

## **Novel graphite-like stacking structure in a discrete molecule and its molecular recognition behavior**

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### **Supporting Information**

## Experimental Procedures

### General.

<sup>1</sup>H NMR spectra were recorded on a Bruker AC300 (300 MHz), a Bruker AVANCE400 (400 MHz), or a Bruker AVANCE600 (600 MHz) spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III. Uncorrected melting points were determined on a Yanaco MP-J3 melting point apparatus. Reagents and solvents were used without further purification unless otherwise noted.

Kanto Silica Gel 60N (spherical, neutral) was used for chromatographic separation. For reactions under inert atmosphere, dehydrated THF, toluene, diethyl ether, and DMF provided by WAKO were used. Dichloromethane, nitromethane, and ethylenediamine were distilled over calcium hydride prior to use.

### Synthesis of 1,2,4,5-tetrabromo-3,6-dichlorobenzene.<sup>[1]</sup>

A mixture of 1,4-dichlorobenzene (6.50 g, 44.2 mmol), bromine (9.2 mL, 0.18 mol), iron powder (241 mg, 4.3 mmol), iodine (0.265 g, 1.04 mmol), and fuming sulfuric acid (SO<sub>3</sub> content, 30%; 70 mL) was heated at 60 °C for 6 h. After the reaction mixture was poured onto ice/water, the formed precipitates were collected on a filter to yield crude product (22.2 g) as grey solid. This was dissolved in toluene (500 mL) by 10 min refluxing and the solution was filtered while hot. After cooling, colorless crystals were grown in the solution, which were collected by filtration to yield 1,2,4,5-tetrabromo-3,6-dichlorobenzene (18.5 g, 40.0 mmol, 90%) as colorless needles, mp 279–280 °C (lit.<sup>[2]</sup> 281 °C), <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 126.6, 135.7.

### Synthesis of 1,4-diiodo-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (2).

A solution of 4-*tert*-butylphenylmagnesium bromide was prepared by adding dropwise a solution of 1-bromo-4-*tert*-butylbenzene (19 mL, 110 mmol) in THF (100 mL) to magnesium (4.02 g, 165 mmol) and subsequent stirring for 2 h at room temperature under argon atmosphere. This solution was introduced into a flask containing a solution of 1,2,4,5-tetrabromo-3,6-dichlorobenzene (6.48 g, 14.0 mmol) in THF (50 mL) via a teflon transfer tube, and the resulting solution was stirred further for 6 h at room temperature. After cooling to 0 °C, iodine (23.5 g, 93 mmol) was added to the solution, which was stirred at room temperature for further 13 h. After addition of water (500 mL), the organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer was washed with an aqueous solution of sodium sulfite and water, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The partially solidified product was treated with hexane and collected on a filter to give 1,4-diiodo-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (2) (10.1 g, 11.8 mmol, 84%) as colorless crystals, mp >300 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.20 (s, 36H), 6.90 (d, *J* = 8.3 Hz, 8H), 7.11 (d, *J* = 8.3 Hz, 8H).

### Synthesis of 4-bromophenylboronic acid (3).<sup>[3]</sup>

A solution of 4-bromophenylmagnesium bromide was prepared by adding dropwise a solution of

1,4-dibromobenzene (14.3 g, 60.4 mmol) in THF (40 mL) to magnesium (1.48 g, 60.9 mmol) and subsequent stirring for 4 h at room temperature under argon atmosphere. This solution was introduced into a flask containing a solution of trimethyl borate (10 mL) in THF (20 mL) under argon atmosphere keeping the temperature at  $-78\text{ }^{\circ}\text{C}$ , and then the resulting solution was stirred for 19 h at room temperature. After addition of 10% hydrochloric acid (20 mL), the mixture was extracted with diethyl ether. The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness to yield crude product (12.6 g) as colorless solid, which was treated with hexane and collected on a filter to give 4-bromophenylboronic acid (**3**) (12.1 g, 60.2 mmol, 99%) as colorless crystals, mp  $277\text{--}279\text{ }^{\circ}\text{C}$  (lit.<sup>[4]</sup>  $277\text{--}278\text{ }^{\circ}\text{C}$ ),  $^1\text{H NMR}$  (400 MHz, acetone- $d_6$ )  $\delta$  7.27 (s, 2H), 7.54 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.79 (d,  $J = 8.4\text{ Hz}$ , 2H).

#### **Synthesis of 1,4-bis(4-bromophenyl)-2,3,5,6-tetrakis(4-tert-butylphenyl)benzene (4).**

Under nitrogen atmosphere, diiodide **2** (4.34 g, 5.05 mmol), boronic acid **3** (4.16 g, 20.7 mmol), tetrakis(triphenylphosphine)palladium(0) (0.308 g, 267  $\mu\text{mol}$ ), potassium carbonate (14.0 g, 101 mmol) and Aliquat 336 (40.5 mg, 100  $\mu\text{mol}$ ) were dissolved in degassed toluene (500 mL) and water (300 mL). The two-phase mixture was heated at reflux for 1 week. After cooling, the mixture was extracted with chloroform. The combined organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness to yield crude product (4.35 g). This was purified by recrystallization from chloroform/methanol to give 1,4-bis(4-bromophenyl)-2,3,5,6-tetrakis(4-tert-butylphenyl)benzene (**4**)<sup>[5]</sup> (3.76 g, 4.10 mmol, 81%) as colorless crystals, mp  $>300\text{ }^{\circ}\text{C}$ ,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.12 (s, 36H), 6.63 (d,  $J = 8.3\text{ Hz}$ , 8H), 6.69 (d,  $J = 8.3\text{ Hz}$ , 4H), 6.84 (d,  $J = 8.3\text{ Hz}$ , 8H), 6.97 (d,  $J = 8.3\text{ Hz}$ , 4H).

