Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Shape-Responsive Adsorption for an Oval Macrocycle Co-deposited with Guest Molecules

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1. Synthesis

The diiodo BDT containing dodecycloxy groups **5** was prepared from 3,3'-bithiophene **1** *via* two-fold acylation with oxalyl chloride, followed by reduction of *o*-quinone **2** with Zinc/acetic anhydride, and subsequent substitution reaction with 1-bromododecane and iodination with N-iodosuccinimide. Diiodo BDT **5** is a suitable precursor for the formation of shape-persistent macrocycles containing extraannular substituents. Sonogashira coupling of **5** with methyl-3-butyn-2-ol gave bis-isopropanol-protected bisacetylene (bisprotected bisacetylene) **6**, partial deisopropanol of **6** gives the monoprotected bisacetylene **7**, which coupled with diiodo BDT **5** under the second sonogashira coupling condition in the presence of CuI and PPh3 provided the half ring **8** in its isopropanol protected form. Subsequent deprotection of **8** with KOH in THF gave bisacetylene **9**. The cyclization of **9** under pseudo-high-dilution condition was carried out by adding the bisacetylene in pyridine at 96 h to a slurry of $CuCl/CuCl_2$ in the same solvent. The final compound BDT ring was purified by column chromatography and crystallization from methylene chloride and methanol mixtures. Detailed synthetic procedures and analytical data are given below. The cyclization reaction is a statistical reaction, so the cyclic dimers BDT ring are formed along with cyclic trimers, oligomers, and polymers. According to the gel permeation chromatography (GPC) data, the crude cyclization product of the BDT ring is about 80%. The molecular weight of the cyclization reaction product is 3 times of the dimer. It is possible the product is one hexamer or 3 dimers aggregated together due to the strong aggregation effect of the BDT.

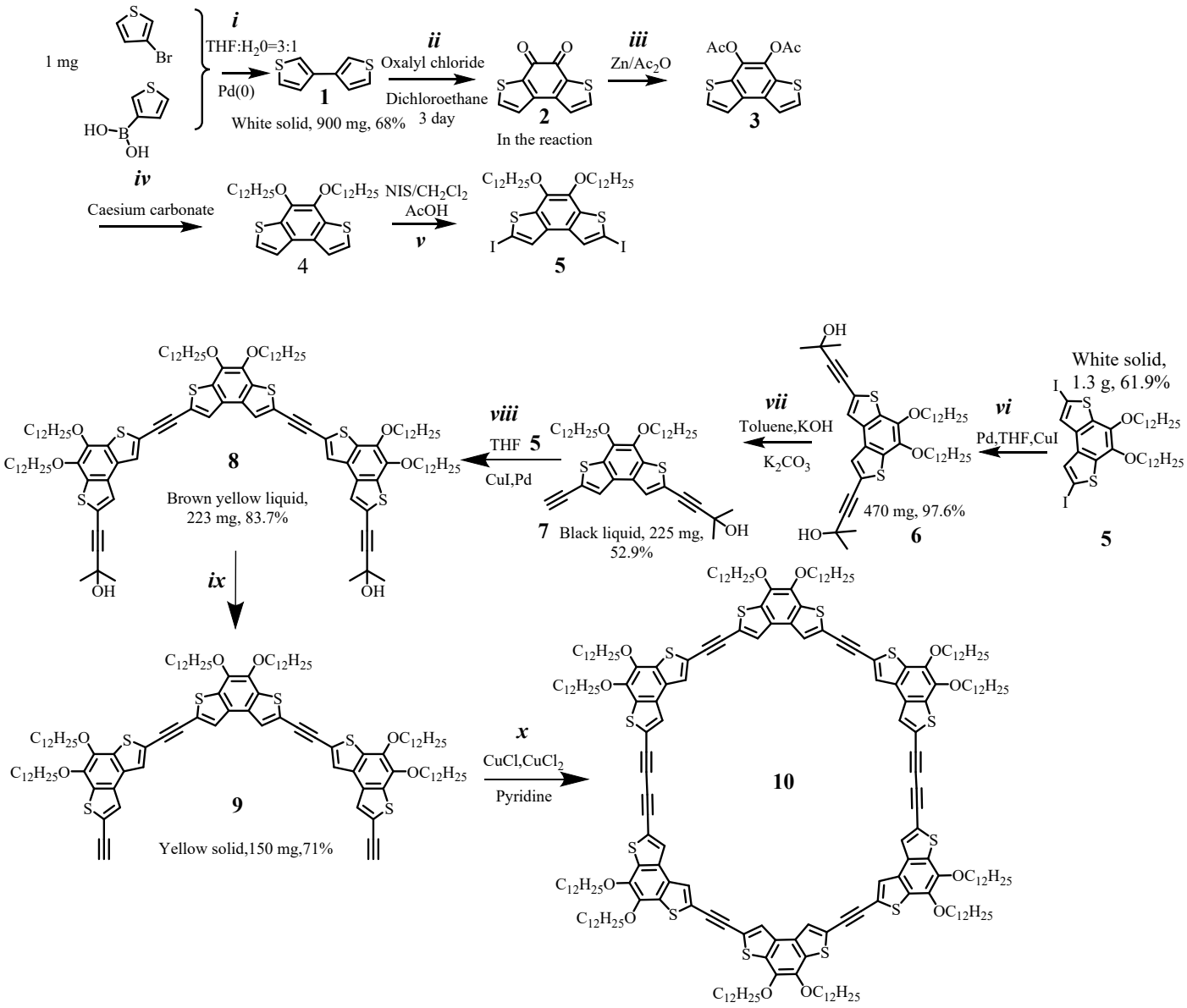
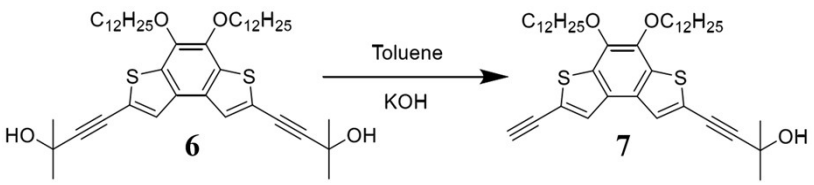
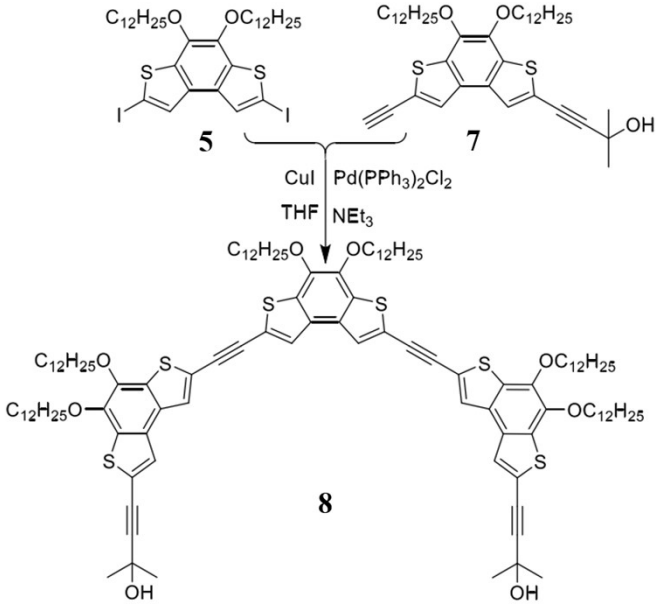


