Supporting Information

Synthesis of Dynamic Imine Macrocyclic Supramolecular Polymers via Synchronized Self-Assembly Based on Dynamic Covalent Bonds and Noncovalent Interactions

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1. General experimental

All the reagents involved in this research were commercially available and used without any further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. Thin layer chromatography (TLC) was carried out on 0.25 mm Yantai silica gel plates (60F-254). Column chromatography was performed on silica gel 60 (Tsingdao 40 – 63 nm, 230 – 400 mesh). ^{1}H-NMR spectra were recorded on a Bruker Avance-400 or 500 spectrometers. All chemical shifts are reported in ppm with residual solvents or tetramethylsilane (TMS) as the internal standards. The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t triplet; m, multiplet.

Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an applied biosystems Elite ESI-QqTOF mass spectrometry system. All the computations were performed at the AM1 level of theory by using Spartan ’14 (Wavefunction, Inc.). Scanning electron microscope (SEM) images were obtained from the field emission SEM (FESEM, ZEISS Merlin).

2. Characterization Data for G1@syn-isomer, G2@anti-isomer, and G3@anti-isomer

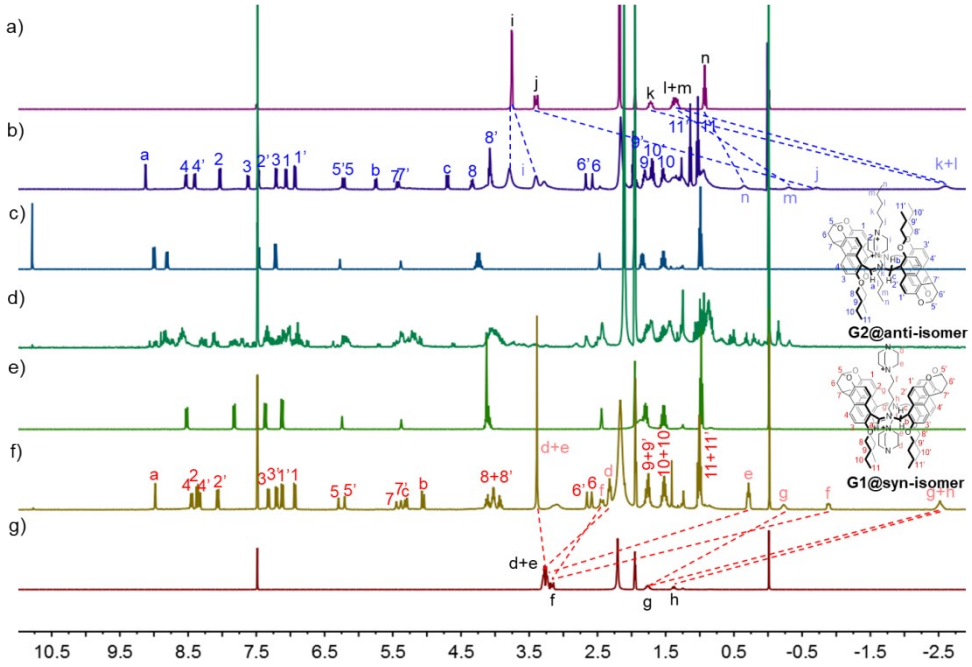


Fig. S1. Full 1H NMR spectra (400 MHz, CDCl3:CD3CN=1:1, 4.0 mM, 300 K) of (a) G2, (b) G2@anti-isomer, (c) BB1, (d) BB1+BB2, (e) BB2, (f) G1@syn-isomer, and (g) G1. For both G1@syn-isomer and G2@anti-isomer, the alkyl signals of the free guests shifted significantly to the upfield, indicating they are encapsulated in the deep cavity of syn-isomer or anti-isomer. This, in addition, suggests that the [1+1] macrocycle capable of forming tight binding with the guests is formed.[1]

