

π -Extended 9b-Boraphenalenenes: Synthesis, Structure, and Physical Properties

Atsuhiko Ikeno[†], Masahiro Hayakawa[†], Mugiho Sakai[‡], Yusuke Tsutsui[§], Soichiro Nakatsuka[†], Shu Seki^{§,*}, Takuji Hatakeyama^{†,*}

[†]Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

[‡]Department of Chemistry, Graduate School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan

[§]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Supporting Information Placeholder

ABSTRACT: Boraphenalenenes, compounds in which the one carbon atom in the phenalenyl skeleton is replaced with a boron atom, have attracted attention for their solid-state and electronic structures; however, the construction of boraphenalene skeletons remains challenging because of the lack of suitable methods. Through this study, we showed that the tandem borylative cyclization of C_3 -symmetric dehydrobenzo[12]annulenes produces a new class of fully fused boron-atom-embedded polycyclic hydrocarbons possessing a 9b-boraphenalene skeleton. The obtained compounds exhibited high electron-accepting characteristics, and their two-step redox process was reversible in the reductive region, involving interconversion of 9b-boraphenalene between Hückel aromaticity and antiaromaticity. Notably, the benzo[*b*]fluorene-fused derivative exhibited a stepwise single-crystal-to-single-crystal (SCSC) phase transition triggered by thermal annealing. Intermolecular electron coupling calculation of the crystal structures suggested significant improvement of charge transporting ability associated with the SCSC phase transition. Moreover, adequate photoconductivity was observed for the single crystals before and after the SCSC phase transition through flash-photolysis time-resolved microwave conductivity.

INTRODUCTION

The incorporation of heteroatoms into polycyclic aromatic hydrocarbons (PAHs) represents a promising strategy for tuning their physical properties without significant alterations to the pristine molecular skeleton. Building upon this robust strategy, numerous molecules have been synthesized, not only to accumulate fundamental findings but also to facilitate the development of various functional materials, ranging from optoelectronics to bio-imaging.¹ Among heteroatom-doped PAHs, boron-doped PAHs (B-PAHs) have garnered great attention owing to their intriguing photophysical and electronic properties attributed to the vacant p_z orbital.² When a three-coordinated boron atom is doped into π -electron systems, the p_z - π^* interaction between the vacant p_z orbital of the boron atom and the π^* orbitals of π -conjugated systems stabilizes the lowest unoccupied molecular orbital (LUMO) level. Additionally, the high Lewis acidity of boron atoms, resulting from the vacant p_z orbital, enables the coordination of Lewis bases to B-PAHs. Consequently, B-PAHs find considerable applications as electron-transporting,³ light-emitting,⁴ and stimuli-responsive materials.⁵ Another crucial aspect of B-PAHs is that the tri-coordinated boron atom is an isostere of a carbocation. While carbon-only systems possess a positive charge, isoelectronic boron-doped systems are charge neutral, facilitating the development of intriguing neutral and closed-shell π -conjugated frameworks,

such as boron-doped polycyclic odd-alternant hydrocarbons and boron-doped nanographene fragments, which serve as defect nanographene models.⁶ In this context, boraphenalene stands as a representative example of boron-doped polycyclic odd-alternant hydrocarbons, displaying an isoelectronic structure with a phenalenyl cation.⁷ Despite theoretical calculations predicting its electronic structure,⁸ including aromaticity/antiaromaticity,⁹ pancake π - π bonding,¹⁰ and singlet-triplet gap,¹¹ the construction of boraphenalene skeletons remains challenging except for nitrogen incorporating boraphenalenenes.¹² Among the boraphenalenenes, categorized into four types (**A**–**D**) based on the doping position of boron, type-**B** compounds (1-boraphenalene) have been independently reported by several research groups (Figure 1a).¹³ Additionally, π -extended 1-boraphenalene shows potential as an acceptor material for organic solar cells. However, 9b-boraphenalene, a type-**A** compound in which the boron atom is doped at the central carbon atom of the phenalenyl motif, has not been well explored because of the lack of suitable methods for constructing its C_3 -symmetric π -conjugated structure.¹⁴

Herein, we report the one-shot construction of C_3 -symmetric π -extended 9b-boraphenalenenes. Our synthetic strategy was inspired by borylative cyclization, a method reported by Ingleson and coworkers in 2015 (Figure 1b).¹⁵ The reaction involves the electrophilic borylation of alkyne-incorporated arenes with BX_3 ,

followed by intramolecular cyclization to form a boracycle. The remaining reactive haloborane moiety after one borylative cyclization facilitates continuous borylation.¹⁶ Accordingly, we envisioned that 9b-boraphenylene analogues can be synthesized from C_3 -symmetric compounds through C–B bond formation via triple intramolecular borylative cyclization. Specifically, dehydrobenzo[12]annulene derivatives are suitable for constructing 9b-boraphenylene skeletons. Therefore, we designed C_3 -symmetric borylative precursors, 1-phenyldehydrotribenzo[12]annulene (**TBC-Ph**) and 1-(naphthalen-2-yl)dehydrotribenzo[12]annulene (**TBC-Nap**), and explored their borylative cyclization. After extensively screening the reaction conditions, we discovered that the combined use of boron triiodide (BI_3) and 2,6-di-*tert*-butylpyridine (dtbpy) enabled triple borylative cyclization. Additionally, we unveiled the photophysical and electrochemical properties of the thus-synthesized 9b-boraphenylene analogues. Moreover, we investigated the characteristic crystal-to-crystal transition behavior and charge transport properties of the fluorene-fused derivative, **BP-BnFI** (Figure 1c).

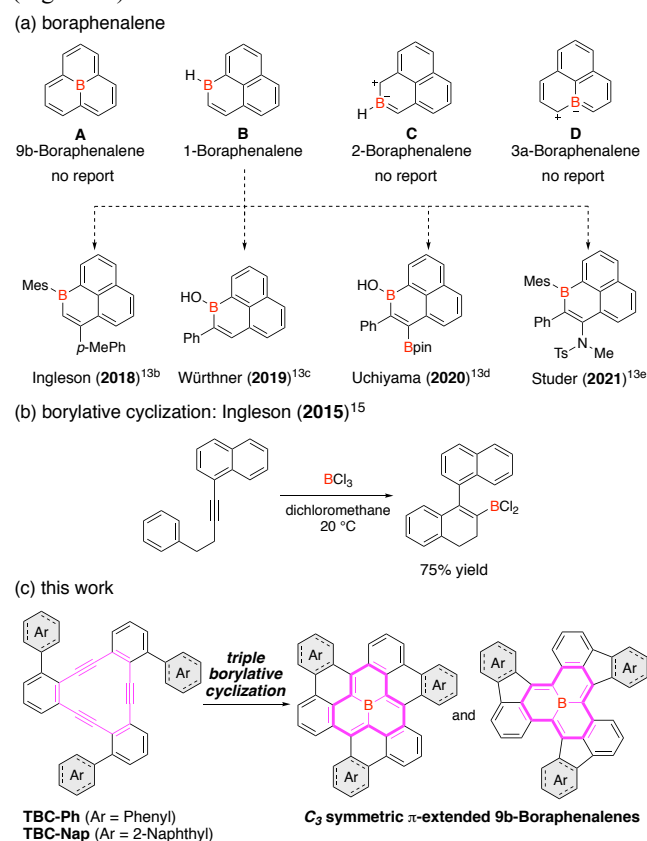
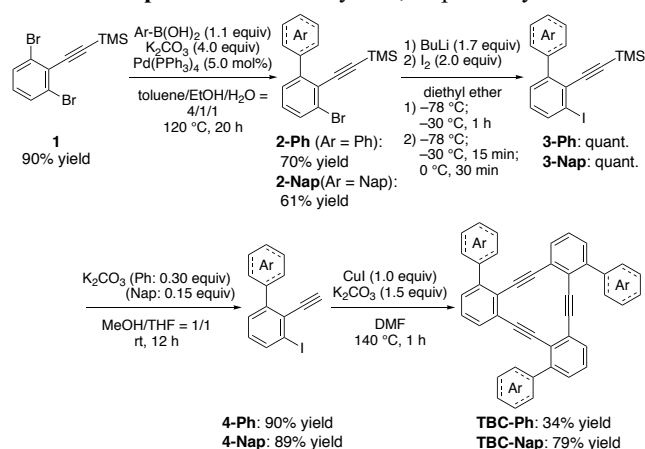


Figure 1. (a) Four isomers of boraphenylene (A–D) and examples of boraphenylene derivatives. (b) Previously reported borylative cyclization. (c) Synthetic strategy for C_3 -symmetric 9b-boraphenylene derivatives with a fully fused boron center.