Fig. S1 Synthesis of macrocycles: *Reagents and conditions*: *i*) I_2, H_2O_2, H_2O, 50 °C, 24 h; *ii*) oxalyl chloride, 1, 2-dichloroethane, 84°C, 48 h; *iii*) acetic anhydride, Zn, Et_3N, CH_2Cl_2, RT, 4 h; *iv*) $C_{12}H_{25}Br$, Cs_2CO_3, DMF, 90 °C, 48 h; *v*) CH_2Cl_2, NIS, acetic acid, RT, 24 h; *vi*) CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, THF, RT, 12 h; *vii*) KOH, Toluene, RT, 1 h; *viii*) CuI, $Pd(PPh_3)_2Cl_2$ NEt_3, THF, N_2, RT, 12 h; *ix*) KOH, Toluene, RT, 1 h; *x*) pyridine, CuCl, $CuCl_2$, N_2, RT, 96 h.

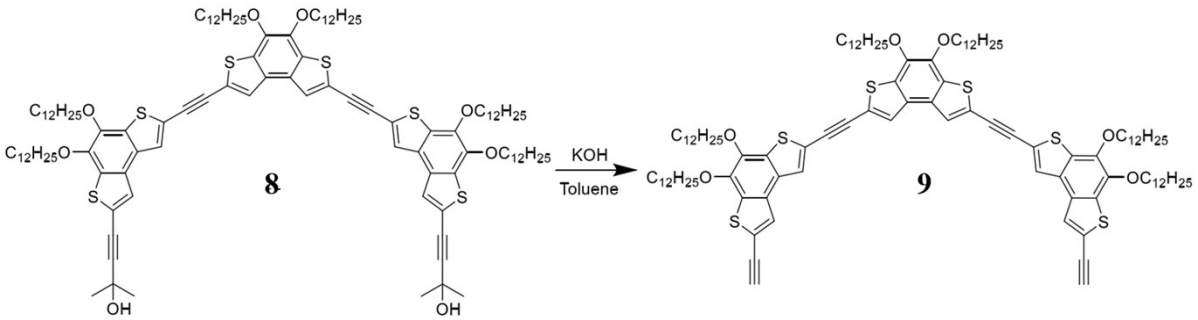
The detailed and key synthesis steps and their yield and ^{1}H NMR