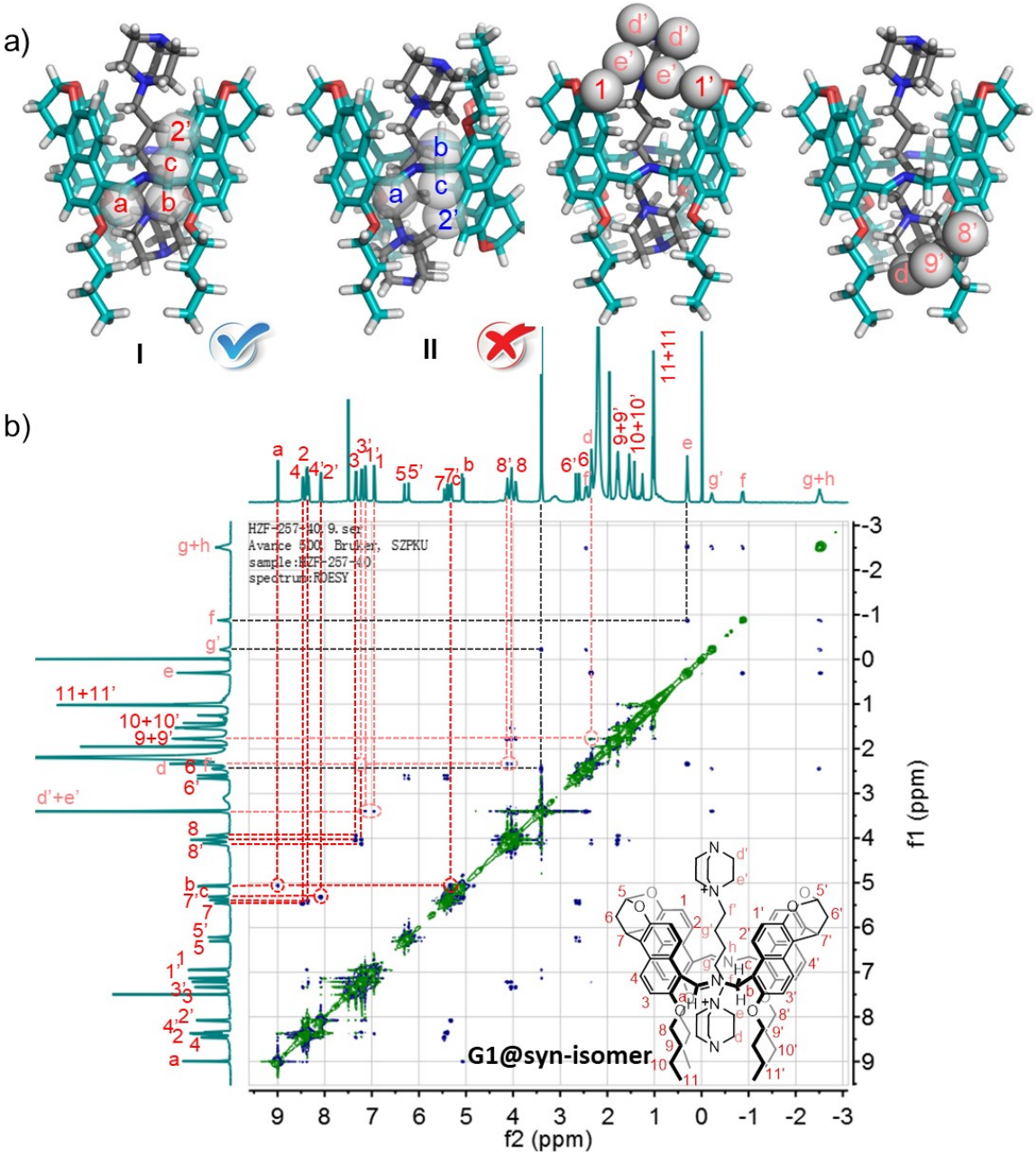


Fig. S2. (a) Molecular models of **G1@syn-isomer** to show the NOE correlations; (b) Full ^{1}H, ^{1}H-ROESY NMR spectrum (500 MHz, $CDCl_3$:CD_3CN=1:1, 4.0 mM, 300 K) of the complex **G1@syn-isomer**. Clearly, the NOE correlations of protons a, b, c, and 2’ are in line with the syn-isomer. In addition, the NOE effects between the host and the guest further confirmed the syn configuration of the host and the guest binding model.[1]

