Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

Crystal structure of a 1,6-bis(phenylethynyl)pyrene-based cyclophane that exhibits mechanochromic luminescence

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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. The reaction to obtain cyclophane **1** was carried out under nitrogen atmosphere. Flash silica gel column chromatography was performed with a Biotage Isolera Flash system using SHOKO-scientific Purif-Pack-EX cartridges. Recycling preparative gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LaboACE. ^{1}H NMR spectrum was measured on a JEOL JNM-ECZ 400S/L1 spectrometer and all chemical shifts are reported on the δ-scale in ppm relative to the signal of tetramethylsilane (TMS, at 0.00). Coupling constants (*J*) are quoted in Hz and relative intensities are also shown. Proton-decoupled ^{13}C NMR spectrum was measured on a JEOL JNM-ECZ 400S/L1 spectrometer and all chemical shifts (δ) are quoted in ppm using the solvent as the internal standard ($CDCl_3$, at 77.16). Elemental analysis was conducted with a J-SCIENCE JM10. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum was obtained on a SHIMADZU AXIMA PERFORMANCE. The DSC measurements were carried out using a Hitachi DSC7020 with a heating rate of 10 ˚C min^{-1} under nitrogen atmosphere. 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.

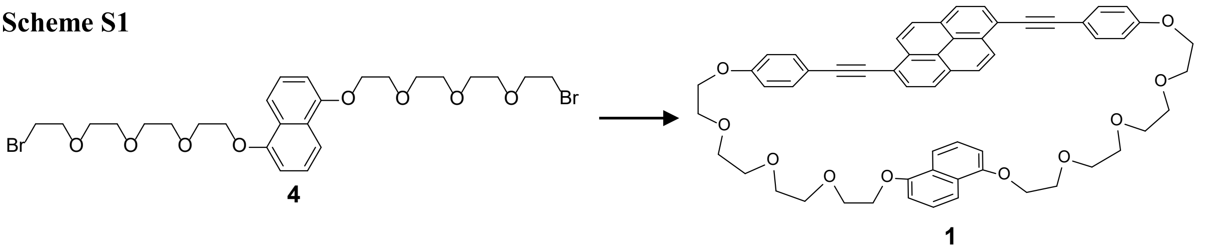
Single crystal X-ray structure analysis.

A single crystal was mounted on a cryoloop with Paratone-N (Hampton Research). Crystallographic data was collected using a Rigaku XtaLab Synergy diffractometer with a single microfocus Mo Kα X-ray radiation source (PhotonJet-S), equipped with a Hybrid Pixel (HyPix) Array detector (HyPix-6000HE) at –100 °C. Data collection, cell refinement, and data reduction were carried out with CrysalisPRO (Rigaku Oxford Diffraction, 2017). The initial structure was solved by SHELXT[S1] and expanded using Fourier techniques and refined on F^2 by the full-matrix least-squares method SHELXL2018/3[S2] package compiled into OLEX2 package.[S3] 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 is summarized in Table S1. CCDC 2104824 (crystal of **1** in the LB-form) contains the supplementary crystallographic data for this paper.

Synthesis

The synthetic route used to prepare compound **1** is shown in Scheme S1. 1,6-Bis(4-hydroxyphenylethynyl)pyrene and compound **4** were prepared according to the reported procedures.[S4,S5] Cyclophane **2** and acyclic reference compound **3** were also obtained through the reported procedures.[S4]

Scheme S1



Conditions: 1,6-bis(4-hydroxyphenylethynyl)pyrene, K_2CO_3, DMF, 85 °C, 17 h.