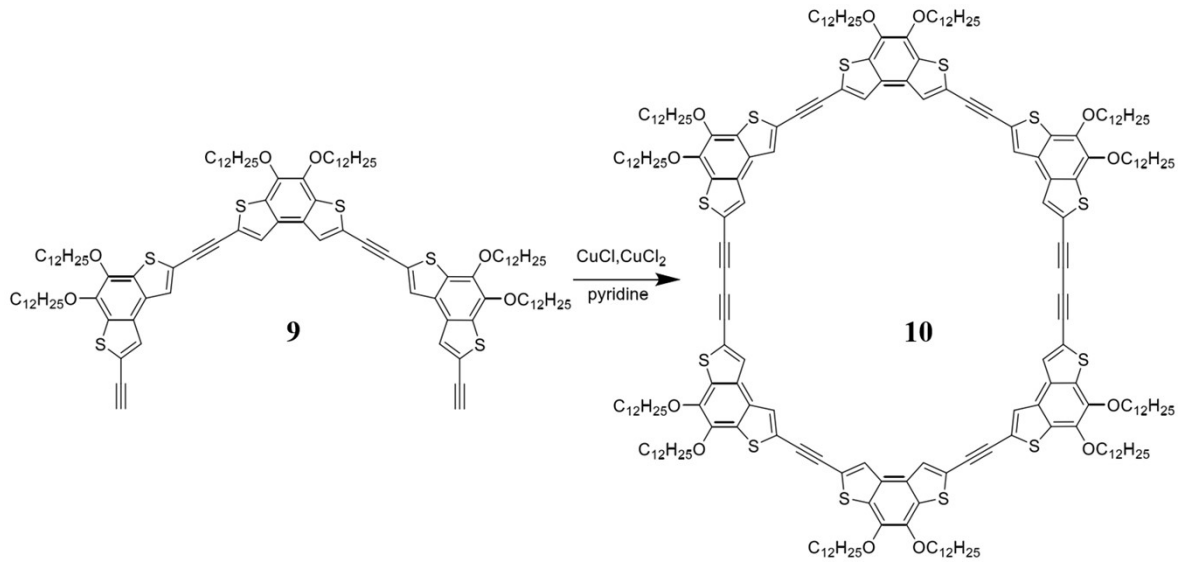
Dissolving **6** (723 mg, 1 mmol) in toluene solution (20 mL) under nitrogen atmosphere, adding 0.03 mL of 1 M KOH aqueous solution, stirring at 90 ° C for 1 hour, and using CH_2Cl_2 (3 × 25 mL) extraction, anhydrous Na_2SO_4 drying, solvent evaporation drying, crude product column chromatography extraction (eluent: petroleum ether: ethyl acetate=5:1) to obtain a black oily liquid **7**. Yield: 346 mg, 52%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70-7.61 (m, 2 H, 2ArH), 4.20 (s, 4 H, $2OCH_2$), 3.48 (s, 1 H, ArCCH), 1.81 (s, 4 H, $2OCH_2CH_2$), 1.65 (s, 6 H, $2CCH_3$), 1.27 (s, 36 H, $18CH_2$), 0.88 (s, 6 H, $2CH_3$).



Dissolving **5** (211 mg, 0.26 mmol) and **7** (346 mg, 0.52 mmol) in 10 mL of dry tetrahydrofuran and 2 mL of dry diisopropylamine under nitrogen atmosphere, then adding $Pd(PPh_3)_2Cl_2$ (50 mg, 0.04 mmol), and CuI (30 mg, 0.16 mmol), stirring overnight at room temperature, and using CH_2Cl_2 (3 × 25 mL) extraction, anhydrous Na_2SO_4 drying, solvent evaporation drying, crude product column chromatography extraction (eluent: petroleum ether: ethylacetate=5:1) to obtain black solid **8**. Yield: 345 mg, 71.4%. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (s, 2 H, 2Ar H), 7.76 (s, 2 H, 2Ar H), 7.66 (s, 2 H, 2Ar H), 4.29-4.23 (m, 12 H, $6OCH_2$), 1.87-1.84 (m, 12 H, $6OCH_2CH_2$), 1.67 (s, 12 H, $4CCH_3$), 1.52 (m, 12 H, $6OCH_2CH_2CH_2$), 1.27 (s, 96 H, $48CH_2$), 0.90-0.85 (m, 18 H, $6CH_3$).



