

## SUPPORTING INFORMATION

### Switchable *trans-cis* Interconversion of an Amphiphilic Anthracene Trimer

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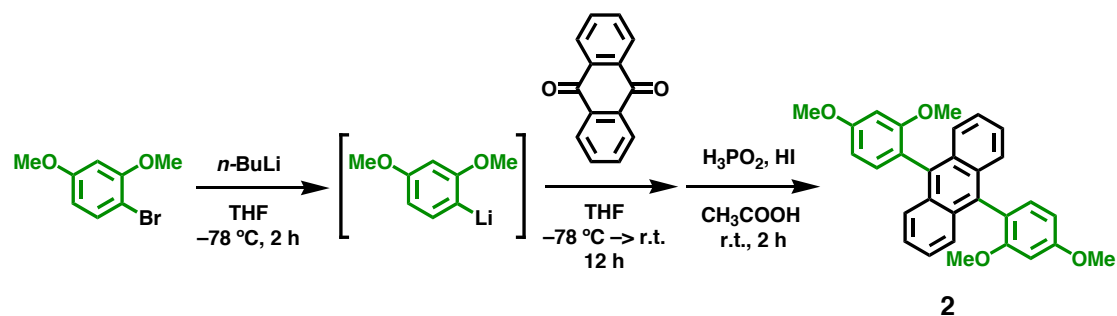
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#### Materials and instrumentations.

NMR spectra were recorded on a Bruker AV-500 (500 MHz) spectrometer. TMS served as internal standard ( $\delta$  0 ppm). MALDI-TOF-MS data were measured on an Applied Biosystem Voyager DE-STR. FAB-MS data were recorded on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL). IR measurements (ATR) were carried out using a DIGILAB Scimitar FTS-2000 instrument. UV-visible and ESR spectral data were recorded on a SHIMADZU UV-3150 and JEOL JMS-RE1X, respectively. Fluorescent spectra were measured on a JASCO FP-6500. Melting points were determined on a Yanaco MF-500V micro melting point apparatus. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co.

### Synthesis of 9,10-bis(2,4-dimethoxyphenyl)anthracene (2).

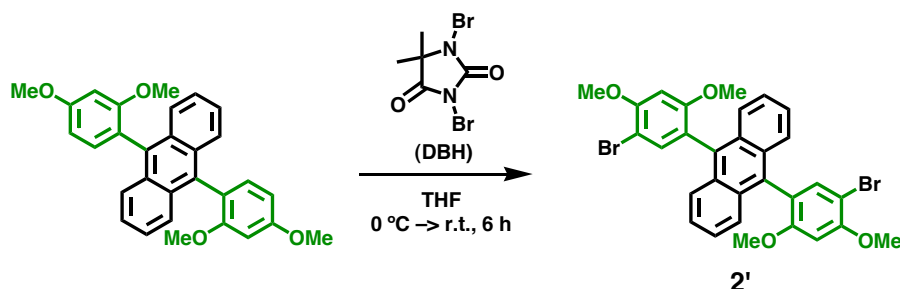


Typical procedure: To a solution of 1-bromo-2,4-dimethoxybenzene (2.0 eq, 5.00 g, 23.0 mmol) in dehydrated THF (154 mL) was added a hexane solution (1.6 M) of *n*-butyllithium (2.0 eq, 14.4 mL, 23.0 mmol) under argon atmosphere at  $-78\text{ }^{\circ}\text{C}$  and the mixture was stirred for 2 hours. Then a dehydrated THF solution of anthraquinone (2.40 g, 11.5 mmol) was added slowly to the mixture at  $-78\text{ }^{\circ}\text{C}$ . After being stirred for 12 hours at room temperature, the mixture was poured into the water. After evaporation, the residue was dissolved in an acetic acid solution (120 mL) of phosphinic acid (33wt%, 7.80 mL) and hydriodic acid (50wt%, 0.73 mL), and then the mixture was stirred at room temperature for 2 hours. The solution was poured into water and the organic compounds were extracted with dichloromethane. When the solvent was evaporated and the crude product was washed several times by hexane and methanol, 9,10-bis(2,4-dimethoxyphenyl)anthracene (**2**) was obtained as a pale yellow solid (2.78 g, 6.10 mmol) in 54% yield.

Physical data of **2**:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $27\text{ }^{\circ}\text{C}$ ):  $\delta$  7.64-7.68 (m, 4H), 7.27-7.32 (m, 4H), 7.19 (d,  $J = 8.5\text{ Hz}$ , 2H), 6.70-6.75 (m, 4H), 3.96 (s, 6H), 3.63 (s, 6H).

Ref. Fudickar, W.; Linker, T.; *Chem. Commun.* **2008**, 1771-1773.

### Synthesis of 9,10-bis(5-bromo-2,4-dimethoxyphenyl)anthracene (2').

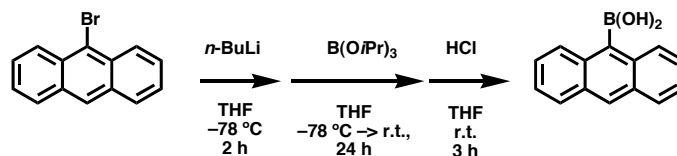


Typical procedure: To the suspended THF solution (154 mL) of 9,10-bis(2,4-dimethoxyphenyl)anthracene (1.00 g, 2.22 mmol) was dropwisely added a THF solution of dibromo-5,5-dimethylhydantoin (1.1 eq, 0.698 g, 2.44 mmol) at  $0\text{ }^{\circ}\text{C}$ . The reaction

was allowed to reach room temperature for 6 hours. After evaporation, the solid was washed several times by hexane and methanol to obtain 9,10-bis(3-bromo-2,4-dimethoxyphenyl)anthracene (**2'**) as a pale yellow solid (1.33 g, 2.19 mmol) in 99% yield. Conformational isomers, *trans*-**2'** and *cis*-**2'** could be separated by recrystallization from chloroform solution.