RESULTS AND DISCUSSION

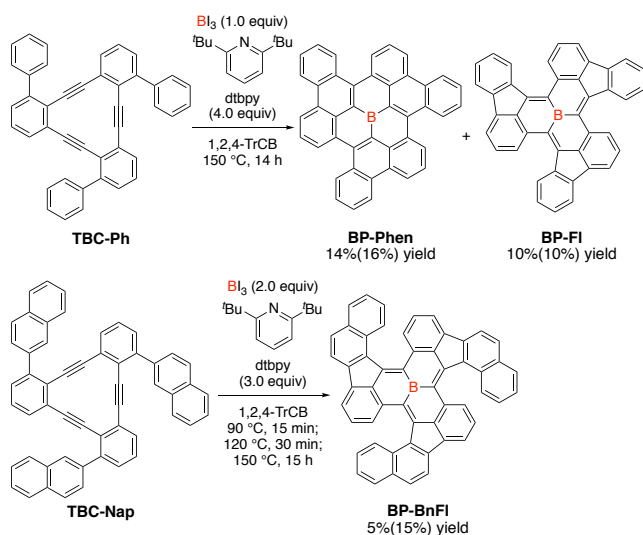
Synthesis of C_3 Symmetric Boraphenylene Analogues. The borylative precursors, **TBC-Ph** and **TBC-Nap**, were synthesized in four steps from 1,3-dibromo-2-trimethylsilylbenzene (**1**) (Scheme 1). Pd-catalyzed Suzuki–Miyaura coupling of **1** with the corresponding arylboronic acid proceeded at 120 °C in a mixed solvent (toluene/EtOH/ H_2O = 4/1/1) to yield mono-aryl-substituted **2-Ph** and **2-Nap** in 70%

and 61% yields, respectively. The remaining bromine was converted to iodine for the subsequent reaction by bromine–lithium exchange and subsequent iodination, resulting in **3-Ph** and **3-Nap** in quantitative yields. After desilylation of **3-Ph** and **3-Nap** by K_2CO_3 , the resulting **4-Ph** and **4-Nap** were subjected to trimerization by Castro–Stephens coupling to afford **TBC-Ph** and **TBC-Nap** in 34% and 79% yields, respectively.



Scheme 1. Synthesis of **TBC-Ph** and **TBC-Nap**.

Finally, borylative cyclization of **TBC-Ph** and **TBC-Nap** was carried out using BI_3 as a borylative reagent (Scheme 2). The triple borylative cyclization of **TBC-Ph** proceeded at 150 °C in the presence of 1.0 equiv of BI_3 and 4.0 equiv of dtbpy to yield two C_3 -symmetric compounds. Notably, other borylative reagents did not yield the products. After careful purification and identification, the two compounds were determined to be phenanthrene-fused boraphenylene **BP-Phen** and fluorene-fused boraphenylene **BP-FI** with isolated yields of 14% and 10%, respectively. In contrast, the borylative cyclization of **TBC-Nap** afforded only one C_3 -symmetric compound. In the presence of 3.0 equiv of dtbpy, borylative cyclization of **TBC-Nap** proceeded using 2.0 equiv of BI_3 under a gradually increasing reaction temperature to afford the benzofluorene-fused-type compound **BP-BnFI** in 15% yield based on 1H NMR analysis. Although this reaction was messy compared to that of the Ph-substituted substrate, **BP-BnFI** was isolated in 5% yield through meticulous purification. It is noteworthy that **BP-BnFI** was obtained in comparable yield (12% yield based on 1H NMR analysis) by using 2,4,6-tri-*tert*-butylpyridine instead of dtbpy (Scheme S1). These obtained compounds were benchtop-stable under ambient conditions and could be handled without precautions. Therefore, single crystals suitable for X-ray analysis were readily grown using the solution diffusion method.



Scheme 2. Borylative cyclization of **TBC-Ph** and **TBC-Nap**. The values in parentheses indicate NMR yields.

A plausible overall reaction mechanism specific to **TBC-Ph** is shown in Figure 2. This reaction consists of three successive borylative cyclizations that proceed by a similar mechanism, in particular, the details of the first borylative cyclization are shown in Figure 2b. The first borylative cyclization commences with the coordination of electrophile BI_3 to the alkyne moiety (**INT1-1** or **INT2-1**). Subsequent 5-*exo-dig* or 6-*endo-dig* cyclization, depending on the coordination position, proceeds to give **INT1-2** and **INT2-2**, which contain a 5-membered or 6-membered ring, respectively. Further deprotonation proceeds to produce a metastable intermediate with a fused fluorene (**INT1**) or phenanthrene structure (**INT2**). The transition state at the cyclization step may be stabilized by the coordination of BI_3 on I⁻ in a realistic system. Subsequent iterative borylative cyclizations follow a similar mechanism to afford desired products **BP-Fl** from the 5-*exo-dig* intermediate (**INT1**) and **BP-Phen** from the 6-*endo-dig* intermediate (**INT2**).

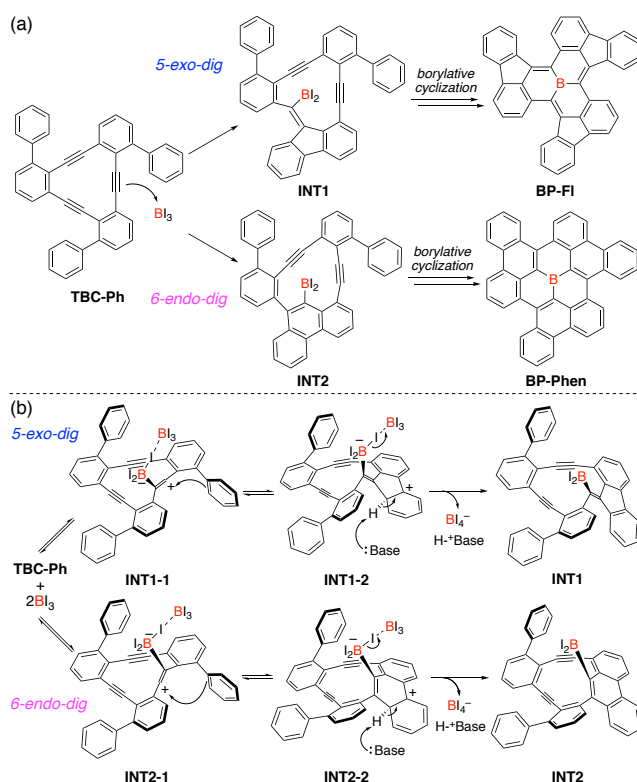


Figure 2. (a) A plausible overall reaction mechanism. (b) Detailed reaction mechanism of the first borylative cyclization.

X-ray Crystallography and Solid-state Phase Transition Behavior. The molecular structures of **BP-Phen**, **BP-Fl**, and **BP-BnFl** were unequivocally confirmed by X-ray crystallography (Figure 3). All compounds adopted windmill-like structures with peripheral aromatic rings deviating from the boraphenylene-like plane because of the steric repulsion of adjacent hydrogen atoms. Consequently, the dihedral angles of the peripheral helical moieties were 33.4/36.2/38.3° (**BP-Phen**), 26.2/34.2/36.7° (**BP-Fl**), and 36.9/45.3/51.5° (**BP-BnFl**). In addition, all the molecules showed a C_1 -symmetric structure in the crystal owing to packing forces and formed a racemic structure containing two enantiomeric isomers—(*P, P, P*) and (*M, M, M*). Based on DFT studies, the isomerization barrier of **BP-Phen** and **BP-Fl** was 11.4 kcal mol⁻¹ and 10.2 kcal mol⁻¹, respectively, which indicates that they readily undergo racemization at room temperature (Figure S14, and Tables S3, S4). Whereas, that of **BP-BnFl** was 31.5 kcal mol⁻¹, which was larger than **BP-Phen** and **BP-Fl** owing to extended π -electron systems (Figure S14c and Table S5). The boraphenylene-like tricyclic skeleton exhibited almost planar, with a 360° sum of the three C–B–C angles (**BP-Phen**: 359.6°, **BP-Fl**: 359.3°, **BP-BnFl**: 359.6°), but slightly contorted geometries owing to the peripheral helical moieties. The C–B bond length was comparable to those of other B-PAHs (1.50–1.56 Å).² The average C–B bond lengths of **BP-BnFl** (1.56 Å) and **BP-Fl** (1.56 Å) were slightly longer than that of **BP-Phen** (1.51 Å) because of the neighboring fused five-membered rings. **BP-Phen** and **BP-Fl** exhibited similar packing structures (Figure 3b and d). The molecules formed face-to-face dimers, rotated by 180°, and these dimers were stacked in a herringbone motif through CH– π interactions. **BP-BnFl** also formed face-to-face dimers, but its packing structure differed significantly (Figure 3f). The face-to-face dimer of **BP-BnFl** adopted a layer-like packing motif along the *b* and *c* axes,

with each layer separated by a strongly disordered cocrystallized solvent (chlorobenzene).