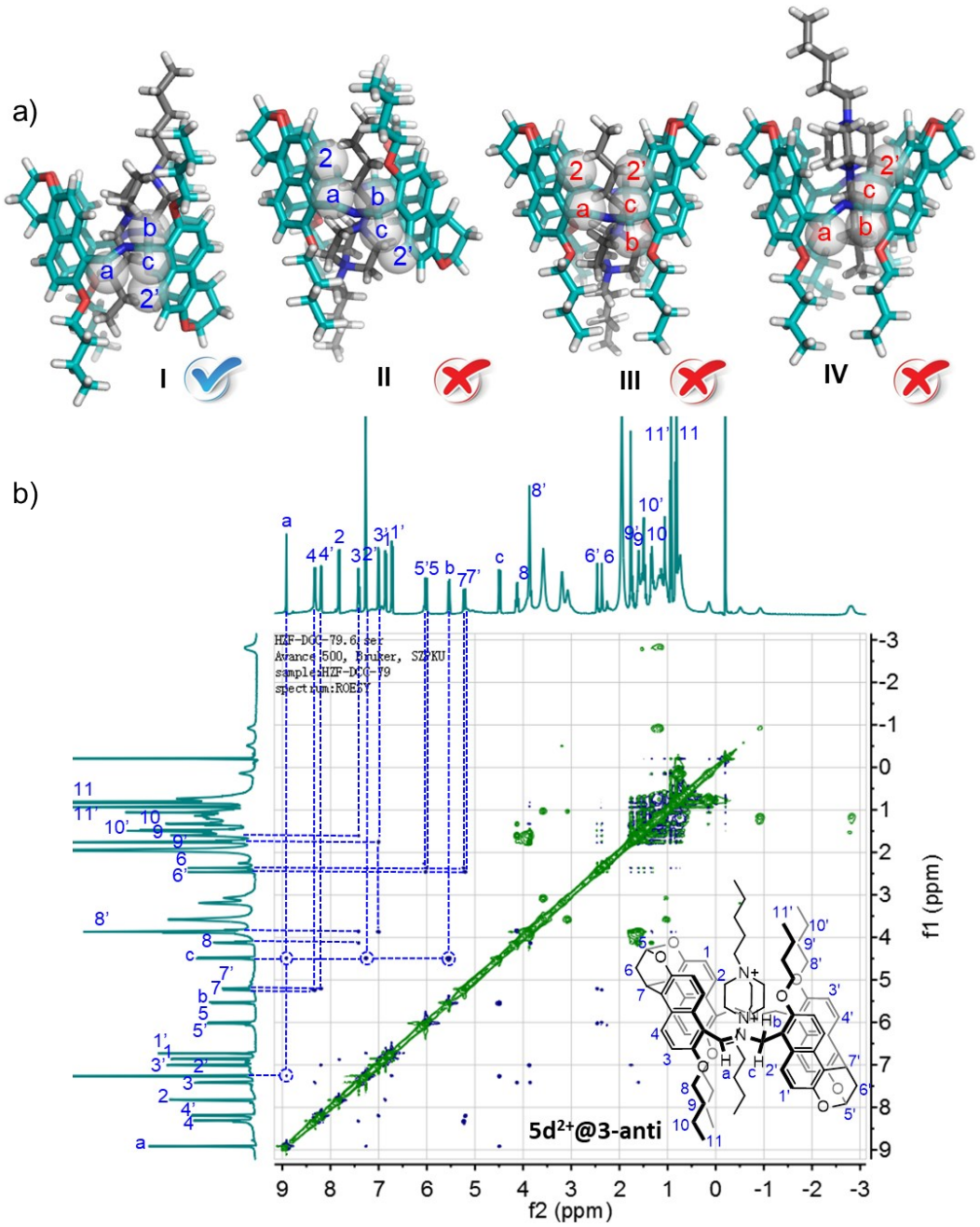


Fig. S3. a) Energy-minimized structures of two possible isomers of **G2@anti-isomer** at the AM1 level of theory. The protons a, b, c, and 2' are rendered to show possible NOE contacts; b) The full ^{1}H, ^{1}H-ROESY NMR spectrum (500 MHz, $CDCl_3$:CD_3CN=1:1, 4.0 mM, 300 K) of the complex **G2@anti-isomer**. Unambiguously, the NOE correlations support the assignment of the anti isomer. The broadening of guest peaks, presumably arising from the intermediate exchange rate between free and encapsulated guests, prevents the unambiguous assignments of guest binding mode. Fortunately, the chemical modelling is sufficient to rule out other possibility and assign the structure to **G2@anti-isomer** as shown in the Figure inset [1].

