SUPPORTING INFORMATION:

2D-Assembly of Metallacycles on HOPG by Shape-Persistent Macrocycle Templates

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STM investigations.

The samples were prepared on freshly cleaved surfaces of HOPG (grade ZYB). Briefly, for the macrocycle arrays, a drop of 1-phenyloctane solution containing **1** or **2** was directly deposited onto HOPG and used for STM measurement. However, for the bilayer structures, a drop of square or rectangular metallacycles dissolved in 1-phenyloctane was directly added onto the macrocycle monolayer.

STM experiments were carried out with a NanoScope IIIa microscope (Digital Instrument). The tunneling tips were prepared by mechanical cutting of Pt/Ir (90/10). The experiments were repeated by using several tips and different samples to check for reproducibility. The imaging parameters are given in the figure captions: bias voltage (V_{bias}), and tunneling current (I_t). All STM images of molecular adsorbates have been corrected for drift with respect to the HOPG lattice.

Additional STM results

4 on HOPG

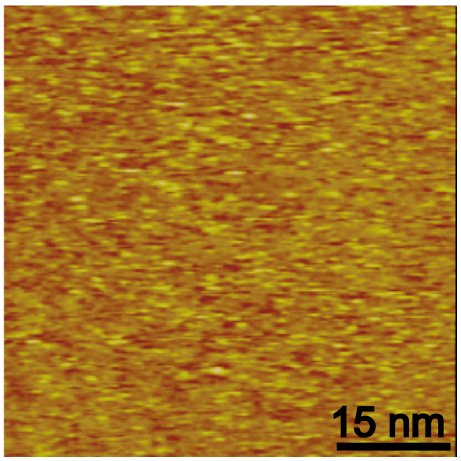


Figure S1. Typical STM image of metallacycles **4** on HOPG. Similar STM image has been recorded for metallacycles **3** on HOPG.

1/4 on HOPG under Different Conditions

Figure S2 is an STM image of **1/4** recorded under the different tunneling conditions from Figure 4 (of the main text), showing an obvious gap between adjacent metallacycles, though the quality is not so good.

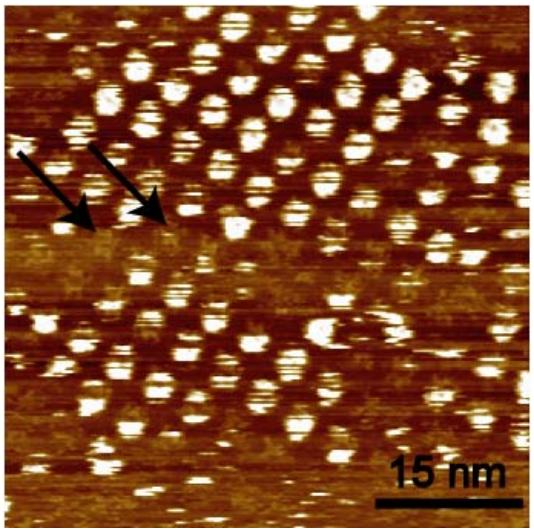
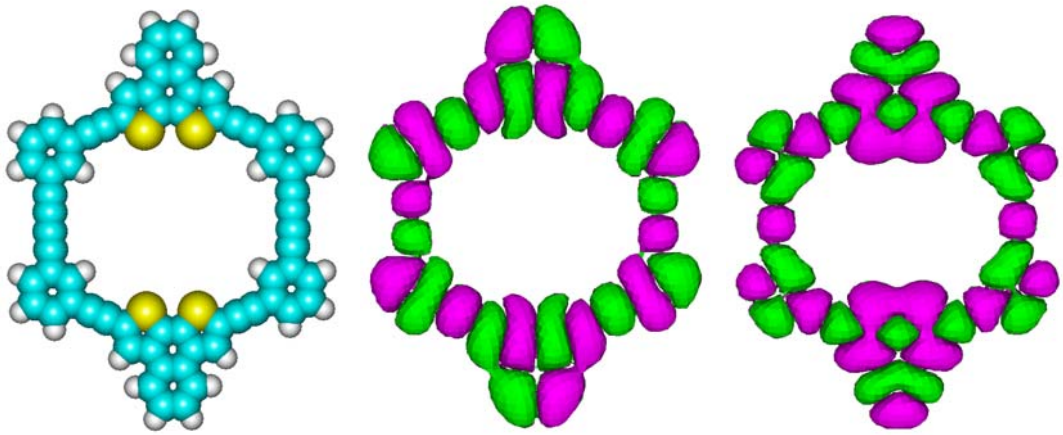


Figure S2: High-resolution STM image of **1/4** on HOPG. V_{bias} = 619.2 mV; I_t = 900.7 pA.

Molecular Modelling.

The optimized geometry and electronic density of the HOMO and LUMO of the rigid ring of the macrocycle calculated by the AM1 method are shown.



HOMO **LUMO**

Figure S3. Frontier orbitals of **1** and **2**.

Macrocycle-Metallacycle Complexes.

The molecular models of macrocycle, square metallacycle, and rectangular metallacycle were built in the Spartan. The interatomic separations and molecular sizes quoted in this study were estimated from these molecular models.

Each individual structure (monomer) is geometry optimized on a force field level, assuming square-planar Pt coordination, high symmetry, planar backbones, and for the macrocycle interaction with a graphene layer. The force field calculations of the dimers (shown here) did not converge, however a few geometry optimization steps were performed in each case to yield realistic distances. The charges of the Pt centers are not considered, and the origin of the host guest interaction is not yet clearly understood.