Compound 1. A solution of compound **4** (582 mg, 0.912 mmol) and 1,6-bis(4-hydroxyphenylethynyl)pyrene (400 mg, 0.912 mmol) in DMF (50 mL) was added to a suspension of K_2CO_3 (2.52 g, 18.2 mmol) in DMF (300 mL) dropwise at 85 °C over 5 h under vigorous stirring. After further stirring for 12 h at 85 °C, the reaction suspension was cooled and most of the DMF was evaporated in vacuo. The crude product was dissolved in chloroform (100 mL) and washed with saturated aq. NH_4Cl solution (5 × 100 mL), followed by saturated aq. NaCl solution (100 mL), the organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 92:8), recycling GPC (eluent: chloroform), and subsequently re-precipitated from a mixture of chloroform and hexane to afford compound **1** (91 mg, 9.9×10^{-2} mmol) as an orange powder in 9.7 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.41–3.44 (m, 4H), 3.46–3.49 (m, 4H), 3.55–3.58 (m, 4H), 3.62–3.65 (m, 4H), 3.78–3.81 (m, 4H), 3.85–3.89 (m, 8H), 4.41 (t, J = 4.0 Hz, 4H), 6.02 (d, J = 7.6 Hz, 2H), 6.46 (t, J = 8.0 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.8 Hz, 4H), 7.68 (d, J = 8.8 Hz, 4H), 7.77 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 9.2 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.41, 67.89, 69.88, 70.40, 70.72, 70.98, 71.11, 88.01, 95.67, 104.23, 113.58, 115.91, 116.32, 118.29, 123.97, 124.93, 125.56, 125.69, 127.89, 129.23, 130.74, 131.71, 133.03, 153.33, 159.47. MS (MALDI-TOF): m/z: 910.24 (calcd. $[M]^+$ = 910.37). Elemental analysis (%) calcd. for $C_{58}H_{54}O_{10}$: C 76.46, H 5.97, N 0.00; found: C 76.19, H 6.05, N 0.13.

Crystallographic data

Table S1. Crystal data, data collection, and reduction parameter for **1** in the LB-form.

	LB-form
Temperature / K	173
Crystal Dimensions / mm^3	0.71 × 0.408 × 0.239
Chemical formula	$C_{58} H_{54} O_{10}$
Formula weight	911.01
Crystal System	Triclinic
Space group	P-1
a, Å	12.3727(4)
b, Å	14.5043(5)
c, Å	14.6034(5)
α, deg	69.637(3)
β, deg	89.791(3)
γ, deg	70.552(3)
V, Å^3	2297.99(15)
Z	2
D_{calc}, g·cm^{-3}	1.317
μ, (Cu Kα) cm^{-1}	0.089
$2\theta_{max}$, deg	62.043
Reflections measured	34248
Independent reflections	11594
Reflections used	11594
R_1 [a]	0.0642
$R_w(F^2)$ [b]	0.1878
GOF	1.060
CCDC number	2104824

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

[b] $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$

Atom numbering for the crystallographically independent molecule in the crystal

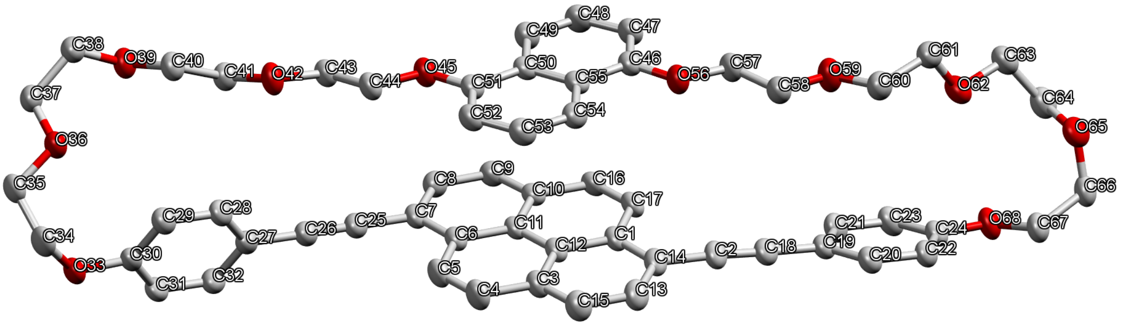


Figure S1. Crystallographically independent molecular structure of **1** in the LB-form with atom numbering.

