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Supporting Information

Two-step Mechanoresponsive Luminescence and Mechanical Stimuliinduced Release of Small Molecules Exhibited by a Luminescent Cyclophane

Yoshimitsu Sagara,* Kiyonori Takahashi, Tatsuya Muramatsu, Atsushi Seki, Nobuyuki Tamaoki E-mail: sagara@es.hokudai.ac.jp

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General methods and materials

All reagents and solvents were purchased from Aldrich, Tokyo Kasei, FUJIFILM Wako Pure Chemical Corporation, and Kanto Chemical. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Flash silica gel column chromatography was performed with a Biotage Isolera Flash system using Biotage Flash Cartridges. ¹H NMR spectra were recorded on a JEOL JNM-ECX 400 spectrometer and all chemical shifts are quoted on the δ -scale in ppm relative to the signal of tetramethylsilane (at 0.00), which worked as an internal standard. Proton-decoupled ¹³C NMR spectra were recorded on a JEOL JNM-ECX 400 spectrometer and all chemical shifts (δ) are reported in ppm using residual solvent as the internal standard (CDCl₃ at 77.16). Coupling constants (*J*) are reported in Hz and relative intensities are also shown. Elemental analysis was conducted with an Exeter Analytical CE440 Elemental Analyzer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on an ABSCIEX TOF/TOF 5800 spectrometer. The DSC measurements were carried out using a Hitachi DSC7020 with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Thermogravimetric analysis was conducted using a Rigaku Thermo plus TG8120 under nitrogen condition. Powder X-ray diffractions were measured with a Rigaku SmartLab. UV-vis absorption spectra were recorded on a JASCO V-550. Steady-state fluorescence spectra were recorded on a JASCO FP-6500. Time-resolved fluorescence measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau. Quantum efficiencies were measured with a Hamamatsu Photonics Quantaurus-QY. Density functional theory (DFT) calculations were carried out using the Gaussian 16 program package with the 6-311G+(d,p) basis set in the gas phase.

Single crystal X-ray structure analysis.

A single crystal was mounted on a cryoloop with Paratone-N (Hampton Research). Crystallographic data were collected using a Rigaku MicroMax-007HF diffractometer and Pilatus 200K detector with Cu K α radiation (λ = 1.54184 Å) at 263 K. Data collection was conducted with CrystalClear-SM Expert 2.1.^{S1} CrysAlisPRO software was used for cell refinement and data reduction.^{S2} The initial structure was solved by SHELXT^{S3} and expanded using Fourier techniques and refined on F^2 by the full-matrix least-squares method SHELXL2018/3^{S4} package compiled into a Yadokari-XG^{S5, S6} or a CrystalStructure 4.2.1.^{S7} All parameters were refined using anisotropic temperature factors, except for hydrogen atoms, which were refined using the riding model, with a fixed C–H bond distance. The crystallographic data are summarized in Table S1 (ESI). CCDC 2033744 (a crystal of 1 in the Y-form) and 2033743 (a crystal of 1 in the YG-form) contain the supplementary crystallographic data for this paper.

Synthesis

The synthetic route used to prepare compound **1** is shown in Schemes S1. 9,10-Bis(4-hydroxyphenylethynyl)anthracene and compound **3** were prepared according to the reported procedures.^{S8,S9} Reference compound **2** was also obtained through the reported procedure.^{S10}



Conditions: 9,10-bis(4-hydroxyphenylethynyl)anthracene, K₂CO₃, DMF, 70 °C, 36 h.

Compound 1. A solution of compound **3** (600 mg, 0.943 mmol) and 9,10-bis(4-hydroxyphenylethynyl)anthracene (387 mg, 0.943 mmol) in DMF (25 mL) was added to a suspension of K₂CO₃ (2.61 g, 18.9 mmol) in DMF (300 mL) dropwise at 70 °C over 12 h under vigorous stirring. After further stirring for 24 h at 70 °C, the reaction suspension was cooled and most of the DMF was evaporated in vacuo. The crude product was dissolved in chloroform and washed with saturated aq. NH₄Cl solution (3×100 mL), followed by saturated aq. NaCl solution, the organic layer was dried over MgSO₄, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/ethyl acetate = 4:1) and subsequently precipitated from a mixture of dichloromethane and ethyl acetate to afford compound **1** (312 mg, 0.352 mmol) as an orange powder in 37 % yield.

¹H NMR (400 MHz, CDCl₃): δ = 3.50–3.57 (m, 8H), 3.59–3.61 (m, 4H), 3.67–3.70 (m, 4H), 3.75 (t, *J* = 5.6 Hz, 4H), 3.84 (t, *J* = 5.6 Hz, 4H), 3.87–3.89 (m, 4H), 4.37–4.40 (m, 4H), 6.16 (d, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 9.2 Hz, 4H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.43–7.45 (m, 4H), 7.71 (d, *J* = 9.2 Hz, 4H), 8.46–8.50 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ = 66.88, 67.98, 69.89, 70.55, 70.63, 70.78, 70.98, 71.12, 85.98, 102.54, 104.76, 113.95, 115.99, 116.05, 118.27, 124.56, 126.03, 126.46, 127.10, 131.80, 133.05, 153.71, 159.56. MS (MALDI-TOF): m/z: 886.17 (calcd. [M]⁺ = 886.37). Elemental analysis (%) calcd. for C₅₆H₅₄O₁₀: C 75.83, H 6.14, N 0.00; found: C 75.88, H 6.06, N 0.30.