#### **Synthesis of 2,11-dibromo-5,8,14,17-tetra-tert-butylhexabenzob[bc,ef,hi,kl,no,qr]coronene (5).**

Under nitrogen atmosphere, a solution of anhydrous iron(III) chloride (303 mg, 1.87 mmol) in nitromethane (2 mL) was added dropwise to a solution of compound **4** (101 mg, 110  $\mu\text{mol}$ ) in dichloromethane (12 mL) and the resulting solution was stirred at room temperature for 12 h. Methanol (50 mL) was added to the solution and the brown precipitates were collected on a filter to yield crude product (442 mg), which was washed thoroughly with methanol to give 2,11-dibromo-5,8,14,17-tetra-tert-butylhexabenzob[bc,ef,hi,kl,no,qr]coronene (**5**)<sup>[5]</sup> (96.5 mg, 107  $\mu\text{mol}$ , 97%) as orange crystals, mp  $>300\text{ }^{\circ}\text{C}$ ,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.92 (s, 36H), 8.57 (s, 4H), 8.58 (s, 4H), 8.98 (s, 4H).

#### **Synthesis of 3,3'-(5,8,14,17-tetra-tert-butylhexabenzob[bc,ef,hi,kl,no,qr]coronene-2,11-diyl)-dibenzaldehyde (7).**

Under nitrogen atmosphere, dibromide **5** (88.5 mg, 97.8  $\mu\text{mol}$ ), 3-formylphenylboronic acid (**6**) (294 mg, 1.96 mmol), tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.010 mmol) and potassium carbonate (270

mg, 1.95 mmol) were dissolved in degassed THF–water (5 mL/1 mL) mixed solvent, and the resulting solution was heated at 100 °C for 48 h. After cooling, the mixture was extracted with chloroform, and the combined organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness to give crude product (72.3 mg). This was purified by column chromatography (SiO<sub>2</sub>, chloroform) to give dialdehyde **7** (50.4 mg, 50.8 μmol, 52%) as yellow crystals, mp >300 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.82 (s, 36H), 7.92 (t, *J* = 7.2 Hz, 2H), 8.12 (d, *J* = 7.2 Hz, 2H), 8.38 (d, *J* = 7.2 Hz, 2H), 8.61 (s, 2H), 9.28 (s, 8H), 9.32 (s, 4H), 10.3 (s, 2H). MALDI-TOF MS: calcd. for C<sub>72</sub>H<sub>58</sub>O<sub>2</sub> [M]<sup>+</sup>: *m/z* = 954.4; found: 954.3. Anal. Calcd for C<sub>72</sub>H<sub>58</sub>O<sub>2</sub>•2H<sub>2</sub>O: C, 87.24; H, 6.30. Found C, 87.08; H, 6.19.

#### Synthesis of 2,2'-oxydiethanamine (**8b**).

Diethylene glycol ditosylate (4.69 g, 11.3 mmol) was added to an aqueous solution (24 mL) of sodium azide (4.26 g, 65.5 mmol) and Aliquat 336 (386 mg, 0.955 mmol), and the resulting solution was heated at 98 °C for 11 h. After cooling, the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to give diazide (1.66 g, 10.6 mmol, ~94%) as yellow oil. The azide (559 mg, 3.58 mmol) was dissolved in degassed ethanol (4 mL) and 5% Pd/C (52.6 mg) was added. The solution was at room temperature under 1 atm hydrogen atmosphere for 17 h. After the insoluble materials were filtered off, the filtrate was concentrated to dryness to give 2,2'-oxydiethanamine (**8b**)<sup>[6]</sup> (314 mg, 3.01 mmol, 84%) as yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.42 (br, 4H), 2.88 (t, *J* = 6.8 Hz, 4H), 3.49 (t, *J* = 6.8 Hz, 4H).

#### Synthesis of 2,2'-(ethane-1,2-diylbis(oxy))diethanamine (**8c**).

1,2-Bis(2-chloroethoxy)ethane (0.80 mL, 5.1 mmol) was added to an aqueous solution of sodium azide (1.41 g, 21.6 mmol) and Aliquat 336 (103 mg, 0.255 mmol), and the resulting solution was heated at 98 °C for 15 h. After cooling, the mixture was extracted with diethyl ether, and the organic layer was concentrated to give crude diazide as yellow oil. This was dissolved in THF (4 mL) under nitrogen atmosphere, and the solution was slowly added to a suspension of lithium aluminum hydride (1.02 g, 26.9 mmol) in THF (4 mL) under nitrogen at 0 °C. After the solution was refluxed for 16 h, an aqueous solution of sodium hydroxide (1 M) was added to the solution, which was stirred for 12 h at room temperature. The reaction mixture was filtered through a Celite pad to remove inorganic salts, and concentrated to dryness to give 2,2'-(ethane-1,2-diylbis(oxy))diethanamine (**8c**)<sup>[6]</sup> (552 mg, 3.72 mmol, 73%) as yellow oil, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 1.68 (br, 4H), 2.88 (t, *J* = 7.0 Hz, 4H), 3.53 (t, *J* = 7.0 Hz, 4H), 3.64 (s, 4H).

