

**Creation of Stimuli-Responsive Luminescent
Materials Based on Charge Transfer Excited
States of *o*-Carborane Derivatives**

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2026

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Preface

This PhD thesis, entitled “Creation of Stimuli-Responsive Luminescent Materials Based on Charge Transfer Excited States of *o*-Carborane Derivatives”, was conducted in the Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University under the supervision of Professor Kazuo Tanaka between April 2021 and March 2026. The author would like to express his sincere gratitude to Professor Kazuo Tanaka for his invaluable guidance and continuous encouragement throughout the PhD study.

The author shows his sincere appreciation to Professor Emeritus Yoshiki Chujo for his persistent support. The author is deeply grateful to Assistant Professors Dr. Masayuki Gon and Dr. Shunichiro Ito for their suggestions and discussions. The author is extremely thankful to Dr. Junki Ochi for his instruction and coaching. The author is also grateful to Ms. Mei Tokutomi, Mr. Sota Takemori, Mr. Takumi Yanagihara, and Mr. Takuji Kohara for their significant contributions. Moreover, the author wishes to acknowledge all the members of the Tanaka Lab.

Moreover, the author greatly appreciates the support by Dr. Daisuke Sakamaki (Osaka Metropolitan University), Dr. Yusuke Tsutsui (Kyoto University), and Professor Shu Seki (Kyoto University) for their support on temperature-dependent circularly polarized luminescence measurements and the collaboration by Professor Tomoki Ogoshi (Kyoto University) and Dr. Shunsuke Ohtani (Kyoto University).

Furthermore, the author wishes to express his special thanks to Professor Christopher R. McNeill and his group members at the Department of Materials Science and Engineering, Monash University, for their support and suggestions during the author’s stay in Melbourne.

Additionally, the author is grateful to the Japan Society for the Promotion of Science and Kyoto University Division of Graduate Studies for their financial supports.

The author expresses deep appreciation to his friends in Kyoto University, and his parents, Mr. Masami Yuhara and Ms. Noriko Yuhara, and his sister Ms. Kahori Uchida, for their continuous assistance and encouragement.

Finally, the author is deeply grateful to his wife, Rio Yuhara, for her patience and constant support throughout the PhD study.

Kazuhiro YUHARA

March 2026

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General Introduction

1. Functional Luminescent Molecules

Luminescent materials have attracted huge attention in basic and applied science.¹⁻³ Their applications have been especially considered for optoelectronic technologies implemented in many items for everyday use. Various kinds of materials have been developed, while, among them, molecule-based luminophores have advantages on synthetic property-adjustability, wet processability, large absorption coefficients, etc.⁴ Over the past decades, toward developing optoelectronics such as light emitting displays, molecular photonics, and telecommunication techniques, a number of molecular skeletons have been designed, created, and evaluated. Their pros and cons were evaluated with several optical parameters: photoluminescence wavelength,⁵ brightness,⁶ rate constants of intersystem crossing,⁷ dissymmetry factors,^{8,9} photon upconversion efficiency,¹⁰ etc. These fields have revealed precise structure-property relationships and have already advanced to practical applications. For example, phosphorescence or thermally-activated delayed fluorescence luminophores can efficiently utilize generated excitons, and then the molecules can be implemented in light emitting flexible displays.¹¹ Additionally, based on the permeability of near-infrared (NIR) light through human skin, water-soluble NIR fluorophores can be employed in tumor targeting bioimaging probes.¹² The author acknowledges that present fields of luminescent materials have primarily focused on one-to-one correlation between molecular structures and functionality-based applications.

2. Stimuli-Responsive Luminescent Materials

Recently, stimuli-responsiveness has emerged as a topic of interest toward one-to-many correlation between structures and properties.¹³ Stimuli-responsive materials change their chemical structures and physical properties in response to external stimuli (Figure 1 top). These materials can convert applied stimuli and molecular-scale environmental changes into observable signals.¹⁴ Lots of papers have been published on the designs, evaluations, and applications of stimuli-responsive materials composed of polymers,¹⁵ metal complexes,¹⁶ liquid crystals,¹⁷ and molecular crystals.¹⁸ Photoluminescence-based detection of stimuli has advantages because luminescence is a non-destructive, high-resolution, and quick-responsive physical signal compared to other detection methods using electromagnetic waves such as UV-vis absorption, infrared, Raman, and nuclear magnetic spectroscopy¹⁹ (Figure 1 bottom left). Moreover, luminescent color change can be clearly recognized by the naked eye, that enables intuitive sensing in material use. Recently, various stimuli and environmental conditions have been employed as triggers such as temperature,²⁰ humidity,²¹ viscosity,²² solvent polarity,²³ mechanical force,²⁴ isotropic compression,²⁵ electric or magnetic fields,²⁶ light irradiation,²⁷ Bronsted or Lewis acid/base interactions,²⁸ host–guest interactions,²⁹ etc.

Stimuli-responsive Materials

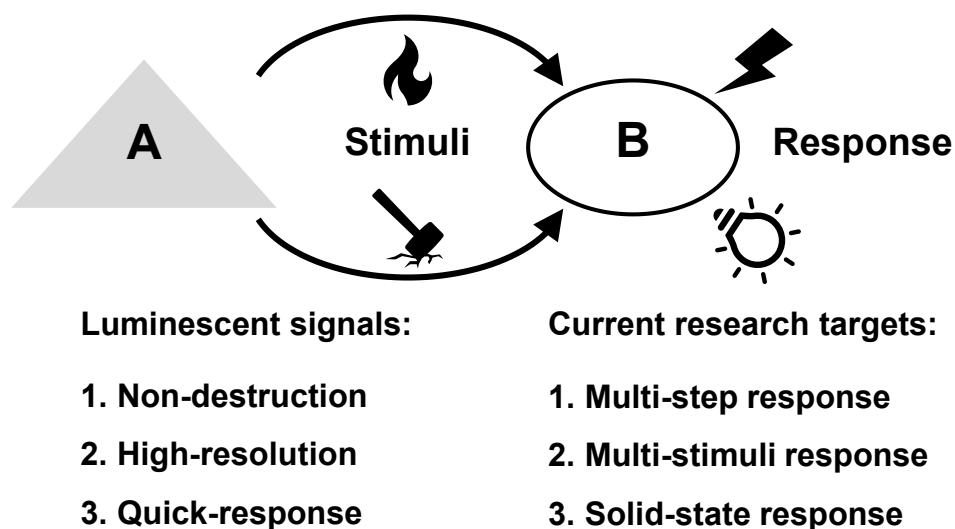


Figure 1. Schematic representation of stimuli-responsive materials.

Based on recent reviews,^{19,30} the author categorizes three major research targets in the field of stimuli-responsive luminescent materials (Figure 1 bottom right).

First, the development of multi-step responsiveness is ongoing. Previous studies have focused on the initial and final stages of the response, which only enables ON–OFF sensing and bicolor switching. If the chromophore can monitor stepwise stimuli-exposure, the users can broaden detection range and enhance sensitivity.

Second, development of multi-stimuli responsive systems, capable of detecting various kinds of stimuli within a single molecular platform, has not matured enough. Previous systems have been constructed by stimuli-oriented design with specific skeletons or functional groups responding to single stimulus. Establishing a mechanism that enables a single molecular framework responding to multiple stimuli can accelerate material designs and applications.

Third, solid-state responsiveness is still its infancy. During the past decades, stimuli-responsive luminescent materials have been evaluated mostly in the solution state because solutions are an ideal media for analyzing basic physical properties. In contrast, solid-state luminescent materials are ideal for applications especially when device implementation is motivated.³¹ Solid-state stimuli-responsive luminophores have often been discovered by chance. Currently, rational design principles for such materials are still under development in material science.

3. Stimuli-Response Based on Excited-State Structural Relaxation

More recently, several stimuli-responsive systems have been constructed based on the excited-state structural relaxation,³² which the author regards as a key to addressing the aforementioned challenges. Luminescent molecules always experience some extent of structural relaxation after photoexcitation.³³ Although it is a fundamental photophysical process, versatile luminescent scaffolds such as polycyclic aromatic hydrocarbons have rigid structure that only allows themselves a little degree of excited-state structural change. Such molecules potentially have superior emission efficiency,³⁴ while their structural rigidity often prevents them from responding to external stimuli because stimuli-induced color change needs at least some degree of structural change. On the other hand, specific molecular systems possess large excited-state structural relaxation including twisted intramolecular charge transfer (TICT),^{35,36} excimer/exciplex formation,³⁷ and excited-state intramolecular proton transfer (ESIPT)³⁸ (Figure 2a). Basic excited-state structure–property relationships have been extensively studied so far. Reported examples showed their high sensitivity to the microenvironment.^{23,38,39} Beyond the conventional processes, recent studies have reported unique flexible π -conjugated skeleton with large relaxation, which can be described as molecular flapping (Figure 2b).^{40–42} Luminescent properties of those systems are sensitive to stimuli because surrounding environments uniformly influence the flexibility of each molecule.³² These types of molecules intrinsically have many intermediate states along the relaxation pathways, which enables multi-step stimuli-responsiveness.⁴³ Furthermore, this relaxation-based mechanism does not require specific functional groups that could limit detectable stimuli. Then this mechanism enables response to multiple stimuli within one skeletal platform.⁴³ Excited-state structural relaxation is a powerful tool to design wide range of stimuli-responsive luminescent materials. However, to the best of the author’s knowledge, systematically studied systems have been limited to a skeleton driven by excited-state aromaticity i.e. cycleoctatetraene, dihydrophenazine,^{44–49}

phenothiazine,^{50,51} and dibenzoheteropin,⁵² except for sporadic reports.^{53,54} Molecular skeletons employing excited-state aromaticity usually have 8π -electron systems folding into anti-aromatic bent geometry in the ground state, while in the excited state it transforms into a planar structure as it gains excited-state Baird aromaticity.^{55–58} The author considers that if more examples of these relaxation-based responses are explored, the research field can expand its scope of designs and applications. In addition, solid-state responsiveness has been rarely reported in the present systems possibly because structural change is often minimized in such a condensed state that reduces molecular sensitivity to the environment. This difficulty motivates the author to study molecular platforms that can be movable and susceptible to external stimuli even in the solid state.

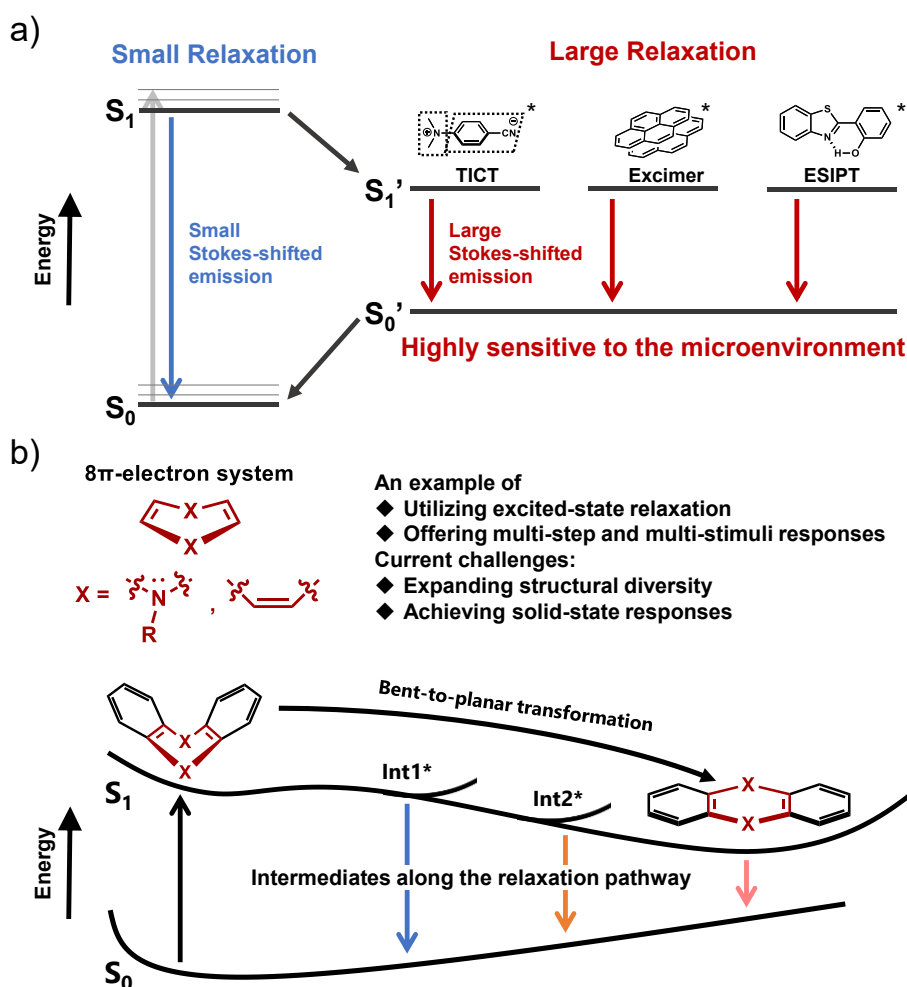


Figure 2. a) Conventional and b) recent luminescent molecules with large excited-state structural relaxations.

4. Carborane

The author focuses on *ortho*-carborane (*o*-carborane) as a promising scaffold for realizing solid-state stimuli-responsive luminescence based on excited-state structural relaxation. Its history, synthesis, properties, and research topics are briefly summarized below. Carborane is a class of boron hydride clusters.⁵⁹ Such clusters are categorized into different sizes and shapes with different physical and chemical properties.⁶⁰ The most-studied carborane is dicarba-*closo*-dodecaborate, which is simply called as carborane. Two BH vertices of $B_{12}H_{12}^{2-}$ are replaced by CH vertices forming a neutralized icosahedron (chemical formula: $C_2B_{10}H_{12}$).⁶¹ Carborane consists of three structural isomers, *ortho*, *meta*, and *para* isomers depending on which position the carbon atoms occupy (Figure 3a). Among them, *o*-carborane has been extensively studied to date because of commercial availability and synthetic accessibility. First synthesis and derivatization of *o*-carborane were achieved in 1963,^{62–67} where reaction of acetylene with decaborane proceeded to form the icosahedral cluster. This protocol is now widely applied with alkynes and decaborane, called as the alkyne insertion reaction (Figure 3b).⁶⁸ Decaborane is commercially available and, if needed, can be prepared in the lab.^{69,70} Lewis bases such as *N,N*-dimethylaniline and acetonitrile are typically used as activators. Recent report showed catalytic amount of silver salt further improves the reaction yield.^{71,72} Polyhedral boranes are generally known to be explosive and were possibly used as rocket fuels in military purposes, while *o*-carborane is thermally stable up to 400 °C.⁵⁹ The stability is based on multiple three-center two-electron bonds that delocalize electrons throughout the icosahedra.^{73,74} From the 1960s, the initial era of carborane research, carborane units have been incorporated into polymer chains to improve their thermal resistance for the development of flame-retardant materials.^{75–77} Successively, especially in the 1980s, carborane has been studied in the field of organometallic and elemental chemistry focusing on synthesis,^{78,79} structure,^{80,81} coordination,^{81–83} and catalysis.^{84,85} Recently the study of carborane has extended into material applications such as medicine,^{86,87} adsorbents,⁸⁸ energy storage,^{89–91} and so on.⁹²

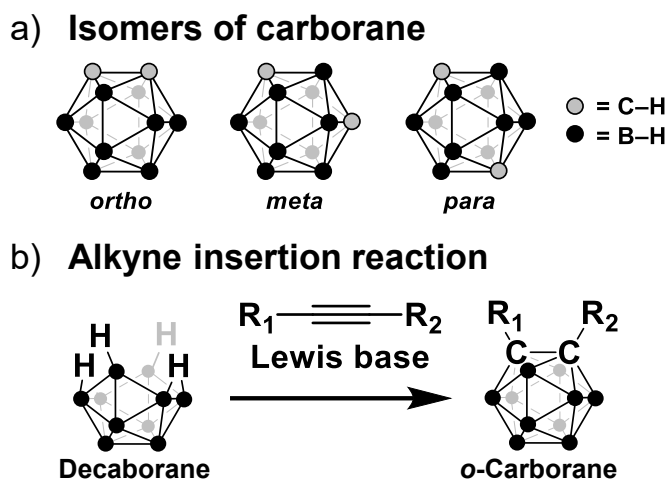


Figure 3. a) Structures of carborane isomers and b) scheme of alkyne insertion reaction.

Over the past decade, the luminescent properties of *o*-carborane derivatives have attracted attention in both basic and applied fields of science.⁹³ The derivatives substituted with π -conjugated units distinctively display intramolecular charge transfer (ICT) emission due to the electronic conjugation between the cluster and conjugated units.^{94–100} ICT emission is a characteristic feature of *o*-carborane derivatives other than *meta*- and *para*-isomers.^{101–103} The electron-accepting nature of the boron-rich *o*-carborane skeleton contributes to this process.^{104,105} Photoexcitation of aryl derivatives first forms a locally-excited (LE) state of the aryl units, whose molecular geometry is close to that of Franck–Condon state i.e. ground-state stable structure under Born–Oppenheimer approximation. Successive excited-state relaxation forms ICT state based on the through-bond electron transfer. The carbon–carbon bond in cluster ($C_{\text{cage}}-C_{\text{cage}}$) plays a key role: σ^* orbital of the bond conjugates with the π^* orbital of the aryl units ($\sigma^*-\pi^*$ conjugation) (Figure 4a).^{106–111} Typically, the $C_{\text{cage}}-C_{\text{cage}}$ bond has a length between 1.6 and 1.9 Å in the ground state, while in the ICT process, the bond significantly elongates to over 2.0 Å, which is a characteristic relaxation process of *o*-carborane derivatives.^{112,113} Furthermore, depending on the aryl units, the emission from ICT states can be combined with that of LE states of the π -conjugated units, resulting in the dual-emission

properties. The rotation of the carborane units affects the dual-emission processes: when the planar aryl moiety is perpendicularly oriented to the $C_{\text{cage}}-C_{\text{cage}}$ bond (twisted conformer), $\sigma^*-\pi^*$ conjugation efficiently occurs to form ICT state, while their parallel orientation (parallel conformer) forms LE state (Figure 4b).^{96,114–118} Most importantly, these ICT-related structural changes are allowed even in the solid state (Figure 4c),^{113,116,119–122} where typical structural relaxation is restricted by surrounding molecules.¹²³ This is an intriguing aspect of this cluster. The author considers here that this unique feature originates from its spherical nature that should minimize free-volume change during the structural relaxation.

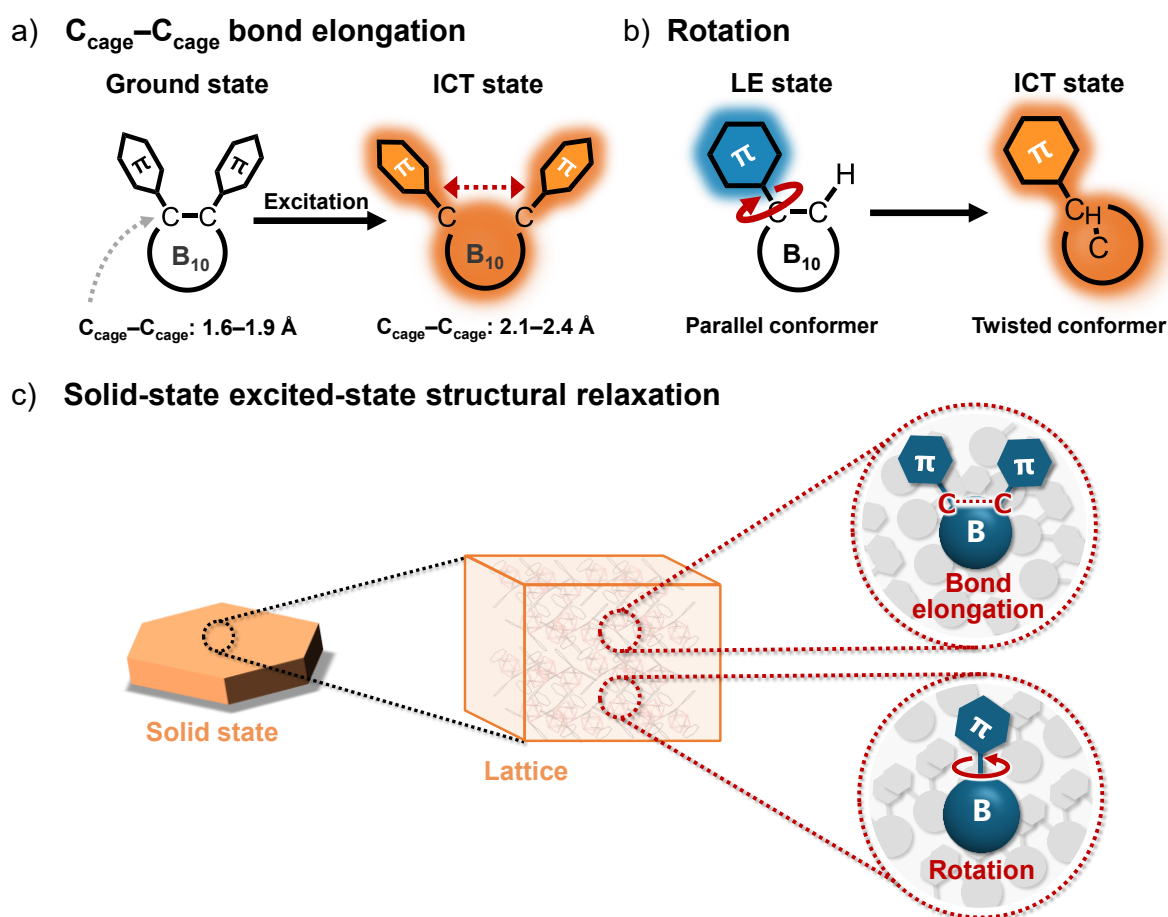


Figure 4. Schematic illustration of a) $C_{\text{cage}}-C_{\text{cage}}$ bond elongation, b) rotation, and c) solid-state excited-state structural relaxation of aryl-*o*-carborane derivatives.

5. Survey of This Thesis

To address the challenges in the field of stimuli-responsive materials, in his PhD work, the author tactically approached the creation of solid-state stimuli-responsive materials based on the ICT state of *o*-carborane. His PhD research is structured into three parts (Figure 5). First, the thesis demonstrates that the structural relaxation process of ICT-based *o*-carborane derivatives can be utilized for the multi-step and multi-stimuli responsiveness, particularly in the solid state. Second, the thesis reveals photophysical stimuli-responsiveness based on the synergistic effect between carborane-induced ICT emission and uni- or multimolecular photophysical processes of π -conjugated units. This thesis not only provides fundamental insights into the structure–property relationships of solid-state stimuli-responsive molecular systems but also expands the design principles and potential applications of smart luminescent materials.

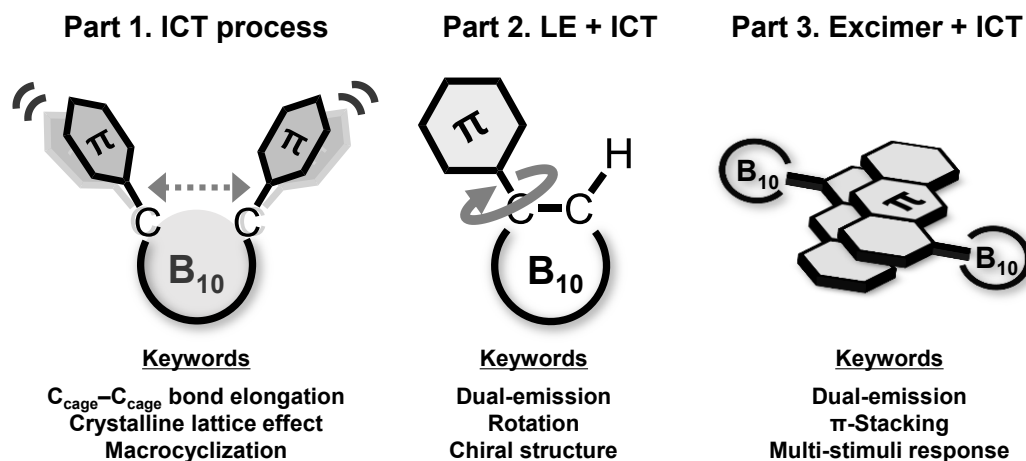
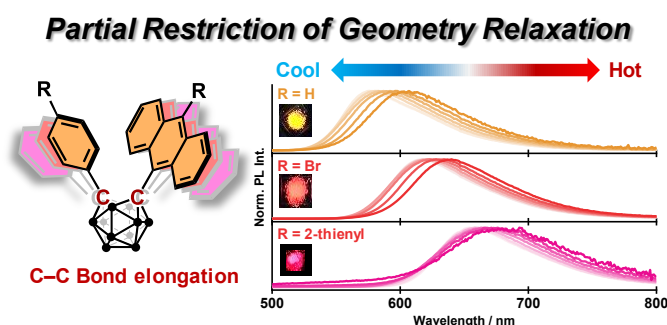


Figure 5. Schematic illustration of the basic concepts in this thesis.

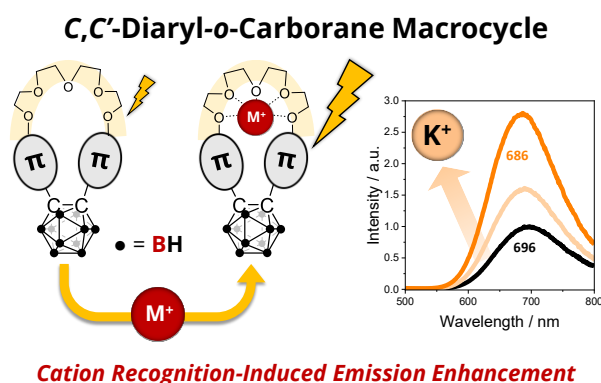
In Part 1, the author undertook research aimed at regulating structural relaxation process to ICT states in *C,C'*-diaryl derivatives. In this part, the regulation of relaxation accompanied by the ICT process was proven to be an effective strategy for controlling stimuli-responsiveness

especially in the solid state. This part comprises Chapters 1–3 working with various mechanisms for the structural regulation.

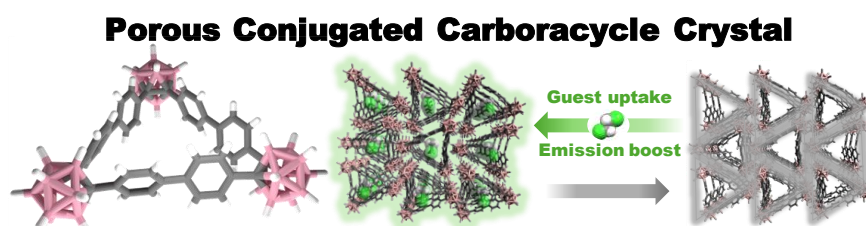
In Chapter 1, the author investigated a mechanism underlying the previously reported crystal-state temperature-dependent luminescence of C,C' -diaryl derivatives. Consequently, extensive analyses revealed that the dependency originated from thermal expansion of crystal lattice that expanded molecular free-volume, which accelerated structural relaxation. The author found that $C_{\text{cage}}-C_{\text{cage}}$ bond elongation was an indispensable process in this responsiveness. The solid-state flexibility of this bond contributed to the successive luminescent spectral shift.



In Chapter 2, the author created macrocyclic compounds incorporated with $C_{\text{cage}}-C_{\text{cage}}$ bond of carborane to regulate the excited-state elongation process studied in the previous chapter. Tetra(ethylene glycol) (TEG) unit was utilized as a guest recognition site. As a result, the author revealed that cation recognition at the TEG moiety induced emission enhancement in solution. The recognition rendered the macrocycle compressed, which suppressed excited-state structural relaxation associated with non-radiative decay channels.



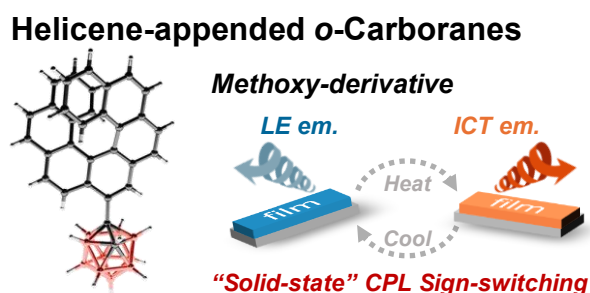
In Chapter 3, the author developed a triangular macrocycle of a C,C' -diaryl derivative to regulate relaxation process by the structural constraints induced by macrocyclization. The macrocycle unfortunately still underwent significant structural relaxation, whereas the author serendipitously found the macrocycle crystallized into a permanent porous crystal. The crystal exhibited emission enhancement upon guest inclusion owing to the suppression of structural relaxation. Theoretical analyses suggested critical role of the guest-induced suppression of structural relaxation in preventing access to the non-emissive ICT state.



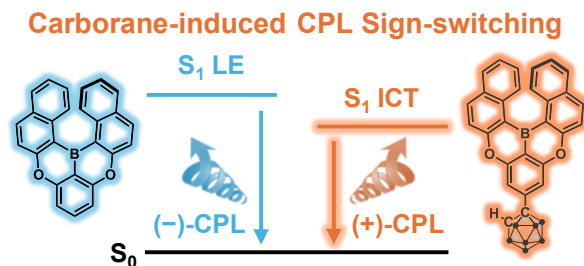
In Parts 2 and 3, the author combined ICT emission with emission species from the incorporated π -conjugated units to exploit their unique characteristics in stimuli-responsiveness.

In Part 2, dual-emissive systems based on LE emission of π -conjugated units and ICT emission were applied to sign control of circularly polarized luminescence (CPL). This part comprises Chapters 4 and 5, which deal with different chiral π -conjugated units.

In Chapter 4, the author demonstrated the utility of a dual-emission property including LE and ICT for solid-state CPL sign-regulation. [7]Helicene-appended *o*-carborane derivatives changed its CPL sign upon switching of the dominant emission species in response to film-state temperature change. The author highlighted the importance of solid-state rotatability.

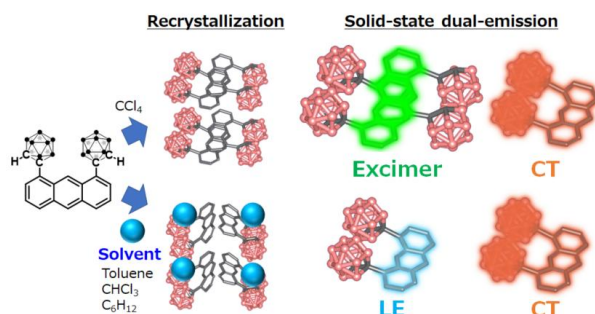


In Chapter 5, the author aimed to improve emission efficiency of the [7]helicene-based compound reported in Chapter 4. Heterohelicene-appended derivative exhibited moderate emission efficiency which was closely associated with the dual-emission-based CPL regulation.

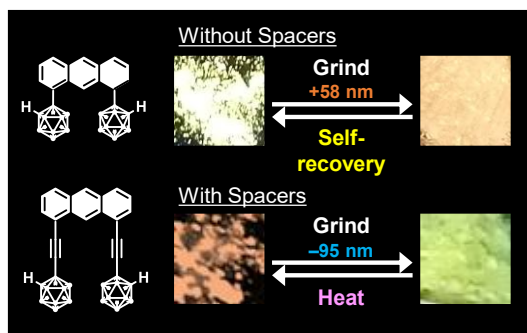


In Part 3, the author developed a crystalline dual-emission system in which excimer emission from π -conjugated units coexisted with ICT emission. This part focuses on the π -stacking structure of a novel anthracene-bis-*o*-carborane triad and comprises Chapters 6–8 dealing with different systems responding to distinct external stimuli.

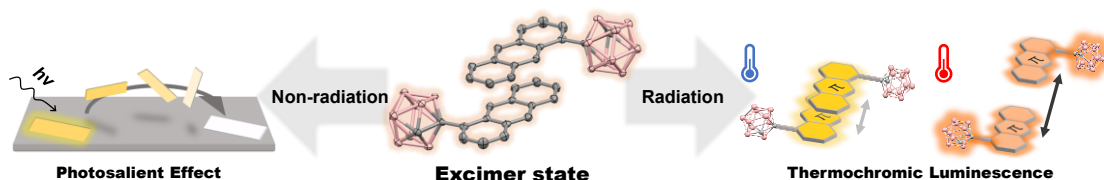
In Chapter 6, the author discovered two pseudo-polymorphs (crystal α and β) of the anthracene-bis-*o*-carborane triad regulated by the inclusion of crystallization solvents. Two polymorphs exhibited distinct dual-emission properties depending on their molecular packing. Crystal α exhibited dual-emission properties composed of excimer and ICT emission due to the π -stacking structure. Crystal β , which lacked such π -stacking, only showed dual-emission composed of LE and ICT emissions. Furthermore, distinct thermochromic luminescence behavior was observed.



In Chapter 7, the author determined crystal structure of crystal α identified in the previous chapter and investigated its stimuli-responsiveness. The π -stacking arrangement of crystal α was characterized by *ab initio* powder X-ray diffraction analysis. Moreover, the author observed mechanochromic properties arising from the collapse and reconstruction of the π -stacking structure. The luminescent processes were affected by whether π -stacking exists or not.



In Chapter 8, the author investigated the relationships between molecular structure and crystalline packing. Carborane units were introduced at various positions on the anthracene core. Consequently, π -stacking structures were observed only for the 1- and 1,8-substituted derivatives. The author conducted an extensive analysis of thermochromic luminescence based on excimer-ICT dual-emission properties and concluded that the increase in the π -plane distance with rising temperature accelerates the formation of the ICT state. Furthermore, the author examined a photosalient effect associated with photodimerization, which is a non-radiative deactivation pathway of excimer.



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Part 1

Stimuli-Responsive Properties Based on the Regulation of Excited-State Structural Relaxation Funneling into Intramolecular Charge Transfer States

Chapter 1

Solid-State Temperature-Dependent Luminescence of *C,C'*-Diaryl-*o*-Carboranes Based on Restriction of Excited-State Structural Relaxation

Abstract

Here, the author shows mechanistic analyses of solid-state temperature-dependent luminescence of *C,C'*-diaryl-*o*-carborane derivatives. Solid-state stimuli-responsiveness is a promising property to visualize environmental changes in molecular scale. Thus, mechanistic study of responsiveness has full of meaning to broaden the scope of materials. Chujo *et al.* previously reported solid-state temperature-dependent luminochromism of *C*-anthryl-*o*-carborane derivatives. Among them, the author re-focused on *C*-anthryl-*C'*-phenyl-*o*-carborane as a prototypical compound and synthesized derivatives with electronically different substituents on aryl units. Based on extensive analyses with crystallography, variable temperature optical measurements and theoretical calculation, the author shows that luminochromic behaviors can be explained by partially-restricted excited-state elongation of the carbon–carbon bond in the cluster. The results indicate that thermal expansion and contraction of crystalline lattice should play a key role in modulating the degree of excited-state structural relaxation including the bond elongation in the cluster.

Introduction

Stimuli-responsive materials change their chemical structures and physical properties in response into external stimuli. These materials can convert applied stimuli and environmental changes to observable signals. Numerous number of materials were reported to have various responsiveness toward external stimuli with changing their properties.^{1,2} Luminescent color change is one of the excellent outputs for stimuli-detection due to its reproducibility, repeatability, and high sensitivity. Some molecular skeletons showed unique responsiveness utilizing excited-state processes such as twisted intramolecular charge transfer,³ excited-state intramolecular proton transfer,⁴ and excimer/exciplex formation.⁵ Basically, luminescent molecules with such processes have large Stokes shifts, which enables users to recognize luminescent color change in response to stimuli.⁶ Recently, excited-state structural relaxation processes of flexible π -conjugated skeletons have gained attention from molecular science and material fields.^{6,7} Upon excitation, such flexible molecules structurally transform to stable structures in the excited state. In an environment where structural change freely occurs, excited molecules can get completely relaxed geometry. In contrast, when the relaxation was partially restricted by outer environment or external stimuli, these compounds show luminescent color change. Based on this excited-state dynamics, stimuli-responsive properties have been reported with flexible π -conjugated skeletons, mainly focusing on responsiveness in the solution states.^{8–11} At this stage, solid-state stimuli-responsive luminescent molecules with flexible skeletons have rarely been reported.^{12,13} Those molecules have advantages on high sensitivity visualizing slight external environmental change based on the abundant stable structures in the excited state even though stimuli-responsiveness accompanying structural change is often cancelled by densely-packed surrounding molecules in the film or crystalline materials. Therefore, the development of molecules with both flexible skeletons and stimuli-responsiveness has been regarded as a challenging research target. Also, for practical usages, solid-state stimuli-

responsive luminescent molecules can be regarded as promising candidates because they are suitable for optoelectronic application such as organic light-emitting diodes, solid-state lasers and sensing devices owing to the durability of the compound against heat and chemical stimuli without vaporization of the solvent and large volume change.^{14,15} This is a stark difference in comparison with the conventional chromophore, which is highly emissive only in the solution state, but suffering from quenching in the solid-state due to the intermolecular interaction such as π – π interactions.¹⁶

An icosahedral compound, *o*-carborane, has been focused on as a key skeleton of solid-state stimuli-responsive luminescent materials.¹⁷ *o*-Carborane is a class of boron cluster compounds composed of two carbon and ten boron atoms in their core units.^{18,19} Optical properties of *C*-aryl-*o*-carborane derivatives have attracted attention from photophysical aspects during the last decade^{20–25} and analyzed in theoretical studies in the recent years.^{26–29} One of the impressive optical properties is intramolecular charge transfer (ICT) emission.³⁰ Owing to the electron deficiency of boron atoms when connected to π -conjugated units, *o*-carborane can work as an electron-acceptor with orbital conjugation. After photoexcitation, locally-excited (LE) state of the π -units is formed, where molecular geometry is close to the Franck–Condon state. Subsequent structural relaxation forms the ICT state through electronic charge transfer from the π -units to the boron cluster. During the relaxation process, the carbon–carbon bond in the *o*-carborane unit ($C_{\text{cage}}\text{--}C_{\text{cage}}$) elongates due to the electronic conjugation from π -orbital of aryl groups to anti-bonding σ^* -orbital of the $C_{\text{cage}}\text{--}C_{\text{cage}}$ bond.^{30–32} In this process, the $C_{\text{cage}}\text{--}C_{\text{cage}}$ bonds get the perpendicular conformation to the π -orbitals of aryl groups and elongate to ca. 2.3 Å.^{26,30} Part of the *C*-aryl derivatives have aggregation-induced emission (AIE)^{1,16} property based on ICT emission. In such systems, only trace of luminescence is observed in solution, while intense emission in aggregate and/or solid can be obtained. The origin of AIE phenomena is often described by suppression of non-radiative decay in the aggregated state.^{33–36} Tanaka *et*

al. experimentally demonstrated that the $C_{\text{cage}}-C_{\text{cage}}$ bond elongation process plays a key role in photophysical process in the excited state leading to AIE property.²⁶ Also, previous studies have discussed the mechanism based on energetic accessibility to non-emissive dark CT state with structure of further elongated $C_{\text{cage}}-C_{\text{cage}}$ bonds (ca. 2.6 Å) and parallel conformation of the $C_{\text{cage}}-C_{\text{cage}}$ bond to aryl π -orbitals.^{27,29} Luminescence can be quenched by structural relaxation in the solution state, while rigid environment in the solid state partially restricts the relaxation, that should lead to AIE phenomena.

In this chapter, the author shows mechanistic analyses of temperature-dependent luminescent properties of *C,C'*-diaryl-*o*-carborane derivatives (Figure 1). Chujo *et al.* previously reported solid-state temperature-dependent luminochromism of *C*-anthryl-*o*-carborane derivatives.³² Theoretical study by Su *et al.* suggested the critical role of the $C_{\text{cage}}-C_{\text{cage}}$ bond elongation process.²⁸ In this chapter, the author focused on the *C*-phenyl-*C'*-anthryl derivative (**H-H**), which can be regarded as a prototypical compound with *C,C'*-diaryl units for further functionalization. The author introduced electronically-different substituents on the phenyl and/or anthryl groups and clarified the mechanism of thermo-responsive luminescent properties based on the results of photophysical measurements, crystallographic data, and thermal analysis. Moreover, these optical properties were well realized by theoretical calculations.

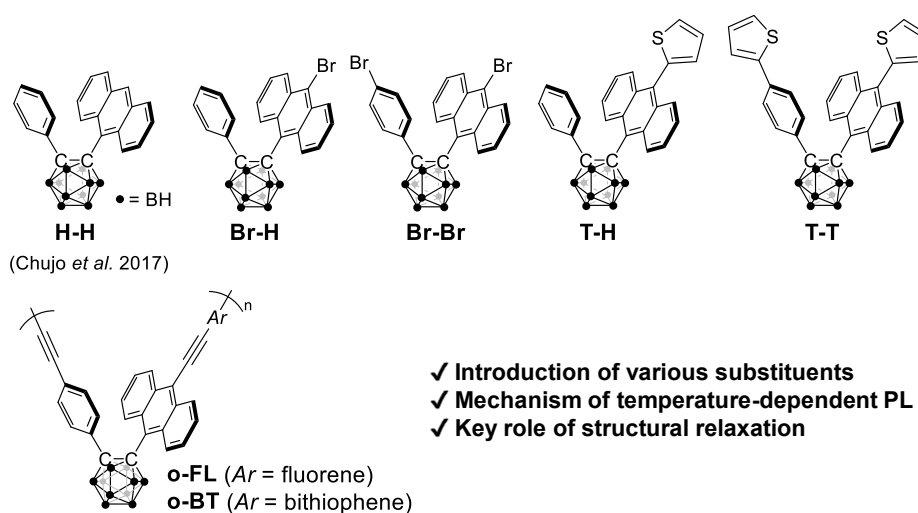
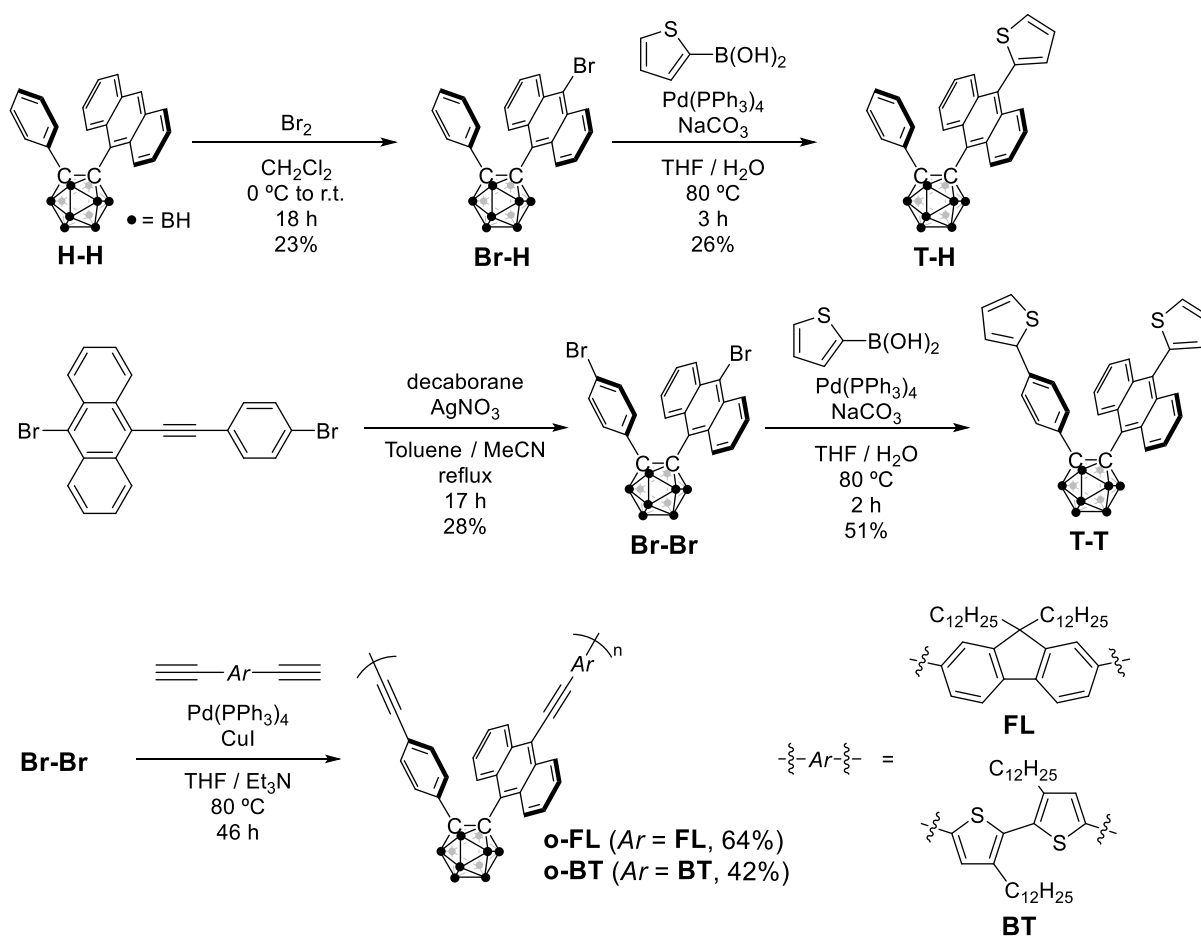


Figure 1. Schematic representation of this chapter.

Results and Discussion

The synthetic scheme of *C,C'*-diaryl-*o*-carborane derivatives is shown in Scheme 1. The author introduced electron-donating 2-thienyl or electron-accepting bromo groups on phenyl and/or 9-anthryl moieties. The prototypical compound, **H-H**, was prepared by the alkyne insertion reaction^{37,38} with 9-(phenylethynyl)anthracene and decarborane ($B_{10}H_{14}$) according to previous literature.³² The mono- and bis-brominated derivatives, **Br-H** and **Br-Br** were synthesized through the nucleophilic aromatic substitution with Br_2 and **H-H** and the alkyne insertion with 9-bromo-10-((4-bromophenyl)ethynyl)anthracene and $B_{10}H_{14}$, respectively. Afterwards, Suzuki–Miyaura coupling reactions of **Br-H** and **Br-Br** with 2-thiopheneboronic acid afforded mono-thienyl derivative, **T-H**, and bis-thienyl derivative, **T-T**, respectively.



Scheme 1. Synthetic scheme of *C,C'*-diaryl-*o*-carborane derivatives.

The author also performed co-oligomerization reactions with fluorene or strong electron-donating bithiophene used as a comonomer unit. Sonogashira–Hagihara coupling reactions between **Br-Br** and corresponding diethynyl-aryl comonomers afforded alternating co-oligomers with fluorene (**o-FL**) and bithiophene (**o-BT**), respectively. Ethynylene spacers were incorporated to reduce steric hindrance of chain-ends during propagation reactions between V-shaped diaryl-*o*-carborane and bis-brominated monomers.

Crystal structures of **H-H**, **Br-H**, **Br-Br**, **T-H**, and **T-T** were determined by single-crystal X-ray diffraction analyses (Figure 2). From diffraction data, molecular structures of the derivatives were unambiguously characterized. All compounds had V-shaped geometries with phenyl and anthryl groups aligned almost perpendicular to the C_{cage}–C_{cage} bonds. The bond lengths between carbon atoms were within a narrow range of 0.01 Å (1.820(4)–1.830(5) Å) and longer than that of parent *o*-carborane (1.62 Å).³⁹ This is attributed to the steric repulsion between phenyl and anthryl groups. Additionally, five compounds had similar values of geometrical parameters such as the dihedral angles of the C_{cage}–C_{cage} bond with the anthryl group and the distance between phenyl and anthryl units. These results indicate that the derivatives have similar ground-state geometries regardless of the substituents.

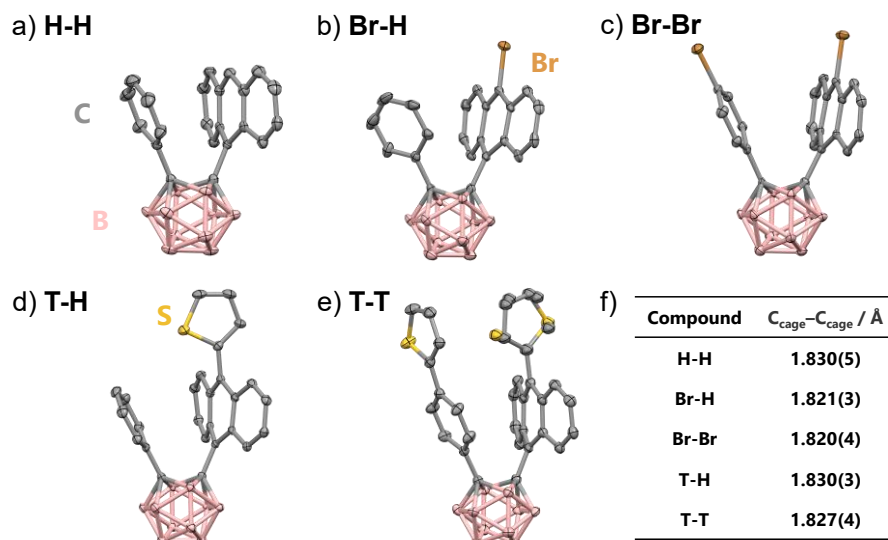


Figure 2. ORTEP drawings of a) **H-H**, b) **Br-H**, c) **Br-Br**, d) **T-H**, and e) **T-T**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The thiophene ring on the anthracene unit of **T-T** is refined with ring flipping disorder. Colors: C, gray; B, pink; S, yellow; Br, brown. f) List of $C_{\text{cage}}-C_{\text{cage}}$ bond lengths.

Temperature dependence of crystalline structures was examined for **H-H**. Diffraction data measured at 143 K was compared with those obtained at 208 and 243 K. In all data, **H-H** crystallized in the same space group ($P2_1/n$) and its molecular geometries were hardly affected by temperature change. However, the lattice constant was affected by temperature change. The author observed the cell volume (V_{cell}) expansion along with the temperature increasing (143 K; 2172.9(19) $\text{\AA}^3$, 208 K; 2180.6(7) $\text{\AA}^3$, 243 K; 2183.5(8) $\text{\AA}^3$). This change should originate from activated molecular vibration by external heat. The void volume in the unit cell (V_{void}) also increased linearly with temperature elevation (143 K; 253 $\text{\AA}^3$, 208 K; 262 $\text{\AA}^3$, 243 K; 267 $\text{\AA}^3$). Additionally, the space occupied by each molecule (V_{mol}) was calculated by $(V_{\text{cell}} - V_{\text{void}})/Z$, where Z denotes the number of molecules in the asymmetric unit. The V_{mol} values were almost consistent across all temperatures (143 K; 480 $\text{\AA}^3$, 208 K; 480 $\text{\AA}^3$, 243 K; 479 $\text{\AA}^3$). These results suggest that each molecule in the crystalline lattice gains more available space to accommodate excited-state structural changes in higher temperature regions.

Optical measurements were conducted to obtain information about electronic structures of the compounds (Figure 3 and Table 1). UV-vis absorption spectra were measured in CHCl_3 . Compared to **H-H**, it was shown that maximum absorption wavelengths (λ_{abs}) of the lowest energy band bathochromically shifted by 24 nm (**T-H**) and 26 nm (**T-T**), implying that the introduction of electron-donating thiophene units could contribute to narrowing energy gaps. Moreover, **o-FL** and **o-BT** had even more red-shifted absorption than the small molecules. This result indicates that electronic conjugation should be developed through polymer main-chains. Photoluminescence (PL) in CHCl_3 also red-shifted in a similar manner to the absorption. Luminescent maximum wavelengths of PL bands (λ_{PL}) of **o-FL** and **o-BT** reached the NIR region (**o-FL**; 709 nm, **o-BT**; 743 nm). To determine luminescent species, optical measurements were performed in several solvents (Figure 4). From all compounds, larger Stokes shifts were observed in highly polar solvents, clearly indicating ICT characters. From small molecules, very weak PL was observed (PL quantum yield (Φ_{PL}) ≤ 0.01) in the solution state, similarly to typical *C*-aryl-substituted *o*-carboranes.^{22,30,32,40} This is because the non-radiative pathways should be activated during the excited-state structural relaxation.²⁶

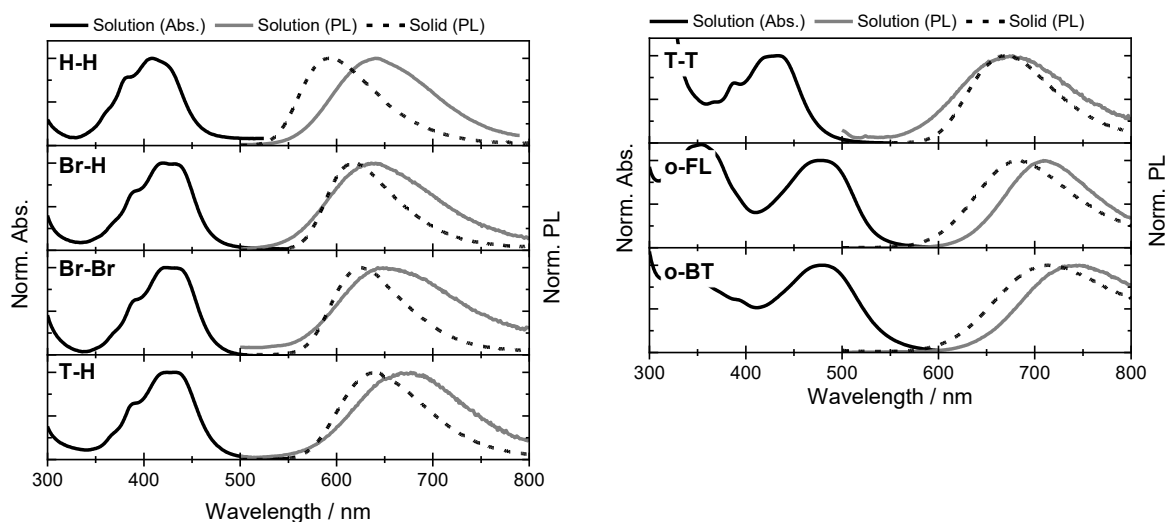


Figure 3. Normalized UV-vis absorption and photoluminescence (PL) spectra of *C,C'*-diaryl-*o*-carborane derivatives (solution: CHCl_3 1.0×10^{-5} M).