A simulated XRD pattern of the LB-form

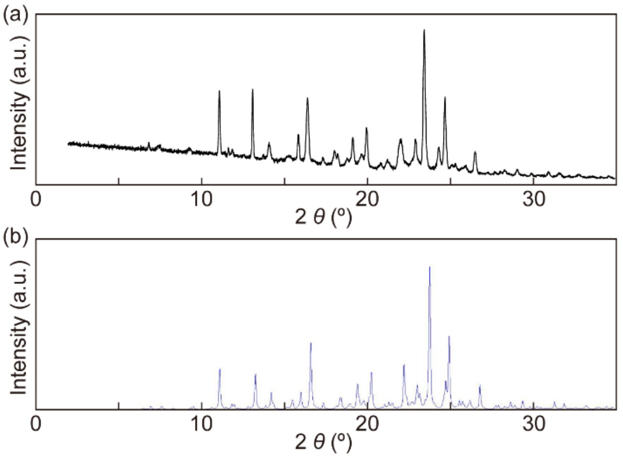


Figure S2. (a) The XRD diffractogram of cyclophane **1** in the LB-form. (b) The simulated XRD pattern based on the crystal structure of **1** in the LB-form.

References

S1. G. M. Sheldrick, *Acta. Cryst.*, 2015, **A71**, 3–8.

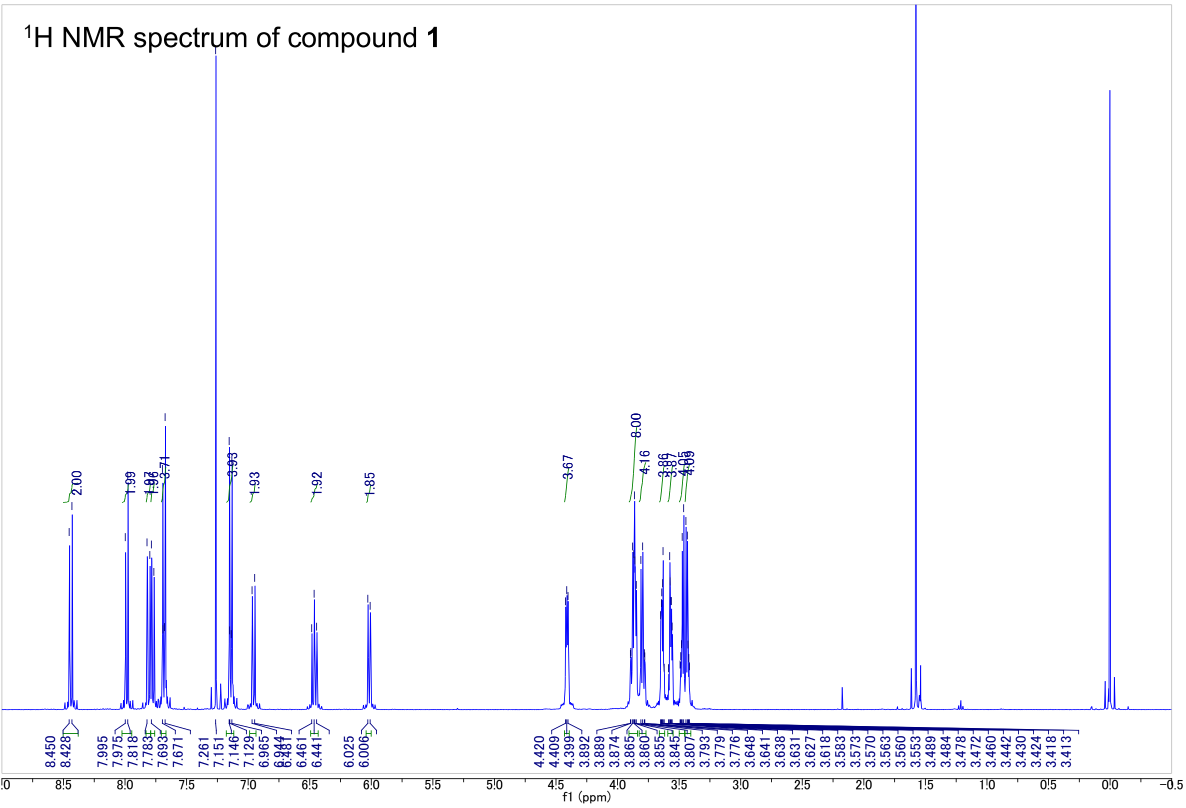
S2. G. M. Sheldrick, *Acta. Cryst.*, 2015, **C71**, 3–8.