#### Synthesis of macrocycle **1a–1c**.

A solution of dialdehyde **7** (9.55 mg, 9.6 μmol) in chloroform (4.5 mL) was mixed with a solution of diamine **8a–8c** in chloroform (0.20 M, 50 μL), and the solution was sand at room temperature or 50 °C for

12–24 h. After solvent was removed under reduced pressure, macrocycles **1a–1c** was obtained as yellow to orange solid, and this was used for spectroscopic measurements without purification procedures.

**1a**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.76 (s, 72H), 4.26 (s, 8H), 7.77 (t,  $J = 7.4$  Hz, 4H), 7.95 (d,  $J = 7.4$  Hz, 4H), 8.02 (d,  $J = 7.4$  Hz, 4H), 8.71 (s, 16H), 8.77 (s, 4H), 8.81 (s, 4H), 8.91 (s, 8H). MALDI-TOF MS: calcd. for  $\text{C}_{148}\text{H}_{124}\text{N}_4$   $[\text{M}]^+$ :  $m/z = 1956.98$ ; found: 1956.96.

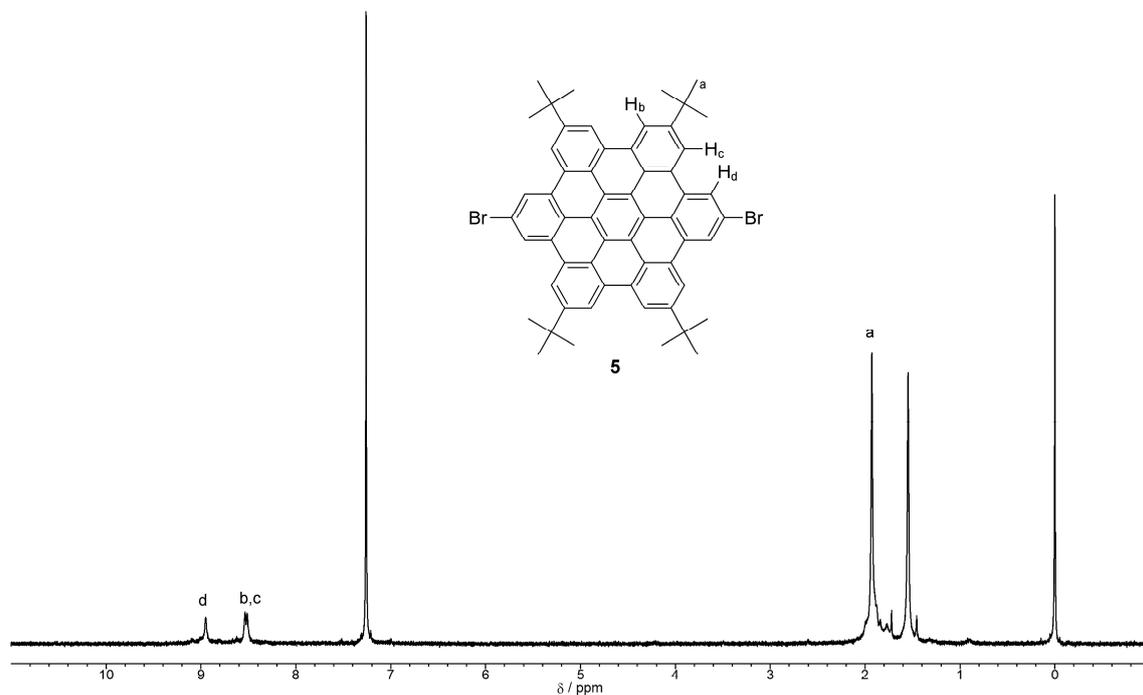
**1b**: yellow crystals,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  1.70 (s, 72H), 4.00 (brs, 16H), 7.63 (t,  $J = 7.5$  Hz, 4H), 7.88 (d,  $J = 7.5$  Hz, 4H), 7.92 (d,  $J = 7.5$  Hz, 4H), 8.28 (s, 4H), 8.53 (s, 4H), 8.67 (s, 8H), 8.73 (s, 8H), 8.75 (s, 8H). MALDI-TOF MS: calcd. for  $\text{C}_{152}\text{H}_{132}\text{N}_4\text{O}_2$   $[\text{M}]^+$ :  $m/z = 2045.0$ ; found: 2044.8.

**1c**: yellow crystals,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  1.80 (s, 72H), 3.78 (s, 8H), 3.90 (t,  $J = 4.9$  Hz, 8H), 3.94 (t,  $J = 4.9$  Hz, 8H), 7.80 (t,  $J = 7.7$  Hz, 4H), 8.08 (d,  $J = 7.7$  Hz, 4H), 8.16 (d,  $J = 7.7$  Hz, 4H), 8.21 (s, 4H), 8.37 (s, 4H), 8.72 (s, 8H), 8.75 (s, 8H), 8.78 (s, 8H). MALDI-TOF MS: calcd. for  $\text{C}_{156}\text{H}_{140}\text{N}_4\text{O}_4$   $[\text{M}]^+$ :  $m/z = 2133.1$ ; found: 2132.8.