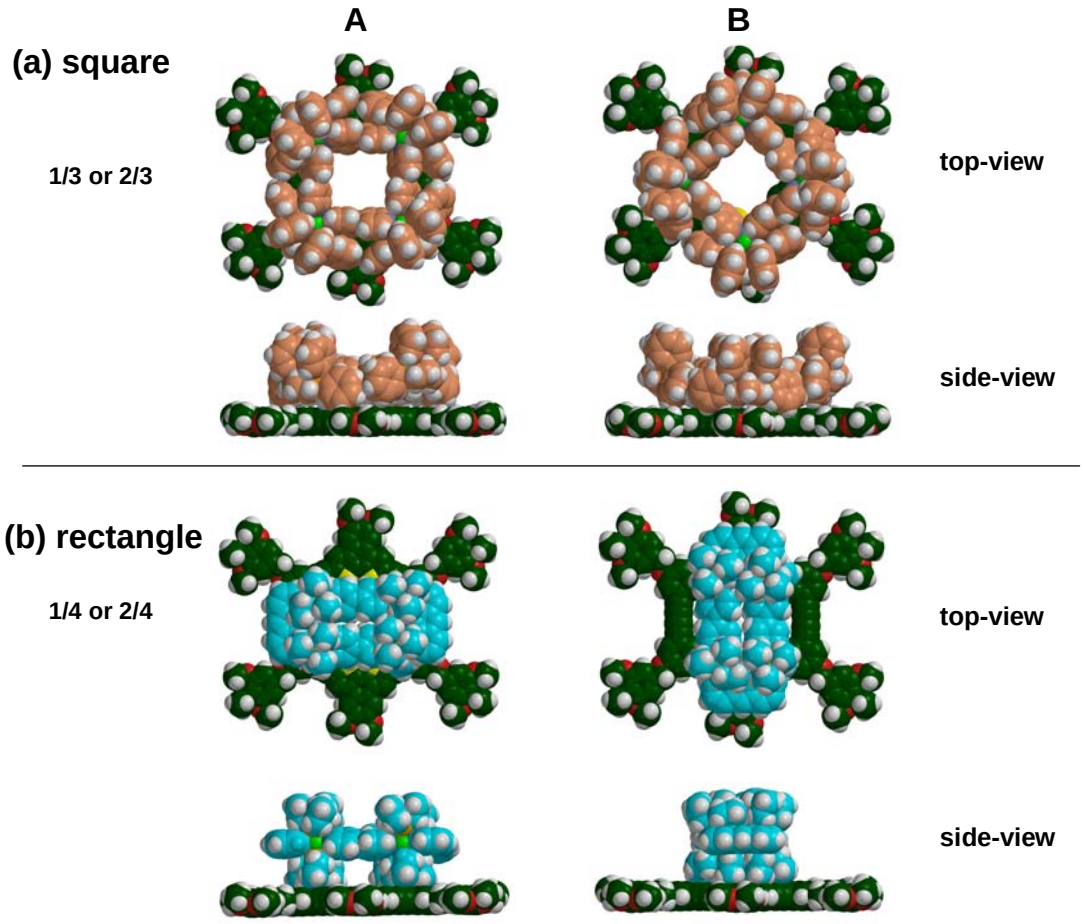
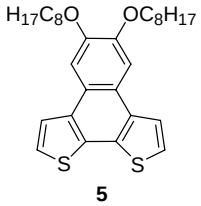


Figure S4: Simulated structures, demonstrating possible dimer geometries and relative sizes of macrocycles (**1,2**) and metallacycles (**3,4**).

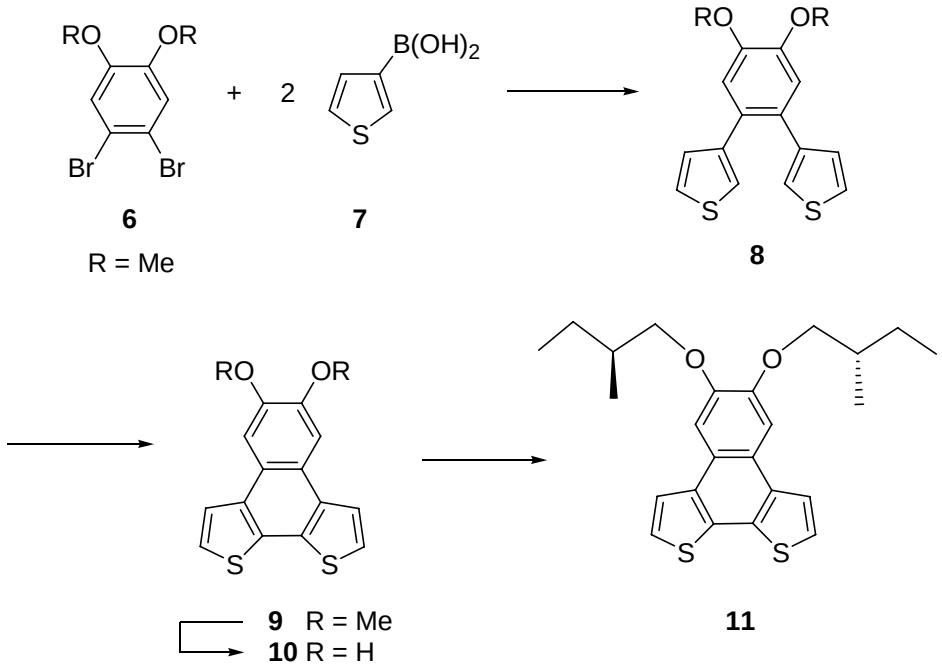
Synthesis.