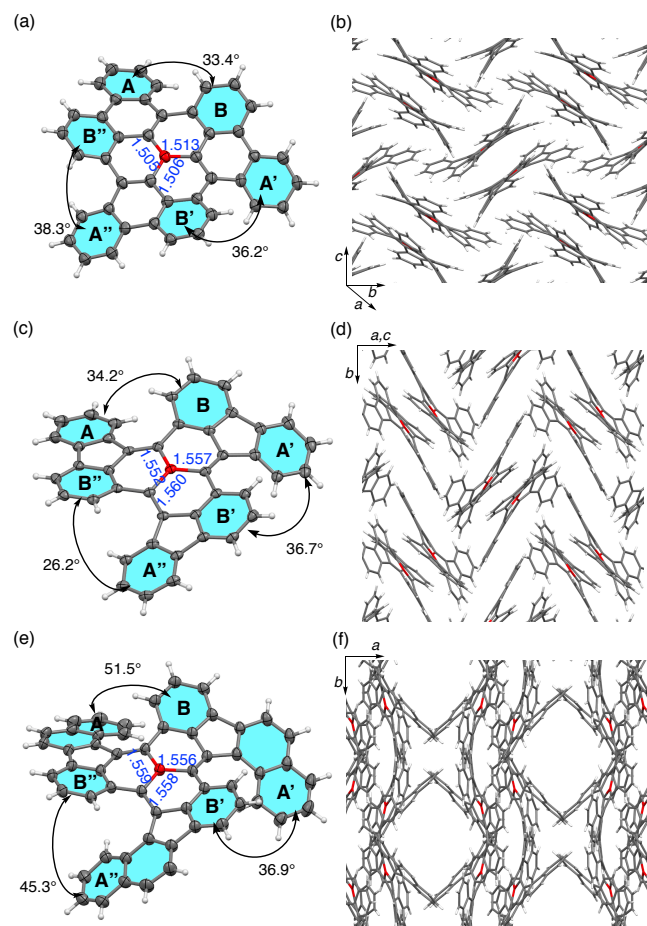


Figure 3. X-ray crystal structures of (a, b) **BP-Phen**, (c, d) **BP-FI**, and (e, f) **BP-BnFI** (C: gray, B: red, H: silver). (a, c, e) Thermal ellipsoid plots (50% probability). (b, d, f) Packing structures. Cocrystallized solvent molecules of toluene (for **BP-Phen**) are omitted for clarity, and chlorobenzene (for **BP-BnFI**) is removed by the *SQUEEZE* program¹⁷ due to high disorder.

Notably, the stepwise single-crystal-to-single-crystal (SCSC) phase transition behavior¹⁸ of **BP-BnFI** was observed, which resulted in two pseudopolymorphs upon heating. For simplicity, the first crystal obtained by the solvent diffusion method was labeled as **BP-BnFI- α** (monoclinic, *I2/a*) and the two pseudopolymorphs obtained by annealing as **BP-BnFI- β** and **- γ** . Annealing **BP-BnFI- α** at 70 °C for 3 h produced **BP-BnFI- β** (triclinic, *P-1*, Figures S2b and S3a), while annealing at 90 °C for 3 h produced **BP-BnFI- γ** (triclinic, *P-1*, Figures S2c and S3b). Further investigation revealed that annealing at 50 °C for 12 h also resulted in **BP-BnFI- γ** , and this transition was irreversible. Therefore, **BP-BnFI- β** was suggested as an intermediate phase, and this SCSC transition behavior inferred an irreversible transition from **BP-BnFI- α** to **BP-BnFI- γ** . In the SCSC transformation of **BP-BnFI**, desorption of the cocrystallized solvent and a significant change in the face-to-face dimeric structure were observed. Notably, the cocrystallized solvent was absent in **BP-BnFI- β** and **- γ** , and the B–B distance between the two molecules forming a dimer increased significantly through heating, expanding from 3.69 Å in **BP-BnFI- α** to 6.22 Å in **BP-BnFI- γ** . These two phenomena led us to infer the SCSC

mechanism from **BP-BnFI- α** to **BP-BnFI- γ** (Figure 4). The driving force of SCSC is presumed to form the most thermodynamically stable crystal structure by external heating. In **BP-BnFI- α** formed by the solvent method, the co-crystallized solvent occupies the intermolecular voids. In the initial transition from **BP-BnFI- α** to **BP-BnFI- β** , the desorption of chlorobenzene, whose positions are indicated by dashed red circles in Figure 4, in the **BP-BnFI- α** crystal upon heating produced large voids, causing the molecules to readily fluctuate and move. To achieve a denser packing and fill in the void, face-to-face dimers shifted and stacked in almost the same orientation. Additionally, half of the face-to-face dimers disengaged and adopted the slipped structure shown in violet in Figure 4. In the subsequent transformation from **BP-BnFI- β** to **BP-BnFI- γ** , the remaining dimers (depicted in sky blue in Figure 4) shifted to slip by each molecule in the reverse direction. Finally, all dimers disengaged and adopted a dense columnar-like slipped π -stacking to form the most thermodynamically stable and densely packed **BP-BnFI- γ** crystals. The crystal density of **BP-BnFI** gradually increased from **BP-BnFI- α** to **BP-BnFI- γ** (α : 1.068 g cm⁻³, β : 1.348 g cm⁻³, and γ : 1.395 g cm⁻³, respectively). The rearrangement into a denser structure upon heating supports the validity of this mechanism. It's noteworthy that **BP-BnFI- β** and **- γ** crystals did not form through the solvent method, indicating that α represents the most kinetically favored crystal in the presence of a solvent.

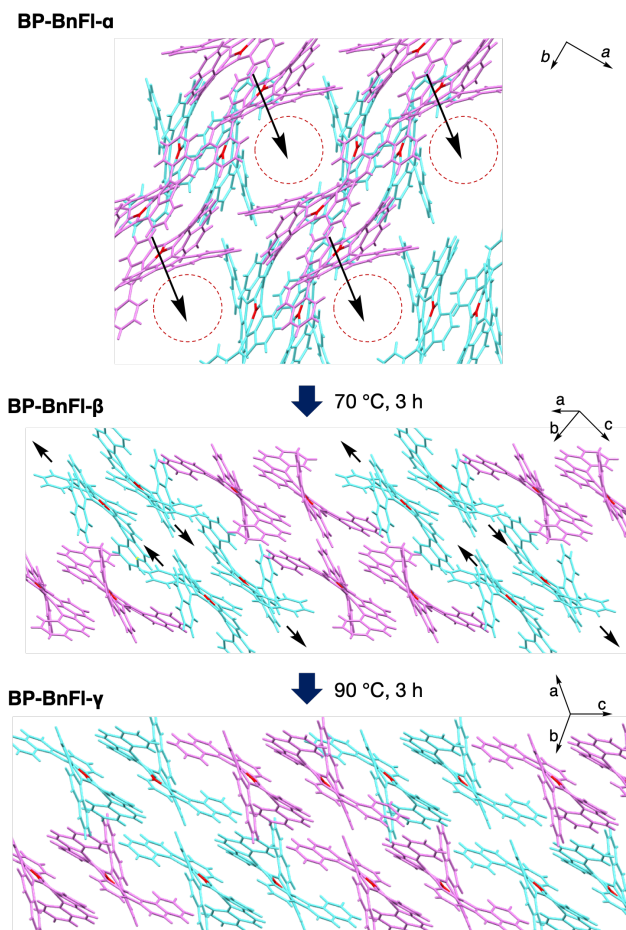


Figure 4. Estimated transformation mechanism from **BP-BnFI- α** to **BP-BnFI- γ** (B: red, C and H: shown in the same color (blue or violet)). Cocrystallized solvent molecules (chlorobenzene) in **BP-**

BnFI-*a* are removed by the *SQUEEZE* program¹⁷ due to high disorder. The positions of the solvent molecules are indicated by dashed red circles.

Photophysical Properties. The ultraviolet–visible (UV–vis) absorption spectra of **BP-Phen**, **BP-FI**, and **BP-BnFI** in CH₂Cl₂ are shown in Figure 5. The absorption maximum of **BP-BnFI** (533 nm) was red-shifted compared to those of **BP-Phen** (488 nm) and **BP-FI** (483 nm) owing to the extended π -conjugated skeleton. According to time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G(d) level of theory, the absorption maximum bands were assigned to symmetry-allowed transitions with a large oscillator strength ($f > 0.2$, **BP-Phen**: $S_0 \rightarrow S_2/S_3$ at 483 nm, **BP-FI**: $S_0 \rightarrow S_5/S_6$ at 498 nm, **BP-BnFI**: $S_0 \rightarrow S_5/S_6$ at 552 nm, Table S2 and Figures S10–S13). While **BP-Phen** exhibited a distinct vibronic structure, **BP-FI** and **BP-BnFI** showed a structureless broad absorption, which is in good agreement with the relatively broad absorption band of PAHs comprising fluorene units.¹⁹ The long-wavelength region of the **BP-FI** and **BP-BnFI** spectra reached 750 nm and was assigned to the $S_0 \rightarrow S_2/S_3$ transition with small f values of 0.0316 and 0.0371, respectively (Table S2 and Figures S10–S13). Because the $S_0 \rightarrow S_1$ transition was symmetry-forbidden, the three compounds did not show any luminescence.