Physical data of **2'** (a *trans* and *cis* mixture): MALDI-TOF-MS (dithranol):  $m/z$  Calcd. 608.0, Found 607.4 [M]<sup>+</sup>; FT-IR (ATR, cm<sup>-1</sup>): 3007, 2937, 2879, 2839, 1596, 1564, 1501, 1462, 1450, 1434, 1402, 1357, 1312, 1288, 1273, 1206, 1169, 1154, 1121, 1057, 1024, 972, 842, 808; E. A. Calcd. for C<sub>30</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>4</sub>: C, 59.23; H, 3.98. Found: C, 58.95; H, 4.14; m. p. 373 °C. Physical data of *trans*-**2'**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27 °C): δ 7.58-7.63 (m, 4H), 7.43 (s, 1H), 7.29-7.33 (m, 4H), 6.72 (s, 2H), 6.70-6.73 (m, 4H), 4.03 (s, 6H), 3.60 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27 °C): δ 158.5, 156.6, 136.4, 132.3, 130.4, 126.8, 125.1, 121.3, 102.2, 97.2, 56.5, 56.2. Physical data of *cis*-**2'**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27 °C): δ 7.58-7.63 (m, 4H), 7.46 (s, 1H), 7.29-7.33 (m, 4H), 6.72 (s, 2H), 6.70-6.73 (m, 4H), 4.03 (s, 6H), 3.62 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27 °C): δ 158.4, 156.6, 136.4, 132.4, 130.4, 126.8, 125.1, 121.3, 102.2, 97.1, 56.5, 56.2.

### Synthesis of 9-anthrylboronic acid.

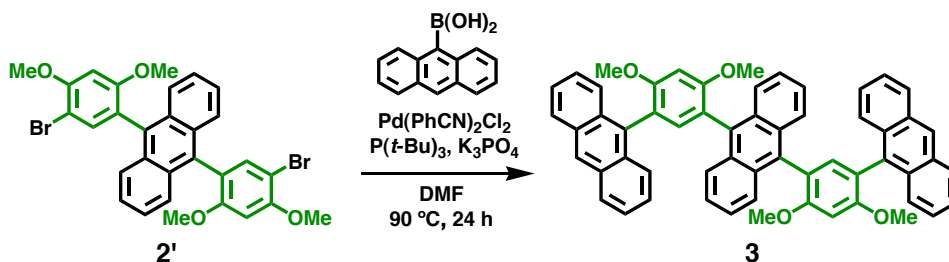


Typical procedure: To a solution of 9-bromoanthracene (5.00 g, 18.4 mmol) in dry THF (156 mL) was added a hexane solution (1.65 M) of *n*-butyllithium (1.5 eq, 17.7 mL, 29.2 mmol) under argon atmosphere at -78 °C and the mixture was stirred for 2 hours. Then triisopropyl borate (2.0 eq, 5.45 g, 38.9 mmol) was added to the suspended solution and the solution was stirred for 24 hours at room temperature. After the addition of water (ca. 5 mL) and HCl (2 M, 6.4 mL), the resulted solution was again stirred for 3 hours. The product was extracted with dichloromethane and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. After evaporation, when the crude product was recrystallized by hexane, 9-anthrylboronic acid was obtained as a pale yellow solid (2.40 g, 10.8 mmol) in 56% yield.

Physical data: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27 °C): δ 8.47 (s, 1H), 8.08 (dd, *J* = 0.8, 5.0 Hz, 4H), 7.43-7.53 (m, 4H), 5.08 (s, 2H).

Ref. Li, Z., H.; Wong, M., S.; Tao, Y.; D'Iorio, M.; *J. Org. Chem.* **2004**, *69*, 921-927.

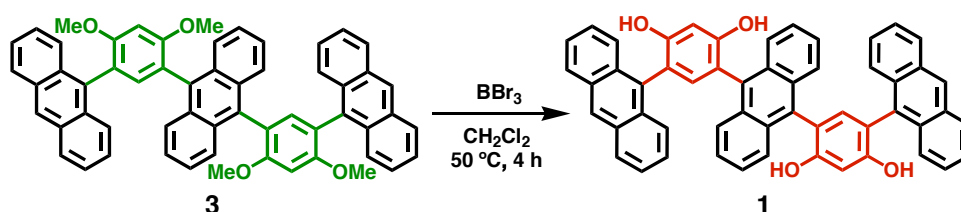
### Synthesis of 9,10-bis[5-(anthracen-9-yl)-2,4-dimethoxyphenyl]anthracene (**3**).



Typical procedure: A mixture of 9,10-bis(3-bromo-2,4-dimethoxyphenyl)anthracene (**2'**; 0.500 g, 0.820 mmol), 9-anthrylboronic acid (4.0 eq, 0.730 g, 3.29 mmol), potassium phosphate (6.0 eq, 1.05 g, 4.90 mmol), and bis(benzonitrile)palladium(II) dichloride (0.1 eq, 31.5 mg, 8.20  $\mu\text{mol}$ ) was suspended in dry DMF (10.0 mL) under argon atmosphere. Tri(*tert*-butyl)phosphine (0.4 eq, 66.5 mg, 0.0329 mmol) was added to the solution and then the reaction mixture was stirred at  $90\text{ }^\circ\text{C}$  for 1 day. After the filtration of the suspended solution, obtained black solid was washed several times by water, acetone, and chloroform. As a result, crude product of 9,10-bis[5-(anthracen-9-yl)-2,4-dimethoxyphenyl]anthracene (**3**) was obtained as a grey solid (0.390 g). Since product **3** had very low solubility in various organic solvents, the characterization was done only by MALDI-TOF-MS.