General. Solvents were dried, distilled and stored under argon if necessary. Reagents were purchased at reagent grade from commercial sources and used without further purification. Unless otherwise stated, acid, base, and salt solutions are aqueous. All water- and/or air-sensitive reactions were carried out in preheated glasware under argon, using standard Schlenk-techniques. Thin-layer chromatography (TLC) was performed on aluminum plates pre-coated with silica gel and fluorescence indicator from Macherey-Nagel (Alugram SIL G/UV 0.25 mm). Column chromatography was performed with Merck silica gel 60 (230 ± 400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 250 (^{1}H, 250 MHz), Bruker AM 300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) and Bruker AM 400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) spectrometers, respectively. Chemical shifts are reported as δ values (ppm) and referenced to residual ^{1}H or ^{13}C signals in deuterated solvents. The MALDI-TOF measurements were carried out on a Bruker Daltronics autoflex TOF/TOF. The mass scale was calibrated with narrow-MWD polystyrene standards. DCTB or Dithranol was used as matrix. EI-MS data were obtained from a MS-50 by A.E.I. Analytical gel permeation chromatography (GPC) measurements were carried out by using an Agilent Technologies instrument with a set of 4 columns (PSS polymer standards service, Mainz, Germany, polystyrene, 8 mm * 300 mm, 10^{2}, 10^{3}, 10^{5} and 10^{6} Å respectively) equipped with IsoPump G1310A, autosampler ALS G1329A, UV-detector VWD G1314B and refractive index (RI) detector RID G1362A, with THF (1 mL / min, HPLC grade, Fisher) as eluent. Universal calibration was performed with polystyrene standards (PSS polymer standards service, Mainz, Germany). Preparative recycling GPC was performed on a Shimadzu instrument equipped with a LC 20-AD pump, a DGU-20 A_3 degasser, a SIL-20 A HAT autosampler, a SPD-20 A UV-Vis detector, a CTO-20 AC column oven, a FRC-10 A fraction collector and FCV-20 AH_2 valves. A set of three GPC columns (PSS polymer standard service, Mainz, Germany; polystyrene, 20mm * 300mm, 10^{3} Å) were used with THF (6 mL / min, HPLC grade, Fisher) as eluent.



5

Figure S5. Structure of bithiophene **5.** **5** was synthesized according to literature procedures.[S1]



Scheme S1. Synthesis of the chiral bthiophene compound **11**.

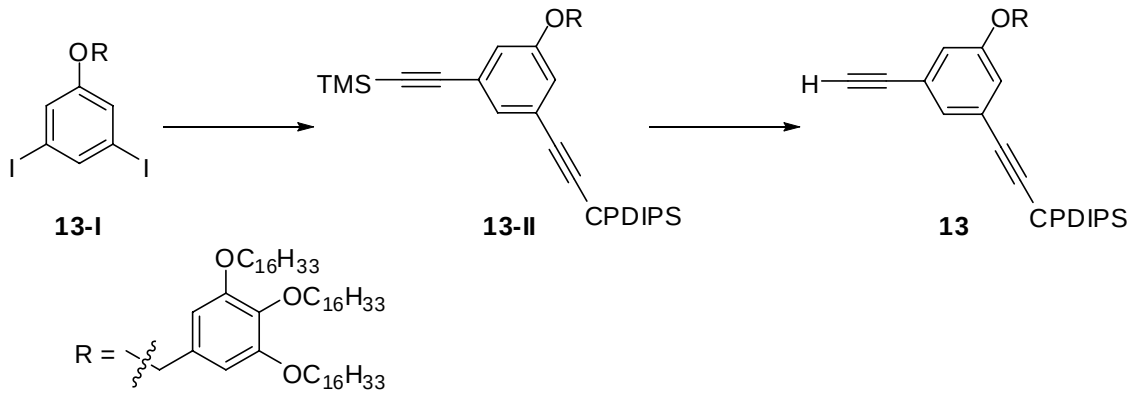
8: 5.0 g (39 mmol) 3-thiophene boronic acid (**7**), 5.24 g (17.7 mmol) dibromo-4,5-dimethoxybenzene (**6**) and 15 g (141 mmol) Na_2CO_3 were suspended in a mixture of toluene (140 mL), ethanol (36 mL) and water (36 mL). The resulting mixture was degassed by passing a slight argon-stream through the solution for 2 h. Afterwards 816 mg (0.71 mmol) $Pd(PPh_3)_4$ was added and the solution heated to reflux for 20 h. After cooling to rt the mixture was diluted with dichloromethane and washed with water, saturated $NaHCO_3$ solution and brine and dried over $MgSO_4$. After removal of the solvent the residue was purified by column chromatography on silica gel using a mixture of dichloromethane – petroluem ether (1:1) as eluent. After evaporation of the solvent, **8** was received as a colourless solid by precipitation from dichloromethane – methanol (4.35 g, 14.4 mmol, 81 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (dd, 2 H, J = 3.0 Hz, J = 4.9 Hz), 7.03 (dd, 2 H, J = 1.3 Hz, J = 3.0 Hz), 6.79 (dd, 2 H, J = 1.3 Hz, J = 5.0 Hz), 3.93 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.2, 141.9, 129.0, 127.9, 124.6, 122.4, 113.2, 56.1; EI MS *m/z* (M^+) calcd for $C_{16}H_{14}O_2S_2$: 301.9; found: 302.0.