Dissolving **8** (339 mg, 0.18 mmol) in 20 mL of toluene solution under a nitrogen atmosphere, slowly add 0.03 mL of 1 M KOH aqueous solution, stirring at 90 ° C for 1 hour, and use CH_2Cl_2 (3 × 25 mL) extraction, anhydrous Na_2SO_4 drying, solvent evaporation drying, crude product column chromatography extraction (eluent: petroleum ether: ethyl acetate=20:1) to obtain yellow solid **9**. Yield: 101.9 mg, 32%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80 (s, 2 H, 2Ar H), 7.79 (s, 2 H, 2Ar H), 7.76 (s, 2 H, 2Ar H), 4.28-4.23 (m, 12 H, 6OCH_2), 3.50 (m, 2 H, 2ArCCH), 1.88-1.81 (m, 12 H, 6OCH_2CH_2), 1.55 (m, 12 H, 6$OCH_2CH_2CH_2$), 1.27 (s, 96 H, 48CH_2), 0.90-0.85 (m, 18 H, 6CH_3).



Adding CuCl (564 mg, 5.7 mmol) and $CuCl_2$ (153 mg, 1.14 mmol) to dried pyridine (20 mL), and slowly adding **9** (100.8 mg, 0.057 mmol) pyridine solution (25 mL) over a period of three days. Stirring at room temperature for 24 hours, adding dichloromethane (100 mL) and water (100 mL), separating the organic layers, and using water (3 × 20 mL), 25% ammonia water (until the aqueous phase is close to colorless), water (3 × 20 mL), 10% acetic acid (3 × 20 mL), Water (3 × 20 mL), 10% sodium hydroxide (3 × 20 mL) and saline water (3 × 20 mL) washing. The organic layer is dried on anhydrous Na_2SO_4 and the solvent is evaporated to dryness. Adding dichloromethane (20 mL) and methanol (20 mL) for recrystallization, filtering, and collecting the precipitate. The crude product was separated and extracted by column chromatography (eluent: dichloromethane: ethyl acetate = 20:1) to obtain a yellow solid **10**. **10**: 42 mg, 42%. ^{1}H NMR (THF-d8, 400 MHz): δ = 7.6-6.8 (m, 12 H, 12Ar H), 4.48-4.02 (s, 24 H, 12OCH_2), 1.89-1.86 (s, 24 H, 12OCH_2CH_2), 1.56-1.21 (m, 216 H, 108CH_2), 0.93 (m, 36 H, 12CH_3).