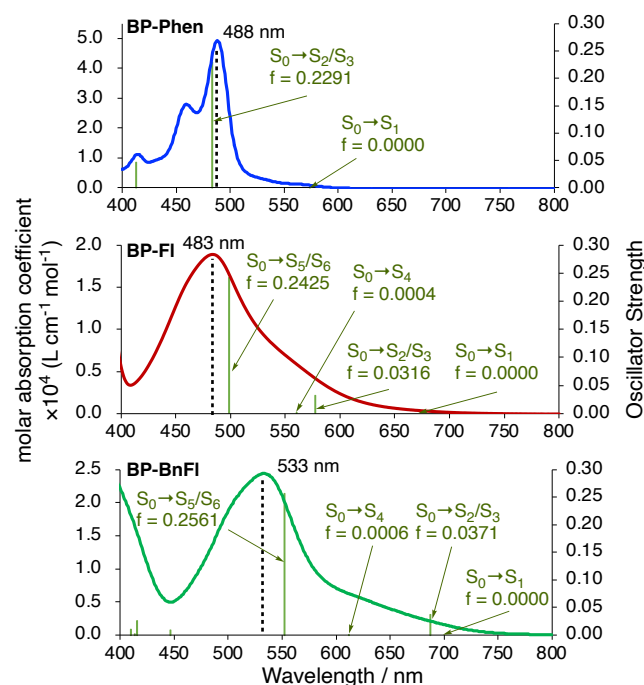


Figure 5. UV–vis absorption spectra of **BP-Phen** (blue), **BP-FI** (red), and **BP-BnFI** (green) in CH₂Cl₂ (2.0×10^{-5} M) with the corresponding oscillator strengths (f ; pale green) were obtained by TD-DFT calculations at the B3LYP/6-31G(d) level of theory.

Lewis Acidity of the Boraphenylene Analogues. One pivotal characteristic of B-PAHs is the Lewis acidity of the boron atom, allowing for the complexation with weak Lewis bases, such as pyridine. To evaluate the Lewis acidity of boraphenylene analogs, titration experiments were conducted using UV–vis spectroscopy. Upon adding pyridine to **BP-Phen** in CH₂Cl₂, the absorbance at 488 nm, corresponding to the absorption maximum, gradually decreased (Figure S4a). By fitting the titration curve using a nonlinear regression model,²⁰ the binding constant of **BP-Phen** against pyridine was determined to be $K_{py} = 30 \text{ M}^{-1}$ (Figure S4b). In the same manner, binding constants of **BP-FI**

and **BP-BnFI** against pyridine were determined to be $K_{py} = 2.9 \times 10^3 \text{ M}^{-1}$ and $1.1 \times 10^3 \text{ M}^{-1}$, respectively (Figures S5 and S6). The binding constants of **BP-FI** and **BP-BnFI**, containing a 5-membered ring as a substructure, were approximately 100 times higher than that of **BP-Phen**, comprising only of a 6-membered ring. Furthermore, these values of **BP-FI** and **BP-BnFI** were highest among the fully fused B-PAHs ($K_{py} = 0.35\text{--}0.66 \text{ M}^{-1}$ in toluene),^{5a,6f} and comparable to that of partially fused B-PAH ($K_{py} = 5.1 \times 10^3 \text{ M}^{-1}$ in toluene) containing a 5-membered ring substructure.^{5a}

Electrochemical Properties. To elucidate the electron affinities of **BP-Phen**, **BP-FI**, and **BP-BnFI**, cyclic voltammetry (CV) measurements were conducted in *o*-dichlorobenzene at room temperature (Figure 6 and Table 1). The cyclic voltammograms of all compounds exhibited two reversible redox processes in the reductive region and irreversible redox processes in the oxidative region (Figure S7). This is in contrast to the fact that typical PAHs possessing one boron atom show only one redox process in the reductive region.^{4c,21} In addition, two reversible redox voltammograms of boraphenylene analogues were identical for at least 10 cycles under CV measurement conditions (Figure S9). Notably, the half-wave potential ($E_{1/2}^{\text{red}}$) of the first redox wave of the fluorene-fused derivatives **BP-FI** and **BP-BnFI** was positive ($E_{1/2}^{\text{red}} = -1.05$ and -1.01 V vs. ferrocene/ferrocenium (Fc/Fc⁺), respectively) compared to that of the phenanthrene-fused derivative **BP-Phen** ($E_{1/2}^{\text{red}} = -1.46 \text{ V}$ vs. Fc/Fc⁺), reflecting the lower LUMO energy levels due to the effective expansion of π^* orbitals via the five-membered rings (Figures S10 and S11). Furthermore, the $E_{1/2}^{\text{red}}$ of the first redox wave of **BP-FI** and **BP-BnFI** is comparable to that of fullerene C₆₀ (-0.98 V vs. Fc/Fc⁺, in CH₃CN/toluene).²² This result demonstrates the potential utility of the 9b-boraphenylene analogues as stable electron-accepting materials.

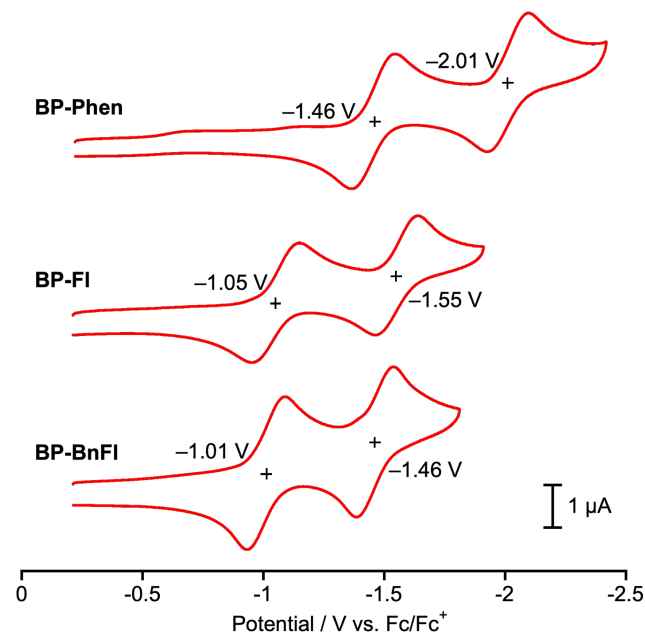


Figure 6. Cyclic voltammograms of **BP-Phen**, **BP-FI**, and **BP-BnFI** measured at a scan rate of 0.1 V s^{-1} in *o*-dichlorobenzene (1.0 mM) at room temperature using Bu_4NPF_6 (0.1 M) as the supporting electrolyte. All potentials are referenced against the ferrocene/ferrocenium (Fc/Fc⁺) couple.

Table 1. Physical properties of boraphenylene analogues

that the γ phase, obtained by thermal annealing of the α phase, would exhibit a higher charge carrier mobility. Therefore, we evaluated the photoconductivity of the α - and γ -phase single crystals using flash-photolysis time-resolved microwave conductivity (FP-TRMC)²⁵ measurements. Several α -phase single crystals prepared by the solution method were affixed to a quartz substrate (Figure S27) and loaded into a microwave cavity. The samples were exposed to 355 nm nanosecond pulses to generate photocarriers. The resulting photoconductivity transients were monitored by measuring the microwave power reflected from the cavity, which enabled us to evaluate the photoconductivity of the compounds without electrodes (Figure S26a). Because of its relatively large intermolecular coupling, the α -phase showed a photoconductivity maxima $(\phi\Sigma\mu)_{\max}$ of $4.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is comparable to that of PC₆₁BM²⁶ ($2.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, ϕ : photocarrier generation efficiency, $\Sigma\mu$: sum of the electron and hole mobilities). The transient conductivity of the γ -phase, obtained by annealing the α -phase crystals, was measured similarly; however, its transient photoconductivity was $(\phi\Sigma\mu)_{\max} = 0.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, smaller than that of the α -phase (Figure S26b). This contradiction with the theoretical predictions was due to the presence of cosolvent molecules in α -phase may facilitate the exciton dissociation giving free charge carrier pairs via the higher reorganization energy for the charged species, which leads the higher ϕ values in α -phase, alternatively, the presence of multiple trap sites in the low-quality crystals and the low SCSC transition efficiency of the α -phase. Indeed, only some of solids obtained by annealing single crystals of the α -phase showed X-ray diffraction patterns. Since most of the crystals did not exhibit clear X-ray diffraction patterns, the powder X-ray diffraction pattern of the TRMC sample did not closely match the ideal γ -phase pattern as simulated in the single crystal (Figure S28). Although the enhancement of charge mobility by the SCSC transition could not be demonstrated, further optimization of the transition process or direct assembly of the γ -phase will improve its charge transport properties and promote its application in organic electronics.

