Supporting Information

Crystal structure and thermoresponsive luminescence of a 9,10-bis(phenylethynyl)anthracene-based cyclophane

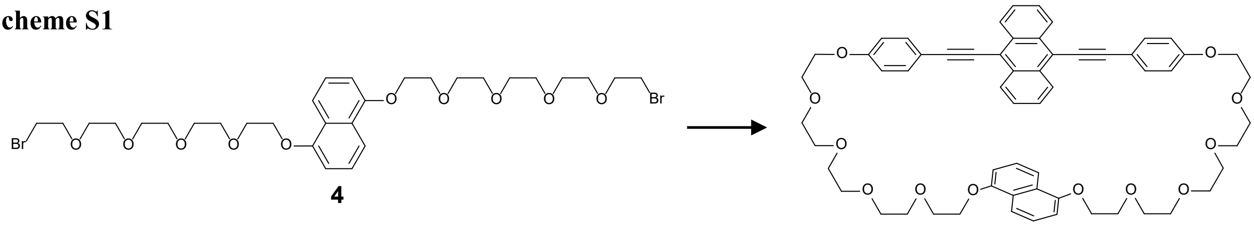
Yoshimitsu Sagara,* Kiyonori Takahashi, Takayoshi Nakamura, Nobuyuki Tamaoki
E-mail: sagara@es.hokudai.ac.jp

Table of Contents

Synthesis of cyclophane 1

Schemes S1 shows the synthetic route used to prepare cyclophane **1**. Compound **4** and 9,10-bis(4-hydroxyphenylethynyl)anthracene were prepared according to the reported procedures.[S1,S2]

Scheme S1



4

1

Conditions: 9,10-bis(4-hydroxyphenylethynyl)anthracene, K_2CO_3, DMF, 70 °C, 36 h.

Cyclophane 1. A solution of compound **4** (449 mg, 0.618 mmol) and 9,10-bis(4-hydroxyphenylethynyl)anthracene (254 mg, 0.618 mmol) in DMF (20 mL) was added to a suspension of K_2CO_3 (1.71 g, 12.4 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. NH_4Cl solution (3 × 100 mL), followed by saturated aq. NaCl solution, 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 = 5:1) and recycling GPC (eluent: chloroform) to afford cyclophane **1** (153 mg, 0.157 mmol) as an orange powder in 25 % yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56–3.66 (m, 20H), 3.70–3.74 (m, 8H), 3.86–3.91 (m, 8H), 4.30–4.32 (m, 4H), 6.34 (d, J = 7.2 Hz, 2H), 6.95 (t, J = 8.0 Hz, 2H), 7.08 (d, J = 9.2 Hz, 4H), 7.46–7.51 (m, 6H), 7.69 (d, J = 8.8 Hz, 4H), 8.55–8.57 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.27, 68.06, 69.79, 70.09, 70.62, 70.82, 70.84, 70.89, 71.19, 85.74, 102.63, 105.16, 114.29, 115.58, 115.91, 118.42, 124.85, 126.37, 126.69, 127.26, 131.93, 133.21, 153.99, 159.54. MS (MALDI-TOF): m/z: 974.73 (calcd. $[M]^+$ = 974.42). Elemental analysis (%) calcd. for $C_{60}H_{62}O_{12}$: C 73.90, H 6.41, N 0.00; found: C 73.75, H 6.36, N 0.30.

Crystallographic data

Table S1. Crystal Data, Data Collection, and Reduction Parameter.

	Cyclophane 1
Temperature / K	273
Crystal size / mm^3	0.600 × 0.400 × 0.020
Chemical formula	$C_{60}H_{62}O_{12}$
Formula weight	975.09
Crystal System	Triclinic
Space group	*P*-1
a, Å	12.0972(7)
b, Å	14.7659(8)
c, Å	15.4910(9)
α, deg	101.433(2)
β, deg	107.441(2)
γ, deg	94.2990(10)
V, Å^3	2560.6(3)
Z	2
D_{calc}, g·cm^{-3}	1.265
μ,(Cu Kα) mm^{-1}	0.087
Reflections measured	24934
Independent reflections	5596
Reflections used	5596
R_1 ^{a}	0.0660
$R_w(F^2)$ ^{b}	0.1642
GOF	1.099

$^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $^bR_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