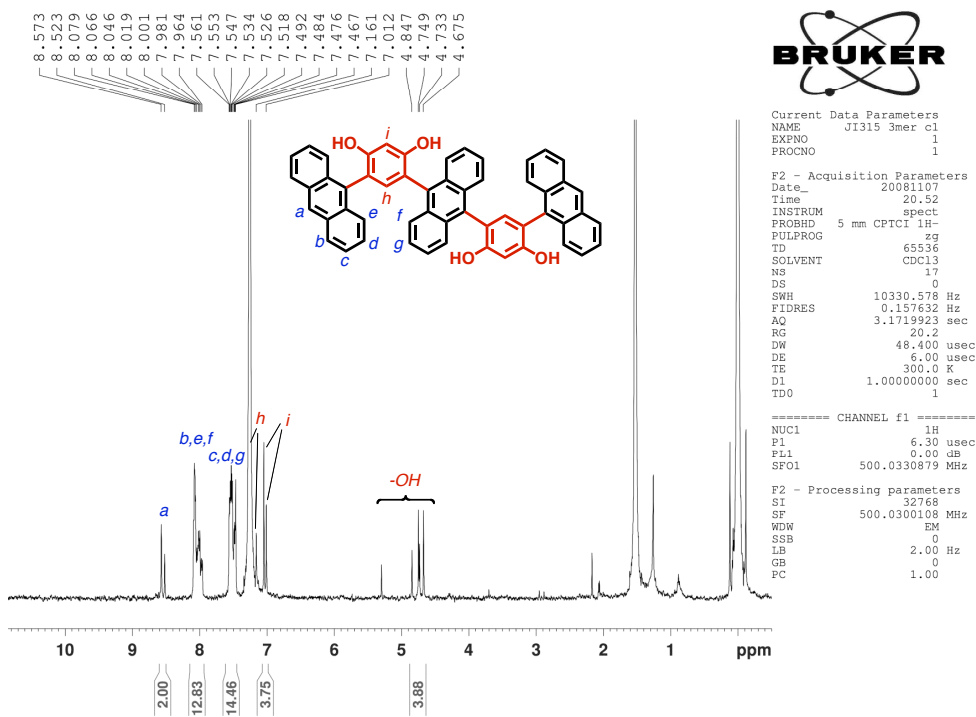
Physical data of **3**: MALDI-TOF-MS (9-nitroanthracene):  $m/z$  calcd. 802.3, found. 802.0 [ $\text{M}$ ]<sup>+</sup>.

### Synthesis of anthracene trimer **1**.



Typical procedure: To a suspended solution of 9,10-Bis[5-(anthracen-9-yl)-2,4-dimethoxyphenyl] anthracene (**3**; 30.0 mg, 0.0374 mmol) in dry dichloromethane (0.560 mL) was added a dichloromethane solution (1.0 M) of boron bromide (20.0 eq, 0.747 mL, 0.747 mmol) under argon atmosphere at  $0\text{ }^\circ\text{C}$ . When the mixture was stirred for 4 hours at  $50\text{ }^\circ\text{C}$ , cold water was added to the solution and the product was extracted with dichloromethane. Then the organic layer was dried over  $\text{Na}_2\text{SO}_4$  and filtrated. After evaporation, the crude product was washed by small amount of hexane to obtain anthracene trimer **1** as a yellow solid (27.0 mg, 0.0362 mmol) in 59% yield (based on **2'**). Conformational isomers, *trans*-**1** and *cis*-**1** were separated by GPC.

Physical data of **1**: FAB-MS (NBA):  $m/z$  calcd. 746.2, found. 746.8  $[M]^+$ ; IR (ATR,  $\text{cm}^{-1}$ ): 3475, 3056, 2854, 1623, 1585, 1499, 1440, 1410, 1390, 1352, 1327, 1260, 1216, 1138, 1085, 1015, 890, 843; E. A.: Calcd. For  $\text{C}_{54}\text{H}_{34}\text{O}_4 \cdot 3\text{H}_2\text{O}$ : C, 80.98; H, 5.03; Found: C, 80.91; H, 5.09; m. p. 330 °C (decomposed). Physical data of *trans*-**1**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27 °C):  $\delta$  8.56 (s, 2H), 7.95-8.17 (m, 12H), 7.46-7.61 (m, 12H), 7.01 (s, 2H), 4.77 (s, 2H), 4.69 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27 °C):  $\delta$  155.4, 155.2, 135.4, 131.7, 131.3, 131.3, 131.1, 129.0, 128.8, 128.2, 126.7, 126.6, 126.5, 126.0, 125.6, 117.0, 116.8, 103.0. Physical data of *cis*-**1**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27 °C):  $\delta$  8.52 (s, 2H), 7.95-8.17 (m, 12H), 7.46-7.61 (m, 12H), 7.16 (s, 2H), 7.04 (s, 2H), 4.90 (s, 2H), 4.76 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27 °C):  $\delta$  155.3, 155.2, 135.5, 131.6, 131.3, 131.2, 131.1, 129.0, 128.7, 128.1, 126.7, 126.5, 126.0, 125.5, 117.0, 116.8, 103.1.