Sample preparation of the Y-form for measurements

As tiny mechanical forces can easily induce partial transitions from the Y-form to the Y_{gc} -form, the crystals of the Y-form were moved to the sample holders for PXRD measurements or quartz containers used for emission spectroscopic measurements, emission lifetime measurements, and quantum yield measurements with significant attention so that any crushing or scratching were avoided. For these gentle procedures, only weighing papers were used to move the samples and no steel sticks were used.

Crystallographic data

	Y-form	YG-form
Temperature / K	263	263
Crystal Dimensions / mm ³	$0.18 \times 0.18 \times 0.05$	$0.17 \times 0.09 \times 0.09$
Chemical formula	C ₅₆ H ₅₄ O ₁₀	C ₅₇ H ₅₅ O ₁₀ Cl ₃
Formula weight	887.04	1006.36
Crystal System	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> , Å	10.375(4)	9.5050(2)
b, Å	13.496(9)	14.5961(4)
<i>c</i> , Å	17.940(7)	19.0950(3)
α , deg	109.313(18)	78.825(2)
β , deg	90.7320(10)	85.325(2)
γ, deg	99.049(19)	87.071(2)
<i>V</i> , Å ³	2335(2)	2588.60(10)
Ζ	2	2
D _{calc} , g·cm ⁻³	1.261	1.291
μ , (Cu K α) cm ⁻¹	0.696	2.080
$2\theta_{max}$, deg	136.20	146.4660
Reflections measured	29930	23454
Independent reflections	8265	8845
Reflections used	8265	8845
R_I^{a}	0.0640	0.0696
$R_w(F^2)$ b	0.1609	0.2127
GOF	0.925	1.124

Table S1. Crystal Data, Data Collection, and Reduction Parameter for the Y-form and YG-form

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

 ${}^{\mathrm{b}}R_{\mathrm{w}} = (\Sigma\omega(|F_{\mathrm{o}}| - |F_{\mathrm{c}}|)^2 / \Sigma\omega F_{\mathrm{o}}^2)^{1/2}$

Atom numbering for the crystallographically independent molecule in the crystalline states



Figure S1. Crystallographically independent molecular structures of **1** in the (a) Y-form and (b) YG-form with atom numbering.

Molecular packed structures in the Y-form and YG-form



Figure S2. Intradimer C-H••• π (light-blue) and C-H•••O interactions (red) in the dimer structure in the Y-form (left) and YG-form (right).



Figure S3. Interdimer C-H••• π (light-blue) and π ••• π interactions (pink) in the (a) Y-form and (b) YG-form.

Shorter distances between the sum of the van der Waals radii of the nearest two atoms can be regarded as sites of effective interactions. Between intradimer of cyclophane 1, C-H••• π and C-H•••O interactions were observed in the Y-form, while only C-H••• π interaction was observed in the YG-form (Fig. S2).

About interdimer interactions in the Y-form, $\pi^{\bullet\bullet\bullet\pi}$ and C-H $\bullet\bullet\bullet$ anthracene π interactions are elongated to the *b* and *c* axes as shown in Fig. S3a. On the other hand, C-H $\bullet\bullet\bullet\pi$ interactions were dominantly observed as interdimer interactions in the YG-form (Fig. S3b). C-H $\bullet\bullet\bullet\pi$ and C-H $\bullet\bullet\bullet\bullet$ interactions play significant roles in constructing the pseudopolymorph structures of the Y- and YG-forms.



Figure S4. Luminophore arrangements of **1** in the Y-form viewed along the [011] direction (left) and the *a* axis (right). The luminophores are partially π -stacked with the shortest distances of 3.290 and 3.502 Å between carbon•••carbon atoms in blue and yellow, and green and yellow molecules, respectively.



Figure S5. Luminophore arrangements in the YG-form parallel to (011) plane (left) and along the c axis (right). The phenylene rings in luminophores are partially π -stacked with the shortest carbon•••carbon distances of 3.615 Å (light blue dotted lines) and partial π -stack between anthracene units is also seen with shortest carbon•••carbon distance of 3.731 Å (red dotted lines).

Photophysical properties of the solution of 1



Figure S6. Molecular structure of acyclic reference compound 2.^{S10}



Figure S7. (a) Absorption and (b) photoluminescent spectra of compounds 1 and 2 ($c = 1.0 \times 10^{-5}$ M). Emission spectra were recorded under excitation light of 365 nm at r.t.



Figure S8. Emission decay profiles recorded for (a) cyclophane 1 and (b) reference compound 2 in chloroform (c = 1×10^{-6} M). Both decays were obtained with excitation of 365 nm at r.t. and well fitted with single exponential decay function.

Appearance of the Y-form and YG-form



Figure S9. A photo representing the appearance of the Y-form (right) and YG-form (left). The photo was taken under room light.



Theoretical calculation for the bent and planer cores

Figure S10. Illustration of computed frontier molecular orbitals for the (a) bent and (b) planer luminophores with methoxy groups. The atom arrangement of the bent luminophore was the same as that in the Y-form. The planer one was optimized based on B3LYP/6-311G+(d,p).

DSC measurements for the Y-form, Ygc-form, and ground Yg-form



Figure S11. DSC traces of the Y-form (top), Y_{gc} -form (middle), and Y_{g} -form (bottom) on heating. The heating rate was 10 °C min⁻¹.

TGA for the YG-form and Y-form



Figure S12. TGA curves of the (a) YG-form and (b) Y-form. The heating rate was 10 °C min⁻¹.

XRD pattern of the YG-form, YGg-form, or YGt-form



Figure S13. X-ray diffraction patterns for the YG-form (top), YGg-form (middle), or YGt-form (bottom).

Gently Crushed YG-form



Figure S14. Photos before and after gentle crushing to the YG-form. All images were taken under excitation light of 365 nm at room temperature. Scale bar: 2 mm.





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NMR data



