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

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1 regardin<del>§</del>5 Abstract: We report luminochromic behaviors mechanochromic luminescence (MCL) of o-carborane-modified anthracene derivatives. We have previously synthesized bis-4-7 carborane-substituted anthracene and found that its cryst $\frac{4}{8}$ polymorphs show dual-emission properties composed of excimer and charge transfer (CT) emission bands in solid. Initially, we observe  $\Delta 0$ the bathochromic MCL behavior from **1a** originating from emission mechanism alteration from dual emission to CT emission. By inserting 2the ethynylene spacers between anthracene and o-carborane 5,3compound 2 was obtained. Interestingly, 2 showed hypsochrom 54 MCL originating from the emission mechanism alteration from CT b5excimer emission. Furthermore, luminescent color of ground 1a cand be recovered to the initial state by allowing to stand at roo 57temperature, meaning that self-recovery proceeds. Detailed analyses 859 are described in this study.

#### Introduction 16

Mechanochromic luminescence (MCL) is the reversible4 17 luminescent color change of solid samples in response 65 18 19 mechanical force such as grinding, compressing or tapping.<sup>1</sup> The 20 property can be broadly utilized as a smart material, such  $as^{1/2}$ 21 pressure sensors, security devices, stimuli memories, and other 22 materials. So far, many reports on MCL have been reported from 9  $\bar{23}$ various molecular systems.<sup>2–5</sup> The emission colors of typical MC2024 dyes are bathochromically shifted upon grinding and recover  $t_0^{-1}$ 25 the initial color when the ground samples are exposed to other  $\frac{1}{2}$ 26 stimuli. Limited reports have proposed the designs for 3 27 hypsochromically shifted MCL.<sup>6</sup> Among the reported examples of 28 MCL, some molecules have characteristic properties. One is5 29 directional controls of the luminescence wavelength shift. In 2015,6 30 our group reported both directional shifts of boronketoiminates 31 based on the difference of the size of the end functional groups in 32 the molecules that induced the change in intermolecular 33 interactions of central aryl moieties.<sup>7</sup> In 2016, Lan, Zou and Yo $^{80}$ 34 et al. reported another strategy that interchanging of two ar  $\frac{1}{2}$ 35 substituents can lead to large difference in the molecular dipole2 36 moments.<sup>8</sup> Another property is self-recovery to the initial emission<sup>3</sup> color. After pristine samples were mechanically treated, usual exposure to solvent vapor or heating was required to recover the 537 38 39 original color. However only under 5% of MCL dyes are set 56 40 recover to initial states even at the room temperature.<sup>5</sup> In 2010,7 41 Fraser et al. reported the pioneering work on self-recovery MOLS 42 emission color of ground samples gradually recovered to the 043 44 original color over the course of a day.<sup>9</sup> This observation was

quantitatively evaluated by Ito and coworkers.<sup>10</sup> They estimated thermodynamic parameters form the transition of the fluorescence spectra. Also, in 2017, Ito et al. reported the systematic study the self-recovery on MCL of indolylbenzothiadiazoles with various substituents.<sup>11</sup> They suggested that the mechanism of self-recovery MCL is based on an amorphization of the crystals upon grinding, followed by recrystallization accelerated by the non-ground crystal phases. Although careful investigations of each property were performed in these reports, general strategies to design those characteristic MCL are still challenging. From this viewpoint, if the MCL can be modulated by adding simple modifications based on a single molecular system, this information would contribute to establishing the molecular design strategies. Also, another evaluation method for self-recovering MCL except for timedependent PL measurements are still required for further comprehension. Thus, not only the discovery of MCL molecules with a self-recovery system but also their detailed characterization is needed.

o-Carborane (1,2-dicarba-closo-dodecaborane) is an icosahedral carbon and boron cluster constructed by three-center two-electron bond. Until now, it has been utilized as versatile skeleton for developing functional molecules such as an agent for boron neutron capture therapy derived from its high boron content<sup>12</sup> and a molecular filler for enhancing heat resistance of polymers derived from its inorganic nature.<sup>13</sup> 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 with neighbored molecules.<sup>14</sup> On the other hand, aryl-substituted o-carborane derivatives have solidstate luminescent properties<sup>15-22</sup> and often show stimuliresponsiveness.<sup>23</sup> It is because the three-dimensional bulky structure of o-carborane can suppress intermolecular interactions, followed by intense solid-state luminescence.<sup>18</sup> The emission process is ascribed to the twisted intramolecular charge transfer (CT) emission from the aryl moiety to the o-carborane unit.24 Some examples of MCL properties utilizing the o-carborane units have been reported over the past decade.<sup>25-28</sup> In 2016, Zhao et al. reported that self-recovery MCL of the o-carborane derivative utilizing the metastable state.<sup>29</sup> It was suggested that the 3D bulkiness of o-carborane can provide sufficient spaces for a molecular conformational change. This observation motivated us to perform detail investigation of the self-recovering MCL of ocarborane derivatives paving a road for diversification and precise control of stimuli-responsiveness.

1 In our previous work, it was revealed that bis-o-carborant 22 substituted anthracene (1, Figure 1) has two crystalline 33 polymorphs with thermochromic dual-emission modes (crystals4 4 **1a** and **1b**).<sup>30</sup> In crystal **1a**, dual emission consisting of CT an $\overline{a}5$ 5 excimer emission bands were obtained. Therefore, the  $\pi$ -stacked 6 structure of the anthracene rings was assumed. In contrast,  $\frac{1}{10}$ -7 7 stacking was disturbed in crystal 1b because of the distorted8 8 anthracene ring stabilized by disturbing the incorporated solve $\mathbf{59}$ 9 molecules according to the single-crystal X-ray structural analys 10 (Figure S1).<sup>30</sup> It was implied that the bulky and spherical shape 6fl11 o-carborane could contribute to the enhancement of stimuto2 12 responsiveness of crystals. 63

13 We herein report that unique luminochromic behaviors 14 concerning MCL based on 1. Initially, we observed the typical 15 MCL from crystal 1a caused by luminescent mechanism alteration 16 from dual-emission composed of excimer and CT emission bands 17 to only CT emission triggered by the grinding treatment. In 18 particular, we accomplished to switch the direction of the 19 wavelength shift to the opposite direction by the simply structural 20 modification with the insertion of the ethynylene spacers (Figure 21 1). The detailed mechanism will be illustrated later. Furthermore. 22 in the case of ground **1a**, we found that the self-recovering 4 23 process to pristine state can proceed even at the roo 6524 temperature. The present study can be expected to provide use 6625 insights into developing advanced MCL materials based on the

26 unique electronical and structural features of o-carborane.