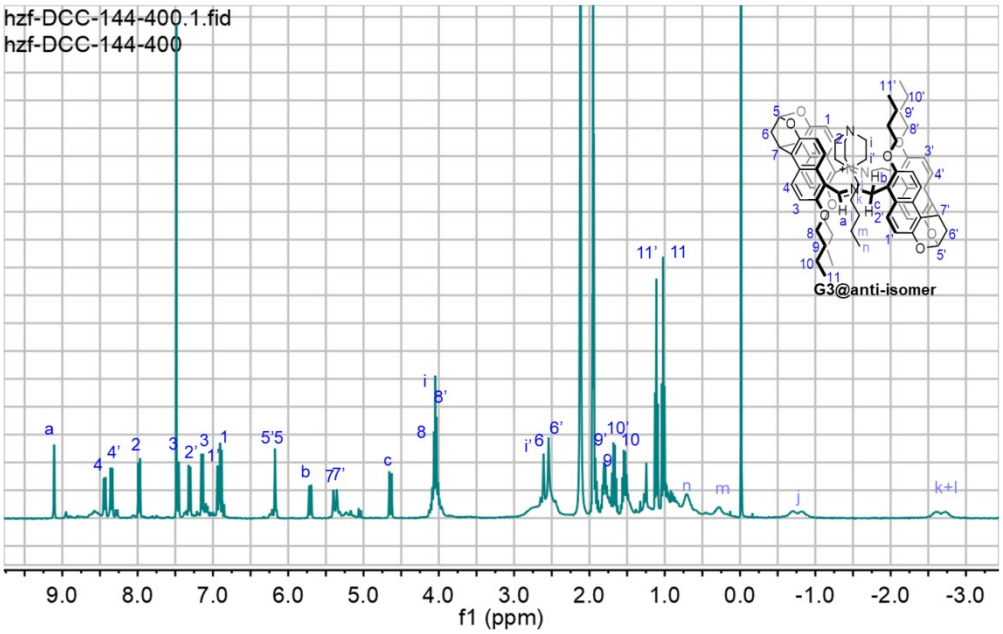


Fig. S4. Full 1H NMR spectra (400 MHz, $CDCl_3$:CD_3CN=1:1, 4.0 mM, 300 K) of G3@anti-isomer, the alkyl signals of the free guests shifted significantly to the upfield, indicating it is encapsulated in the deep cavity of anti-isomer. This, in addition, suggests the [1+1] macrocycle capable of forming tight binding with the G3 is formed.

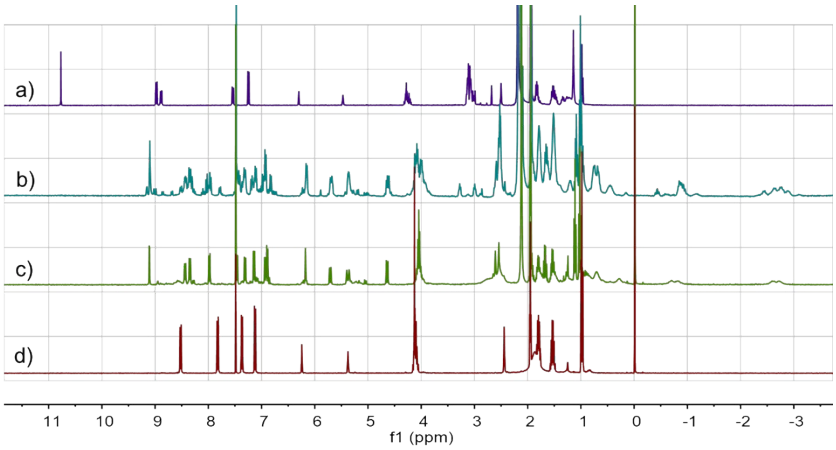


Fig. S5. Full ^{1}H-NMR spectra (400 MHz, $CDCl_3$:CD_3CN=1:1, 4.0 mM, 300 K) of a) BB1-DABCO, b) DIMPs, c) G3@anti-isomer and d) BB2. The aldehyde of BB1-DABCO and the amine of BB2 disappear. Imines appear at 5.5 and 4.6 ppm.