Table 1. Photophysical properties of *C,C'*-diaryl-*o*-carboranes

Compounds	State	λ_{abs} / nm	λ_{PL} / nm ^[c]	Φ_{PL} ^[c,d]
H-H	Solution ^[a]	408	643	0.01
	Crystal	—	592	0.70
Br-H	Solution ^[a]	419	637	< 0.01
	Crystal	—	619	0.26
Br-Br	Solution ^[a]	422	643	< 0.01
	Crystal	—	625	0.26
T-H	Solution ^[a]	432	676	< 0.01
	Crystal	—	637	0.66
T-T	Solution ^[a]	434	677	< 0.01
	Crystal	—	671	0.22
o-FL	Solution ^[a]	478	709	0.05
	Film ^[b]	491	700	0.06
o-BT	Solution ^[a]	479	743	0.01
	Film ^[b]	494	729	0.02

^[a] 1.0×10^{-5} M in CHCl_3 solution (per repeating units for oligomers). ^[b] Prepared by spin coating method.

^[c] Excited at λ_{abs} . ^[d] Absolute quantum yield determined by an integrating sphere method. ^[e] Excited at 369 or 375 nm. —: not measured. n.d.: cannot be determined reliably due to weak luminescence.

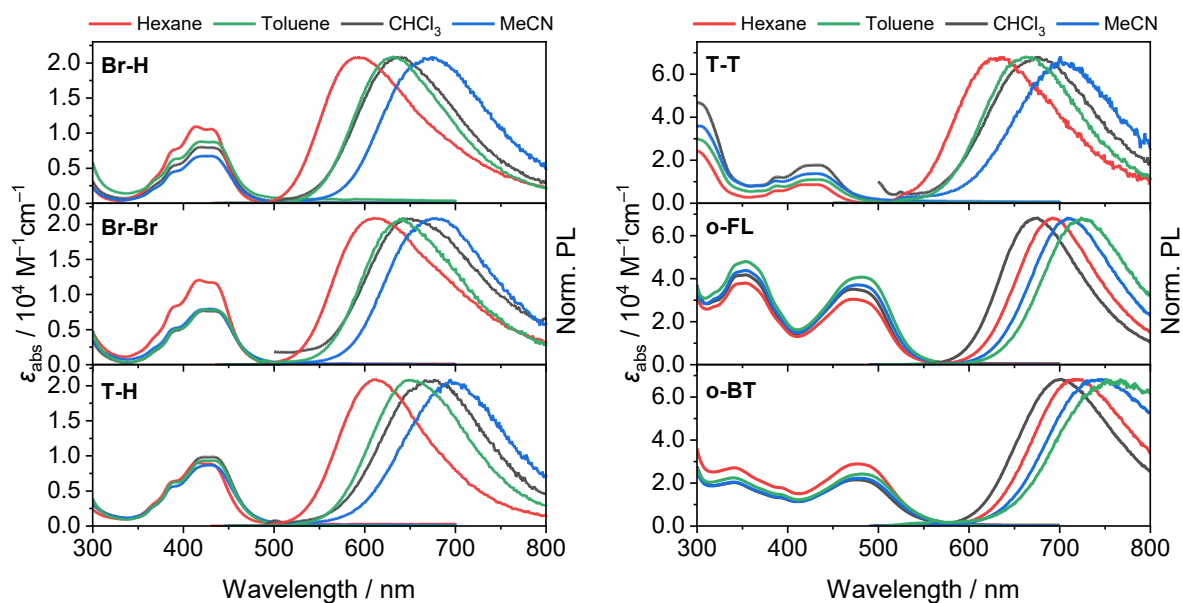


Figure 4. Solvent-dependence of UV-vis absorption and PL spectra of *C,C'*-diaryl-*o*-carborane derivatives recorded in 1.0×10^{-5} M solution.

Solid-state luminescent properties were measured with crystal samples of the compounds and oligomer films (Figure 3 and Table 1). The maximum emission wavelengths were red-shifted by the introduction of electron-donating groups as observed in the solution state (**H-H**; 592 nm, **T-H**; 637 nm, **T-T**; 671 nm) originating from elevation of highest occupied molecular orbital (HOMO) energy levels. In all compounds, higher Φ_{PL} values in solid were observed than those in solution, representing that these compounds have AIE properties. In addition, in all compounds the λ_{PL} values were shorter than those in CHCl_3 and longer than those in low-polarity solvent (hexane or CCl_4). The degree of structural relaxation of ICT-emissive aryl-*o*-carborane system can be strongly affected by the polarity around the molecule.^{20,26,41,40} Then depending on the polarity, the solution-state luminescent wavelength can locate at both shorter and longer wavelength regions in comparison with that in the solid state.

Temperature dependence of luminescent properties was examined to gain deeper insight into the relaxation process in the excited state. Solid-state variable-temperature PL (VTPL) properties were monitored (Figure 5). It should be noted that VTPL spectra of oligomers were recorded below glass transition temperatures (ca. 340 K, determined by DSC) to exclude consideration on glass transition. All compounds showed continuous red-shifts of the luminescent bands with increasing temperature although wavelength regions were dependent on the substituents on aryl units as observed in **H-H** previously.³² The maximum luminescent wavelengths consecutively increased with the temperature increase (e.g. **H-H**; 576 nm (80 K), 587 nm (230 K), and 607 nm (410 K), **Br-Br**; 617 nm (80 K), 622 nm (230 K), and 640 nm (410 K), **T-T**; 654 nm (80 K), 668 nm (230 K), and 693 nm (410 K)). As observed in temperature-dependent X-ray diffraction of **H-H**, solid-state organic compounds have lower density at higher temperature region due to the thermal expansion of the crystal lattice.⁴² It is suggested that this lattice expansion should form larger void volume in crystal where larger degree of excited-state structural relaxation can be allowed.

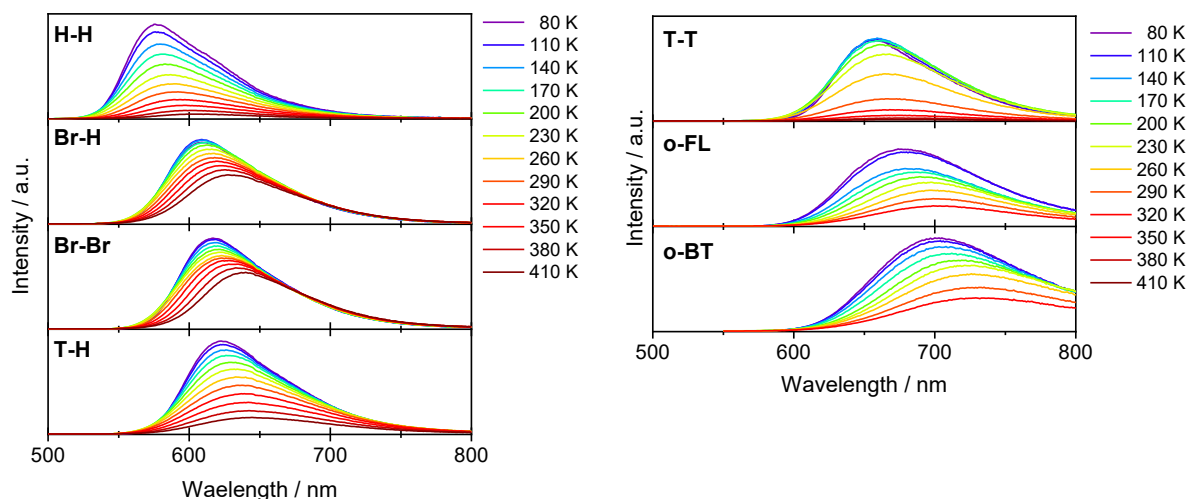


Figure 5. Solid-state temperature-dependent luminescent spectra of *C,C'*-diaryl-*o*-carboranes.

Additionally, the author investigated the temperature dependence of radiative and non-radiative decay constants (k_r and k_{nr} , respectively) (Figure 6). It was revealed that k_r values were almost independent of or slightly decreased with increasing temperature. In contrast, k_{nr} values exponentially increased with temperature although each compound had different extent of increase. **T-T**, **o-FL**, and **o-BT** had one order of magnitude larger k_{nr} values than those of other compounds, especially in higher temperature regions. Due to the narrower energy gaps, these three compounds should have more non-radiative decay pathways as explained by the energy gap law.⁴³ Therefore, emission quenching proceeds by heating. Larger k_{nr} values of brominated derivatives, **Br-H** and **Br-Br**, than **H-H** over the entire temperature change can be explained by the heavy atom effect of bromine atoms, which may accelerate intersystem crossing from the singlet to the triplet excited dark state.⁴⁴ These kinetic analyses suggest that molecular thermal vibration in the excited state should accelerate at higher temperature, which can facilitate non-radiative decay pathways.

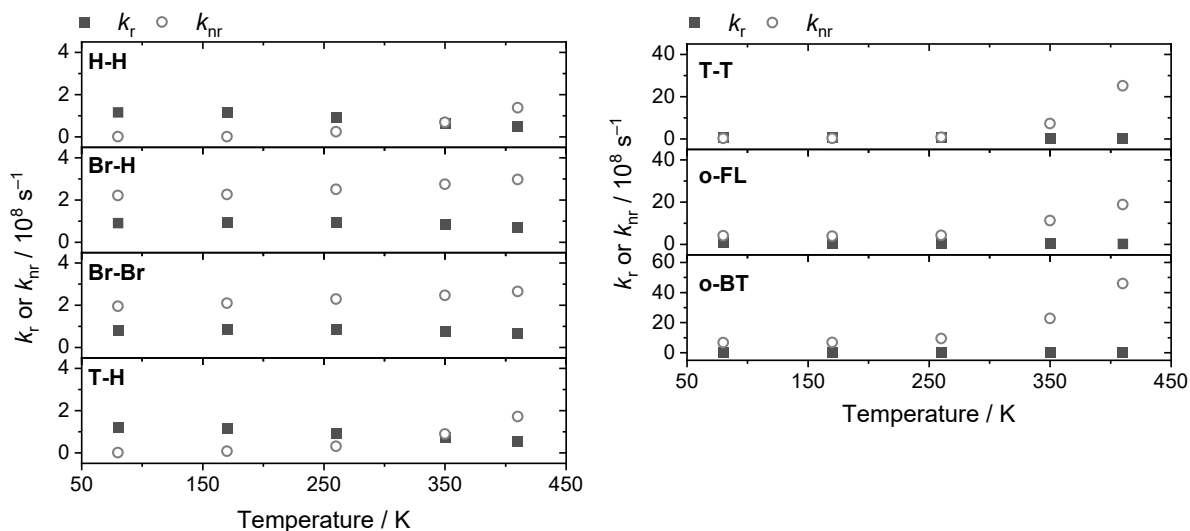


Figure 6. Temperature dependence of k_r and k_{nr} in the solid state.

To elucidate the mechanistic insight of photophysical properties, the author performed theoretical calculation on **H-H**, **Br-H**, **Br-Br**, **T-H**, and **T-T**. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to optimize molecular structures in the S_0 and S_1 states. The solvent effect of CHCl_3 was modeled with polarized continuum model (PCM)^{45–47} in the solution state. Quantum mechanics and molecular mechanics (QM/MM) calculation^{26,30,48} was used for structural optimization in the crystal.

Firstly, based on the energy levels and the distribution of the frontier molecular orbitals, the luminescent characters of the derivatives were evaluated (Figure 7). Calculation indicated that transition between HOMO and LUMO dominantly contributed to the emission character. Compared to **H-H**, electron-donating thiophene units induced the elevation of the HOMO level resulting in narrower energy gap between HOMO and the lowest unoccupied molecular orbital (LUMO). This result supports the red-shifted absorption and luminescent bands of **T-H** and **T-T** relative to those of **H-H**. Indeed, TD-DFT calculation reproduced the trends of the absorption and luminescence wavelengths. Then the validity of the selected calculation level was confirmed (Table 2). Also, luminescence was driven by electronic transition between HOMO

and LUMO in the S_1 state. Emission species were characterized by distribution analysis of orbitals. In the S_1 state, HOMO orbitals mainly localized on anthracene and *o*-carborane moieties, whereas LUMO orbitals spread over the entire molecule. Along with the luminescent transition, the charge transfer between aryl units and *o*-carborane moieties should occur, supporting the characterization of ICT luminescence. The oligomerization was supposed to enhance ICT character through introduction of electron-donating groups, fluorene and bithiophene. As a result, far more red-shifted luminescence is therefore expected compared to other compounds.

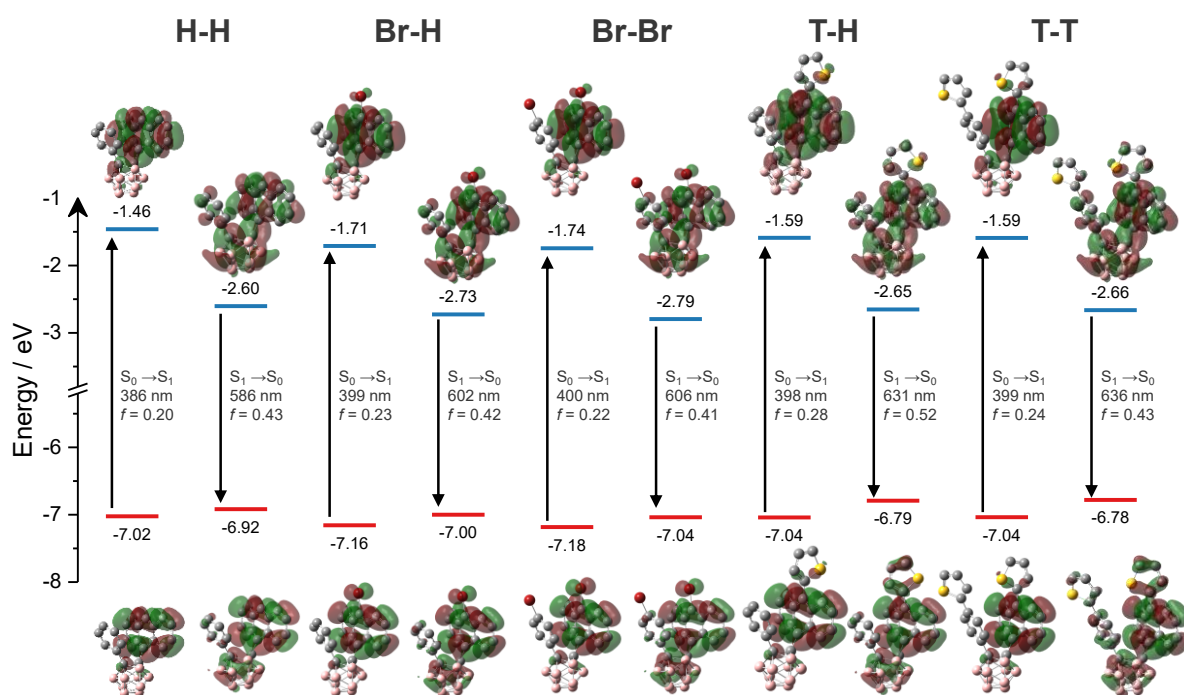


Figure 7. Calculated Kohn–Sham frontier orbital distribution and S_0 – S_1 electronic transition energy in nm for energy minimum geometries of S_0 and S_1 states (Colors: C, gray; B, pink; S, yellow; Br, red). Hydrogen atoms were omitted for clarity. Solvent effect of chloroform was considered with polarized continuum model. f denotes the oscillator strength. Isovalues are 0.02. CAM-B3LYP functional with 6-31+G(d,p) (for H, B, and C) and LanL2DZ (for Br) basis sets were used. Red and blue line plots indicate HOMO and LUMO energy levels, respectively.

Table 2. Relationship between optimized C_{cage}–C_{cage} bond length in the excited state and luminescence wavelength

Compounds	Solution			Crystal		
	C _{cage} –C _{cage} / Å ^[a]	$\lambda_{\text{em}}^{\text{calc[a]}}$	$\lambda_{\text{em}}^{\text{exp[b]}}$	C _{cage} –C _{cage} / Å ^[c]	$\lambda_{\text{em}}^{\text{calc[c]}}$	$\lambda_{\text{em}}^{\text{exp}}$
H-H	2.334	586	643	2.216	517	592
Br-H	2.290	602	637	2.230	515	619
Br-Br	2.293	606	643	2.254	520	625
T-H	2.305	631	676	2.238	537	637
T-T	2.307	636	677	2.227	553	671

^[a] Solvent effect of chloroform was considered with polarized continuum model. ^[b] Measured in chloroform solution (1.0×10^{-5} M). ^[c] Estimated by QM/MM analyses.

Next, the author found stark differences in the molecular structures between ground and excited states. The most characteristic difference was observed in the C_{cage}–C_{cage} bond length (Table 2). In the solution state, the bond lengths were 1.778–1.791 Å in the ground state, meanwhile the bond extension was observed to 2.290–2.334 Å in the excited state. In the crystal, the excited-state C_{cage}–C_{cage} bond elongation was also induced to 2.216–2.254 Å. These results suggest that the bond elongation process should be one of the main excited-state structural relaxation processes. The crystal-state suppression of relaxation can induce smaller Stokes shifts in solid than those in CHCl₃ solution. Additionally, these relaxations should lead to non-radiative decays. In the solution state, emission from C,C'-diaryl-*o*-carborane derivatives is quenched by free relaxation. However, in the crystal, such processes should be partially restricted by surrounding molecules, and subsequently intense AIE properties can be induced.

Finally, thermochromic luminescence was theoretically analyzed. Correlation between the C_{cage}–C_{cage} bond length and electronic states suggested the role of the C_{cage}–C_{cage} bond in consecutive shifts of luminescent bands upon temperature change. The S₀ and S₁ potential energy curves (PESs) were calculated through the scan method with variance of the C_{cage}–C_{cage} bond length (Figure 8). By changing the C_{cage}–C_{cage} bond length between 1.8 Å and 2.7 Å in

0.1 Å increment, energy levels were estimated in both ground (S_0^{opt}) and excited states (S_1^{opt}) and corresponding vertically de-excited state (S_0^{FC}). Energy difference between S_1^{opt} and S_0^{FC} states represents luminescent energy with consideration of Franck–Condon approximation. In the S_0 state, elongation of the bond resulted in monotonical increase of potential energy, while S_1 PES had a global minimum around 2.3 Å in the solution state. Here the author applied the method to QM/MM analyses in crystal. PES in the crystalline state showed a steeper energy change along with the lengths of the $C_{\text{cage}}-C_{\text{cage}}$ bond compared to those in the solution state. This difference suggests that structural relaxation processes in solid were restricted because solid-state molecules were confined in the condensed packing state. Global minimum in the crystalline state located around 2.2 Å, reflecting restriction of relaxation. Moreover, differences of energy levels between S_1^{opt} and S_0^{FC} states decreased by increasing the $C_{\text{cage}}-C_{\text{cage}}$ bond length. These data correspond to red-shifts of calculated luminescent wavelengths along with the $C_{\text{cage}}-C_{\text{cage}}$ bond elongation. Based on the above analyses, the author proposes the plausible description of temperature-dependent consecutive PL spectral shifts. By heating solid-state samples, void volume increased. This structural alteration provided more void volumes as enlarged available spaces to proceed larger degree of excited-state structural relaxation mainly triggered through the $C_{\text{cage}}-C_{\text{cage}}$ bond elongation. Then incomplete, but larger degree of elongation results in luminescence in longer wavelength regions at higher temperature regions.

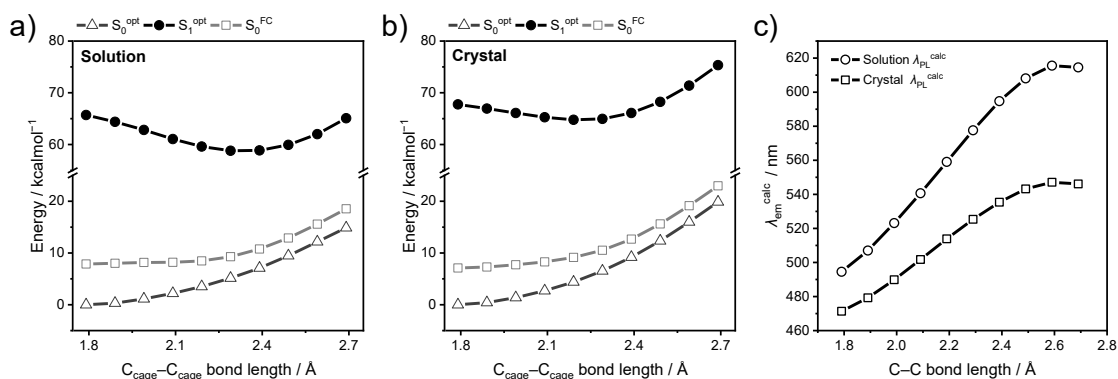


Figure 8. Energy levels of the S_0 and S_1 states modeled in a) solution and b) crystal, and c) calculated emission wavelengths of **H-H** with variable $C_{\text{cage}}-C_{\text{cage}}$ bond lengths.

Conclusion

In this chapter, the author performed mechanistic analyses of temperature dependent luminescence of *C,C'*-diaryl-*o*-carborane derivatives in the solid states. Six novel derivatives were synthesized by bromine-substituted derivatives as key intermediates. Temperature dependence of optical properties and theoretical calculations indicate that the compounds can show the $C_{\text{cage}}-C_{\text{cage}}$ bond elongation as a key excited-state structural relaxation pathway. Thermally-induced expansion or contraction of crystalline lattice affected crystal void volume where excited-state structural changes should be accommodated. The consecutive shifts of the luminescence bands could be explained by the changes in the degree of the relaxation upon thermally-induced micro-environmental alteration in the crystalline state. These results have meanings on the study of excited-state chemistry and material applications of *C*-aryl-*o*-carborane derivatives. These mechanistic analyses of excited-state photophysical dynamics and exploration of stimuli-responsiveness of aryl-*o*-carborane derivatives are promised to be significant information for creating advanced sensing materials.

Experimental Section

Materials

Commercially available reagents used without purification

Decaborane ($B_{10}H_{14}$) (Toronto Research Chemicals), $AgNO_3$ (Fujifilm Wako Pure Chemical Corporation), 2-thiopheneboronic acid (Tokyo Chemical Industry Co., Ltd.), tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) (Tokyo Chemical Industry Co., Ltd.), CuI (Fujifilm Wako Pure Chemical Corporation), Celite® (No. 535, Fujifilm Wako Pure Chemical Corporation), 9-bromoanthracene (Fujifilm Wako Pure Chemical Corporation), 9-anthracenecarbaldehyde (Tokyo Chemical Industry Co., Ltd.), 2,7-dibromo-9,9-didodecyl-9H-fluorene (BLDpharm), 2-bromo-3-dodecylthiophene (Tokyo Chemical Industry Co., Ltd.), bromine (Br_2) (Fujifilm Wako Pure Chemical Corporation), Na_2CO_3 (Fujifilm Wako Pure Chemical Corporation), $NaHSO_3$ (Fujifilm Wako Pure Chemical Corporation), $MgSO_4$ (Fujifilm Wako Pure Chemical Corporation)

Commercially available solvents used after purification

Tetrahydrofuran (THF) (Super deoxidized, stabilizer free, Fujifilm Wako Pure Chemical Corporation) and triethylamine (Et_3N) (Guaranteed reagent, KANTO CHEMICAL CO., INC.) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA).

Commercially available solvents used without purification

Toluene (Deoxidized, Fujifilm Wako Pure Chemical Corporation), acetonitrile (MeCN) (Deoxidized, Fujifilm Wako Pure Chemical Corporation), dichloromethane (CH_2Cl_2) (Deoxidized, Fujifilm Wako Pure Chemical Corporation), ethyl acetate (EtOAc) (Fujifilm Wako Pure Chemical Corporation), *n*-hexane (Fujifilm Wako Pure Chemical Corporation), $CHCl_3$ (Fujifilm Wako Pure Chemical Corporation), methanol (MeOH) (Fujifilm Wako Pure Chemical Corporation), $CDCl_3$ (Eurisotop), CD_2Cl_2 (Eurisotop)

Compounds prepared as described in the literature

H-H³² (2steps, 20% overall yield from 9-bromoanthracene), 9-bromo-10-(4-bromophenylethynyl)anthracene⁴⁹ (2steps, 18% overall yield from 9-anthracenecarbaldehyde), 9,9-didodecyl-2,7-diethynyl-9H-fluorene⁵⁰ (2steps, 80% overall yield from 2,7-dibromo-9,9-didodecyl 9H-fluorene), 3,3'-didodecyl-5,5'-diethynyl-2,2'-bithiophene⁵¹ (4steps, 2% overall yield from 2-bromo-3-dodecylthiophene)

Synthesis

General. Synthetic experiments were performed under dry N₂ atmosphere with typical Schlenk technique unless otherwise noted. ¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR spectra were recorded on a JEOL JNM-ECZ400 and JNM-ECZ400S FT-NMR instrument at 400, 100, and 128 MHz, respectively. Some of ¹H and ¹³C{¹H} spectra were recorded on a JNM-ECZ600R FT-NMR instrument at 600 and 150 MHz, respectively. The ¹H and ¹³C chemical shift values were expressed relative to tetramethylsilane (TMS) (0.00 ppm) or non-deuterated solvent in CD₂Cl₂ (5.32 ppm for ¹H and 53.84 ppm for ¹³C) as an internal standard. The ¹¹B chemical shift values were expressed relative to BF₃·Et₂O (0.00 ppm) as an external standard. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel® C-300 silica gel. High-resolution mass spectrometry (HRMS) spectra were obtained on a Thermo Fisher Scientific Exactive Plus for atmospheric pressure chemical ionization (APCI, mass accuracy < 3ppm RMS) or a Bruker Daltonics ultrafleXtreme for matrix-assisted laser desorption ionization (MALDI, mass accuracy < 1ppm). Characterization of compounds by HRMS was based on the difference between simulated and measured data within 5ppm. Gel permeation chromatography (GPC) was carried out on a SHIMADZU Prominence system equipped with three consecutive polystyrene gel columns (TSK gels: G4000HXL, G3000HXL, G2500HXL) using chloroform as an eluent after calibration with standard polystyrene samples (1.0 mL·min⁻¹) at 40 °C. ¹³C{¹H} NMR measurements on JNM-ECZ600R FT-NMR instrument and HRMS were performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University).

Synthesis of Br-H. To the CH₂Cl₂ (10 mL) solution of **H-H** (77 mg, 0.19 mmol), CH₂Cl₂ (1.0 mL) solution of Br₂ (16 μ L, 0.31 mmol) was added at 0 °C under ambient atmosphere. The reaction mixture was stirred by magnetic stirrer for 30 min at 0 °C, then the reaction temperature was raised to room temperature. After stirred for 18 h at room temperature, the mixture was quenched by aqueous NaHSO₃. Then the organic layer was washed with water and brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed by a rotary evaporator to afford an orange solid. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give an orange solid. Recrystallization of the residual solid from MeOH/CHCl₃ ca. 10/1 (v/v) at 85 °C afforded **Br-H** as an orange crystal (21 mg, 44 μ mol, 23%). ¹H NMR (400MHz, CDCl₃): δ (ppm) 8.98 (d, *J* = 8.8 Hz, 2H), 8.28 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.52–7.44 (m, 4H), 6.92 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.55 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.39 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.39–1.35 (m, 10H). ¹³C{¹H} NMR (150 MHz, CDCl₃): 134.10, 130.39, 130.06, 129.85, 129.72, 128.71, 127.23, 127.22, 126.49, 126.43, 125.49, 119.41, 94.60, 89.79. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ (ppm) 0.17, –2.73, –9.34, –10.46. HRMS (n-APCI): calcd. for C₂₂H₂₃B₁₀Br⁺ [M]⁺ 476.1971, found 476.1965, error 1.3ppm.

Synthesis of T-H. In the 2-necked test tube, **Br-H** (27 mg, 57 μ mol), 2-thiopheneboronic acid (10 mg, 78 μ mol), Pd(PPh₃)₄ (2 mg, 2 μ mol) and Na₂CO₃ (15 mg, 0.14 mmol) were dissolved in THF (0.9 mL) and distilled water (0.1 mL, bubbling with dried N₂ for ca. 15 min was performed before use) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer and heated at 80 °C for 3 h. The black-red solution was diluted with EtOAc and H₂O, then the organic layer was washed with water and brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed by a rotary evaporator to afford an orange solid. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give a red solid. Recrystallization of the residual solid from MeOH/CHCl₃ ca. 5/1 (v/v) at 85 °C afforded **T-H** as an orange crystal (7 mg, 15 μ mol, 26%). ¹H NMR (400MHz, CD₂Cl₂): δ (ppm) 9.03 (d, *J* = 6.0 Hz, 2H), 7.60 (dd, *J* = 3.4, 0.6 Hz, 1H), 7.55 (dd, *J* = 6.0, 0.8 Hz, 2H), 7.50–7.47 (m, 2H), 7.32–7.29 (m, 2H), 7.24 (dd, *J* = 3.6, 2.4 Hz, 1H), 7.08 (tt, *J* = 5.0, 0.6 Hz, 1H), 6.91 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.66–6.63 (m, 2H), 6.48 (dd, *J* = 6.0, 0.8 Hz, 2H) 4.23–1.56 (br, 10H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 137.83, 135.04, 133.62, 132.03, 130.70, 130.41, 130.39, 130.35, 127.66, 127.53, 127.41, 126.61, 126.58, 125.54, 125.43, 120.25, 95.50, 91.19. ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂): δ (ppm) –0.21, –3.01, –9.30, –10.60. HRMS (n-APCI): calcd. for C₂₆H₂₆B₁₀S+Cl⁺ [M+Cl]⁺ 515.2380, found 515.2403, error 4.5ppm.

Synthesis of Br-Br. In the 30 mL 2-necked round bottom flask, 9-Bromo-10-(4-bromophenylethynyl)anthracene (438 mg, 1.00 mmol), decaborane (277 mg, 2.27 mmol) and AgNO₃ (37 mg, 0.22 mmol) were dissolved in toluene (5.0 mL) and MeCN (0.63 mL) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer and refluxed at 110 °C for 3 h. After additional amount of toluene (2.5 mL) and MeCN (0.3 mL) were added, the reaction mixture was refluxed for 14 h. After filtration to remove any insoluble impurities, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/20 (v/v)) to give an orange solid. Recrystallization of the residual solid from MeOH/CHCl₃ ca. 2/1 (v/v) at 90 °C afforded **Br-Br** as an orange crystal (156 mg, 0.17 mmol, 28%). ¹H NMR (400MHz, CDCl₃): δ (ppm) 8.95 (dd, *J* = 8.0, 2.0 Hz, 2H), 8.34 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.54–7.47 (m, 4H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.22 (d, *J* = 9.2 Hz, 2H), 4.38–1.65 (br, 10H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 134.13, 131.38, 130.46, 130.39, 128.81, 128.78, 127.30, 126.55, 126.38, 125.70, 125.16, 118.85, 93.45, 90.09. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ (ppm) 0.29, -2.48, -9.32, -10.28. HRMS (n-APCI): calcd. for C₂₂H₂₂B₁₀Br₂⁻ [M]⁻ 554.1076, found 554.1079, error 0.5ppm.

Synthesis of T-T. In the 2-necked test tube, **Br-Br** (56 mg, 0.10 mmol), 2-thiopheneboronic acid (30 mg, 0.23 mmol), Pd(PPh₃)₄ (3 mg, 3 μmol) and Na₂CO₃ (27 mg, 0.25 mmol) were dissolved in THF (1.6 mL) and distilled water (0.3 mL, bubbling with dried N₂ for ca. 15 min was performed before use) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer and heated at 80 °C for 2 h. The black-red solution was diluted with EtOAc and water, then the organic layer was washed with water and brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed by a rotary evaporator to afford a red solid. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give a red solid. Recrystallization of the residual solid from MeOH/CHCl₃ ca. 5/1 (v/v) at 80 °C afforded **T-T** as a red crystal (29 mg, 52 μmol, 51%). ¹H NMR (400MHz, CD₂Cl₂): δ (ppm) 9.05 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.50 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.34–7.29 (m, 3H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.07 (dd, *J* = 3.1, 1.6 Hz, 1H), 7.03 (dd, *J* = 5.4, 3.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 2H), 4.64–1.60 (br, 10H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 142.62, 137.71, 136.35, 135.24, 133.63, 132.07, 130.95, 130.20, 129.48, 128.56, 127.37, 127.23, 126.69, 126.56, 126.50, 125.63, 125.47, 124.81, 125.57, 120.28, 95.64, 91.83. ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂): δ (ppm) -0.19, -2.94, -9.27, -10.49. HRMS (n-APCI): calcd. for C₃₀H₂₈B₁₀S₂+H⁺ [M+H]⁺ 563.2636, found 563.2660, error 4.3ppm.

Synthesis of o-FL. In the 2-necked test tube, **Br-Br** (150 mg, 0.27 mmol), 9,9-didodecyl-1,7-diethynyl-9*H*-fluorene (148 mg, 0.27 mmol), Pd(PPh₃)₄ (6 mg, 5 μmol) and CuI (1 mg, 5 μmol) were dissolved in THF (1.2 mL) and Et₃N (0.5 mL) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer and refluxed at 80 °C for 46 h. The black-red solution was diluted with CHCl₃ and filtrated with Celite[®], then the CHCl₃ solution was reprecipitated into MeOH. After filtration under reduced pressure, a reddish orange solid (231 mg) was obtained. The small molecules were extracted by Soxhlet extractor with MeOH at 110 °C for 7 h and *n*-hexane at 90 °C for 13.5 h, then the residual solid was dissolved in hot CHCl₃ at 105 °C. After the solvent was removed by rotary evaporator, the CHCl₃ solution of the red solid was reprecipitated into MeOH. After filtration under reduced pressure, **o-FL** was obtained as a reddish orange solid (163 mg, 64%). $M_n = 3,200$, $M_w = 4,200$, $M_w/M_n = 1.31$. ¹H NMR (400MHz, CDCl₃): δ (ppm) 9.20–8.88 (br, 8H), 8.64–8.38 (m, 8H), 7.92–6.94 (m, 40H), 6.92–6.64 (m, 8H), 6.34–6.40 (br, 5H), 6.32–6.14 (m, 3H), 4.79–1.65 (br, 49H), 1.37–0.24 (br, 177H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 151.49, 151.40, 151.32, 151.13, 141.18, 141.06, 140.62, 140.50, 133.50, 132.49, 132.23, 132.07, 131.43, 131.26, 131.11, 130.34, 130.12, 130.00, 129.88, 129.07, 127.14, 126.79, 126.67, 126.45, 126.36, 126.16, 125.81, 125.70, 125.33, 125.27, 123.44, 123.36, 123.03, 121.92, 121.77, 121.57, 120.47, 120.33, 120.23, 119.66, 119.19, 105.67, 105.59, 105.40, 94.83, 93.97, 92.71, 91.35, 90.86, 88.68, 86.42, 86.26, 77.77, 77.63, 77.33, 77.22, 77.02, 76.70, 55.46, 55.34, 55.24, 40.52, 40.32, 40.23, 40.04, 31.87, 31.72, 30.18, 30.03, 29.96, 29.61, 29.31, 28.86, 28.71, 23.94, 23.79, 22.64, 14.10. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ (ppm) –4.50, –10.70.

Synthesis of o-BT. In the 2-necked test tube, **Br-Br** (168 mg, 0.30 mmol), 3,3'-didodecyl-5,5'-diethynyl-2,2'-bithiophene (168 mg, 0.30 mmol), Pd(PPh₃)₄ (7 mg, 6 μmol) and CuI (1 mg, 5 μmol) were dissolved in THF (1.3 mL) and Et₃N (0.6 mL) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer and refluxed at 80 °C for 46 h. The black-red solution was diluted with CHCl₃ and filtrated with Celite[®], then the CHCl₃ solution was reprecipitated into MeOH. After filtration under reduced pressure, a red solid (267 mg) was obtained. The small molecules were extracted by Soxhlet extractor with MeOH at 110 °C for 4.5 h and *n*-hexane at 95 °C for 13.5 h, then the residual solid was dissolved in hot CHCl₃ at 105 °C. After the solvent was removed by rotary evaporator, the CHCl₃ solution of the red solid was reprecipitated into MeOH. After filtration under reduced pressure, **o-BT** was obtained as a reddish orange solid (119 mg, 42%). $M_n = 3,500$, $M_w = 5,700$, $M_w/M_n = 1.64$. ¹H NMR (400MHz, CDCl₃): δ (ppm) 9.48–8.66 (m, 2H), 8.62–7.86 (m, 2H), 7.86–7.29 (m, 6H), 7.13–6.00 (m, 4H),

4.94–1.78 (br, 14H), 1.72–1.42 (br, 4H), 1.42–0.93 (br, 36H), 0.93–0.35 (br, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 143.41, 143.20, 135.12, 134.60, 134.05, 133.44, 133.13, 132.09, 131.79, 131.63, 131.43, 131.01, 130.93, 130.40, 130.26, 129.95, 129.86, 129.00, 126.68, 126.28, 126.16, 125.98, 125.72, 125.31, 122.82, 122.71, 122.47, 97.45, 94.00, 90.78, 77.62, 77.33, 77.22, 77.01, 76.69, 31.92, 30.71, 29.72, 29.48, 29.38, 28.98, 22.68, 22.50, 14.13. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) –3.20, –10.31.

Single-crystal X-ray Diffraction Analysis

The X-ray crystallographic analysis was carried out with a Rigaku Saturn 724+ with MicroMax-007 HF CCD diffractometer with Varimax Mo optics using graphite-monochromated Mo $\text{K}\alpha$ radiation. Temperature control was performed by Rigaku nitrogen gas splaying cooler (temperature controller: CHINO KP 1000, gas generator: Iwatani gas GN-12). The structures were solved with SHELXT 2015⁵² and refined on F^2 with SHELXL 2015⁵³ on Olex 2-1.2.⁵⁴ All hydrogen atoms were placed at calculated positions and refined using a riding model. The program *Mercury 2020.3.0*⁵⁵ and *ORTEP-3*⁵⁶ was used to generate the X-ray structural diagram. The volume of void in the crystal structure was calculated by the program *CrystalExplorer 21.5*.⁵⁷ Isovalue was set as $0.002 \text{ e} \cdot \text{au}^{-3}$.

Table 3. Crystallographic data

Compound name	H-H	Br-H	Br-Br	T-H	T-T
CCDC number	2411824	2411825	2411826	2411827	2411828
Empirical formula	C ₂₂ H ₂₄ B ₁₀	C ₂₂ H ₂₃ B ₁₀ Br	C ₂₂ H ₂₂ B ₁₀ Br ₂	C ₂₆ H ₂₆ B ₁₀ S	C ₃₀ H ₂₈ B ₁₀ S ₂
Formula weight	396.51	475.41	554.31	478.63	560.74
Temperature / K	143(2)	143(2)	143(2)	143(2)	143(2)
Wavelength / Å	0.71075	0.71075	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ /n (No.14)	<i>C</i> 2/c (No.15)	<i>C</i> 2/c (No.15)	<i>P</i> $\bar{1}$ (No.2)	<i>P</i> 2 ₁ /c (No.14)
<i>a</i> / Å	11.896(6)	30.080(8)	30.140(7)	9.459(4)	11.075(4)
<i>b</i> / Å	12.504(6)	10.105(3)	10.366(2)	11.316(5)	19.436(8)
<i>c</i> / Å	14.801(7)	17.857(5)	17.799(4)	12.775(6)	13.485(5)
α / °	90	90	90	109.650(5)	90
β / °	99.230(7)	124.970(3)	123.658(2)	100.826(3)	97.585(7)
γ / °	90	90	90	99.410(5)	90
<i>V</i> / Å ³	2172.9(19)	4448(2)	4629.1(18)	1226.3(9)	2877(2)
<i>Z</i>	4	8	8	2	4
ρ / g·cm ⁻³	1.212	1.420	1.591	1.296	1.294
<i>a</i> / cm ⁻¹	0.061	1.859	3.514	0.149	0.208
<i>F</i> (000)	824	1920	2192	496	1160
θ range / °	3.230–27.486	3.140–27.490	3.100–27.485	3.057–27.488	3.048–27.527
Limiting indices	$-15 \leq h \leq 12$ $-16 \leq k \leq 16$ $-18 \leq l \leq 19$	$-38 \leq h \leq 37$ $-13 \leq k \leq 12$ $-22 \leq l \leq 23$	$-34 \leq h \leq 39$ $-13 \leq k \leq 13$ $-21 \leq l \leq 23$	$-11 \leq h \leq 12$ $-13 \leq k \leq 14$ $-16 \leq l \leq 16$	$-14 \leq h \leq 13$ $-25 \leq k \leq 25$ $-17 \leq l \leq 13$
Collected unique reflections	17387/4974	17643/5079	18383/5309	10041/5379	23165/6496
<i>R</i> _{int} ^[a]	0.1491	0.0410	0.0631	0.0486	0.0847
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.130	0.777	0.824	0.872	1.092
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.1187	0.0370	0.0281	0.0416	0.0742
<i>wR</i> ₂ (all data) ^[d]	0.2188	0.1153	0.0631	0.0990	0.1864

^[a] $R_{\text{int}} = \sum ||F_o|^2 - \langle |F_o|^2 \rangle| / \sum |F_o|^2$ ^[b] $S = [\{\sum w(|F_o|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\sum (|F_o|^2 - |F_c|^2)^2 / \sum (|F_o|^2)^2]^{1/2}$

^[d] $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_o|^2) + (ap)^2 + bp]$, where $p = [|F_o|^2 + 2|F_c|^2] / 3$

Table 4. Crystallographic data of **H-H** measured at different temperatures

Temperature / K	143(2)	208(2)	243(2)
CCDC number	2411824	2425738	2425739
Empirical formula	C ₂₂ H ₂₄ B ₁₀	C ₂₂ H ₂₄ B ₁₀	C ₂₂ H ₂₄ B ₁₀
Formula weight	396.51	396.51	396.51
Wavelength / Å	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /n (No.14)	<i>P</i> 2 ₁ /n (No.14)	<i>P</i> 2 ₁ /n (No.14)
<i>a</i> / Å	11.896(6)	11.912(2)	11.910(3)
<i>b</i> / Å	12.504(6)	12.511(2)	12.514(3)
<i>c</i> / Å	14.801(7)	14.825(3)	14.838(3)
α / °	90	90	90
β / °	99.230(7)	99.261(3)	99.142(3)
γ / °	90	90	90
<i>V</i> / Å ³	2172.9(19)	2180.6(7)	2183.5(8)
<i>Z</i>	4	4	4
ρ / g·cm ⁻³	1.212	1.208	1.206
<i>a</i> / cm ⁻¹	0.061	0.061	0.061
<i>F</i> (000)	824	824	824
θ range / °	3.230–27.486	3.257–27.487	3.223–27.478
Limiting indices	–15 ≤ <i>h</i> ≤ 12 –16 ≤ <i>k</i> ≤ 16 –18 ≤ <i>l</i> ≤ 19	–11 ≤ <i>h</i> ≤ 15 –16 ≤ <i>k</i> ≤ 15 –19 ≤ <i>l</i> ≤ 19	–15 ≤ <i>h</i> ≤ 13 –15 ≤ <i>k</i> ≤ 14 –19 ≤ <i>l</i> ≤ 19
Collected unique reflections	17387/4974	17321/4980	17258/4922
<i>R</i> _{int} ^[a]	0.1491	0.0328	0.0488
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.130	1.083	0.962
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.1187	0.0462	0.0488
<i>wR</i> ₂ (all data) ^[d]	0.2188	0.1294	0.1381

^[a] $R_{\text{int}} = \sum ||F_0|^2 - \langle |F_0|^2 \rangle| / \sum |F_0|^2$ ^[b] $S = [\{\sum w(|F_0|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\sum (|F_0|^2 - |F_c|^2)^2 / \sum (|F_0|^2)^2]^{1/2}$

^[d] $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w(|F_0|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Optical Properties

UV–vis absorption and diffusion reflectance spectra were obtained on a SHIMADZU UV3600i plus spectrophotometer. PL spectra were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer and an Oxford Optistat DN for temperature control. The fluorescence quantum yield (QY) was recorded on a HAMAMATSU Quantaurus-QY Plus C13534-01 model. The PL lifetime measurement was performed on a HORIBA FluoroCube spectrofluorometer system with a UV diode laser (NanoLED 369 nm) or a HORIBA Deltaflex spectrofluorometer system with a UV diode laser (DeltaDiode 375 nm). Spectroscopic measurements were performed at room temperature unless otherwise noted. Solvents guaranteed as spectroscopic grade were used for the measurements.

Theoretical Calculation

General. The Gaussian 16 program Revision C.01 package⁵⁸ was used for density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. CAM-B3LYP/6-31+G(d,p) (for H, B, and C) and LanL2DZ (for Br) levels were used. Effective core potential was calculated with LanL2DZ level. Geometry optimization was conducted for each compound in ground singlet (S_0) and excited singlet (S_1) states. Optimized structures at S_0 states were obtained for all compounds and confirmed as local minimum on each potential energy surface using frequency calculations. Kohn-Sham orbitals of HOMOs and LUMOs were generated from the optimized structure using GaussView 6 (isovalue: 0.02).

QM/MM. The molecular structures in crystalline state were optimized by the quantum mechanics / molecular mechanics (QM/MM) method. The molecular coordinates for QM/MM analyses were extracted from single-crystal structures. The calculation models were constructed by adding molecules until fully covering central one molecule with surrounding molecules in ball and stick drawing mode. The central one molecule in the high layer was calculated at QM calculation and the surround molecules in the low layer were dealt in the universal force field.⁵⁹

Scan calculation. The S_0 and S_1 potential energy curves (PESs) were calculated through scan method with variance of $C_{\text{cage}}-C_{\text{cage}}$ bond between 1.8–2.7 Å (0.1 Å increments). Opt=modredundant keyword was used for restricted structural optimization.

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Chapter 2

Macrocyclic *C,C'*-Diaryl-*o*-Carborane Derivatives Containing Pseudo-Crown Ether: Emission Enhancement upon Cation Recognition

Abstract

Luminescent properties of aggregation-induced emission (AIE)-active chromophores are critically affected by the presence of non-radiative decay processes from the excited state to ground state. Mechanistic understanding of the excited-state structural relaxation pathways is of importance to design and manipulate their photophysics. Here the author reports AIE properties of macrocyclic *C,C'*-diaryl-*o*-carborane derivatives and modulation of luminescent properties by adding cations through the regulation of excited-state structural relaxation. The *C,C'*-diaryl-*o*-carborane moieties were incorporated into pseudo-crown ether unit that captures alkali metal cations through electrostatic interactions. It was demonstrated that cation recognition induced the emission enhancement and suppression of non-radiative decay process by the construction of the macrocyclic structures.

Introduction

Aggregation-induced emission (AIE) is a photophysical phenomenon that molecules exhibit only trace luminescence in the solution state, but bright luminescence in the aggregate or solid state.¹ AIE-active luminogens (AIEgens) have attracted tremendous attention in material science because of their huge potential for the platform of solid-state luminescent materials in organic device applications. Since the discovery of AIE by Tang,² various types of AIEgens have been reported so far. Mechanistic studies revealed the critical role in the manipulation of non-radiative decay processes from the photo-excited state to ground state based on the restriction of intramolecular motion (RIM).^{3,4} Recent review has summarized several possible models of RIM, in which excited-state structural relaxation process has a pivotal role,⁵ suggesting that precise regulation of the excited-state geometrical change enables further manipulation of AIEgens and their material applications.

Tanaka and Chujo *et al.* have focused on the aryl-modified *o*-carborane⁶ as an emerging AIEgens.^{7,8} AIE properties accompanying intramolecular charge transfer (ICT) emission have been observed from a series of *C*-aryl derivatives.^{9–17} The charge transfer is supposed to occur via electronic conjugation between $\pi^{(*)}$ -orbital of aryl units and σ^{*} -orbital of carbon–carbon bond in the cluster ($C_{\text{cage}}-C_{\text{cage}}$), which causes the elongation of $C_{\text{cage}}-C_{\text{cage}}$ bond.^{18,19} Previously, Tanaka *et al.* reported that the bond elongation was involved in the emission annihilation in the AIE behaviors.²⁰ Recently the author reported solid-state temperature-dependent luminescent properties based on the manipulation of the degree of bond elongation in crystals, which showed controllability of the relaxation processes of aryl-*o*-carboranes.²¹ It was suggested that excited-state intramolecular rotation of aryl groups can be related to AIE properties as well. At this stage, further investigation into the excited-state relaxation processes is needed toward full understanding of the AIE behavior of aryl-*o*-carboranes.

Herein, the author reports molecular recognition as a new strategy to control the excited-state relaxation process because the degree of structural change can be easily modified by changing guests. Utilizing *C,C'*-diaryl-*o*-carborane scaffold presented in Chapter 1 as a key building block,²¹ the author synthesized macrocycles containing tetraethylene glycol (TEG), pseudo-crown ether, units (Figure 1), which can act as molecular recognition sites and regulate the structural change.^{22–25} V-shaped model compounds bearing two methoxy groups were also synthesized to discuss the effects of macrocyclization. The author found that macrocycles and V-shaped compounds have AIE properties. Macrocycles can capture alkali metal cations, which induced emission enhancement accompanied by hypochromic shifts. Photophysical analyses indicate that the suppression on non-radiative decays should occur upon cation recognition.

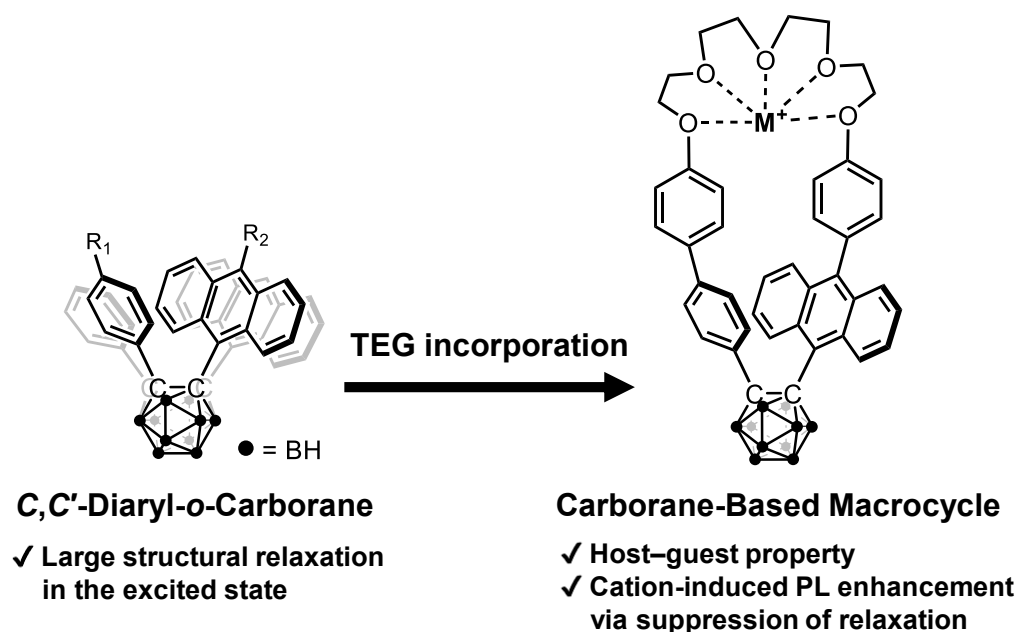


Figure 1. Schematic illustration of this chapter.

Bpin-Ph-TEG
 $\text{Pd}(\text{PPh}_3)_4$
 Na_2CO_3
 KPF_6
 THF / H_2O
 reflux
 19 h
 20%

C1

Bpin-Ph-OMe
 $\text{Pd}(\text{PPh}_3)_4$
 Na_2CO_3
 THF / H_2O
 reflux
 38 h
 47%

M1

Bpin-Ph-TEG
 $\text{Pd}(\text{PPh}_3)_4$
 Na_2CO_3
 KPF_6
 THF / H_2O
 reflux
 21 h
 28%

C2

Bpin-Ph-OMe
 $\text{Pd}(\text{PPh}_3)_4$
 Na_2CO_3
 THF / H_2O
 reflux
 24.5 h
 10%

M2

Bpin-Ph-TEG

Bpin-Ph-OMe

The host–guest properties of **C1** and **C2** were examined by ^1H NMR titration. Alkali metal salts of hexafluorophosphate (MPF_6 , $\text{M} = \text{K}, \text{Rb}, \text{Cs}$) were used as guests. As shown in Figure 2, the addition of K^+ or Rb^+ to macrocycles **C1** and **C2** resulted in downfield shifts of the signal peaks (+0.05 ppm for **C2** with 12 eq. of K^+) of the protons assignable to tetraethylene glycol (TEG) moieties, indicating that both macrocycles can interact with cations. For V-shaped compounds of **M1** and **M2**, no change in chemical shifts of methoxy moiety was observed in the presence of K^+ ($\Delta\delta < 0.01$ ppm), meaning that **M1** and **M2** hardly capture cations.