27 Figure 1. Chemical structures of 1 and 2.

#### 28 Results and Discussion

#### 29 Synthesis

30 Compound 1 was prepared according to our previous report.<sup>30</sup> 31 The synthetic scheme of the o-carborane derivative 2 is shown in 32 Scheme S1. 2 was synthesized through the Sonogashira-33 Hagihara cross-coupling reaction with 1,8-diiodoanthracene and 34 1-ethynyl-o-carborane. Purification by silica-gel column 35 chromatography followed by crystallization from CHCI<sub>3</sub> gave the 36 desired product. The chemical structure of the product was 37 characterized by <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and 38 high-resolution mass spectrometry (Charts S1-S4). As 39 mentioned later, the chemical structure of the product was also 40 confirmed by the X-ray diffraction measurement. From these 41 characterization data, we concluded that the product should have 42 the expected structure and enough purity for further analyses. 43

#### 44 X-ray Structural Analysis

Due to fragility of crystal samples of **1** and **2**, significant data were not obtained from single-crystal X-ray diffraction. Instead, we investigated their structures through the Rietveld method with the data of powder X-ray diffraction (PXRD). Fortunately, the packing structure of crystal **1a** was able to be determined (Figure 2 and S1 and 2, Table S1). Accordingly, in the crystal **1a**, 4 stacked in face-to-face manner avoiding steric hindrance of bulky o-carborane. In particular, it was found that columnar  $\pi$ -stacking arrangement of the anthracene rings was constructed and each column was separated by the o-carborane units. The distance between the anthracene rings was measured as 3.271 Å and 3.387 Å, suggesting that intermolecular interaction can be sufficiently formed through  $\pi$ -stacking. It should be noted that due to the limited diffractions form powder X-ray diffraction analysis we could not obtain the analyzed results without the distorsion of benzene rings in anthracene units. On the other hand, in the case of crystal **2** we were not able to refine the packing structure by any available methods including single-crystal X-ray diffraction analyses and PXRD analyses using the Rietveld method.



Figure 2. Crystal structure of 1a.

#### **Photoluminescent Properties**





Table 1. Photophysical properties of solution and crystalline state

e	λ <sub>abs,max</sub> / nm	λ <sup>abs,onset</sup> / nm	λ <sub>PL,max</sub> / nm	τ / ns <sup>f,g</sup>	$oldsymbol{\phi}_{PL}$
	202	445	435°	n.d.	0.006
1 (CHCI3) <sup>4</sup>	383	415	622 <sup>c</sup>	9.0	0.33°
<b>2</b> (CHCl <sub>3</sub> ) <sup>a</sup>	393	431	446 <sup>d</sup>	0.3	0.03 <sup>d</sup>
<b>1a</b> (crystal)	-	492 <sup>b</sup>	553°	53 (89%) 16 (11%)	0.23 <sup>e</sup>
<b>1a</b> (ground)	-	483 <sup>b</sup>	611 <sup>e</sup>	10 (81.5%), 2.5 (18.5%)	0.39 <sup>e</sup>
2 (crystal)	-	489 <sup>b</sup>	590 <sup>d</sup>	16 (93%), 0.6 (7%)	0.04 <sup>d</sup>
<b>2</b> (ground)	-	517 <sup>b</sup>	495 <sup>d</sup>	6.8 (43%), 1.2 (57%)	0.05 <sup>d</sup>

[a] Solution state at 1.0 x 10<sup>-5</sup> M [b] Data from diffuse reflectance spectra [c] Excited at 383 nm [d] Excited at 393 nm [e] Excited at 382 nm [f] Excited at 369 nm [g] Detected at  $\lambda_{PL,max}$  [n.d.] Not determined due to weak photoluminescence [–] Not obtained

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1 The electronic structure in the ground state was initially 2 2 examined with UV-vis absorption measurements in solution state33 (Figure 3a (top), Table 1). In the spectrum of 2 in CHCl<sub>3</sub>, the 4 4 typical vibrational structure attributable to  $\pi - \pi^*$  transition in the 5 5 anthracene moiety was observed. The slight red-shift compared 6 to that of **1** can be explained by the expansion of  $\pi$ -conjugation 7 7 through the ethynylene spacers. To support these optical dat6,88 we performed density functional theory (DFT) calculations agg9 CAM-B3LYP 6-31+G(d,p) level (Figure S3, Table S2). The frontiat molecular orbitals in 2 were expanded through the ethynylenel spacers, and the smaller HOMO–LUMO gap was obtained from 22than that of **1**. These theoretical results show good agreement 3with the experimental data in UV-vis absorption spectra. 74 To evaluate the electronic structures in the excited state,5 photoluminescent (PL) properties were examined in the solution6 state (Figure 3a (bottom) and S4 and S5, Table 1). As depicted  $i\hbar7$ previous work. 1 exhibited dual-emission consisting of locall 7-8 excited (LE) emission from the anthracene moiety with the 49 vibrational structure and CT emission from the whole molecule where anthracene and o-carborane should work as an electron 1donor and acceptor, respectively.<sup>30</sup> The LE emission band was 2observed at almost same wavelength in various solvents, and the 3CT emission band appeared in the longer wavelength regions &4relatively-higher polar solvents. In contrast, 2 showed the single 5 emission band with the vibrational structure of anthracene and the 6Stokes shift was not affected by solvent polarity, meaning that &7exhibited only LE emission from the anthracene moiety (Figure 8) S4 and S5, Table S3). This observation corresponds with oar9previous data on aryl-o-carborane with the ethynylened spacers.<sup>31,32</sup> In these studies, it was revealed that the ary 1ethynyl-carboranes should potentially show the emission bands2 of LE and CT. It is probably because only the CT emission couddbe guenched in the solution state due to intermolecular vibration at the C-C bond in the o-carborane unit. In the case of 1 where 5 the o-carborane units exit in parallel arrangement, molecular6 motions should be suppressed owing to steric hindrance of each 7o-carborane. Thus, both emission bands can be expressed even 8in the solution state. 99 Next, we examined crystal state PL properties. Differed behaviors were obtained between crystal 1a and 2 (Figure 3b, 16) and S7, Table 1). As discussed in the previous work, the  $n_{10}^{10}$ unimodal PL spectrum with two distinct PL lifetime components3 was observed from crystal 1a.30 That spectrum was characterized4 as the sum of two emission species in crystal. One in the excine 5emission from the anthracene rings with relatively long emission lifetime (53 ns) in the shorter wavelength region. Another one 16747 the CT emission from anthracene to o-carborane with shorters 48 emission lifetimes (16 ns) in the longer wavelength region. In the 49 work, from the crystal structural data, the refined  $\pi$ -stacking 0 50 structure was observed, proposing that intense excimer emission h 51 could be generated. In contrast, crystal 2 exhibited a unimoldal2 52 emission band in the longer wavelength region ( $\lambda_{PL}$  = 590 nm<sup>1</sup>.3 53 From the PL lifetime measurements, it was shown that crystal b4 54 has relatively shorter lifetime (16 ns) than the excimer emission df5 55 crystal 1a but that was almost same as the CT emission6 56 component of crystal 1a. Therefore, it was suggested that the 7 57 emission species of crystal **2** could be assigned as the b t 858 emission through the ethynylene spacers. 119 120 121 59 60 61