**Figure S1.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 27 °C) of **1**.

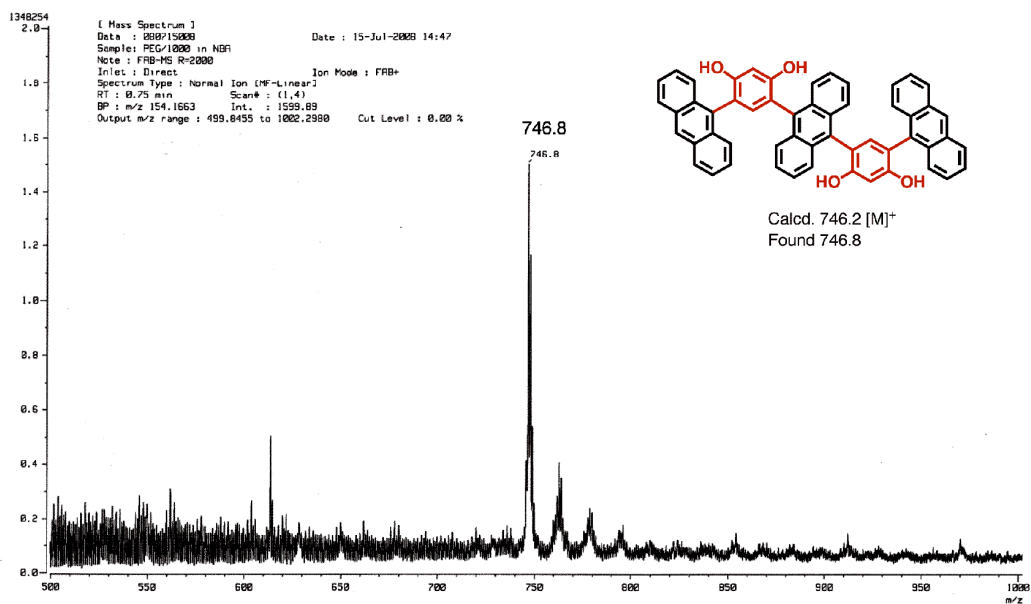


Figure S2. FAB-MS spectrum (NBA) of 1.

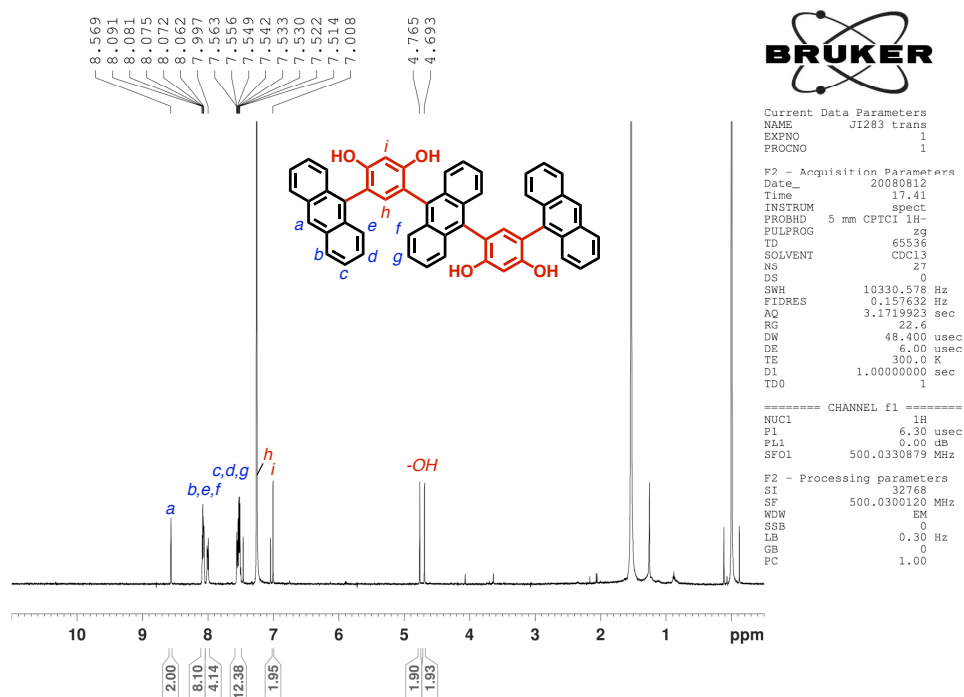


Figure S3. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 27 °C) of *trans*-1.

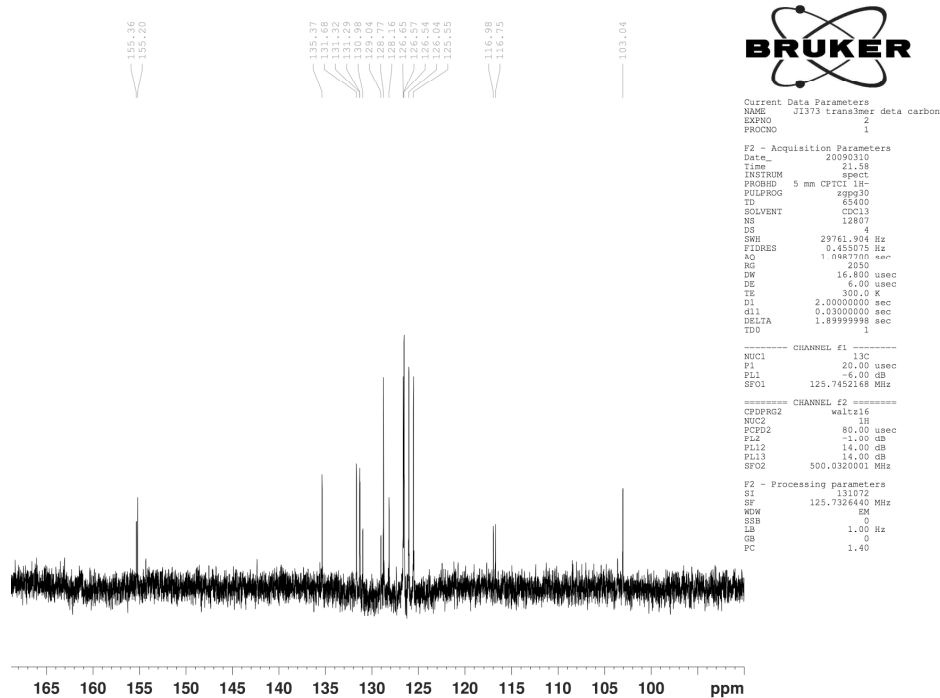


Figure S4. <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>, 27 °C) of *trans*-1.