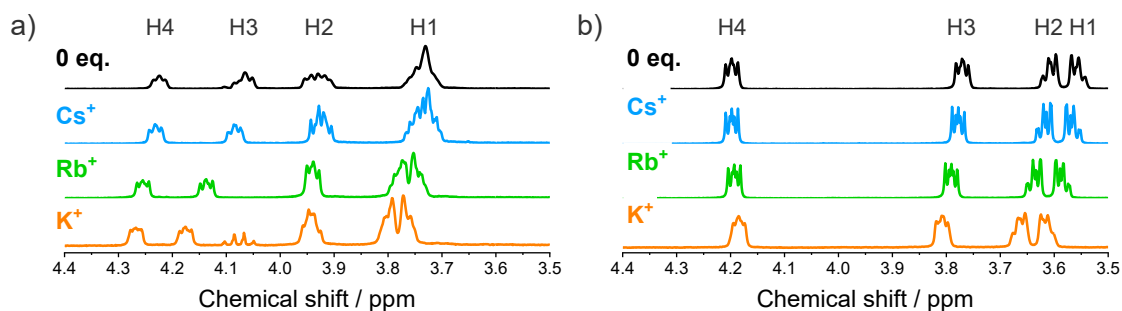


Figure 2. ^1H NMR spectra of a) **C1** and b) **C2** without any cations or with K^+ , Rb^+ , or Cs^+ (12 eq.) in acetone- d_6 / CDCl_3 (3/2, v/v) (2.0×10^{-3} M) solution. The labelled H1–4 peaks represent the proton signals assignable to TEG segments.

Job plots of **C1** and **C2** with K^+ and Rb^+ were prepared by monitoring the chemical shift changes of H4 peak of **C1** and H1 peak of **C2**. The plots indicated a 1:1 binding stoichiometry (Figure 3). From the ^1H NMR titration data, association constants (K_a) were estimated from spectral fitting with a 1:1 stoichiometry model (Table 1).²⁶ In contrast in the titration with Cs^+ , the chemical shift changes were not large enough to determine stoichiometry and K_a , suggesting that macrocycles may weakly interact with Cs^+ in different stoichiometries probably due to the larger cation radius of Cs^+ . For Na^+ , the iodide salt was used instead of PF_6 salt for titration of **C2** because of the low solubility of NaPF_6 , but only weak binding was detected ($\log K_a = 1.33 \pm 0.08$). These results suggest that macrocycles have a suitable size for capturing K^+ or Rb^+ .

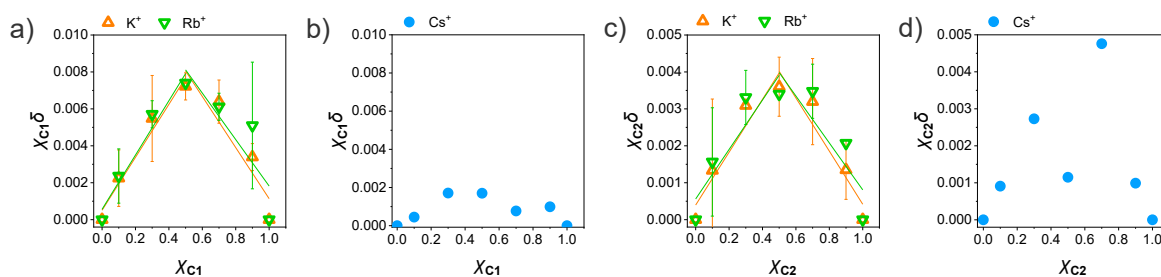


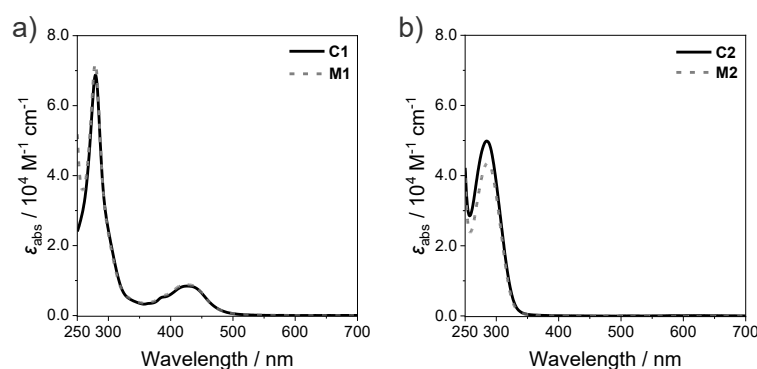
Figure 3. Job plots obtained from ^1H NMR measurements of (a, b) **C1** and (c, d) **C2** with hexafluorophosphate salt of (a, c) K^+ and Rb^+ , and (b, d) Cs^+ . Error bars represent standard deviation of uncertainty.

Table 1. Association constants (K_a) for alkali metal cations

M^+	Radius / pm ^[a]	$\log K_a$	
		C1	C2
K^+	138	2.13 ± 0.06	1.80 ± 0.05
Rb^+	152	2.73 ± 0.07	2.55 ± 0.16

[a] Ref.²⁷

The author conducted photophysical measurements of the compounds. According to the UV–vis absorption spectra between **C1** and **M1** and those of **C2** and **M2**, it is indicated that macrocyclization hardly affects the electronic structures in the ground state (Figure 4).

**Figure 4.** UV–vis absorption spectra of a) **C1** and **M1** and b) **C2** and **M2** in $CHCl_3$ (1.0×10^{-5} M).

Then, the author focused on the excited-state electronic structure. In both solution and crystal states, four compounds showed broad photoluminescence (PL) spectra with large Stokes shifts. As observed in previous reports on the *C*-anthryl-*C'*-phenyl-*o*-carborane derivatives,^{17,21} these luminescence bands should be assigned to the typical ICT emission character. By comparing the properties of macrocycles and corresponding V-shaped compounds, the author found that cyclization had almost no effect on emission wavelengths in solution state (Figure 5). This result suggests that the structural transformation upon macrocyclization only has a small effect on excited-state relaxation processes in solution. In addition, all compounds showed only slight luminescence in solution (PL quantum yields (Φ_{PL}) ≤ 0.01). This is because of the fully allowed intramolecular motion, which should activate non-radiative decays. In contrast, Φ_{PL} values in

crystal were significantly enhanced ($\Phi_{\text{PL}} \geq 0.54$), indicating AIE properties. Also, the emission wavelengths in crystal hypsochromically shifted from those in solution (Figure 5). In the crystal state, molecular motions should be restricted due to the proximity of surrounding molecules and therefore excited-state relaxation could be suppressed.²⁸ Additionally, macrocyclization caused a blue-shift of luminescence in crystal compared to model compounds, which implies that structural restriction by macrocyclization works more in solid than in solution.

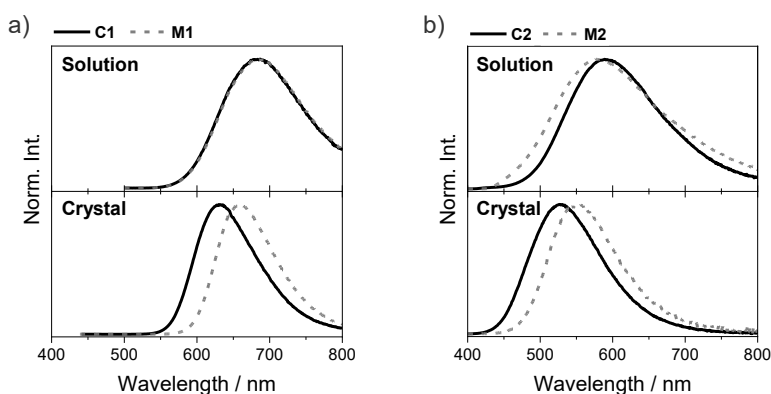


Figure 5. PL spectra of a) **C1** and **M1** and b) **C2** and **M2** in CHCl_3 (1.0×10^{-5} M) (top) and crystal (bottom).

Next, the effects of complexation with cations on optical properties were investigated. Photophysical measurements of **C1** and **C2** were conducted with variable equivalents of M^+ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) (Figure 6). Upon cation addition, emission enhancement and hypsochromic shift of $\lambda_{\text{PL,max}}$ were observed in both macrocyclic compounds. For example, **C1** showed 2.8-fold emission enhancement accompanying 10 nm PL blue shift with 500 eq. of K^+ . Compared with Rb^+ , complexation with K^+ led to a larger emission enhancement despite its smaller K_a value. For Cs^+ , only slight changes of emission properties were observed, meaning the low ability of complexation. In contrast, no significant change in optical properties was observed in **M1** and **M2** even with 500 eq. of K^+ (Figure 7). These data clearly indicate that the complexation with cations affected the change in optical properties.

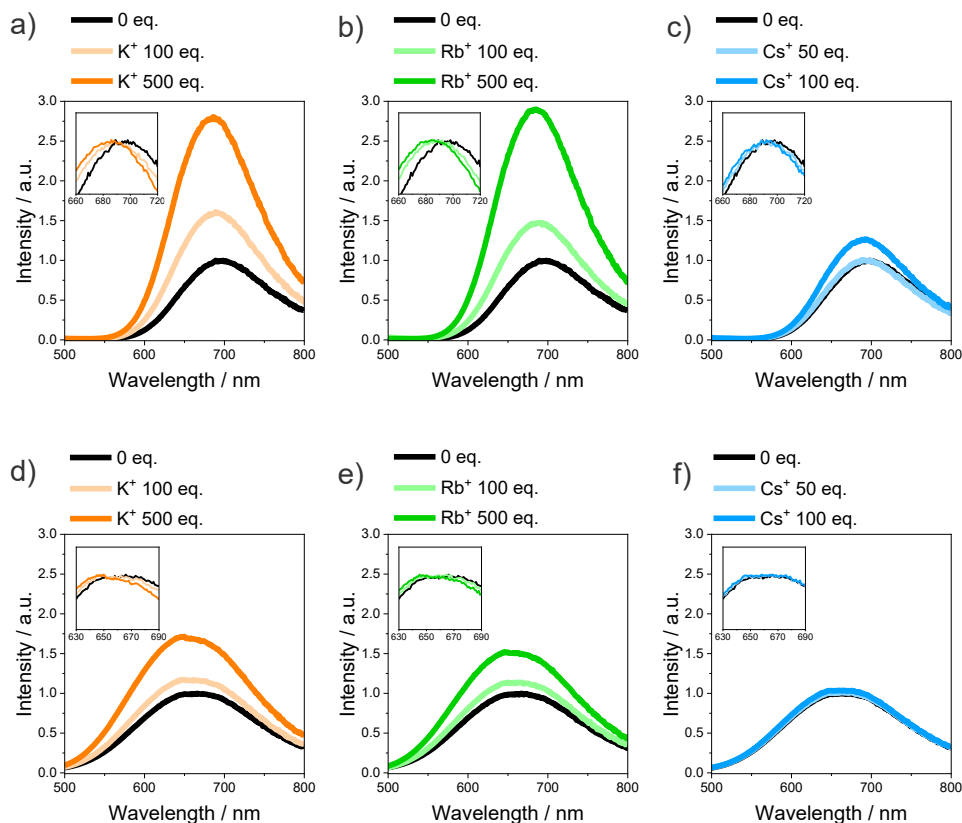


Figure 6. PL spectra of **C1** in acetone/ CHCl_3 (3/2, v/v) (1.0×10^{-5} M) (a–c) and **C2** in MeCN/ CHCl_3 (3/2, v/v) (1.0×10^{-5} M) (d–f) with K^+ (a, d), Rb^+ (b, e), and Cs^+ (c, f). Insets: magnified PL spectra.

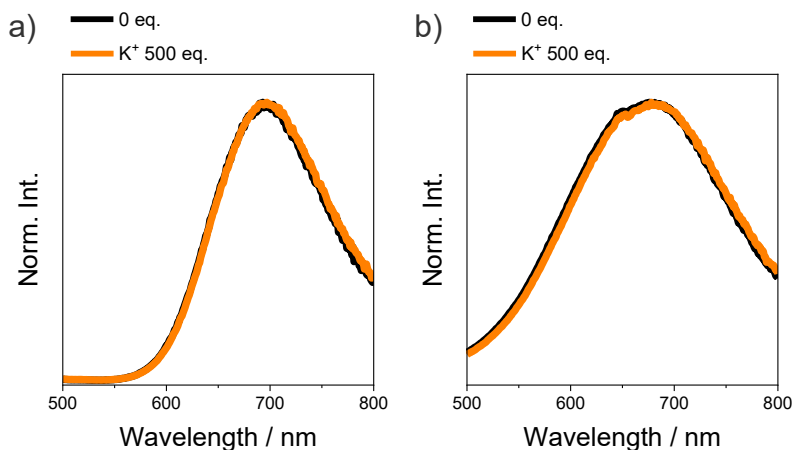


Figure 7. PL spectra of a) **M1** in acetone/ CHCl_3 (3/2, v/v) (1.0×10^{-5} M) and b) **M2** in MeCN/ CHCl_3 (3/2, v/v) (1.0×10^{-5} M) with 0 or 500 eq. of KPF_6 .

To investigate the optical behaviors of macrocycles upon cation addition, further measurements were performed for calculating radiative and non-radiative decay constants (k_r

and k_{nr} , respectively). Optical properties were obtained at low temperature (213 K) to enhance luminescence intensity (Figure 8). The relative PL quantum yields ($\Phi_{\text{PL,rel}}$) were calculated compared to $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$. As shown in Table 2, decreases in k_{nr} values were observed by the addition of 500 eq. of K^+ , suggesting that complexation with cation suppressed non-radiative decay process of *o*-carborane containing macrocycles through RIM.

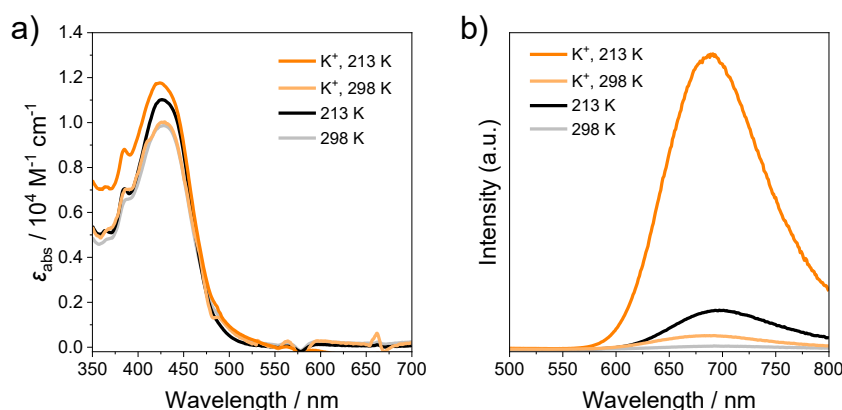


Figure 8. a) UV-vis absorption and b) PL spectra of **C1** in acetone/ CHCl_3 (3/2, v/v) (1.0×10^{-5} M) with 0 or 500 eq. of KPF_6 at 213 or 298 K.

Table 2. Optical properties of **C1** with or without KPF_6 at 213 K^[a]

Eq. of KPF_6	τ / ns ^[b]	τ_{ave} / ns ^[c]	$\Phi_{\text{PL,rel}}$ (%) ^[d]	k_{r} / 10^7 s^{-1} ^[e]	k_{nr} / 10^8 s^{-1} ^[f]
0	1.51 (78%), 0.32 (22%)	1.2	4.7	4.6	7.7
500	3.38 (91%), 0.96 (9%)	3.2	42	13	1.8

^[a] Measured in 1.0×10^{-5} M acetone/ CHCl_3 (3/2, v/v). ^[b] Excited at 375 nm and detected at 683 nm. ^[c] $\sum_i \tau_i f_i$, τ_i : luminescent lifetime of *i*th component (ns), f_i : relative amplitude of *i*th component (%). ^[d] Relative quantum yield. ^[e] Radiative decay constant calculated by $\Phi_{\text{PL,rel}}/\tau_{\text{ave}}$. ^[f] Non-radiative decay constant calculated by $(1-\Phi_{\text{PL,rel}})/\tau_{\text{ave}}$.

To elucidate the mechanism behind the cation-induced emission changes, the quantum chemical calculations were performed using density functional theory (DFT) and time-dependent DFT (TD-DFT). According to the previous study,²⁹ B3PW91-D3/6-31+G(d,p) level was selected. From the calculations with **C1** and its K^+ complex (**K@C1**), it was shown that the theoretical emission wavelengths (λ_{em}) of **K@C1** were hypsochromically shifted compared with **C1** (**K@C1**, 606 nm; **C1**, 633 nm), suggesting that complexation with cations affect the relaxation processes in the excited state (Figure 9). As for the $C_{cage}-C_{cage}$ bond distance in the S_1 state, almost the same values were obtained with or without cations (**K@C1**, 2.23 Å; **C1**, 2.24 Å), suggesting that coordination of cations should lead to a contraction of the whole macrocyclic structures and suppression of excited-state structural relaxation. These results suggest that complexation with cations should be effective in suppressing the excited-state structural relaxation process accompanied by non-radiative decay pathways.

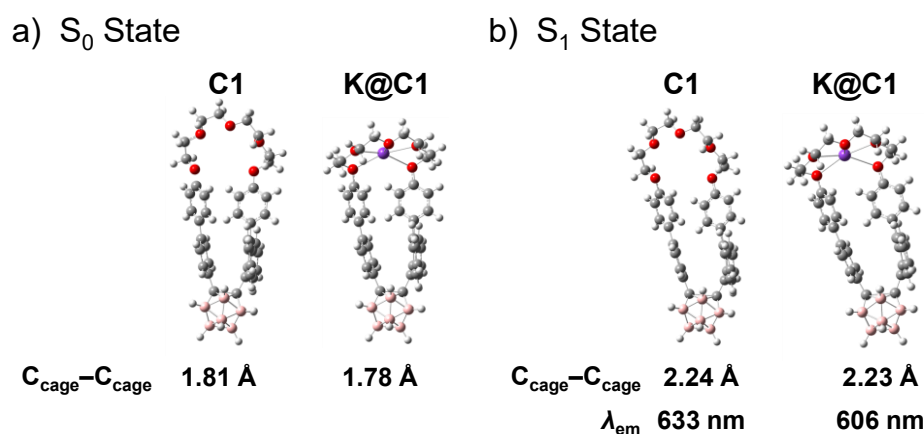


Figure 9. Optimized structures in a) S_0 and b) S_1 states and corresponding $C_{cage}-C_{cage}$ bond lengths and emission wavelengths (λ_{em}) of **C1** and **K@C1**. (Colors: C, gray; B, pink; H, white; O, red; K, purple)

Conclusion

In this chapter, the host–guest and optical property of *o*-carborane based macrocycles were investigated. Upon cation recognition, the macrocycles showed emission enhancement based on the suppression of non-radiative decay pathways. It is proposed that excited-state structural relaxation can be regulated by cation recognition depending on the cation size. These findings provide the design strategy for the modulation of AIE properties based on the regulation of excited-state molecular motions by adding external molecules.

Experimental Section

The experimental details followed that described in Chapter 1, with the differences and additional details summarized below.

Materials

Commercially available reagents used without purification

KPF₆ (Fujifilm Wako Pure Chemical Corporation), K₂CO₃ (Fujifilm Wako Pure Chemical Corporation), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (**Bpin-Ph-OMe**) (Tokyo Chemical Industry Co., Ltd.), 4-bromobenzyl bromide (Tokyo Chemical Industry Co., Ltd.), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (Fujifilm Wako Pure Chemical Corporation), ammonium hexafluorophosphate (Fujifilm Wako Pure Chemical Corporation), tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate (Tokyo Chemical Industry Co., Ltd.)

Commercially available solvents

N,N-Dimethylformamide (Deoxidized, Fujifilm Wako Pure Chemical Corporation), acetone-*d*₆ (Tokyo Chemical Industry Co., Ltd.)

Compounds prepared and characterized as described in the literatures

Br1²¹ (4 steps, 18% overall yield from 4-bromobenzyl bromide (1 step, 29% yield from 9-bromo-10-[2-(4-bromophenyl)ethynyl]anthracene)), **Br2**³⁰ (1 step, 27% overall yield from 1,2-bis(4-bromophenyl)ethyne), **Bpin-Ph-TEG**³¹ (1 step, 58% yield from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol), RbPF₆³² (1 step, 33% yield from ammonium hexafluorophosphate), CsPF₆³² (1 step, 63% yield from ammonium hexafluorophosphate)

Synthesis

General. Part of HRMS spectra were obtained on a Thermo Fisher Scientific Exactive Plus for electron spray ionization (ESI) or atmospheric pressure chemical ionization (APCI).

Synthesis of C1. THF (4.0 mL) solution of **Bpin-Ph-TEG** (0.326 g, 0.55 mmol) was stirred at room temperature under N₂ atmosphere. To a 1 L 2-necked round-bottom flask, THF (ca. 700 mL), **Br1** (0.279 g, 0.50 mmol), KPF₆ (0.466 g, 2.53 mmol), Na₂CO₃ (0.275 g, 2.60 mmol), Pd(PPh₃)₄ (0.017 g, 0.014 mmol), **Bpin-Ph-TEG** solution in THF, and H₂O (125 mL) were added under N₂ atmosphere. The mixture was refluxed for 15 h under N₂ atmosphere. After cooling to room temperature, the solvent was evaporated with a rotary evaporator. The mixture was extracted with CH₂Cl₂. The organic layer was washed with brine and dried over MgSO₄. After filtration and evaporation of the solvent to afford orange solid, the crude was supported

by silica in CHCl_3 and purified by silica gel column chromatography (eluent: $\text{AcOEt}/n\text{-hexane} = 2/1(\text{v/v})$). Recrystallization from MeOH afforded **C2** as a orange powder (0.068 g, 0.09 mmol, 20%). ^1H NMR (600 MHz, CDCl_3 at 0 °C): δ (ppm) = 9.03 (d, $J = 9.0$ Hz, 2H), 7.47 (ddd, $J = 7.5, 1.8, 1.2$ Hz, 2H), 7.35 (dd, $J = 8.7, 0.9$ Hz, 2H), 7.33 (d, $J = 9.0$, 2H), 7.24 (dd, $J = 6.6, 0.6$ Hz, 1H), 7.22 (dd, $J = 6.6, 0.6$ Hz, 1H), 7.19 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.01 (d, $J = 8.4$, 2H), 6.97 (dd, $J = 8.1, 2.1$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 6.54 (d, $J = 8.4$ Hz, 2H), 6.15 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.01 (dd, $J = 7.2, 1.2$ Hz, 1H), 4.20 (t, $J = 4.5$ Hz, 2H), 4.05 (m, 2H), 3.97 (m, 2H), 3.94 (m, 2H), 3.79 (m, 4H), 3.76 (m, 4H), 4.2–2.0 (br, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3 at 0 °C): δ (ppm) = 159.1, 158.2, 142.8, 141.6, 133.4, 132.2, 131.3, 131.1, 130.8, 130.5, 129.6, 128.9, 128.1, 126.6, 126.3, 124.9, 124.8, 124.5, 118.6, 114.9, 114.3, 113.6, 95.6, 92.0, 71.1, 70.8, 70.6, 70.2, 69.5, 69.4, 67.9, 67.2. (Note: Due to the high rotational barrier of the phenyl ring on the anthracene unit, the atoms at inside and outside of the macrocycle were magnetically inequivalent.) $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) = 0.36 (2B), -2.02 (2B), -9.25 (6B). HRMS (ESI) calcd. for $\text{C}_{42}\text{H}_{46}\text{B}_{10}\text{O}_5\text{K}_1^+ [\text{M}+\text{K}]^+$ 779.3934, found 779.3977.

Synthesis of M1. To a 100 mL 2-necked round-bottom flask, **Br1** (0.166 g, 0.30 mmol), **Bpin-Ph-OMe** (0.223 g, 0.90 mmol), Na_2CO_3 (0.085 g, 0.75 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.013 g, 0.0068 mmol) were added under N_2 atmosphere. Then, THF (4.8 mL) and H_2O (0.8 mL) were added and refluxed for 38 h. After cooling to room temperature, the mixture was extracted with AcOEt . The organic layer was washed with brine and dried over MgSO_4 . After filtration and evaporation of the solvent to afford orange solid, the crude was supported by silica in CHCl_3 and purified by silica gel chromatography (eluent: $\text{AcOEt}/n\text{-hexane} = 1/5(\text{v/v})$). Recrystallization from $\text{MeOH}/\text{CHCl}_3$ afforded **M1** as a deep orange powder (0.085 g, 0.14 mmol, 47%). ^1H NMR (600 MHz, CDCl_3 at 0 °C): δ (ppm) = 9.06 (d, $J = 9.0$ Hz, 2H), 7.48 (ddd, $J = 9.0, 6.6, 1.2$ Hz, 2H), 7.37 (dd, $J = 9.0, 1.2$ Hz, 2H), 7.32 (d, $J = 9.0$ Hz, 2H), 7.24 (dd, $J = 5.7, 0.6$ Hz, 1H), 7.23 (dd, $J = 6.6, 0.6$ Hz, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.00 (d, $J = 6.6$ Hz, 1H), 6.96 (d, $J = 9.0$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 6.56 (d, $J = 9.0$ Hz, 2H), 6.38 (d, $J = 7.2$ Hz, 1H), 6.18 (d, $J = 7.8$ Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 4.0–1.8 (br, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3 at 0 °C): δ (ppm) = 159.6, 158.8, 142.6, 141.7, 133.3, 131.8, 131.5, 131.2, 130.6, 130.4, 129.6, 128.7, 128.1, 126.6, 126.3, 125.0, 124.9, 124.4, 118.5, 114.1, 113.7, 113.0, 95.2, 91.5, 55.4, 55.2. (Note: Due to the high rotational barrier of the phenyl ring on the anthracene unit, the atoms that face other phenyl group side and those that do not were magnetically inequivalent.) $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) = 0.48 (1B), -1.95 (1B), -9.63 (8B). HRMS (APCI) calcd. for $\text{C}_{36}\text{H}_{37}\text{B}_{10}\text{O}_2^+ [\text{M}+\text{H}]^+$ 609.3791, found 609.3807.

Synthesis of C2. THF (4.0 mL) solution of **Bpin-Ph-TEG** (0.474 g, 0.79 mmol) was stirred at room temperature under N₂ atmosphere. To a 1 L 2-necked round-bottom flask, THF (ca. 700 mL), **Br2** (0.316 g, 0.70 mmol), KPF₆ (0.647 g, 3.50 mmol), Na₂CO₃ (0.381 g, 3.60 mmol), Pd(PPh₃)₄ (0.020 g, 0.017 mmol), **Bpin-Ph-TEG** solution in THF, and H₂O (100 mL) were added under N₂ atmosphere. The mixture was refluxed for 21 h under N₂ atmosphere. After cooling to room temperature, the solvent was evaporated with a rotary evaporator. The mixture was extracted with CH₂Cl₂. The organic layer was washed with brine and dried over MgSO₄. After filtration and evaporation of the solvent to afford brown solid, the crude was supported by silica in CHCl₃ and purified by silica gel column chromatography (eluent: AcOEt/*n*-hexane = 2/1(v/v)). Recrystallization from MeOH and decantation from *n*-hexane afforded **C2** as a white powder (0.124 g, 0.20 mmol, 28%). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) = 7.36 (d, *J* = 8.8 Hz, 4H), 7.31 (d, *J* = 9.2 Hz, 4H), 7.22 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 4.17 (m, 4H), 3.74 (m, 4H), 3.58 (m, 4H), 3.53 (m, 4H), 3.5–1.6 (br, 10H). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) = 159.3, 142.6, 131.9, 131.6, 128.6, 128.3, 126.1, 115.6, 86.4, 70.9, 70.9, 69.8, 68.2. ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂): δ (ppm) = -2.67 (2B), -10.81 (8B). HRMS (APCI) calcd. for C₃₄H₄₂B₁₀O₅Cl₁⁻ [M+Cl]⁻ 640.3968, found 640.4000.

Synthesis of M2. To a 50 mL 2-necked round-bottom flask, **Br2** (0.091 g, 0.20 mmol), **Bpin-Ph-OMe** (0.141 g, 0.60 mmol), Na₂CO₃ (0.058 g, 0.55 mmol), Pd(PPh₃)₄ (0.019 g, 0.016 mmol) was added under N₂ atmosphere. Then, THF (4.0 mL) and H₂O (0.5 mL) was added and refluxed for 24.5 h. After cooling to room temperature, the mixture was extracted with AcOEt. The organic layer was washed with brine and dried over MgSO₄. After filtration and evaporation of the solvent to afford brown solid, the crude was supported by silica in CHCl₃ and purified by silica gel chromatography (eluent: AcOEt/*n*-hexane = 1/5(v/v)). Recrystallization from MeOH and decantation from hexane afforded **M1** as a light-yellow powder (0.010 g, 0.02 mmol, 10%). **M2** was characterized according to the literature.³³

NMR titration

NMR titration was conducted by using the modified procedures according to the literature.³⁴ ¹H NMR titration experiments were performed on JEOL JNM-ECZ 400 or JEOL JNM-ECZ 400S spectrometers. In this experiment, a solution of hexafluorophosphate salt (potassium, rubidium, and cesium) in acetone-*d*₆ was added to a solution of macrocycle in CDCl₃ at 298 K.

A 40.0 mM solution of the salt was added to 200 μL of a 5.0 mM solution of macrocycle, where 1.0 equivalent of salt added corresponds to 25.0 μL of the salt solution. As for titration of cesium hexafluorophosphate and **C2**, 10.0 mM of the salt was prepared and added in addition of 40.0 mM salt solution. All titration was performed in the mixed solvent of acetone- d_6 /CDCl₃ 3/2(v/v). Association constants were estimated by using the non-linear fitting tool provided by the open access web portal *Supramolecular.org* (<http://supramolecular.org>).

The stoichiometry of the interaction of macrocycles and cations was determined by Job's method based on the chemical shift change (δ) of the TEG protons (H4 for **C1** and H1 for **C2**) and the molar fraction of **C1** or **C2** (χ). All titration was performed in the mixed solvent of acetone- d_6 /CDCl₃ (3/2, v/v). [**C1** or **C2**] + [MPF₆] = 4 mM.

Optical Properties

Relative quantum yield ($\Phi_{\text{PL,rel}}$) was calculated by the following equation³⁵

$$\Phi_{\text{PL,rel}} = \Phi_s \times \left(\frac{A_s}{A_x}\right) \times \left(\frac{F_x}{F_s}\right) \times \left(\frac{n_x}{n_s}\right)^2$$

in which Φ_s , A , F , and n are quantum yield of the standard, absorption, integrated emission intensities, and refractive index, respectively. The subscript x and s refer to the unknown and the reference, respectively. A CHCl₃ solution (1.0×10^{-5} M) of Ru(bpy)₃Cl₂·6H₂O was used as a reference.

Theoretical Calculation

Calculation was performed at DFT B3PW91-D3/6-31+G(d,p) level.

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Chapter 3

Guest-Induced Emission Enhancement in the Permanent Porous Conjugated Carboracycle Crystal

Abstract

Stimuli-responsive aggregation-induced emission is attracting platform for the next-generation smart materials. Macrocyclization can provide available space for host–guest-mediated molecular sensing based on the regulation of excited-state structural change. Here the author found guest-induced photoluminescence (PL) change of crystalline *o*-carborane-based conjugated macrocycle, which forms intrinsic porous crystal with 1D channels. The crystal can be loaded with halogenated ethane derivatives and exhibited guest-induced emission enhancement due to the suppression of excited-state structural relaxation. Notably, the crystal showed successful reversible guest loading without losing its crystalline porosity and heat resistance up to 500 °C.

Introduction

Solid-state emissive molecular materials have attracted tremendous attention toward application for optoelectronics.¹ Conventional chromophores suffer from aggregation-caused quenching, whereas aggregation-induced emission (AIE) can overcome this drawback: AIE luminogens (AIEgens) show slight emission in dispersed states, while exhibiting strong luminescence in solid states.² AIE has a strong relationship with excited-state structural relaxation processes.^{3,4} Surrounding molecules restrict excited-state motion of the chromophore, suppressing non-radiative deactivation processes.⁵ Structure–property relationships of AIEgens have been extensively studied for applications.⁶ Currently expanding their applications to the next-stage smart devices, AIEgens are expected to have stimuli-responsiveness i.e. change emission properties in response to external stimuli.⁷ However, motional restrictions in solid-state often hinder molecular responses to surrounding environments, which potentially decreases their luminescent responsiveness.⁸ In this context, macrocyclization of AIEgens can provide internal cavities accommodating molecular motion, while maintaining AIE properties. Furthermore, host–guest properties of macrocycles enable control of solid-state optical properties.⁹ To date, many studies have reported AIEgen-based macrocycles,¹⁰ whereas only a few reports have addressed solid-state host–guest properties and their effect on luminescence.

A boron and carbon cluster, *o*-carborane, is known as a skeleton to design functional AIEgens.¹¹ *C*-aryl *o*-carborane derivatives typically show intramolecular charge transfer (ICT) emission originating from orbital conjugation between aryl units and the cluster (Figure 1a).¹² The ICT process occurs when planar aryl moieties perpendicularly oriented to carbon–carbon bond in the cluster ($C_{\text{cage}}-C_{\text{cage}}$ bond), accompanied with significant elongation of the bond.¹³ Recent theoretical results suggested the formation of non-emissive charge separated dark state, where planar aryl units parallelly aligned to $C_{\text{cage}}-C_{\text{cage}}$ bond accompanied with further elongation.^{14,15} These emissive ICT and non-emissive dark states may competitively contribute

to emission properties. In Chapter 2, the author found that host–guest interaction can mediate the excited-state structural relaxation pathways of *o*-carborane-based macrocycles containing pseudo-crown ether (Figure 1b).¹⁶ The macrocycles showed emission enhancement upon solution-state host–guest complexation owing to the suppression of molecular motion.

There have been a number of C_3 -symmetric macrocyclic compounds with precise host–guest chemistry (Figure 1c).^{17,18} C,C' -Di-functionalized *o*-carborane can be implemented into the corner of molecular triangles.¹⁹ This chapter reports a macrocycle of cyclo-trimerized diphenyl *o*-carborane (**CB3Ph6**, Figure 1d) as a conjugated type of carboracycle.²⁰ **CB3Ph6** formed permanent intrinsic porous crystal,²¹ where guest-accessible 1D channels were constructed through columnar stacking of macrocycles. **CB3Ph6** showed AIE properties, and its porous crystal showed emission enhancement upon encapsulation of guests. Theoretical calculation suggested that cavity filling by guests can restrict the excited-state structural relaxation leading to non-emissive dark states. Furthermore, the crystal showed reversible guest release and capture without changing its crystalline porosity and no chemical decomposition up to 500 °C.

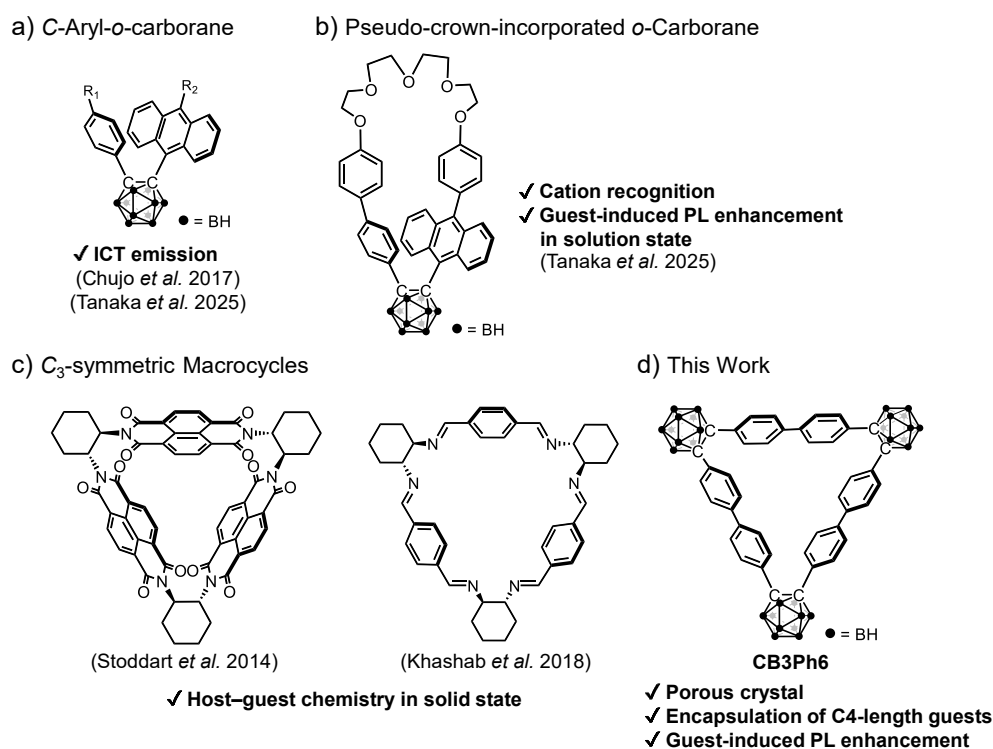
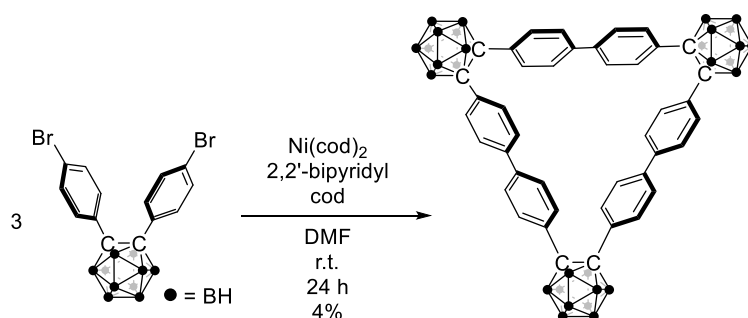


Figure 1. Summary of previous and present works.

Results and Discussion

The targeted macrocycle, **CB3Ph6**, was successfully synthesized by Ni(0)-mediated trimerization of 1,2-bis(4-bromophenyl)-*o*-carborane²² (Scheme 1). A crystal of **CB3Ph6** loaded with 1,2-dichloroethane (DCE) was obtained by vapor diffusion of MeOH into a DCE solution at $-30\text{ }^{\circ}\text{C}$, followed by slow evaporation of solvent at room temperature (**DCE@CB3Ph6**). Single-crystal X-ray diffraction (SCXRD) analysis revealed that DCE molecules occupied the centroid of the cavity in each macrocycle to form a 1:1 host–guest complex (Figure 2ab). Included DCE molecules had multiple C–H $\cdots\pi$ interactions with biphenyl sides located between *o*-carborane corners. **CB3Ph6** molecules aligned in a columnar structure with 1D channels (Figure 2c). Stacked **CB3Ph6** molecules were involved in B–H $\cdots$ H–B and B–H $\cdots$ H–C contacts. Columns were assembled to form packed structure, where several B–H $\cdots$ B, B–H $\cdots$ H–B, and B–H $\cdots$ H–C contacts were observed between them (Figure 2d).



Scheme 1. Synthesis of **CB3Ph6** by Ni(0)-mediated cyclo-trimerization reaction.

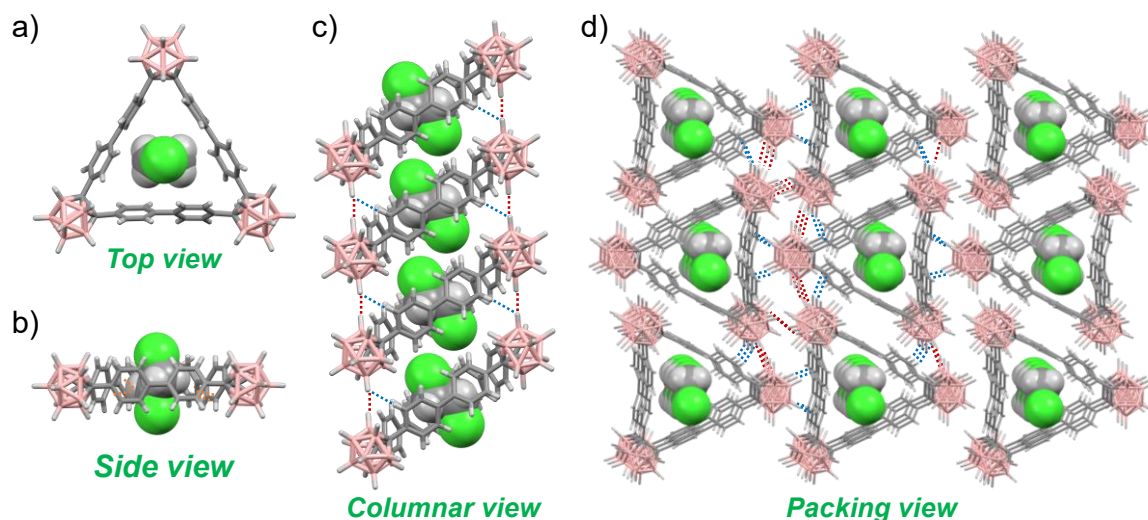


Figure 2. Single-crystal structures of **DCE@CB3Ph6** drawn in a) top, b) side, c) columnar, and d) packing views. Orange, red and blue dotted lines indicate C-H... π , B-H...(H-)B, and B-H...H-C contacts (< sum of vdW radii), respectively. Colors: C, gray; B, pink; H, white; Cl, green.

To investigate the effects of solvent inclusion on physical properties, guest-free crystal (**CB3Ph6 α**) was prepared by heating **DCE@CB3Ph6** at 100 °C under vacuum for 3 h. Crystal structure of **CB3Ph6 α** was studied by powder X-ray diffraction (PXRD) analysis. Initially, the PXRD peak positions of **CB3Ph6 α** were almost consistent with those of **DCE@CB3Ph6**, suggesting their similarity in molecular packing (Figure 3a). Moreover, indexing on PXRD patterns revealed that **CB3Ph6 α** has the same space group (*C2/c*) to **DCE@CB3Ph6** with slight change in the crystal lattice upon guest removal (Figure 3b). These results indicate that crystalline molecular arrangement of **CB3Ph6 α** remained intact during the guest-removing process. From these data, it was expected that **CB3Ph6 α** would have available unfilled channels where guest molecules can be accommodated. To test this, N₂ adsorption isotherm of **CB3Ph6 α** was measured (Figure 3c). It revealed that **CB3Ph6 α** had a typical type-I N₂ isotherm, indicating the presence of microporosity. The specific surface area was calculated as $1.5 \times 10^2 \text{ m}^2 \cdot \text{g}^{-1}$, which was on the same order of magnitude as that of a porous crystal based on triangle compounds.¹⁸ These results support that **CB3Ph6 α** has permanent intrinsic porosity,¹⁸ while

maintaining its crystalline molecular arrangement even after removal of guest molecules. Furthermore, adsorption isotherms were collected for CO₂, methane, ethane, butane, and *n*-hexane (Figure 3c). **CB3Ph6 α** showed the highest adsorption capability on butane, which has multiple C–H moieties and the most similar molecular size to DCE among the tested gases. The adsorption data suggest that **CB3Ph6 α** can capture C4-length guests via C–H $\cdots\pi$ interactions.

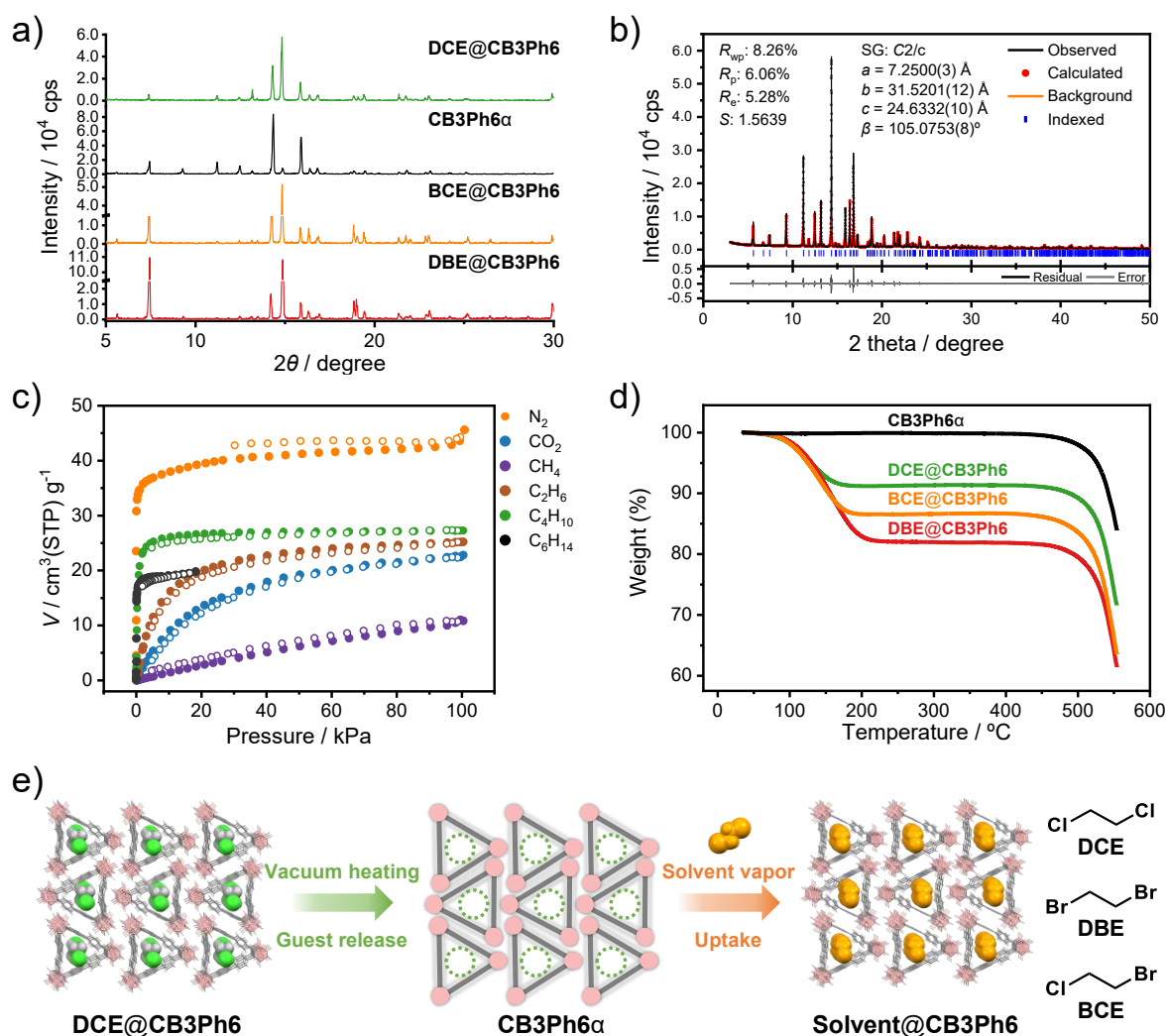


Figure 3. a) PXRD patterns of **CB3Ph6** crystals. b) Whole powder pattern fitting (WPPF) profile of **CB3Ph6 α** with indexing. c) Gas sorption isotherms of **CB3Ph6 α** recorded at 77 K for N₂ and 298 K for the others. Solid and open circles represent adsorption and desorption, respectively. d) TGA thermograms of **CB3Ph6** crystals. e) Representation of guest removal and encapsulation processes.

Guest uptake of **CB3Ph6 α** was studied by solid-vapor adsorption experiments. Samples were prepared by exposing **CB3Ph6 α** to gaseous vapor of 1,2-dibromoethane (DBE) and 1-bromo-2-chloroethane (BCE) (**DBE@CB3Ph6** and **BCE@CB3Ph6**, respectively). ^1H NMR spectra indicated 1:1 encapsulation of the solvent molecules in **CB3Ph6** (Table 1). PXRD patterns of **DBE@CB3Ph6** and **BCE@CB3Ph6** were almost identical to those of **DCE@CB3Ph6** and **CB3Ph6 α** , indicating that crystal-state arrangement was unchanged by reuptake (Figure 3a). Thermogravimetric analysis (TGA) showed that solvated crystals had 10–20% weight loss between 100–200 °C that is assignable to solvent release (Figure 3d). TGA curves supported 1:1 complexation (Table 1). In contrast, **CB3Ph6 α** had no weight loss below 400 °C, indicating complete removal of the guest solvents during activation. Reported porous organic compounds lose their porosity over approximately 100 °C²³ or, at best, ~400 °C.²⁴ Notably, decomposition temperature of **CB3Ph6** is over 500 °C (Table 1), which highlights material robustness owing to the *o*-carborane scaffolds. Furthermore, SCXRD analysis on **DBE@CB3Ph6** revealed its same crystalline packing to **DCE@CB3Ph6** except for the replacement of halogen atoms (Figure 3e right). Space group remained *C2/c*. The difference in lattice constants between the crystals was less than 1%. These results indicate that the removal and reuptake of vaporous guests proceed without crystal phase transition, amorphization, or chemical decomposition (Figure 3e).

Table 1. Summary of host–guest ratio and thermal properties of the crystals

Crystals	Sol : CB3Ph6 (TGA) ^[a]	Sol : CB3Ph6 (NMR) ^[b]	$T_{\text{sol}} / ^\circ\text{C}^{[c]}$	$T_{\text{d}} / ^\circ\text{C}^{[d]}$
CB3Ph6α	0.00 : 1	0.00 : 1	n.d.	504
DCE@CB3Ph6	0.85 : 1	0.96 : 1	92	509
DBE@CB3Ph6	1.03 : 1	0.99 : 1	109	507
BCE@CB3Ph6	0.95 : 1	1.00 : 1	97	505

^[a] Solvent molecules to **CB3Ph6** molar ratio determined by TGA analyses. ^[b] Solvent molecules to **CB3Ph6** molar ratio determined by ^1H NMR analyses. ^[c] Temperature at which vaporous solvent guests were released. ^[d] Temperature at which decomposition occurred.

Optical measurements were conducted to understand the effect of macrocyclization and crystalline state host–guest complexation on excited-state relaxation processes. **CB3Ph6** showed only slight photoluminescence (PL) in CHCl_3 solution (PL quantum yield (Φ_{PL}) < 0.01), whereas crystals recorded over 10 times higher efficiency ($\Phi_{\text{PL}} > 0.10$) (Table 2), indicating AIE properties of **CB3Ph6**. Solvent polarity had no effect on UV–vis absorption spectra, whereas PL spectra red-shifted as the polarity increased (Figure 4ab), supporting ICT luminescent character in solution state. Crystals showed structureless PL bands as observed in solution state, indicating their ICT character. These results suggest macrocyclic **CB3Ph6** has excited-state relaxation path that is still allowed under rigid environment. Next, the effect of guest uptake was investigated with **CB3Ph6** crystals (Figure 4c, Table 2). The guest-free crystal, **CB3Ph6 α** , showed PL spectrum with maximum wavelength (λ_{PL}) at 461 nm and Φ_{PL} of 0.11. Host–guest complexation in solvated crystals resulted in 14–23% increase of Φ_{PL} and 4–12 nm blue-shift of λ_{PL} . PL spectra of the solvated crystals were completely overlapped with each other, which suggests that similar luminescent mechanism worked on them despite including different guests. Reversible guest uptake was confirmed by the correspondence of PL spectra between **DCE@CB3Ph6** and **CB3Ph6 α** exposed to DCE vapor (**DCE-fumed**) (Figure 4d), and re-enhanced Φ_{PL} value to 0.33 for **DCE-fumed**. Additionally, radiative and non-radiative constants (k_{r} and k_{nr} , respectively) were calculated to assess mechanistic insights (Table 2). It revealed that guest uptake had almost no effect on k_{r} values, while it decreased k_{nr} values by an order of magnitude. This result suggests that guest molecules restricted access to non-radiative decay channels. It is widely known that cryogenic temperature can suppress molecular motion leading to emission quenching. For **CB3Ph6** crystals, cooling from room temperature to 77 K induced blue-shift of PL spectra by 15–17 nm (Figure 4e) and significant emission enhancement (Figure 4f). These cryogenic results corresponded to the phenomena observed upon solvent uptake, which further implies that included guest solvents should block molecular motions.