9: 1.0 g (3.3 mmol) **8** were dissolved in 250 mL of dry dichloromethane. Under vigorous stirring a solution of 1.12 g (6.9 mmol) $FeCl_3$ in dry nitromethane (20 mL) was added and the resulting mixture was stirred for additional 15 min. Then 1.0 g (16.5 mmol) zinc powder was added and the slurry was filtered. The organic solvent was removed from the filtrate and the residue was purified by column chromatography on silica gel using a dichloromethane –

petroleum ether (1:3) as eluent. **9** was received as a colourless solid (557 mg, 1.85 mmol, 56 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, 2 H, J = 5.4 Hz), 7.68 (s, 2 H), 7.49 (d, 2 H, J = 5.4 Hz), 4.10 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.7, 133.8, 130.6, 123.6, 122.6, 122.4, 104.7, 56.0; EI MS *m/z* (M^+) calcd for $C_{16}H_{12}O_2S_2$: 300.0; found: 300.0.

10: 527 mg (1.75 mmol) **9** were dissolved in dry dichloromethane (10 mL) and cooled to -78 °C. 8.8 mL of a 1M solution of BBr_3 in dichloromethane was added dropwise. The resulting mixture was allowed to warm to rt and stirred over night. The solution was diluted with dichloromethane and water. The organic phase was separated, washed with water, saturated $NaHCO_3$-solution and brine, dried and the solvent was removed. The greenish solid of crude **10** was used for the next step without further purification (467 mg, 1.72 mmol, 98 %). ^{1}H NMR (MeOH-d4, 400 MHz) δ 7.80 (d, 2 H, J = 5.4 Hz), 7.70 (s, 2 H), 7.42 (d, 2 H, J = 5.4 Hz), 4.67 (bs, 2 H); ^{13}C NMR ($CDCl_3$ + MeOH-d4, 100 MHz) δ 144.8, 133.3, 129.2, 122.5, 122.1, 122.0, 107.6; EI MS *m/z* (M^+) calcd for $C_{14}H_8O_2S_2$: 272.0; found 272.0.

11: A mixture of crude **10** (224 mg, 0.82 mmol), (S)-(+)-1-bromo-2-methylbutane (273 mg, 1.81 mmol), Cs_2CO_3 (1.34 g, 4.11 mmol) and KI (14 mg, 0.08 mmol) in DMF (8 mL) was stirred for 4 d at 80 °C. After cooling to rt the reaction mixture was diluted with diethyl ether and water. The organic layer was separated, washed with water, saturated $NaHCO_3$ solution and brine, dried and the solvent was removed. Purification was achieved by column chromatography on silica gel using petroleum ether – dichloromethane (3:1) as eluent. **11** was received as a colourless solid (204 mg, 0.49 mmol, 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, 2 H, J = 5.4 Hz), 7.69 (s, 2 H), 7.46 (d, 2 H, J = 5.4 Hz), 4.09 – 3.97 (m, 4 H), 2.09 – 2.02 (m, 2 H), 1.76 – 1.65 (m, 2 H), 1.45 – 1.34 (m, 2 H), 1.14 (d, J = 6.8 Hz, 6 H), 1.03 (t, J = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.1, 133.9, 130.3, 123.3, 122.7, 122.6, 106.7, 73.9, 34.9, 26.3, 16.7, 11.5; EI MS *m/z* (M^+) calcd for $C_{24}H_{28}O_2S_2$: 412.2; found: 412.2.



Scheme S2. Synthesis of compound **13**.

13-II

A mixture of **13-I**[S2] (5.70 g, 4.93 mmol), $PdCl_2(PPh_3)_2$ (173 mg, 0.25 mmol), CuI (116mg, 0.61 mmol) and PPh_3 (173 mg, 0.66 mmol) was dissolved in THF (40 mL) and piperidine (1.5 mL, 14.8 mmol). CPDIPS-acetylene[S3] was added and the mixture was stirred at rt for 4.5 h. After addition of TMS-acetylene (726 mg, 7.4 mmol) the reaction mixture was continuously stirred at rt over night. The reaction mixture was diluted with diethyl ether and water. The organic layer was separated, washed with water and brine, dried over $MgSO_4$ and the solvent was removed in vacuum. Purification was achieved by column chromatography on silica gel using petroleum ether – dichloromethane (3:2, then 1:1) as eluent. After precipitation from CH_2Cl_2 / cold EtOH, **14** was received as a greyish solid (2.65 g, 2.2 mmol, 45 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19 (t, 1 H, J = 1.3 Hz), 7.06 – 7.01 (m, 2 H), 6.59 (s, 2 H), 4.92 (s, 2 H), 4.00 – 3.92 (m, 6 H), 2.43 (t, 2 H, J = 6.9 Hz), 1.90 – 1.70 (m, 8 H), 1.52 – 1.41 (m, 6 H), 1.38 – 1.21 (m, 76 H), 1.13 – 1.06 (m, 12 H), 0.91 – 0.85 (m, 9 H), 0.26 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.2, 153.3, 138.0, 131.1, 128.3, 124.3, 124.0, 119.6, 118.9, 118.5, 106.7, 106.1, 103.8, 94.9, 89.9, 73.4, 70.6, 69.1, 31.9, 30.3, 29.7, 29.7, 29.7, 29.6, 29.6, 29.6, 29.6, 29.4, 29.4, 29.3, 26.1, 26.1, 22.6, 21.2, 20.7, 18.1, 17.9, 14.1, 11.6, 9.5, -0.1; ESI MS *m/z* (M^+) calcd for $C_{78}H_{135}NO_4Si_2$: 1206.9; found: 1229.9 [M^+ + Na].