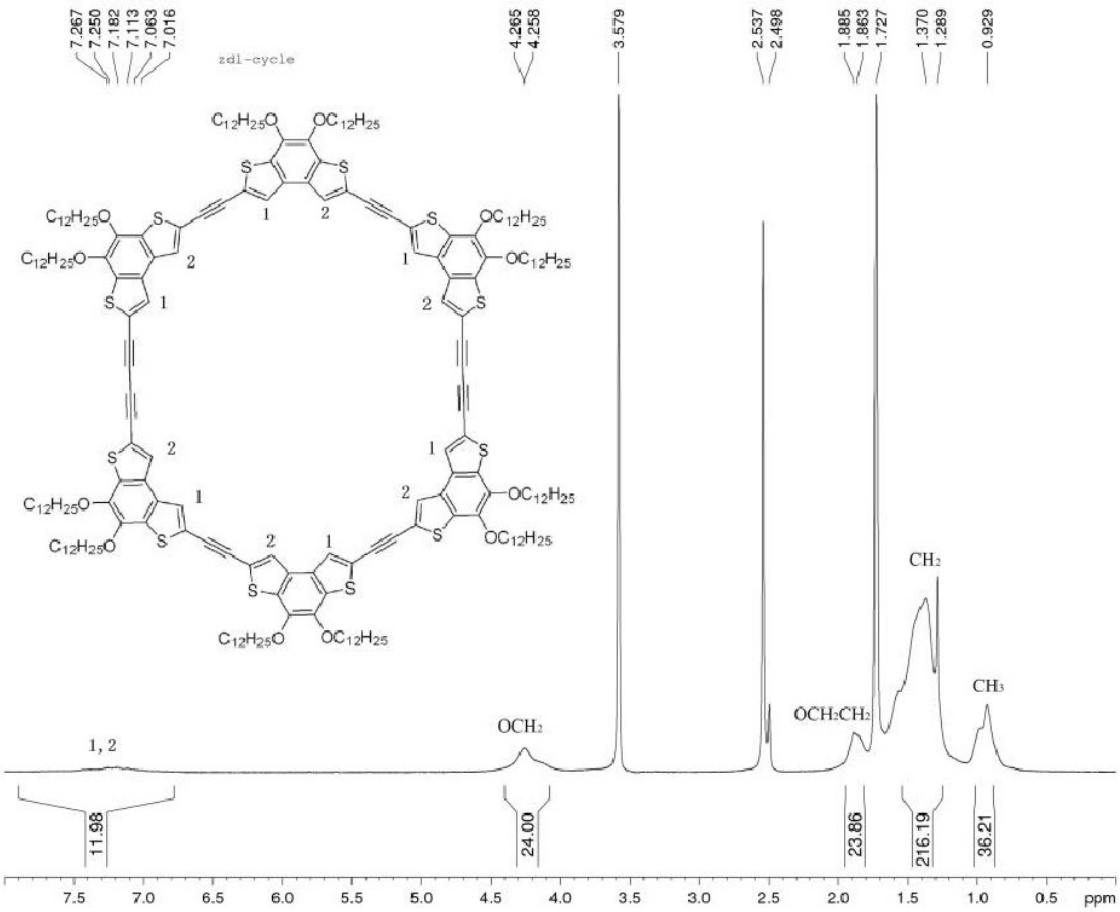


Fig. S2 ^{1}H-NMR Spectrum of M1 (THF-d8, 400 MHz): δ = 7.6-6.8 (m, 12 H, 12Ar H), 4.48-4.02 (s, 24 H, 12OCH_2), 1.89-1.86 (s, 24 H, 12OCH_2CH_2), 1.56-1.21 (m, 216 H, 108CH_2), 0.93 (m, 36 H, 12CH_3).

GPC for half ring 2.5x10^3 and the ring 1.1x10^4

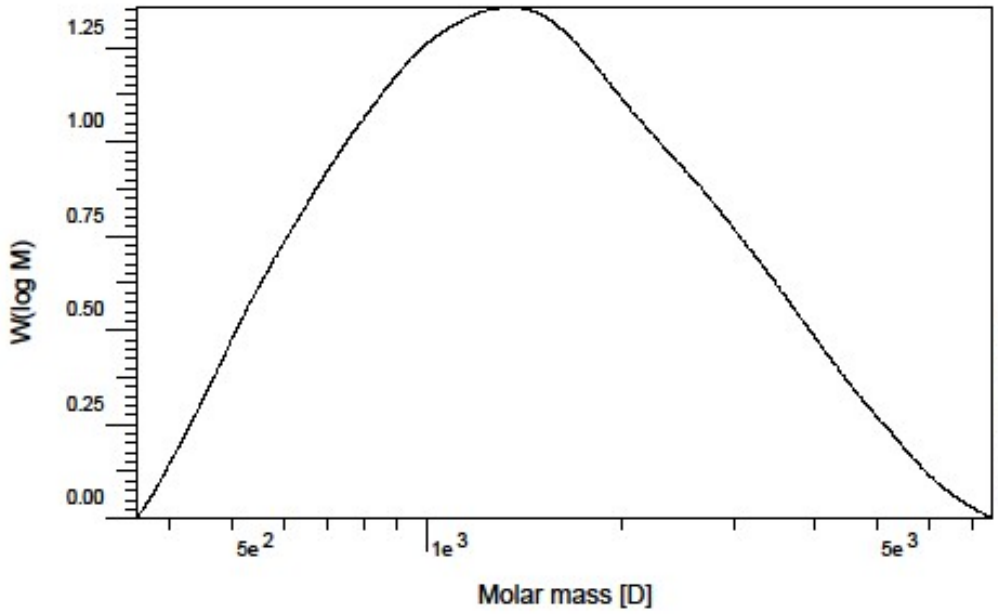


Fig. S3 GPC for the half ring 1.1x10^4.