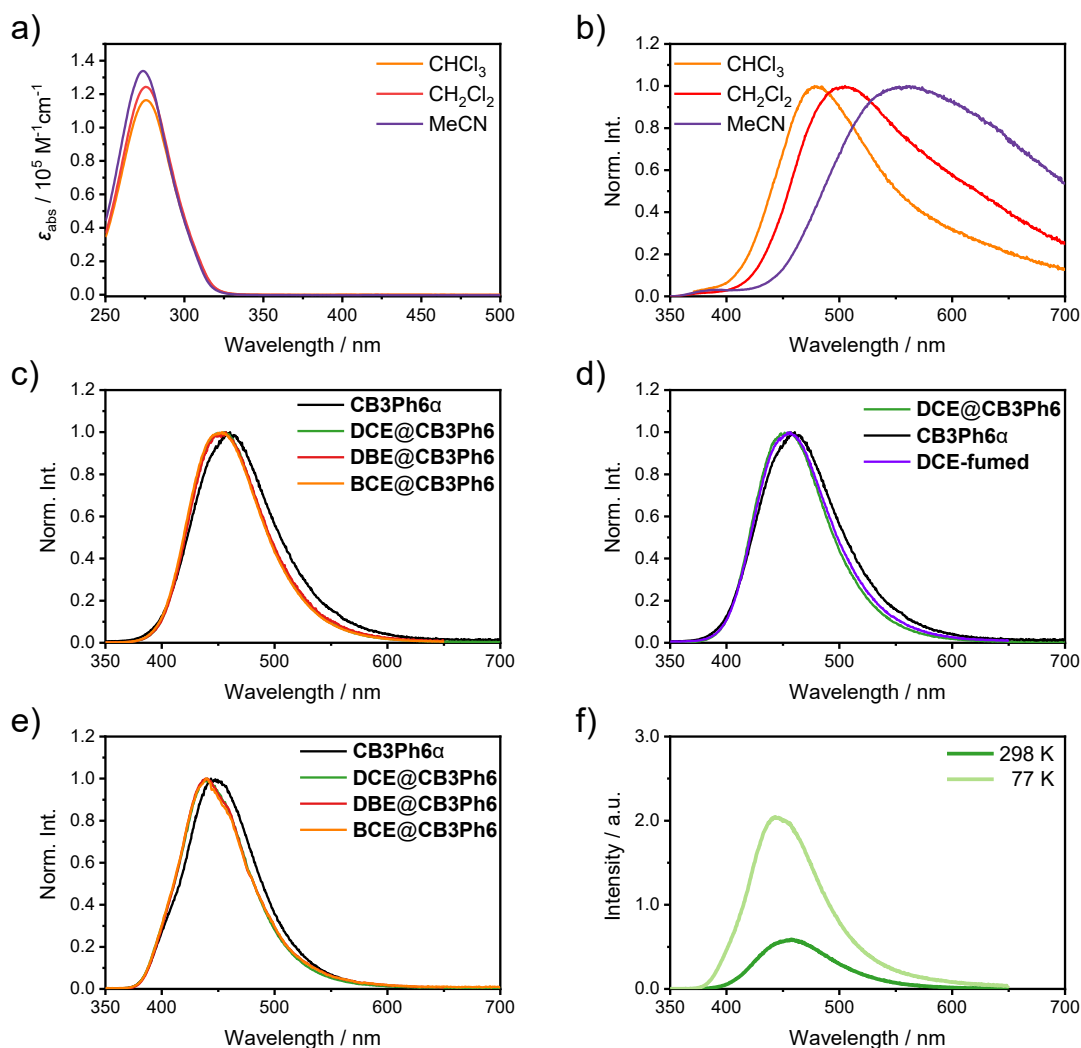


Figure 4. a) UV–vis absorption and b) PL spectra of **CB3Ph6** in CHCl_3 , CH_2Cl_2 , or MeCN (1.0×10^{-5} M). PL spectra of c) **CB3Ph6** crystals and d) **DCE@CB3Ph6** before and after removal of vaporous guests (**CB3Ph6 α**) and after reuptake of DCE (**DCE-fumed**). e) PL spectra of **CB3Ph6** crystals recorded at 77 K. f) Variable-temperature PL spectra of **DCE@CB3Ph6**.

Table 2. Summary of solid-state optical properties

Crystal	λ_{PL} / nm ^[a]	Φ_{PL} ^[a,b]	τ_{PL} / ns ^[c,d]	χ^2	k_r / ns ⁻¹ ^[e]	k_{nr} / ns ⁻¹ ^[f]
CB3Ph6α	461	0.11	0.5	1.22	0.22	1.8
DCE@CB3Ph6	456	0.29	1.1	1.06	0.26	0.65
DBE@CB3Ph6	457	0.25	0.9	1.09	0.28	0.83
BCE@CB3Ph6	454	0.34	1.1	0.99	0.28	0.63

^[a] Excited at 276 nm. ^[b] Absolute quantum yield determined by the integrating sphere method. ^[c] Excited at 375 nm. ^[d] $\sum_i \tau_i f_i$, where f_i : relative amplitude of i th component (%), τ_i : luminescent decay lifetime of i th component(s). ^[e] $k_r = \Phi_{\text{PL}}/\tau_{\text{PL}}^{\text{ave}}$. ^[f] $k_{\text{nr}} = (1-\Phi_{\text{PL}})/\tau_{\text{PL}}^{\text{ave}}$.

To discuss mechanism behind guest-induced emission enhancement, theoretical calculation was performed with density functional theory (DFT) and time-dependent DFT (TD-DFT). DFT calculations for the ground state show that the calculated structure is identical to the SCXRD structure (Figure 2a), and isolated **CB3Ph6** should have C_3 -symmetry with equal length of the $C_{\text{cage}}-C_{\text{cage}}$ bonds in three *o*-carborane units (1.75 Å) and vertically oriented biphenyl sides to the $C_{\text{cage}}-C_{\text{cage}}$ bonds (Figure 5a). Absorption transition (S_0 to S_1) contained molecular orbitals (MOs) contributed by biphenyl units (Figure 6 left). TD-DFT calculations for the excited state suggest a locally-stable geometry with the elongated $C_{\text{cage}}-C_{\text{cage}}$ bond to 2.36 Å (Figure 5b). Emission transition (S_1 to S_0) is calculated as ICT character between lowest unoccupied MO (LUMO) and highest occupied MO (HOMO). HOMO contains π^* orbitals of two biphenyl units, while LUMO is mainly located on the *o*-carborane unit (Figure 6 middle). These results support that **CB3Ph6** exhibits ICT emission contributed by one *o*-carborane unit and two biphenyl units connected to it.

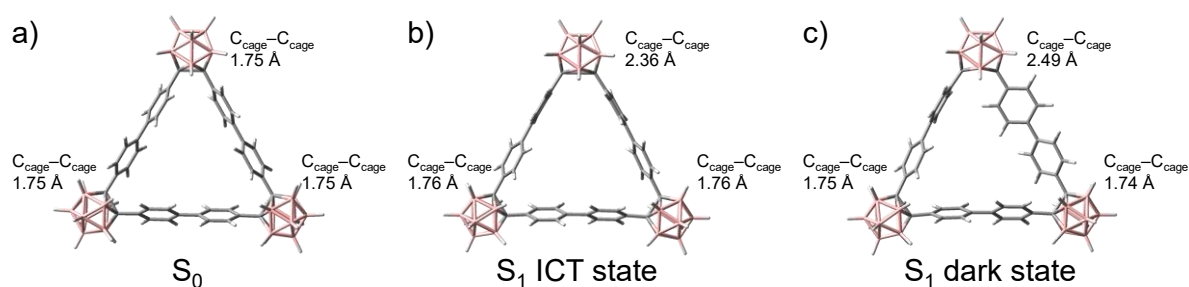


Figure 5. Optimized geometries of a) S_0 , b) S_1 ICT, and c) S_1 dark states of isolated **CB3Ph6**. $C_{\text{cage}}-C_{\text{cage}}$ bond lengths were indicated. (Colors: C, gray; B, pink; H, white)

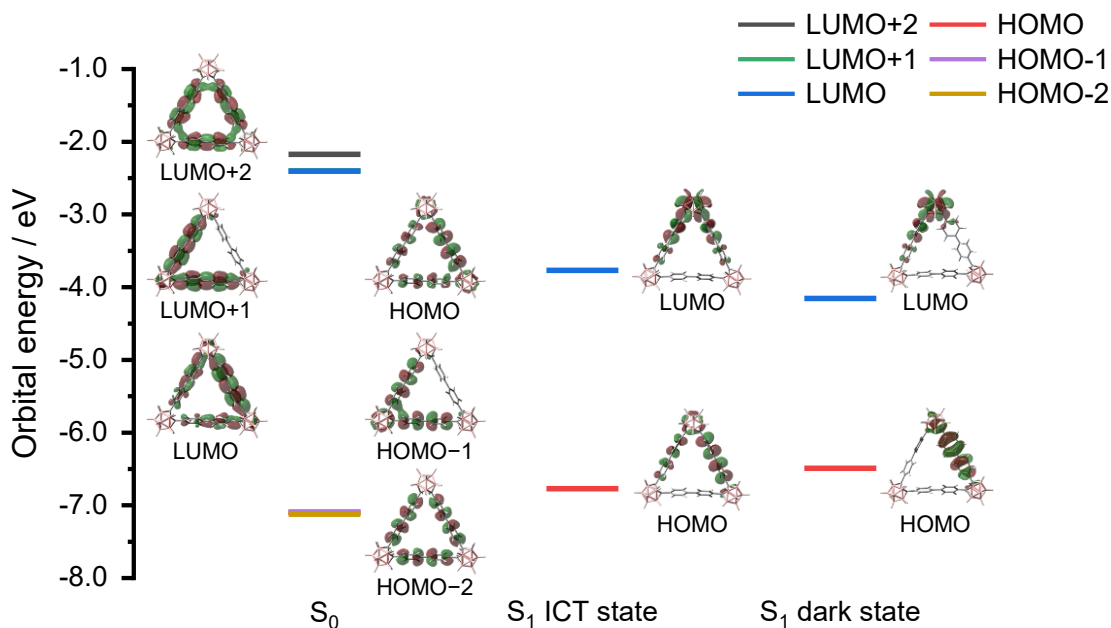


Figure 6. Energy diagram of selected orbitals with corresponding calculated Kohn–Sham frontier orbital distribution of **CB3Ph6** in the S_0 (left), S_1 ICT (middle), and S_1 dark states (right). HOMO–2 to LUMO+2 orbitals were displayed in the S_0 state. Only HOMO and LUMO orbitals were displayed in the S_1 states. Isovalues are 0.02. B3LYP/6-31+G(d,p) level was used. (Colors: C, gray; B, pink; H, white)

To understand the guest-induced PL change, quantum mechanics and molecular mechanics (QM/MM) method was used for crystal-state calculation.²⁵ Guest inclusion of DCE and DBE was calculated to induce 4 and 6 nm blue shifts of PL, which is almost consistent with experimentally observed up to 7 nm blue-shifts (Table 3). Guest inclusions slightly restricted $C_{\text{cage}}-C_{\text{cage}}$ bond elongation (Figure 7a–c), which may suppress excited-state structural relaxation followed by a PL blue shift. Furthermore, significant emission enhancement can be explained with the existence of excited-state non-emissive dark states, where slight overlap exists between HOMO and LUMO (Figure 6 right). As a result, corresponding emission transitions have almost vanished oscillator strength. In dark state, isolated **CB3Ph6** had a $C_{\text{cage}}-C_{\text{cage}}$ bond of 2.49 Å and parallel orientation of one biphenyl unit to the elongated bond (Figure 5c). The rotated biphenyl moieties partially filled internal cavities of **CB3Ph6**. Crystalline dark

states were also revealed with QM/MM method (Figure 7d–f). Dark state of **CB3Ph6** α was destabilized by 0.19 eV as compared to the corresponding ICT state. Such unstabilization was enhanced by guest loading; dark states of solvent-included crystals had 0.38 and 0.44 eV higher energy than ICT states. These results suggest that guest molecules partially block the formation of non-emissive dark states and allow more excitons to be trapped in emissive ICT states.

Table 3. Summary of calculated crystal-state ICT states^[a]

Crystal	C _{cage} –C _{cage} / Å	$\lambda_{\text{PL}}^{\text{calc}}$ / nm ^[b]	Oscillator strength (<i>f</i>)
CB3Ph6 α	2.36, 1.77, 1.76	480	0.30
DCE@CB3Ph6	2.35, 1.76, 1.76	476	0.31
DBE@CB3Ph6	2.34, 1.76, 1.75	474	0.29
BCE@CB3Ph6	—	—	—

^[a] Calculated by QM/MM method. ^[b] Calculated emission wavelength. —: Not calculated due to the unavailability of SCXRD result.

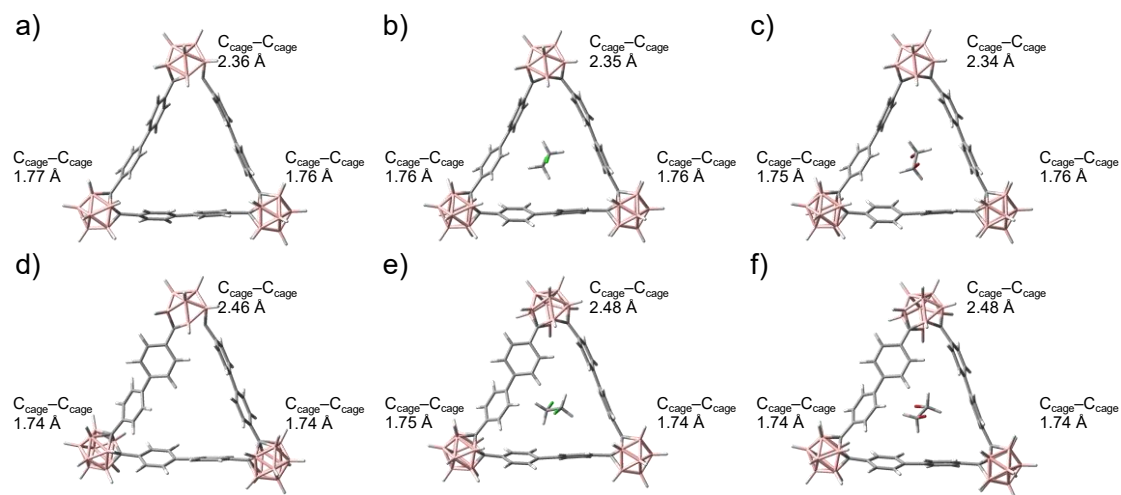


Figure 7. Optimized geometries of S₁ ICT (a–c) and dark states (d–f) of **CB3Ph6** in QM/MM modelling of **CB3Ph6** α (a,d), **DCE@CB3Ph6** (b,e), and **DBE@CB3Ph6** (c,f). Only QM-treated one molecule (accompanied with a guest molecule if existed) was shown for clarity. (Colors: C, gray; B, pink; H, white; Cl, green; Br, red)

Conclusion

In this chapter, the author has shown that **CB3Ph6**, a novel AIE-active *o*-carborane-based macrocycle, can form a permanent intrinsic porous crystal with 1D channels. Solid-vapor adsorption indicated that vaporous halogenated ethane derivatives can thread into the channel to construct 1:1 host–guest complex. The crystal can be processed with reversible guest removal and encapsulation without losing its porosity and crystallinity. Vapor-loading induced a blue shift and enhancement of PL. Theoretical calculation suggests that cavity-filling by vaporous guests restricted excited-state structural relaxation in crystal state. The loaded guests may destabilize available non-emissive dark states and guide excitons to emissive ICT states in the excited states. Surprisingly, the porous crystal has excellent thermal stability up to 500 °C. This finding expands design and application of smart materials based on porous molecular crystals utilizing AIEgens.

Experimental Section

The experimental details followed that described in Chapter 1, with the differences and additional details summarized below.

Materials

Commercially available reagents used without purification

1,2-Bis(4-bromophenyl)ethyne (Tokyo Chemical Industry Co., Ltd), bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) (Fujifilm Wako Pure Chemical Corporation), 2,2'-bipyridyl (Tokyo Chemical Industry Co., Ltd), 1,5-cyclooctadiene (cod) (Tokyo Chemical Industry Co., Ltd)

Commercially available solvents used without purification

CHCl₃ (Fujifilm Wako Pure Chemical Corporation), *N,N*-dimethylformamide (DMF) (Deoxidized, Fujifilm Wako Pure Chemical Corporation), 1,2-dichloroethane (DCE) (Fujifilm Wako Pure Chemical Corporation), 1,2-dibromoethane (DBE) (Tokyo Chemical Industry Co., Ltd), 1-bromo-2-chloroethane (BCE) (Tokyo Chemical Industry Co., Ltd)

Synthesis

General. An MBRAUN glovebox system, UNIlab, was used for treating air-unstable reagent.

Synthesis of 1,2-Bis(4-bromophenyl)-*o*-carborane. 1,2-Bis(4-bromophenyl)ethyne (2.689 g, 8.0 mmol), decaborane (1.102 g, 9.0 mmol) and AgNO₃ (0.270 g, 1.6 mmol) were added to a 100 mL 2-neck round bottom flask. To the flask, toluene (40 mL) and MeCN (5.0 mL) were added under N₂ atmosphere, and the mixture was refluxed at 110 °C for 18 h. After filtration and evaporation of the solvents to afford orange solid, the crude was supported by silica in CHCl₃ and purified by silica gel column chromatography (eluent: *n*-hexane/DCM = 30/1 (v/v)). Recrystallization from boiling MeOH/CHCl₃ afforded colorless crystal of 1,2-bis(4-bromophenyl)-*o*-carborane (1.163 g, 2.6 mmol, 32%). The product was characterized by ¹H NMR analysis according to the literature.²²

Synthesis of CB3Ph6. To a 300 mL round bottom flask, 1,2-bis(4-bromophenyl)-*o*-carborane (1.135 g, 2.50 mmol), Ni(cod)₂ (1.374 g, 5.00 mmol), 2,2'-bipyridyl (0.194 g, 1.24 mmol), and DMF (150 mL) were added in an MBRAUN glovebox system under N₂ atmosphere. The flask was capped with septum and taken out from glovebox. To the flask, cod (0.50 mL, 4.07 mmol) was added, and the mixture was stirred at room temperature for 24 h. To the resultant mixture, pure water (ca. 200 mL) was added. Brown precipitate was collected by vacuum filtration and

extracted with CHCl_3 concentrated with rotary evaporator to afford brown solid. The crude solid was purified by silica gel column chromatography (eluent: *n*-hexane/AcOEt = 5/1 (v/v)). Recrystallization was performed by vapor diffusion method: filtrated DCE solution of the semi-purified solid and MeOH vapor. The colorless co-crystal of **CB3Ph6** and DCE (34 mg, 0.03 mmol, 4%) was obtained by vacuum filtration. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.45 (d, J = 8.4 Hz, 12H), 7.32 (d, J = 8.4 Hz, 12H), 3.8–1.6 (br, 30H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) = 139.8, 131.1, 130.6, 126.3, 84.70. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) = -2.90, -10.49. HRMS (APCI) calcd. for $\text{C}_{42}\text{H}_{54}\text{B}_{30}\text{Cl}^-$ $[\text{M}+\text{Cl}]^-$ 923.6824, found 923.6806.

Preparation of crystalline samples

DCE@CB3Ph6: Recrystallization by slow evaporation of DCE solution at rt.

CB3Ph6 α : Vacuum drying of **DCE@CB3Ph6** at 100 °C for 3 h.

DBE@CB3Ph6: Solid-vapor adsorption of **CB3Ph6 α** to DBE for several hours at rt.

DBE@CB3Ph6: Solid-vapor adsorption of **CB3Ph6 α** to BCE for several hours at rt.

Single-crystal X-ray Diffraction Analysis

Crystalline sample of **DCE@CB3Ph6** for this study is prepared by vapor diffusion of MeOH into DCE solution at -30 °C, followed by slow evaporation of the solvent at rt.

Table 4. Crystallographic data

Compound name	DCE@CB3Ph6	DBE@CB3Ph6
CCDC number	2495493	2495494
Empirical formula	C ₂₆ H ₂₈ B ₁₀ •C ₂ H ₄ Cl ₂	C ₂₆ H ₂₈ B ₁₀ •C ₂ H ₄ Br ₂
Formula weight	982.10	1071.02
Temperature / K	143(2)	143(2)
Wavelength / Å	0.71075	0.71075
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / Å	7.2450(12)	7.2884(17)
<i>b</i> / Å	31.353(5)	31.271(7)
<i>c</i> / Å	23.751(4)	23.733(6)
α / °	90	90
β / °	91.880(3)	92.054(3)
γ / °	90	90
<i>V</i> / Å ³	5392.1(15)	5406(2)
<i>Z</i>	4	4
ρ / g·cm ⁻³	1.210	1.316
<i>a</i> / cm ⁻¹	0.156	1.535
<i>F</i> (000)	2024	2168
θ range / °	3.038–27.460	3.026–27.485
Limiting indices	$-9 \leq h \leq 9$ $-39 \leq k \leq 36$ $-22 \leq l \leq 30$	$-9 \leq h \leq 9$ $-40 \leq k \leq 40$ $-29 \leq l \leq 30$
Collected unique reflections	21828/6058	21870/6128
<i>R</i> _{int} ^[a]	0.0456	0.0411
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.586	1.082
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.1211	0.0807
<i>wR</i> ₂ (all data) ^[d]	0.3971	0.2454

^[a] $R_{\text{int}} = \Sigma ||F_0|^2 - |F_c|^2| / \Sigma |F_0|^2$ ^[b] $S = [\{\Sigma w(|F_0|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\Sigma (|F_0|^2 - |F_c|^2) / \Sigma (|F_0|^2)^2]^{1/2}$

^[d] $wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w(|F_0|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Powder X-ray Diffraction Analysis

Powder X-ray diffraction (PXRD) data for indexing was obtained using Rigaku SmartLab with a Ge (111) Johansson monochromator ($\text{Cu K}\alpha_1 = 1.54059 \text{ \AA}$; 50 kV and 40 mA; transmittance mode), a HyPix-3000 detector, a borosilicate capillary (outside diameter, 0.7 mm; wall thickness, 0.01 mm; sample loading height, $\sim 30 \text{ mm}$), and a capillary rotation attachment. Measurement parameters were set as follows: 2 theta range, $3\text{--}50^\circ$; step, 0.005° ; speed, $0.5^\circ \cdot \text{min}^{-1}$; rotation speed, 120 rpm. The analysis was carried out with the powder X-ray diffraction analysis software SmartLab Studio II (Rigaku). Indexing programs DICVOL²⁶ or ITO²⁷ were used for the determination of cell dimensions. The diffraction profiles were decomposed with the whole powder pattern fitting (WPPF) method. Following these data, corresponding space groups were determined based on systematic extinctions. Fitting parameters for the indexing including weighted-profile of R (R_{wp}), profile-refinement of R (R_{p}), expected R (R_{e}), and goodness-of-fit (S) values were defined as follows:

$$R_{\text{wp}} = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\}^{\frac{1}{2}}$$

$$R_{\text{p}} = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i}$$

$$R_{\text{e}} = \left(\frac{N - P}{\sum_i w_i y_i^2} \right)^{\frac{1}{2}}$$

$$S = \frac{R_{\text{wp}}}{R_{\text{e}}}$$

in which y_i is a diffraction intensity, $f_i(x)$ is a calculated diffraction intensity, P is a parameter for the least-squares method, w_i is a statistical weight and N is the number of data points.

Typical PXRD data were collected with a Rigaku SmartLab Diffractometer (sealed tube (50 kV, 40 mA); $\text{Cu K}\alpha$, $1.542 \text{ \AA}$; Bragg–Brentano geometry). PXRD samples were placed on a single-crystal silicon substrate.

Adsorption Properties

Gas and vapor sorption isotherms were obtained using a BELSORP-max (BEL Japan Inc., Osaka, Japan) sorption analyzer at room temperature. The equilibrium points were determined

if the pressure change for 300 s is less than 0.3% of the pressure gauge values. Sample was activated by overnight heating at 80 °C under vacuum.

Surface area of the material was calculated by Brunauer-Emmett-Teller (BET) theory.^{28,29} The following equation was used at standard temperature and pressure (STP).

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} - \frac{C - 1}{CV_m} \cdot \frac{P}{P_0}$$

in which V is the weight of adsorbate per unit mass at a given relative pressure, P is equilibrium pressure of adsorbate, P_0 is saturation pressure of adsorbate, C is BET constant, and V_m is monolayer adsorbate volume per unit mass. Experimental adsorption data was subjected to linear fitting of $P/\{V(P_0 - P)\}$ vs P/P_0 plot in the range where C is positive. Then, V_m was calculated by the following equation with the slope (s) and intercept (i) values.

$$V_m = \frac{1}{s + i}$$

Finally, the specific surface area per unit mass (S_{BET}) was calculated by the following equation:

$$S_{\text{BET}} = \frac{V_m N_A \sigma}{M_v}$$

in which N_A is Avogadro's number ($= 6.02 \times 10^{23}$ molecules $\cdot\text{mol}^{-1}$), σ is cross-sectional area of the adsorbate ($= 0.162$ nm² for N₂), and M_v is the molar volume of adsorbate ($= 22414$ cm³).

Thermal Analysis

Thermogravimetric analyses (TGA) were performed by a HITACHI STA 7200RV instrument with an aluminum pan and a heating rate of 10 °C $\cdot\text{min}^{-1}$ up to 550 °C under nitrogen flow (200 mL $\cdot\text{min}^{-1}$).

Theoretical Calculation

General. Calculation was performed at B3LYP/6-31+G(d,p) level.

QM/MM calculation. Model for guest-free crystal, **CB3Ph6 α** , was constructed with solvent-removed **DCE@CB3Ph6**.

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Chapter 3

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Part 2

Regulation of Circularly Polarized Luminescent Properties Based on the Dual-Emission from Locally Excited and Intramolecular Charge Transfer States

Chapter 4

[7]Helicene-Appended *o*-Carboranes: Sign-Changing Circularly Polarized Luminescence Based on Dual-Emissive Properties and Its Temperature Dependency

Abstract

Circularly polarized luminescence (CPL) attracts tremendous attention owing to their applicability for the next-generation optoelectronics. Precise control over CPL sign as well as its stimuli-responsiveness is one of the next goals, especially for developing solid-state chiroptical materials. Herein, the author synthesized [7]helicene-appended *o*-carborane derivatives and observed temperature-dependent CPL sign-switching behaviors. Similar to the reported aryl-*o*-carborane derivatives, the synthesized [7]helicene-appended derivatives showed dual-emission properties between locally-excited (LE) and intramolecular charge transfer (ICT) emission accompanied by excited-state deformation of *o*-carborane units. It should be noted that CPL sign inversion was observed upon emission species change because of their different spatial orientation of the transition electric and magnetic dipole moments. Owing to the spherical structure of the *o*-carborane scaffold, the dual-emission can be exhibited even in the condensed solid state, where structural relaxation is usually suppressed by the structural restriction caused by surrounding molecules. Finally, from temperature-dependent CPL measurements in film state, the author observed stimuli-responsive CPL sign-switching properties based on the change in LE/ICT dual-emission intensity ratio.

Introduction

Circularly polarized luminescence (CPL) is the difference in emission intensity between left-handed and right-handed light (I_L and I_R , respectively) produced by chiral luminescent scaffolds.¹ The sign of CPL is defined as follows: when the left CPL is stronger than the right one ($I_L - I_R > 0$), CPL sign is determined as positive, if otherwise ($I_L - I_R < 0$), the sign becomes negative. Quantitative analyses are performed by g_{CPL} factor based on the intensity bias of both-handed CPL as experimentally calculated by the following equation: $g_{\text{CPL}} = 2(I_L - I_R)/(I_L + I_R)$. In the field of CPL, the extreme goal has been regarded as establishing molecular and material designs reaching maximum g_{CPL} values ($= \pm 2$). To achieve the goal, many platforms exhibiting CPL performances have been reported such as metal complexes,^{2,3} distorted conjugated systems,^{4,5} and supramolecular systems.⁶ In terms of organic compounds, helically twisted chiral molecules have been reported with high g_{CPL} values.⁷⁻⁹ CPL-active materials are currently regarded as light-emitting sources for 3D projecting display¹⁰ or asymmetric photosynthesis¹¹ and ink for encryption¹² or anti-counterfeiting techniques.¹³ Toward such applications, precise control over CPL handedness is an emerging research target. CPL properties including its intensity, wavelengths, and handedness are affected by molecular structure and surrounding environments. The sign-inversion and ON/OFF switching of CPL have been reported utilizing structural change upon anion¹⁴ or metal recognition,¹⁵⁻¹⁷ acid/base addition,¹⁸⁻²¹ or solvent alteration.²²⁻²⁴ More recently, there have been some reports on the CPL sign-switching molecules dependent on the change in luminescence species. Ito and Asami *et al.* presented the CPL sign-switching of the pyrene-based molecule utilizing locally-excited (LE) and excimer emission species.²⁵ Also, there have been several examples of CPL sign-switching systems utilizing excimer emission,²⁵⁻³⁰ phosphorescence,³¹ and intramolecular charge transfer (ICT) emission (Figure 1a).^{32,33} However, solid-state CPL sign-switching materials have rarely been developed so far except for a few mechanochromic luminescent

systems.^{34–36} Since solid-state emitters are highly desirable toward device fabrications, further investigation is needed for logical design of solid-state CPL sign-switching materials.

The author has been focusing on *o*-carborane³⁷ as a functional skeleton for luminescent materials. Interestingly, *C*-aryl derivatives show synergistic effects between the attached conjugated and carborane units based on orbital conjugation. In early 2010s, Fox *et al.* reported ICT emission properties of *C*-benzodiazaborolyl derivatives owing to donor–acceptor electronic communication between the cluster and aryl groups.^{38–41} Chujo *et al.* reported that *C*-anthryl-*o*-carborane shows solid-state ICT emission properties accompanied by the rotation of the *o*-carborane unit around the single bond between anthryl and carborane units (Figure 1b).⁴² The rotation resulted in the twisted orientation between π -plane and carbon–carbon bond in the cluster ($C_{\text{cage}}-C_{\text{cage}}$), and ICT occurs from π orbitals of aryl units to σ^* orbitals of $C_{\text{cage}}-C_{\text{cage}}$ bond, accompanied by $C_{\text{cage}}-C_{\text{cage}}$ bond elongation.^{43–45} Many works have been presented on the synthesis and optical properties of the modified *o*-carboranes with various aryl units and some of them show intense solid-state luminescence and aggregation-induced emission properties attributable to the ICT emission. Moreover, from the reported ICT emissive aryl-*o*-carborane derivatives, dual-emission properties consisting of the ICT emission band from whole molecule and the LE emission band of the aryl units were often observed. Despite the fact that such switching of emission species between LE and ICT states in aryl-modified *o*-carboranes should be associated with the structural change in the excited state, the *o*-carborane unit can rotate in the solid state owing to its spherical shape,^{46,47} and sensitive thermochromic behaviors based on the alteration of intensity ratios between ICT/LE emission have been obtained.^{48,49} For the next-generation light emitting materials, stimuli-responsiveness is important to visualize environmental factors at the molecular scale and to monitor tiny environmental changes.

In this chapter, the author targeted the combination of solid-state dual-emissive aryl-*o*-carborane and CPL-active π -systems to realize environment-dependent CPL sign-controllable luminescent materials. There have been several reports on chiral *o*-carborane derivatives functionalized with point,⁵⁰ axial,^{51,52} planar,⁵³ cage,^{54,55} and cage-planar chirality⁵⁶ (Figure 1c). In a stark contrast, this is the first synthesis of *o*-carborane derivatives with helical chirality. Carbo[*n*]helicene derivatives are well known to possess sufficient chiral stability when $n \geq 6$.⁵⁷ Also, their structures and (chir)optical properties have been extensively studied by various experiments coupled with theoretical analyses.^{58,59} The author took advantage of such well-studied carbo[*n*]helicene scaffolds to accomplish the research target. The author herein reports novel aryl-*o*-carborane derivatives with the [7]helicene moiety as a chiral π -conjugated unit (Figure 1d). [7]Helicene-appended *o*-carborane (**1**) was successfully synthesized via step-by-step construction of [7]helicene and *o*-carborane moieties. Methoxy derivative (**2**) was synthesized as well to enhance its ICT character. Both compounds showed dual-emission properties based on two distinctive excited states: LE states of [7]helicene moieties and ICT states formed by the electronic perturbation of *o*-carborane. In dispersed films, sign-different CPL signals were obtained from each emission band. Temperature-dependent measurements showed that the film exhibited the alteration of its CPL signals accompanied by the change in the dual-emission intensity ratio.

a) CPL-switching Utilizing Dual-emission

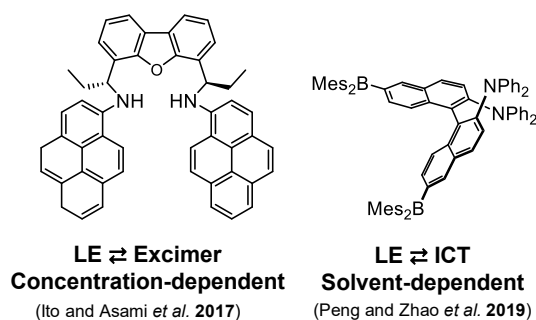
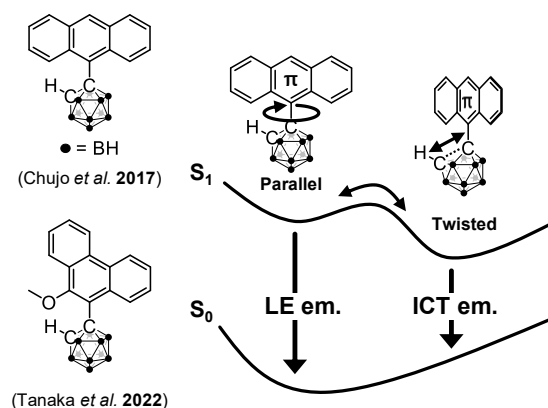
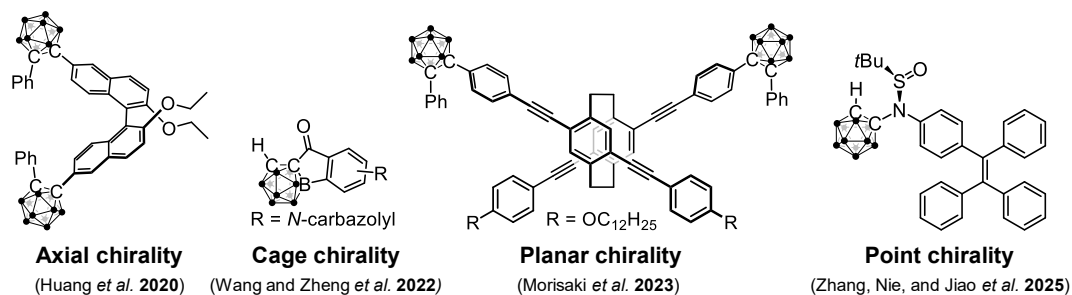
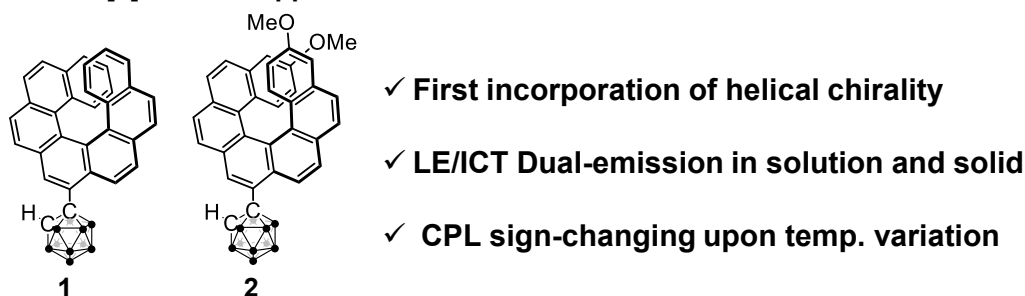
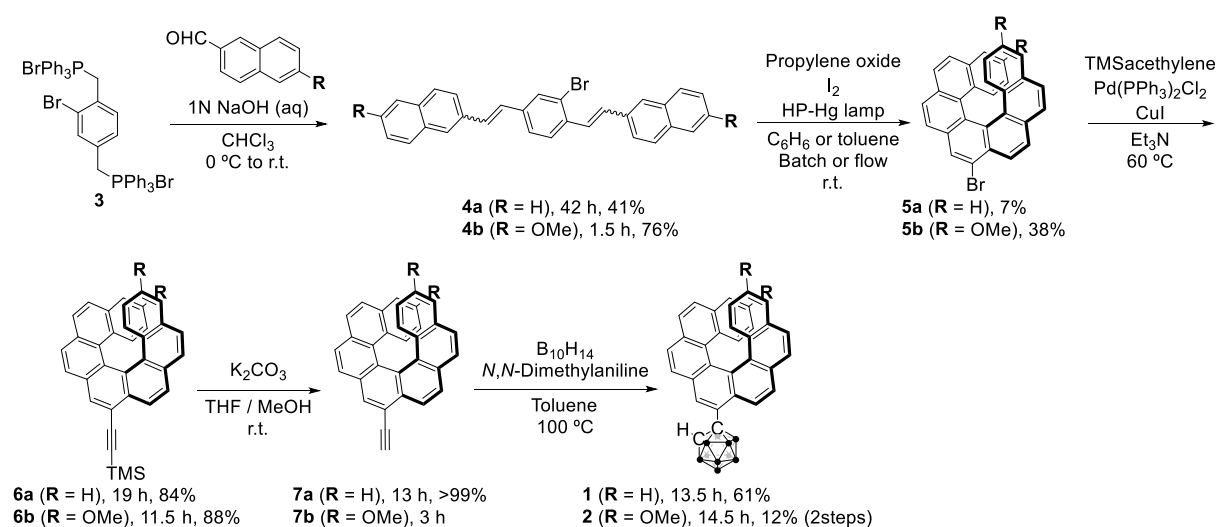
b) Dual-emission of C-Aryl-*o*-carboranesc) CPL-active Chiral *o*-Carborane Derivativesd) This Work: [7]Helicene-appended *o*-Carboranes

Figure 1. Reported examples of a) CPL sign-switching molecules based on multiple emission species, b) *C*-aryl-*o*-carborane derivatives showing dual-emission properties, and c) chiral *o*-carborane derivatives with CPL properties. d) Structures of [7]helicene-appended *o*-carboranes and overview of this research. (LE: locally-excited, ICT: intramolecular charge transfer)

Results and Discussion

Compounds **1** and **2** were synthesized as shown in Scheme 1. A precursor with two vinylene bridges linking bromo-phenylene and 2-naphthyl units (**4a**) was synthesized using a phosphonium salt (**3**)⁶⁰ and 2-naphthaldehyde in Wittig reaction. The photocyclization reaction of **4a** in the presence of iodine as an oxidizing agent produced 9-bromo-[7]helicene (**5a**).^{61,62} The terminal ethynyl group was incorporated by the successive Sonogashira–Hagihara coupling reaction with TMSacetylene and subsequent desilylation. Alkyne insertion of **7a** into decaborane ($B_{10}H_{14}$) yielded [7]helicene-appended *o*-carborane (**1**). Compound **2**, which has two methoxy groups at 3 and 16 positions of [7]helicene, was synthesized by the same reaction sequence with 6-methoxy-2-naphthaldehyde used instead in the Wittig reaction. The enantiomeric pairs of **1** and **2** were optically separated by chiral high-performance liquid chromatography (HPLC) (Figure 2). Both compounds were separated as two fractions: 1st and 2nd fractions (Fr1 and Fr2, respectively). Optical purities were determined to be over 99% for all enantiomers. Absolute structures of the compounds in each fraction were determined by the correspondence of the experimental and calculated CD spectra. Also, optical rotation was measured for all fractions. Consequently, the fractions were characterized as follows: **1**-Fr1 → (+)-(*P*)-**1**; **1**-Fr2 → (–)-(*M*)-**1**; **2**-Fr1 → (+)-(*P*)-**2**; **2**-Fr2 → (–)-(*M*)-**2**.



Scheme 1. Synthetic route of [7]helicene-appended *o*-carborane derivatives.

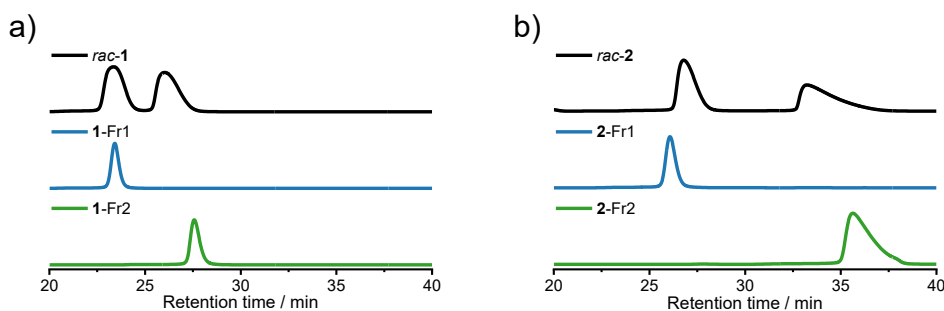


Figure 2. Chiral HPLC chromatogram of a) **1** and b) **2**.

The structure of **1** was confirmed by single-crystal X-ray diffraction analysis (Figure 3). The geometrical feature of the [7]helicene moiety was evaluated by torsion angle and helical pitch defined as the dihedral angle of C19–C20–C21–C22 atoms and the centroid–centroid distance of the terminal benzene rings, respectively.⁶³ Torsion angle and helical pitch of **1** were determined as 25.2(4)° and 3.688 Å, respectively. These values were similar to the averaged values of the reported structures of [7]helicene (24.3° and 3.835 Å), supporting that the carborane moieties had little effect on the helical scaffold. The compound had twisted conformation between carborane and helicene moiety, where C_{cage}–C_{cage} bond and π -plane of [7]helicene crossed vertically. The dihedral angle of C10–C9–C_{cage1}–C_{cage2} atoms ($\varphi_{\text{Ar-CB}}$) was measured as 83.7°. This result suggests that the twisted conformation is one of the stable conformers at least in the ground state.

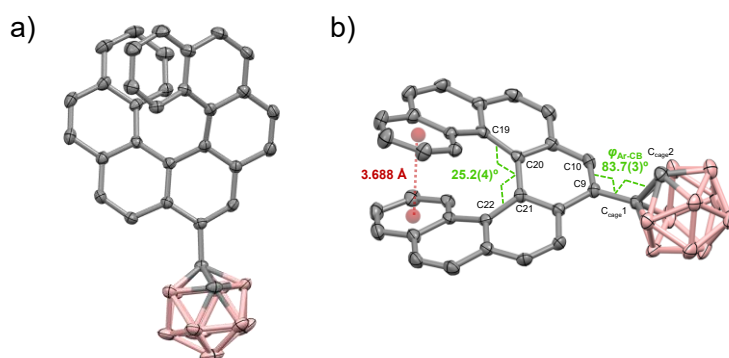


Figure 3. ORTEP drawing of **1** measured at 143 K. a) Top and b) side view of the asymmetric unit including structural parameters. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Colors: C, gray; B, pink.

To study the electronic structures of the [7]helicene-appended carborane derivatives, optical measurements were conducted on racemate samples of **1** and **2** (*rac*-**1** and *rac*-**2**, respectively) in solution state (Table 1, Figure 4). Both **1** and **2** had similar UV–vis absorption spectra with [7]helicene (Figure 4a)⁶⁴ although **2** had red-shifted absorption as compared to **1** (Table 1). In contrast, both compounds showed different photoluminescence (PL) spectra from [7]helicene.⁶⁵ The spectra contained two emission bands: vibrational bands around 460 nm and broad bands spread from 600 to 800 nm (Figure 4b). [7]Helicene typically shows vibrational PL spectra attributable to LE emission.⁶⁶ To identify the emission character of the additional broad band, solvent effect was investigated (Figure 5). The broad PL bands were polarity-sensitive: in polar solvents, red-shift was observed. In contrast, absorption and vibrational PL bands were almost independent of solvent polarity. Lippert–Mataga plots^{67,68} were prepared for quantitative analysis (Figure 6). Stokes shifts of the broad PL bands were linearly correlated with the solvent polarity, whereas those of the vibrational bands showed almost no correlation. From these results, the author assigned the vibrational and broad bands to emission from LE and ICT states, respectively. In addition, based on the plot, the differences of dipole moments in the ground and excited states ($\Delta\mu$) were calculated. Accordingly, compound **2** had a larger $\Delta\mu$ value (19.8 Debye) than compound **1** (14.2 Debye), indicating that compound **2** has a stronger ICT character.

Table 1. Summary of optical properties

Compound	State	λ_{abs} / nm	λ_{PL} / nm ^[c]	Φ_{PL} ^[c,d]
<i>rac</i> - 1	Solution ^[a]	342	456, 637	0.04
	Dispersed film ^[b]	343	455, 600	0.03
<i>rac</i> - 2	Solution ^[a]	359	464, 697	0.03
	Dispersed film ^[b]	359	464, 657	0.04

^[a] Toluene solution (1.0×10^{-5} M). ^[b] Dispersed in β -estradiol (1 wt%). ^[c] Excited at λ_{abs} . ^[d] Absolute PL quantum yield determined by integrating sphere method.

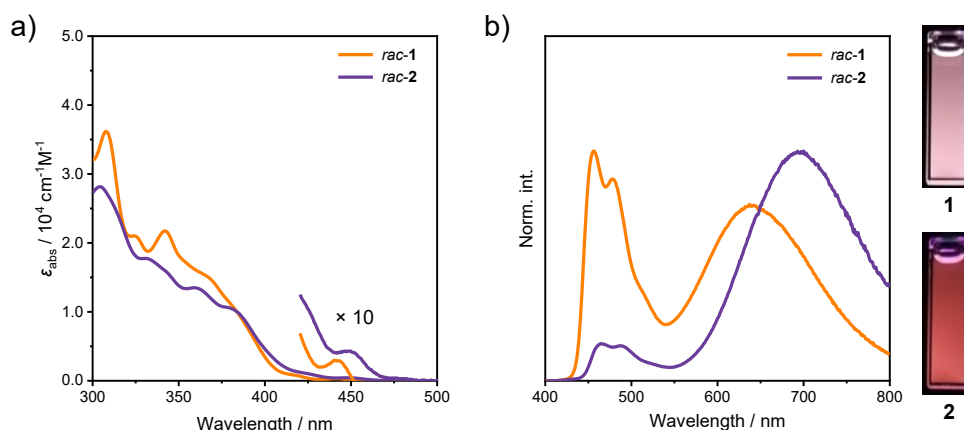


Figure 4. a) UV-vis absorption and b) PL spectra of *rac-1* and *rac-2* in toluene (1.0×10^{-5} M). Inserted photographs were taken under irradiation of UV light (365 nm).

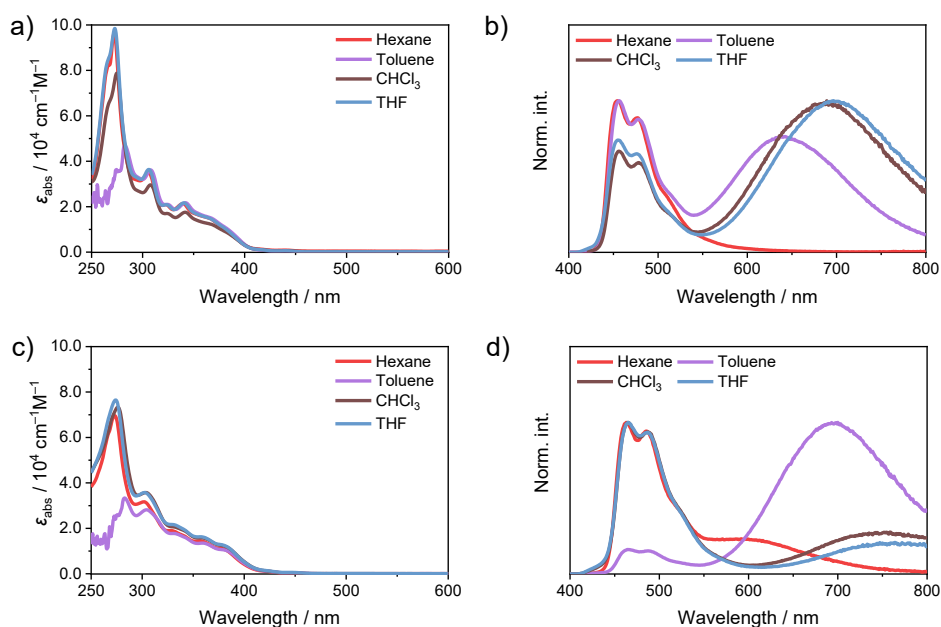


Figure 5. UV-vis absorption (a,c) and PL spectra (b,d) of *rac-1* (a,b) and *rac-2* (c,d) in various solvents (1.0×10^{-5} M).

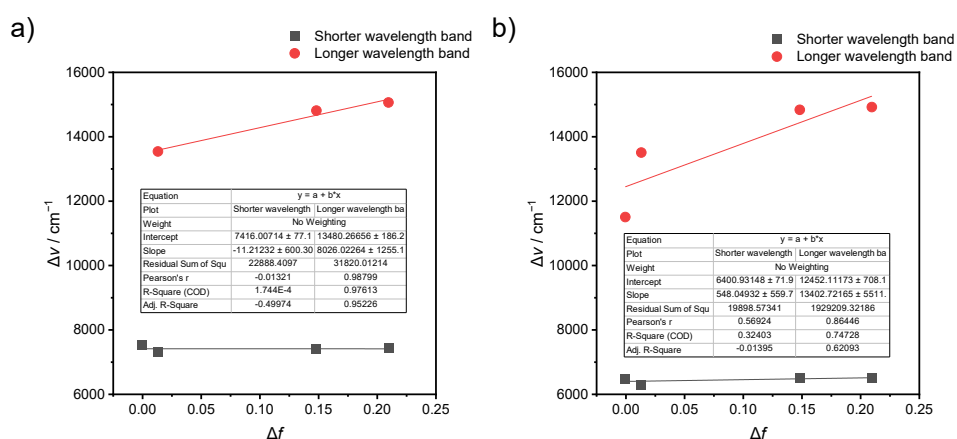


Figure 6. Lippert-Mataga plots of a) *rac-1* and b) *rac-2*.

Next, the author investigated emission properties in the solid matrix of β -estradiol, which forms a transparent, thick amorphous film with sufficient temperature durability.^{69–71} In the matrix, compounds are isolated, and molecular motions are basically restricted. UV–vis absorption spectra had almost no difference from those measured in solution (Table 1, Figure 7a). Solid-state dual-emission properties were observed from PL measurements (Table 1, Figure 7b). Similar to the solution state, both compounds showed vibrational LE and broad ICT bands. Compound **2** had a larger ICT/LE emission intensity ratio, supporting stronger ICT property of **2** as proposed from the Lippert–Mataga plot. These results suggest that structural changes correlated with dual-emission can occur even in the solid state.

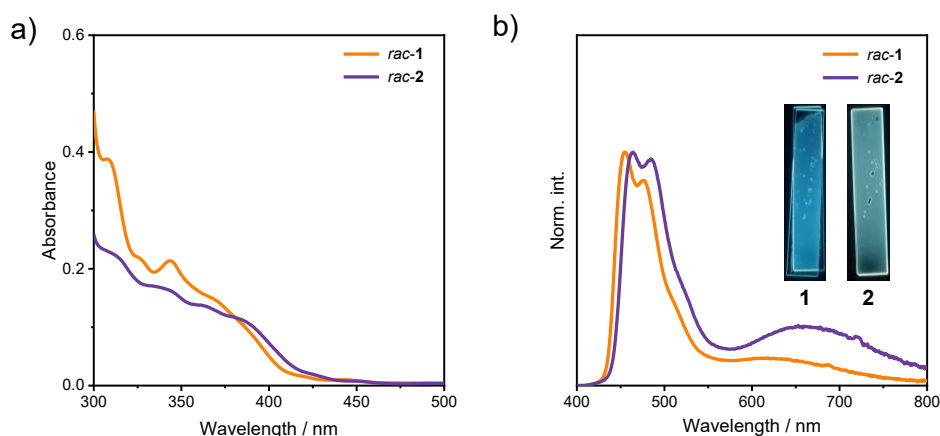


Figure 7. a) UV–vis absorption and b) PL spectra of *rac-1* and *rac-2* dispersed in β -estradiol films (1wt%). Inserted photographs were taken under irradiation of UV light (365 nm).

Photophysical properties of the [7]helicene-appended carborane derivatives were theoretically studied by time-dependent density functional theory (TD-DFT) calculations performed at B3LYP-GD3BJ 6-311G(2d,p) level.^{66,72} It should be noted that **1** and **2** had conformational dependence on rotation around the single bond connecting *o*-carborane and [7]helicene. The dihedral angle, ϕ_{Ar-CB} , was used as a variable representing conformational difference. Here the lowest-energy conformers were used for both parallel and twisted

conformers. Dual-emission properties were predicted from the calculations on transitions from the S_1 to S_0 states (Figure 8). It was shown that in the parallel conformations (**1**, $\varphi_{\text{Ar-CB}} = -157^\circ$; **2**, $\varphi_{\text{Ar-CB}} = -160^\circ$) molecular orbitals responsible for the emission transitions mainly located on [7]helicene units, meaning that LE character should be assigned to the emission from parallel conformations. In contrast, in twisted conformations ($\varphi_{\text{Ar-CB}} = -84^\circ$ for both **1** and **2**), cluster deformation could proceed through $\text{C}_{\text{cage}}\text{--C}_{\text{cage}}$ bond elongation, accompanied by orbital overlap between σ^* orbitals of $\text{C}_{\text{cage}}\text{--C}_{\text{cage}}$ bonds and π^* orbitals of the helicene moieties. The orbital localization on the electron deficient *o*-carborane unit significantly stabilizes the LUMO, allowing charge transfer emission from the helicene moiety to the *o*-carborane unit.