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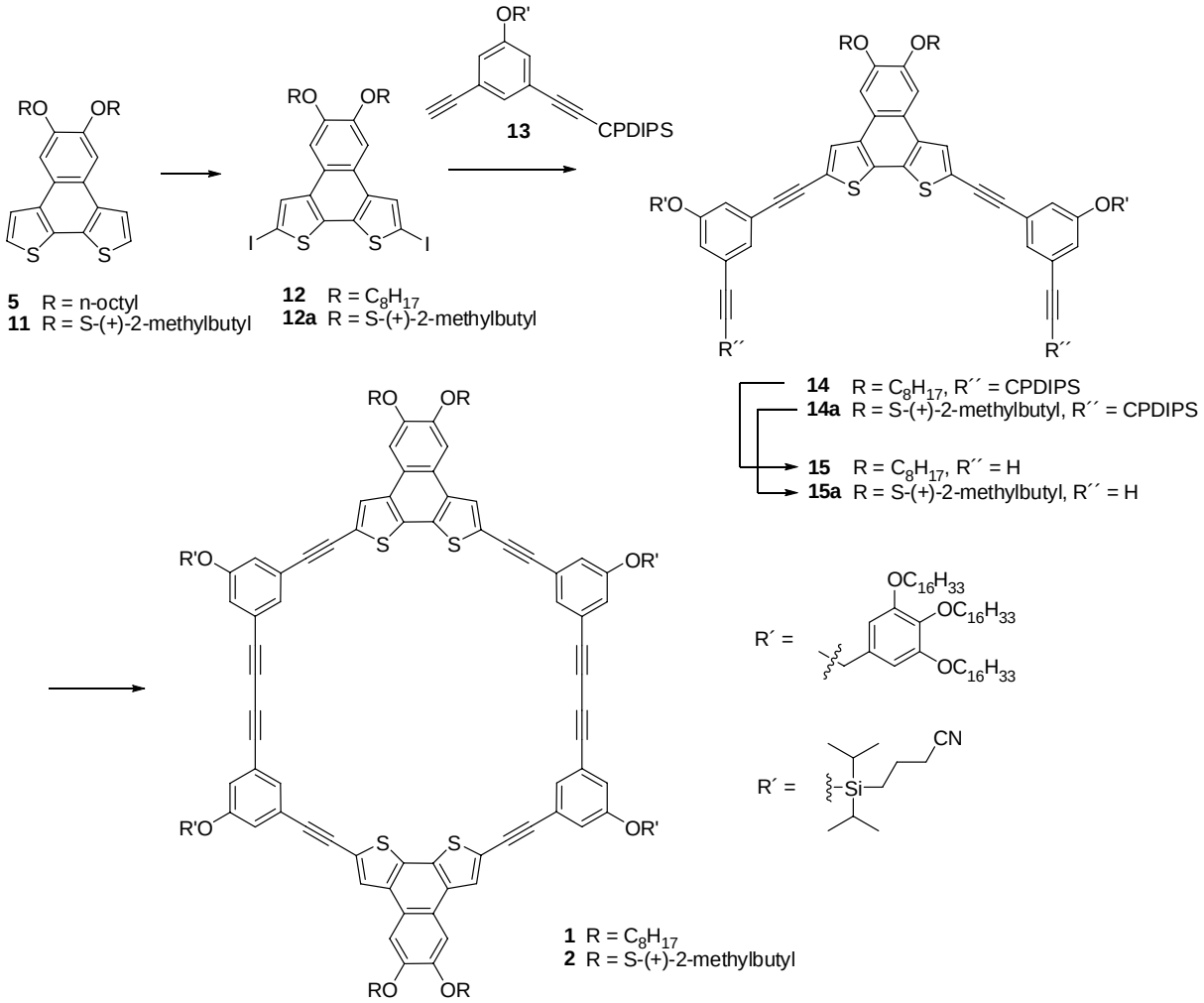
Compound **13-II** (1.33 g, 1.1 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) were suspended in THF (100 mL) and MeOH (40 mL) and stirred at rt over night. The reaction mixture was diluted with diethyl ether and water. The organic layer was separated, washed with water, saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$ and the solvent was removed in vacuum. Purification was achieved by column chromatography on silica gel using petroleum ether –

dichloromethane (1:1) as eluent. **14** was received as a colourless, waxy solid (900 mg, 0.79 mmol, 72 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (t, 1 H, J = 1.3 Hz), 7.07 – 7.05 (m, 2 H), 6.59 (s, 2 H), 4.93 (s, 2 H), 3.99 – 3.92 (m, 6 H), 3.06 (s, 1 H), 2.43 (t, 2 H, J = 6.9 Hz), 1.90 – 1.70 (m, 10 H), 1.51 – 1.42 (m, 6 H), 1.39 – 1.22 (m, 74 H), 1.12 – 1.06 (m, 12 H), 0.91 – 0.85 (m, 9 H); 13C NMR ($CDCl_3$, 100 MHz): δ 158.2, 153.3, 138.0, 131.0, 128.5, 124.2, 123.3, 119.6, 119.0, 118.8, 106.5, 106.1, 90.1, 82.5, 77.7, 73.4, 70.6, 69.1, 31.9, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 26.1, 26.1, 22.6, 21.2, 20.7, 18.1, 17.9, 14.1, 11.6, 9.5; MS (MALDI-TOF, DCTB) *m/z* (M^+) calcd for $C_{75}H_{127}NO_4Si$: 1134.0; found: 1133.9.



Scheme S3. Synthesis of macrocycles **1** and **2**, respectively.