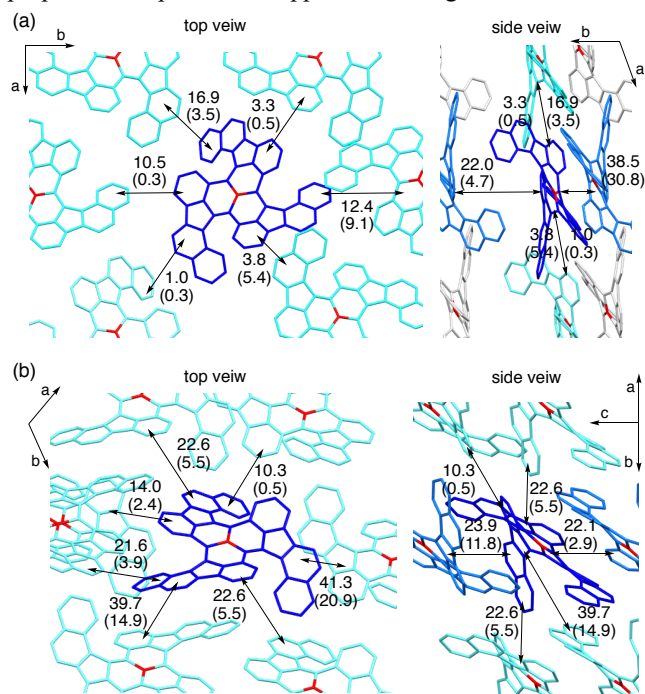


Figure 8. Electron couplings (meV) of neighboring molecules in the X-ray crystal structures of (a) BP-BnFI- α and (b) BP-BnFI- γ at the PW91/TZP level on the ADF2020 program. The LUMO–LUMO interaction values are shown in parenthesis below the HOMO–HOMO interaction values. Hydrogen atoms are omitted for clarity.

CONCLUSION

The reaction of C_3 -symmetric dehydro[12]annulenes containing three alkyne moieties with the highly reactive BI_3 through tandem borylative cyclization resulted in the 9b-boraphenylene skeleton. Electrochemical measurements revealed that the obtained boraphenylene analogues exhibited two reversible redox processes in the reduction region, a distinctive feature compared to that of conventional mono-boron embedded B-PAHs. According to theoretical calculations, the driving force for these two-electron reduction processes is the acquisition of Hückel aromaticity by the two-electron reduction of the 12π antiaromatic boraphenylene moiety. Notably, the five-membered ring-fused derivatives, BP-FI and BP-BnFI, displayed a high electron-accepting characteristics comparable to that of fullerene C_{60} due to the effective expansion of π^* orbitals. Single-crystal X-ray diffraction analyses of the resulting compounds unequivocally confirmed the tricyclic boraphenylene skeleton. Furthermore, a significant change in the packing structure was observed in the BP-BnFI crystal due to the stepwise single-crystal-to-single-crystal (SCSC) transition behavior. Compared to BP-BnFI- α (α -phase) obtained by the solution method, BP-BnFI- γ (γ -phase) obtained by the SCSC transition formed a dense packing structure. This change to a denser packing structure attributed to the SCSC transition led to a significant improvement in intermolecular charge coupling. Indeed, the α - and γ -phases exhibited some transient conductivity in flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements, albeit with a low transition efficiency from the α -phase to the γ -phase. This result underscores the potential of boraphenylene analogues as charge transport materials with high electron-accepting characteristics. Further investigations into the potential applications of boraphenylenes as electronic materials, as well as the extension of this synthetic strategy to other classes of B-PAHs, are currently underway in our laboratory.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

The details of synthesis, X-ray crystallographic analysis, photo-physical and electrochemical measurements, DFT studies, and evaluation of photoconductivity, as well as the NMR spectra of newly synthesized compounds (PDF).

AUTHOR INFORMATION

Corresponding Author

*Shu Seki

E-mail: seki@moleng.kyoto-u.ac.jp

*Takuji Hatakeyama

E-mail: hatake@kuchem.kyoto-u.ac.jp

ACKNOWLEDGMENT

This work was supported by the Japan Society for the Promotion of Science (JSPS) Grants-in-Aid for Transformative Research Areas (A) “Condensed Conjugation” (Grant Number 20H05863 for

T.H. and 20H05867 for S.S.) and Core-to-Core Program (JPJSCCA20220004 for T.H.). The synchrotron X-ray crystallography experiments were performed at the BL40XU beamline of SPring-8, with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Project No. 2023A1337). We thank Dr. Masakazu Kondo (JNC Co., Ltd.) for his support and for the band calculations. We would also like to thank Profs. Satoshi Horike and Kentaro Kadota (Kyoto Univ.) for their help with XRD measurement, Dr. Mika Sakai (Nagoya Univ.) for her advice on pyridine titration experiments, and Ms. Akiko Fujihashi (Kyoto Univ.) for her advice on Mass spectroscopy.