#### Mechanochromic Luminescence

In both compounds, luminescent color changes can be induced by grinding with a metal spatula on a quartz substrate, meaning that these compounds have MCL properties (Figure 3b). It was interesting that crystals 1 and 2 exhibited bathochromic and hypsochromic shift in response to the stimuli, respectively. Upon mechanical grinding, the yellow emission ( $\lambda_{PL}$  = 553 nm) of crystal 1 was bathochromically shifted to orange emission ( $\lambda_{PL}$  = 611 nm). In contrast, the emission color of crystal 2 hypsochromically shifted from orange ( $\lambda_{PL}$  = 590 nm) to yellow green ( $\lambda_{PL}$  = 495 nm) by the same treatment. From the PXRD analysis with both compounds, weaker intensity of the diffraction peaks was observed in the ground samples than those in crystal samples (Figure S8). Moreover, <sup>1</sup>H NMR spectroscopy confirmed that degradation or chemical reactions were hardly induced upon the mechanical treatment (Chart S5-6). These results indicate that the emission color change in both compounds should originate from the difference of the molecular arrangement in crystal and amorphous.<sup>33,34</sup> Furthermore, the additional measurement was performed to obtain the detail information about the difference in molecular arrangements between crystal and amorphous. We focused on the fact that the molecular structures and arrangements in the solid samples can be evaluated from the diffuse reflectance spectra.35,36 In general, from solid samples with  $\pi$ -stacked structures, red-shifted spectra can be obtained compared to the corresponding non- $\pi$ -stacked sample .<sup>37</sup> Taking this issue into consideration, we evaluated our molecules. Comparing the diffuse reflectance spectra of the crystal and ground 1a, obvious blue-shift was observed (Figure S9a). Moreover, the emission spectrum and lifetime of ground 1a were almost the same as those of CT emissive crystal **1b** with no  $\pi$ stacking structure (Figure S1 and S7, Table S3). These results suggest that the collapse of  $\pi$ -stacking structure should be induced by grinding, and subsequently CT emission should be induced after grinding. In addition, MCL properties were not observed in crystal 1b (Figure S7), which was probably due to the absence of π-stacking structure. This fact supports the role of the π-stacking structure in MCL properties of **1a**. On the other hand, ground 2 showed the red-shifted diffuse reflectance spectrum comparing to crystal 2 (Figure S9b). In addition, the spectrum shape and the peak position were identical to the previously reported examples of the excimer emission of anthracene.38,39 Also, excimer emission of anthracene and pyrene were reported to be blue-shifted compared with CT emission originated from the charge transfer between  $\pi$ -conjugated systems and o-carborane units.<sup>27,40</sup> Moreover, in the cases of excimer emission in crystalline states, because of the low radiative transition rate originated from symmetry-forbidden transitions, long emission lifetimes can be observed.<sup>31,32,41,42</sup> In our case, relatively longer emission lifetime (53 ns) was observed in crystal 1a, while in ground 2 (6.8 ns (43%) and 1.2 ns (57%)) such large value was not observed (Table S3). We assume that molecular motion might occur in the amorphous state and the non-radiative processes could be accelerated. Actually, the non-radiative rate constant  $(k_{nr})$  of ground 2 increased one order of magnitude larger than corresponding crystalline samples (Table S3). Thus, it is assumed that excimer emission should be generated from partial π-stacking orientations in amorphous.



Figure 4. PL spectra of pristine, ground, annealed and fumed a) 1a and b) 2 64 Annealed: ground samples heated at 150 °C for 30 min. Fumed: ground samples exposed to  $CCl_4$  vapor for 30 min for 1a and  $CH_2Cl_2$  vapor for 30 min 5 for 2. 66

Next, intriguing behaviors, such as recovering, were discovered  $\overset{\prime}{0}_{8}$ 67 from both compounds. Emission colors of the ground samples 97 were almost restored to that of the initial crystalline state  $H_0$ 8 response to other external stimuli such as heating or furning  $\frac{40}{12}$ 9 solvent vapor (Figure 4). It should be noted that in the spectra  $\dot{e}_{2}^{1}$ annealed and fumed samples, baselines were elevated. This could be attributed to scattering light from surface roughness  $\dot{e}_4$ heated or solvent vapor fumed samples. After heating of the5 ground samples, the peak intensity of the PXRD pattern $\frac{6}{6}$ increased and sharp peaks emerged (Figure S8). Moreover, the differential scanning calorimetry (DSC) measurements of the ground samples showed endothermic peaks in the 1st heating cycle (Figure S10). It should be noted that the DSC measurements were performed under degradation points estimated by thermogravimetric analyses (Figure S11). These results suggest that recrystallization should proceed triggered by heating of the ground samples. Interestingly, the self-recovery behavior was observed in 1a. When ground 1a were just left at room temperature (298 K), the emission color was automatically partially restored in the time range of several hours (Figure 5a). In compound 2, such spontaneous recovery was little observed (Figure 5b). These findings indicate that 1a has self-recovery MCL properties.<sup>5</sup> Also, when the recovery process was monitored at 323 K, the emission spectra of 1a were restored into the crystal state in 7 hours and those of 2 became more closer to crystal one in 23 hours than at 298 K (Figure 5cd). Also the relative intensity at the wavelength corresponding to the maximum emission wavelength of ground samples to those of crystal samples were plotted (Figures 5e and 5f). It can be qualitatively recognized that in both compounds, recovery processes were faster at 323 K than at 298 K. Therefore, we thought that the temperature had significant role in the recovery processes. Furthermore, reproducibility of self-recovery MCL in 1a was confirmed by measuring time-dependent PL spectra with three different 40 samples. The degree of recovery was diverse in each sample, and this was probably due to the heterogeneity of ground amorphous samples (Figure S12). Even if the ground 1a was left for a long enough time (over a day), complete restoration was not able to be observed. It is suggested that even at low temperature the partial recrystallization should be induced. However, the long, range ordered structure was not reconstructed to result in the formation of semi-stable partially recovered state. Then, we tried to investigate these recovery processes by thermal analyses and variable temperature PXRD measurements.