12: A mixture of THF (10 mL) and TMEDA (428 mg, 3.68 mmol) was cooled to -78 °C and then 1.73 mL of a 1.6M solution of n-BuLi in hexane was added. After 10 min a solution of **5** (459 mg, 0.92 mmol) in THF (10 mL) was added dropwise and stirred for another 30 min at -78 °C. A solution of iodine (1.64 g, 6.44 mmol) in THF (5 mL) was added and the reaction mixture was allowed to warm to rt over night. The reaction mixture was diluted by adding 10 mL of an aqueous 2M KOH solution. Chloroform was added, the organic layer separated and washed with water and brine, dried and the solvent was removed. The resulting solid was reprecipitated from chloroform – methanol to give **12** as a faint yellow solid (619 mg, 0.83 mmol, 90 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (s, 2 H), 7.50 (s, 2 H), 4.17 (t, 4 H, J = 6.6 Hz), 1.94 (m, 4 H), 1.61 – 1.51 (m, 4 H), 1.46 – 1.27 (m, 16 H), 0.90 (t, 6 H, J = 6.9 Hz); 13C NMR ($CDCl_3$, 100 MHz) δ 149.2, 134.9, 134.0, 132.3, 121.3, 106.1, 73.9, 69.2, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1; EI MS *m/z* (M^+) calcd for $C_{30}H_{38}I_2O_2S_2$: 748.0; found: 748.0.

12a: **12a** was synthesized analogue to **12**. Precipitation from chloroform – methanol provides **12a** as faint yellow crystals (345 mg, 0.52 mmol, 87 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (s, 2 H), 7.44 (s, 2 H), 4.04 – 3.93 (m, 4 H), 2.08 – 1.99 (m, 2 H), 1.75 – 1.64 (m, 2 H), 1.44 – 1.33 (m, 2 H), 1.13 (d, J = 6.8 Hz, 6 H), 1.03 (t, J = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.5, 134.9, 133.8, 132.3, 121.2, 105.9, 73.8, 34.9, 26.3, 16.7, 11.4; EI MS *m/z* (M^+) calcd for $C_{24}H_{28}I_2O_2S_2$: 664.0; found: 663.9.

14: A mixture of **12** (178 mg, 0.24 mmol), **13** (600 mg, 0.53 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), CuI (6mg, 0.03 mmol) and PPh_3 (10 mg, 0.04 mmol) in THF/piperidine (13 mL/6 mL) was stirred at rt for 48 h. The reaction mixture was diluted with diethyl ether and water. The organic layer was separated, washed with water, saturated $NaHCO_3$-solution and brine, dried and the solvent was removed in vacuum. Purification was achieved by column chromatography on silica gel using petroleum ether – dichloromethane (1:2) as eluent. **14** was received as a yellow solid (615 mg, 0.22 mmol, 93 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (s, 2 H), 7.62 (s, 2 H), 7.32 (t, 2 H, J = 1.3 Hz), 7.17 – 7.15 (m, 2 H), 7.11 – 7.09 (m, 2 H), 6.64 (s, 4 H), 4.99 (s, 4 H), 4.20 (t, 4 H, J = 6.6 Hz), 4.04 – 3.94 (m, 12 H), 2.46 (t, 4 H, J = 6.9 Hz), 2.00 – 1.72 (m, 24 H), 1.61 – 1.22 (bm, 180 H), 1.17 – 1.08 (m, 24 H), 0.95 – 0.84 (m, 24 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 153.3, 149.3, 138.1, 134.3, 131.1, 130.5, 127.9, 127.7, 124.3, 123.9, 122.4, 120.9, 119.6, 1190, 117.9, 106.6, 106.1, 94.2, 90.3, 83.7, 73.4, 70.7, 69.1, 31.9, 31.8, 30.3, 29.7, 29.6, 29.4, 29.3, 29.3, 29.2, 26.1, 22.7, 21.3, 20.7, 18.2,

17.9, 14.1, 11.7, 9.5; MS (MALDI-TOF, DCTB) calcd for $C_{180}H_{290}N_2O_{10}S_2Si_2$: 2760.1; found: 2760.2.

14a: **14a** was synthesized analogue to **14**. Purification was achieved by column chromatography using petroleum ether – dichloromethane (1:1) as eluent. **14a** was received as a yellow solid (280 mg, 0.104 mmol, 97 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (s, 2 H), 7.61 (s, 2 H), 7.31 (t, 2 H, J = 1.3 Hz), 7.15 (m, 2 H), 7.09 (m, 2 H), 6.63 (s, 4 H), 4.98 (s, 4 H), 4.06 – 3.95 (m, 16 H), 3.75 (m, 2 H), 2.45 (t, 4 H, J = 6.9 Hz), 2.07 – 2.01 (m, 2 H), 1.92 – 1.65 (m, 24 H), 1.51 – 1.22 (bm, 158 H), 1.15 – 1.08 (m, 24 H), 1.02 (t, 6 H, J = 7.5 Hz), 0.90 – 0.84 (m, 24 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 153.3, 149.6, 138.1, 134.4, 131.1, 130.5, 127.9, 127.8, 124.4, 123.9, 122.4, 120.9, 119.7, 118.9, 117.9, 106.7, 106.2, 106.1, 94.1, 90.2, 83.7, 73.8, 73.4, 70.7, 69.1, 67.9, 34.9, 31.9, 30.3, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.4, 29.3, 26.2, 26.1, 26.1, 25.6, 22.6, 22.6, 21.2, 20.7, 18.1, 18.1, 17.9, 17.9, 16.6, 14.1, 11.7, 11.6, 11.4, 9.5; MS (MALDI-TOF, DCTB) calcd for $C_{180}H_{278}N_2O_{10}S_2Si_2$: 2677.0; found: 2676.0.