REFERENCES

- Recent reviews: (a) Narita, A.; Wang, X.-Y.; Feng, X.; Müllen, K. New Advances in Nanographene Chemistry. *Chem. Soc. Rev.* **2015**, *44*, 6616–6643. DOI: 10.1039/c5cs00183h (b) Stepień, M.; Gońka, E.; Żyła, M.; Sprutta, N. Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications. *Chem. Rev.* **2017**, *117*, 3479–3716. DOI: 10.1021/acs.chemrev.6b00076 (c) Hirai, M.; Tanaka, N.; Sakai, M.; Yamaguchi, S. Structurally Constrained Boron-, Nitrogen-, Silicon-, and Phosphorus-Centered Polycyclic π -Conjugated Systems. *Chem. Rev.* **2019**, *119*, 8291–8331. DOI: 10.1021/acs.chemrev.8b00637 (d) Dhbaibi, K.; Favereau, L.; Crassous, J. Enantioenriched Helicenes and Helicenoids Containing Main-Group Elements (B, Si, N, P) *Chem. Rev.* **2019**, *119*, 8846–8953. DOI: 10.1021/acs.chemrev.9b00033 (e) Schaub, T. A.; Padberg, K. Kivala, M. Bridged Triarylboranes, -silanes, -amines, and -phosphines as Minimalistic Heteroatom-Containing Polycyclic Aromatic Hydrocarbons: Progress and Challenges. *J. Phys. Org. Chem.* **2020**, *33*, e4022. DOI: 10.1002/poc.4022 (f) Biagiotti, G.; Perini, I.; Richichi, B.; Cicchi, S. Novel Synthetic Approach to Heteroatom Doped Polycyclic Aromatic Hydrocarbons: Optimizing the Bottom-Up Approach to Atomically Precise Doped Nanographenes. *Molecules* **2021**, *26*, 6306. DOI: 10.3390/molecules26206306 (g) Borissov, A.; Maurya, Y. K.; Moshniha, L.; Wong, W.-S.; Żyła-Karwowska, M.; Stepień, M. Recent Advances in Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds. *Chem. Soc. Rev.* **2022**, *122*, 565–788. DOI: 10.1021/acs.chemrev.1c00449
- Recent reviews of B-PAHs: (a) Wakamiya, A.; Yamaguchi, S. Designs of Functional π -Electron Materials Based on the Characteristic Features of Boron. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1357–1377. DOI: 10.1246/bcsj.20150151 (b) Escande, A.; Ingleston, M. J. Fused Polycyclic Aromatics Incorporating Boron in the Core: Fundamentals and Applications. *Chem. Commun.* **2015**, *51*, 6257–6274. DOI: 10.1039/c5cc00175g (c) Ji, L.; Griesbeck, S.; Marder, T. B. Recent Developments in and Perspectives on Three-Coordinate Boron Materials: A Bright Future. *Chem. Sci.* **2017**, *8*, 846–863. DOI: 10.1039/c6sc04245g (d) von Grotthuss, E.; John, A.; Kaese, T.; Wagner, M. Doping Polycyclic Aromatics with Boron for Superior Performance in Materials Science and Catalysis. *Asian J. Org. Chem.* **2018**, *7*, 37–53. DOI: 10.1002/ajoc.201700495 (e) He, J.; Rauch, F.; Finze, M.; Marder, T. B. (Hetero)arene-Fused Boroles: A Broad Spectrum of Applications. *Chem. Sci.* **2021**, *12*, 128–147. DOI: 10.1039/D0SC05676F (f) Oda, S.; Hatakeyama, T. Development of One-Shot/One-Pot Borylation Reactions toward Organoboron-Based Materials. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 950–960. DOI: 10.1246/bcsj.20200327 (g) Shi, J.; Ran, Z.; Peng, F.; Chen, M.; Li, L.; Ji, L.; Huang, W. High-Performance Three-Coordinated Organoboron Emitters for Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2022**, *10*, 9165–9191. DOI: 10.1039/d2tc01243j (h) Guo, Y.; Chen, C.; Wang, X.-Y. Recent Advances in Boron-Containing Acenes: Synthesis, Properties, and Optoelectronic Applications. *Chin. J. Chem.* **2023**, *41*, 1355–1373. DOI: 10.1002/cjoc.202200700 (i) Wang, R.; Lee, C.-S.; Lu, Z. Recent Development of Three-Coordinated Boron-Doped Aromatics for Optoelectronic Applications. *J. Organomet. Chem.* **2023**, *984*, 122564. DOI: 10.1016/j.jorganchem.2022.122564 (j) Chang, Z.; Chen, C.; Wang, X.-Y. Boron-Containing Triangulenes and Their Analogues: Synthesis, Properties, and Applications. *Chem. Lett.* **2023**, *52*, 586–597. DOI: 10.1246/cl/230195 (k) Yuan, L.; Wang, Y.; Dou, C. Progress of Polycyclic Boron-Doped Molecular Carbons. *Org. Mater.* **2023**, *5*, 191–201. DOI: 10.1055/a-2213-1732 (l) Mamada, M.; Hayakawa, M.; Ochi, J.; Hatakeyama, T. Organoboron-Based Multiple-Resonance Emitters: Synthesis, Structure–Property Correlations, and Prospects. *Chem. Soc. Rev.* **2024**, *53*, 1624–1692. DOI: 10.1039/D3CS00837
- (a) Shuto, A.; Kushida, T.; Fukushima, T.; Kaji, H.; Yamaguchi, S. π -Extended Planarized Triphenylboranes with Thiophene Spacers. *Org. Lett.* **2013**, *15*, 6234–6237. DOI: 10.1021/ol403084x (b) Kushida, T.; Shuto, A.; Yoshio, M.; Kato, T.; Yamaguchi, S. A Planarized Triphenylborane Mesogen: Discotic Liquid Crystals with Ambipolar Charge-Carrier Transport Properties. *Angew. Chem. Int. Ed.* **2015**, *54*, 6922–6925. DOI: 10.1002/anie.201502678 (c) Miyamoto, F.; Nakatsuka, S.; Yamada, K.; Nakayama, K.; Hatakeyama, T. Synthesis of Boron-Doped Polycyclic Aromatic Hydrocarbons by Tandem Intramolecular Electrophilic Arene Borylation. *Org. Lett.* **2015**, *17*, 6158–6161. DOI: 10.1021/acs.orglett.5b03167 (d) Matsuo, K.; Saito, S.; Yamaguchi, S. A Soluble Dynamic Complex Strategy for the Solution-Processed Fabrication of Organic Thin-Film Transistors of a Boron-Containing Polycyclic Aromatic Hydrocarbon. *Angew. Chem. Int. Ed.* **2016**, *55*, 11984–11988. DOI: 10.1002/anie.201605221 (e) Kushida, T.; Shirai, S.; Ando, N.; Okamoto, T.; Ishii, H.; Matsui, H.; Yamagishi, M.; Uemura, T.; Tsurumi, J.; Watanabe, S.; Takeya, J.; Yamaguchi, S. Boron-Stabilized Planar Neutral π -Radicals with Well-Balanced Ambipolar Charge-Transport Properties. *J. Am. Chem. Soc.* **2017**, *139*, 14336–14339. DOI: 10.1021/jacs.7b056471 (f) Sun, W.; Guo, J.; Fan, Z.; Yuan, L.; Ye, K.; Dou, C. Ribbon-Type Boron-Doped Polycyclic Aromatic Hydrocarbons: Conformations, Dynamic Complexation and Electronic Properties. *Angew. Chem. Int. Ed.* **2022**, *61*, e202209271. DOI: 10.1002/anie.202209271
- (a) Reus, C.; Weidlich, S.; Bolte, M.; Lerner, H.-W.; Wagner, M. C-Functionalized, Air- and Water-Stable 9,10-Dihydro-9,10-diboraanthracenes: Efficient Blue to Red Emitting Luminophores. *J. Am. Chem. Soc.* **2013**, *135*, 12892–12907. DOI: 10.1021/ja406766e (b) Hertz, V. M.; Bolte, M.; Lerner, H.-Q.; Wagner, M. Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores. *Angew. Chem. Int. Ed.* **2015**, *54*, 8800–8804. DOI: 10.1002/anie.201502977 (c) Schickedanz, K.; Trageser, T.; Bolte, M.; Lerner, H.-W.; Wagner, M. A Boron-Doped Helicene as a Highly Soluble, Benchtop-Stable Green Emitter. *Chem. Commun.* **2015**, *51*, 15808–15810. DOI: 10.1039/C5CC07208E (d) John, A.; Bolte, M.; Lerner, H.-W.; Meng, G.; Wang, S.; Peng, T.; Wagner, M. Doubly Boron-Doped Pentacenes as Emitters for OLEDs. *Chem. Commun.* **2018**, *6*, 10881–10887. DOI: 10.1039/C8TC03954B (e) Kotadiya, N. B.; Blom, P. W. M.; Wetzelaer, G.-J. A. H. Efficient and Stable Single-Layer Organic Light-Emitting Diodes Based on Thermally Activated Delayed Fluorescence. *Nat. Photon.* **2019**, *13*, 765–769. DOI: 10.1038/s41566-019-0488-1 (f) Lee, Y. H.; Lee, W.; Lee, T.; Lee, D.; Jung, J.; Yoo, S.; Lee, M. H. Blue TADF Emitters Based on B-Heterotriangulene Acceptors for Highly Efficient OLEDs with Reduced Efficiency Roll-Off. *ACS Appl. Mater. Interfaces* **2021**, *13*, 45778–45788. DOI: 10.1021/acsami.1c10653 (g) Ito, M.; Shirai, S.; Xie, Y.; Kushida, T.; Ando, N.; Soutome, H.; Fujimoto, K. J.; Yanai, T.; Tabata, K.; Miyata, Y.; Kita, H.; Yamaguchi, S. Fluorescent Organic π -Radicals Stabilized with Boron: Featuring a SOMO–LUMO Electronic Transition. *Angew. Chem. Int. Ed.* **2022**, *61*, e202201965. DOI: 10.1002/anie.202201965 (h) Liu, Y.; Yuan, L.; Guo, J.; Sun, W.; Wang, Y.; Dou, C. Photonic Modulation Enabled by Controlling the Edge Structures of Boron-Doped Molecular Carbons. *Angew. Chem. Int. Ed.* **2023**, *62*, e202306911. DOI: 10.1002/anie.202306911