To obtain deeper insight on the recovery of MCL behaviors, we 51 initially analyzed the DSC thermograms. In the profile, the onset 52 temperature ( $T_c^{onset}$ ), which represents the starting temperature for recrystallization, of the endothermic peaks were 308.0 K and 342.1 K in 1a and 2, respectively (Figure S13, Table 2). The fact that  $T_{c}^{onset}$  values of **1a** was close to the room temperature, which indicated that the activation barriers in the recrystallization can be exceeded even at room temperature. Furthermore, this process should be assisted by the partially-residual crystalline components in the ground samples to compensate the difference of the  $T_{c}^{onset}$  values and room temperature. In addition, variable temperature PXRD measurements of the samples were carried out. Diffraction patterns were measured in increments of about 2 K/min as temperature rising from room temperature (each measurement was performed with ca. 4 K increments) (Figure S14 and 15). In the ground samples, constant patterns were observed at near room temperature, while in the middle of the measurement that changed to the upward trend. In addition, when the crystalline samples were heated under the same conditions as control experiments, significant changes in diffraction intensity were hardly observed. Therefore, the variation points in the ground samples can be chosen as the start of recrystallization. We also tried to monitor the self-recovery process of 1a by timedependent PXRD measurement of ground 1a at 298 K. However, obvious diffraction intensity change was not observed (Figure S16). It is suggested that formed crystalline region upon recovery could be too small to detect.



Figure 5. Time-dependent PL spectra (a,b) at 298 K and (c,d) 323 K after grinding crystal of (a,c) 1a and (b,d) 2 and plot of relative intensity at the peak wavelength of ground samples to those of crystal samples of e) 1a and f) 2.

Next, the diffraction counts of the strongest peaks were plotted versus temperature and the  $T_{c}^{onset}$  values were also obtained from the intersection of approximate straight lines obtained by the mean-square method in the two regions (Figure S17, Table  $2\xi_5^+$ From both measurements, the smaller values of  $T_c^{\text{onset}}$  were  $\widetilde{e_6}$ observed in 1a (311.9 K) than that of 2 (324.8 K), suggesting that 7 the self-recovery processes can smoothly occur in 1a. In fact, this 8 suggestion is consistent with the fact that the emission spectru $\mathbf{59}$ of **1a** can be more likely to recover spontaneously. From the above analyses, it was confirmed that self-recovery MCL exist  $\frac{9}{2}$ It is proposed that the self-recovery processes can proceed owing  $3^{12}$ to loose molecular packings created by the sphere and bulky 64carboranes. 65

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1. <b>Tablez.</b> Determined recrystalization temperature	15	Table2. Determined recrystallization temperature
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sample	Method	7c <sup>onset</sup> / K
1a	DSC	308.0
1a	VT-PXRD	311.9
2	DSC	342.1
2	VT-PXRD	324.8

#### 18 Conclusion

80 19 It has been discovered that some of aryl-modified o-carboranes1 20 show emission mechanism alterations in solid triggered by2 21 external stimuli or environmental changes as shown here. Base 22 on these alterations of two kinds of bis-o-carborane-modified anthracene, in this paper we demonstrated the direction switching 23 24 of wavelength shifts in MCL. Moreover, we also found that the self-recovering process in MCL. The bulky and sphere structure  $^{6}$ 25 of o-carborane substitutions seems to be responsible for this 26 process. Although it is still challenging to design the molecule  $\xi_0^\prime$ 27 28 presenting not only the stimuli-responsive emission mechanismo 29 alteration but also self-recovering process, o-carborane could be() 30 a key building block for controlling these stimuli-responsivel 31 92 luminochromic behaviors.

#### 32 **Experimental Section**

Synthesis and characterization methods: <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B NMB 33 34 spectra were recorded on a JEOL JNM-AL400 instrument at 400, 100, ar(0) 128 MHz, respectively and analyzed by NMRV4 spectrum software / 35 <sup>11</sup>B{<sup>1</sup>H} NMR spectrum was recorded on a JEOL ECZ400 instrument 3936 128 MHz and analyzed by Delta NMR software. The <sup>1</sup>H and <sup>13</sup>C chemical nbb 37 38 shift values were expressed relative to Me<sub>4</sub>Si and/or residual n <u>0</u>1 39 deuterated solvents as an internal standard in CDCl<sub>3</sub>. The <sup>11</sup>B chemi **Q**2 40 shift values were expressed relative to BF3. Et2O as an external standa 03 41 Reaction was performed under N2 atmosphere using Schlenk 42 techniques. Analytical thin-layer chromatography (TLC) was perform 05 43 with silica gel 60 Merck F254 plates. Column chromatography v **Q**6 44 performed with Wakogel® C-300 silica gel. High-resolution mass (HRM 45 spectrometry was performed at the Technical Support Office (Departm 46 of Synthetic Chemistry and Biological Chemistry, Graduate School 09 47 Engineering, Kyoto University), and the HRMS spectra were obtained Thermo Fisher Scientific Exactive Plus for and atomospheric pressure 1 48 chemical ionization (APCI) method. Elemental analyses were performed 49 50 at the Microanalytical Center of Kyoto University. 113

Materials: 1,8-diiodoanthracene (Tokyo Chemical Industry Co., Ltd.), Pd(PPh<sub>3</sub>)<sub>4</sub> (Tokyo Chemical Industry Co., Ltd.), Cul (Fujifilm Wako Pure Chemical Corporation), N,N-dimethylaniline (Fujifilm Wako Pure Chemical Corporation), Toluene (Deoxidized, Fujifilm Wako Pure Chemical Corporation), CHCl<sub>3</sub> (Fujifilm Wako Pure Chemical Corporation), CH<sub>2</sub>Cl<sub>2</sub> (Fujifilm Wako Pure Chemical Corporation), MeOH (Fujifilm Wako Pure Chemical Corporation), MeCN (Fujifilm Wako Pure Chemical Corporation), n-hexane (Fujifilm Wako Pure Chemical Corporation), CCl4 (Fujifilm Wako Pure Chemical Corporation), cyclohexane (Fujifilm Wako Pure Chemical Corporation), CDCl<sub>3</sub> (Eurisotop) and CD<sub>2</sub>Cl<sub>2</sub> (Eurisotop) were purchased and used without purification. Tetrahydrofuran (THF) and NEt<sub>3</sub> (Tokyo Chemical Industry Co., Ltd.) were purchased and purified using a twocolumn solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA) under N<sub>2</sub> pressure. 1-Ethynyl-o-carborane<sup>43</sup> and 1<sup>30</sup> were synthesized and characterized according to the literatures.