S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

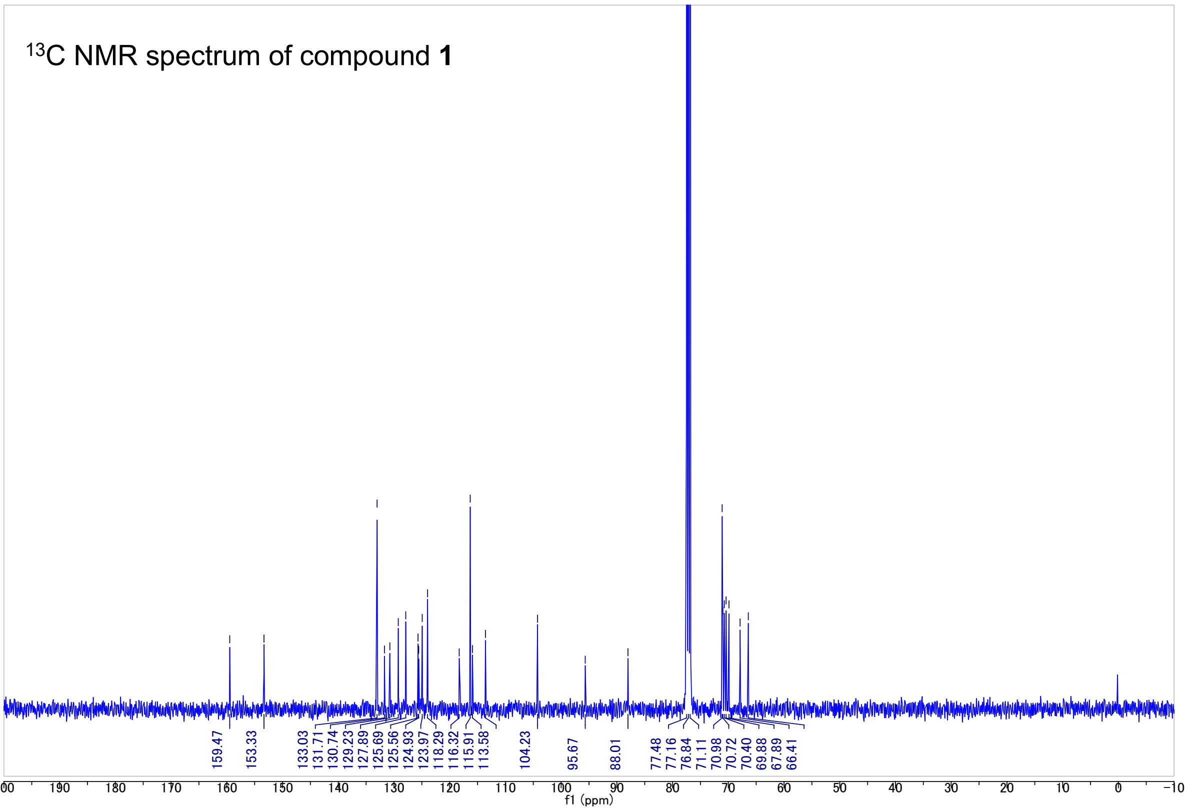
S4. Y. Sagara, C. Weder, N. Tamaoki, *Chem. Mater.*, 2017, **29**, 6145–6152.

S5. Y. Sagara, M. Karman, E. Verde-Sesto, K. Matsuo, Y. Kim, N. Tamaoki, C. Weder, *J. Am. Chem. Soc.*, 2018, **140**, 1584–1587.

NMR data



^{1}H NMR spectrum of compound **1**



^{13}C NMR spectrum of compound **1**