15: **14** (615 mg, 0.22 mmol) was dissolved in 20 mL of THF, 0.9 mL of a 1M solution of TBAF in THF was added and the resulting mixture was stirred for 1 h at rt. The reaction mixture was diluted with diethyl ether and water. The organic phase was separated and washed with water and brine, dried over $MgSO_4$ and the solvent was removed. Purification was achieved by column chromatography on silica gel using petroleum ether – dichloromethane (2:1, later 1:1) as eluent. **15** was received as a yellow solid (480 mg, 0.20 mmol, 91 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 2 H), 7.60 (s, 2 H), 7.32 (t, 2 H, J = 1.3 Hz), 7.17 – 7.15 (m, 2 H), 7.12 – 7.10 (m, 2 H), 6.62 (s, 4 H), 4.98 (s, 4 H), 4.19 (t, 4 H, J = 6.6 Hz), 4.03 – 3.93 (m, 12 H), 3.10 (s, 2 H), 1.99 – 1.90 (m, 4 H), 1.85 – 1.71 (m, 12 H), 1.60 – 1.21 (bm, 176 H), 0.93 – 0.84 (m, 24 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 153.3, 149.3, 138.1, 134.3, 131.0, 130.5, 127.9, 127.7, 123.9, 123.5, 122.4, 120.9, 119.1, 118.2, 106.1, 94.1, 83.6, 82.5, 77.8, 73.4, 70.6, 69.1, 31.9, 31.8, 30.3, 29.7, 29.6, 29.4, 29.3, 29.3, 29.2, 26.1, 22.6, 14.1; MS (MALDI-TOF, DCTB) calcd for $C_{160}H_{252}O_{10}S_2$: 2397.9; found 2397.8.

15a: **15a** was synthesized analogue to **15**. Purification by column chromatography on silica gel using petroleum ether – dichloromethane (1:1) as eluent provided **15a** as a yellow solid (195 mg, 0.084 mmol, 80 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (s, 2 H), 7.57 (s, 2 H), 7.30

(t, 2 H, *J* = 1.3 Hz), 7.16 (m, 2 H), 7.10 (m, 2 H), 6.61 (s, 4 H), 4.96 (s, 4 H), 4.05 – 3.90 (m, 16 H), 3.16 (s, 2 H), 2.04 – 1.96 (m, 2 H), 1.82 – 1.62 (m, 14 H), 1.60 – 1.21 (bm, 158 H), 1.11 (d, 6 H, *J* = 6.8 Hz), 1.01 (t, 6 H, *J* = 7.5 Hz), 0.88 – 0.84 (m, 18 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 153.7, 150.1, 138.2, 134.7, 131.6, 130.7, 128.3, 128.0, 124.3, 123.9, 122.6, 121.2, 119.4, 118.6, 106.5, 106.2, 94.3, 83.9, 82.7, 78.1, 74.2, 73.7, 71.0, 69.4, 35.3, 32.3, 30.7, 30.1, 30.1, 30.1, 30.0, 29.8, 29.7, 26.6, 26.5, 23.0, 16.7, 14.2, 11.6; MS (MALDI-TOF, DCTB) calcd for $C_{154}H_{240}O_{10}S_2$: 2313.8; found 2313.8.

1: Under an argon atmosphere, CuCl (250 mg, 2.5 mmol) and $CuCl_2$ (50 mg, 0.37 mmol) were suspended in pyridine (100 mL) and heated to + 40 °C. A solution of **10** (60 mg, 0.025 mmol) in pyridine (50 mL) was added dropwise over a period of 96 h. After further stirring for 24 h at 40 °C the reaction mixture was diluted with diethyl ether and water. The organic layer was separated and washed with water, 25% aqueous NH_3 solution, saturated $NaHCO_3$-solution and brine. The organic phase was dried over $MgSO_4$ and the solvent removed. The residue was solved in dichloromethane and filtered over silica gel using petroleum ether – dichloromethane (1:1) as eluent. **1** was finally purified by preparative recycling GPC and obtained as a yellow solid (12 mg, 0,0025 mmol, 20 %). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.81 (bs, 4 H), 7.39 (bs, 4 H), 7.11 (bs, 4 H), 6.80 (bs, 4 H), 6.74 (bs, 4 H), 6.62 (s, 8 H), 4.72 (bs, 8 H), 4.13 (m, 8 H), 4.00 – 3.93 (m, 24 H), 1.97 – 1.88 (m, 8 H), 1.85 – 1.73 (m, 24 H), 1.54 – 1.46 (m, 24 H), 1.40 – 1.22 (m, 328 H), 0.96 – 0.92 (m, 12 H), 0.91 – 0.85 (m, 36 H); MS (MALDI-TOF, Dithranol) calcd for $C_{320}H_{500}O_{20}S_4$: 4795.8; found: 4796.1.

2: **2** was synthesized analogue to **1**. After filtration over short column of silica gel (eluent petroleum ether – dichloromethane (1:1)), **1** was finally purified by preparative recycling GPC and obtained as a yellow solid (3 mg, 0,648 µmol, 3 %). MS (MALDI-TOF, Dithranol) calcd for $C_{308}H_{476}O_{20}S_4$: 4623.5; found: 4627.3.