Synthetic procedure 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(PPh<sub>3</sub>)<sub>4</sub> (94 mg, 0.081 mmol) and Cul (60 mg, 0.32 mmol) were dissolved in THF (16 mL) and NEt<sub>3</sub> (12 mL). The reaction mixture was stirred by a magnetic stirrer 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 MgSO<sub>4</sub>. 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 CHCl<sub>3</sub> at 60 °C afforded 2 as a yellow solid (51 mg, 0.10 mmol, 25% isolated yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 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. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>): δ (ppm) -2.21, -3.78, -9.04, -10.14, -10.58 (sh), -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. The 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 CCl<sub>4</sub> for 30 min and CH<sub>2</sub>Cl<sub>2</sub> 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 analysis with Rietveld refinement: The PXRD data for structural refinement with Rietveld method were measured using Rigaku SmartLab with a Ge (111) Johannson monochromator (Cu K $\alpha_1$  radiation  $\lambda$ =1.54059 Å, 50 kV and 40 mA, transmittance mode), a HyPix-3000 detector, and a capillary rotation attachment (120 % sec). The analyses were carried out with the powder X-ray diffraction analysis software SmartLab Studio II (Rigaku). Indexing programs DICVOL44 or ITO<sup>45</sup> 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 our previous cif data with insufficient quality<sup>30</sup> (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 (±1.000 ° width for restraint). The bond length and angle of anthracene moiety were restrained to the previously reported anthracene ones (cif deposition number 1103070).46 We determined converged

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structure, confirming residual sum of squares ( $R_{wp}$ ) was less than 10  $\frac{1}{20}$ , 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<sup>47</sup>.

6 Fitting parameters for the Rietveld refinement were defined as following equations (eq. 1–4):

8 
$$R_{wp} = \left\{ \frac{\sum_{i} w_{i} [y_{i} - f_{i}(x)]^{2}}{\sum_{i} w_{i} y_{i}^{2}} \right\}^{\frac{1}{2}}$$
 (62)

9 
$$R_p = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i}$$

$$R_e = \left(\frac{N-P}{\sum_i w_i y_i^2}\right)^{\frac{1}{2}}$$
(3)

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

12in which  $y_i$  is a diffraction intensity,  $f_i(x)$  is a calculated diffraction intensity, P is13a parameter for the least-squares method,  $w_i$  is a statistical weight and N is the<br/>number of data points.14number of data points.15Deposition15Number(s)

16 href="https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.59 02301189"> 2256549 (for 1a)
18 crystallographic data for this paper. These data are provided free of charge by 1
19 the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum.2
20 Karlsruhe <url href="http://www.ccdc.cam.ac.uk/structures">http://www.ccdc.cam.ac.uk/structures

Karlsruhe <url href="<u>http://www.ccdc.cam.ac.uk/structures</u>">Access Structures
 Service</url>

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23 24 Diffractometer (sealed tube (50 kV, 40 mA); Cu Ka, 1.542 Å; Braggrad Brentano geometry; HyPix-3000 detector). The heating treatment for 25 26 27 28 29 PXRD measurement was performed at 473 K for 5 min and 523 K for 50min for 1a and 2, respectively. Variable temperature PXRD (VT-PXR $\widetilde{p}_{1}$ was carried out by Anton paar DCS500 while samples were covered with a Poly Ether Ether Ketone (PEEK) dome. Samples were placed on §3 single-crystal silicon substrate for room temperature measurements and  $\underline{1}$ 30 Inconel® substrate under constant heating mode with repeated measurements and heating rate 2 K/min from room temperature. The 31 32 onset values of graphs were calculated by Origin Pro 2020 software with 33 Onset Of Slope app. 88

34 diffus@0 Photophysical measurements: UV-vis absorption and 35 reflectance spectra was obtained on a SHIMADZU UV3600i plus 36 spectrophotometer. Diffuse reflectance spectra were obtained by  $usir \hat{q} \hat{j}$ 37 integrated sphere method and the concentration was 1wt% in BaSO $\hat{\Phi}$ . 38 Photoluminescence (PL) spectra were measured with a HORIBA JOBIO 39 YVON Fluorolog-3 spectrofluorometer. Fluorescence quantum yield (QØ)5 40 was recorded on a HAMAMATSU Quantaurus-QY Plus C13534-01 mode)6 41 The PL lifetime measurement was performed on a Horiba FluoroCubie 42 spectrofluorometer system; excitation was carried out using a UV diodex 43 laser (NanoLED 369 nm).

10044 Differential scanning calorimetry Thermal analvses: (D\$C)1 45 measurements were carried out on a HITACHI DSC 7020 instrument with 2 46 the aluminum pan and the heating rate of 10 K/min under nitrogen flow 130347 mL/min). Thermogravimetric analyses (TGA) were performed by 04 48 HITACHI STA 7200RV instrument with the aluminum pan and the heat 10549 rate of 10 K/min up to 773 K under nitrogen flow (200 mL/min). The onset 50 values of graphs were calculated by Origin Pro 2020 software with Onser 51 Of Slope app. 108 109

31+G(d,p) levels. The energy level of the optimized geometry was confirmed to be the local minima by performing frequency calculations and obtaining only positive frequencies. The calculation data of **1** and anthracene were according to our pervious literature.<sup>30</sup>

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# **RESEARCH ARTICLE**

#### Entry for the Table of Contents

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Mechanochromic luminescence of bis-*o*-carborane-anthracene triad is described. By introducing ethynylene spacers, the direction of luminescence wavelength shift was changed. Recrystallization of ground samples occur even at room temperature and then the self-recovery of emission color can be observed.

# **Supporting Information**

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### Materials

<u>Commercially available compounds used without purification</u> 1,8-diiodoanthracene (Tokyo Chemical Industry Co., Ltd.) Pd(PPh<sub>3</sub>)<sub>4</sub> (Tokyo Chemical Industry Co., Ltd.) CuI (Fujifilm Wako Pure Chemical Corporation) *N,N*-dimethylaniline (Fujifilm Wako Pure Chemical Corporation)

#### Commercially available solvents used with purification

Tetrahydrofuran (THF) and NEt<sub>3</sub> were purchased and purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA) under N<sub>2</sub> pressure.