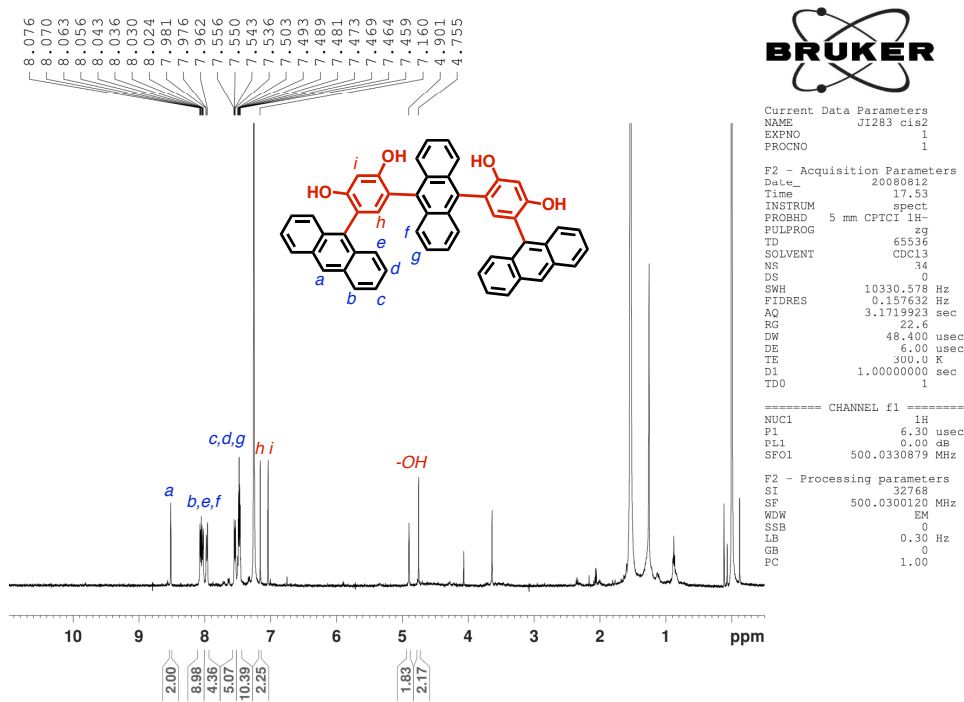


Figure S5. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 27 °C) of *cis*-1.

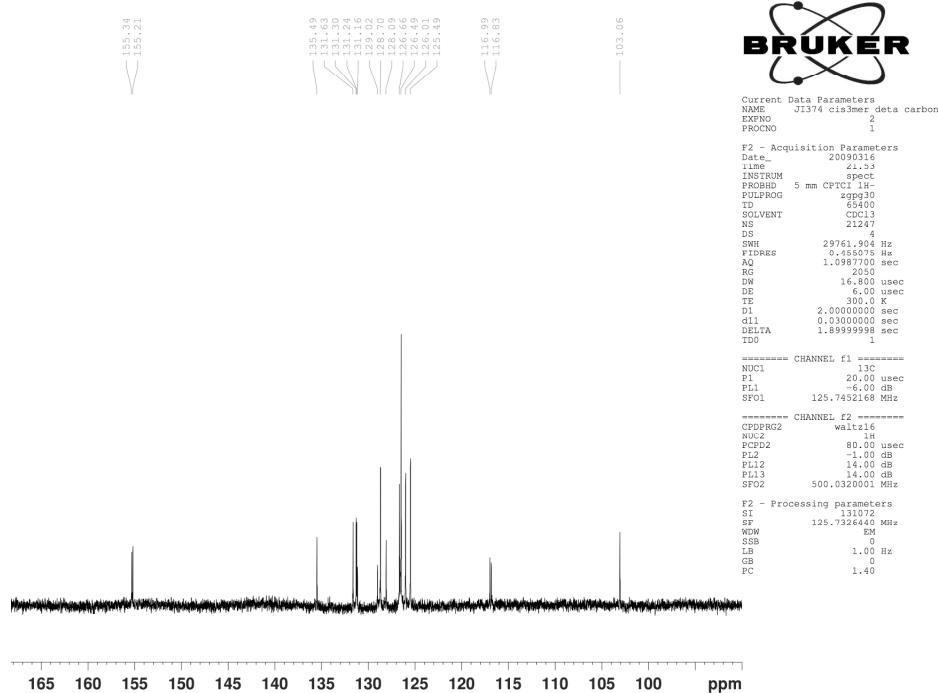
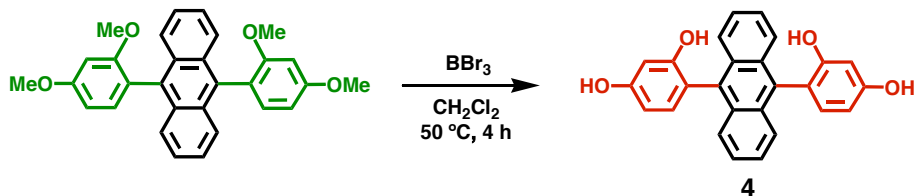


Figure S6.  $^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{CDCl}_3$ , 27  $^\circ\text{C}$ ) of *cis*-1.