Atom numbering for the crystallographically independent molecule in the crystal

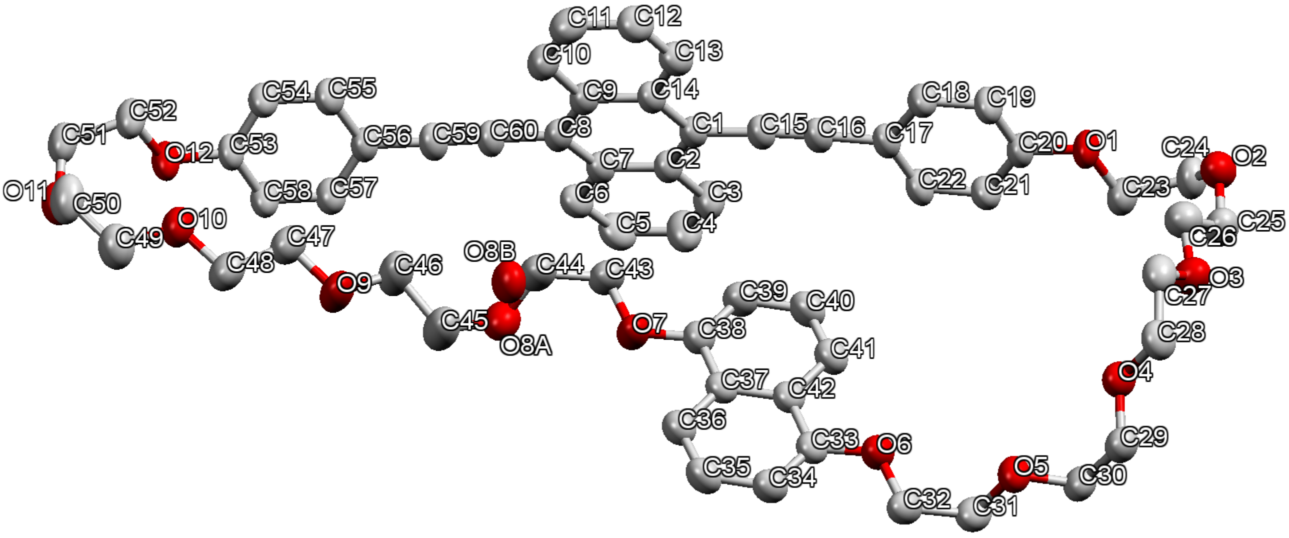


Figure S1. Crystallographically independent molecular structure with atom numbering.

Hirshfeld surface analysis for 1

Hirshfeld surface analysis was applied to the crystal structure of cyclophane **1** (Figure S2). Hirshfeld surface is depicted as d_{norm} surface. Red and blue surface in d_{norm} expression correspond to the surface that is smaller and larger than the sum of the van der Waals radii between the inner and outer nearest atoms from the surface, while white one is same as van der Waals radii with the same manner to red and blue ones. Relatively strong interactions were observed around phenylene rings and oxygen atom bonded to phenylene ring. This interaction corresponded to C-H•••O interaction between phenylene ring and oxygen atom in alkoxy chain. Percentage contribution of the type of interatomic contact between inter-molecules was summarized in Figure S2b. 58.3% contact is between hydrogen atoms. The C•••C contact is contributed as 2.5%, corresponding to π•••π interactions.