Commercially available solvents used without purification Toluene (Deoxidized, Fujifilm Wako Pure Chemical Corporation) CHCl<sub>3</sub> (Fujifilm Wako Pure Chemical Corporation) CH<sub>2</sub>Cl<sub>2</sub> (Fujifilm Wako Pure Chemical Corporation) MeOH (Fujifilm Wako Pure Chemical Corporation) MeCN (Fujifilm Wako Pure Chemical Corporation) *n*-hexane (Fujifilm Wako Pure Chemical Corporation) CCl<sub>4</sub> (Fujifilm Wako Pure Chemical Corporation) cyclohexane (Fujifilm Wako Pure Chemical Corporation) CDl<sub>4</sub> (Eurisotop) CD<sub>2</sub>Cl<sub>2</sub> (Eurisotop)

### Compounds prepared as described in the literatures

1-Ethynyl-o-carborane<sup>43</sup> and 1.<sup>30</sup>

#### **Synthetic Procedures**

Reaction was performed under N<sub>2</sub> atmosphere using Schlenk line techniques. 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 (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained a Thermo Fisher Scientific Exactive Plus for and atomospheric pressure chemical ionization (APCI) method. Elemental analyses were performed at the Microanalytical Center of Kyoto University.



Scheme S1 Synthetic scheme of 2.

2

In the 100 mL light shaded round-bottomed flask, 1,8-diiodoanthracene (172 mg, 0.400 mmol), 1ethynyl-*o*-carborane (151 mg, 0.898 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (94 mg, 0.081 mmol) and CuI (60 mg, 0.32 mmol) were dissolved in THF (16 mL) and NEt<sub>3</sub> (12 mL). The reaction mixture was stirred by a magnetic stirrer at 60 °C for 0.5 h under N<sub>2</sub> atmosphere. The reaction mixture was added to ethyl acetate and washed with saturated aqueous NH<sub>4</sub>Cl solution. The organic phase was dried over anhydrous MgSO<sub>4</sub>. After filtration, the solvent was removed by a rotary evaporator. The crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 1/5 (v/v)) to give yellow solid. Recrystallization of the yellow solid from CHCl<sub>3</sub> at 60 °C afforded **2** as a yellow solid (51 mg, 0.10 mmol, 25% isolated yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –2.21, –3.78, –9.04, –10.14, –10.58 (shoulder peak), –13.078. HRMS (n-APCI): calcd. for C<sub>22</sub>H<sub>30</sub>B<sub>20</sub>+Cl<sup>-</sup> [M+Cl]<sup>-</sup> 549.3946, found 549.3950. Anal. Calcd for C<sub>22</sub>H<sub>30</sub>B<sub>20</sub>: C, 51.74; H, 5.92. Found: C, 51.71; H, 5.95.

### **NMR Spectra**

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B NMR spectra were recorded on a JEOL JNM-AL400 instrument at 400, 100, and 128 MHz, respectively and analyzed by NMRV4 spectrum software. <sup>11</sup>B{<sup>1</sup>H} NMR spectrum was recorded on a JEOL ECZ400 instrument at 128 MHz and analyzed by Delta NMR software. The <sup>1</sup>H and <sup>13</sup>C chemical shift values were expressed relative to Me<sub>4</sub>Si and/or residual non-deuterated solvents as an internal standard in CDCl<sub>3</sub>. The <sup>11</sup>B chemical shift values were expressed relative to BF<sub>3</sub>·Et<sub>2</sub>O as an external standard.



Chart S1. <sup>1</sup>H NMR spectrum of 2 in CDCl<sub>3</sub>.



Chart S2. <sup>13</sup>C NMR spectrum of 2 in CDCl<sub>3</sub>.



Chart S3. <sup>11</sup>B NMR spectrum of 2 in CDCl<sub>3</sub>.



Chart S4.  $^{11}B\{^{1}H\}$  NMR spectrum of 2 in CDCl<sub>3</sub>.



Chart S5. <sup>1</sup>H NMR spectrum of 1 after grinding in CDCl<sub>3</sub>.



Chart S6. <sup>1</sup>H NMR spectrum of 2 after grinding in CDCl<sub>3</sub>.

# Preparation method of ground samples

#### For PL measurements

The crystal samples were scratched on quartz substrates by metal spatula. The 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  $CCl_4$  for 30 min and  $CH_2Cl_2$  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) Johannson monochromator (Cu K $\alpha_1$  radiation  $\lambda$ =1.54059 Å, 50 kV and 40 mA, transmittance mode), a HyPix-3000 detector, and a capillary rotation attachment (120 °/sec). The analyses were carried out with the powder X-ray diffraction analysis software SmartLab Studio II (Rigaku). Indexing programs DICVOL<sup>44</sup> or ITO<sup>45</sup> 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 our previous cif data with insufficient quality for structure determination by single-crystal X-ray diffraction analysis<sup>30</sup> (cif deposition number 2155816). These obtained structures were refined using the Rietveld method under restrained conditions for bond lengths ( $\pm 0.0200$  Å width for restraint) and angles (±1.000 ° width for restraint). The bond length and angle of anthracene moiety were restrained to the previously reported anthracene ones (cif deposition number 1103070)<sup>46</sup>. We determined converged structure, confirming residual sum of squares ( $R_{wp}$ ) was less than 10 %, and goodness-offit 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<sup>47</sup>.

Fitting parameters for the Rietveld refinement were defined as follows:

$$R_{wp} = \left\{ \frac{\sum_{i} w_{i} [y_{i} - f_{i}(x)]^{2}}{\sum_{i} w_{i} {y_{i}}^{2}} \right\}^{\frac{1}{2}}$$
(1)

$$R_p = \frac{\sum_i |y_i - f_i(x)|}{\sum_i y_i} \tag{2}$$

$$R_e = \left(\frac{N-P}{\sum_i w_i y_i^2}\right)^{\frac{1}{2}} \tag{3}$$

$$S = \frac{R_{wp}}{R_e} \tag{4}$$

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.

	1a
CCDC deposition number	2256549
Chemical formula	$C_{18}B_{20}H_{30}$
Space group	$P2_{1}/c$
<i>a</i> , <i>b</i> , <i>c</i> / Å	7.1473(6), 18.8081(17), 19.3300(17)
$\alpha, \beta, \gamma / ^{\circ}$	90, 95.955(2), 90
$R_{ m wp}$	2.83%
$R_{ m p}$	1.97%
Re	1.66%
S	1.6892
Max Shift	0.000

 Table S1. Selected X-ray data collection and Rietveld refinement parameters for 1a.