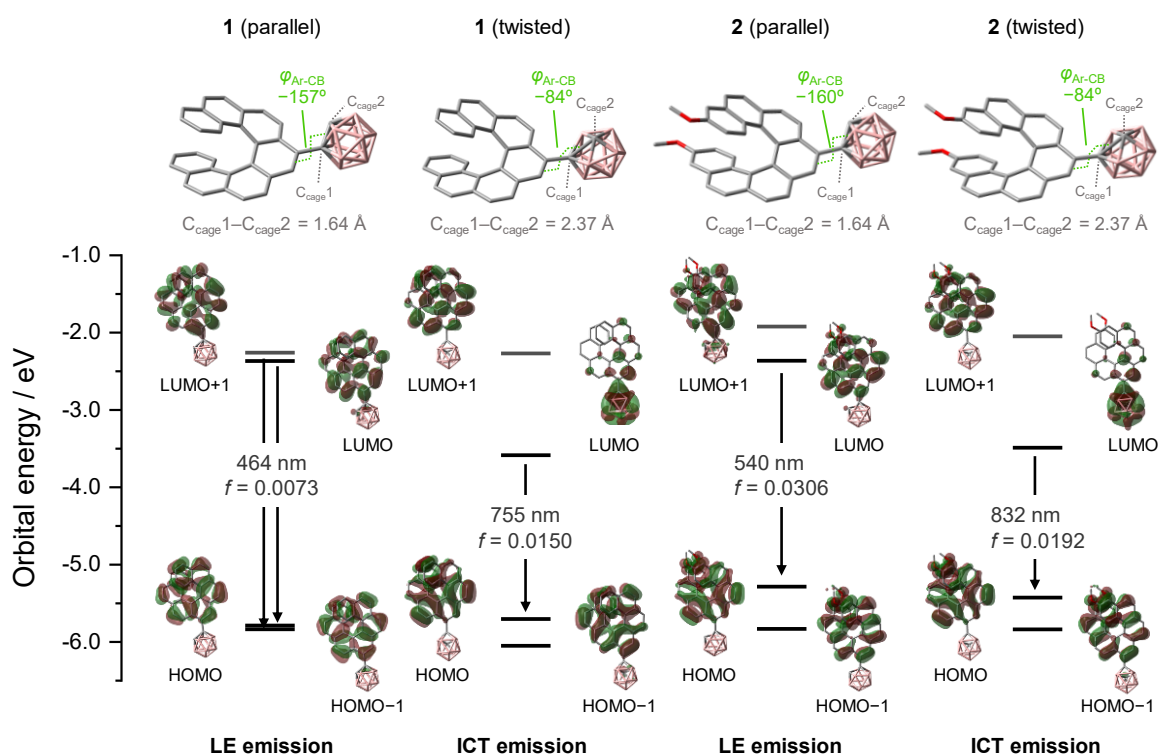


Figure 8. Optimized structures with geometrical parameters and calculated Kohn–Sham frontier orbital distributions, S_0 – S_1 electronic transition energy in nm, and assigned emission characters for energy-minimum geometries of parallel and twisted conformers in the S_1 states (colors: C, gray; B, pink; O, red). (*P*)-isomers were used for calculation. Hydrogen atoms were omitted. f denotes the oscillator strength. Isovalues are 0.02. Bar plots indicate HOMO–1, HOMO, LUMO, and LUMO+1 orbitals from lower to higher energy.

To assess chiral electronic structures of the [7]helicene-appended carboranes, chiroptical measurements were performed in film state. Similar CD spectra were obtained from both compounds (Figure 9a), indicating that similar ground-state chiral electronic structures should be obtained in molecularly dispersed states. Similar to the UV–vis absorption spectra, almost identical CD spectra were observed between the compounds and [7]helicene,^{64,66} meaning their similar chiral ground-state electronic structures localized on helicene moieties.

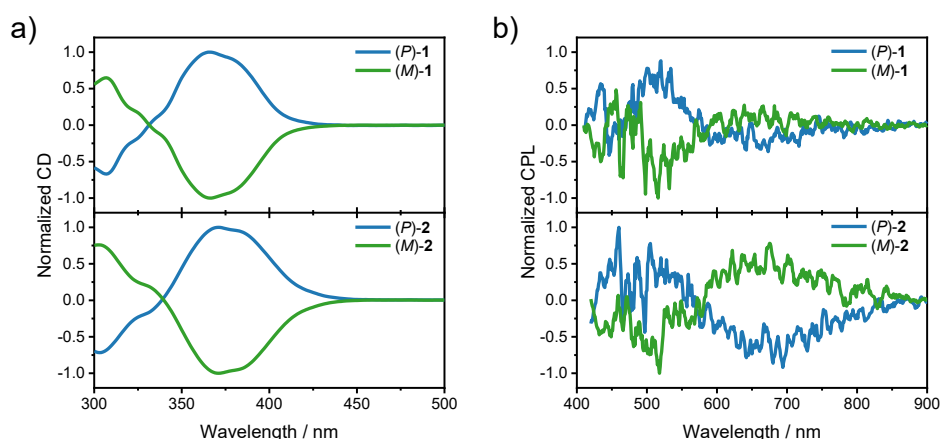


Figure 9. a) CD and b) CPL spectra of **1** (top) and **2** (bottom) in β -estradiol films (1wt%).

CPL spectra were obtained to investigate the excited-state chiral electronic structures. In β -estradiol films, both compounds showed dual emission properties consisting of the emission band between 420 and 550 nm, attributable to LE emission, and the stretched broad band between 550 and 900 nm attributable to ICT emission (Figure 9b). Notably, each band had opposite CPL signs: (P)-**1** showed positive and negative CPL in LE and ICT regions, respectively, and *vice versa* from (M)-**1**. The same situation regarding CPL signs were obtained from **2**, while the intensity ratio of ICT to LE bands was larger than that of **1** because of the stronger charge transfer interaction in **2**. It should be emphasized that in the film state the author confirmed that [7]helicene-appended carborane derivatives, **1** and **2**, had CPL dual-emission properties and sign-difference in each emission band.

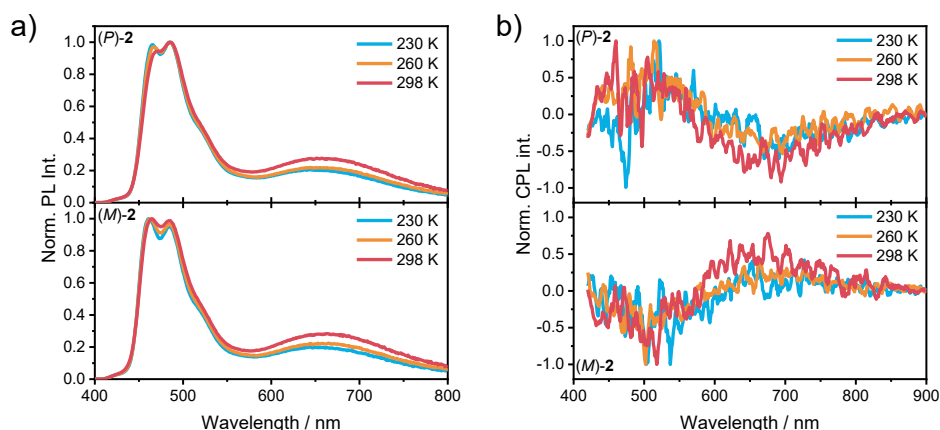


Figure 10. Variable-temperature a) PL and b) CPL spectra of **2**.

The author further investigated stimuli-responsiveness of the CPL sign-switching behaviors. LE/ICT dual-emission properties of *C*-aryl-*o*-carborane derivatives have been reported to show unique temperature dependence, in which ICT/LE relative intensity ratio changed in response to temperature variation.^{44,48,49,73–79} Despite the fact that switching of emission characters accompanies conformational change, these temperature-sensitivities can be observed even in condensed states such as crystals^{48,78} and films⁷⁹ owing to the spherical structure of *o*-carborane units. Initially, variable-temperature PL (VTPL) spectra were monitored with the film sample of **2** (Figure 10a). The film exhibited continuous enhancement of the relative emission intensity of ICT to LE emission bands. Based on the results of VTPL measurements, variable-temperature CPL spectra were measured to assess the effect of change in dual-emission intensity on CPL properties (Figure 10b). As temperature increasing, (*P*)-**2** showed enhanced ICT emission in the negative region. Temperature change had almost no impact on g_{CPL} values in both (*P*)-**2** and (*M*)-**2**. Based on these results, with increasing temperature, the change in the relative intensity of each PL band led to CPL sign-inversion. In contrast, **1** hardly showed observable temperature-dependence in CPL spectra probably because of the weaker ICT. This result supports the discussion on CPL sign-switching property in **2** originating from the temperature-dependent emission species change.

As a next step, the author performed theoretical analysis on the chiroptical properties with TD-DFT method according to the previous reports.^{66,80,81} Calculated dissymmetry factors ($g_{\text{CPL}}^{\text{calc}}$) were used for the analysis. The $g_{\text{CPL}}^{\text{calc}}$ values were calculated by the theoretical equation: $g_{\text{CPL}}^{\text{calc}} = 4|\boldsymbol{\mu}'||\boldsymbol{m}'|\cos\theta_{\mu',m'}/(|\boldsymbol{\mu}'|^2 + |\boldsymbol{m}'|^2)$, where $\boldsymbol{\mu}'$ and $\boldsymbol{m}'$ are transition electric and magnetic dipole moments (TEDM and TMDM), respectively, and $\theta_{\mu',m'}$ is angle between TEDM and TMDM vectors for de-excitation transitions. The sign of CPL is theoretically determined by $\cos\theta_{\mu',m'}$ values. The $\theta_{\mu',m'}$ values in LE and ICT emissions from (*P*)-isomers were calculated as acute and obtuse angle which result in the positive and negative signs, respectively. The calculation suggested that the origin of sign-changing CPL can be different spatial orientation of TEDM and TMDM vectors (Figure 11, Table 2). At this stage, it can be said that the difference of dipole moment vectors in two emission species probably due to the change in orbital distribution included in the emission transitions.

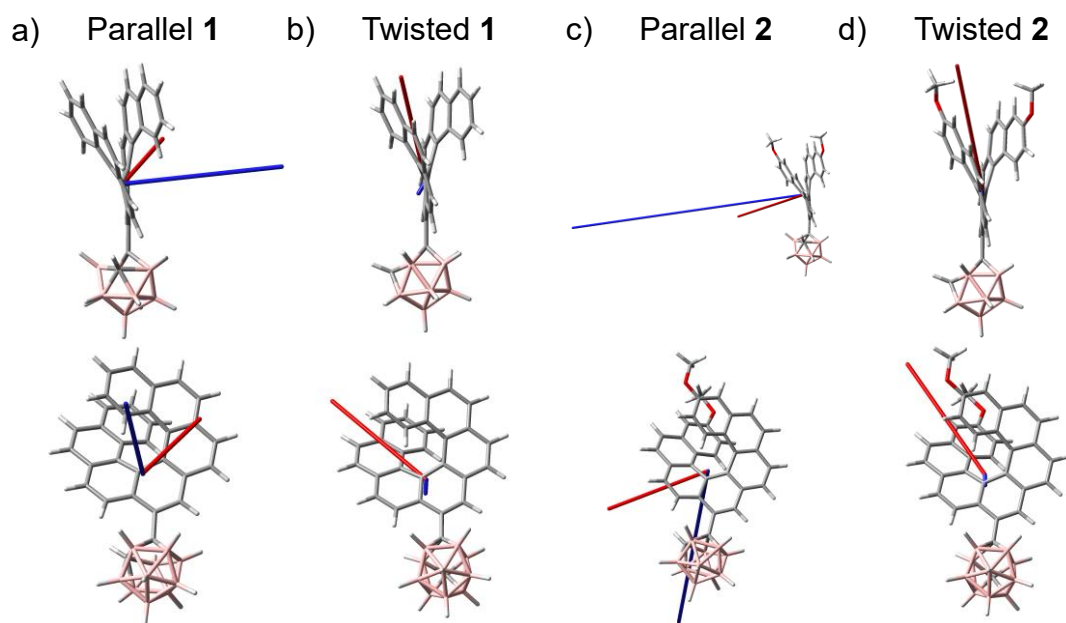


Figure 11. The visualized arrangements of TEDM ($\boldsymbol{\mu}'$, red) and TMDM ($\boldsymbol{m}'$, blue) vectors for S₁ to S₀ transitions of parallel (a,c) and twisted conformers (b,d) of **1** (a,b) and **2** (c,d), where the length of the TMDM vectors are multiplied by 200 for visibility. Side (top) and diagonal views (bottom) were visualized.

Table 2. Calculated chiroptical properties^[a]

	$\varphi_{\text{Ar-CB}} / ^\circ$	$\lambda_{\text{PL}}^{\text{calc}} / \text{nm}$	Emission character	$ \mu' / 10^{-20} \text{ esu}\cdot\text{cm}$	$ m' / 10^{-20} \text{ erg}\cdot\text{G}^{-1}$	$\theta_{\mu',m'} / ^\circ$	$g_{\text{CPL}}^{\text{calc}}$
1	−157	464	LE	85.19	0.8466	59	+0.021
1	−84	755	ICT	155.07	0.0768	116	−0.00088
2	−160	540	LE	187.66	2.5223	37	+0.042
2	−84	832	ICT	184.11	0.0655	148	−0.0012

^[a] Calculated for the (*P*)-isomers at the TD-B3LYP-GD3BJ/6-311G(2d,p) level of theory in the gas phase using the geometry optimized in the S_1 state, corresponding to the S_1 – S_0 transitions. Calculated properties of energy minimum conformers for each emission character were listed.

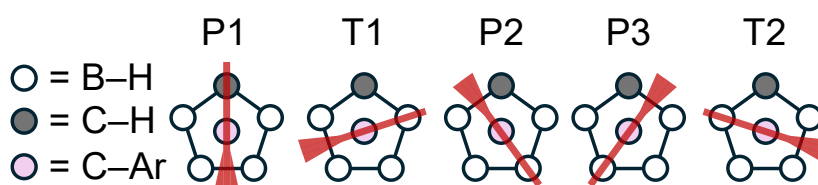


Figure 12. Schematic drawings of the conformers with different dihedral angles between [7]helicene and carborane units, where red arrows indicate [7]helicene units.

Additional calculations were performed in the solid-state models to support solid-state dual-emission properties which should include intramolecular rotation in the condensed state. Quantum mechanics and molecular mechanics (QM/MM) calculation was applied to **1** in S_0 and S_1 structural optimization in the solid state. Single-crystalline packing structure was employed for modelling. The author obtained five locally stable conformers; three in parallel conformations (P1–3) and two in twisted conformations (T1, T2) (Figure 12). The most stable conformer in the ground state among the five was the twisted conformer (T2, $\varphi_{\text{Ar-CB}} = 86^\circ$) which is almost identical to that refined in SCXRD analysis ($\varphi_{\text{Ar-CB}} = 83.7(3)^\circ$). This correspondence represents the validity of the QM/MM calculation. Interconvertibility between

pairs of conformers was evaluated by the calculated rotational barrier estimated with the energy difference between the most unstable transition state and the most stable conformer. As a result, the rotational barrier was calculated as 6.84 and 11.99 kcal·mol⁻¹ in the ground and excited states, respectively. The higher value in the excited state than that in the ground state is because of the stabilized twisted conformers in the ICT states. The calculated solid-state rotational barrier in both ground and excited states were slightly higher than those calculated for the corresponding isolated molecule (ground state, 4.89 kcal·mol⁻¹; excited state, 10.92 kcal·mol⁻¹). These elevations of the rotational barrier should be likely caused from the closely located surrounding molecules in the solid state. The barrier in solid states was still low (< 20 kcal·mol⁻¹), which plays a critical role in rotatability at room temperature in both ground and excited states. Experimentally, the author utilized β -estradiol film to prepare isotropic dispersion of chromophore in the solid state. The density of amorphous β -estradiol was recently reported as 1.158 g·cm⁻³,⁸² which is lower than that of crystalline **1** modeled for QM/MM calculation (1.242 g·cm⁻³). It can be assumed that the lower density of the matrix is expected to induce more flexible molecular conformational change. Therefore, these calculations can rationalize the rotatability of *o*-carborane units connected to [7]helicene even dispersed in the β -estradiol film. The rotation induced the switching of emission species especially facilitated when temperature is varied.

Conclusion

In this chapter, based on temperature-dependent dual-emission properties of aryl-*o*-carborane derivatives in solid, [7]helicene-appended *o*-carboranes (**1** and **2**) were designed, and the author successfully demonstrated temperature-dependent CPL sign-switching in the solid state. The compounds were synthesized by the sequential construction with [7]helicene scaffolds and *o*-carborane cages. X-ray structural analysis indicated the successful incorporation of cluster unit into [7]helicene with keeping its helical skeletal feature. Optical and chiroptical measurements showed the combination between dual-emission properties consisting of LE and ICT emission, and CPL signals from chiral helicene moieties. The author utilized amorphous steroidal matrix, β -estradiol, for preparing homogeneous films, which showed sign-different CPL signals from each emission character. In variable temperature measurements, the sign-switching of whole CPL spectra upon heating was observed, originating from the change in relative emission intensity of two emission characters. Theoretical analysis on the optical and chiroptical properties suggests that the orientational difference of TEDM and TMDM in the emission transition from energy-minimum LE and ICT states should play an important role in the CPL sign-switching in response to temperature change. Moreover, QM/MM calculations can rationalize the rotatability of the carborane units connected to [7]helicene even dispersed in the film. The findings could not only contribute to expanding photophysical chemistry of aryl-*o*-carborane derivatives but also provide useful suggestions on the material science for design and development of CPL-active solid-state materials toward future optoelectronic applications.

Experimental Section

The experimental details followed that described in Chapter 1, with the differences and additional details summarized below.

Materials

Commercially available reagents used without purification

2-Naphtaldehyde (Tokyo Chemical Industry Co., Ltd.), 6-methoxy-2-naphtaldehyde (Tokyo Chemical Industry Co., Ltd.), 1N NaOH solution (for Volumetric Analysis, Fujifilm Wako Pure Chemical Corporation), propylene oxide (Tokyo Chemical Industry Co., Ltd. or Nacalai Tesque, Inc.), iodine (I₂) (Guaranteed Reagent, Fujifilm Wako Pure Chemical Corporation), copper iodide (CuI) (Wako 1st Grade, Fujifilm Wako Pure Chemical Corporation), Pd(PPh₃)₂Cl₂ (Tokyo Chemical Industry Co., Ltd.), trimethylsilylacetylene (TMSacetylene) (BLDpharm), *N,N*-dimethylaniline (Wako Special Grade, Fujifilm Wako Pure Chemical Corporation), Na₂SO₄ (Anhydrous, Guaranteed Reagent, Fujifilm Wako Pure Chemical Corporation), NH₄Cl (Guaranteed Reagent, Fujifilm Wako Pure Chemical Corporation), K₂CO₃ (Guaranteed Reagent, Fujifilm Wako Pure Chemical Corporation), Na₂S₂O₃ (Extra Pure, Fujifilm Wako Pure Chemical Corporation), β -estradiol (Tokyo Chemical Industry Co., Ltd.)

Commercially available solvents used without purification

Benzene (Super dehydrated, Wako Pure Chemical Corporation)

Compounds prepared as described in the literature

((2-Bromo-1,4-phenylene)bis(methylene))bis(bromotriphenyl- λ^5 -phosphane) (**3**)⁶⁰ (2 steps, 29% overall yield from 2-bromo-*p*-xylene)

Synthesis

General. ¹³C{¹H} and part of ¹H spectra were recorded on a JNM-ECZ600R FT-NMR instrument at 150 and 600 MHz, respectively. ¹³C{¹H} NMR spectra were recorded with using inverse-gated decoupling pulse sequences with long relaxation delays to minimize the NOE effect. High-resolution mass spectrometry (HRMS) spectra were obtained on a JEOL JMS for electron ionization (EI) or Thermo Fisher Scientific Exactive Plus for atmospheric pressure chemical ionization (APCI). Specific rotation ([α]_D^T) was measured with a Rudolph Research AUTOPOL IV polarimeter. Optical separation was performed on Shimadzu Prominence LC-20A HPLC equipped with YMC CHIRAL ART Amylose-SA (particle size: 5 μ m, length: 250 mm, diameter: 20 mm) and UV absorption detector (detected at 250 nm).

Synthesis of 2,2'-((2-bromo-1,4-phenylene)bis(ethene-2,1-diyl))dinaphthalene (4a). To a CHCl_3 (108 mL) solution of **3** (5.216 g, 6.01 mmol, 1.0 eq.) and 2-naphthaldehyde (2.066 g, 13.23 mmol, 2.2 eq.), 1N aqueous NaOH (48 mL, 48 mmol, 8.0 eq.) was added at 0 °C over 5 min. The yellow solution was stirred at room temperature under an ambient atmosphere for 42 h. The reaction mixture was diluted by pure water (ca. 50 mL). The organic components were extracted by CHCl_3 (ca. 15 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated to afford yellow solid. The crude mixture was purified with column chromatography on SiO_2 (eluent: *n*-hexane/EtOAc = 10/1 (v/v), R_f = 0.40) to give compound **4a** as a yellow solid (1.142 g, 2.47 mmol, 41% yield). Note that the production of **4a** was confirmed by EI-MS. ^1H NMR spectrum of the product was complicated probably due to the mixture of *trans-cis* isomers. HRMS (APCI): calcd. for $\text{C}_{30}\text{H}_{21}\text{Br}^+ [\text{M}]^+$ 460.0821, found 460.0822.

Synthesis of 9-bromo[7]helicene (5a). A 500 mL photoreactor (SEN LIGHTS Corporation, VG500-4) attached with a water-cooled quartz immersion well was used for the reaction. To a benzene (320 mL) solution of compound **4a** (456 mg, 0.988 mmol, 1.0 eq.) in a batch photoreactor, propylene oxide (36 mL) and I_2 (521 mg, 2.05 mmol, 2.1 eq.) were added under N_2 atmosphere. A 400 W high-pressure Hg lamp (SEN LIGHTS Corporation, HL400BH-8) was equipped in the immersion well. The reddish black solution was irradiated at 365 nm by the lamp for 2 h at room temperature. The same procedure was performed again with 2.306 g (5.00 mmol) of **4a**, 2.611 g (10.3 mmol) of I_2 and 182 mL of propylene oxide in 1600 mL of benzene for 2 h irradiation of UV light. The combined reaction mixture was concentrated to afford black oil. The crude oil was dissolved and purified with column chromatography on SiO_2 (eluent: gradient from *n*-hexane/EtOAc = 10/1 to 1/1 (v/v), R_f = 0.58 for *n*-hexane/EtOAc = 10/1 (v/v)) to give a mixture of brown solid and oil (2.10 g). The mixture was again subjected to column chromatography on SiO_2 (eluent: gradient from *n*-hexane/EtOAc = 40/1 to 1/1 (v/v), R_f = 0.35 for *n*-hexane/EtOAc = 40/1 (v/v)) to give a yellow solid (0.870 g). Recrystallization from MeOH/ CHCl_3 (ca. 1/1 (v/v)) afforded compound **5a** as a yellow solid (183 mg, 0.400 mmol, 7% isolated yield), which was characterized according to the literature.⁶²

Synthesis of 9-trimethylsilyl[7]helicene (6a). To a Et_3N (30 mL) solution of compound **5a** (463 mg, 1.01 mmol, 1.0 eq.), CuI (20 mg, 0.11 mmol, 0.11 eq.), and $\text{Pd(II)(PPh}_3)_2\text{Cl}_2$ (139 mg, 0.198 mmol, 0.20 eq.), TMSacethylene (0.28 mL, 2.02 mmol, 2.0 eq.) was added under N_2 atmosphere. The solution was stirred at 60 °C for 19 h. The black suspension was filtered by Celite® (No.535) with washing by EtOAc. The filtrate was washed with aqueous NH_4Cl (ca.

25 mL $\times$ 2). The organic layer was dried over MgSO_4 , filtered, and concentrated to afford black solid. The crude solid was purified by column chromatography on SiO_2 (eluent: *n*-hexane, R_f = 0.30) to give compound **6a** as a yellow solid (402 mg, 0.85 mmol, 84% yield), which was characterized by ^1H NMR spectra according to the literature.⁸³

Synthesis of 9-ethynyl-[7]helicene (7a). Compound **6a** (402 mg, 0.847 mmol, 1.0 eq.) and K_2CO_3 (585 mg, 5.96 mmol, 7.0 eq.) were suspended in THF (17 mL) and MeOH (17 mL) at room temperature under ambient atmosphere. After 13 h, the reaction mixture was diluted by EtOAc. The organic layer was washed with pure water (ca. 15 mL), dried over MgSO_4 , filtered, and concentrated to afford yellow solid and oil (451 mg). The crude mixture was purified with column chromatography on SiO_2 (eluent: *n*-hexane/EtOAc = 20/1 (v/v), R_f = 0.38) to give compound **7a** as a yellow foam (339 mg, 0.84 mmol, >99% yield). The foam was used in the next reaction without further purification. ^1H NMR (400MHz, CDCl_3): δ (ppm) 8.58 (d, J = 8.2 Hz, 1H), 8.31 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 8.7 Hz, 1H, overlapped), 7.30 (d, J = 8.7 Hz, 1H, overlapped), 7.08 (d, J = 7.8 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 6.94–6.89 (m, 2H), 6.42 (dd, J = 8.7, 1.4 Hz, 1H), 6.40 (dd, J = 8.7, 1.4 Hz, 1H), 3.61 (s, 1H).

Synthesis of 9-(1-*o*-carboranyl)-[7]helicene (1). To a toluene (8.3 mL) solution of Compound **7a** (333 mg, 0.827 mmol, 1.0 eq.) and $\text{B}_{10}\text{H}_{14}$ (117 mg, 0.957 mmol, 1.2 eq.), *N,N*-dimethylaniline (0.2 mL) was added under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 13.5 h. The mixture was filtered to remove any insoluble impurities and concentrated to afford crude oil. The crude mixture was purified with column chromatography on SiO_2 (eluent: *n*-hexane/toluene = 10/1 (v/v), R_f = 0.35) to give compound **1** as a yellow foam (262 mg, 0.50 mmol, 61% isolated yield). ^1H NMR (600MHz, CD_2Cl_2): δ (ppm) 8.94 (d, J = 8.9 Hz, 1H), 8.33 (s, 1H), 8.01–8.00 (m, 3H), 7.73 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.504 (d, J = 8.4 Hz, 1H), 7.497 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 6.95 (ddd, J = 7.9, 6.9, 1.1 Hz, 1H), 6.91–6.88 (m, 2H), 6.80 (d, J = 8.5 Hz, 1H), 6.46 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 6.42 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 4.97 (s, 1H), 3.83–1.84 (br, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CD_2Cl_2): 132.36, 132.10, 132.09, 130.47, 129.89, 129.67, 129.37, 129.18, 129.09, 128.69, 128.67, 128.59, 128.55, 128.04, 127.45, 127.43, 127.07 (2C), 127.04, 126.83, 126.40, 125.90, 125.54, 125.41, 125.08, 125.00, 124.58, 124.51, 124.42, 123.08, 78.08, 62.51. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2): δ (ppm) –2.88, –9.11, –9.76, –13.29. HRMS (APCI): calcd. for $\text{C}_{32}\text{H}_{28}\text{B}_{10}^- [\text{M}]^-$ 522.3127, found 522.3152. Optical resolution was performed with

chiral HPLC. Conditions: HPLC column, Chiralpak IA; eluent, *n*-hexane/CHCl₃ = 3/1 (v/v); flow rate, 3.5 mL·min⁻¹; detection wavelength, 250 nm; retention time, 23.4 and 27.6 min for (*P*)-(+)-**1** and (*M*)-(-)-**1**, respectively. (*P*)-(+)-**1**: $[\alpha]^{23}_{\text{D}} = +3429$ (*c* 0.1, CHCl₃). (*M*)-(-)-**1**: $[\alpha]^{23}_{\text{D}} = -3449$ (*c* 0.1, CHCl₃).

Synthesis of 6,6'-(-(2-bromo-1,4-phenylene)bis(ethene-2,1-diyl))bis(2-methoxy naphthalene) (4b). To a CHCl₃ (150 mL) solution of **3** (7.284 g, 8.40 mmol, 1.0 eq.) and 6-methoxy-2-naphthaldehyde (3.125 g, 16.78 mmol, 2.0 eq.), 1N aqueous NaOH (67 mL, 67 mmol, 8.0 eq.) was added dropwisely at 0 °C over 5 min. The yellow solution was stirred at room temperature under ambient atmosphere for 1.5 h. The reaction mixture was diluted by pure water (ca. 20 mL). The organic components were extracted by CHCl₃ (ca. 15 mL × 4). The combined organic layer was dried over MgSO₄, filtered, and concentrated to afford yellow solid (9.095 g). The crude mixture was purified with flash column chromatography on SiO₂ (eluent: *n*-hexane/EtOAc = 5/1 (v/v), *R*_f = 0.40) to give a yellow solid. Recrystallization MeOH/CHCl₃ (ca. 1/2 (v/v)) afforded compound **4b** as a yellow solid (3.324 g, 6.37 mmol, 76% isolated yield). Note that the production of **4b** was confirmed by APCI-MS. ¹H NMR spectrum of the product was complicated probably due to the mixture of *trans-cis* isomers. HRMS (APCI): calcd. for C₃₂H₂₆O₂Br⁺ [M+H]⁺ 521.1111, found 521.1109.

Synthesis of 9-bromo-3,16-dimethoxy[7]helicene (5b). Compound **4b** (105 mg, 0.201 mmol, 1.0 eq.), I₂ (108 mg, 0.426 mmol, 2.1 eq.), and propylene oxide (7.3 mL) were dissolved in toluene (320 mL). The solution was subjected to N₂ bubbling for 15 min. The solution was passed through a photochemical flow reactor equipped with high-pressure Hg lamp (400 W) and FEP tubing at a flow rate of 6.4 mL·min⁻¹. The same procedures were repeated two times using 0.6 mmol of compound **4b**. The flow rate was changed to 9.6 mL·min⁻¹ in the two successive reactions. The combined drain solution was concentrated to ca. 300 mL volume. The excess I₂ was quenched by aqueous Na₂S₂O₃. The organic layer was dried over MgSO₄, filtered, and concentrated to afford brown oil. The crude oil was purified with column chromatography on SiO₂ (eluent: *n*-hexane/toluene = 1/3 (v/v), *R*_f = 0.30) to give compound **5b** as a yellow solid (280 mg, 0.541 mmol, 38% isolated yield). ¹H NMR (600MHz, CDCl₃): δ (ppm) 8.37 (d, *J* = 8.4 Hz, 1H), 8.29 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.69 (d, *J* = 2.7 Hz, 1H, overlapped), 6.69 (d, *J* = 2.7 Hz, 1H, overlapped), 6.074 (dd, *J* = 9.2, 2.2 Hz, 1H), 6.069 (dd, *J* = 9.2, 2.2 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H). ¹³C{¹H} NMR (150 MHz, CDCl₃): 156.89, 156.87,

133.40, 133.35, 132.01, 130.30, 129.92, 129.90, 129.87, 128.28, 128.22, 128.19, 128.02, 127.49, 127.03, 126.90, 126.28, 126.07, 125.77, 125.44, 124.74, 124.62, 124.58, 124.50, 124.35, 121.16, 114.74, 114.70, 106.25, 106.22, 55.24 (2C). HRMS (APCI): calcd. for $C_{32}H_{22}O_2Br^+ [M+H]^+$ 517.0798, found 517.0794.

Synthesis of 3,16-dimethoxy-9-trimethylsilylethynyl[7]helicene (6b). To a Et_3N (16.5 mL) solution of compound **5b** (280 mg, 0.541 mmol, 1.0 eq.), CuI (12 mg, 0.063 mmol, 0.12 eq.), and $Pd(II)(PPh_3)_2Cl_2$ (78 mg, 0.111 mmol, 0.21 eq.), $TMSacethylene$ (0.15 mL, 1.08 mmol, 2.0 eq.) was added under N_2 atmosphere. The solution was stirred at 60 °C for 11.5 h. The reaction mixture was washed with aqueous NH_4Cl (ca. 10 mL $\times$ 2). The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford brown oil. The crude solid was purified by column chromatography on SiO_2 (eluent: *n*-hexane/toluene = 1/3 (v/v), R_f = 0.40) to give compound **6a** as a yellow oil (256 mg, 0.479 mmol, 89% yield). 1H NMR (600MHz, $CDCl_3$): δ (ppm) 8.48 (d, J = 8.3 Hz, 1H), 8.24 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.01 (d, J = 9.2 Hz, 1H), 6.98 (d, J = 9.2 Hz, 1H), 6.690 (d, J = 2.8 Hz, 1H), 6.685 (d, J = 2.7 Hz, 1H), 6.07 (dd, J = 9.2, 2.7 Hz, 1H), 6.06 (dd, J = 9.2, 2.7 Hz, 1H), 3.709 (s, 3H), 3.708 (s, 3H), 0.41 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): 156.85, 156.78, 133.29, 133.28, 131.67, 131.56, 131.01, 130.32, 129.86, 128.18, 128.15, 127.85, 127.80, 127.18, 127.04, 126.29, 126.26, 125.76, 125.49, 125.42, 125.36, 125.24, 124.56, 124.47, 123.69, 119.08, 114.61, 114.57, 106.23 (2C), 103.39, 99.76, 55.23 (2C), 0.19. HRMS (APCI): calcd. for $C_{37}H_{31}O_2Si^+ [M+H]^+$ 535.2088, found 535.2086.

Synthesis of 3,16-dimethoxy-9-ethynyl[7]helicene (7b). Compound **6b** (256 mg, 0.479 mmol, 1.0 eq.) and K_2CO_3 (343 mg, 3.49 mmol, 7.3 eq.) were suspended in THF (9 mL) and MeOH (10 mL) at room temperature under ambient atmosphere. After 3 h, the reaction mixture was poured into pure water (ca. 20 mL). The organic layer was extracted with EtOAc (ca. 20 mL $\times$ 2), dried over $MgSO_4$, filtered, and concentrated to afford brown oil (222 mg). The product was unstable and used in the next reaction without further purification. The isolation of the product was not conducted because impurities were detected in 1H NMR analysis even just after column chromatography. That is probably because of high reactivity of ethynyl group. 1H NMR (400MHz, $CDCl_3$): δ (ppm) 8.50 (d, J = 8.2 Hz, 1H), 8.27 (s, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 9.6 Hz, 1H), 6.99 (d, J = 9.2 Hz, 1H), 6.71–6.69 (m, 2H), 6.09–6.06 (m, 2H), 3.71 (s, 3H, overlapped), 3.71 (s, 3H,

overlapped), 3.59 (s, 1H). HRMS (APCI): calcd. for $C_{34}H_{23}O_2^+$ $[M+H]^+$ 463.1693, found 463.1691.

Synthesis of 9-(1-*o*-carboranyl)-3,16-dimethoxy[7]helicene (2). To a toluene (4.8 mL) solution of Compound **7b** (222 mg, 0.479 mmol, 1.0 eq.) and $B_{10}H_{14}$ (74 mg, 0.605 mmol, 1.3 eq.), *N,N*-dimethylaniline (0.11 mL) was added under N_2 atmosphere. The reaction mixture was stirred and refluxed for 14.5 h. The mixture was filtered with toluene washing to remove any insoluble impurities and concentrated to afford crude oil. The crude mixture was purified with column chromatography on SiO_2 (eluent: *n*-hexane/EtOAc = 5/1 (v/v), R_f = 0.23) to give yellow oil and solid. Recrystallization from *n*-hexane afforded compound **2** as a yellow solid (33 mg, 0.057 mmol, 12% isolated yield for 2 steps). 1H NMR (600MHz, CD_2Cl_2): δ (ppm) 8.84 (d, J = 8.9 Hz, 1H), 8.30 (s, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.493 (d, J = 8.5 Hz, 1H), 7.485 (d, J = 8.2 Hz, 1H), 6.82 (d, J = 9.2 Hz, 1H), 6.74–6.71 (m, 3H), 6.10 (dd, J = 9.2, 2.7 Hz, 1H), 6.05 (dd, J = 9.2, 2.8 Hz, 1H), 4.96 (s, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.56–1.84 (br, 10H). $^{13}C\{^1H\}$ NMR (150 MHz, CD_2Cl_2): 157.43, 157.28, 133.77 (2C), 131.27, 129.93, 129.39, 129.36, 128.99, 128.75, 128.58, 128.05, 128.03, 127.96, 127.33 (2C), 126.96, 126.60, 126.32, 126.30, 125.79 (2C), 125.75, 124.75, 124.26, 122.04, 115.53, 115.47, 106.61, 106.57, 78.15, 62.43, 55.54, 55.52. $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ (ppm) –2.88, –9.13, –10.07, –13.29. HRMS (APCI): calcd. for $C_{32}H_{33}B_{10}O_2^+$ $[M]^+$ 583.3406, found 583.3436. Optical resolution was performed with chiral HPLC. Conditions: HPLC column, Chiralpak IA; eluent, *n*-hexane/ $CHCl_3$ = 3/1 (v/v); flow rate, 3.5 mL·min^{–1}; detection wavelength, 250 nm; retention time, 26.1 and 35.6 min for (*P*)-(+)-**2** and (*M*)-(–)-**2**, respectively. (*P*)-(+)-**1**: $[\alpha]^{24}_D$ = +3240 (*c* 0.1, $CHCl_3$). (*M*)-(–)-**1**: $[\alpha]^{24}_D$ = –3372 (*c* 0.1, $CHCl_3$).

Single-crystal X-ray Diffraction Analysis

Table 3. Crystallographic data

Compound name	1	$\gamma / ^\circ$	90
CCDC number	2473185	$V / \text{\AA}^3$	2784.4(11)
Empirical formula	$\text{C}_{32}\text{H}_{28}\text{B}_{10}$	Z	4
Formula weight	520.64	$\rho / \text{g}\cdot\text{cm}^{-3}$	1.242
Temperature / K	143(2)	a / cm^{-1}	0.065
Wavelength / \AA	0.71075	$F(000)$	1080
Crystal system	Orthorhombic	θ range / $^\circ$	3.077–27.471
Space group	$P2_12_12_1$ (No. 19)	Limiting indices	$-9 \leq h \leq 10$ $-10 \leq k \leq 14$ $-39 \leq l \leq 39$
$a / \text{\AA}$	8.2403(19)	Collected unique reflections	22670/6340
$b / \text{\AA}$	11.115(3)	$R_{\text{int}}^{[\text{a}]}$	0.0533
$c / \text{\AA}$	30.399(7)	S (Goodness-of-fit on F^2) ^[b]	1.066
$\alpha / ^\circ$	90	$R_1 [I > 2\sigma(I)]^{[\text{c}]}$	0.0477
$\beta / ^\circ$	90	wR_2 (all data) ^[d]	0.1159

^[a] $R_{\text{int}} = \Sigma ||F_0|^2 - |F_c|^2| / \Sigma |F_0|^2$ ^[b] $S = [\{ \Sigma w(|F_0|^2 - |F_c|^2)^2 \} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\Sigma (|F_0|^2 - |F_c|^2)^2 / \Sigma (|F_0|^2)^2]^{1/2}$

^[d] $wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w(|F_0|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Optical Properties

Circular dichroism (CD) spectra were recorded on a JASCO J-820 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were recorded on a JASCO CPL-200S and a Unisoku CoolSpek USP-203 for temperature control.

Preparation procedure of β -estradiol dispersion films

The dispersed films were prepared according to the literature method.⁶⁹ The carborane derivatives (1 wt%) were dissolved in the melted β -estradiol at 200 $^\circ\text{C}$. The viscous mixed liquid was dropped on a 200 $^\circ\text{C}$ -heated quartz substrate (9.0 mm $\times$ 50 mm), onto which another hot quartz substrate (9.0 mm $\times$ 50 mm) was placed. Then, the sandwich was removed from the hot plate and quenched to form a glassy transparent matrix.

Lippert–Mataga plot

Lippert–Mataga plots were generated to discuss the relationship between solvent polarity and optical properties.^{68,84} Solvent polarity parameter (Δf) and Stokes shift ($\Delta\tilde{\nu}$) were used as parameters calculated by the following equations.

$$\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$$

in which ε and n represent dielectric constant and refractive index of the solvents, respectively.⁸⁵

$$\Delta\tilde{\nu} = \tilde{\nu}_{\text{em}} - \tilde{\nu}_{\text{abs}}$$

in which $\tilde{\nu}_{\text{em}}$ and $\tilde{\nu}_{\text{abs}}$ denote wavenumber of the absorption and emission maxima.

The difference of dipole moments between excited and ground states ($\Delta\mu$) was calculated by the linear fitting of the $\Delta\tilde{\nu}$ plots against Δf according to the following equation.

$$\Delta\tilde{\nu} = 2\Delta\mu^2/(hca^3)\Delta f + \Delta\tilde{\nu}^\circ$$

in which h is Planck constant, c is the propagating speed of light in vacuum, a is Onsager cavity radius and superscript “°” indicates the absence of solvents. Linear fitting was performed by *Origin 2020* software. Onsager cavity radii of **1** and **2** were calculated as 6.31 and 6.66 Å performed at DFT B3LYP-GD3BJ/6-311G(2d,p) level with “volume” keyword used in energy calculations.

Theoretical Calculation

General. Calculations were performed at B3LYP-GD3BJ 6-311G(2d,p) level.

Conformational dependence. The compounds have at least five possible conformations at the local minimum, and there are significant rotation barriers between those conformations. Thus, the optimized structure depends on the initial structure. The author obtained locally stable five conformers just by changing the initial structure. The interconvertibility of the conformers were calculated by the rotation barriers which were estimated by optimizing the structure at transition states (TS) using QST2 or QST3 keywords. The TS structure was confirmed by performing frequency resulting in only one imaginary frequency and intrinsic reaction coordinate (IRC) calculations connecting the two conformers around the considering TS. For QM/MM models, TS structures were calculated by using QUADMAC with QST2 or QST3 keywords and IRC calculation for excited states cannot be performed due to the unavailability of the method.

Reference

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Chapter 5

Regulating Circularly Polarized Luminescent Properties of Oxabora[6]helicene by Introduction of *o*-Carborane Scaffold for Inducing Dual-Emission Character

Abstract

Circularly polarized luminescence (CPL)-active materials have been attracting attention for improving optoelectrical technologies where handedness-control of CPL emitter is of importance. Here the author manipulated CPL properties of oxabora[6]helicene skeleton by introducing a boron and carbon cluster, *o*-carborane scaffold. In addition to a locally-excited (LE) emission band from the helicene, electron-accepting ability of *o*-carborane induced intramolecular charge-transfer (ICT) excited states, resulting in dual-emission character. Introduction of the cluster into the helicene skeleton realized high emission efficiency while maintaining dual-emission properties. Oxabora[6]helicene itself showed simple LE CPL bands, while its *o*-carborane derivative exhibited sign-inverted ICT CPL bands, meaning that introduced *o*-carborane scaffold regulated both CPL sign and wavelength of the conjugated skeleton. Theoretical calculations suggested that the CPL regulation was enabled by the spatial orientational change of transition dipole moments in the two emission characters.

Introduction

Circularly polarized luminescence (CPL) is a photophysical process that represents intensity difference between strength of right- and left-handed light (I_R and I_L , respectively) produced by chiral luminophore.^{1,2} Material applications of CPL-active materials have been considered for security ink for anti-counterfeiting techniques.³ Naked eyes cannot distinguish the handedness of CPL, while specific spectrophotometers can resolve it and identify counterfeit items.⁴ CPL-active molecules can be used as hidden codes on authentic products. Handedness and efficiency of CPL are quantified with sign and dissymmetry factor (g_{CPL}).² When $I_L > I_R$, sign is positive; otherwise, it is negative. The factor, g_{CPL} , is defined as $2(I_L - I_R)/(I_L + I_R)$. Materials with higher g_{CPL} values have been highlighted as research targets especially studied in lanthanide complexes,⁵ while molecular design for sign-controlling is currently attracting attention for security applications.⁶ Recently, several reports suggested that chiral luminophores with dual-emission properties including excimer emission⁷ and intramolecular charge-transfer (ICT) emission^{8,9} can switch their CPL sign upon changing emission characters.

The author focuses on *o*-carborane^{10,11} as a useful scaffold for CPL sign-controlling. Over the last decade, *C*-aryl derivatives have been revealed to form ICT species in the excited state owing to the electron acceptability of *o*-carborane.^{12–15} Orbital interaction between a carbon–carbon bond in the cluster ($\text{C}_{\text{cage}}\text{--}\text{C}_{\text{cage}}$) and π orbital is assumed to have a significant role. Excitation on aryl units initially forms its locally-excited (LE) state, whose π^* orbital electronically conjugates with σ^* orbital of $\text{C}_{\text{cage}}\text{--}\text{C}_{\text{cage}}$ bond when planar aryl units have perpendicular orientation to the bond ($\sigma^*\text{--}\pi^*$ conjugation).¹⁶ The excited-state conjugation initiates significant elongation of $\text{C}_{\text{cage}}\text{--}\text{C}_{\text{cage}}$ bond from 1.6–1.8 Å in the ground state to 2.2–2.4 Å in the excited-state.^{12,17–19} Theoretical analyses revealed that formation of LE and ICT states is dependent on molecular conformations.^{12,13,20} LE state is formed when $\text{C}_{\text{cage}}\text{--}\text{C}_{\text{cage}}$ bond is parallel to the π -plane (parallel conformer), while perpendicular orientation results in ICT state (twisted

conformer). Typical C-aryl derivatives show dual-emission properties based on ICT emission combined with LE emission of aryl units,^{21–26} which is a promising property for CPL sign-controlling materials. In Chapter 4, the author synthesized [7]helicene-introduced derivatives and found their sign-changing CPL properties depending on emission species i.e. the CPL shows different signs in the LE and ICT emission bands.²⁷ However, due to the low emission ability of [7]helicene unit,²⁸ the compound showed only several percent of emission quantum yield (Φ_{PL}). Furthermore, the strategy of dual-emission-based CPL sign-controlling needs more examples and analysis to confirm its generality and applicability.

This chapter focuses on a strategy to create CPL sign-controllable molecules with high luminescence efficiency (Figure 1). Recently, heterohelicenes have been reported to show highly efficient emission properties.²⁹ Especially, boron-doped helicene, borahelicene, can be synthesized by a single-step introduction of helical structure and three-coordinate boron atom via Friedel–Crafts borylation.^{30,31} Here the author utilizes oxabora[6]helicene (**OB[6]H**) skeleton reported by Hatakeyama *et al.*³² The author introduced the unit onto *o*-carborane (**CB-OB[6]H**) and studied its (chir)optical properties combined with theoretical calculation.

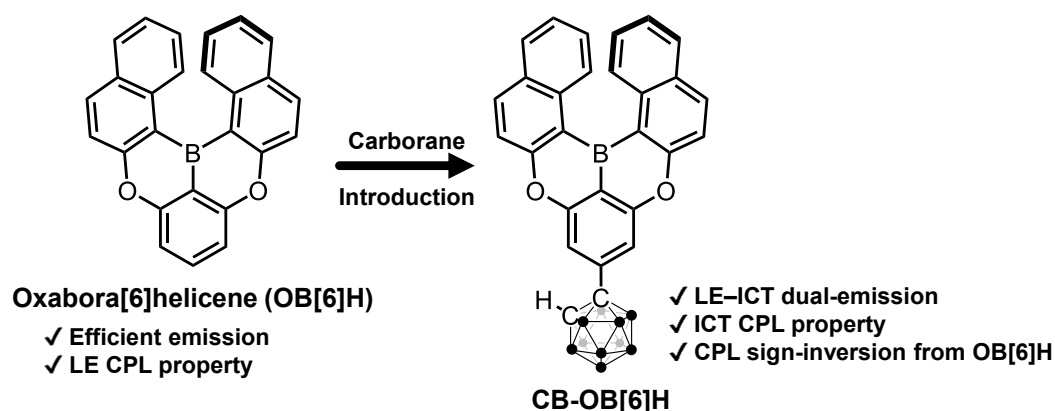
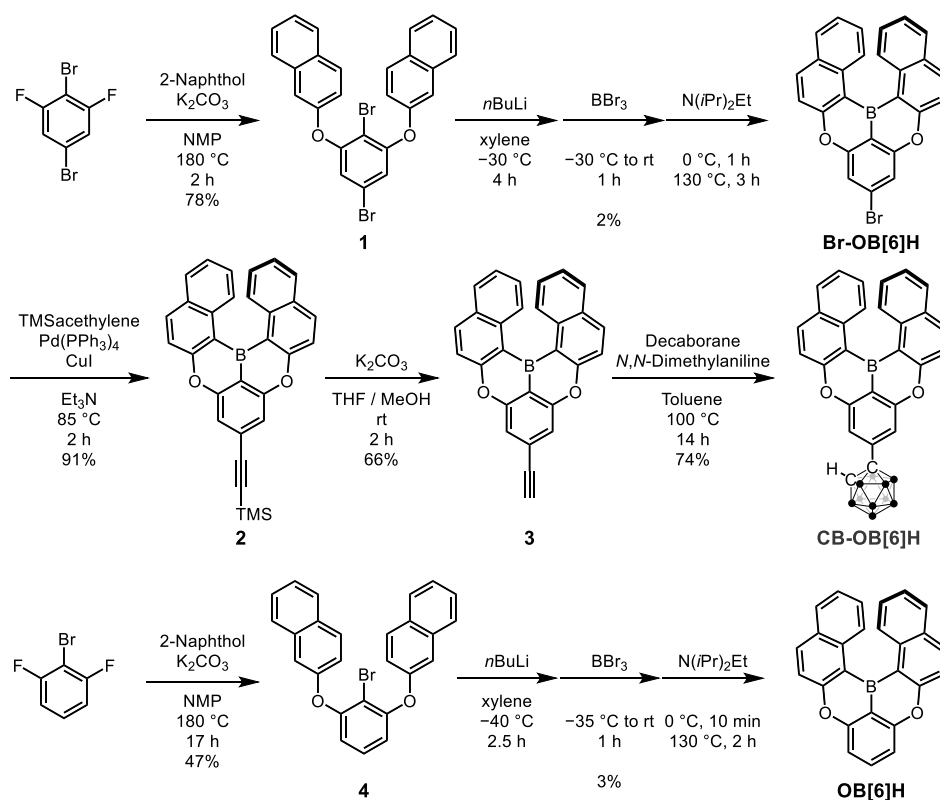


Figure 1. Schematic representation of this chapter.

Results and Discussion

The oxabora[6]helicene skeleton and its *o*-carborane derivative were synthesized according to Scheme 1. **CB-OB[6]H** was synthesized through five steps starting from 2,5-dibromo-1,3-difluorobenzene. S_NAr reaction with 2-naphthol produced naphthyloxy precursor (**1**), which was subjected to Friedel–Crafts borylation³³ to prepare bromo-functionalized derivative (**Br-OB[6]H**). Bromo group was utilized in the following Sonogashira–Hagihara coupling with trimethylsilylacetylene. Successive deprotection of a silyl unit and alkyne insertion reaction with decaborane formed **CB-OB[6]H**. In a similar manner, **OB[6]H** was synthesized from 2-bromo-1,3-difluorobenzene via naphthyloxy precursor (**4**).



Scheme 1. Synthetic scheme of oxabora[6]helicene derivatives.

X-ray diffraction unambiguously determined chemical structures of **Br-OB[6]H** and **CB-OB[6]H** (Figure 2). It confirmed helical structures associated with three-coordinate boron atoms doped in π -conjugated scaffolds. The carborane unit was also characterized in **CB-**

OB[6]H. Comparison of geometrical features was performed between oxabora[6]helicene derivatives and carbo[6]helicene. For **OB[6]H**, previously reported SCXRD data was used.³² B1–C2 bond lengths of **OB[6]H**, **Br-OB[6]H**, and **CB-OB[6]H** were 1.557(3), 1.549, and 1.57(1) Å, respectively. The lengths are ~0.1 Å longer than those of corresponding C–C bonds (1.447 Å in average) in the reported crystal structure of [6]helicene. Helical structures were further evaluated by torsion angle and helical pitch defined as the dihedral angle of C1–C2–B1–C3 and the centroid–centroid distance between 1st and 6th benzene rings of helicene, respectively.³⁴ Calculated torsion angles (helical pitch) of **OB[6]H**, **Br-OB[6]H**, and **CB-OB[6]H** were $-19.7(3)^\circ$ (4.970 Å), -20.2° (4.820 Å), and $-20(1)^\circ$ (4.952 Å) respectively, while those reported for [6]helicene were -30.3° (4.466 Å) in average. Longer B–C bond decreases helicity of oxabora[6]helicene than that of [6]helicene, while slight differences of structural parameters in three oxabora[6]helicene derivatives mean that the influence of substituents on their structure can be negligible in the ground state.