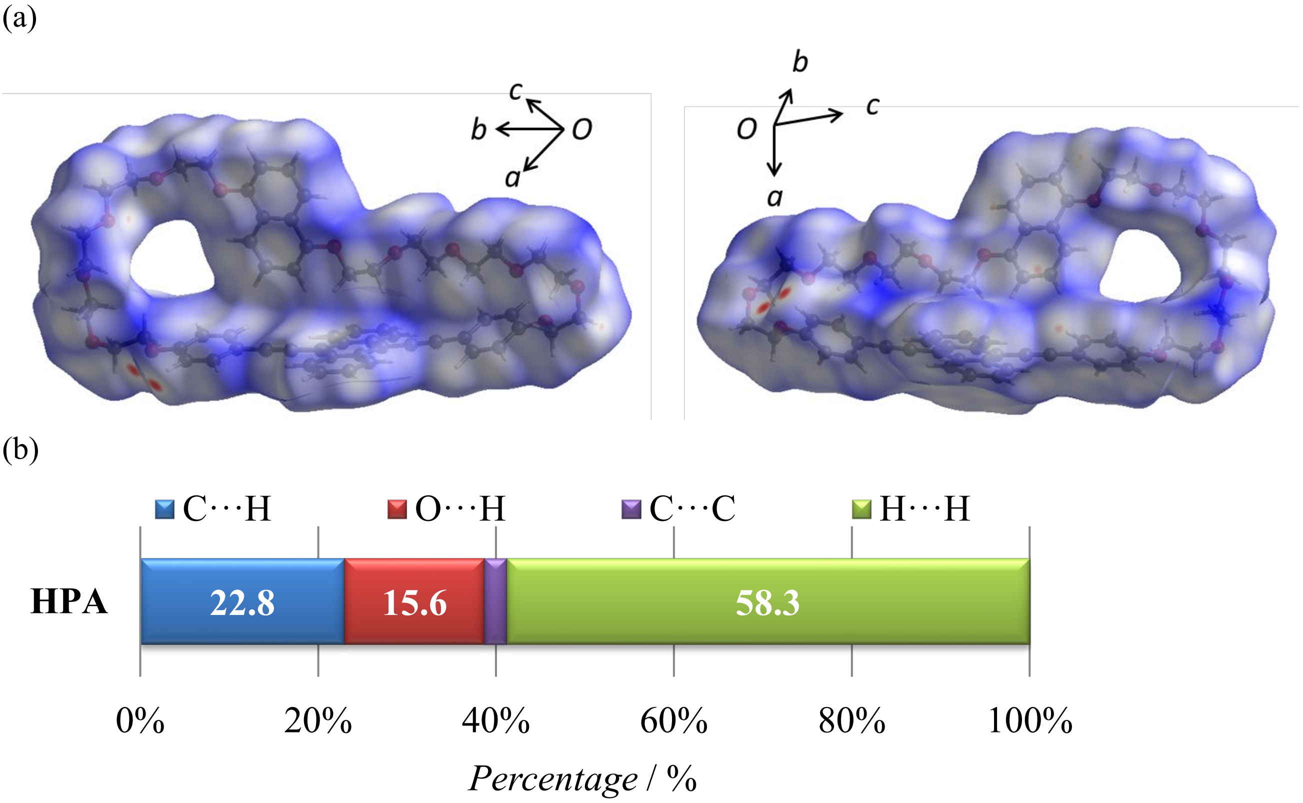


Figure S2. Hirshfeld surface analysis of cyclophane **1**. (a) Hirshfeld surface for crystallographically independent molecule depicted as d_{norm} expression. The surfaces were shown from the different views (left and right). (b) Percentage contribution of the types of interatomic contact between inter- and outer-molecules.

Simulated XRD pattern of 1 in the Cr$_1$ phase

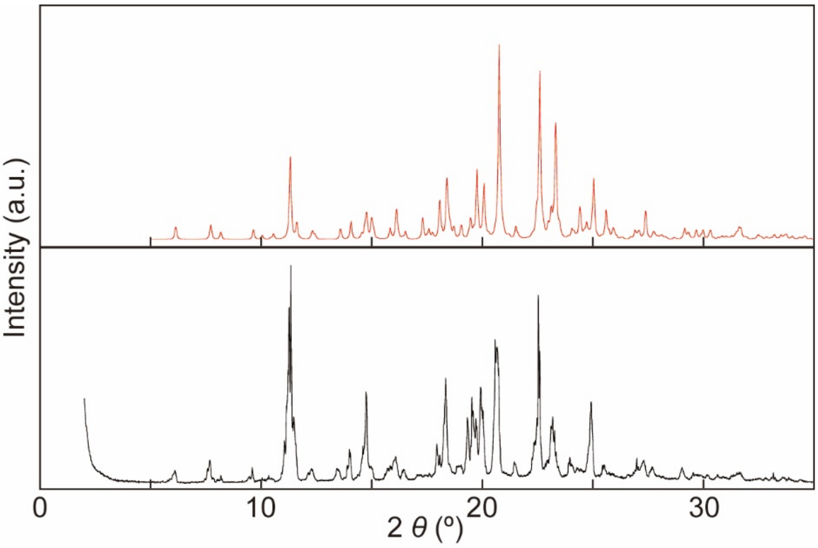


Figure S3. Simulated (red) and measured (black) XRD patterns of **1** in the Cr$_1$ phase.

Absorption and emission spectra of 1 in THF

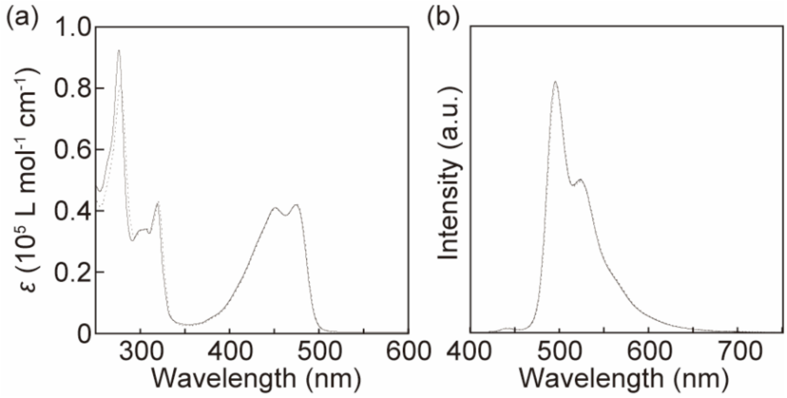


Figure S4. (a) Absorption and (b) photoluminescence spectra of cyclophane **1** in THF (solid line) and CHCl$_3$ (dotted line) (c = 1.0 × 10^{-5} M). All spectra were recorded at r.t. The excitation wavelength for the photoluminescence spectra was 400 nm.