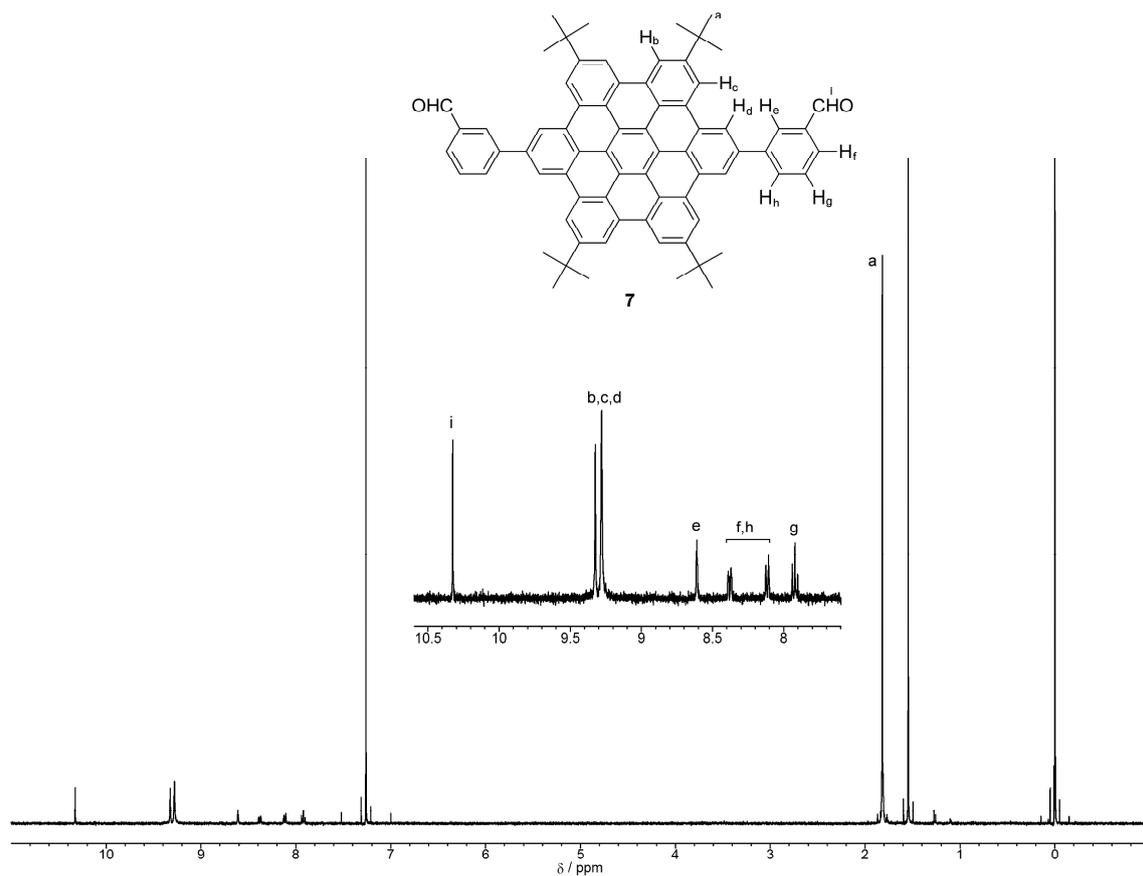
## References

- [1] K. Harada, H. Hart and C.-J. F. Du, *J. Org. Chem.*, 1985, **50**, 5524–5528.
- [2] G. Hugel, M. Lerer and C. Fabre, *Bull. Chim. Soc. Fr.* 1954, 836–842.
- [3] H. Konno, S. Aimoto, S. O. Smith, K. Nosaka and K. Akaji, *Bioorg. Med. Chem.*, 2009, **17**, 5769–5774.
- [4] G. W. Kabalka, U. Sastry, K. A. R. Sastry, F. F. Knapp, Jr. and P. C. Srivastava, *J. Organomet. Chem.*, 1983, **259**, 269–274.
- [5] C. M. Thompson, G. T. McCandless, S. N. Wijenayake, O. Alfarawati, M. Jahangiri, A. Kokash, Z. Tran and R. A. Smaldone, *Macromolecules*, 2014, **47**, 8645–8652.
- [6] Y. Li, C. Zhang and S. Zheng, *Eur. Polym. J.*, 2011, **47**, 1550–1562.