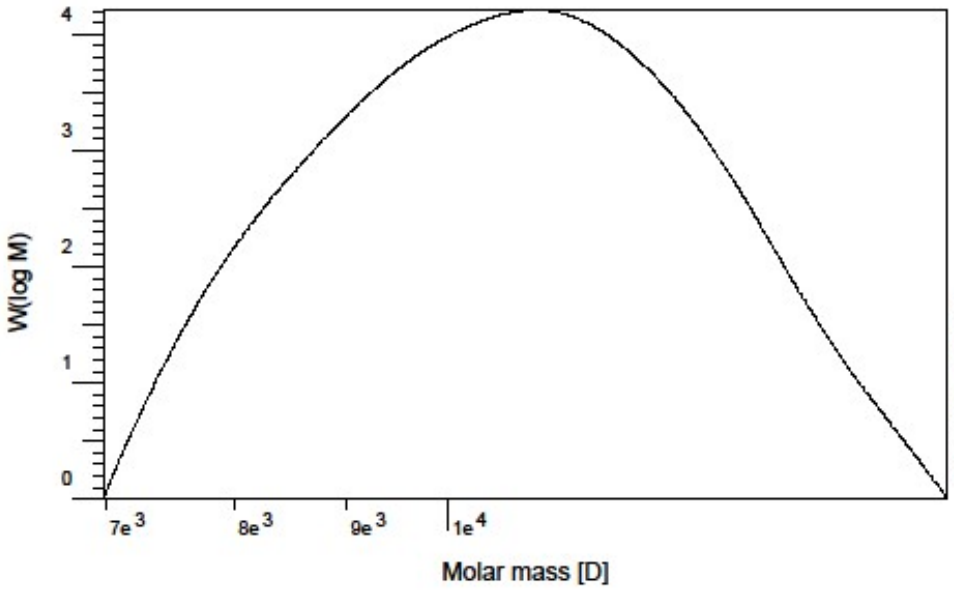


Fig. S4 GPC for the ring 2.5x10^3.

Reference

1. L. J. Shu, M. Mayor, *Chem. Commun.,* 2006, **39**, 4134–4136.
2. C. Grave, A. D. Schlüter, *Eur. J. Org. Chem.*, 2002, **18**, 3075–3098.

2. The UV-Vis absorption spectrum of M1 by adding Tp and Py in toluene solutions.

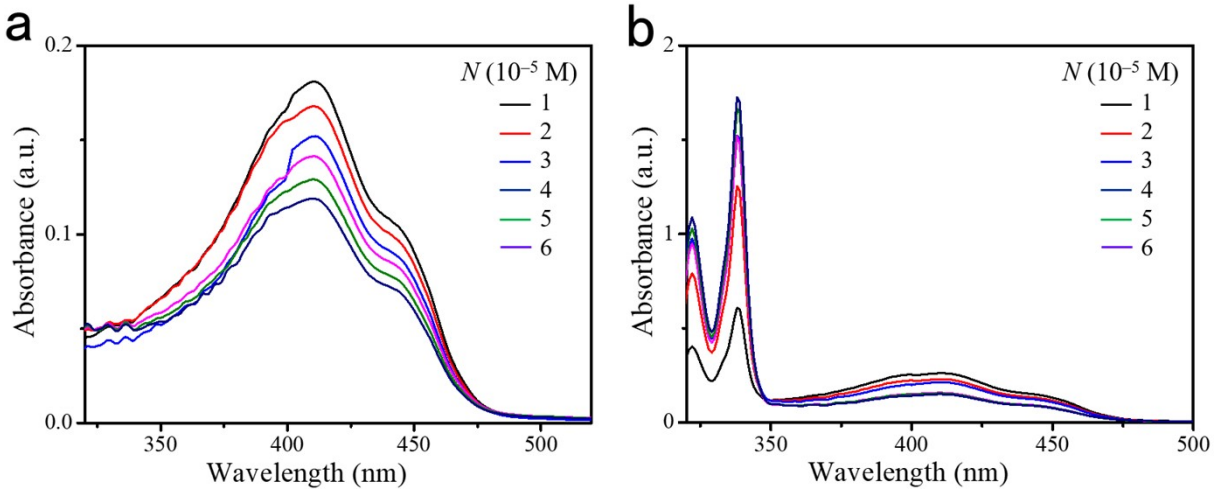


Fig. S5 UV-Vis absorption spectrum of the mixtures with varying guest concentrations in M1 toluene solution with constant concentration (Concentration = 10^{-5} M). (a) M1 with the addition of Tp, and (b) M1 with the addition of Py in toluene solution at room temperature, respectively. The concentration of guest molecules is N × 10^{-5} M.