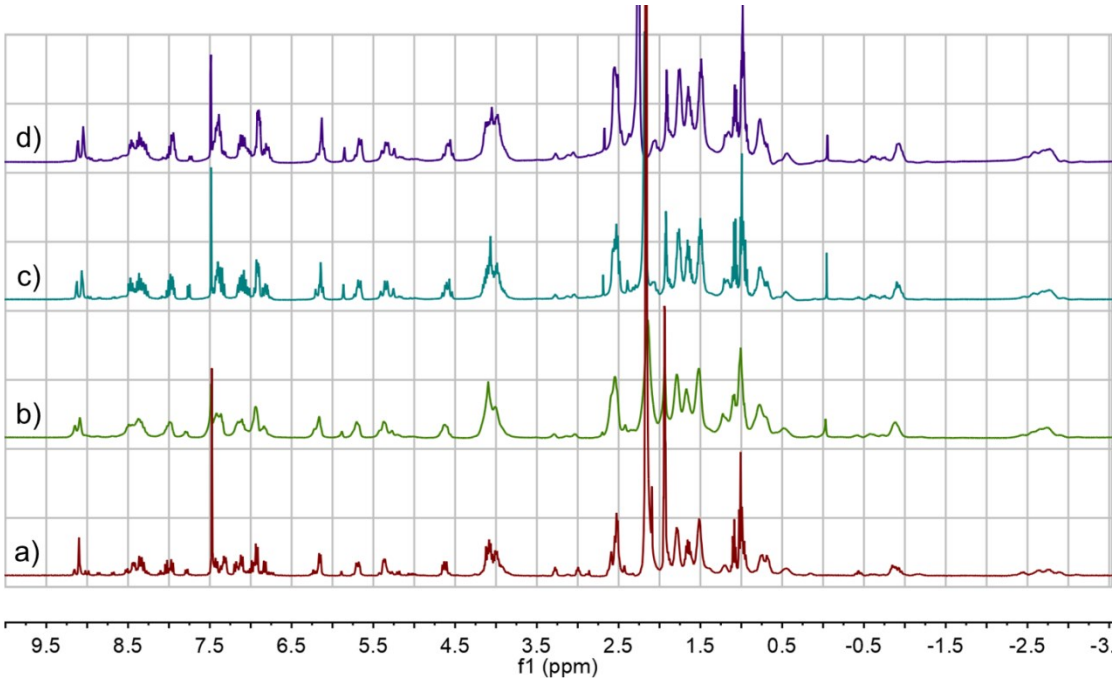


Fig. S6. Full ^{1}H NMR spectra (400 MHz, CDCl3:CD3CN=1:1, 4.0 mM, 300 K) of supramolecular polymer (DIMPs) at different concentrations of self-assembly a) 4 mM, b) 16.5 mM, c) 33.7 mM, d) 55.4 mM.

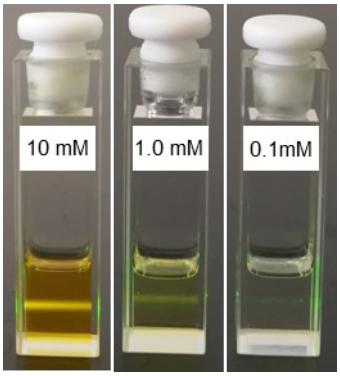


Fig. S7. The tyndall effect of DIMPs in different concentrations, which illustrate that big aggregate could be formed with increasing the concentration.