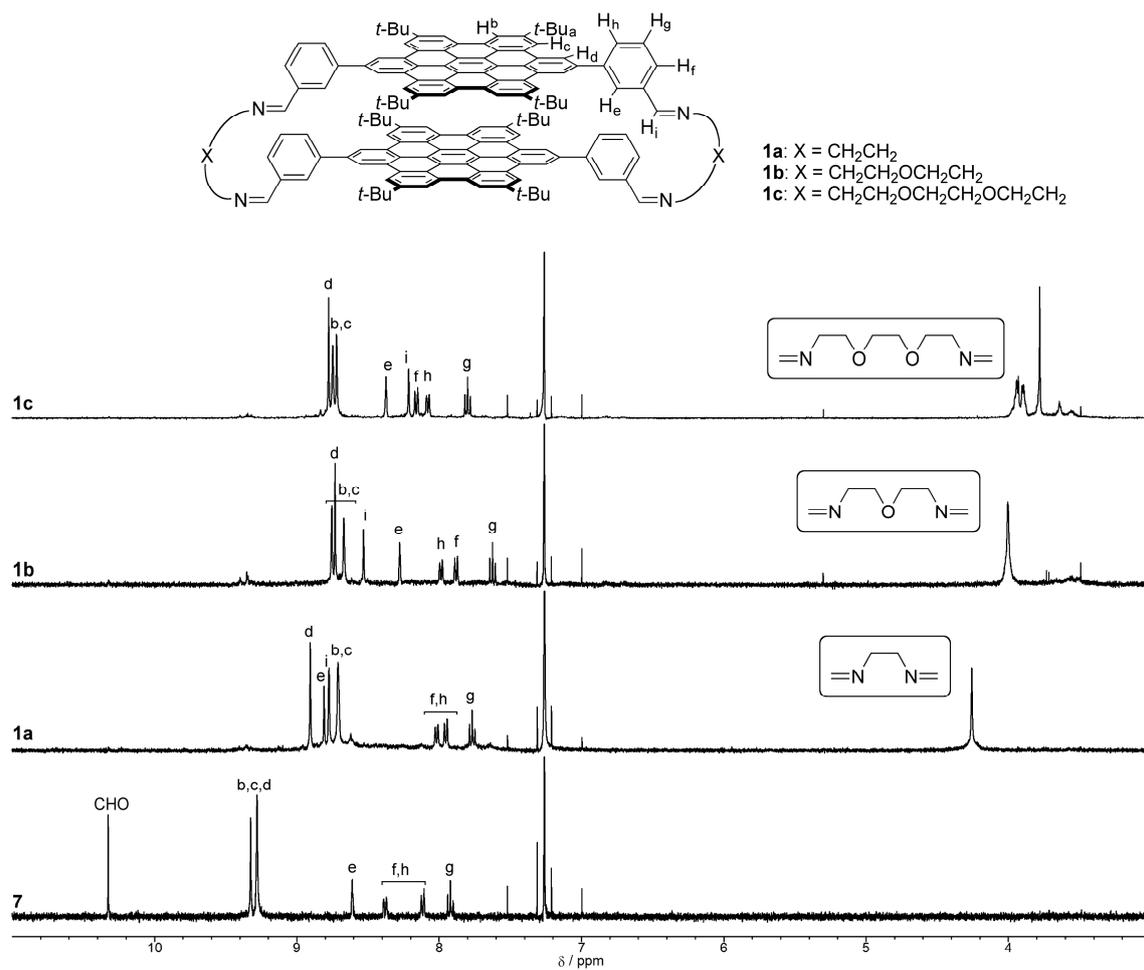
## Supporting Figures



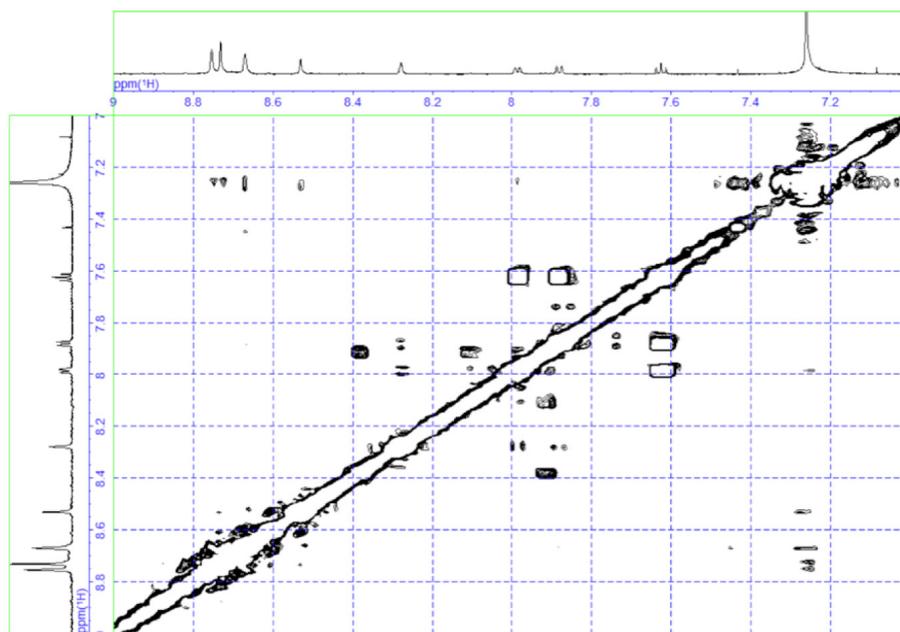
**Figure S1.** <sup>1</sup>H NMR spectrum of 5 (400 MHz, CDCl<sub>3</sub>)



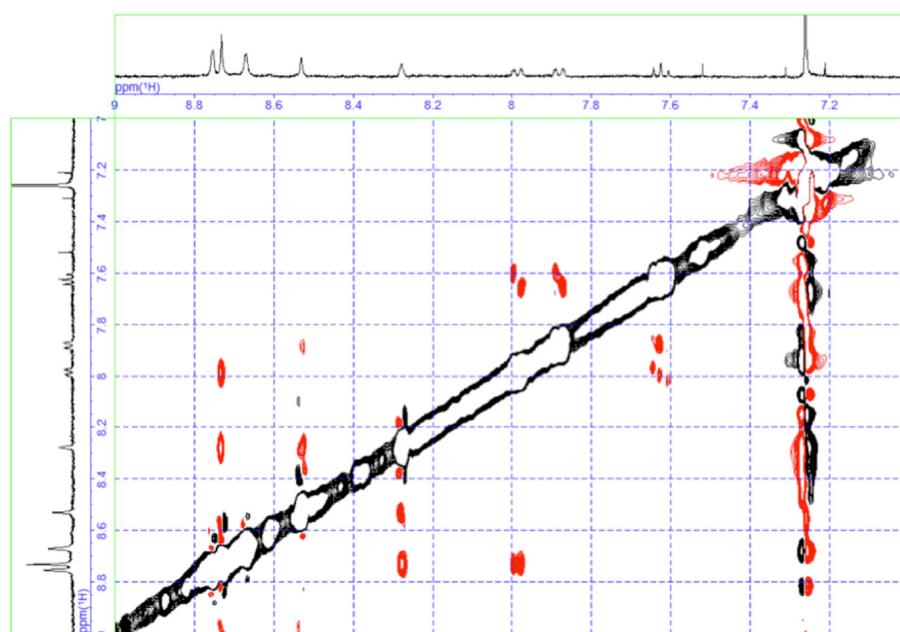
**Figure S2.** <sup>1</sup>H NMR spectrum of 7 (400 MHz, CDCl<sub>3</sub>).