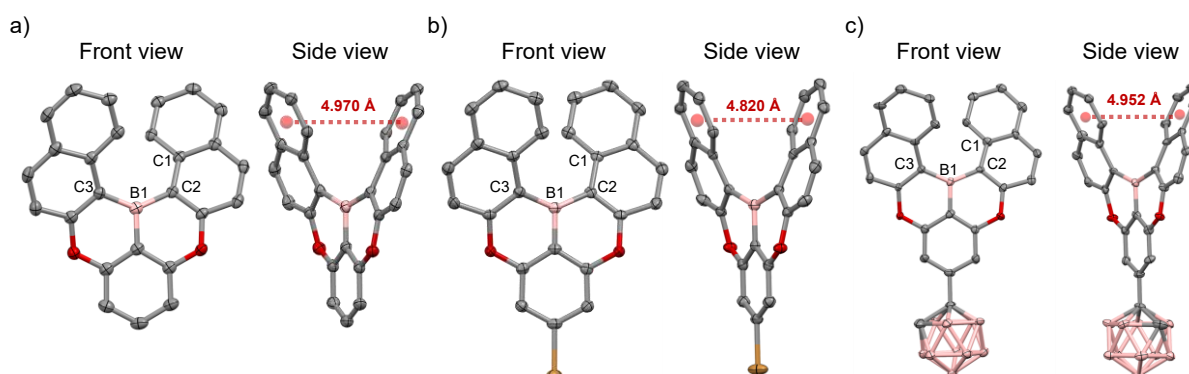


Figure 2. ORTEP drawing of a) **OB[6]H**,³² b) **Br-OB[6]H**, and c) **CB-OB[6]H**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Colors: C, gray; B, pink; O, red; Br, brown.

Optical measurements revealed that **CB-OB[6]H** has dual-emission properties with moderate luminescence efficiency in solution state. As an initial assessment, UV absorption and photoluminescence (PL) measurements were performed for racemates in dilute CHCl_3 solution

(Figure 3, Table 1). In UV absorption spectra, **OB[6]H**, **Br-OB[6]H**, and **CB-OB[6]H** showed similar spectrum shape with prominent bands at around 400 and 320 nm, meaning that the three compounds have similar ground-state electronic structures (Figure 3a). However, **CB-OB[6]H** showed different PL spectra from the others. **OB[6]H** and **Br-OB[6]H** showed only one sharp PL band around 400 nm. This sharp emission band is assignable to LE emission from the oxabora[6]helicene skeleton. In contrast, **CB-OB[6]H** exhibited a second broadly stretched PL band between 500–750 nm in addition to the sharp one. To clarify the emission species, solvent-dependency was evaluated (Figure 4). Polarity difference had no effect on the absorption and sharp PL bands, while it affected broad PL band observed in **CB-OB[6]H**: the broad band was not detected in less polar solvent, toluene, but observed in other relatively polar solvents. This result indicates that the broad PL band is polarity-sensitive and correlates with charge transfer properties. Furthermore, solvent-dependency of radiative and non-radiative constants (k_r and k_{nr} , respectively) supported the formation of charge-transfer states (Table 1). **OB[6]H** and **Br-OB[6]H**, compounds showing only LE emission band, had almost identical k_r and k_{nr} values in solvents. **CB-OB[6]H** showed no solvent-dependency of k_r value, whereas k_{nr} value increased as polarity increased. This result suggests that **CB-OB[6]H** had effective exciton funneling into charge transfer states. Then partial formation of non-emissive charge separated states was facilitated in polar solvents as reported in previous works.^{35–37}

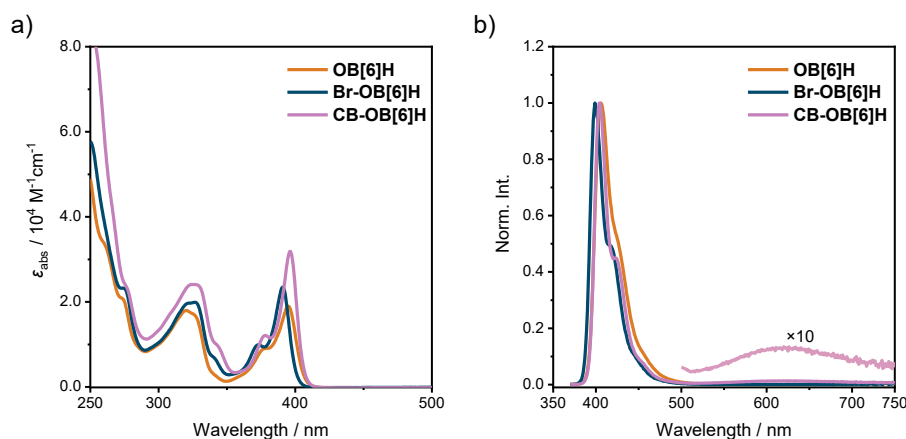


Figure 3. a) UV absorption and b) PL spectra of oxabora[6]helicene derivatives recorded in CHCl_3 (1.0×10^{-5} M)

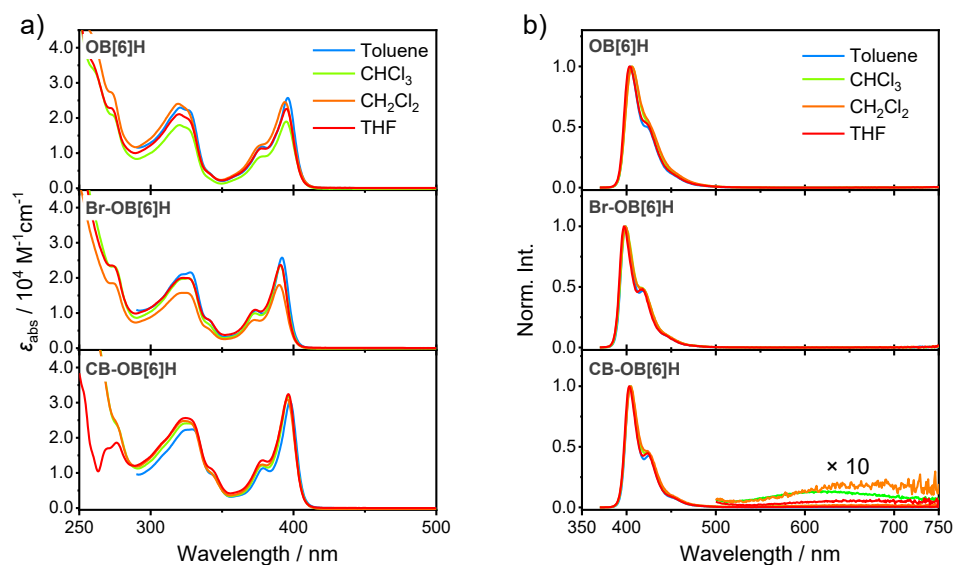


Figure 4. a) UV absorption and b) PL spectra of oxabora[6]helicene derivatives in various solvents (1.0×10^{-5} M).

Table 1. Summary of optical properties

Compound	Solvent ^[a]	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{PL}} / \text{nm}$ ^[b]	Φ_{PL} ^[b,c]	$k_{\text{r}} / \text{ns}^{-1}$ ^[d]	$k_{\text{nr}} / \text{ns}^{-1}$ ^[e]
OB[6]H	Toluene	320, 396	404	0.42	0.095	0.13
	CHCl ₃	320, 395	405	0.33	0.089	0.18
	CH ₂ Cl ₂	319, 394	406	0.36	0.088	0.16
	THF	320, 395	404	0.41	0.085	0.12
Br-OB[6]H	Toluene	328, 392	399	0.05	0.10	1.9
	CHCl ₃	326, 391	399	0.05	0.10	1.9
	CH ₂ Cl ₂	325, 390	398	0.05	0.10	1.9
	THF	322, 391	397	0.05	0.10	1.9
CB-OB[6]H	Toluene	329, 397	404	0.49	0.12	0.12
	CHCl ₃	325, 396	404, 636	0.25	0.14	0.42
	CH ₂ Cl ₂	323, 395	405, 663	0.04	0.13	3.2
	THF	324, 396	403, 643	0.11	0.11	0.89

^[a] Measured in 1.0×10^{-5} M. ^[b] Excited at λ_{abs} . ^[c] Absolute quantum yield determined by integrating sphere method. ^[d] $k_{\text{r}} = \Phi_{\text{PL}}/\tau_{\text{PL}}^{\text{ave}}$. ^[e] $k_{\text{nr}} = (1-\Phi_{\text{PL}})/\tau_{\text{PL}}^{\text{ave}}$.

The optical results were further discussed by theoretical calculations. Energy levels and distribution of the orbitals included in $S_1 \rightarrow S_0$ emission transitions were calculated with time-dependent density functional theory (TD-DFT) (Figure 5). For the emission calculation on **CB-OB[6]H**, parallel and twisted conformers were used. LE emission properties were suggested for **OB[6]H**, **Br-OB[6]H**, and parallel conformer of **CB-OB[6]H**, in which frontier molecular orbitals mainly distributed over oxabora[6]helicene scaffolds. In the twisted conformer of **CB-OB[6]H**, as expected, ICT character between *o*-carborane and π -conjugated units was suggested: highest occupied molecular orbital (HOMO) distributed on helicene unit, while structural relaxation stabilized lowest unoccupied molecular orbital (LUMO), which was localized on the cluster moiety. The twisted conformer had an elongated $C_{\text{cage}}-C_{\text{cage}}$ bond to 2.37 Å (1.63 Å for parallel conformer) because of the $\sigma^*-\pi^*$ conjugation. Experimental observation and theoretical study revealed that **CB-OB[6]H** shows dual-emission property based on LE and ICT emission characters.

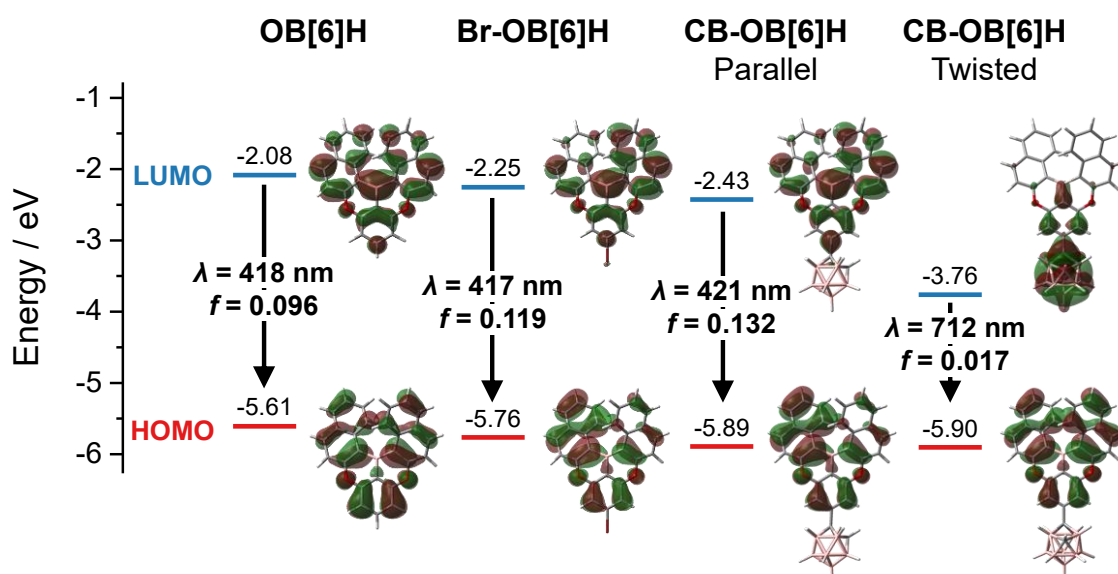


Figure 5. Calculated Kohn–Sham frontier orbital distribution and S_0 – S_1 electronic transition energy in nm for S_1 states (colors: C, gray; B, pink; H, white; O, red; Br, brown). All transitions were composed of 100% HOMO–LUMO character. f denotes the oscillator strength. Isovalues are 0.02. B3LYP-GD3BJ 6-311G(2d,p) level was used. Red and blue line plots indicate energy levels of HOMOs and LUMOs, respectively.

An additional feature is moderate emission efficiency of the heterohelicene skeleton (Table 1): Φ_{PL} values of **OB[6]H** and **CB-OB[6]H** were 0.33 and 0.25 in CHCl_3 , which is much higher than that of previously reported [7]helicene-appended *o*-carborane ($\Phi_{\text{PL}} \leq 0.04$ in solutions and films). **CB-OB[6]H** still showed dual-emission character in more polar solvents such as CH_2Cl_2 and THF, while Φ_{PL} reached only 0.11 at maximum.

Enantiomeric pairs of **OB[6]H** and **CB-OB[6]H** were successfully separated into two fractions by chiral HPLC. Enantiomeric excess (e.e.) of both isomers was over 99%, confirming their sufficient optical purity. The racemization Gibbs activation energy of **CB-OB[6]H** was determined as $25.9 \text{ kcal}\cdot\text{mol}^{-1}$, which means that an enantiopure sample is expected to retain its e.e. over 99% for at least 3 h (Figure 6). The experimental racemization barrier was in good agreement with the calculated values (**OB[6]H**, $27.4 \text{ kcal}\cdot\text{mol}^{-1}$; **CB-OB[6]H**, $27.1 \text{ kcal}\cdot\text{mol}^{-1}$). Absolute helicity of enantiomeric pairs was also determined with the correspondence of circular dichroism (CD) spectra between experimental and theoretical results. First and second fractions in chiral chromatography were characterized as (*P*) and (*M*)-isomers, respectively.

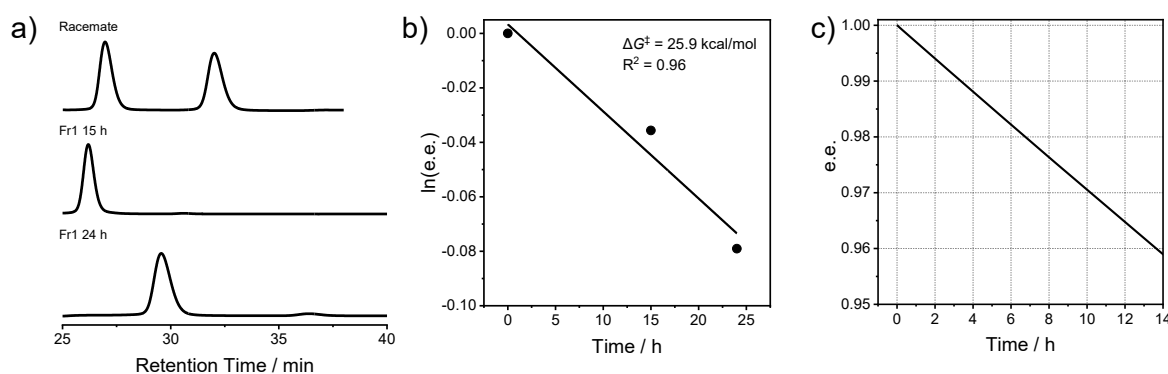


Figure 6. Time-dependency of a) chiral HPLC chromatogram of **CB-OB[6]H** (1st fraction) after separation (eluent: $\text{CHCl}_3/\text{Hex} = 1/3$, v/v) at 298 K and b) experimentally observed results (filled circle) with linear fitting (solid line) at 298 K. c) Simulation of e.e. against time with consideration of $\Delta G^\ddagger = 25.9 \text{ kcal}\cdot\text{mol}^{-1}$ and $T = 298 \text{ K}$.

Chiroptical measurements were performed with enantiopure samples. Initially, CD spectra were obtained in CHCl_3 solution (Figure 7a). **OB[6]H** and **CB-OB[6]H** showed clear CD signals and their (*P*)-isomers had similar sign of spectra, while **CB-OB[6]H** showed weaker CD signals than that of **OB[6]H**. CD measurements indicated that the introduction of *o*-carborane unit maintained ground-state chiral electronic structure, while weakened CD signals probably because of the reduced rigidity of chiral structure. Next, CPL spectra were obtained to evaluate correlation between dual-emission character and chiral excited-state electronic structure (Figures 7bc). **OB[6]H** showed clear CPL signal in the same wavelength region to LE emissive PL band with negative and positive signals of CPL for (*P*)- and (*M*)-isomers, respectively. In contrast, **CB-OB[6]H** showed only noisy signals between 370–500 nm, where LE band was clearly observed in PL spectra. **CB-OB[6]H** only showed a broad CPL band between 500–800 nm, where ICT PL band is weakly observed. Moreover, the CPL sign was inverted upon introduction of carborane unit: (*P*)- and (*M*)-**CB-OB[6]H** showed positive and negative CPL signal in ICT region, respectively. These results indicate that wavelength and sign of CPL spectra were mediated by incorporating *o*-carborane.

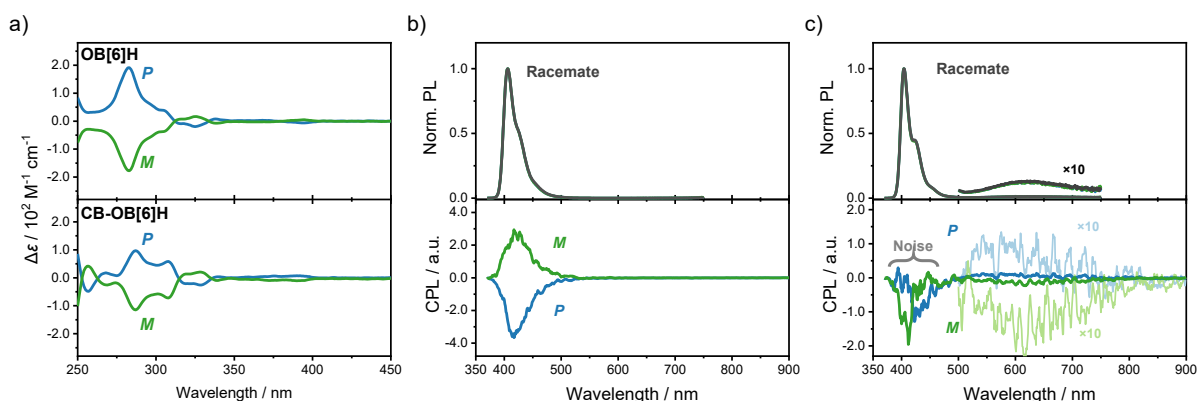


Figure 7. a) CD spectra of **OB[6]H** and **CB-OB[6]H**. CPL spectra of b) **OB[6]H** and c) **CB-OB[6]H** with corresponding PL spectra. All spectra were recorded in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$).

For mechanistic understanding of CPL properties, theoretical calculation was utilized.^{38,39} Theoretical *g* value of CPL ($g_{\text{CPL}}^{\text{calc}}$) was calculated by the following equation: $g_{\text{CPL}}^{\text{calc}} = 4|\boldsymbol{\mu}'||\boldsymbol{m}'|\cos\theta_{\boldsymbol{\mu}',\boldsymbol{m}'} / (|\boldsymbol{\mu}'|^2 + |\boldsymbol{m}'|^2)$, where $\boldsymbol{\mu}'$ is the transition electric dipole moment (TEDM), $\boldsymbol{m}'$

is the transition magnetic dipole moment (TMDM) and $\theta_{\mu',m'}$ is the angle between TEDM and TMDM vectors for de-excitation transitions. The observed and calculated g values are listed in Table 2. The $g_{\text{CPL}}^{\text{calc}}$ for (*P*)-**OB**[6]**H** and twisted conformer of (*P*)-**CB-OB**[6]**H** were consistent in sign and almost on the same order of magnitude as those observed ($\sim 10^{-3}$), supporting validity of the calculation method. Calculated dipole moment vectors were superimposed on molecular geometry (Figure 8). It suggested that relative orientation of the vectors was flipped upon switching of the emission species, which changed sign of CPL. Consequently, the introduced carborane moiety induced ICT emission in the oxabora[6]helicene skeleton and altered CPL wavelength and sign. Additionally, lower $g_{\text{CPL}}^{\text{calc}}$ value ($\sim 10^{-4}$) was calculated for the parallel conformer of (*P*)-**CB-OB**[6]**H**, which is consistent with weakened CD signal and the absence of LE CPL signal from **CB-OB**[6]**H**. This suggests that the chiroptical nature of oxabora[6]helicene skeleton was reduced by the introduction of *o*-carborane unit, although it induced dual-emission.

Table 2. CPL dissymmetry factors of oxabora[6]helicene derivatives

	Emission species	$ g_{\text{CPL}} / 10^{-3} (\lambda / \text{nm})^{[a]}$	$ g_{\text{CPL}}^{\text{calc}} / 10^{-3}^{[b]}$
OB [6] H	LE	0.69 (425–525)	1.4
	LE	n.d.	0.25
CB-OB [6] H	ICT	0.78 (550–650)	0.86

^[a] Averaged values of both isomers within specified wavelength range. ^[b] Calculated values of (*P*)-isomers.

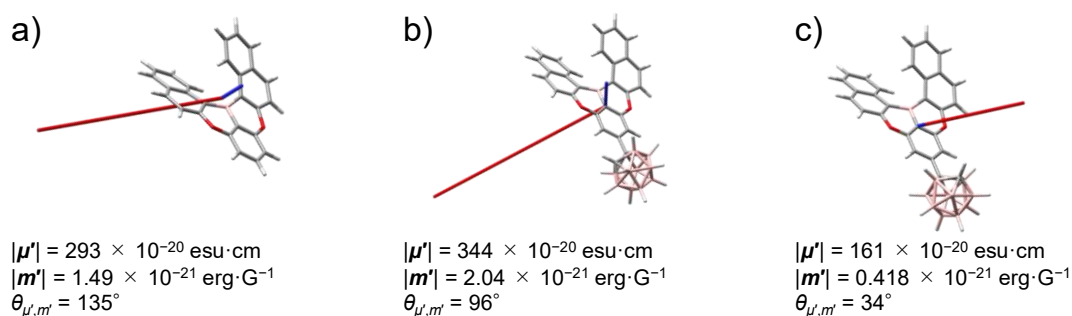


Figure 8. Visualized arrangements of TEDM (μ' , red) and TMDM (m' , blue) vectors for S_1 to S_0 transitions of a) (*P*)-**OB**[6]**H**, and b) parallel and c) twisted conformers of (*P*)-**CB-OB**[6]**H**, where the length of TMDM vectors are multiplied by 200 times for visibility.

Conclusion

In this chapter, regulation of CPL properties of **OB[6]H**, a hetero-atom-doped π -conjugated helical skeleton, was enabled by introduction of *o*-carborane scaffold. The cluster induced ICT excited states in the brightly emissive heterohelicene scaffold, which resulted in high emission efficiency with dual-emission properties. **OB[6]H** showed clear CPL bands originating from LE emission. In contrast, its *o*-carborane derivative, **CB-OB[6]H**, exhibited ICT CPL bands with inverted sign from LE CPL of **OB[6]H**, indicating the CPL sign and wavelength of the heterohelicene skeleton were regulated by the simple introduction of *o*-carborane scaffold. Computational analysis suggests that CPL from LE and ICT excited states has different spatial orientation of transition electric and magnetic dipole moments, leading to sign inversion. This work contributes not only to basic photophysical chemistry but also to material science based on CPL-active materials.

Experimental Section

The experimental procedure followed that described in Chapters 1 and 4, with the differences and additional details summarized below.

Materials

Commercially available reagents used without purification

2,5-Dibromo-1,3-difluorobenzene (Tokyo Chemical Industry Co., Ltd), 2-naphthol (Tokyo Chemical Industry Co., Ltd), *n*-butyllithium (*n*BuLi), 1.6 mol·L⁻¹ in *n*-hexane (KANTO CHEMICAL CO., INC.), BBr₃, (Ampoule, Fujifilm Wako Pure Chemical Corporation), N(*i*Pr)₂Et (Fujifilm Wako Pure Chemical Corporation), trimethylsilylacetylene (TMSacetylene) (Tokyo Chemical Industry Co., Ltd), 2-bromo-1,3-difluorobenzene (Tokyo Chemical Industry Co., Ltd), K₂CO₃ (Fujifilm Wako Pure Chemical Corporation), NH₄Cl (Fujifilm Wako Pure Chemical Corporation)

Commercially available solvents used without purification

N-Methyl-2-pyrrolidone (NMP) (Super dehydrated, Fujifilm Wako Pure Chemical Corporation), xylene (Super dehydrated, Fujifilm Wako Pure Chemical Corporation), pyridine-*d*₅ (Eurisotop)

Synthesis

General. The ¹H and ¹³C chemical shift values recorded in pyridine-*d*₅ were expressed relative non-deuterated solvent (¹H, 7.19 ppm; ¹³C, 123.50 ppm) as internal standards. Column chromatography was performed with Nacalai Tesque Silica Gel 60 (spherical, neutral, averaged particle diameter; 75 μm). Optical resolution was performed with chiral HPLC. Conditions: HPLC column, Chiralpak IA; flow rate, 3.5 mL·min⁻¹; detection wavelength, 250 nm.

Synthesis of 1,3-bis(2-naphthyloxy)-2,5-dibromobenzene (1). A modified procedure from a published paper was applied.⁴⁰ 2,5-Dibromo-1,3-difluorobenzene (3.217 g, 11.83 mmol), 2-naphthol (3.416 g, 23.69 mmol) and K₂CO₃ (6.615 g, 47.86 mmol) were added to a 200 mL 2-necked round bottom flask. After equipped with a stirring bar, a 3-necked cock, and a septum, the flask was filled with N₂ flow. NMP (super dehydrated, 48 mL) was added to form a colorless suspension. The suspension was heated at 180 °C by mantle heater, when the mixture turned into a green-blue suspension. After 2 h, the mixture turned into a reddish-brown suspension, which was then cooled to room temperature. The mixture was washed with brine and extracted with CHCl₃. The combined organic component was dried over MgSO₄, filtered, and

concentrated by a rotary evaporator to afford NMP solution. MeOH (ca. 250 mL) was added to the solution. Precipitated solid was collected by vacuum filtration and then recrystallized by MeOH/CHCl₃ (ca. 1/10 (v/v), ca. 150 mL) at 80 °C to afford **1** as a colorless solid. Filtrate solution was concentrated and subjected to second recrystallization at the same condition. Combined solid (4.829 g, 9.283 mmol, 78% isolated yield) was used for a successive reaction. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.91 (d, J = 9.2 Hz, 2H), 7.87 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.52 (ddd, J = 7.4, 7.4, 1.6 Hz, 2H), 7.47 (ddd, J = 7.6, 7.6, 1.4 Hz, 2H), 7.42 (d, J = 2.3 Hz, 2H), 7.30 (dd, J = 8.9, 2.5 Hz, 2H), 6.83 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) = 156.5, 153.4, 134.2, 130.7, 130.4, 127.9, 127.4, 126.8, 125.4, 121.3, 119.7, 117.2, 115.1, 105.9. HRMS (APCI) calcd. for C₂₆H₁₆Br₂O₂+H⁺ [M+H]⁺ 518.9590, found 518.9586.

Synthesis of Br-OB[6]H. A modified procedure from a published paper was applied.^{32,40} To an oven-dried 300 mL 2-necked round bottom flask, **1** (3.105 g, 5.969 mmol) was added. After equipped with an oven-dried stirring bar, a 3-necked cock, and a septum, the flask was filled with N₂ flow. Xylene (super dehydrated, 120 mL) was added to form colorless suspension. The suspension was cooled down to -40 °C by dry ice/MeOH/H₂O bath. *n*BuLi (1.6 M, 4.15 mL, 6.64 mmol) was added in a dropwise manner within 5 min. The mixture turned into a yellowish suspension and was stirred at -30 to -40 °C for 4 h. BBr₃ (0.67 mL, 7.2 mmol) was added in a dropwise manner within 5 min. The mixture turned into a reddish-brown suspension. Then the mixture was warmed to room temperature and stirred for 1 h. At 0 °C, N(*i*Pr)₂Et (1.9 mL, 10.9 mmol) was added in a dropwise manner. The mixture turned into a yellowish suspension. After 1 h stirred at 0 °C, the mixture was heated at 130 °C for 3 h to form a yellow solution with colorless precipitates. After cooling to room temperature, the mixture was concentrated to afford a brown solid. CHCl₃ (ca. 200 mL) was added to form suspension, which was filtrated by celite[®]. An orange filtrate solution was concentrated. Column chromatography was performed on neutral SiO₂ four times. Eluent was toluene/*n*-hexane = 1/4 (v/v) (R_f = 0.70) for first three times and CHCl₃/*n*-hexane = 1/5 (v/v) (R_f = 0.43) for the last. Combined product-rich solid was recrystallized by *n*-hexane/CHCl₃ (ca. 1/2 (v/v)) at 80 °C to afford **Br-OB[6]H** (63 mg, 0.14 mmol, 2% isolated yield) as a colorless solid. This procedure was repeated to get enough amount of the product for the next reaction. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.17 (d, J = 8.7 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 9.2 Hz, 2H), 7.56 (s, 2H), 7.44 (ddd, J = 8.0, 6.7, 1.1 Hz, 2H), 7.11 (ddd, J = 8.6, 7.0, 1.5 Hz, 2H). ¹³C{¹H} NMR (100 MHz, pyridine-*d*5): δ (ppm) = 157.6, 157.5, 137.7, 131.9, 130.5, 130.2,

128.7, 125.5, 124.1, 120.4, 119.7, 113.3 (NMR signals of the α -positioned carbon atoms to a boron atom were not observed). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) = 40.9. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, pyridine-*d*5): δ (ppm) = -5.9. HRMS (APCI) calcd. for $\text{C}_{26}\text{H}_{14}\text{BBrO}_2 + \text{H}^+$ $[\text{M} + \text{H}]^+$ 449.0343, found 449.0340.

Synthesis of (7,11-dioxa-17c-boraphenanthro[2,3,4-*no*]tetraphen-9-ylethynyl) trimethylsilane (2). To a 100 mL 2-necked round bottom flask, **Br-OB[6]H** (155 mg, 0.345 mmol), CuI (9 mg, 0.05 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (82 mg, 0.071 mmol) were added. After equipped with a stirring bar, a 3-necked cock, and a septum, the flask was filled with N_2 flow. Et_3N (11 mL) and TMSacetylene (0.10 mL, 0.73 mmol) were added. The solution was stirred at 85 °C for 2 h. The mixture was washed with aqueous NH_4Cl (ca. 20 mL). The organic component was extracted with EtOAc (ca. 15 mL $\times$ 3). The combined organic component was dried over MgSO_4 , filtered, and concentrated by a rotary evaporator to afford black oil. Column chromatography was performed on neutral SiO_2 (eluent: CHCl_3/n -hexane = 1/3 (v/v), R_f = 0.55) to give **2** as a colorless solid (147 mg, 0.315 mmol, 91% isolated yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.13 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 7.3 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.9 Hz, 2H), 7.45 (s, 2H), 7.41 (ddd, J = 7.8, 7.3, 0.9 Hz, 2H), 7.08 (ddd, J = 8.4, 7.0, 1.3 Hz, 2H), 0.32 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) = 160.2, 155.3, 135.0, 134.8, 130.7, 130.0, 127.7, 127.3, 126.3, 125.0, 118.9, 112.2, 104.6, 96.7, -0.1 (NMR signals of the α -positioned carbon atoms to a boron atom were not observed). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) = 40.6. HRMS (APCI): calcd. for $\text{C}_{31}\text{H}_{23}\text{BO}_2\text{Si}^+$ $[\text{M} + \text{H}]^+$ 467.1633, found 467.1637.

Synthesis of 9-ethynyl-7,11-dioxa-17c-boraphenanthro[2,3,4-*no*]tetraphene (3). To a 300 mL round bottom flask, **2** (127 mg, 0.272 mmol) and K_2CO_3 (196 mg, 2.00 mmol) were added. After the flask was equipped with a stirring bar, MeOH (6.0 mL) and THF (6.0 mL) were added to form a white suspension. The solution was stirred at room temperature for 2 h. The mixture was washed with H_2O (ca. 10 mL). The organic component was extracted with EtOAc (ca. 10 mL $\times$ 3–5). The combined organic component was dried over MgSO_4 , filtered, and concentrated by a rotary evaporator to afford **3** as a colorless solid (71 mg, 0.18 mmol, 66% isolated yield). ^1H NMR (400 MHz, pyridine-*d*5): δ (ppm) = 8.07 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 9.2 Hz, 2H), 7.40 (s, 2H), 7.29 (ddd, J = 7.6, 7.6, 0.9 Hz, 2H), 6.98 (ddd, J = 7.7, 7.7, 1.4 Hz, 2H), 4.07 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, pyridine-*d*5): δ (ppm) = 157.6, 156.9, 137.7, 136.0, 131.9, 130.5, 130.1, 128.7, 125.4, 121.9, 119.8, 113.7, 84.5, 78.7 (NMR signals of the α -positioned carbon atoms to a boron atom were not observed).

$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, pyridine-*d*5): δ (ppm) = -7.1. HRMS (APCI): calcd. for $\text{C}_{28}\text{H}_{15}\text{BO}_2^+$ $[\text{M}+\text{H}]^+$ 395.1238, found 395.1241.

Synthesis of CB-OB[6]H. To a 100 mL 2-necked round bottom flask, **3** (71 mg, 0.180 mmol) and $\text{B}_{10}\text{H}_{14}$ (28 mg, 0.23 mmol) were added. After equipped with a stirring bar, a 3-necked cock, and a septum, the flask was filled with N_2 flow. Toluene (5.5 mL) and *N,N*-dimethylaniline (0.05 mL, 0.40 mmol) were added to form yellow solution. The solution was stirred at 100 °C for 14 h. The yellow mixture was filtrated to remove any insoluble components and the filtrate solution was concentrated to afford a yellow solid. Column chromatography was performed on neutral SiO_2 (eluent: CHCl_3/n -hexane = 1/3 (v/v), R_f = 0.40). to give **CB-OB[6]H** as a yellow solid (68 mg, 0.13 mmol, 74% isolated yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 8.19 (d, J = 8.7 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H, overlapped), 7.51 (s, 2H), 7.45 (ddd, J = 8.1, 7.0, 1.0, 2H), 7.11 (ddd, J = 8.4, 7.0, 1.3, 2H), 4.17 (s, 1H), 3.50–1.70 (br, 10H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) = 160.3, 155.6, 138.1, 135.3, 134.9, 130.7, 130.2, 127.9, 126.5, 125.3, 119.6, 118.7, 118.4, 108.2, 75.8, 60.0. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3): δ (ppm) = 40.2, -2.3, -4.2, -9.0, -10.9, -12.9. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, pyridine-*d*5): δ (ppm) = -3.0, -9.2, -10.8. HRMS (APCI): calcd. for $\text{C}_{28}\text{H}_{25}\text{B}_{11}\text{O}_2^+ \text{Cl}^-$ $[\text{M}+\text{Cl}]^-$ 549.2615, found 549.2626. Chiral HPLC: eluent, *n*-hexane/ CHCl_3 = 3/1 (v/v); retention time, 30.6 and 38.6 min for (*P*)- and (*M*)-**CB-OB[6]H**, respectively.

Synthesis of 1,3-bis(2-naphthyloxy)-2-bromobenzene (4). A modified procedure from a published paper was applied.⁴⁰ 2-Naphtol (2.895 g, 20.08 mmol) and K_2CO_3 (5.248 g, 37.97 mmol) were added to a 2-necked round bottom flask. After equipped with a stirring bar, a 3-necked cock, and a septum, the flask was filled with N_2 flow. 2-Bromo-1,3-difluorobenzene (1.20 mL, 10.7 mmol) and NMP (super dehydrated, 40 mL) were added to form a colorless suspension. The suspension was heated at 180 °C by mantle heater, when the mixture turned into a black-green suspension. After 2.5 and 4 h, 0.7104 g and 0.7124 g of 2-naphtol were added, respectively. 17 h after the reaction began, the mixture turned into a reddish-brown suspension, which was then cooled to room temperature. The mixture was washed with H_2O and extracted with CHCl_3 . The combined organic component was dried over MgSO_4 , filtered, and concentrated by a rotary evaporator to afford black NMP solution. MeOH (ca. 150 mL) was added to the solution. The mixture was placed at -30 °C freezer for 4 h. Precipitated solid was collected by vacuum filtration to afford **4** as a colorless solid (2.199 g, 4.983 mmol, 47% isolated yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.87 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.48 (ddd, J = 8.2, 6.8, 1.4 Hz, 2H), 7.43 (ddd, J = 8.2,

6.8, 1.4 Hz, 2H), 7.34 (d, $J = 2.3$ Hz, 2H), 7.32 (dd, $J = 8.4, 2.3$ Hz, 2H), 7.21 (t, $J = 8.4$ Hz, 1H), 6.80 (d, $J = 8.2$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) = 155.7, 154.4, 134.2, 130.4, 130.1, 128.5, 127.8, 127.2, 126.7, 124.9, 119.5, 115.2, 113.9, 108.0. HRMS (APCI) calcd. for $\text{C}_{26}\text{H}_{17}\text{BrO}_2 + \text{H}^+ [\text{M} + \text{H}]^+$ 441.0485, found 441.0479.

Synthesis of OB[6]H. A modified procedure from a published paper was applied.^{32,40} To an oven-dried 300 mL 2-necked round bottom flask, **4** (1.094 g, 2.478 mmol) was added. After equipped with an oven-dried stirring bar, a 3-necked cock, and a septum, the flask was filled with N_2 flow. Xylene (super dehydrated, 50 mL) was added to form a colorless solution. The solution was cooled down to -40 °C by dry ice/MeOH/ H_2O bath. $n\text{BuLi}$ ($1.6 \text{ mol} \cdot \text{L}^{-1}$, 1.75 mL, 2.8 mmol) was added in a dropwise manner within 5 min. The mixture turned into a white suspension and was stirred at -30 to -40 °C for 2.5 h. $n\text{BuLi}$ (1.6 M, 0.3 mL, 0.48 mmol) was additionally added. BBr_3 (0.28 mL, 3.0 mmol) was added in a dropwise manner within 5 min. The mixture turned into a brownish solution. Then the mixture was warmed to room temperature and stirred for 1 h. At 0 °C, $\text{N}(i\text{Pr})_2\text{Et}$ (0.8 mL, 4.6 mmol) was added in a dropwise manner. The mixture turned into a yellowish suspension. After 10 min stirred at 0 °C, the mixture was heated at 130 °C for 2 h to form a yellow solution with colorless precipitates. After cooling to room temperature, the mixture was concentrated to afford a brown solid. CHCl_3 (ca. 50 mL) was added to form suspension, which was filtrated by celite[®]. An orange filtrate solution was concentrated to be approx. 20% initial volume. Column chromatography was performed on neutral SiO_2 (eluent: $\text{CHCl}_3/n\text{-hexane} = 1/3$ (v/v), $R_f = 0.65$) to give a yellow solid. Recrystallization from $\text{CHCl}_3/n\text{-hexane}$ (ca. $1/5$ (v/v)) was performed twice. Re-column chromatography was performed on neutral SiO_2 (eluent: $\text{CHCl}_3/n\text{-hexane} = 2/3$ (v/v), $R_f = 0.70$) to afford **OB[6]H** (31 mg, 0.083 mmol, 3% isolated yield) as a yellowish solid. The product was characterized by ^1H NMR according to literature.³² Chiral HPLC: eluent, $n\text{-hexane}/\text{CHCl}_3 = 9/1$ (v/v); retention time, 31.7 and 34.8 min for (*P*)- and (*M*)-**OB[6]H**, respectively.

Theoretical Calculation

The chiral stability of enantiomeric samples at specified temperatures (T) were examined by the following equation,⁴¹ where ee is enantiomeric excess, t is time, κ is transmission coefficient ($= 0.5$), k_B is Boltzmann constant, h is Planck constant, R is gas constant, and $\Delta G^\ddagger$ is racemization barrier:

$$\ln(ee) = -t \times 2 \frac{\kappa k_B T}{h} \exp \left(-\frac{\Delta G^\ddagger}{RT} \right)$$

Single-crystal X-ray Diffraction Analysis

Table 3. Crystallographic data

Compound name	Br-OB[6]H	CB-OB[6]H
CCDC number	2496906	2496907
Empirical formula	C ₂₆ H ₁₄ BBrO ₂	C ₂₈ H ₂₅ B ₁₁ O ₂
Formula weight	449.09	512.39
Temperature / K	143	143
Wavelength / Å	0.71075	0.71075
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> bcn (No.60)	<i>P</i> 2 ₁ /c
<i>a</i> / Å	16.6469(19)	12.815(10)
<i>b</i> / Å	13.4057(15)	6.557(5)
<i>c</i> / Å	8.3868(11)	30.61(2)
α / °	90	90
β / °	90	95.076(12)
γ / °	90	90
<i>V</i> / Å ³	1871.6(4)	2562(3)
<i>Z</i>	4	4
ρ / g·cm ⁻³	1.594	1.329
<i>a</i> / cm ⁻¹	2.218	0.074
<i>F</i> (000)	904	1056
θ range / °	3.039–27.494	3.178–27.501
Limiting indices	–21 ≤ <i>h</i> ≤ 18 –17 ≤ <i>k</i> ≤ 17 –10 ≤ <i>l</i> ≤ 10	–16 ≤ <i>h</i> ≤ 14 –8 ≤ <i>k</i> ≤ 8 –34 ≤ <i>l</i> ≤ 39
Collected unique reflections	14107/2151	18021/5744
<i>R</i> _{int} ^[a]	0.0797	0.1097
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.159	1.123
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.0613	0.1649
<i>wR</i> ₂ (all data) ^[d]	0.0983	0.4311

^[a] $R_{\text{int}} = \Sigma ||F_o|^2 - \langle |F_o|^2 \rangle| / \Sigma |F_o|^2$ ^[b] $S = [\{\Sigma w(|F_o|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\Sigma (|F_o|^2 - |F_c|^2)^2 / \Sigma (|F_o|^2)^2]^{1/2}$

^[d] $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(|F_o|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_o|^2) + (ap)^2 + bp]$, where $p = [|F_o|^2 + 2|F_c|^2] / 3$

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Part 3

Solid-State Stimuli-Responsiveness Based on the Dual-Emission Including Excimer and Intramolecular Charge Transfer Emission

Chapter 6

Regulation of Solid-State Dual-Emission Properties by Switching Luminescent Processes Based on the Bis-*o*-Carborane-Modified Anthracene Triad

Abstract

The author herein demonstrates not only design of combination of luminescent processes in dual-emission properties by selecting preparation protocols but also temperature-driven switching of luminescent processes in dual-emission properties based on a bis-*o*-carborane-substituted anthracene triad in crystal. The author synthesized the triad and obtained crystal polymorphs with or without included solvent molecules by changing the type of solvent used in recrystallization. From the optical measurements, it is shown that dual-emission properties arise from distinct photophysical mechanisms. In the absence of the solvent molecules the crystal exhibits dual-emission of charge transfer (CT) and excimer, while in the presence of them the crystal exhibits that of locally-excited (LE) and CT emission. Furthermore, relative intensities of these emissions are sensitive to temperature changes. These luminochromic behavior is well-suited for application to ratiometric sensing systems.

Introduction

The dual-emission system, in which two emission bands are simultaneously observed in the spectra, is a versatile optical behavior.¹ For example, to obtain white luminescence, dual-emission is necessary with appropriate color balance.² Generally, by loading several dyes having different luminescent color onto matrices, desired luminescent color is generated. As another instance, if intensity ratios of the components are varied by environmental changes, precise detection for the changes can be realized through ratiometric analyses.³ By comparing emission intensities at various wavelength positions, influence from the heterogeneity of local concentration of luminophores on the signals can be minimized. This function is of importance especially for realizing quantitative analyses.⁴ Therefore design and synthesis of dual-emission systems should be of significance for developing advanced luminescent materials.

In solution system, several approaches have been established for obtaining dual-emission. By suppressing transitions between locally-excited (LE) and charge transfer (CT) states in the excited state, dual-emission has often been achieved.⁵ Owing to the environmental sensitivity, dual emissive materials can be utilized as key components for optical chemical sensors.⁶ The dual-emission consisting of LE and excimer emission has been also accomplished.⁷ Drastic color changes can be obtained because of intrinsic intense emission from excimer. Additionally, by connecting different types of molecules and suppressing energy-transfer efficiency, dual-emission can be produced.⁸ Thus, dual-emission properties are suitable for designing luminescent sensors. However, there are still difficulties in the design of dual-emission systems in the solid state. Luminescent properties are generally spoiled by non-specific intermolecular interactions in the condensed state. Moreover, due to structural restrictions, it is challenging to design luminochromic behaviors based on dual-emission properties.

o-Carborane is an icosahedral boron and carbon cluster compound.⁹ Tremendous attention has been paid to aryl-modified *o*-carboranes as a platform for obtaining functional solid-state

luminescent materials. From the first report on aggregation-induced emission of *o*-carborane-containing polymers,¹⁰ a series of stimuli-responsive luminescent materials have been developed.¹¹ According to the mechanistic studies, it was revealed that molecular rotation in the *o*-carborane unit in the condensed state is allowed, and various luminescent colors can be expressed by regulating the angle between the direction of the C–C bond in *o*-carborane and π -plane.^{12,13} In the planar and vertical conformations between them, LE and CT emission can be respectively induced even in the solid state. On the basis of these structure-related optical properties, stimuli-responsive luminochromic behaviors have been observed from the solid materials by regulating the degree of molecular rotation.¹⁴ Thus, the author presumed that introduction of multiple *o*-carborane substituents could be a promising strategy for obtaining diverse solid-state luminochromic behaviors as well as highly sensitive stimuli-responsiveness.

Herein, the author reports bis-*o*-carborane-modified anthracene triad (**1**) (Figure 1). The author obtained crystal polymorphs depending on solvation. Each polymorph provides characteristic solid-state dual-emission behaviors. In the absence of solvents, dual-emission consisting of CT and excimer emissions was detected, while dual-emission composed of LE and CT emissions was observed in their presence. Remarkably, both crystals showed thermochromic luminescence based on intensity ratio changes between dual-emission bands.

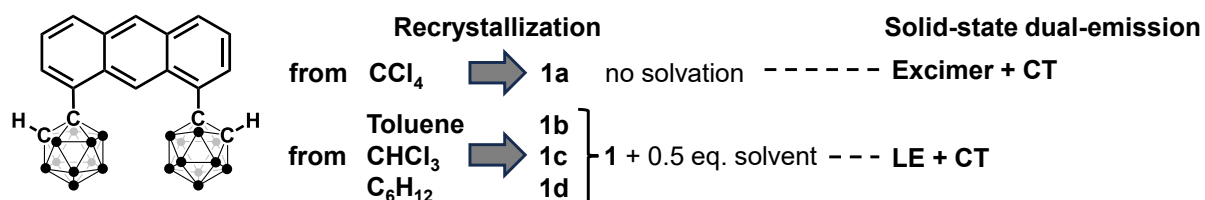
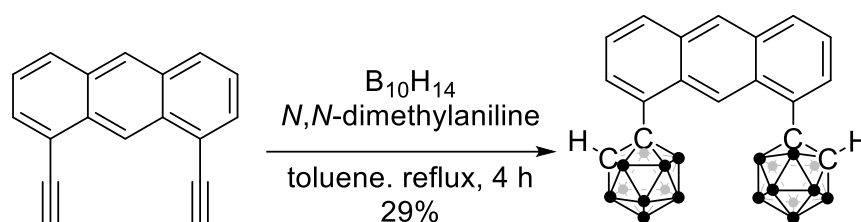


Figure 1. Chemical structure of **1** and schematic illustration for the preparation of crystal polymorphs and their dual emission properties.

Results and Discussion

The author designed a bis-*o*-carborane-substituted anthracene triad **1**. Anthracene is known as a typical aromatic ring with luminescent properties and has been employed as an aryl moiety for constructing *o*-carborane dyads because of its efficient absorption and emission properties. The triad **1** was synthesized by the alkyne insertion reaction¹⁵ with decaborane ($B_{10}H_{14}$) and 1,8-diethynylantracene (Scheme 1).



Scheme 1. Synthesis of **1** by alkyne insertion reaction.

By changing the type of solvents for recrystallization, the author was able to obtain polymorphs with different optical properties. When **1** was recrystallized from CCl_4 , a yellow crystal (**1a**) was obtained, while from toluene, $CHCl_3$, and cyclohexane, light-yellow crystals (**1b–1d**) were obtained, respectively. From 1H NMR spectroscopy and thermogravimetric analyses, **1a** has no solvent molecules, whereas **1b–1d** included 0.5 equivalent of solvent molecules (Tables 1 and 2). Also, crystals had different powder X-ray diffraction (PXRD) patterns (Figure 2a). Based on these results, **1** was shown to have crystal pseudo-polymorphs depending on conditions. Additionally, transition from **1b–1d** to **1a** can be achieved by heating. When **1b** was heated at 200 °C for 5 min (named as **1b'**), the transformation to **1a** with the clear color change from light yellow to yellow occurred. PXRD patterns of the heated **1b'** were identical to those of **1a**. Moreover, in the profile of differential scanning calorimetry (DSC) of **1b**, the endothermic peak was observed at 156 °C, corresponding to the desorption of solvents (Figure 2b). These results suggest that crystal polymorphism of **1** and the associated optical properties can be controlled by choosing recrystallization solvents and heating temperature.

Table 1. Thermal properties of the crystals

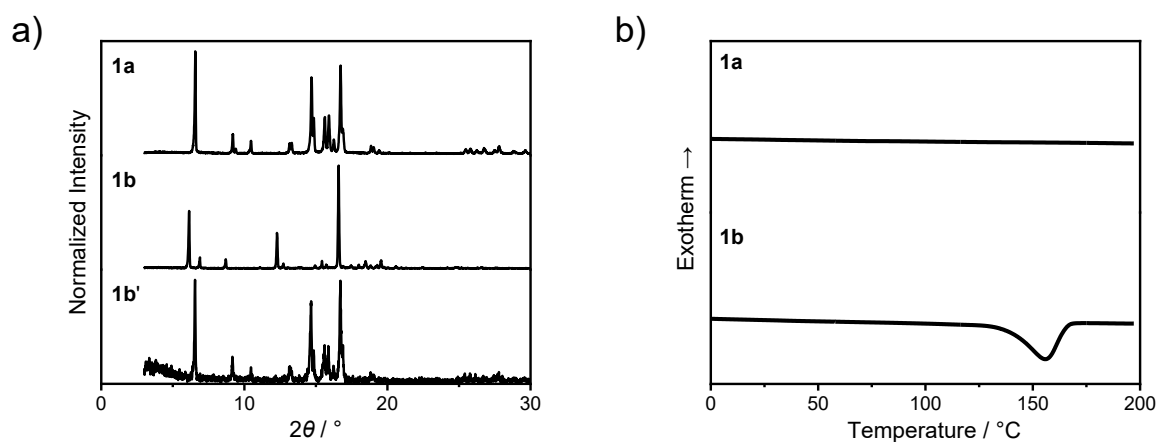
	1a	1b	1c	1d
T_p (°C) ^[a]	n.d.	156	129	143
T_d (°C) ^[b]	376	372	375	376

^[a] Phase transition temperature determined with DSC. ^[b] Thermal degradation temperature determined with TGA. n.d.: not detected.

Table 2. The molar ratio of included solvents

	1b	1c	1d
SCXRD (mol%) ^[a]	0.50	—	—
TGA (mol%) ^[b]	0.45	0.48	0.42

^[a] Determined with diffraction data of the single-crystal X-ray analysis. ^[b] Determined with weight loss of the TGA. —: Crystals suitable for X-ray analyses were not obtained.

**Figure 2.** a) PXRD patterns of **1a**, **1b** and **1b'** and b) DSC thermograms of **1a** and **1b**.

To obtain insight into the crystal packings, single-crystal X-ray structures were analyzed (Figure 3). From **1b**, the suitable sample for the analysis was obtained by slow evaporation from toluene. **1b** included 0.5 equivalents of toluene as mentioned above, although the disordered solvent molecules were removed during the analysis by the SQUEEZE method.¹⁶

According to the result, it was found that **1b** has no intermolecular π - π interaction between anthracene rings because of the twisted anthracene rings ($\varphi_{\text{C1-C4-C5-C8}} = 22.0(1)^\circ$), which disturbs the interaction. The twisted anthracene ring in **1b** might be formed by bulky *o*-carborane units, and this distorted conformation could be stabilized by solvation. The X-ray analysis of **1a** was also performed, but the *R* value was too large to discuss detailed structural properties. Since the crystal packing could be determined only from **1b** and similar optical properties were obtained from **1b–1d**, the author mainly focuses on the differences in optical properties between **1a** and **1b**.

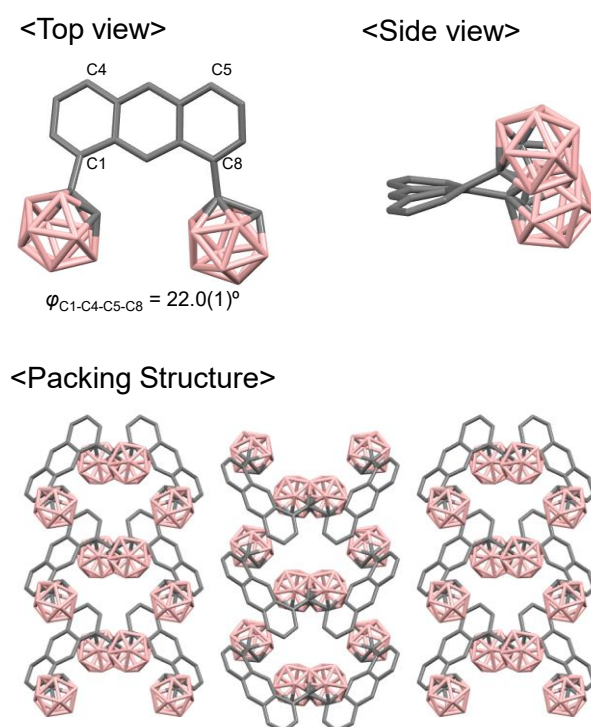


Figure 3. Single-crystal X-ray structure of **1b**. Hydrogen atoms were omitted for clarity. Colors: C, gray; B, pink.