### Synthesis of 9,10-bis(2,4-hydroxyphenyl)anthracene (**4**).

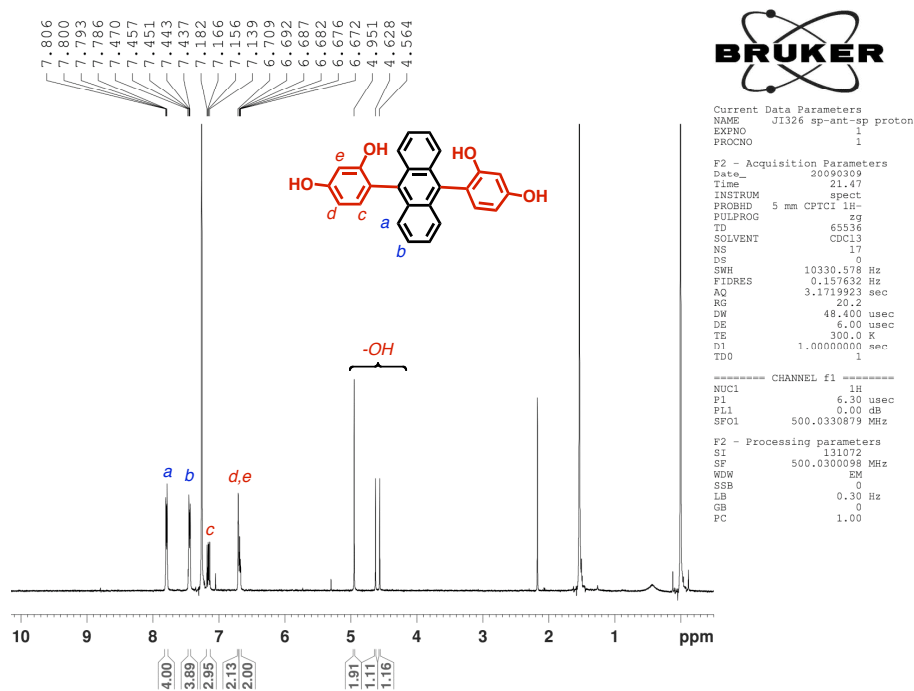


Typical procedure: To a solution of 9,10-bis(2,4-dimethoxyphenyl)anthracene (1.0 eq, 200 mg, 0.444 mmol) in dry dichloromethane (8.88 mL) was added a dichloromethane solution (1.0 M) of boron bromide (20.0 eq, 8.88 mL, 8.88 mmol) under argon atmosphere at 0  $^\circ\text{C}$ . When the mixture was stirred at 50  $^\circ\text{C}$  for 4 hours, cold water was added to the solution and the product was extracted with dichloromethane. Then the organic layer was dried over  $\text{Na}_2\text{SO}_4$  and filtrated. After evaporation, the crude product was washed by hexane and chloroform to obtain 9,10-bis(2,4-dihydroxyphenyl)anthracene (**4**) as a yellow solid (150 mg, 0.381 mmol) in 86% yield.

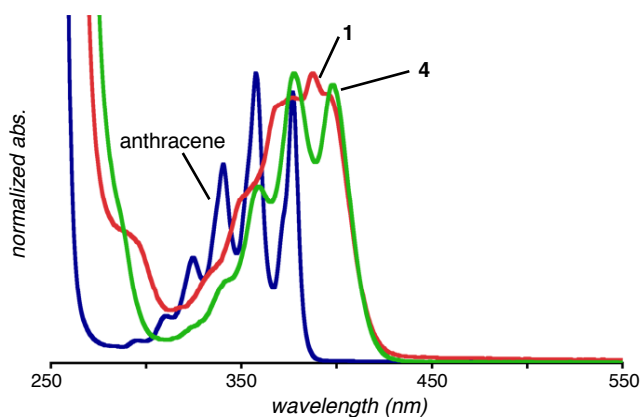
Physical data of **4**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27  $^\circ\text{C}$ ):  $\delta$  7.76-7.82 (m, 4H), 7.43-7.49 (m, 4H), 7.13-7.19 (m, 2H), 6.66-6.73 (m, 4H), 4.99 (s, 2H), 4.64 (s, 1H), 4.56 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ , 27  $^\circ\text{C}$ ):  $\delta$  159.49, 157.33, 134.41, 134.24, 133.89, 132.05, 131.99, 127.95, 127.88, 125.74, 125.55, 117.32, 117.22, 108.07, 103.79; MALDI-TOF-MS (dithranol):  $m/z$



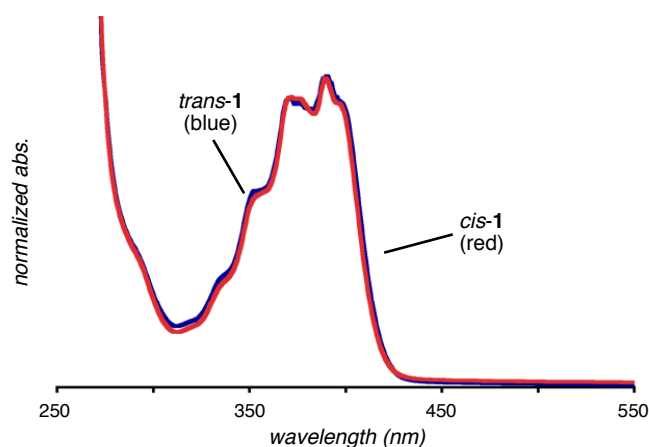
calcd. 394.1, found. 393.8 [M]<sup>+</sup>; IR (ATR, cm<sup>-1</sup>): 3459, 1619, 1590, 1508, 1438, 1391, 1307, 1138, 1095, 972, 831, 810, 768; m. p. 330 °C (decomposed); E. A.: Calcd. For C<sub>26</sub>H<sub>18</sub>O<sub>4</sub>•1.2H<sub>2</sub>O: C, 75.06; H, 4.94; Found: C, 75.06; H, 5.00.