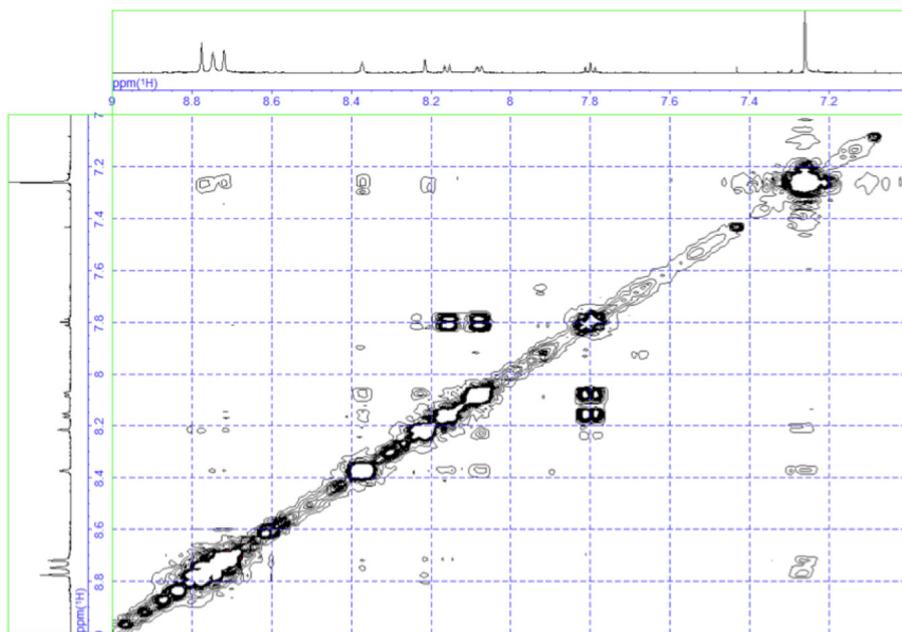
**Figure S3.** <sup>1</sup>H NMR spectra of macrocycles **1a**, **1b**, **1c**, and **7** (400 MHz, CDCl<sub>3</sub>).



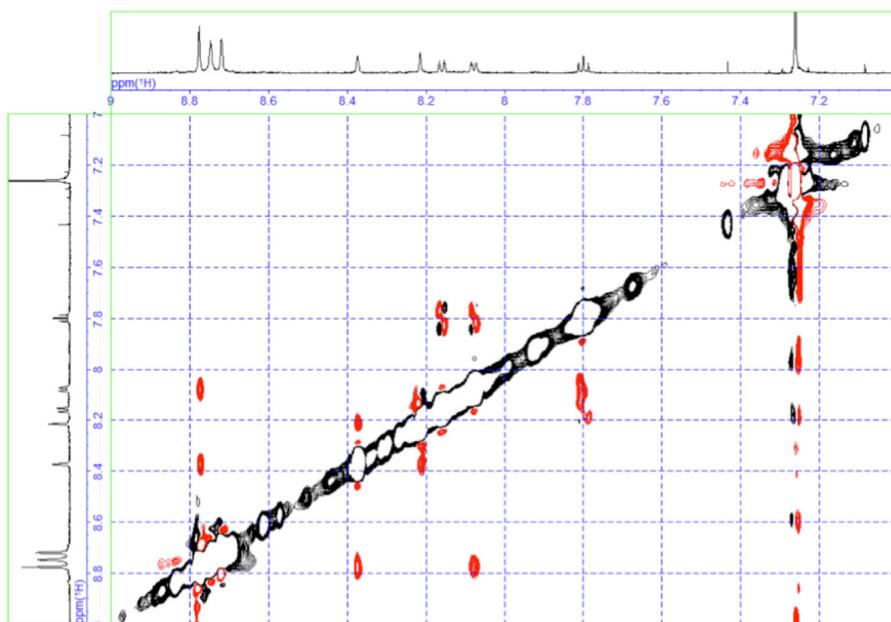
**Figure S4.** HH COSY spectrum of macrocycle **1b** (400 MHz, CDCl<sub>3</sub>).