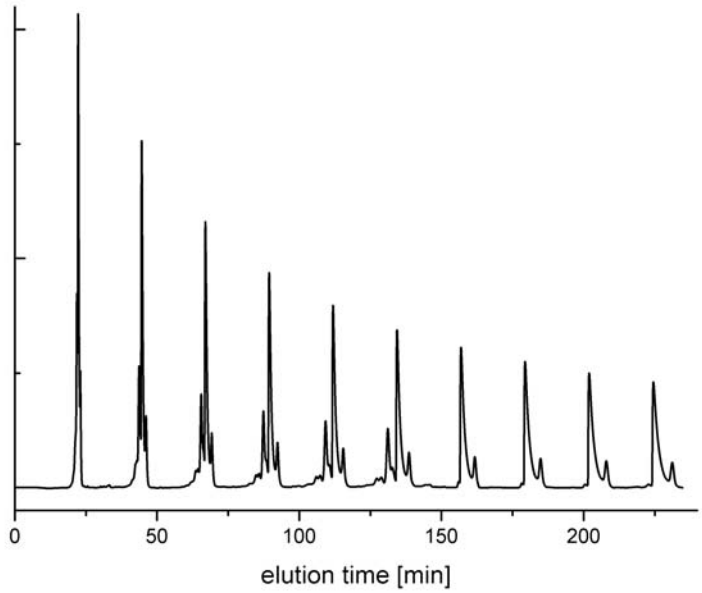


Figure S6. Elution diagram of the purification of macrocycle **1** by recycling GPC.

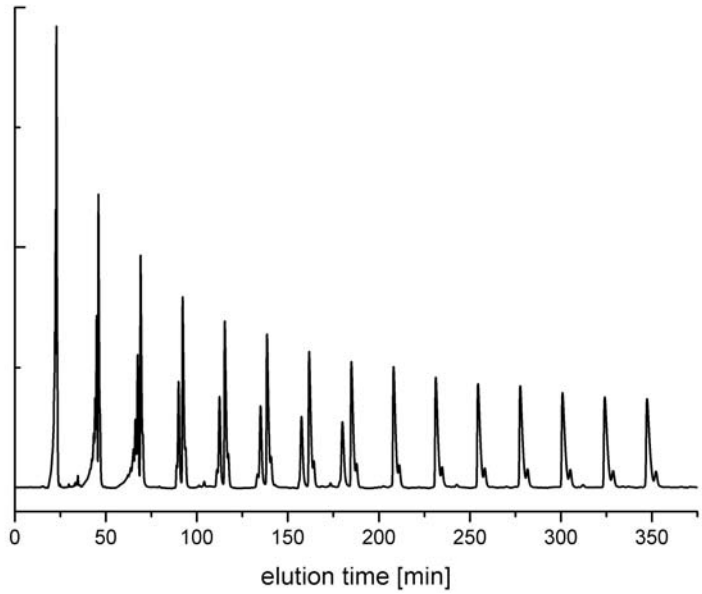


Figure S7. Elution diagram of the purification of macrocycle **2** by recycling GPC.

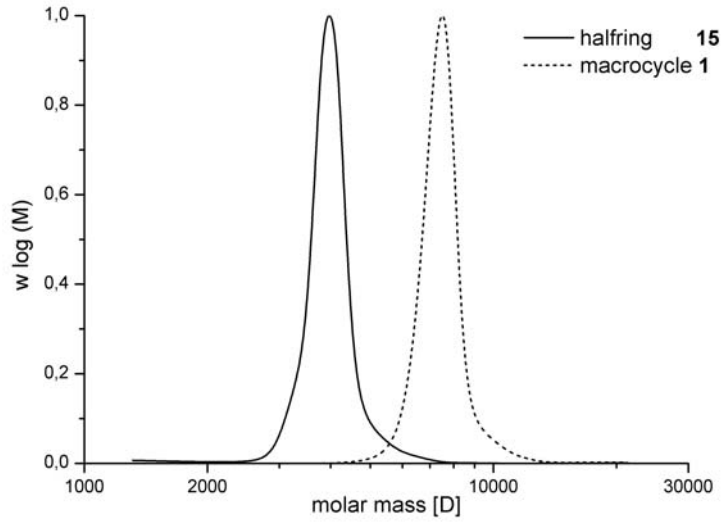


Figure S8. Normalized molar weight distribution from analytical GPC of halfring **15** and macrocycle **1** after purification by recycling GPC.

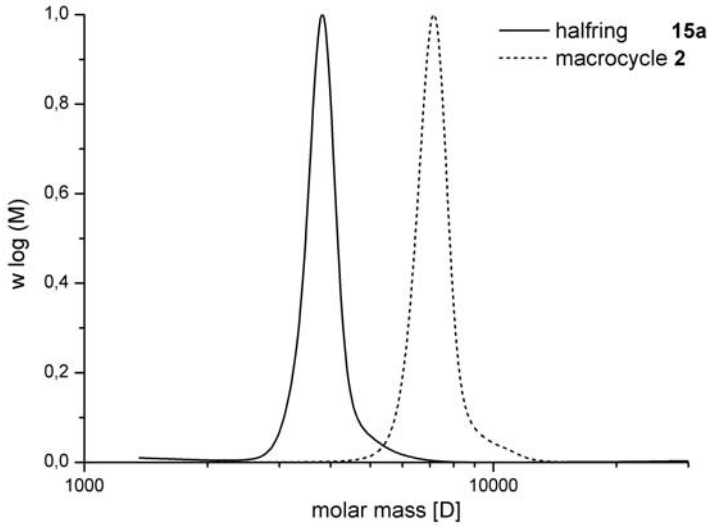


Figure S9. Normalized molar weight distribution from analytical GPC of halfring **15a** and macrocycle **2** after purification by recycling GPC.

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