**Figure S7.** <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>, 27 °C) of **4**.

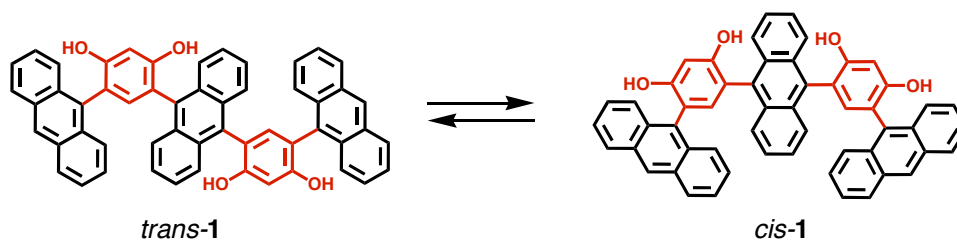


**Figure S8.** UV-vis spectra (THF, r.t.) of **1** (0.033 mM), **4** (0.10 mM), and anthracene (0.010 mM).



**Figure S9.** UV-vis spectra ( $\text{CHCl}_3$ , 0.033 mM, r.t.) of *trans*-**1** and *cis*-**1**.

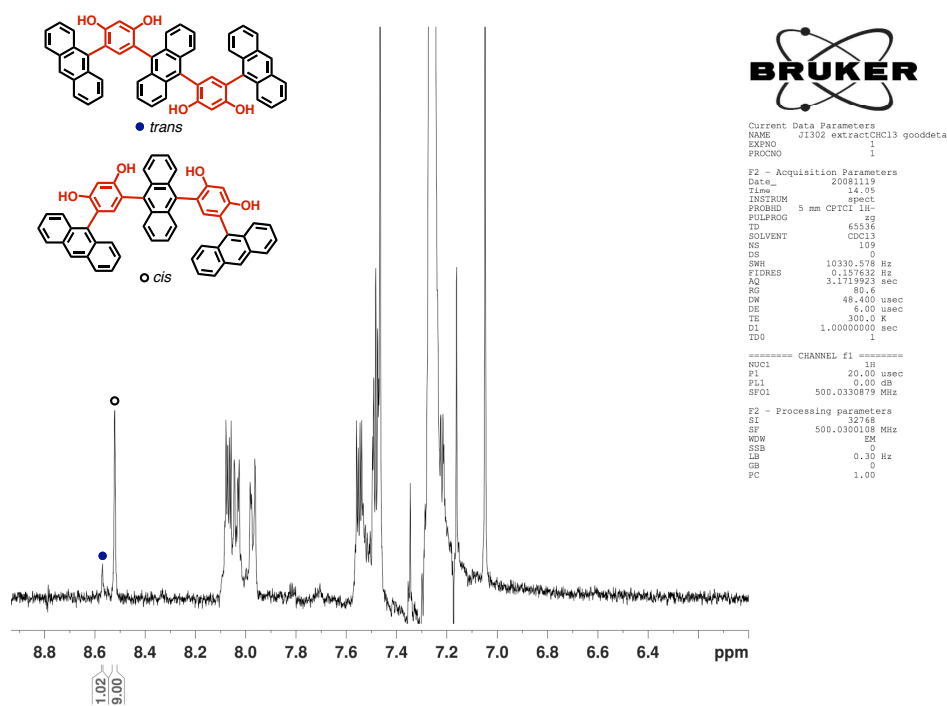
### Studies of *trans-cis* interconversion of anthracene trimer **1**.



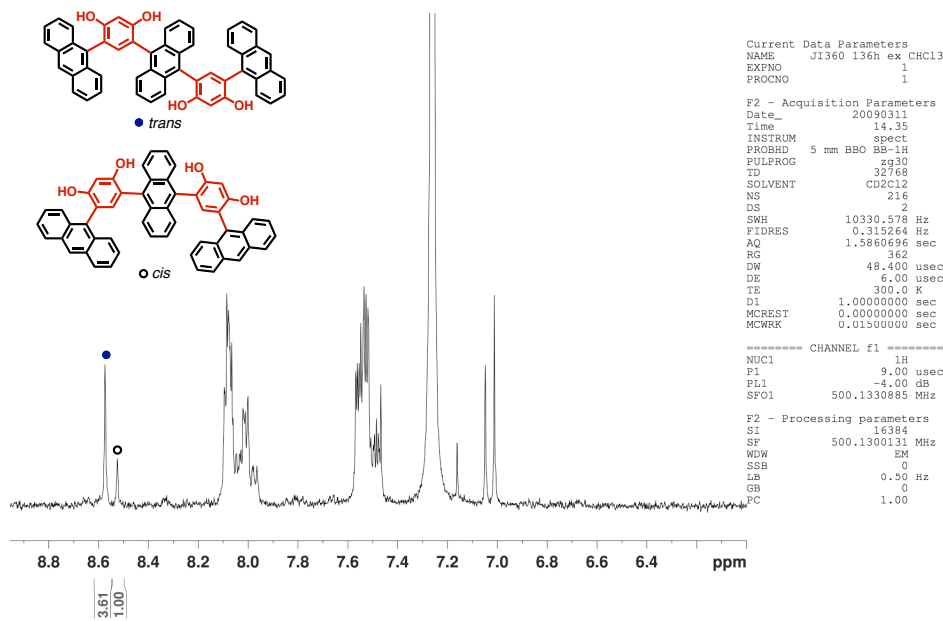
Typical procedure 1: A deuterated THF solution of *trans*-**1** (0.100 mg, 0.134  $\mu\text{mol}$ ; 1.0 mM) was stirred at 80  $^\circ\text{C}$  for 12 hours. Conformational interconversion of *trans*-**1** was monitored by  $^1\text{H-NMR}$  analysis and then thermodynamic equilibrium of **1** in THF was determined to be *trans* : *cis* = 6:4 by  $^1\text{H-NMR}$ .

Typical procedure 2: A 1M NaOH aqueous solution of *trans*-**1** (0.020 mg, 0.027  $\mu\text{mol}$ ; 1.0 mM) was kept at 30  $^\circ\text{C}$  for one week in the dark. The aqueous solution was neutralized with 1M HCl(aq.) and then the products were extracted by chloroform. The thermodynamic equilibrium ratio of *trans* and *cis* was estimated to be 1:9 by  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ).