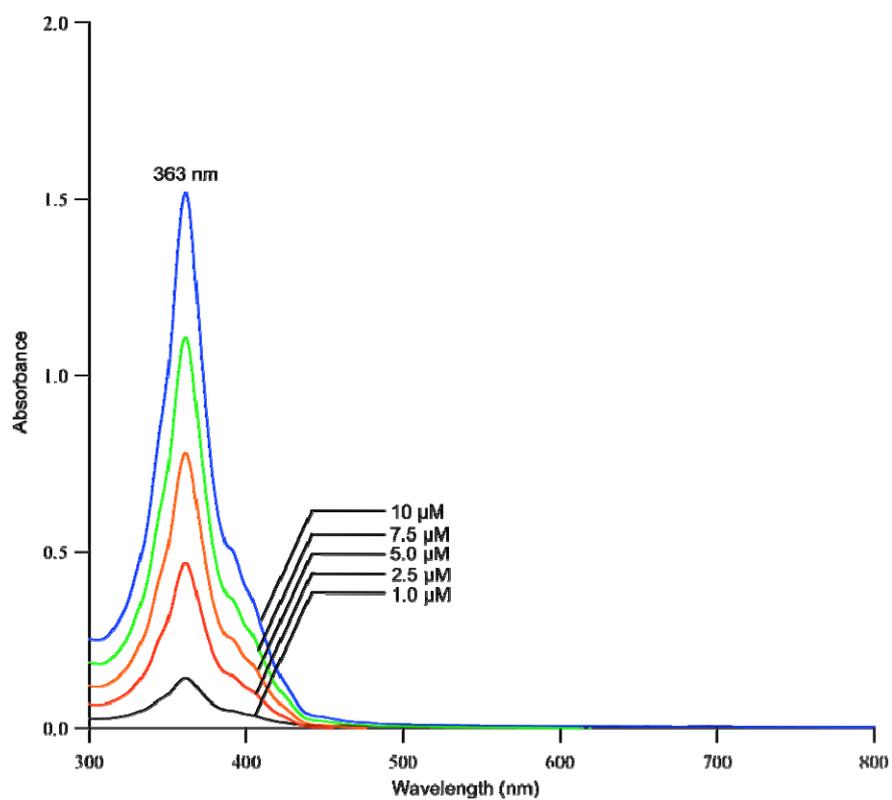
**Figure S5.** ROESY spectrum of macrocycle **1b** (600 MHz, CDCl<sub>3</sub>).



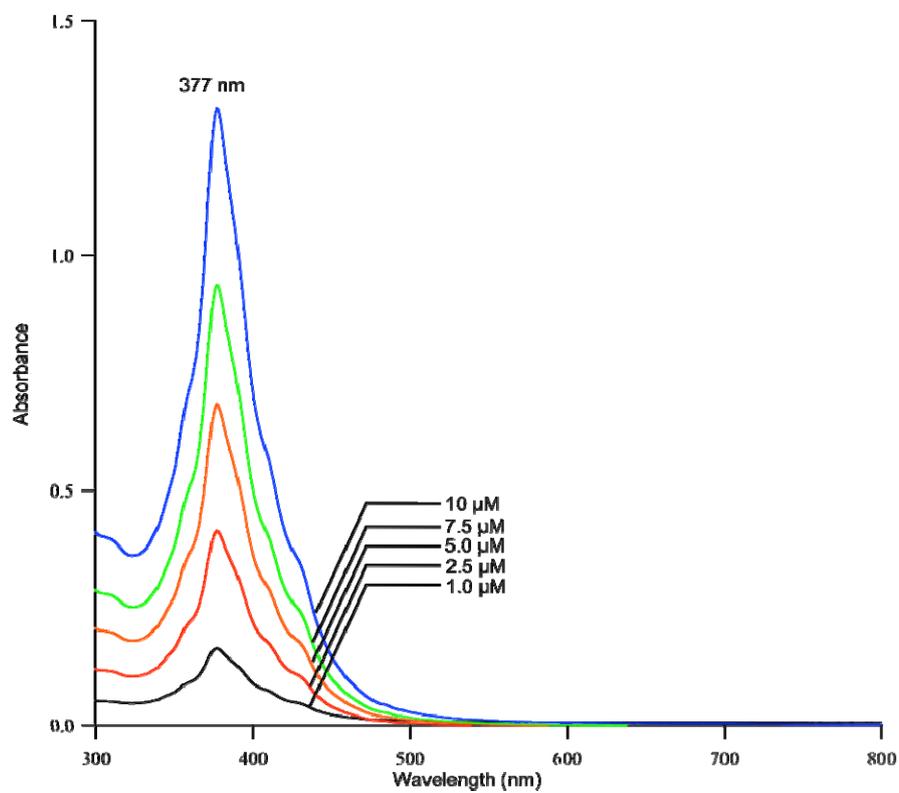
**Figure S6.** HH COSY spectrum of macrocycle **1c** (600 MHz, CDCl<sub>3</sub>).



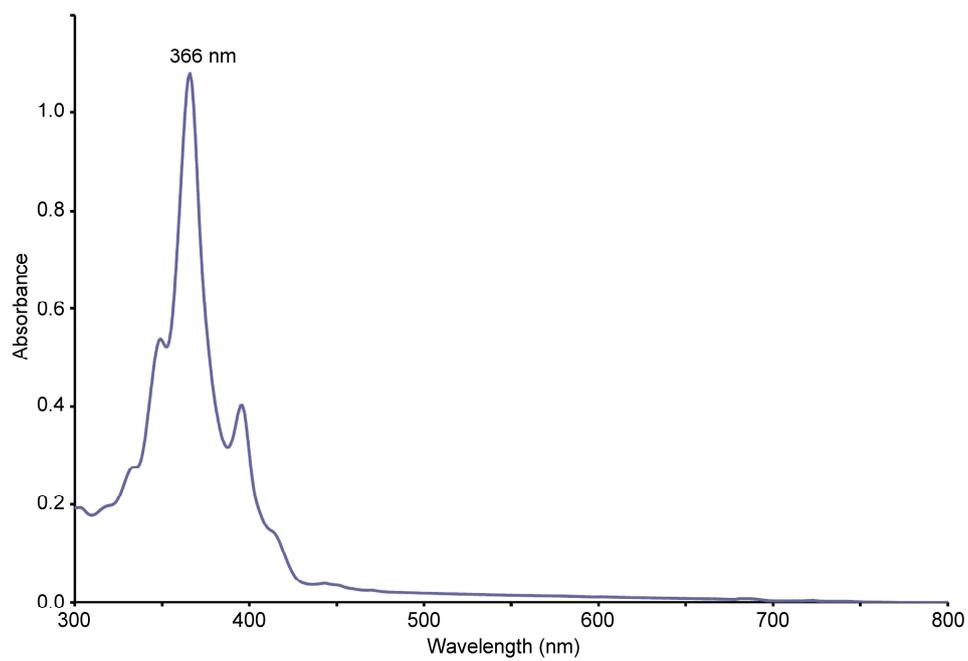
**Figure S7.** ROESY spectrum of macrocycle **1c** (600 MHz, CDCl<sub>3</sub>).