Photophysical properties of **1** were investigated. Initially, to evaluate the electronic structure of **1**, optical measurements were performed in dilute solution (Figure 4a, Table 3). UV-vis absorption spectra of **1** exhibited vibrational structures attributed to the π - π^* transition at the

anthracene moiety. Compared to anthracene, the slight red shift of the absorption band from the modified anthracene could be explained by the electron-withdrawing effect of *o*-carborane. Then, to estimate electronic structure of **1** in the excited state, photoluminescence (PL) properties were examined. Accordingly, two distinct emission bands were detected. Since the bathochromic shift was observed only from the longer-wavelength emission band, the author concluded that the emission bands with vibrational structure in shorter wavelength region and the broad band in the longer one should be attributable to the emission from the LE state and the intramolecular CT states, respectively.

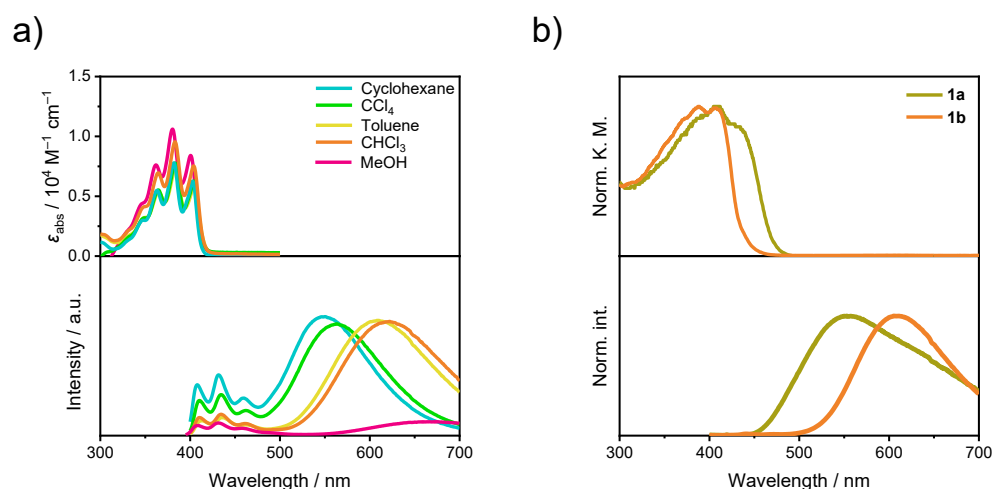


Figure 4. a) UV–vis absorption (top) and PL (bottom) spectra of **1** in solvents (1.0×10^{-5} M). b) Diffusion reflectance (top) and PL (bottom) spectra of **1a** and **1b**.

Table 3. Photophysical Properties of **1**

Sample	$\lambda_{\text{PL,max}} / \text{nm}$	$\tau / \text{ns}^{[\text{c},\text{d}]}$	Φ_{PL}
1 (CHCl_3)	435 ^[a]	n.d.	0.33 ^[a]
	622 ^[a]	9.0 (100%)	
1a	553 ^[b]	53 (89%), 16 (11%)	0.23 ^[b]
1b	608 ^[b]	11 (100%)	0.69 ^[b]

^[a] Excited at 383 nm. ^[b] Excited at 382 nm. ^[c] Excited at 369 nm. ^[d] Detected at $\lambda_{\text{PL,max}}$. n.d.: not determined.

Next, solid-state optical properties of **1** were investigated (Figure 4b, Table 3). Diffusion reflectance spectra revealed that the offset wavelength of **1a** was about 50 nm longer than those of **1b**. This result suggests that π - π overlapping of the anthracene rings should exist in the crystalline structure of **1a**. In the PL spectra, **1a** showed far broader emission band, whereas **1b** exhibited similar unimodal emission bands with the peak around 608 nm. To gain deep insight into the emission mechanism, the author performed PL lifetime measurements. **1a** had relatively longer lifetime component (53 ns) and shorter component (16 ns), while **1b** mainly had relatively shorter components (11 ns). Furthermore, when **1** was dispersed in polystyrene with a concentration of 1wt%, the emission band with the shorter lifetime was observed at almost the same wavelength as in the crystalline sample. Since each molecule should be isolated in the polystyrene matrix, the emission band in the longer wavelength region with the shorter lifetime is attributable to CT emission.

Spectrum shape alteration was observed from **1a** in time-resolved emission spectra (TRES) (Figure 5a). The emission spectrum of **1a** converged into a unimodal band in the shorter wavelength region after 30 ns, meanwhile a significant shape change was hardly observed from the spectrum of **1b** even after 50 ns (Figure 5b). This fact implies that additional emission species that is different from CT emission might be generated in the crystalline sample of **1a**. As mentioned above, **1** showed only CT emission in the polystyrene matrix, where intermolecular interaction would be negligible, and basically, the longer lifetime than those from conventional fluorescence was observed from **1a**. From these data, the author concluded that the converged emission should be excimer emission from the anthracene moieties. In summary, **1** can exhibit three types of emission bands: LE, CT, and excimer emission, and the latter two processes are dominant in the solid state.

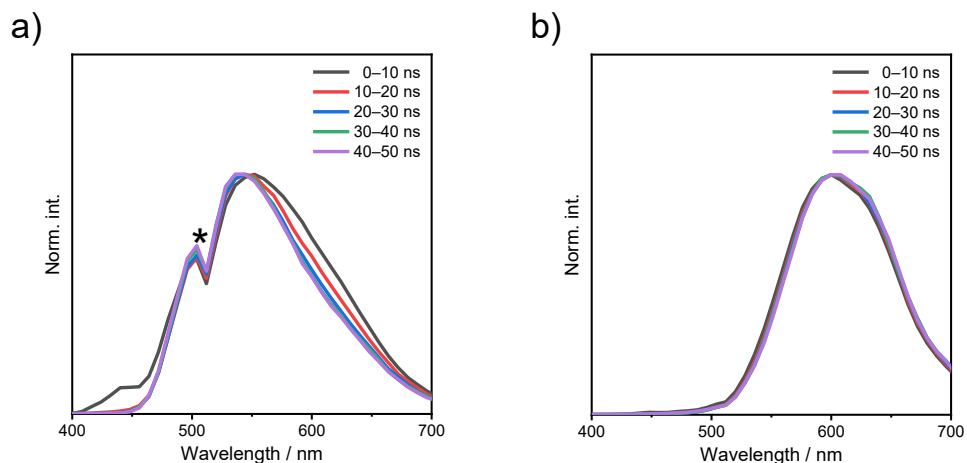


Figure 5. TRES of a) **1a** and b) **1b**. * Noise from instrument setup.

Finally, the author examined stimuli-responsivity of dual-emission of **1** in the crystalline state. Characteristic thermochromic luminescence behaviors were observed from the crystalline samples of **1** in the wide temperature range between 80 and 440 K (Figure 6).

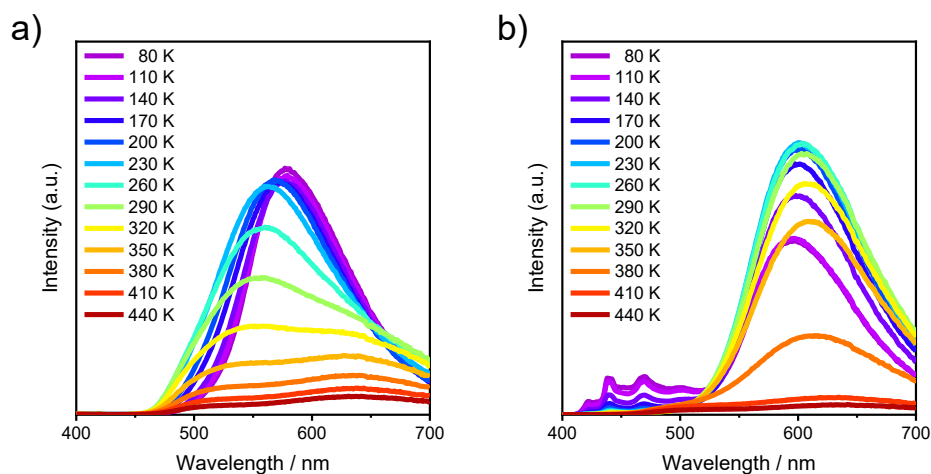


Figure 6. Variable-temperature PL spectra of a) **1a** and b) **1b**.

Below 200 K, **1a** showed the broad and unimodal emission band, while in the case of **1b**, additional emission band with vibrational structures in the shorter wavelength regions was also

detected. This emission band is attributable to LE emission. It is likely that the planar conformation of the C–C bonds in *o*-carborane units and π plane, which is suitable for providing LE emission, should be maintained by suppressing molecular rotation at the *o*-carborane unit in the low temperature region. Different behaviors were also obtained over 200 K. **1a** continuously exhibited the unimodal broad emission band with the peak around 570 nm. Subsequently, by heating, this emission band hypsochromically shifted, and dual-emission involving the new band around 640 nm was observed. Taking the peak positions into consideration, the former and latter emission could be assigned as excimer and CT emission, respectively. In contrast, the broad emission band in the longer wavelength region exhibited bathochromic shift in **1b**. Judging from the peak position, this emission band can be attributable to CT emission. Chujo *et al.* previously reported the same results of emission band shifts upon heating.^{17,18} From excimer emission, hypsochromic shifts were observed, and it was suggested that intermolecular interaction through π – π stacking should be weakened by the gradual expansion of crystal lattice. In contrast, bathochromic shifts were detected from CT emission and it was proposed that larger structural relaxation could be allowed in weakened crystal packing where thermal motions at the substituents vigorously occur. In the case of **1a**, as temperature increased, excimer/CT intensity ratio increased. It is probably because gradual expansion of the π – π stacking distance leads to more favorable conformation for CT emission than for excimer emission. In the case of **1b**, intensity of LE emission was lowered by heating, and bathochromic shift of the CT emission band was simultaneously observed. It is reasonable that molecular rotations should be enhanced to form CT state. After heating of **1b** at 440 K, the author cooled the crystalline sample to 80 K and monitored the luminescent properties during heating. Accordingly, the same behavior to **1a** was obtained. Due to the desorption of solvent molecules by heating, **1a** was generated without significant pyrolysis. Then, switching of the dual-emission property was realized.

Conclusion

In this chapter, solid-state thermochromic luminescence of bis-*o*-carborane-modified anthracene triad **1** is investigated. By incorporating dual *o*-carborane substituents, solid-state excimer emission can be introduced. It should be emphasized that dual-emission properties consisting of excimer/CT emission or LE/CT emission can be controlled by the choice of preparation protocol. Moreover, characteristic thermochromic luminescence arose from changes in the intensity ratio between the emission species. The findings might be applicable not only to establish precise temperature measurement technologies based on ratiometric analyses but also to design advanced luminochromic materials with high environmental sensitivity.

Experimental Section

The experimental details followed that described in Chapter 1, with the differences and additional details summarized below.

Materials

Commercially available compounds used without purification

1,8-Diiodoanthracene (Tokyo Chemical Industry Co., Ltd.), polystyrene (Fujifilm Wako Pure Chemical Corporation)

Commercially available solvents

CCl₄ and cyclohexane (Fujifilm Wako Pure Chemical Corporation)

Compounds prepared as described in the literature

1,8-Diethynylanthracene.⁴⁴

Synthesis

General. ¹H, ¹³C {¹H}, and ¹¹B NMR spectra were recorded on a JEOL JNM-AL400 instrument at 400, 100, and 128 MHz, respectively.

Synthesis of 1. In the 100 mL round bottom flask, 1,8-diethynylanthracene (624 mg, 2.76 mmol), B₁₀H₁₄ (779 mmol, 3.44 mmol) and *N,N*-dimethylaniline (1.25 mL, 9.90 mmol) were dissolved in toluene (27.6 mL) under N₂ atmosphere. The reaction mixture was stirred and refluxed for 4.5 h. After filtration to remove any insoluble impurities, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give a yellow solid. Recrystallization of the residual solid from CCl₄ at 60 °C afforded **1a** (80 mg, 0.17 mmol, 6% isolated yield) as a yellow solid and that from CHCl₃ at 60 °C afforded **1c** (369 mg, 0.63 mmol, 23% isolated yield) as a light-yellow solid. ¹H NMR (400MHz, CD₂Cl₂): δ (ppm) 9.60 (s, 1H), 8.57 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.94 (dd, *J* = 7.4, 0.9 Hz, 2H), 7.46 (dd, *J* = 8.2, 7.6 Hz, 2H), 4.81 (s, 2H), 3.77–1.63 (br, 20H). ¹³C {¹H} NMR (100 MHz, CD₂Cl₂): δ (ppm) 132.34, 132.10, 130.77, 130.64, 129.28, 128.59, 124.96, 119.86, 78.17, 62.07. ¹¹B NMR (128 MHz, CD₂Cl₂): −3.34, −8.44, −9.62, −10.89, −12.56, −13.84. HRMS (n-APCI): calcd. for C₁₈H₃₀B₂₀+Cl[−] [M+Cl][−] 501.3946, found 501.3950. Anal. Calcd for C₁₈H₃₀B₂₀: C, 46.73; H, 6.54. Found: C, 46.52; H, 6.60.

Crystals **1b** and **1d** were prepared by recrystallization of the crude product from toluene at 110 °C and cyclohexane at 85 °C, respectively. Both **1b** (14 mg, 0.03 mmol) and **1d** (41 mg, 0.07 mmol) were obtained as a light-yellow solid.

Single-crystal X-ray Diffraction Analysis

Table 4. Crystallographic data

Compound name	1a	1b
CCDC number	2155816	2155817
Empirical formula	C ₁₈ H ₃₀ B ₂₀	C ₁₈ H ₃₀ B ₂₀
Formula weight	462.62	462.62
Temperature / K	143(2)	143(2)
Wavelength / Å	0.71075	0.71075
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / Å	7.115(6)	6.926(3)
b / Å	18.754(18)	28.794(13)
c / Å	19.216(16)	14.201(7)
α / °	89.60(3)	90
β / °	83.73(4)	95.438(7)
γ / °	87.73(3)	90
V / Å ³	2547(4)	2819(2)
Z	4	4
ρ / g·cm ⁻³	1.207	1.090
a / cm ⁻¹	0.056	0.051
$F(000)$	952	952
θ range / °	3.042–27.464	3.038–27.481
Limiting indices	$-8 \leq h \leq 9$ $-23 \leq k \leq 24$ $-23 \leq l \leq 24$	$-8 \leq h \leq 8$ $-37 \leq k \leq 37$ $-18 \leq l \leq 18$
Collected unique reflections	16814/2340	22760/4770
$R_{\text{int}}^{[a]}$	0.1360	0.1429
S (Goodness-of-fit on F^2) ^[b]	0.971	1.063
R_1 [$I > 2\sigma(I)$] ^[c]	0.1751	0.0980
wR_2 (all data) ^[d]	0.4529	0.2200

^[a] $R_{\text{int}} = \Sigma ||F_0|^2 - |F_c|^2| / \Sigma |F_0|^2$ ^[b] $S = [\{\Sigma w(|F_0|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\Sigma (|F_0|^2 - |F_c|^2) / \Sigma (|F_0|^2)]^{1/2}$

^[d] $wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w(|F_0|^2)]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Powder X-ray Diffraction Analysis

PXRD data were collected with a Rigaku SmartLab Diffractometer (sealed tube (50 kV, 40 mA); Cu K α , 1.542 Å; Bragg–Brentano geometry). PXRD samples were placed on a single-crystal silicon substrate.

Thermal Analysis

Thermogravimetric analyses (TGA) were performed by a HITACHI STA 7200RV instrument with the aluminum pan and the heating rate of 10 °C·min⁻¹ up to 500 °C under nitrogen flow (200 mL·min⁻¹). Differential scanning calorimetry (DSC) measurements were carried out on a HITACHI DSC 7020 instrument with the aluminum pan and the heating rate of 10 °C·min⁻¹ under nitrogen flow (50 mL·min⁻¹).

Optical Measurement

TRES was measured on HORIBA Deltaflex spectrofluorometer system. Excitation was carried out using a UV diode laser (DeltaDiode 375 nm).

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Chapter 7

Direction Switching and Self-Recovering Mechanochromic Luminescence of Anthracene-Modified *o*-Carboranes

Abstract

Mechanochromic luminescence (MCL) of *o*-carborane-modified anthracene derivatives was studied. The author has previously synthesized bis-*o*-carborane-substituted anthracene and found that its crystal polymorphs exhibited dual-emission properties composed of excimer and charge transfer (CT) emission bands. The author observed bathochromic MCL behavior from the compound, which originated from a change in the emission mechanism from dual emission to exclusive CT emission. Interestingly, a compound with ethynylene spacers inserted between anthracene and *o*-carborane units showed hypsochromic MCL originating from the emission mechanism change from CT to excimer emission. Furthermore, luminescent color of ground sample can be recovered to the initial state by allowing it to stand at room temperature, indicating that self-recovery occurs.

Introduction

Mechanochromic luminescence (MCL) is the reversible luminescent color change of solid samples in response to mechanical force.¹ This property can be broadly utilized in the development of smart materials. To date, many MCL-active skeletons have been reported.²⁻⁵ The emission colors of typical MCL dyes shift bathochromically upon grinding and recover to their initial color when the ground samples are exposed to other stimuli. Limited reports have proposed the designs for hypsochromically shifted MCL.⁶ Among the reported examples of MCL, some molecules have characteristic features. One is the directional controls of the luminescence wavelength shift. Chujo *et al.* reported both directional MCL shifts of boronketoiminates.⁷ Lan, Zou, and You *et al.* reported another chromophore that utilizes a difference in molecular dipole moments.⁸ Another property is self-recovery to the initial emission color. After pristine samples were mechanically treated, exposure to solvent vapor or heating was usually required to recover the original color. However only less than 5% of MCL dyes can self-recover to initial states even at room temperature.⁵ Fraser *et al.* reported the pioneering work on self-recovery MCL in the difluoroavobenzene dye.⁹ Although careful investigations of each property were performed in previous reports, general strategies for designing those characteristic MCL systems remain to be established. From this viewpoint, if the MCL can be modulated by adding simple modifications based on a single molecular system, this would contribute to diversifying MCL molecular designs.

o-Carborane is an icosahedral carbon and boron cluster, which has been utilized as a versatile skeleton for developing functional molecules.^{10,11} Recently, it has been revealed that aryl-substituted *o*-carborane derivatives have attractive solid-state luminescent properties. Basically, luminescence of conventional organic dyes is quenched in the solid state due to concentrated quenching caused by intermolecular interactions.¹² In contrast, aryl-*o*-carboranes have solid-state luminescent properties^{13,14} and often exhibit stimuli-responsiveness.¹⁵ The emission

process is ascribed to the intramolecular charge transfer (CT) emission from the aryl moiety to the *o*-carborane unit.¹⁶ Some examples of MCL properties utilizing *o*-carborane units have been reported over the past decade.^{17–18} Zhao *et al.* reported that self-recovery MCL of an *o*-carborane derivative utilizing a metastable state.¹⁹ It was suggested that the 3D bulkiness of *o*-carborane can provide sufficient space for a molecular conformational change. This observation motivates the author to investigate self-recovering MCL of *o*-carborane derivatives.

Previously, the author revealed that bis-*o*-carborane substituted anthracene (**1**, Figure 1) has two crystalline polymorphs with thermochromic dual-emission modes (crystals **1a** and **1b**).²⁰ In crystal **1a**, dual emission consisting of CT and excimer emission bands were obtained. Therefore, the π -stacked structure of the anthracene rings was assumed. In contrast, π -stacking was disturbed in crystal **1b** because of the distorted anthracene ring stabilized by the incorporated solvent molecules.³⁰ Here the author reports that unique MCL behavior of **1**. Initially, the author observed MCL from crystal **1a** caused by luminescent mechanism convergence from dual-emission to only CT emission. Then, the author accomplished switching the direction of the wavelength shift to the opposite direction by the simply structural modification with the insertion of the ethynylene spacers (**2**, Figure 1). Furthermore, in the case of ground **1a**, the author found that the self-recovering process at the room temperature.

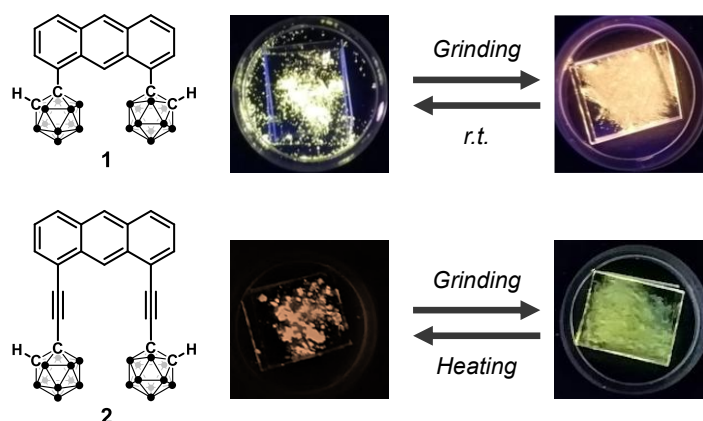
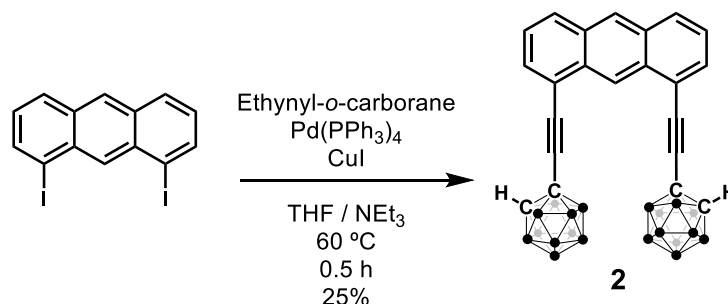


Figure 1. Chemical structures of **1** and **2** and their mechanochromic luminescent properties.

Results and Discussion

Compound **1** was prepared according to the previous report.²⁰ As shown in Scheme 1, compound **2** was synthesized through the Sonogashira–Hagihara cross-coupling reaction with 1,8-diiodoanthracene and 1-ethynyl-*o*-carborane.



Scheme 1. Synthesis of **2** by Sonogashira–Hagihara coupling.

Due to fragility of crystal samples of **1** and **2**, sufficient data were not obtained from single-crystal X-ray diffraction. Instead, the author investigated their structures through the Rietveld method with the powder X-ray diffraction (PXRD) data (Figure 2a). Fortunately, packing structure of crystal **1a** was determined (Figure 2b). Accordingly, in the crystal **1a**, **1** stacked in face-to-face manner avoiding steric hindrance of bulky *o*-carborane. In particular, columnar π -stacking of anthracenes was constructed. Distances between anthracene planes were 3.271 Å and 3.387 Å, suggesting that intermolecular interaction was formed through π -stacking.

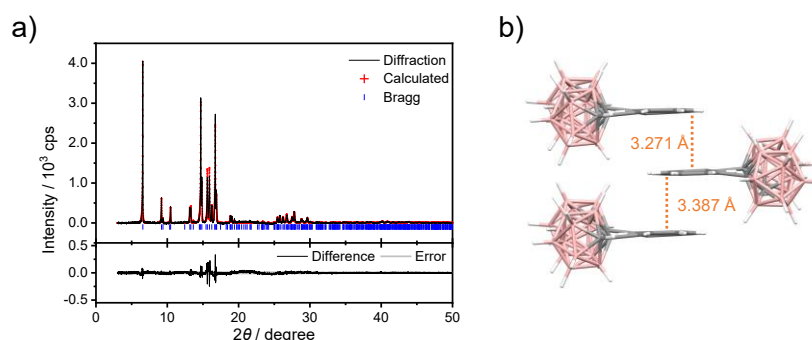


Figure 2. a) Rietveld plot of **1a** and b) its crystal structure determined from the plot (colors: C, gray; B, pink; H, white).

The electronic structure in the ground state was initially examined by UV–vis absorption measurements in the solution state (Figure 3a (top), Table 1). In the spectrum of **2** in CHCl_3 , the typical vibrational structure attributable to π – π^* transition of the anthracene moiety was observed. The slight red-shift compared to that of **1** can be explained by the expansion of π -conjugation through the ethynylene spacers. To evaluate the electronic structures in the excited state, photoluminescent (PL) properties were examined in the solution state (Figure 3a (bottom), Table 1). As described in Chapter 6, **1** exhibited dual-emission consisting of locally-excited (LE) and CT emission.²⁰ The LE emission bands were observed at almost same wavelength in various solvents, and the CT bands appeared in the longer wavelength regions in relatively more polar solvents. In contrast, **2** showed the single emission band with the vibrational structure of anthracene and the Stokes shift was not affected by solvent polarity, indicating that **2** exhibited only LE emission from the anthracene moiety (Figure 4).

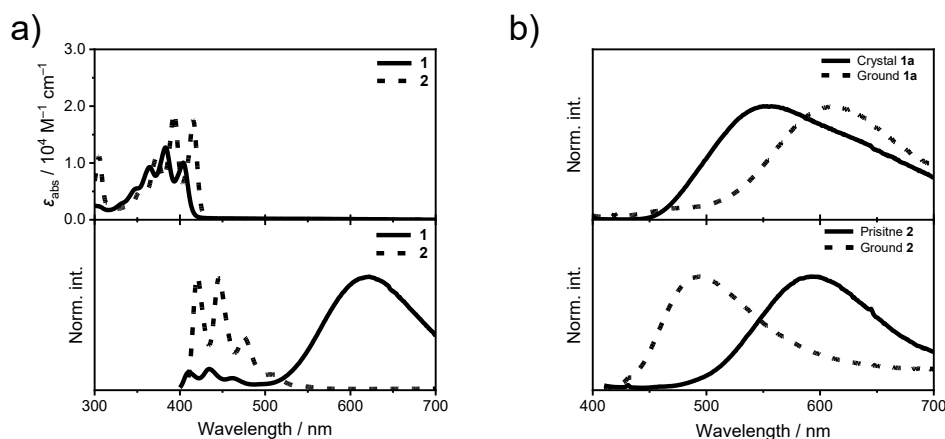


Figure 3. a) UV–vis absorption (top) and PL spectra (bottom) in CHCl_3 (1.0×10^{-5} M) of **1** and **2**. b) PL spectra of crystal and ground state of **1a** (top) and **2** (bottom)

Next, the author examined crystal state PL properties. Different behaviors were observed between crystals **1a** and **2** (Figure 3b, Table 1). As discussed in Chapter 6, the non-unimodal PL spectrum with two distinct PL lifetime components was observed for crystal **1a**.²⁰ The

spectrum was characterized as the overlap of excimer and CT emission bands. In the crystal structural analysis, the π -stacking structure was refined, suggesting that excimer emission could be generated. In contrast, crystal **2** exhibited a unimodal emission band in the longer wavelength region ($\lambda_{\text{PL}} = 590$ nm). Based on the PL lifetime measurements, crystal **2** exhibited relatively shorter lifetime (16 ns) than the excimer emission of crystal **1a** (53 ns) but this was almost identical to the CT emission component of crystal **1a** (16 ns). Therefore, it was suggested that the emission of crystal **2** could be originated from CT through the ethynylene spacers.

Table 1. Summary of the photophysical properties

Sample	$\lambda_{\text{abs,max}} / \text{nm}$	$\lambda_{\text{PL,max}} / \text{nm}$	$\tau / \text{ns}^{[\text{d,e}]}$	Φ_{PL}
1 (CHCl_3)	383	435 ^[a]	n.d.	0.33 ^[a]
		622 ^[a]	9.0 (100%)	
2 (CHCl_3)	393	446 ^[b]	0.3 (100%)	0.03 ^[b]
1a (crystal)	—	553 ^[c]	53 (89%), 16 (11%)	0.23 ^[c]
1a (ground)	—	611 ^[c]	10 (82%), 2.5 (19%)	0.39
2 (crystal)	—	590 ^[b]	16 (93%), 0.6 (7%)	0.04
2 (ground)	—	495 ^[b]	6.8 (43%), 1.2 (57%)	0.04

[a] Excited at 383 nm. [b] Excited at 393 nm. [c] Excited at 382 nm. [d] Excited at 369 nm. [e] Detected at $\lambda_{\text{PL,max}}$. n.d.: not determined.

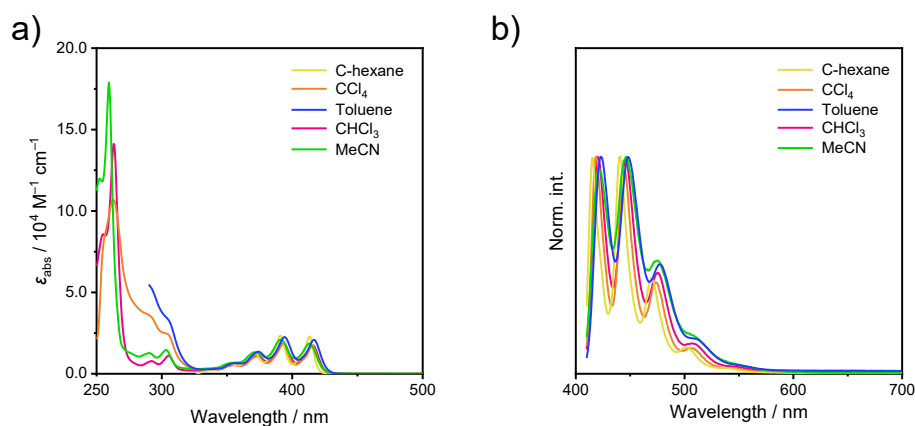


Figure 4. a) UV-vis and b) PL spectra of **2** in various solvents (1.0×10^{-5} M).

In both compounds, luminescent color changes can be induced by grinding with a metal spatula on a quartz substrate, demonstrating MCL properties (Figure 3b). Crystals **1** and **2** exhibited bathochromic and hypsochromic shifts in response to the stimuli, respectively. Upon mechanical grinding, yellow emission ($\lambda_{\text{PL}} = 553 \text{ nm}$) of crystal **1** was bathochromically shifted to orange emission ($\lambda_{\text{PL}} = 611 \text{ nm}$). In contrast, under the same treatment, the emission color of crystal **2** hypsochromically shifted from orange ($\lambda_{\text{PL}} = 590 \text{ nm}$) to yellow green ($\lambda_{\text{PL}} = 495 \text{ nm}$). From the PXRD analysis of both compounds, the diffraction peaks in the ground samples had lower intensity than those in crystal samples (Figure 5). Moreover, ^1H NMR spectroscopy confirmed that degradation or chemical reactions were hardly induced by the mechanical treatment. These results indicate that the emission color change in both compounds should originate from the difference in the molecular arrangements between the crystal and amorphous states.^{21,22}

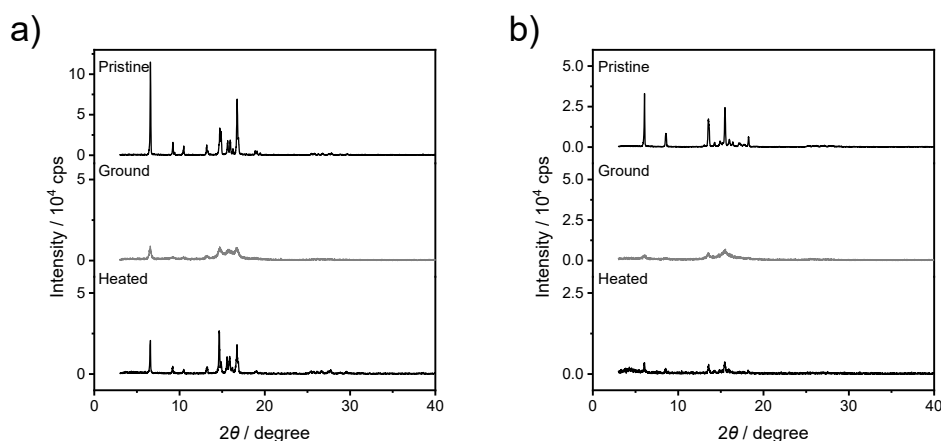


Figure 5. PXRD patterns of a) **1a** and b) **2**.

Furthermore, the author focused on the fact that the molecular structures and arrangements in the solid samples can be evaluated from diffuse reflectance spectra.^{23,24} In general, from solid samples with π -stacked structures, red-shifted spectra can be obtained compared to their non-

π -stacked counterparts.²⁵ Taking this into consideration, the author evaluated the present molecules. Comparing the diffuse reflectance spectra of the crystal and ground **1a**, an obvious blue-shift was observed (Figure 6a). This suggests that the collapse of π -stacking structure should be induced by grinding, thereby leading to CT emission. In addition, MCL properties were not observed in crystal **1b** probably due to the absence of π -stacking structure. This observation qualitatively supports the MCL mechanism of **1a**. On the other hand, ground **2** showed the red-shifted diffuse reflectance spectrum compared to crystal **2** (Figure 6b). In addition, the spectrum shape and the peak position were consistent with the previously reported excimer emission of anthracene.^{26,27} Also, excimer emission is known to be blue-shifted compared with CT emission between π -systems and carborane units.^{27,40} Moreover, in the cases of excimer emission in crystalline states, because of the low radiative transition rate originated from symmetry-forbidden transitions, excimer emission generally shows long emission lifetimes.^{31,32,41,42} In this case, relatively longer emission lifetime (53 ns) was observed in crystal **1a**, but in ground **2** (6.8 ns (43%) and 1.2 ns (57%)) such large value was not observed. The author assumed that molecular motion was likely to occur in the amorphous, that accelerates non-radiative decays. Actually, the non-radiative rate constant of ground **2** ($2.6 \times 10^8 \text{ s}^{-1}$) increased one order of magnitude higher than that of the corresponding crystal ($0.64 \times 10^8 \text{ s}^{-1}$). Thus, excimer emission should be generated from partial π -stacking orientations in amorphous.

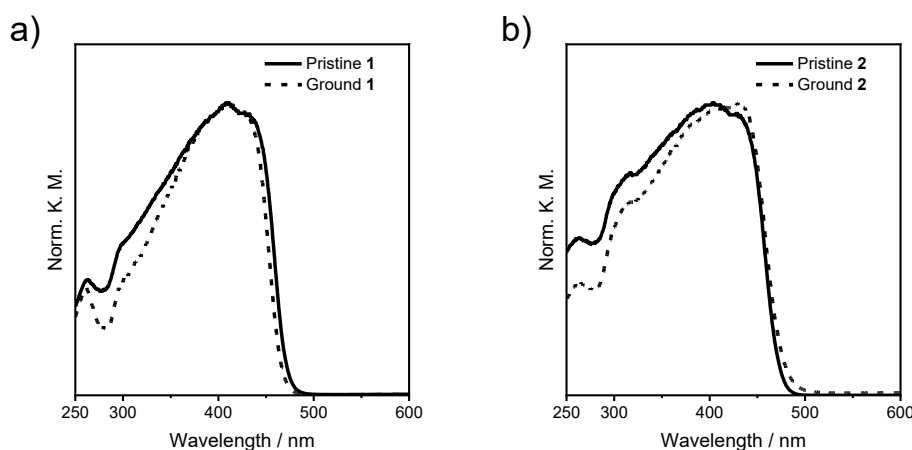


Figure 6. Diffuse reflectance spectra of crystal and ground samples of a) **1a** and b) **2**.

Next, recovery behaviors were observed in both compounds. Emission colors of the ground samples were almost restored to those of the initial crystalline state in response to other external stimuli such as heating or solvent vapor fuming (Figure 7). After heating of the ground samples, the peak intensity of the PXRD patterns increased and sharp peaks emerged (Figure 5). Moreover, differential scanning calorimetry (DSC) measurements of the ground samples exhibited endothermic peaks in the first heating cycle (Figure 8). These results suggest that recrystallization was induced by heating of the ground samples. Interestingly, the self-recovery behavior was observed for **1a**.

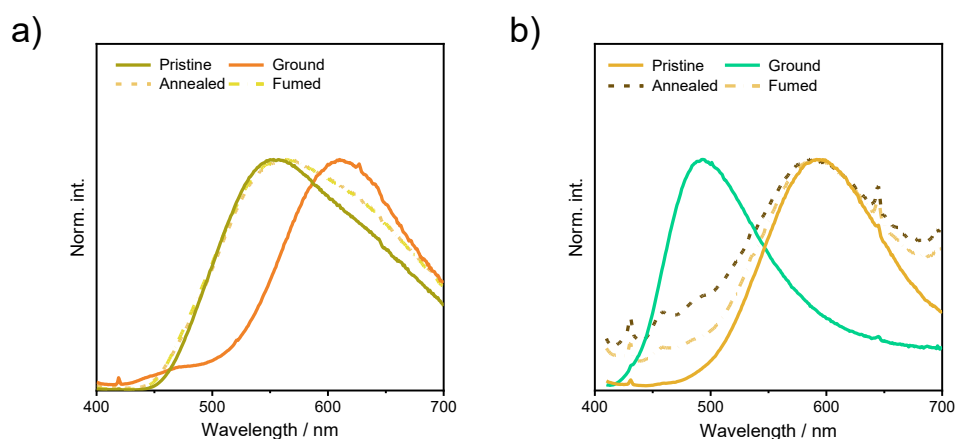


Figure 7. PL spectra of ground a) **1a** and b) **2** after heated at 150 °C for 30 min (Annealed) and exposed to CCl₄ and CH₂Cl₂ vapor for 30 min for **1** and **2**, respectively (Fumed).

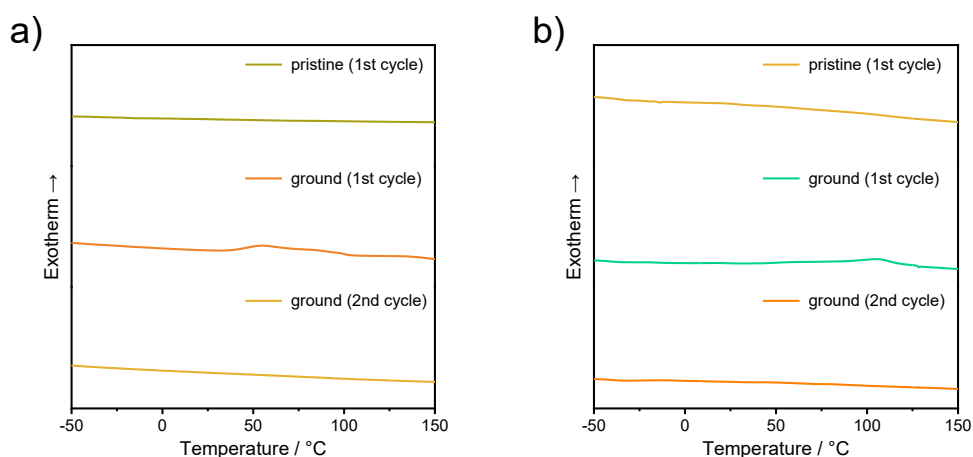


Figure 8. DSC thermogram of pristine and ground samples of a) **1a** and b) **2**.

When ground **1a** was just left standing at room temperature (298 K), the emission color was spontaneously and partially restored within several hours (Figure 9a). In compound **2**, such spontaneous recovery was scarcely observed (Figure 9b). These findings indicate that **1a** exhibits self-recovery MCL properties.⁵

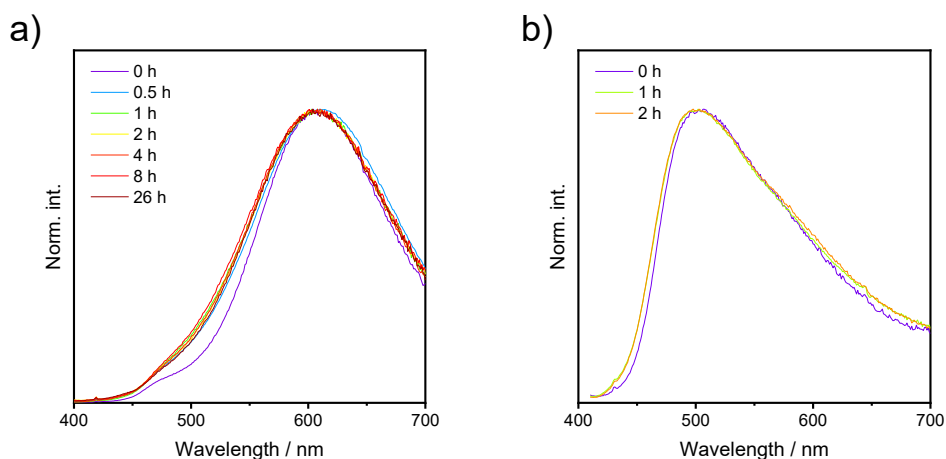


Figure 9. Time dependent PL spectra of ground a) **1** and b) **2** at 298 K.

To gain deeper insight into the recovery of MCL behavior, the author initially analyzed the DSC thermograms. In the profile, the onset temperatures (T_c^{onset}), which represents the starting temperature for recrystallization, of the endothermic peaks were 308.0 K and 342.1 K for **1a** and **2**, respectively (Figure 8, Table 2). The fact that T_c^{onset} value of **1a** was close to the room temperature, which indicates that the activation barriers in the recrystallization can be overcome even at room temperature. Furthermore, this process should be assisted by the partially residual crystalline components in the ground samples which compensate the difference between the T_c^{onset} values and room temperature. In addition, variable temperature PXRD (VT-PXRD) measurements of the samples were carried out. Diffraction patterns were recorded in increments of approximately $2 \text{ K} \cdot \text{min}^{-1}$ during heating from room temperature. In the ground samples,

constant patterns were observed at near room temperature, but began to increase at high temperature. In contrast, when the crystalline samples were heated under the same conditions as control experiments, significant changes in diffraction intensity were hardly observed. Therefore, the onset of recrystallization was determined based on the changes in PXRD patterns of the ground samples.

Next, the diffraction intensity of the strongest peaks were plotted against temperature. The T_c^{onset} values were also obtained from the intersections of approximate straight lines obtained by the mean-square method in the two regions (Table 2). From both measurements, the lower value of T_c^{onset} were observed for **1a** (311.9 K) than that for **2** (324.8 K), suggesting that the self-recovery processes can proceed more smoothly in **1a**. In fact, this suggestion is consistent with the fact that the emission spectrum of **1a** is more likely to recover spontaneously. From the above analyses, it was confirmed that self-recovery MCL exists. It is proposed that the self-recovery processes can proceed owing to the loose molecular packing created by the spherical and bulky *o*-carborane units.

Table 2. Determined thermophysical parameter for recrystallization

Sample	Method	T_c^{onset} / K
1a	DSC	308.0
1a	VT-PXRD	311.9
2	DSC	342.1
2	VT-PXRD	324.8

Conclusion

In this chapter, aryl-modified *o*-carboranes were found to exhibit emission mechanism alterations in solid triggered by external stimuli or environmental changes. Based on these alterations observed in two kinds of bis-*o*-carborane-modified anthracenes, the author demonstrated the direction switching of wavelength shifts in MCL. Moreover, the author also identified a self-recovering process in MCL. The bulky and spherical structure of *o*-carborane substituents appears to be responsible for this process. Although it is still challenging to design the molecules that exhibit not only stimuli-responsive emission mechanism alteration but also self-recovering behavior, *o*-carborane could be a key building block for controlling these stimuli-responsive luminochromic properties.

Experimental Section

The experimental details followed that described in Chapters 1 and 6, with the differences and additional details summarized below.

Materials

Commercially available compounds used without purification

CuI (Fujifilm Wako Pure Chemical Corporation), *N,N*-dimethylaniline (Fujifilm Wako Pure Chemical Corporation).

Compounds prepared as described in the literature

1-Ethynyl-*o*-carborane²⁸ and **1**.²⁰

Synthesis

Synthesis of 2. In the 100 mL light shaded round-bottomed flask, 1,8-diiodoanthracene (172 mg, 0.400 mmol), 1-ethynyl-*o*-carborane (151 mg, 0.898 mmol), Pd(PPh₃)₄ (94 mg, 0.081 mmol) and CuI (60 mg, 0.32 mmol) were dissolved in THF (16 mL) and NEt₃ (12 mL). The reaction mixture was stirred at 60 °C for 0.5 h under N₂ atmosphere. The reaction mixture was added to ethyl acetate and washed with saturated aqueous NH₄Cl solution. The organic phase was dried over anhydrous MgSO₄. After filtration, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give yellow solid. Recrystallization of the yellow solid from CHCl₃ at 60 °C afforded **2** as a yellow solid (51 mg, 0.10 mmol, 25% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.77 (s, 1H), 8.50 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.81 (dd, *J* = 7.0, 0.9 Hz, 2H), 7.47 (dd, *J* = 8.5, 7.1 Hz, 2H), 4.12 (s, 2H), 3.73–1.70 (br, 20H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 134.88, 131.30, 131.03, 130.92, 128.81, 125.07, 122.18, 117.96, 88.27, 77.59, 63.18, 61.55. ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ (ppm) –2.21, –3.78, –9.04, –10.14, –10.58 (shoulder peak), –13.078. HRMS (n-APCI): calcd. for C₂₂H₃₀B₂₀+Cl[–] [M+Cl][–] 549.3946, found 549.3950. Anal. Calcd for C₂₂H₃₀B₂₀: C, 51.74; H, 5.92. Found: C, 51.71; H, 5.95.

Preparation Method of Ground Samples

For PL measurements. The crystal samples were scratched on quartz substrates by metal spatula. PL spectra were obtained by irradiation of excitation light to the substrates attached with ground samples. The heating treatment was performed at 150 °C for 30 min on hot plate

and the fuming to solvent vapor was performed to CCl₄ for 30 min and CH₂Cl₂ for 30 min vapor for **1a** and **2**, respectively.

For X-ray diffraction, diffuse reflectance and thermophysical measurements. The crystal samples were grinded by agate motor and the ground samples were scraped off by metal spatula.

Powder X-ray diffraction (PXRD) analysis with Rietveld refinement

PXRD data for structural refinement with Rietveld method were measured using Rigaku SmartLab with a Ge (111) Johansson monochromator (Cu K α_1 radiation $\lambda=1.54059$ Å, 50 kV and 40 mA, transmittance mode), a HyPix-3000 detector, and a capillary rotation attachment (120 rpm). The analyses were carried out with the powder X-ray diffraction analysis software SmartLab Studio II (Rigaku). Indexing programs DICVOL²⁹ or ITO³⁰ were used for the determination of cell dimensions. The diffraction profiles were decomposed with the whole powder pattern fitting (WPPF) method. Following these data, corresponding space groups were determined based on systematic extinctions. After additional WPPF methods, the initial phase was obtained by direct space method using the previous cif data with insufficient quality for structure determination by single-crystal X-ray diffraction analysis²⁰ (cif deposition number 2155816). These obtained structures were refined using the Rietveld method under restrained conditions for bond lengths (± 0.0200 Å width for restraint) and angles ($\pm 1.000^\circ$ width for restraint). The bond length and angle of anthracene moiety were restrained to the previously reported anthracene ones (cif deposition number 1103070).³¹ Convergence was judged by confirming residual sum of squares (R_{wp}) was less than 10 %, and goodness-of-fit indicator (S), sufficiently closed to unity. The distance between anthracene rings was defined as the distance between mean planes formed by all carbon atoms of anthracene moiety. The mean planes were calculated by *Mercury 2020.3.0* software.³² Fitting parameters for the indexing including weighted-profile of R (R_{wp}), profile-refinement of R (R_p), expected R (R_e), and goodness-of-fit (S) values were defined as follows:

$$R_{wp} = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\}^{\frac{1}{2}}$$

$$R_p = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i}$$

$$R_e = \left(\frac{N - P}{\sum_i w_i y_i^2} \right)^{\frac{1}{2}}$$

$$S = \frac{R_{wp}}{R_e}$$

in which y_i is a diffraction intensity, $f_i(x)$ is a calculated diffraction intensity, P is a parameter for the least-squares method, w_i is a statistical weight and N is the number of data points.

Table 3. Selected X-ray data collection and Rietveld refinement parameters for **1a**.

	1a
CCDC deposition number	2256549
Chemical formula	C ₁₈ B ₂₀ H ₃₀
Space group	<i>P2₁/c</i>
<i>a</i> , <i>b</i> , <i>c</i> / Å	7.1473(6), 18.8081(17), 19.3300(17)
<i>α</i> , <i>β</i> , <i>γ</i> / °	90, 95.955(2), 90
<i>R</i> _{wp}	2.83%
<i>R</i> _p	1.97%
<i>R</i> _e	1.66%
<i>S</i>	1.6892
<i>Max Shift</i>	0.000

Diffuse Reflectance Spectra

Diffuse reflectance spectra were obtained on a SHIMADZU UV3600i plus spectrophotometer by using integrated sphere method. The concentration was 1wt% in BaSO₄.

Variable-Temperature PXRD

Variable temperature PXRD (VT-PXRD) was carried out by Anton Paar DCS500 while samples were covered with a Poly Ether Ether Ketone (PEEK) dome. Samples were placed on a single-crystal silicon substrate for room temperature measurements and Inconel[®] substrate under constant heating mode with repeated measurements and heating rate of 2 K·min⁻¹ from room temperature.

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Chapter 8

Photosalient Effect and Thermochromic Luminescence Based on *o*-Carborane-Assisted π -Stacking in the Crystalline State

Abstract

Herein, the author reports a unique multiple-stimuli responsiveness of anthracene-tethered *o*-carborane derivatives. The author designed and synthesized anthracene derivatives with different substitution positions and numbers of the *o*-carborane units. Two compounds exhibited characteristic crystal structures, featuring columnar π -stacking structures of the anthracene units. From the analysis of crystalline-state structure–property relationships, it was revealed that the crystals exhibited the photosalient effect accompanied by photochemical [4+4] cycloaddition reactions and temperature-dependent photophysical dual-emission properties including excimer emission of anthracene. Those properties were considered as non-radiative and radiative deactivation pathways via excimer formation in the excited state and the formation of excimer species was facilitated by the π -stacking structure of anthracene units. Moreover, the author observed an unusual temperature dependency on the occurrence of the photosalient effect. Variable-temperature X-ray crystallography data suggested a strong correlation between lattice shrinkage and strain accumulation.

Introduction

Stimuli-responsive materials can change their physical and/or chemical properties in response to external stimuli or environmental changes.¹ Their design and fabrication attract tremendous attention for the development of advanced sensing materials. Crystalline materials are promising scaffolds because molecular arrangements in crystal can be defined at the atomic level by X-ray crystallography. It is convenient to obtain information on structure-property relationships, which is essential for elucidating the origin of functionalities. However, obtaining crystalline materials with multi-stimuli-responsiveness is still challenging due to the difficulty in regulating molecular arrangements. Thus, there is a huge interest in the discovery of unusual crystal structures as well as the development of novel functions.

Mechanical motion of crystalline materials has attracted attention for the development of dynamic crystalline materials.^{2,3} Among the dynamic motion of the crystals, light-induced crystal jumping is referred to as the photosalient effect.⁴ This phenomenon has potential application in sensors and micro-actuators that can convert light into macroscopic physical force. Several mechanisms underlying the photosalient effect have been studied such as [2+2] photocycloaddition,⁵⁻⁷ [4+4] photocycloaddition,^{8,9} *E/Z* isomerization,¹⁰ reversible cyclization,¹¹⁻¹⁴ and intermetallic interactions.¹⁵ The intrinsic origin of dynamic motion is commonly understood as accumulated strain in the crystals during photochemical processes without phase transitions.^{4,9,12,14,16,17} Although molecular skeletons exhibiting photosalient effect have been sporadically discovered, there are few examples that simultaneously modulate physical properties including the photosalient effect and other functions.⁹

A carbon–boron cluster compound, *o*-carborane, has been utilized as a functional scaffold in various fields.¹⁸⁻²¹ Since the first report on aggregation-induced emission of *o*-carborane-containing polymers,²² various solid-state luminescent materials have been developed.²³⁻²⁸ Typical solid-state emission process of aryl-substituted *o*-carboranes is derived from

intramolecular charge transfer (ICT) from the aryl moieties to the *o*-carborane units.²⁷ In addition, aryl-substituted *o*-carborane can serve as a versatile building block for the development of crystalline stimuli-responsive luminescence.²⁹ Previously, the author reported thermochromic and mechanochromic luminescent properties of bis-*o*-carborane-modified anthracene (**18-H**, Scheme 1).^{30,31} These multiple luminochromic properties were shown to originate from the π -stacking crystal structure. Thermochromic luminescence was attributed to the elongation and shortening of π - π distance,³⁰ and mechanochromic luminescence was induced by the destruction and construction of the π -stacking.³¹

In this chapter, the author synthesized anthracene-tethered *o*-carborane derivatives and serendipitously discovered their photosalient effect. From the crystallographic studies, the author revealed that the photosalient effect originates from the π -stacking structure of anthracene in crystal. Unusual temperature dependency was discovered under a microscope and investigated by variable temperature X-ray crystallography. Moreover, thermochromic luminescent properties were examined. Accordingly, photophysical processes can be regulated by the substitution patterns of *o*-carborane units tethered to the anthracene core (Figure 1).