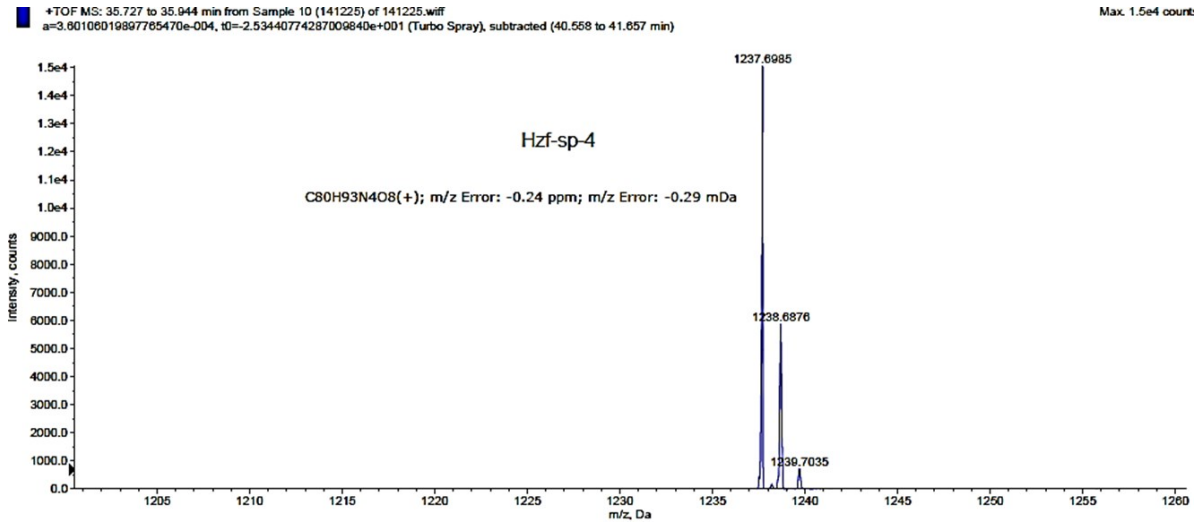


Fig. S8. The ESI-MS datum of isotopic pattern of the single repeating unit of DIMPs.

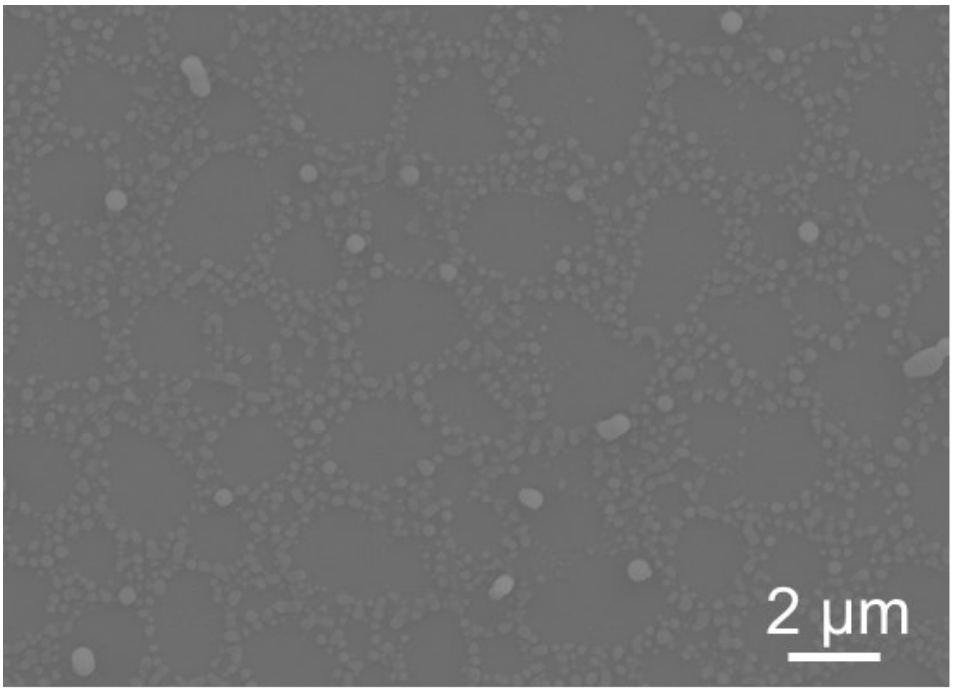
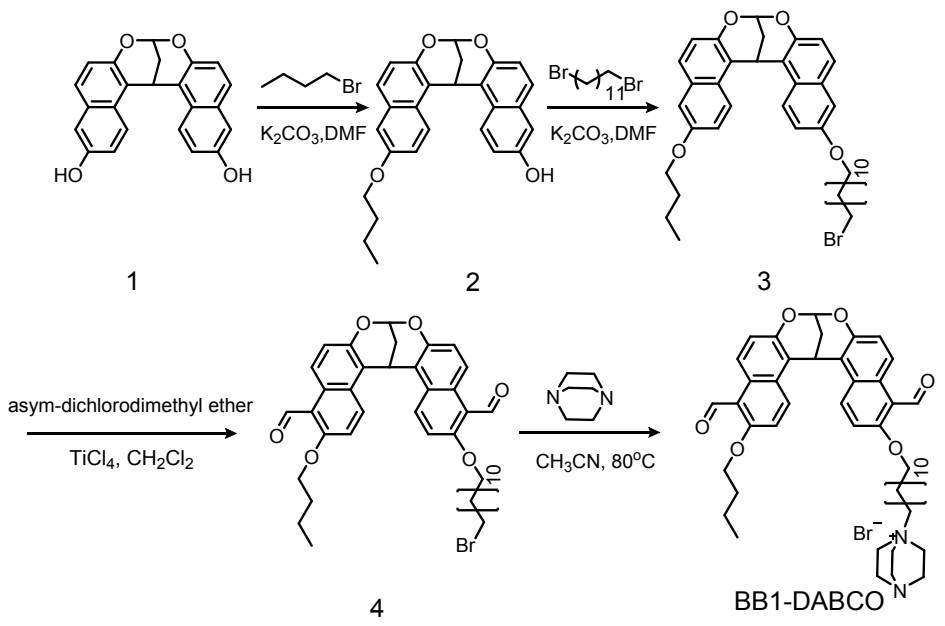