Packing structure



b)

Side view

Top view





Packing structure



**Figure S1.** Crystal structures of polymorphic crystals a) **1a** and b) **1b**<sup>30</sup>. Hydrogen atoms were omitted for clarity.



Figure S2. Rietveld plot of crystal 1a.

### **Computational Methods**

The Gaussian 16 program package<sup>48</sup> was used for structural optimization. First, optimized structures of isolated molecules in the ground  $S_0$  states and calculated their electric structures were calculated. The density functional theory (DFT) was applied for the optimization of the structures in the  $S_0$  states at the CAM-B3LYP 6-31+G(d,p) levels. The energy level of the optimized geometry was confirmed to be the local minima by performing frequency calculations and obtaining only positive frequencies. The calculation data of **1** and anthracene were according to our pervious literature.<sup>30</sup>



**Figure S3.** Molecular orbital distribution and energy levels of HOMO and LUMO of anthracene, **1** and **2** in the ground state calculated with DFT in CAM-B3LYP 6-31+G(d,p) level

Center	Center Atomic Coo			oms)
Number	Number	X	У	Z
1	6	-3.479455	-3.658561	-0.11647
2	6	-2.748919	-2.495778	-0.071328
3	6	-3.420806	-1.217763	-0.036307
4	6	-4.855143	-1.217037	-0.040744
5	6	-5.565546	-2.455169	-0.08584
6	6	-4.897607	-3.640965	-0.124629
7	6	-2.737255	-0.000004	-0.000028
8	6	-5.532564	-0.000009	-0.000057
9	6	-4.855149	1.217022	0.040644
10	6	-3.420812	1.217752	0.036238
11	6	-2.74893	2.49577	0.071272
12	6	-3.479471	3.65855	0.116399
13	6	-4.897623	3.640949	0.124528
14	6	-5.565557	2.45515	0.085725
15	1	-1.652264	-0.000002	-0.000017
16	1	-2.957656	-4.60871	-0.145084
17	1	-6.650979	-2.429233	-0.089295
18	1	-5.439799	-4.579628	-0.160445
19	1	-6.619122	-0.000011	-0.000068
20	1	-2.957676	4.608701	0.145024
21	1	-5.439819	4.579611	0.160333
22	1	-6.65099	2.42921	0.089158
23	6	-1.321592	2.598205	0.052339
24	6	-0.130065	2.785714	0.035598
25	6	1.2799	3.065574	0.012828
26	5	2.420596	1.979688	-0.634641
27	5	2.37263	2.345947	1.10521
28	5	3.65643	3.005621	-1.383866
29	5	1.965249	3.441935	-1.528972
30	5	3.916029	2.327565	0.243405
31	1	2.013883	0.945188	-1.029513
32	5	1.884844	4.039102	1.306424
33	1	1.933138	1.553273	1.861623
34	5	3.576819	3.601471	1.44176
35	5	4.378711	4.005896	-0.097527
36	5	3.16265	4.695258	-1.182705
37	1	4.251004	2.64529	-2.342201
38	6	1.727389	4.608678	-0.299916

#### Table S2. Optimized geometry of 2 in $S_0$ state

39	1	1.227845	3.454984	-2.448202
40	1	4.70596	1.469353	0.446143
41	5	3.113203	5.060344	0.549763
42	1	1.09916	4.41374	2.101103
43	1	4.114259	3.665871	2.494941
44	1	5.50566	4.367618	-0.141765
45	1	3.27523	5.571366	-1.968324
46	1	0.909679	5.296218	-0.468344
47	1	3.192758	6.180039	0.92056
48	6	-1.321581	-2.598208	-0.052365
49	6	-0.130054	-2.785713	-0.035599
50	6	1.279912	-3.065569	-0.012801
51	5	2.420592	-1.979681	0.634693
52	5	2.372662	-2.345938	-1.10516
53	5	3.656413	-3.005612	1.383942
54	5	1.965229	-3.441931	1.529012
55	5	3.916043	-2.327553	-0.243324
56	1	2.013867	-0.945183	1.029559
57	5	1.884884	-4.039093	-1.306386
58	1	1.933183	-1.553264	-1.86158
59	5	3.576861	-3.601458	-1.441687
60	5	4.378722	-4.005884	0.097615
61	5	3.162642	-4.69525	1.182767
62	1	4.250966	-2.645281	2.342289
63	6	1.727398	-4.608673	0.29995
64	1	1.227807	-3.454984	2.448227
65	1	4.705976	-1.469339	-0.446044
66	5	3.113231	-5.060333	-0.549702
67	1	1.099217	-4.413732	-2.101081
68	1	4.114322	-3.665855	-2.494857
69	1	5.505672	-4.367602	0.141876
70	1	3.275208	-5.571359	1.968388
71	1	0.909687	-5.296215	0.46836
72	1	3.192796	-6.180028	-0.920499

### **Photophysical Data**

UV-vis absorption spectra were obtained on a SHIMADZU UV3600i plus spectrophotometer. Photoluminescence (PL) spectra were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer. 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; excitation was carried out using a UV diode laser (NanoLED 369 nm) except for ground **1b**, whose PL lifetime was measured on HORIBA Deltaflex spectrofluorometer system (excitation was carried out using a UV diode laser (DeltaDiode 375 nm). Radiative rate constants ( $k_r$ ) and non-radiative rate constants ( $k_{nr}$ ) were calculated by using averaged PL lifetime ( $\tau$ ave =  $\tau_1 f_1 + \tau_2 f_2, f$ : relative amplitude (%))