3. Additional STM Data

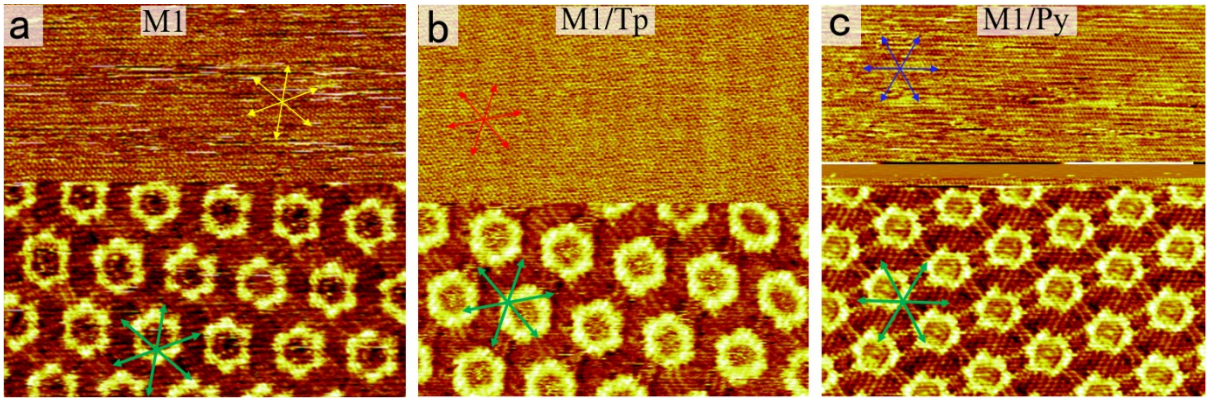


Fig. S6 (a-c**)** Composite STM images (M1, M1+Tp, M1+Py) showing the underlying HOPG lattice and the M1 array at the 1-phenylacetate/graphite interface (24 × 24 nm^2, 20 × 20 nm^2, and 27 × 27 nm^2). V_{bias} = 700 mV, I_t = 420 pA for the molecular adlayer (Lower), and V_{bias} = 100 mV, I_t = 560 pA for the HOPG lattice (Upper). The image was obtained by switching the bias during the STM scan from the bottom to the upper frame.

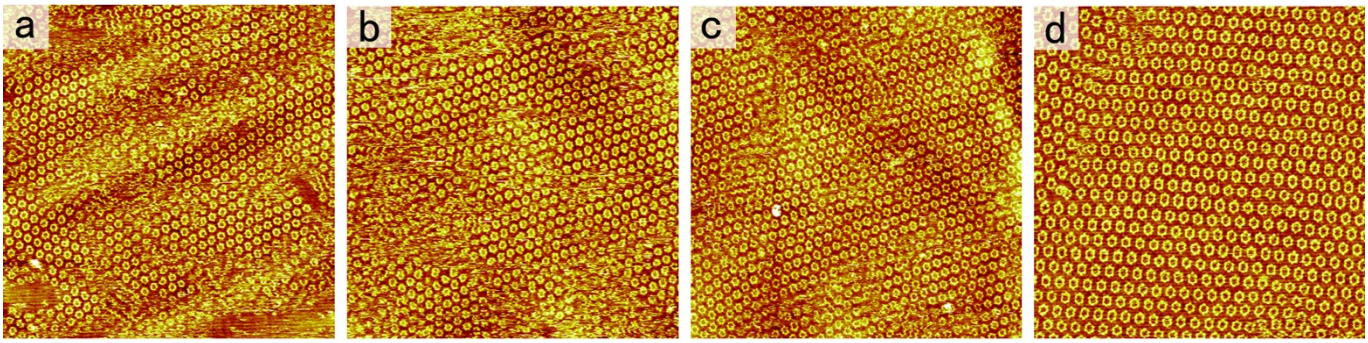


Fig. S7 (a) Large-scale STM images for the self-assemblies of M1 at the 1-phenyloctane/HOPG interface with various concentrations: (a) 1.0 × 10^{-3} M, (b) 5.0 × 10^{-4} M, (c) 2.5 × 10^{-4} M, (d) 1.2 × 10^{-4} M. Image size: (a-c) 108 × 108 nm^2, (d) 80 × 80 nm^2.

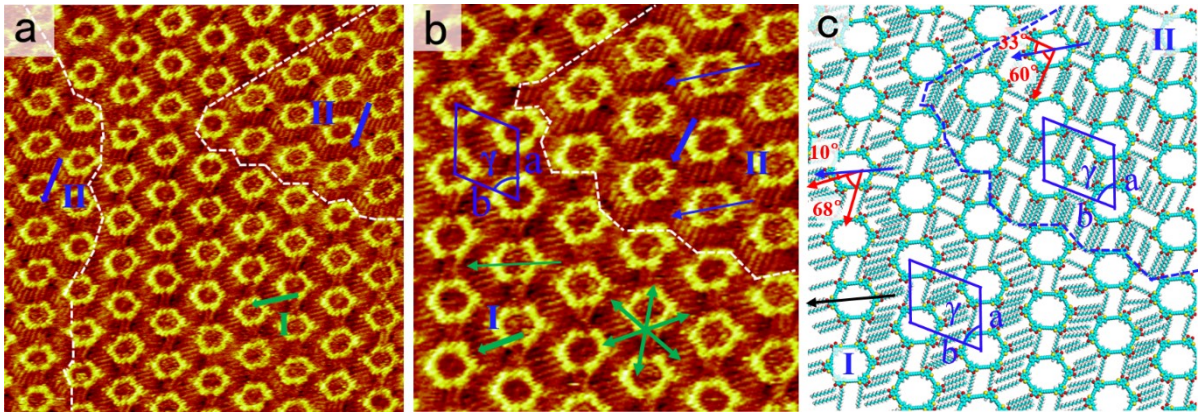


Fig. S8 (a) Medium-scale and (b) high-resolution STM images for the assembled adlayer of M1 at the octanoic acid/HOPG interface (1.0 × 10^{-4} M, 40 × 40 nm^2; 27 × 27 nm^2, V_{bias} = 603 mV and I_{set} = 405 pA). (c) Proposed molecular model for the self-assembled nanostructure.