Fig. S9. SEM of BB1-DABCO showing the spherical shape.

3. Synthetic details



Scheme S1. Synthetic procedures of BB1-DABCO.

Compound 2 & 3:

Compound 1[2] (2.00 g, 5.61 mmol), 1-bromobutane (0.38 g, 2.80 mmol), and K_2CO_3 (0.78 g, 5.61 mmol) were mixed in dry DMF (30 mL). The mixture was stirred for 24 h at room temperature under an argon protection. The solution was poured into H_2O (100 mL). The suspension was filtered off. The filter cake was re-dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under a reduced pressure. The crude product was subjected to column chromatography (SiO_2, petroleum ether: CH_2Cl_2 = 1:1) to give **2** as a white solid (1.00 g, 43 %), which was used directly in the next step. **Compound 2** (0.40 g, 1.0 mmol), 1,12-Dibromododecane (2.50 g, 8.0 mmol), and K_2CO_3 (0.54 g, 4.0 mmol) were mixed in dry DMF (15 mL). The mixture was stirred for 24 h at room temperature under an argon protection. The solution was poured into H_2O (60 mL). The suspension was filtered off. The filter cake was re-dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under a reduced pressure. The crude product was subjected to column chromatography (SiO_2, petroleum ether : CH_2Cl_2 = 3:1) to give **compound 3** as a white solid (0.20 g, 31.3 %). ^{1}H-NMR (400 MHz, CDCl3, 300 K): ppm = δ 8.49 (d, J = 9.3 Hz, 2H), 7.49 (d, J = 8.9 Hz, 2H), 7.25 (dd, J = 9.2, 2.7 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 2.4 Hz, 2H), 6.28 (m, 1H), 5.31 (m, 1H), 4.03 (m, 4H), 3.42 (q,

J = 6.7 Hz, 4H), 2.47 (t, J = 2.7 Hz, 2H), 1.95 – 1.73 (m, 8H), 1.45 (m, 4H), 1.29 (m, 12H), 1.00 (t, J = 7.4 Hz, 4H)