5. (a) Matsuo, K.; Saito, S.; Yamaguchi, S. Photodissociation of B–N Lewis Adducts: A Partially Fused Trinaphthylborane with Dual Fluorescence. *J. Am. Chem. Soc.* **2014**, *136*, 12580–12583. DOI: 10.1021/ja506980p (b) Adams, I. A.; Rupar, P. A. A Poly(9-Borafluorene) Homopolymer: An Electron-Deficient Polyfluorene with “Turn-On” Fluorescence Sensing of NH₃ Vapor. *Macromol. Rapid. Commun.* **2015**, *36*, 1336–1340. DOI: 10.1002/marc.201500107 (c) Møllerup, S. K.; Wang, S. Boron-Based Stimuli Responsive Materials. *Chem. Soc. Rev.* **2019**, *48*, 3537–3549. DOI: 10.1039/c9cs00153k (d) Srivastava, S.; Jain, S. K.; Gupta, G.; Senguttuvan, T. D.; Gupta, B. K. Boron-Doped Few-Layer Graphene Nanosheet Gas Sensor for Enhanced Ammonia Sensing at Room Temperature. *RSC Adv.* **2020**, *10*, 1007–1014. DOI: 10.1039/C9RA08707A (e) Ando, N.; Yamada, T.; Narita, H.; Oehlmann, N. N.; Wagner, M.; Yamaguchi, S. Boron-Doped Polycyclic π -Electron Systems with an Antiaromatic Borole Substructure That Forms Photoresponsive B–P Lewis Adducts. *J. Am. Chem. Soc.* **2021**, *143*, 9944–9951. DOI: 10.1021/jacs.1c04251 (f) Narita, H.; Choi, H.; Ito, M.; Ando, N.; Ogi, S.; Yamaguchi, S. Fully Fused Boron-Doped Polycyclic Aromatic Hydrocarbons: Their Synthesis, Structure–Property Relationships, and Self-Assembly Behavior in Aqueous Media. *Chem. Sci.* **2022**, *13*, 1484–1491. DOI: 10.1039/D1SC06710A
6. (a) Saito, S.; Matsuo, K.; Yamaguchi, S. Polycyclic π -Electron System with Boron at Its Center. *J. Am. Chem. Soc.* **2012**, *134*, 9130–9133. DOI: 10.1021/ja3036042 (b) Dou, C.; Saito, S.; Matsuo, K.; Hisaki, I.; Yamaguchi, S. A Boron-Containing PAH as a Substructure of Boron-Doped Graphene. *Angew. Chem. Int. Ed.* **2012**, *51*, 12206–12210. DOI: 10.1002/anie.201206699 (c) Kawai, S.; Saito, S.; Osumi, S.; Yamaguchi, S.; Foster, A. S.; Spijker, P.; Meyer, E. Atomically Controlled Substitutional Boron-Doping of Graphene Nanoribbons. *Nat. Commun.* **2015**, *6*, 8098. DOI: 10.1038/ncomms9098 (d) Osumi, S.; Saito, S.; Dou, C.; Matsuo, K.; Kume, K.; Yoshikawa, H.; Awaga, K.; Yamaguchi, S. Boron-Doped Nanographene: Lewis Acidity, Redox Properties, and Battery Electrode Performance. *Chem. Sci.* **2016**, *7*, 219–227. DOI: 10.1039/c5sc02246k (e) Kahan, R. J.; Crossley, D. L.; Cid, J.; Radcliffe, J. E.; Woodward, A. W.; Fasano, V.; Endres, S.; Whitehead, G. F. S.; Ingleson, M. J. Generation of a Series of B_n Fused Oligo-naphthalenes (*n* = 1 to 3) from a B₁-Polycyclic Aromatic Hydrocarbon. *Chem. Commun.* **2018**, *54*, 9490–9493. DOI: 10.1039/C8CC04701D (f) Kawai, S.; Nakatsuka, S.; Hatakeyama, T.; Pawlak, R.; Meier, T.; Tracey, J.; Meyer, E.; Foster, A. S. Multiple Heteroatom Substitution to Graphene Nanoribbon. *Sci. Adv.* **2018**, *4*, eaar7181. DOI: 10.1126/sciadv.aar7181 (g) Radtke, J.; Schickedanz, K.; Bamberg, M.; Menduti, L.; Schollmeyer, D.; Bolte, M.; Lerner, H.-W.; Wagner, M. Selective Access to Either a Doubly Boron-Doped Tetrabenzopentacene or an Oxadiborepin from the Same Precursor. *Chem. Sci.* **2019**, *10*, 9017–9027. DOI: 10.1039/C9SC03115D (h) Yuan, L.; Guo, J.; Yang, Y.; Ye, K.; Dou, C.; Wang, Y. A C₃₄B₂ Polycyclic π -System with Bilayer Assembly and Multi-Redox Activity. *CCS Chem.* **2023**, *5*, 876–884. DOI: 10.31635/ccschem.022.202101738 (i) Yuan, L.; Yang, J.; Qi, S.; Liu, Y.; Tian, X.; Jia, T.; Wang, Y.; Dou, C. Diradicaloid Boron-Doped Molecular Carbons Achieved by Pentagon-Fusion. *Angew. Chem. Int. Ed.* **2023**, *62*, e202314982. DOI: 10.1002/anie.202314982
7. Pettit, R. The Synthesis and Properties of the Perinaphthenylium Cation. *J. Am. Chem. Soc.* **1960**, *82*, 1972–1975. DOI: 10.1021/ja01493a033
8. (a) Zoellner, M. J.; Zoellner, W. R. Uncharged Analogues of the Phenalenyl Cation: Hartree-Fock, Møller-Plesset, and Density Functional Computational Investigations of the Isomers of Bora-phenalene. *J. Mol. Struct.* **2009**, *904*, 49–56. DOI: 10.1016/j.theochem.2009.02.032 (b) Irham, M. A.; Anrokhi, M. S.; Anggraini, Y.; Sutjahja, I. M. Dopant Effect on Phenalene Bandgap Control: A Huckel Molecular Orbital Perspective. *Quim. Nova* **2021**, *44*, 1204–1209. DOI: 10.21577/0100-4042.20170765
9. (a) Cyrański, M. K.; Havenith, R. W. A.; Dobrowolski, M. A.; Gray, B. R.; Krygowski, T. M.; Fowler, P. W.; Jenneskens, L. W. The Phenalenyl Motif: A Magnetic Chameleon. *Chem. Eur. J.* **2007**, *13*, 2201–2207. DOI: 10.1002/chem.200601619 (b) Havenith, R. W. A.; Fowler, P. W. Ipsocentric Ring Currents in Density Functional Theory. *Chem. Phys. Lett.* **2007**, *449*, 347–353. DOI: 10.1016/j.cplett.2007.10.083 (c) Tsiapis, A. C. Efficiency of the NICS_{zz}-Scan Curves to Probe the Antiaromaticity of Organic and Inorganic Rings/Cages. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8244–8261. DOI: 10.1039/B903677F (d) Trujillo, C.; Sánchez-Sanz, G.; Alkorta, I.; Elguero, J. An Insight on the Aromatic Changes in Closed Shell Icosagen, Tetrel, and Pnictogen Phenalenyl Derivatives. *Struct. Chem.* **2017**, *28*, 345–355. DOI: 10.1007/s11224-016-0882-y
10. (a) Kolb, B.; Kertesz, M.; Thonhauser, T. Binding Interactions in Dimers of Phenalenyl and Closed-Shell Analogues. *J. Phys. Chem. A* **2013**, *117*, 3642–3649. DOI: 10.1021/jp3095424 (b) Cui, Z.; Lischka, H.; Beneberu, H. Z.; Kertesz, M. Rotational Barrier in Phenalenyl Neutral Radical Dimer: Separating Pancake and van der Waals Interactions. *J. Am. Chem. Soc.* **2014**, *136*, 5539–5542. DOI: 10.1021/ja412862n (c) Tian, Y.-H.; Sumpter, G. B.; Du, S.; Huang, J. Pancake π - π Bonding Goes Double: Unexpected 4e/All-Sites Bonding in Boron- and Nitrogen-Doped Phenalenyls. *J. Phys. Chem. Lett.* **2015**, *6*, 2318–2325. DOI: 10.1021/acs.jpclett.5b00857 (d) Gao, F.-W.; Xu, H.-L.; Su, Z.-M. Tuning the Inter-molecular Charge Transfer, Second-Order Nonlinear Optical and Absorption Spectra Properties of a π -Dimer under an External Electric Field. *Phys. Chem. Chem. Phys.* **2017**, *19*, 31958–31964. DOI: 10.1039/C7CP06412H (e) Gao, F.-W.; Zhang, F.-Y.; Zhong, R.-L.; Xu, H.-L.; Sun, S.-L.; Su, Z.-M. Boron/Nitrogen Substituted the Staggered Heterodimers: Fascinating Intermolecular Charge-Transfer and Large NLO Responses. *Dyes Pigm.* **2017**, *145*, 21–28. DOI: 10.1016/j.dyepig.2017.05.039 (f) Zhong, R.-L.; Gao, F.-W.; Xu, H.-L.; Su, Z.-M. Strong Pancake 2e/12c Bond in π -Stacking Phenalenyl Derivatives Avoiding Bond Conversion. *Chem. Phys. Chem.* **2019**, *20*, 1879–1884. DOI: 10.1002/cphc.201900280 (g) Gao, F.-W.; Li, S.-B.; Xu, H.-L.; Su, Z.-M. Periodic B- and N-Doped Phenalenyl π -Aggregates: Unexpected Nonlinear Optical Properties by Tuning Pancake π - π Bonding. *Phys. Chem. Chem. Phys.* **2021**, *23*, 23998–24003. DOI: 10.1039/D1CP03540A (h) Janesko, B. G.; Brothers, E. N. Half-Pancake Bonding in Asphaltenes. *Energy Fuels* **2021**, *35*, 15657–15662. DOI: 10.1021/acs.energyfuels.1c02240
11. (a) Sanz-Rodrigo, J.; Ricci, G.; Olivier, Y.; Sancho-García, J. C. Negative Singlet–Triplet Excitation Energy Gap in Triangle-Shaped Molecular Emitters for Efficient Triplet Harvesting. *J. Phys. Chem. A* **2021**, *125*, 513–522. DOI: 10.1021/acs.jpca.0c08029 (b) Dreuw, A.; Hoffmann, M. The Inverted Singlet–Triplet Gap: A Vanishing Myth? *Front. Chem.* **2023**, *11*, 1239604. DOI: 10.3389/fchem.2023.1239604
12. (a) Dewar, M. J. S.; Jones, R. New heteroaromatic compounds Part XXXI: The 12,11-borazarophenalenium cation. *Tetrahedron Lett.* **1968**, *9*, 2707–2708. DOI: 10.1016/S0040-4039(00)89679-3 (b) Hergel, A.; Pritzknaw, H.; Siebert, W. Synthesis and Reactivity of a Naphto[1,8-*bc*]boret. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1247–1248. DOI: 10.1002/anie.199412471 (c) Wei, H.; Liu, Y.; Gopalakrishna, T. Y.; Phan, H.; Huang, X.; Bao, L.; Guo, J.; Zhou, J.; Luo, S.; Wu, J.; Zeng, Z. B–N–B Bond Embedded Phenalenyl and Its Anions. *J. Am. Chem. Soc.* **2017**, *139*, 15760–15767. DOI: 10.1021/jacs.7b07375 (d) Scholz, A. S.; Massoth, J. G.; Bursch, M.; Mewes, J.-M.; Hetzke, T.; Wolf, B.; Lerner, H.-W.; Grimme, S.; Wagner, M. BNB-Doped Phenalenyls: Modular Synthesis, Optoelectronic Properties, and One-Electron Reduction. *J. Am. Chem. Soc.* **2020**, *142*, 11072–11083. DOI: 10.1021/jacs.0c03118 (e) Crumbach, M.; Ayhan, O.; Fritze, L.; Sprenger, J. A. P.; Zapf, L.; Finze, M.; Helten, H. BNB-doped phenalenyls – aromaticity switch upon one-electron reduction. *Chem. Commun.* **2021**, *57*, 2408–2411. DOI: 10.1039/D0CC07671F
13. (a) Crossley, D. L.; Kahan, R. J.; Endres, S.; Warner, A. J.; Smith, R. A.; Cid, J.; Dunsford, J. J.; Jones, J. E.; Vitorica-Yrezabal, I.; Ingleson, M. J. A Modular Route to Boron Doped PAHs by