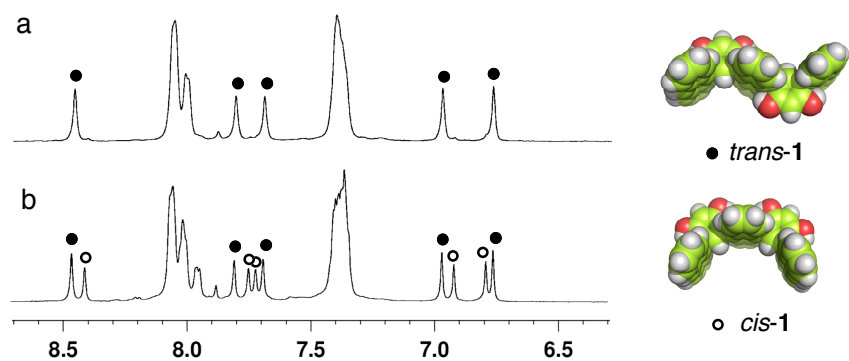
Typical procedure 3: A pyridine solution of *cis*-**1** (0.100 mg, 0.134  $\mu\text{mol}$ ; 1.0 mM) was stirred at 80  $^\circ\text{C}$  for 6 days. After evaporation, the mixture was dissolved in  $\text{CDCl}_3$  and analyzed by  $^1\text{H-NMR}$  spectroscopy. The equilibrium ratio was determined to be *trans* : *cis* = 8:2.



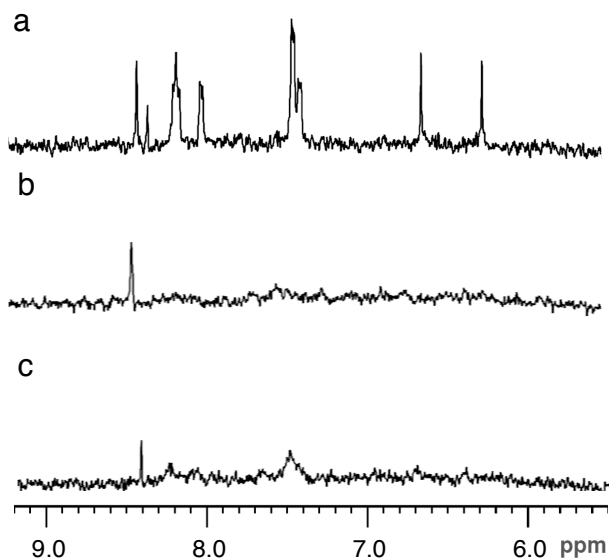
**Figure S10.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 27 °C) of *trans*-1 after one week at room temperature in aqueous NaOH solution.



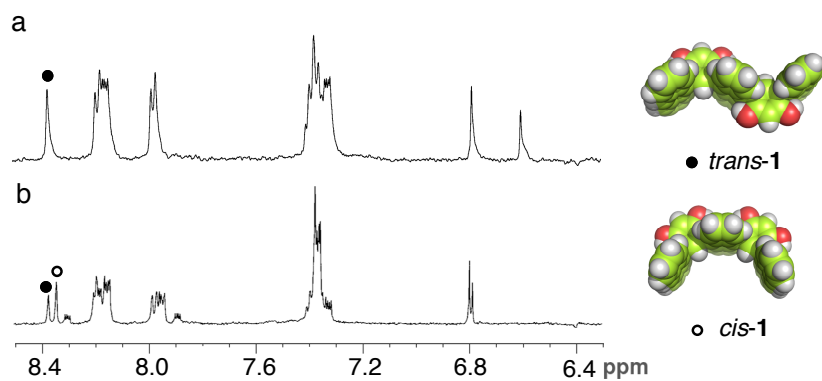
**Figure S11.**  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 27 °C) of *cis*-1 after 6 days at 80 °C in pyridine.



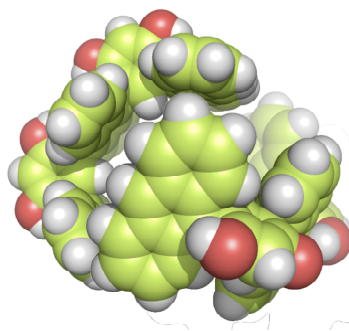
**Figure S11.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{THF-}d_8$ , 27 °C) of *trans-1* (a) before and (b) after the isomerization in THF at 80 °C for 12 hours.



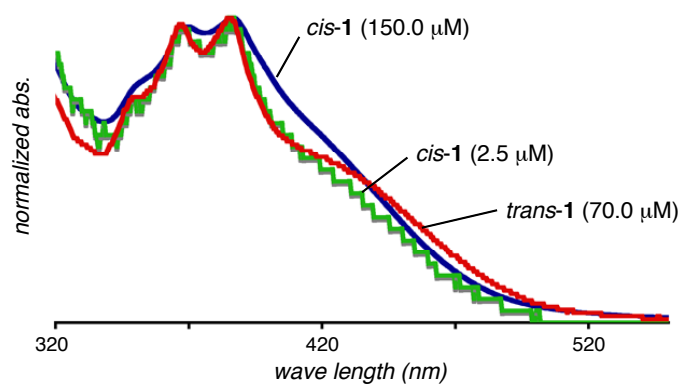
**Figure S12.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{NaOD/D}_2\text{O}$ , 27 °C) of (a) *trans-1*, (b) *cis-1*, and (c) *trans-1* after one week at room temperature in  $\text{NaOHaq}$ .



**Figure S13.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_3\text{OD}$ , 27 °C) of *trans-1* (a) before and (b) after one day in  $\text{CD}_3\text{OD/NaOHaq}$ . at 30 °C.



**Figure S14.** Proposed structure of the hydrophobic self-aggregation of amphiphilic *cis-1* in water.



**Figure S15.** Concentration-dependent UV-vis spectra (NaOH aq., r.t.) of *cis-1* (150.0 μM) (red line), *trans-1* (70.0 μM) (blue line), and *cis-1* (2.5 μM) (green line).