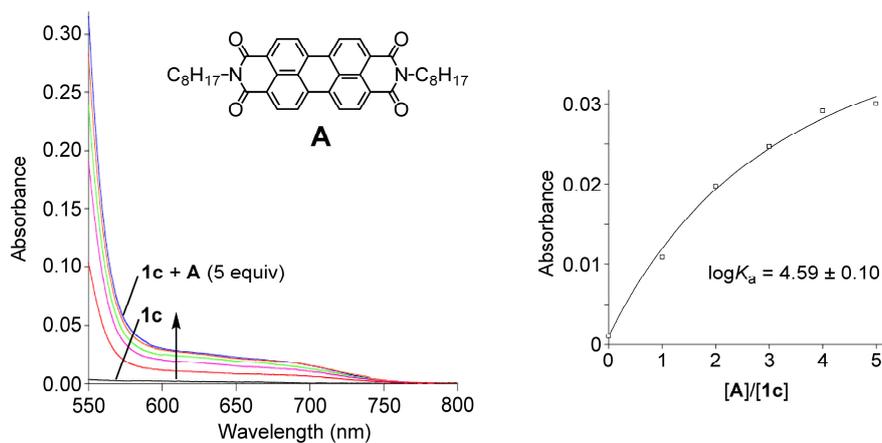
**Figure S8.** UV-vis absorption spectra of macrocycle **1b** in different concentrations.



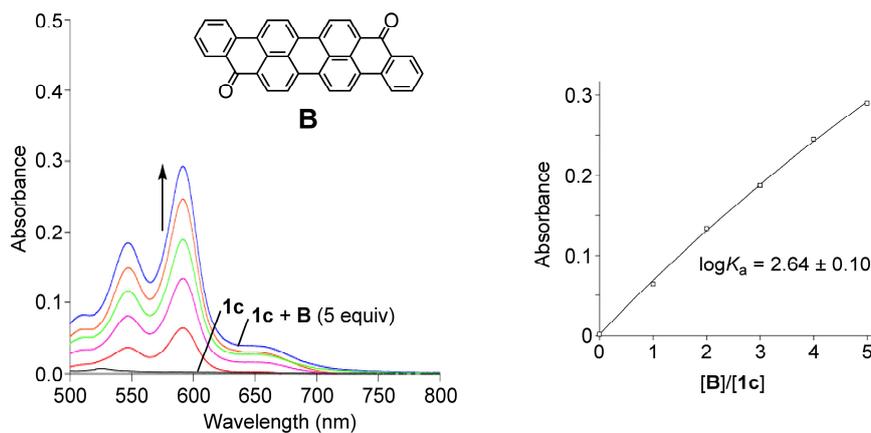
**Figure S9.** UV-vis absorption spectra of macrocycle **1c** in different concentrations.



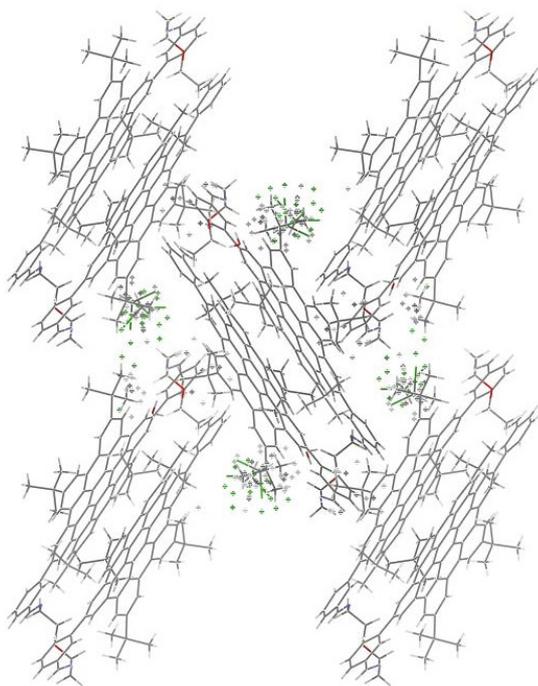
**Figure S10.** UV-vis absorption spectrum of dialdehyde **7** (5 μM).



**Figure S11.** UV-vis spectral changes of macrocycle **1c** upon the addition of perylene bisimide derivative **A** in chloroform,  $[1c] = 10 \mu\text{M}$ .



**Figure S12.** UV-vis spectral changes of macrocycle **1c** upon the addition of isoviolanthrone (**B**) in chloroform,  $[1c] = 10 \mu\text{M}$ .



**Figure S13.** Packing diagram of the crystal of macrocycle **1b**.