^{1}H NMR and ^{13}C NMR spectra of 1

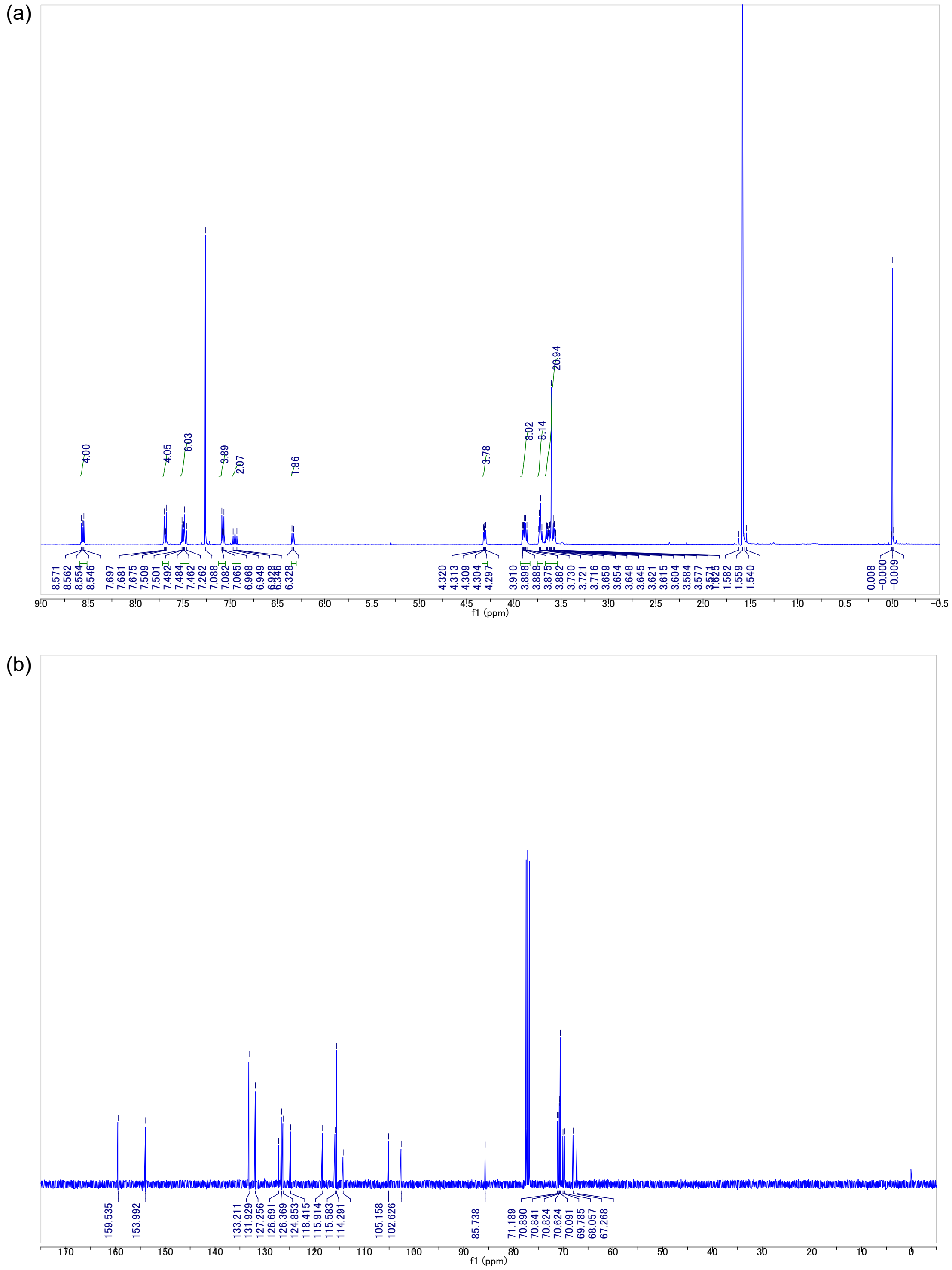


Figure S5. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of cyclophane **1** in $CDCl_3$ at r.t.

References

S1. Y. Sagara, A. Seki, Y. Kim and N. Tamaoki, *J. Mater. Chem. C*, 2018, **6**, 8453–8459.

S2. Y. Sagara, Y. C. Simon, N. Tamaoki and C. Weder, *Chem. Commun.*, 2016, **52**, 5694–5697.