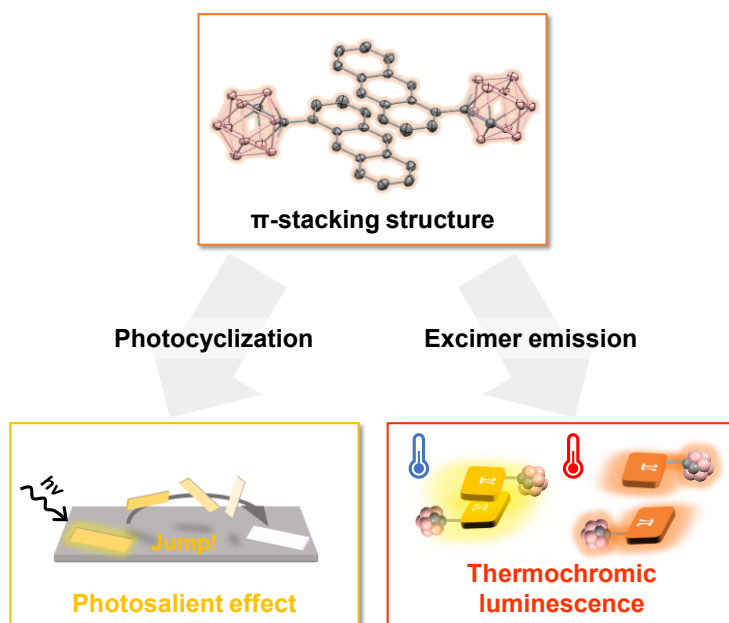
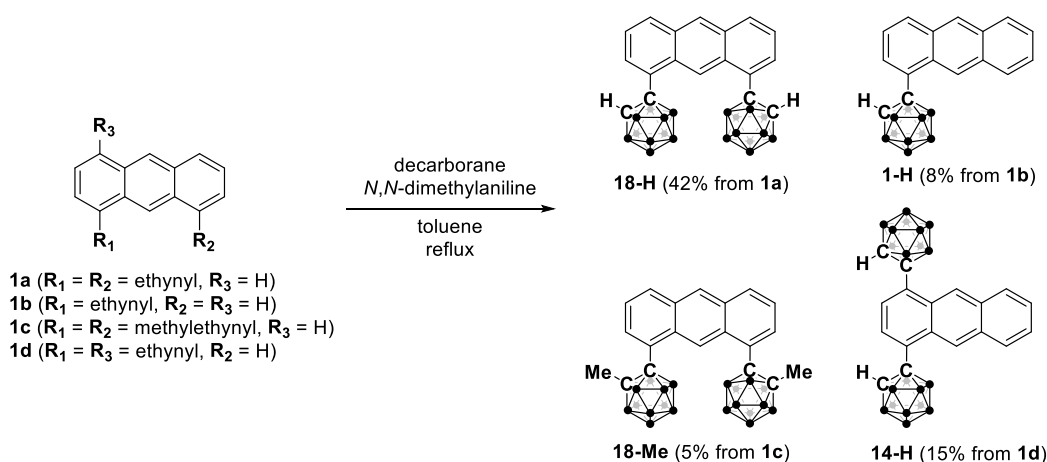


Figure 1. Overview of the multi-stimuli-responsiveness in this chapter.

Results and Discussion

According to the previous work, **18-H** was synthesized and characterized.³⁰ It should be noted that **18-H** can form both non-solvated and solvated crystals. Each crystal can be separately obtained by careful selection of recrystallization solvent. When **18-H** is recrystallized from CCl₄, a non-solvated yellow crystal with π -stacking of anthracenes is solely obtained (crystal **a**). In contrast, from toluene, CHCl₃, and cyclohexane, a solvated, colorless crystals without π -stacking interactions is alternatively obtained (crystal **b**).⁵⁵ In this chapter, the author will discuss only crystal **a**, whose crystal structure was determined in Chapter 7.³¹ In addition, to gain deeper insight into the structure–property relationship, the series of compounds were prepared by introducing *o*-carborane to the 1-position of anthracene (**1-H**) and 1,4-positions (**14-H**). Also, methyl groups were introduced at the unsubstituted carbon atoms in *o*-carborane units of **18-H** (**18-Me**) (Scheme 1).



Scheme 1. Synthetic scheme of anthracene-substituted *o*-carborane derivatives

The relationship between crystal and chemical structures was initially examined by SCXRD (Figure 2). **1-H** had anthracene-faced π -stacked dimers in the unit cell. The π – π distance (the distance between the carbon atom at the 9-position of one molecule and that at the 10-position of the other molecule) in a dimer unit was 3.637(4) Å. In contrast, in the crystal of **18-Me**,

although parallel arrangement of the anthracene units was observed, only weak π -stacking was formed. Two methyl groups were arranged in anti conformation relative to anthracene planes, and the π - π distance was measured as 4.486(3) Å, which is significantly longer than those of **18-H** and **1-H**. This means that the π -stacking of anthracene was disrupted by the methyl groups. **14-H** crystal exhibited a completely different arrangement. Each anthracene unit crossed their long axes almost orthogonally to each other and π -stacking of anthracene units was not formed. As a result of crystal evaluation, π -stacking crystal structure of anthracene units can be modulated by choosing incorporated positions and numbers of *o*-carborane units.

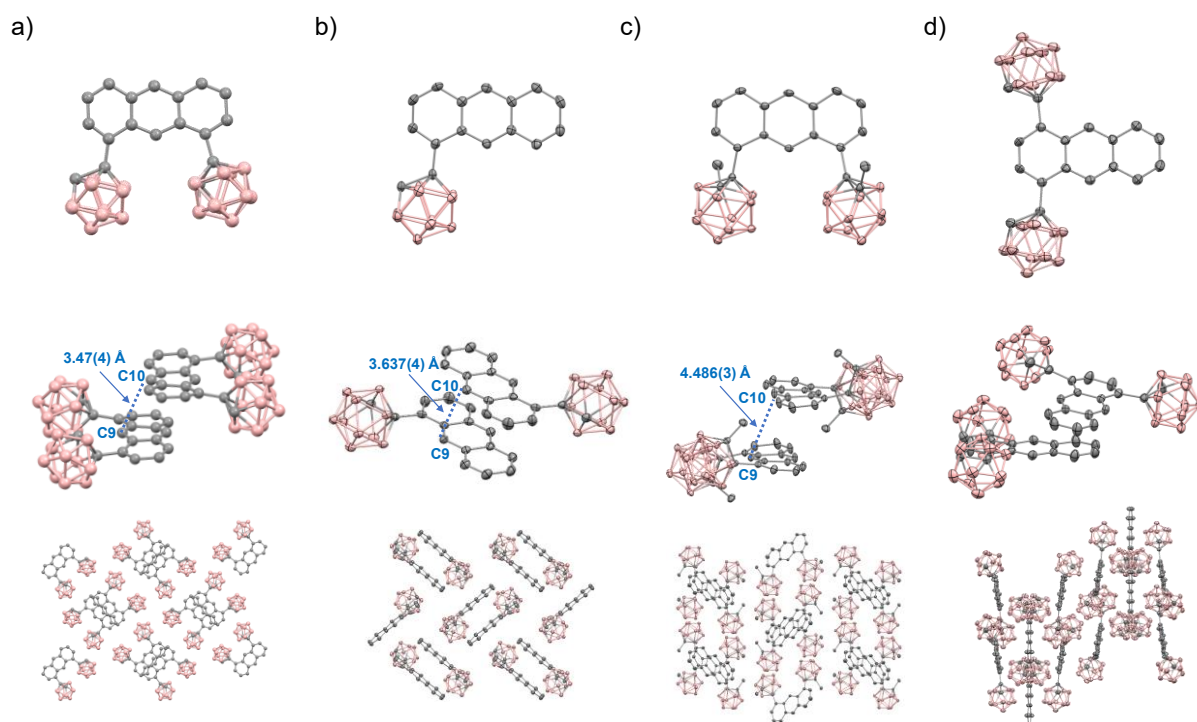


Figure 2. Molecular structures (top), stacking two molecules (middle) and packing structures along *a* axis (bottom) of a) **18-H**, b) **1-H**, c) **18-Me**, and d) **14-H**. The structure of **18-H** was refined from powder X-ray diffraction data at room temperature by using the Rietveld method and those of **1-H**, **18-Me**, and **14-H** were determined by single-crystal X-ray diffraction analysis at 143 K. Thermal ellipsoids for **1-H**, **18-Me**, and **14-H** were drawn at the 50% probability level. All hydrogen atoms were omitted for clarity. Colors: C, gray; B, pink.

When the author observed **18-H** crystal under UV light, **18-H** crystal exhibited physical motions accompanied by decolorization (Figures 3ab). This dynamic photomechanical motion was identified as photosalient effect. Analysis of the resulting colorless crystal revealed the product to be a dimer (**18-H**_{dimer}), in which two **18-H** molecules are connected by C–C bonds (Figure 3c). The C–C bond length was 1.638(6) Å and the angles of C4A–C10–C10A and C8A–C9–C9A atoms were 110.8(3)° and 111.1(3)°, respectively. Furthermore, the C–C bonds involving bridgehead positions (C4A–C10, C8A–C9, C9–C9A and C10–C10A) were elongated from 1.394(3)–1.401(3) Å in anthracene³² to 1.522(5)–1.547(5) Å, indicating that lost of the aromaticity at the central benzene ring. Accordingly, the face-to-face stacked anthracenes of **18-H** underwent [4+4] cycloaddition. In **18-H** crystal, the distance of photoreactive carbon atoms of anthracene (C9 and C10) was 3.87(3) Å. This intermolecular distance is shorter than upper limit of 4.2 Å for dimerization, indicating its ability to form a photodimer under UV.³³

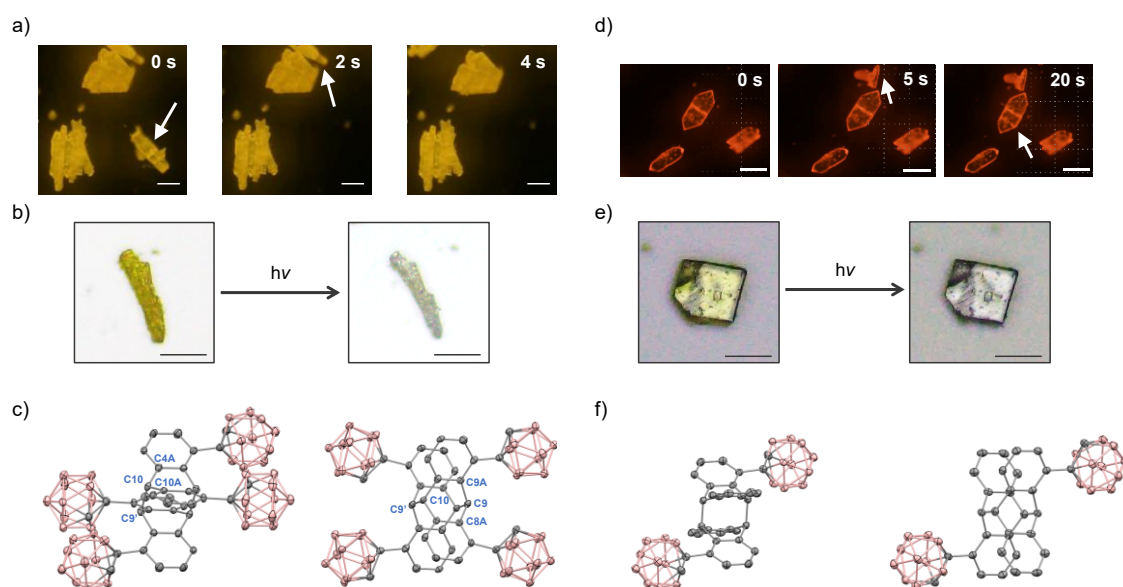


Figure 3. Photosalient effect of **18-H** (a–c) and **1-H** (d–f). Fluorescence microscope images showing the photosalient effect under UV light (a,d). Scale bars represent 50 μm (a) and 100 μm (d). The pictures of the crystals before (left) and after (right) irradiated by UV light (b,e). Scale bars represent 50 μm . Side view (left) and top view (right) of the molecular structure of dimerized products (c,f). Thermal ellipsoids were drawn at the 50% probability level. All hydrogen atoms were omitted for clarity. Colors: C, gray; B, pink.

Photoreactivity of **1-H**, **14-H**, and **18-Me** crystals was also investigated by fluorescence microscope. Similar to **18-H**, **1-H** crystal exhibited photosolient effect (Figure 3d). After the pale yellow **1-H** crystal was irradiated by UV light, jumping, cracking, and splitting accompanied by decolorization were observed (Figure 3e). SCXRD analysis revealed the photoproduct as a dimer of **1-H** (**1-H**_{dimer}, Figure 3f). Moreover, the structure of the dimerized anthracene unit was almost identical to that of **18-H**_{dimer}. Therefore, as observed in **18-H**, photomechanical motion was induced by photo-induced dimerization of the anthracene units. In addition, the photoreactivity of the bulk samples of **18-H** and **1-H** was investigated by UV light irradiation with Xe lamps and analyzed by powder X-ray diffraction (PXRD) (Figure 4). Through comparison of PXRD patterns between irradiated samples and simulated PXRD patterns, it was confirmed that the dimerized compound was the only product of the photoreaction because all PXRD patterns of photo-irradiated bulk samples were explained by the sum of the simulated patterns of monomer and dimer. In contrast, photomechanical effects were hardly observed in the crystals of **14-H** and **18-Me**. Considering the crystal structure, **18-H** and **1-H** had π -stacking structure with the face-to-face arrangement of anthracene units, where π - π distance (3.87(3) Å for **18-H** and 3.684(3) Å for **1-H** at r.t.) are sufficiently short for photoinduced dimerization. However, the crystals of **18-Me** and **14-H** had arrangement unsuitable for intermolecular photoreaction, resulting in the absence of photoreactivity.

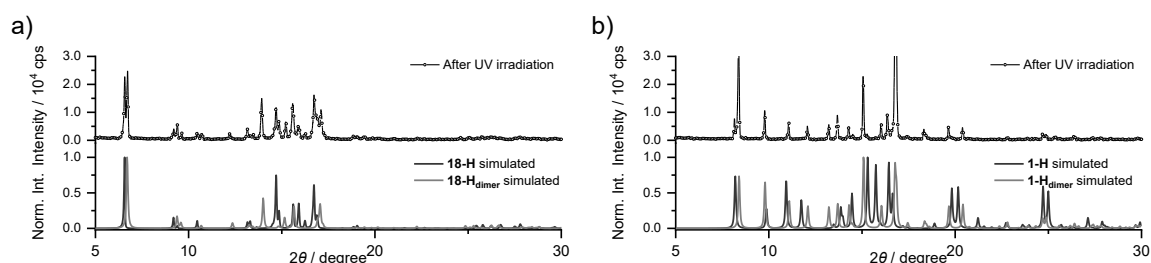


Figure 4. PXRD patterns of UV irradiated polycrystalline samples (top) and simulated patterns of corresponding monomers and dimers (bottom) of a) **18-H** and b) **1-H**.

For the crystal of **1-H**, the change of crystal lattice parameters during the photodimerization was evaluated (Table 1). At 298 K, the change in the unit cell volume was as small as -2.05% ($-36.6 \text{ \AA}^3$), and the lattice constants were anisotropically transformed. The elongation of c axis ($+0.58\%$) and the shrinkage of a axis (-3.73%) and b axis (-0.18%) were observed. These structural changes satisfied the requirements for the crystals exhibiting salient effects.³⁴ In addition, the elongated c axis was parallel to the direction of π -stacking. These observations suggest that the strain was generated by a bond-forming photodimerization reaction and accumulated due to molecular disordering. When the strain was eventually released without being cancelled inside the crystal, the macroscopic force could be generated.¹⁶ Although the author also tried to check the lattice changes in **18-H** and **18-H_{dimer}**, due to the difficulty in preparing single crystals, comparable data could not be obtained.

Table 1. Comparison of crystallographic data between **1-H** and **1-H_{dimer}**^[a]

Temperature (K)	Δa (%)	Δb (%)	Δc (%)	$\Delta \alpha$ (%)	$\Delta \beta$ (%)	$\Delta \gamma$ (%)	ΔV (%)	$\Delta \rho$ (%)
143	-4.57	1.04	0.37	0	-4.07	0	-1.63	1.73
178	-4.13	0.96	0.11	0	-4.13	0	-1.51	1.57
213	-4.17	0.8	0.21	0	-4.08	0	-1.64	1.75
263	-3.79	0.18	0.23	0	-3.63	0	-2.02	2.09
298	-3.73	-0.18	0.58	0	-3.33	0	-2.05	2.1

^[a] Difference of the parameter (Δx (%)) were calculated by the equation: $(x_{\text{1-Hdimer}} - x_{\text{1-H}}) / x_{\text{1-H}}$.

From fluorescence microscopic observations on a temperature-tunable stage, temperature dependency of the photosalient effect was revealed in both **18-H** and **1-H**. Naumov and co-workers have utilized the latent period of strain tolerance for the occurrence of the photosalient effect.⁴ The latent period is defined here as the elapsed time from the start of UV irradiation when the first photo-induced mechanical motion was observed.¹² In the temperature range from 143 to 373 K, it was found that the latent period decreased with temperature increasing (Figure 5). At low temperatures, there was a dormant region, in which no photosalient effect was

observed within 2 minutes. From thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis, both compounds exhibited negligible degradation and no phase transition in this temperature region. The author also checked the possibility of the thermo-induced salient (thermosalient) effects generated by heating during photoirradiation. When the crystals were gradually heated from 143 K to 373 K without UV light irradiation, no thermosalient effect was observed. Then it could be inferred that the observed temperature dependency did not originate from thermal reactions and phase transitions. To analyse this temperature dependency, variable temperature SCXRD (VT-SCXRD) analysis of **1-H** and **1-H_{dimer}** was performed at 143, 178, 213, 263, and 298 K. The difference in the lattice parameters before and after photoreaction was compared (Table 1). In all measurements, the space group was unchanged as monoclinic, $P2_1/c$ in both **1-H** and **1-H_{dimer}**, and the percentage difference in the lattice constants (Δa , Δb , Δc , and $\Delta \beta$) were almost constant or approached zero with temperature increasing. In contrast, the volume change (ΔV) was accelerated by heating from -1.63% at 213 K to -2.05% at 298 K. The photosalient effect is considered to occur when internal strain accumulates above a threshold.^{4,14} In addition, the anisotropic lattice deformation was maintained in this temperature range. Larger volume changes should enhance the frequency of the photosalient effects at higher temperatures.^{12,16} The author suggests here that the acceleration of the degree of anisotropic lattice deformation plays a crucial role.

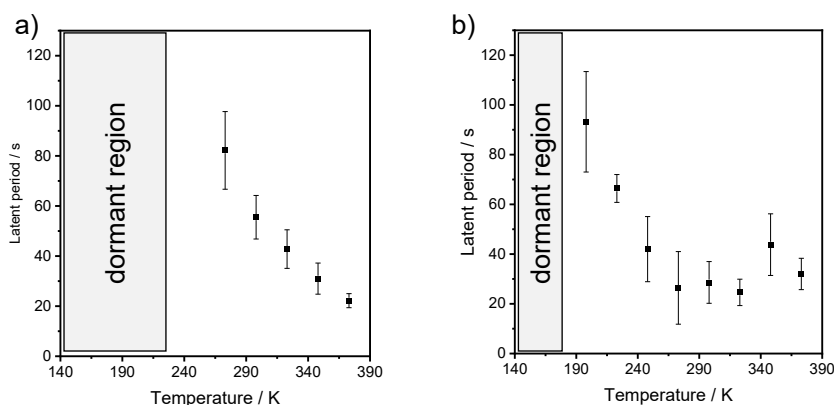


Figure 5. Variable temperature observations of the photosalient effect of a) **18-H** and b) **1-H**. The error bars indicate standard deviations.

Moreover, the photodimerization of anthracene is considered to proceed *via* the formation of an excimer as an excited-state intermediate.³⁵ The fate of the excimer state depends on the competition between radiative and non-radiative decay pathways, which result in excimer emission and photodimerization, respectively.³⁶ Therefore, excimer emission can be observed from these crystals. Subsequently, the author investigated their photophysical properties.

PL properties were obtained in crystal states at room temperature (Figure 6). **18-H** showed a broad bimodal emission band. According to the previous work,³⁰ this originates from the combination of ICT emission including *o*-carboranes and excimer emission of face-to-face-stacked anthracene units. In addition, a bimodal band was also observed in **1-H**. The major emission band is located at $\lambda_{\text{em}} = 679$ nm, while a minor shoulder peak was detected between 500–600 nm. The major and minor components can be attributed to ICT and excimer emission, respectively. In contrast, for the crystal samples of **18-Me** and **14-H**, yellow to orange luminescence ($\lambda_{\text{em}} = 562$ nm for **18-Me** and 638 nm for **14-H**) with unimodal emission bands were observed. Notably the shoulder peak of **18-Me** can originate from LE emission of the anthracene units. The shape of the spectra and luminescence lifetimes were consistent with the data from other ICT emissive aryl *o*-carborane derivatives.^{25,27,37,38} Therefore, as a result, the dominant luminescent species of **18-Me** and **14-H** can be assigned as ICT emission.

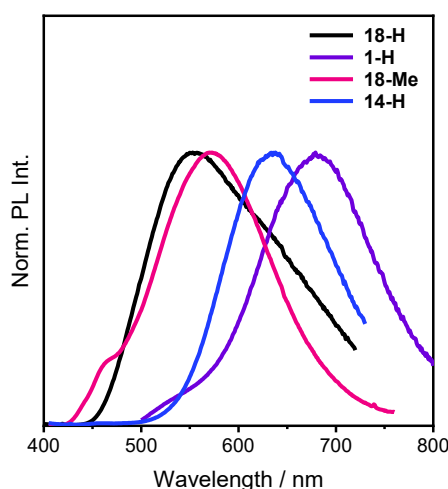


Figure 6. PL spectra of **18-H**, **1-H**, **18-Me**, and **14-H** in the crystalline state at room temperature.

Although the π -stacking structure of **1-H** has a potential for exhibiting excimer emission in the crystalline state, such emission band was only weakly detected at room temperature. Excimer emission in crystals is generally dependent on the distance between the π -planes of the chromophores.^{39–43} Hence, it was presumed that the temperature-dependent change in the unit cell volume can influence the luminescent properties of crystalline **1-H**. Based on this assumption, variable temperature PL (VT-PL) spectra were recorded from 80 to 410 K in 30 K increments with the crystalline samples (Figure 7ab). Accordingly, spectral changes were observed for all compounds. In **18-H**, the relative intensity of ICT to excimer emission increased with temperature increasing, as previously reported. In the VT-PL spectra of **1-H**, in addition to the ICT band around 680 nm, the new emission band appeared around 580 nm.

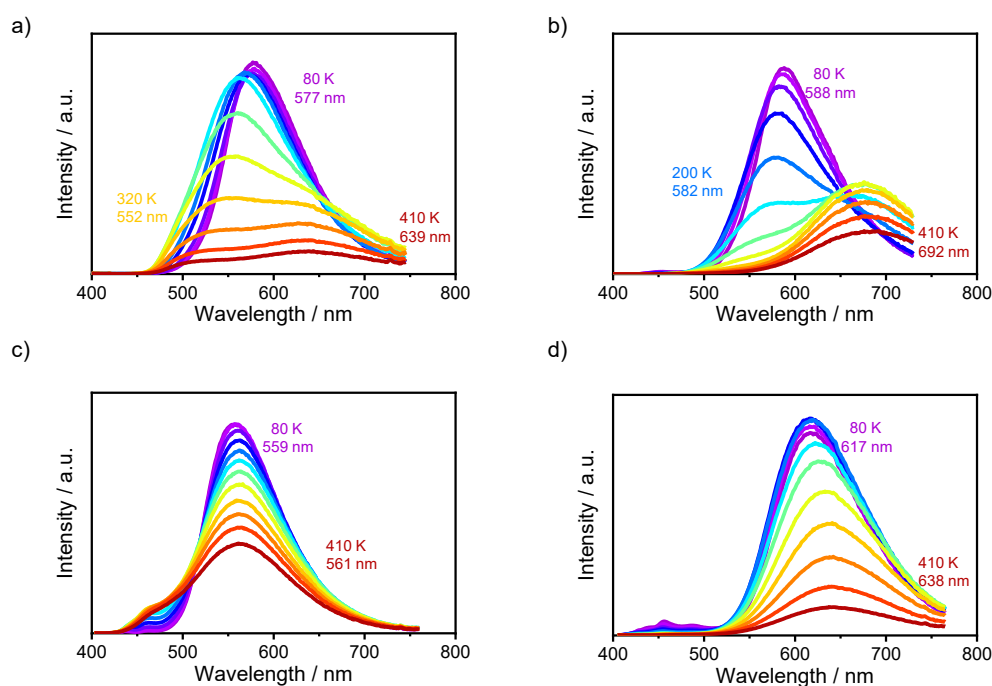


Figure 7. Variable temperature PL spectra of a) **18-H**, b) **1-H**, c) **18-Me**, and d) **14-H** in the crystalline state from 80 to 410 K in 30 K increments.

On the other hand, in **14-H** and **18-Me**, unimodal emission spectra were observed as the major component (Figure 7cd). In the lower temperature region (below *ca.* 200 K), weak emission bands with the vibrational structure appeared around 400–500 nm attributable to the

LE emission of anthracene. These data support that the π -stacking structure in these crystals plays a critical role in the formation of excimer followed by the photodimerization and excimer emission. To deconvolute the spectra into individual emission component, time-resolved emission spectra (TRES) were obtained (Figure 8ab). The detection temperature was fixed at 320 K for **18-H** and 230 K for **1-H** where two emission bands were observed. In both compounds, the emission components in the longer wavelength region (*ca.* 600 nm for **18-H** and *ca.* 650 nm for **1-H**) were observed in the earlier period (0–20 ns for **18-H**, 0–35 ns for **1-H**). As time progressed, these components converged into the unimodal bands in the shorter wavelength region (*ca.* 550 nm for **18-H** and *ca.* 575 nm for **1-H**), indicating the presence of two emission species. Considering the photochemical and photophysical processes of π -stacking structures, the photodimerization of **18-H** and **1-H** indicates that these compounds form excimers of the anthracene units as precursors in the excited state. When the excimers follow non-radiative decay processes, photodimerization can be induced. In contrast, when they followed radiative processes, excimer emission can be observed. The TRES analyses were also performed in the crystals of **18-Me** and **14-H** at 230 K (Figure 8cd). As expected, the change in spectral shapes was not observed and therefore these compounds emit solely ICT emission. The absence of π -stacking structures in **18-Me** and **14-H** prevents excimer formation, supporting the assignment of emission species.

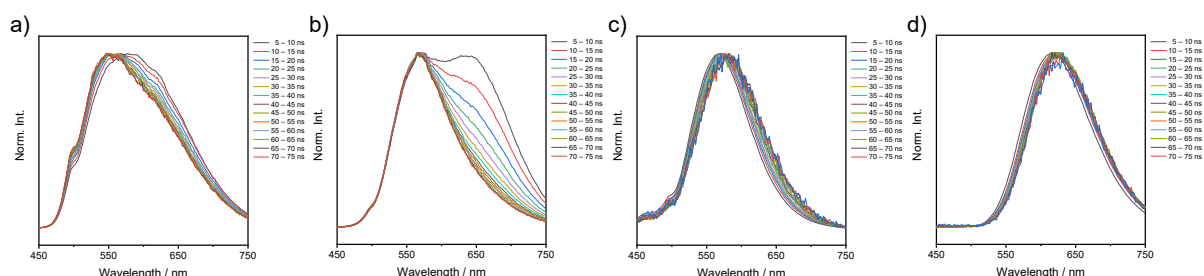


Figure 8. Time-resolved emission spectra (TRES) in the crystalline state of a) **18-H** at 320 K, b) **1-H** at 230 K, c) **18-Me** at 230 K, and d) **14-H** at 230 K.

In **18-H** and **1-H**, sequential enhancements of ICT/excimer intensity ratios were observed with temperature increasing. Taking crystal expansion into consideration, further analyses of these behaviors were conducted. VT-SCXRD analysis of **1-H** revealed gradual elongation of π - π distance (from 3.637(4) Å at 143 K to 3.684(3) Å at 298 K) as the temperature increased. This expansion suppressed excimer formation in the crystal.⁴⁴ In contrast, ICT emission originates from a single molecular process. In this case, the emission spectra were interpreted as the result of the competition between excimer and ICT emission in the crystal state. Therefore, at higher temperatures, ICT emission became dominant due to the suppression of excimer formation.

Moreover, consecutive shifts of the luminescent bands were observed with temperature increasing. In **18-H** and **1-H**, hypsochromic shifts of the excimer emission bands (577 nm at 80 K to 552 nm at 320 K for **18-H**, 588 nm at 80 K to 582 nm at 200 K for **1-H**) were observed in the shorter wavelength region. In contrast, bathochromic shifts of the ICT emission bands were observed in longer wavelength region (627 nm at 350 K to 639 nm at 410 K for **18-H**, 662 nm at 230 K to 692 nm at 410 K for **1-H**). Similar bathochromic shifts of ICT emission were also observed in **18-Me** and **14-H** (559 nm at 80 K to 561 nm at 410 K for **18-Me**, 617 nm at 80 K to 638 nm at 410 K for **14-H**). Hypsochromic shifts of solid-state excimer emission were previously reported in anthracene,⁴⁵ acridine,⁴⁶⁻⁴⁸ and pyrene⁴⁹ derivatives and explained by gradual crystal lattice expansion accompanied by elongation of π - π distances.^{45,48} A strong correlation was found between unit cell volume and π - π distance ($R^2 > 0.99$). Therefore, the gradual elongation of π - π distance also occurred in **1-H** along with the expansion of crystal lattice volume. In the case of ICT bands, the bathochromic shifts were also found in the previous reports on aryl-substituted *o*-caboranes^{25,50} and analyzed theoretically as that the thermally promoted structural relaxation in the excited state.^{51,52} These results further support the assignment of the emission species for all observed bands.

Conclusion

In this chapter, the unique stimuli-responsiveness of anthracene-tethered *o*-carborane derivatives was investigated. Based on the previous results on π -stacking-mediated thermochromic and mechanochromic luminescence of 1,8-bis-*o*-carborane-substituted anthracene, additional structurally modified compounds were synthesized to investigate structure-property relationships. Among them, anthracene with an *o*-carborane unit at 1-position exhibited a π -stacking crystal structure. As a result of this π -stacking arrangement, excimer emission and [4+4] photodimerization could be observed, resulting in the thermochromic luminescence and photosalient effect, respectively. The mechanism of the unique properties was confirmed by X-ray crystallographic analysis including variable temperature method. It could be expected that the π -stacking structure of aryl-substituted *o*-carborane derivatives can be a promising platform for stimuli-responsive luminescent materials with intermolecular interaction in the solid state without suffering from concentration quenching that typically limits conventional luminescent dyes.

Experimental Section

The experimental details followed that described in Chapters 1 and 6, with the differences and additional details summarized below.

Materials.

Commercially available compounds used without purification

N,N-Dimethylaniline (Fujifilm Wako Pure Chemical Corporation), 1,4-bis(diphenylphosphino)butane (dppb) (Fujifilm Wako Pure Chemical Corporation), PdCl₂(PPh₃)₂ (Tokyo Chemical Industry Co., Ltd.), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Fujifilm Wako Pure Chemical Corporation), tetrolic acid (Tokyo Chemical Industry Co., Ltd.), CuI (Fujifilm Wako Pure Chemical Corporation), trimethylsilylacetylene (TMSacetylene) (BLDpharm), 1-aminoanthraquinone (Tokyo Chemical Industry Co., Ltd.), 1,4-diaminoanthraquinone (Tokyo Chemical Industry Co., Ltd.)

Commercially available solvents

Dimethyl sulfoxide (DMSO) (Deoxidized, Fujifilm Wako Pure Chemical Corporation)

Compounds prepared as described in the literature

1-bromoanthracene⁵³ (2 steps, 12% overall yield from 1-aminoanthraquinone),
1-ethynylanthracene (**1b**)⁵⁴ (2 steps, 66% overall yield from 1-bromoanthracene),
1,4-dibromoanthracene^{55,56} (2 steps, 3% overall yield from 1,4-diaminoanthraquinone),
1,4-diethynylanthracene (**1d**)⁵⁷ (2 steps, 92% overall yield from 1,4-dibromoanthracene)

Synthesis

General. ¹H and ¹³C{¹H} NMR spectra were recorded on a JEOL JNM-AL400 or JEOL ECZ400 instrument at 400 and 100 MHz, respectively. ¹¹B{¹H} NMR spectra were recorded on a JEOL ECZ400 instrument at 128 MHz. UV irradiation was performed by Asahi Spectra two MAX-303 300 W Xe lamps equipped with LX0365 band pass filters (365 nm) and the light was integrated by two-branched light guide, QLGΦ5×2M-2Connection. The samples were placed in micro vials or 5 mL sample bottles. Micro vials were jointed with rotating motors of rotary evaporators.

Synthesis of 1-H. In a 50 mL 2-necked round bottom flask, 1-ethynylanthracene (**1b**) (134 mg, 0.66 mmol), decaborane (89 mg, 0.73 mmol) and *N,N*-dimethylaniline (0.15 mL, 1.2 mmol) were dissolved in toluene (7.0 mL) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer at 100 °C (reflux) for 4 h. After filtration to remove any insoluble impurities, the solvent was removed by a rotary evaporator. The crude product was purified by column

chromatography (eluent: CH₂Cl₂/*n*-hexane 1/20 (v/v)) to give a pale-yellow solid. Recrystallization of the residual solid from CCl₄ at 80 °C afforded **1-H** as a pale-yellow solid (17 mg, 0.053 mmol, 8% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.31 (s, 1H), 8.47 (s, 1H), 8.08–8.04 (m, 2H), 8.00–7.97 (m, 1H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.56–7.52 (m, 2H), 7.36 (dd, *J* = 8.2, 7.7 Hz, 1H), 4.71 (s, 1H), 3.85–1.63 (br, 10H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 132.54, 132.18, 131.90, 131.07, 129.03, 128.51, 128.20, 128.06, 127.61, 127.42, 126.71, 126.44, 124.10, 123.39, 119.86, 77.53, 61.32. ¹¹B{¹H} NMR (128 MHz, CDCl₃): –2.82 (2B), –9.02 (3B), –10.16 (3B), –13.42 (2B). HRMS (APCI): calcd. for C₁₆H₂₀B₁₀[–] [M][–] 322.2501, found 322.2501.

Synthesis of 1,8-bis(methylethynyl)anthracene (1c). In a 50 mL 2-necked round bottom flask, 1,8-diiodoanthracene (432 mg, 1.0 mmol), dppb (87 mg, 0.20 mmol), PdCl₂(PPh₃)₂ (74 mg, 0.11 mmol), DBU (0.45 mL, 3.0 mmol) and tetrolic acid (187 mg, 2.2 mmol) were dissolved in DMSO (2.0 mL). The reaction mixture was stirred by magnetic stirrer at 110 °C for 8.5 h. The black solution was extracted with CH₂Cl₂, then the organic layer was washed with water and brine (3 times) and dried over MgSO₄. After filtration, the solvent was removed by a rotary evaporator to afford brown oil. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give 1,8-bis(methylethynyl)anthracene (**1c**) as a pale-yellow solid (76 mg, 30 % isolated yield). The product was characterized by ¹H NMR spectra according to the literature.⁵⁸

Synthesis of 18-Me. In a 50 mL 2-necked round bottom flask, 1,8-bis(methylethynyl)anthracene (**1c**) (76 mg, 0.30 mmol), decaborane (88 mg, 0.72 mmol) and *N,N*-dimethylaniline (0.14 mL, 1.1 mmol) were dissolved in toluene (3.0 mL) under N₂ atmosphere. The reaction mixture was stirred by magnetic stirrer at 115 °C (reflux) for 21.5 h. After filtration to remove any insoluble impurities, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane 1/5 (v/v)) to give yellow solid. Recrystallization of the residual solid from CCl₄ at 85 °C afforded **18-Me** as a yellow solid (8 mg, 0.016 mmol, 5% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.16 (s, 1H), 8.53 (s, 1H), 8.34 (d, *J* = 7.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H), 7.51 (dd, *J* = 7.9, 7.9 Hz, 2H), 3.21–1.87 (br, 20H), 1.47 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 135.88, 132.70, 132.11, 129.75, 129.73, 126.54, 124.52, 122.53, 83.75, 80.64, 23.25. ¹¹B{¹H} NMR (128 MHz, CDCl₃): –1.81 (2B), –4.80 (2B), –9.40 (16B). HRMS (APCI): calcd. for C₂₀H₃₄B₂₀+Cl[–] [M+Cl][–] 529.4259, found 529.4262.

Synthesis of 14-H. In a 30 mL 2-necked round bottom flask, 1,4-diethynylantracene (**1d**) (61 mg, 0.30 mmol), decaborane (47.5 mg, 0.39 mmol) and *N,N*-dimethylaniline (0.068 mL, 0.63 mmol) were dissolved in toluene (3.0 mL) under N₂ atmosphere. After the reaction mixture was stirred by magnetic stirrer at 100 °C (reflux) for 1.5 h, additional amount of decaborane (46.5 mg, 0.38 mmol) was added. Then the mixture was further stirred at 100 °C (reflux) for 1 h. After filtration to remove any insoluble impurities, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (eluent: CH₂Cl₂/*n*-hexane gradient from 1/20 to 1/5 (v/v)) to give colorless solid. Recrystallization of the residual solid from *n*-hexane/CHCl₃ at 80 °C afforded **14-H** as a pale yellow solid (14 mg, 0.044 mmol, 15% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.45 (s, 2H), 8.06 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.64–7.61 (m, 4H), 4.62 (s, 2H), 4.17–1.59 (br, 20H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 131.66, 130.89, 128.36, 128.32, 127.79, 126.05, 125.15, 76.34, 61.60. ¹¹B{¹H} NMR (128 MHz, CDCl₃): –2.44 (4B), –8.81 (6B), –9.84 (6B), –13.12 (4B). HRMS (APCI): calcd. for C₂₀H₃₄B₂₀+Cl[–] [M+Cl][–] 501.3946, found 501.3955.

Synthesis of 18-H_{dimer}. The photoreactor was constructed using high pressure mercury lamp as a light source and a water-cooled quartz immersion well. **18-H** (16 mg, 0.035 mmol) was placed in the 5 mL sample bottle. Irradiation to UV light for 10 h with manual stirring at roughly 1 h intervals yielded pale yellow solid. Without any treatments, the resulted solid was used for analyses. ¹H NMR analysis of the soluble part indicated that it contained 39mol% of the starting monomer **18-H**. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.39 (d, *J* = 6.8 Hz, 4H), 7.17 (d, *J* = 8.4 Hz, 4H), 7.00 (dd, *J* = 8.4, 6.8 Hz, 4H), 5.99 (d, *J* = 11.2 Hz, 2H), 4.98 (d, *J* = 11.6 Hz, 2H), 4.19 (s, 4H), 3.78–1.72 (br, 40H). HRMS (APCI): calcd. for C₃₂H₆₀B₄₀+Cl[–] [M+Cl][–] 967.8224, found 967.8215.

Synthesis of 1-H_{dimer}. The photoreactor was constructed using high pressure mercury lamp as a light source and a water-cooled quartz immersion well. **1-H** (5 mg, 0.016 mmol) was placed in the 5 mL sample bottle. Irradiation to UV light for 7 h with manual stirring at roughly 1 h intervals yielded pale yellow solid. Without any treatments, the resulting solid was used for analyses. ¹H NMR analysis of the soluble part indicated that it contained 7mol% of the starting monomer **18-H**. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.13–7.11 (m, 2H), 7.06 (dd, *J* = 4.4, 4.4 Hz, 2H), 7.02–7.00 (m, 2H), 6.91–6.89 (m, 4H), 6.81–6.80 (m, 4H), 5.79 (d, *J* = 11.2 Hz, 2H), 4.71 (d, *J* = 11.6 Hz, 2H), 4.29 (s, 2H), 3.82–1.63 (br, 20H). HRMS (APCI): calcd. for C₃₂H₄₀B₂₀+Cl[–] [M+Cl][–] 679.4728, found 679.4749.

Table 2. Crystallographic data

Compound name	18-H_{dimer}	1-H	1-H_{dimer}	18-Me	14-H
CCDC number	2279749	2279750	2279755	2279260	2279761
Empirical formula	C ₃₆ H ₆₀ B ₄₀	C ₁₆ H ₂₀ B ₁₀	C ₃₂ H ₄₀ B ₂₀	C ₂₀ H ₃₄ B ₂₀	C ₁₈ H ₃₀ B ₂₀
Formula weight	925.24	320.42	640.84	490.67	462.62
Temperature / K	143(2)	143(2)	143(2)	143(2)	143(2)
Wavelength / Å	0.71075	0.71075	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /n (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>C</i> 2/c (No.15)
<i>a</i> / Å	7.296(5)	11.168(5)	10.658(7)	1.849(4)	20.213(12)
<i>b</i> / Å	18.436(13)	12.060(5)	12.186(6)	21.870(6)	15.812(8)
<i>c</i> / Å	19.181(14)	13.467(6)	13.517(8)	11.064(3)	25.624(15)
α / °	90	90	90	90	90
β / °	100.755(10)	104.400(8)	100.151(10)	107.132(4)	101.221(9)
γ / °	90	90	90	90	90
<i>V</i> / Å ³	2535(3)	1756.8(13)	1728.2(17)	2740.0(14)	8033(8)
<i>Z</i>	2	4	2	4	12
ρ / g·cm ⁻³	1.212	1.211	1.232	1.189	1.148
<i>a</i> / cm ⁻¹	0.056	0.060	0.061	0.056	0.053
<i>F</i> (000)	952	664	664	1016	2856
θ range / °	3.049–27.393	3.123–27.473	3.062–27.435	3.140–27.486	3.044–27.536
Limiting indices	$-9 \leq h \leq 9$ $-23 \leq k \leq 29$ $-24 \leq l \leq 22$	$-12 \leq h \leq 14$ $-14 \leq k \leq 15$ $-17 \leq l \leq 17$	$-9 \leq h \leq 13$ $-15 \leq k \leq 14$ $-17 \leq l \leq 17$	$-15 \leq h \leq 14$ $-25 \leq k \leq 28$ $-14 \leq l \leq 14$	$-26 \leq h \leq 26$ $-19 \leq k \leq 20$ $-33 \leq l \leq 28$
Collected unique reflections	19872/5724	14070/3943	13710/3918	22031/6261	31869/9182
<i>R</i> _{int} ^[a]	0.1390	0.1237	0.0781	0.0431	0.0897
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.195	1.052	1.118	1.046	1.096
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.1359	0.0777	0.0797	0.0491	0.0809
<i>wR</i> ₂ (all data) ^[d]	0.2603	0.1883	0.1573	0.1461	0.2193

^[a] $R_{\text{int}} = \sum ||F_0|^2 - \langle |F_0|^2 \rangle| / \sum |F_0|^2$ ^[b] $S = [\{\sum w(|F_0|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\sum (|F_0|^2 - |F_c|^2)^2 / \sum (|F_0|^2)^2]^{1/2}$

^[d] $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w(|F_0|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Table 3. Crystallographic data of **1-H** measured at different temperature

Temperature / K	143(2)	178(2)	213(2)	263(2)	298(2)
CCDC number	2279750	2279751	2279752	2279753	2279754
Empirical formula	C ₁₆ H ₂₀ B ₁₀	C ₁₆ H ₂₀ B ₁₀	C ₁₆ H ₂₀ B ₁₀	C ₁₆ H ₂₀ B ₁₀	C ₁₆ H ₂₀ B ₁₀
Formula weight	320.42	320.42	320.42	320.42	320.42
Wavelength / Å	0.71075	0.71075	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)
<i>a</i> / Å	11.168(5)	11.105(4)	11.130(3)	11.097(4)	11.112(3)
<i>b</i> / Å	12.060(5)	12.088(3)	12.125(3)	12.200(4)	12.239(3)
<i>c</i> / Å	13.467(6)	13.501(4)	13.524(3)	13.530(5)	13.536(4)
α / °	90	90	90	90	90
β / °	104.400(8)	104.295(4)	104.290(4)	104.130(5)	104.112(6)
γ / °	90	90	90	90	90
<i>V</i> / Å ³	1756.8(13)	1756.2(9)	1768.5(7)	1776.3(10)	1785.4(9)
<i>Z</i>	4	4	4	4	4
ρ / g·cm ⁻³	1.211	1.212	1.203	1.198	1.192
<i>a</i> / cm ⁻¹	0.060	0.060	0.059	0.059	0.059
<i>F</i> (000)	664	664	664	664	664
θ range / °	3.123–27.473	3.114–27.508	3.109–27.479	3.197–27.470	3.191–27.476
Limiting indices	–12 ≤ <i>h</i> ≤ 14 –14 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 17	–10 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 17	–14 ≤ <i>h</i> ≤ 13 –15 ≤ <i>k</i> ≤ 15 –15 ≤ <i>l</i> ≤ 17	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 12 –17 ≤ <i>l</i> ≤ 17	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 13
Collected unique reflections	14070/3943	14056/4025	13988/4008	14078/4040	14124/4076
<i>R</i> _{int} ^[a]	0.1237	0.0798	0.0329	0.0478	0.0565
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.052	1.073	1.102	1.110	1.083
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.0777	0.0834	0.0633	0.0813	0.0690
<i>wR</i> ₂ (all data) ^[d]	0.1883	0.2092	0.1898	0.2136	0.1919

^[a] $R_{\text{int}} = \Sigma ||F_0|^2 - \langle |F_0|^2 \rangle| / \Sigma |F_0|^2$ ^[b] $S = [\{\Sigma w(|F_0|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\Sigma (|F_0|^2 - |F_c|^2)^2 / \Sigma (|F_0|^2)^2]^{1/2}$

^[d] $wR_2 = [\Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w(|F_0|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Table 4. Crystallographic data of **1-H_{dimer}** measured at different temperature

Temperature / K	143(2)	178(2)	213(2)	263(2)	298(2)
CCDC number	2279755	227976	2279757	2279758	2279759
Empirical formula	C ₃₂ H ₄₀ B ₂₀	C ₃₂ H ₄₀ B ₂₀	C ₃₂ H ₄₀ B ₂₀	C ₃₂ H ₄₀ B ₂₀	C ₃₂ H ₄₀ B ₂₀
Formula weight	640.84	640.84	640.84	640.84	640.84
Wavelength / Å	0.71075	0.71075	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)	<i>P</i> 2 ₁ /c (No.14)
<i>a</i> / Å	10.658(7)	10.646(6)	10.666(4)	10.676(5)	10.698(4)
<i>b</i> / Å	12.186(6)	12.204(7)	12.222(4)	12.222(5)	12.217(4)
<i>c</i> / Å	13.517(8)	13.516(8)	13.552(5)	13.561(6)	13.615(5)
α / °	90	90	90	90	90
β / °	100.151(10)	99.992(7)	100.036(5)	100.354(7)	100.646(5)
γ / °	90	90	90	90	90
<i>V</i> / Å ³	1728.2(17)	1729.6(17)	1739.5(11)	1740.5(14)	1748.8(11)
<i>Z</i>	2	2	2	2	1
ρ / g·cm ⁻³	1.232	1.231	1.224	1.223	1.217
<i>a</i> / cm ⁻¹	0.061	0.061	0.060	0.060	0.060
<i>F</i> (000)	664	664	664	664	664
θ range / °	3.062–27.435	3.152–27.519	3.053–27.461	3.054–27.517	3.034–27.458
Limiting indices	–9 ≤ <i>h</i> ≤ 13 –15 ≤ <i>k</i> ≤ 14 –17 ≤ <i>l</i> ≤ 17	–13 ≤ <i>h</i> ≤ 10 –15 ≤ <i>k</i> ≤ 13 –17 ≤ <i>l</i> ≤ 17	–13 ≤ <i>h</i> ≤ 12 –15 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 17	–13 ≤ <i>h</i> ≤ 13 –11 ≤ <i>k</i> ≤ 15 –15 ≤ <i>l</i> ≤ 17	–13 ≤ <i>h</i> ≤ 13 –14 ≤ <i>k</i> ≤ 14 –17 ≤ <i>l</i> ≤ 17
Collected unique reflections	13710/3918	13705/3929	13815/3959	13889/3965	13849/3902
<i>R</i> _{int} ^[a]	0.0781	0.0789	0.0751	0.0663	0.0642
<i>S</i> (Goodness-of-fit on <i>F</i> ²) ^[b]	1.118	1.114	1.115	1.147	1.173
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[c]	0.0797	0.0787	0.0788	0.0800	0.0834
<i>wR</i> ₂ (all data) ^[d]	0.1573	0.1636	0.1556	0.1582	0.1725

^[a] $R_{\text{int}} = \sum ||F_0|^2 - \langle |F_0|^2 \rangle| / \sum |F_0|^2$ ^[b] $S = [\{\sum w(|F_0|^2 - |F_c|^2)^2\} / (N_o - N_p)]^{1/2}$ ^[c] $R_1 = [\sum (|F_0|^2 - |F_c|^2)^2 / \sum (|F_0|^2)^2]^{1/2}$

^[d] $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w(|F_0|^2)^2]^{1/2}$. $w = 1 / [\sigma^2(|F_0|^2) + (ap)^2 + bp]$, where $p = [|F_0|^2 + 2|F_c|^2] / 3$

Microscope Analysis of the Photosalient Effect

Observation of photo-induced mechanical motion was conducted under OLYMPUS BX53M fluorescence microscope. Pictures and videos were obtained by OLYMPUS DP74 camera using *Stream Basic* software. MPlanFLN 10x and WHN10X were used for objective and eyepiece lens, respectively. Built-in USH-1030L 100W mercury lamp was used as light source. BFL, FL(WUS), and FL(WBS) mirror units were used for bright field observation, ultraviolet light excitation and blue light excitation, respectively. For observation with different UV light strength, Asahi Spectra MAX-303 two 300W Xe lamps equipped with two-branched light guide, QLG Φ 5 $\times$ 2M-2Connection were used in the dark room with the sample placed on a glass plate. Temperature control was carried out with LINKAM 10002L variable temperature stage. The mechanical motion of the crystals was quantitatively analyzed by observation under fluorescence microscope. The crystals were set exactly at the same position (center of the field of view). The latent period was defined as the duration initiated by UV light irradiation to the time of the first observation of the crystal movement. For reaching constant temperature, variable temperature observation was carried out at least 1 minutes after the temperature display showed target temperature. The latent period at each temperature was determined as averaged time of at least five measurements.

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List of Publications

Part 1.

Stimuli-Responsive Properties Based on the Regulation of Excited-State Structural Relaxation Funneling into Intramolecular Charge Transfer States

Chapter 1

Solid-state temperature-dependent luminescence of *C,C'*-diaryl-*o*-carboranes based on restriction of excited-state structural relaxation

Yuhara, K.; Tanaka, K.

Chem. Sci. **2025**, *16*, 6495–6506.

Chapter 2

Macrocyclic *C,C'*-diaryl-*o*-carborane derivatives containing pseudo-crown ether: emission enhancement upon cation recognition

Tokutomi, M.; Yuhara, K.; Tanaka, K.

Phys. Chem. Chem. Phys. **2025**, *27*, 15845–15849.

Chapter 3

Guest-induced emission enhancement in the permanent porous conjugated carboracycle crystal

Yuhara, K.; Takemori, S.; Yanagihara, T.; Ohtani, S.; Ogoshi, T.; Tanaka, K.

Chem. Sci. **2026**, *in press*. DOI: 10.1039/D5SC08753H.

Part 2.

Regulation of Circularly Polarized Luminescent Properties Based on the Dual-Emission from Locally Excited and Intramolecular Charge Transfer States

Chapter 4

[7]Helicene-Appended *o*-Carboranes: Sign-Changing Circularly Polarized Luminescence Based on Dual-Emissive Properties and Its Temperature Dependency

Yuhara, K.; Tanaka, K.

Adv. Opt. Mater. in press. DOI: 10.1002/adom.202502647.

Chapter 5

Regulation of circularly polarized emission properties of oxabora[6]helicene by inducing dual-emission properties using *o*-carborane introduction

Yuhara, K.; Tanaka, K.

Bull. Chem. Soc. Jpn. in press. DOI: 10.1093/bulcsj/uoaf117.

Part 3.

Solid-State Stimuli-Responsiveness Based on the Dual-Emission Including Excimer and Intramolecular Charge Transfer Emission

Chapter 6

Regulation of solid-state dual-emission properties by switching luminescence processes based on a bis-*o*-carborane-modified anthracene triad

Yuhara, K.; Tanaka, K.; Chujo, Y.

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Chapter 7

Direction Switching and Self-Recovering Mechanochromic Luminescence of Anthracene-Modified *o*-Carboranes

Yuhara, K.; Tanaka, K.

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Chapter 8

The Photosalient Effect and Thermochromic Luminescence Based on *o*-Carborane-Assisted π -Stacking in the Crystalline State

Yuhara, K.; Tanaka, K.

Angew. Chem. Int. Ed. **2024**, 63, e202319712.

Other Publications

Controlling the Dual-Emission Character of Aryl-Modified *o*-Carboranes by Intramolecular CH $\cdots$ O Interaction Sites

Ochi, J.; Yuhara, K.; Tanaka, K.; Chujo, Y.

Chem. Eur. J. **2022**, 28, e202200155.

Switching between intramolecular charge transfer and excimer emissions in solids based on aryl-modified ethynyl-*o*-carboranes

Yamamoto, H; Ochi, J.; Yuhara, K.; Tanaka, K.; Chujo, Y.

Cell Rep. Phys. Sci. **2022**, 3, 100758.

Highly Efficient and Thermally Durable Luminescence of 1D Eu³⁺ Coordination Polymers with Arsenic Bridging Ligands

Shimoji, H.; Aoyama, Y.; Inage, K.; Nakamura, M.; Yanagihara, T.; Yuhara, K.; Kitagawa, Y.;

Hasegawa, Y.; Ito, S.; Tanaka, K.; Imoto, H.; Naka, K.

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