- Combining Borylative Cyclization and Electrophilic C-H Borylation. *Chem. Sci.* **2017**, *8*, 7969–7977. DOI: 10.1039/C7SC02793A (b) Kahan, J. R.; Crossley, D. L.; Cid, J.; Radcliffe, J. E.; Ingleson, M. J.; Synthesis, Characterization, and Functionalization of 1-Boraphenalenenes. *Angew. Chem. Int. Ed.* **2018**, *57*, 8084–8088. DOI: 10.1002/anie.201803180 (c) Farrell, J. M.; Mützel, C.; Bialas, D.; Rudolf, M.; Menekse, K.; Krause, A.-M. Stolte, M.; Würthner, F. Tunable Low-LUMO Boron-Doped Polycyclic Aromatic Hydrocarbons by General One-Pot C–H Borylations. *J. Am. Chem. Soc.* **2019**, *141*, 9096–9104. DOI: 10.1021/jacs.9b04675 (d) Hirano, K.; Morimoto, K.; Fujiooka, K.; Miyamoto, K.; Muranaka, A.; Uchiyama, M. Nucleophilic Diboration Strategy Targeting Diversified 1-Boraphenarene Architectures. *Angew. Chem. Int. Ed.* **2020**, *59*, 21448–21453. DOI: 10.1002/anie.202009242 (e) You, C.; Sakai, M.; Daniliuc, C. G.; Bergander, K.; Yamaguchi, S.; Studer, A. Regio- and Stereoselective 1,2-Carboboration of Ynamides with Aryldichloroboranes. *Angew. Chem. Int. Ed.* **2021**, *60*, 21697–21701. DOI: 10.1002/anie.202107647
14. Non-C₃ symmetric B-PAHs with 9b-boraphenylene as a substructure can be found in refs. 4f, 5f, 6h, and 6i.
 15. Warner, A. J.; Lawson, J. R.; Fasono, V.; Ingleson, M. J. Formation of C(sp²)-Boronate Esters by Borylative Cyclization of Alkynes Using BCl₃. *Angew. Chem. Int. Ed.* **2015**, *54*, 11245–11249. DOI: 10.1002/anie.201505810
 16. (a) Yuan, K.; Kahan, R. J.; Si, C.; Williams, A.; Kirschner, S.; Uzelac, M.; Zysman-Colman, E.; Ingleson, M. J. The Synthesis of Brominated-Boron-Doped PAHs by Alkyne 1,1-Bromoboration: Mechanistic and Functionalisation studies. *Chem. Sci.* **2020**, *11*, 3258–3267. DOI: 10.1039/C9SC05404A (b) Zhang, J.-J. Tang, M.-C.; Fu, Y.; Low, K. -H.; Ma, J.; Yang, L.; Weigand, J. J.; Liu, J.; Yam, V. W.-W.; Feng, X. One-Pot Synthesis of Boron-Doped Polycyclic Aromatic Hydrocarbons via 1,4-Boron-Migration. *Angew. Chem. Int. Ed.* **2021**, *60*, 2833–2838. (c) Zhang, J.-J.; Tang, M.-C.; Fu, Y.; Low, K.-H.; Ma, J.; Yang, L.; Weigand, J. J.; Liu, J.; Yam, V. W.-W.; Feng, X. A Modular Cascade Synthetic Strategy Toward Structurally Constrained Boron-Doped Polycyclic Aromatic Hydrocarbons. *Angew. Chem. Int. Ed.* **2021**, *60*, 25695–25700. DOI: 10.1002/anie.202109840 (d) Guo, J.; Zhang, K.; Wang, Y.; Wei, H.; Xiao, W.; Yang, K.; Zeng, Z. Fully-Fused Boron-Doped Olympicenes: Modular Synthesis, Tunable Optoelectronic Properties, and One-Electron Reduction. *Chem. Sci.*, **2023**, *14*, 4158–4165. DOI: 10.1039/D3SC00342F
 17. Spek, A. L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Cryst.* **2015**, *C71*, 9–18. DOI: 10.1107/S2053229614024929
 18. (a) Chaudhary, A.; Mohammad, A.; Mobin, S. M. Recent Advances in Single-Crystal-to-Single-Crystal Transformation at the Discrete Molecular Level. *Cryst. Growth. Des.* **2017**, *17*, 2893–2910. DOI: 10.1021/acs.cgd.7b00154 (b) Fernandez-Bartolome, E.; Martinez-Martinez, A.; Resines-Urien, E.; Piñeiro-Lopez, L.; Costa, J. S. Reversible single-crystal-to-single-crystal transformations in coordination compounds induced by external stimuli. *Coord. Chem. Rev.* **2022**, *452*, 214281. DOI: 10.1016/j.ccr.2021.214281 (c) Zheng, Y.; Jia, X.; Li, K.; Xu, J.; Bu, X.-H. Energy Conversion in Single-Crystal-to-Single-Crystal Phase Transition Materials. *Adv. Energy Mater.* **2022**, *12*, 2100324. DOI: 10.1002/aenm.202100324 (d) Wu, W.; Chen, K.; Wang, T.; Wang, N.; Huang, X.; Zhou, L.; Wang, Z.; Hao, H. Stimuli-responsive flexible organic crystals. *J. Mater. Chem. C* **2023**, *11*, 2026–2052. DOI: 10.1039/D2TC04642C
 19. (a) Liu, T.; Qi, C.; Zhou, Q.; Dai, W.; Lan, Y.; Xu, L.; Ren, J.; Pan, Y.; Yang, L.; Ge, Y.; Qu, Y.-K.; Li, W.; Li, H.; Xiao, S. Divergent Synthesis of Contorted Polycyclic Aromatics Containing Pentagons, Heptagon, and/or Azulene. *Org. Lett.* **2022**, *24*, 472–477. DOI: 10.1021/acs.orglett.1c03498 (b) Tropp, J.; Ihde, M. H.; Williams, A. K.; White, N. J.; Eedugurala, N.; Bell, N. C.; Azoulay, J. D. Bonizzoni, M. A Sensor Array for the Discrimination of Polycyclic Aromatic Hydrocarbons Using Conjugated Polymers and the Inner Filter Effect. *Chem. Sci.* **2019**, *10*, 10247–10255. DOI: 10.1039/C9SC03405F
 20. Solé, S.; Gabbai, F. P. A bidentate borane as colorimetric fluoride ion sensor. *Chem. Commun.* **2004**, 1284–1285. DOI: 10.1039/B403596H
 21. (a) Zhou, Z.; Wakamiya, A.; Kushida, T.; Yamaguchi, S. Planarized Triarylboranes: Stabilization by Structural Constraint and Their Plane-to-Bowl Conversion. *J. Am. Chem. Soc.* **2012**, *134*, 4529–4532. DOI: 10.1021/ja211944q (b) Hertz, V. M.; Ando, N.; Hirai, M.; Bolte, M.; Lerner, H.-W.; Yamaguchi, S.; Wagner, M. Steric Shielding vs Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon. *Organometallics* **2017**, *36*, 2512–2519. DOI: 10.1021/acs.organomet.6b00800
 22. (a) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. Electrochemical Detection of C₆₀⁶⁻ and C₇₀⁶⁻: Enhanced Stability of Fullerides in Solution. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980. DOI: 10.1021/ja00036a056 (b) Zhou, F.; Jehoulet, C.; Bard, A. J. Reduction and Electrochemistry of C₆₀ in Liquid Ammonia. *J. Am. Chem. Soc.* **1992**, *114*, 11004–11006. DOI: 10.1021/ja00053a072
 23. Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, *23*, 2367–71. DOI: 10.1002/adma.201004554
 24. Takimiya, K.; Nakano, M.; Sugino, H.; Osaka, I. Design and Elaboration of Organic Molecules for High Field-Effect-Mobility Semiconductors. *Synth. Met.* **2016**, *217*, 68–78. DOI: 10.1016/j.synthmet.2016.02.018
 25. (a) Acharya, A.; Seki, S.; Saeki, A.; Koizumi, A.; Tagawa, S. Study of Transport Properties in Fullerene-Doped Polysilane Films using Flash Photolysis Time-Resolved Microwave Technique. *Chem. Phys. Lett.* **2005**, *404*, 356–360. DOI: 10.1016/j.cplett.2005.02.003 (b) Seki, S.; Saeki, A.; Sakurai, T.; Sakamaki, D. Charge Carrier Mobility in Organic Molecular Materials Probed by Electromagnetic Waves. *Phys. Chem. Chem. Phys.* **2014**, *16*, 11093–11113. DOI: 10.1039/C4CP00473F
 26. Ie, Y.; Karakawa, M.; Jinnai, S.; Yoshida, H.; Saeki, A.; Seki, S.; Yamamoto, S.; Ohkita, H.; Aso, Y. Electron-Donor Function of Methanofullerenes in Donor-Acceptor Bulk Heterojunction Systems. *Chem. Commun.* **2014**, *50*, 4123–4125. DOI: 10.1039/C4CC00940A