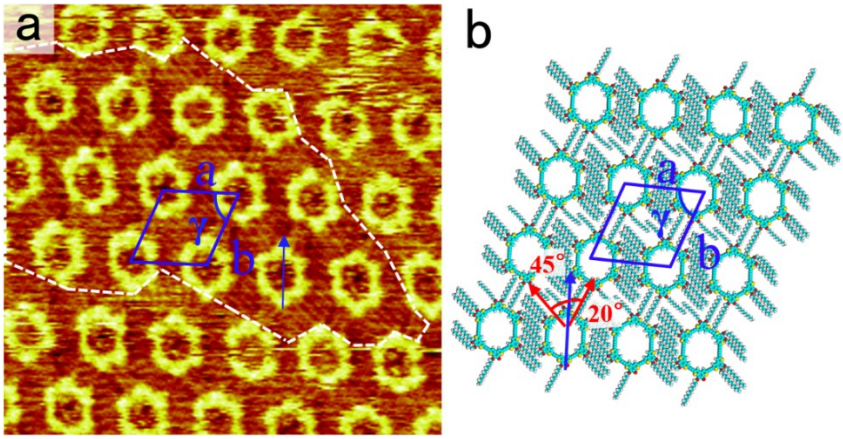


Fig. S9 (a) High-resolution STM image for assembly of M1 adlayer at the octanoic acid/HOPG interface (1.0 × 10^{-4} M, 27 × 27 nm^2; V_{bias} = 632 mV, and I_{set} = 479 pA). (b) Suggested molecular model for M1 self-assembly nanostructure.

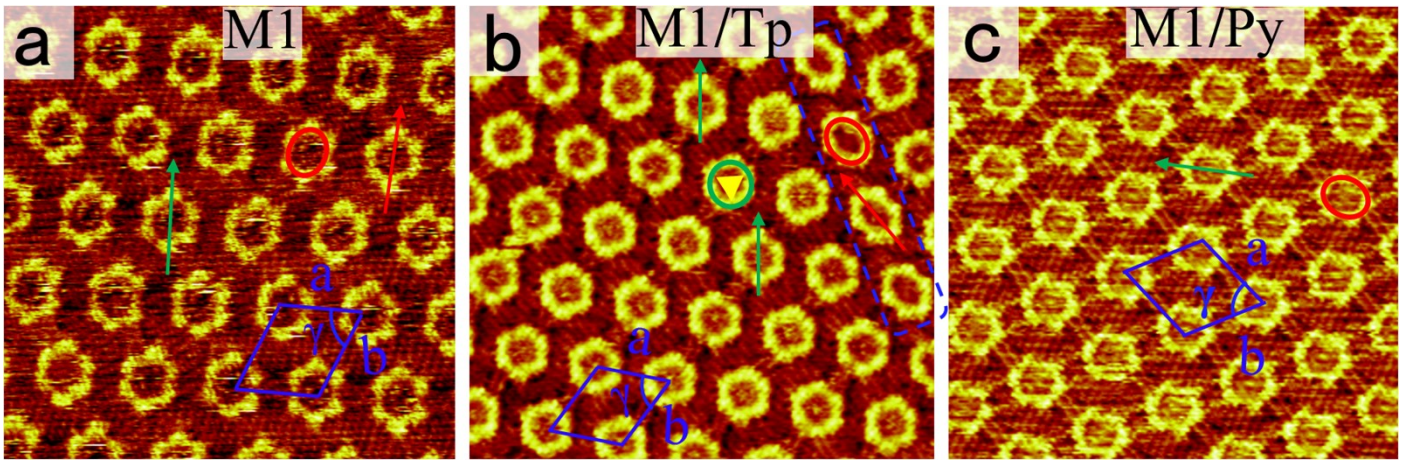


Fig. S10. (a) High-resolution STM images showing the M1, M1/Tp, and M1/Py patterns in 1-phenyloctane at a low concentration (10^{-4} M). Image sizes (a-c): 22 × 22 nm^2, 30 × 30 nm^2, 30 × 30 nm^2.

Table S1. Angles between alkyl chains and macrocycle (long axis) of M1, M1/Tp and M1/Py.

Compound	*M1(1-phenyloctane)*		*M1(Octanoic acid)*		M1/Tp	M1/Py
Angles between alkyl chains and macrocycle (long axis)	Domain I	10/70 ± 1°	Domian I	10/68 ± 1°		
	Domian II	41/56 ± 1°	Domain II	33/60 ± 1°	34/47 ± 1°	42/79 ± 1°
	Domian III	14/45 ± 1°	Domain III	20/45 ± 1°		