sample	λ <sub>abs,max</sub> / nm	$\varepsilon_{abs}$ / $10^4 M^ ^1 cm^{-1}$	A <sub>abs,onset</sub> / nm	λ <sub>PL,max</sub> / nm	au / ns <sup>h</sup>	$\chi^2$	Φ	<i>k</i> <sub>r</sub> / 10 <sup>7</sup> s <sup>-</sup>	$k_{ m nr}$ / 10 <sup>8</sup> s <sup>-1</sup>
<b>1</b> (CUC1 )a	202	1.27	415	435°	n.d. <sup>i</sup>	_	0.220	27	0.74
<b>I</b> (CHCl <sub>3</sub> )"	383	1.27	415	622°	9.0 <sup>i</sup>	1.24	0.33	3.7	0.74
2 (Cyclohexane) <sup>a</sup>	391	2.34	431	441 <sup>d</sup>	3.7 <sup>i</sup>	1.41	0.37 <sup>d</sup>	10	1.7
<b>2</b> (CCl <sub>4</sub> ) <sup>a</sup>	393	1.79	432	444 <sup>e</sup>	2.4 <sup>i</sup>	1.70	0.23 <sup>e</sup>	9.6	3.2
<b>2</b> (Toluene) <sup>a</sup>	394	2.25	433	448 <sup>f</sup>	$0.5^{i}$	2.51	0.06 <sup>f</sup>	12	19
<b>2</b> (CHCl <sub>3</sub> ) <sup>a</sup>	393	1.88	431	446 <sup>e</sup>	0.3 <sup>i</sup>	1.07	0.03 <sup>e</sup>	10	32
<b>2</b> (MeCN) <sup>a</sup>	391	2.10	433	446 <sup>d</sup>	n.d. <sup>i</sup>	_	0.01 <sup>d</sup>	_	_
1a (crystal)	_	_	492 <sup>b</sup>	553 <sup>g</sup>	53 (89%), 16 (11%) <sup>i</sup>	1.57	0.23 <sup>g</sup>	0.47	0.16
1a (ground)	_	_	483 <sup>b</sup>	611 <sup>g</sup>	10 (81.5%), 2.5 (18.5%) <sup>i</sup>	2.52	0.39 <sup>g</sup>	4.5	0.71
1b (crystal)	_	_	477 <sup>b</sup>	608 <sup>g</sup>	11 <sup>i</sup>	2.30	0.69 <sup>g</sup>	6.3	0.3
1b (ground)	_	_	_	604 <sup>g</sup>	12 (76%), 5.3 (24%) <sup>j</sup>	1.20	0.36 <sup>g</sup>	3.5	0.62
2 (crystal)	_	_	489 <sup>b</sup>	590 <sup>e</sup>	16 (93%), 0.6 (7%) <sup>i</sup>	3.19	0.04 <sup>e</sup>	0.27	0.64
2 (ground)	_	_	517 <sup>b</sup>	495 <sup>e</sup>	6.8 (43%), 1.2 (57%) <sup>i</sup>	4.83	0.05 <sup>e</sup>	1.4	2.6

**Table S3.** Photophysical properties of 1 and 2.

<sup>a</sup> Solution state at 1.0 x 10<sup>-5</sup> M <sup>b</sup> Data from diffuse reflectance spectra <sup>c</sup> Excited at 383 nm <sup>d</sup> Excited at 391 nm <sup>e</sup> Excited at 393 nm <sup>f</sup> Excited at 394 nm <sup>g</sup> Excited at 382 nm <sup>h</sup> Detected at  $\lambda_{PL,max}$  <sup>i</sup> Excited at 369 nm <sup>j</sup> Excited at 375 nm [n.d.] Not determined due to weak photoluminescence [–] Not obtained



Figure S4. a) UV-Vis and b) PL spectra of 2 in various solvents  $(1.0 \times 10^{-5} \text{ M})$ .



Figure S5. Photoluminescence decay profile of 2 in cyclohexane, CCl<sub>4</sub>, Toluene and CHCl<sub>3</sub> (detected at  $\lambda_{PL,max}$  for all samples,  $1.0 \times 10^{-5}$  M)



**Figure S6.** Photoluminescence decay profile of crystal (a,c) and ground (b,d) samples of **1a** (a,b) and **2** (c,d).



**Figure S7.** a) PL spectra of crystal **1b** and ground **1b** and PL decay profile of b) crystal **1b** and c) ground **1b**.

### Powder X-ray diffraction (PXRD) analyses

PXRD data were collected with a Rigaku SmartLab Diffractometer (sealed tube (50 kV, 40 mA); Cu K $\alpha$ , 1.542 Å; Bragg–Brentano geometry; HyPix-3000 detector). Heating treatments to obtain PXRD data of "heated" samples were performed by heating the samples at 473 K for 5 min and 523 K for 5 min for **1a** and **2**, respectively.



**Figure S8.** PXRD pattern of pristine, ground and heated after ground samples of a) **1a** and b) **2**, respectively.

## **Diffuse Reflectance Spectra**

Diffuse reflectance spectra were obtained on a SHIMADZU UV3600i plus spectrophotometer by using integrated sphere method. The concentration was 1wt% in BaSO<sub>4</sub>.



Figure S9. Diffuse reflectance spectra of crystal and ground samples of a) 1a and b) 2.

### **Thermal Analyses**

Differential scanning calorimetry (DSC) measurements were carried out on a HITACHI DSC 7020 instrument with the aluminum pan and the heating rate of 10 K/min under nitrogen flow (50 mL/min). Thermogravimetric analyses (TGA) were performed by a HITACHI STA 7200RV instrument with the aluminum pan and the heating rate of 10 K/min up to 773 K under nitrogen flow (200 mL/min).



Figure S10. DSC thermogram of pristine and ground samples of a) 1a and b) 2, respectively.



Figure S11. TGA thermogram of pristine and ground samples of a) 1a and b) 2, respectively.

# Photophysical data of reproducibility on self-recovery MCL

Photoluminescence (PL) spectra were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer. The ground samples were prepared by scratching crystal samples on quartz substrates by metal spatula.



**Figure S12.** Time-dependent PL spectra at 298 K of three different ground samples of **1a** prepared by the same method.

# Analyses of DSC thermograms

The onset values of graphs were calculated by Origin Pro 2020 software with Onset Of Slope app.



**Figure S13.** The analyzed DSC thermograms to read  $T_c^{\text{onset}}$  from the intersection of approximate straight lines obtained by the mean-square method in the two regions of ground a) **1a** and b) **2**.

## 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<sup>®</sup> substrate under constant heating mode with repeated measurements and heating rate 2 K/min from room temperature.



**Figure S14.** Variable temperature PXRD profile of ground a) **1a** and b) **2** and the maximum values of ground c) **1a** and d) **2** between 16–18 ° for **1a** and 14-16 ° for **2**.



Figure S15. Variable temperature PXRD profile of crystal a) 1a and b) 2 and the maximum values of crystal c) 1a and d) 2 between 16–18 ° for 1a and 14-16 ° for 2.



Figure S16. Time-dependent PXRD profile of ground a) **1a** at 298 K and b) the maximum counts between 16–18 ° of each diffraction profile were plotted. The samples were placed on the diffractometer as soon as possible after grinding.

## Analyses of variable temperature PXRD

The onset values of graphs were calculated by Origin Pro 2020 software with Onset Of Slope app.



Figure S17. The analyzed variable temperature PXRD profile to read  $T_c^{\text{onset}}$  from the intersection of approximate straight lines obtained by the mean-square method in the two regions of ground a) 1a and b) 2.

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