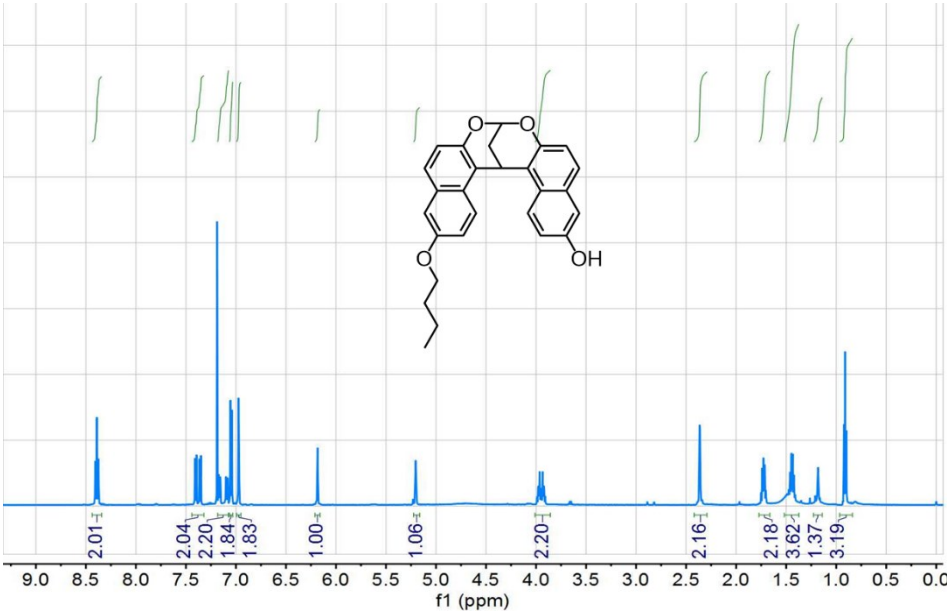


Fig. S10. ^{1}H-NMR spectrum of Compound 2 (400 MHz, $CDCl_3$, 298 K).

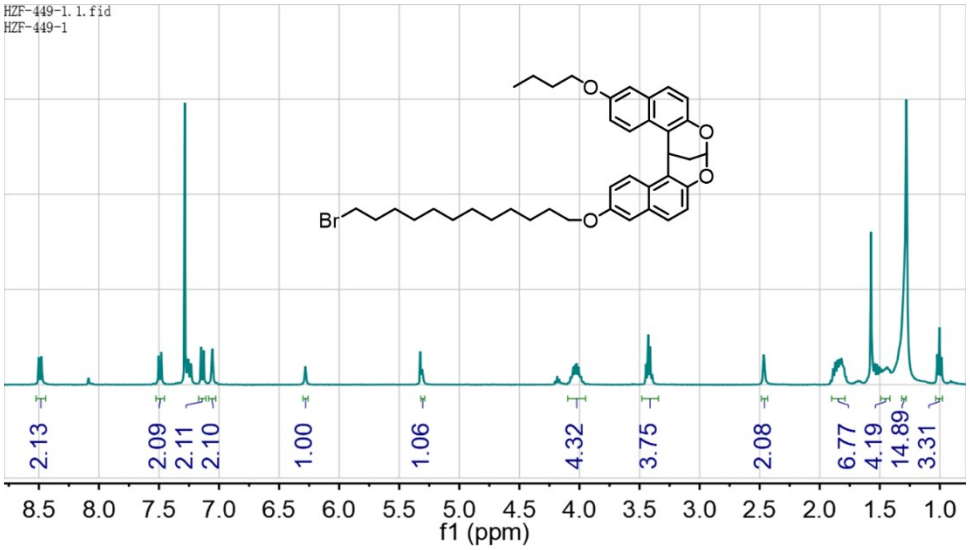


Fig. S11. ^{1}H-NMR spectrum of Compound 3 (400 MHz, $CDCl_3$, 298 K).

Compound 4:

To the solution of compound 3 (100 mg, 0.15 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C, α,α-dichloromethyl methyl ether (0.11 mL, 1.2 mmol) was added. It was followed by the slow addition of $TiCl_4$ (230 mg, 1.2 mmol) via syringe. After stirring at 0 °C for 1 h, the resulting mixture was warmed to room temperature and stirred for

another 2.5 h. The solution was then poured into saturated aqueous $NaHCO_3$. The resulting suspension was extracted with CH_2Cl_2 (20 mL×3). The combined organic phase was washed consecutively with saturated aqueous $NaHCO_3$ (50 mL) and H_2O (100 mL), then dried over anhydrous Na_2SO_4. After filtration, the crude product was obtained by removing the solvent under a reduced pressure. Pure compound 4 as a yellow solid (75 mg, 70%) was afforded after column chromatography (SiO_2, hexane : CH_2Cl_2 = 2: 1). 1H NMR (400 MHz, CDCl3, 300 K): ppm =10.86 (s, 2H), 9.13 (d, J = 9.4 Hz, 2H), 8.73 (d, J = 9.5 Hz, 2H), 7.38 (dd, J = 9.5, 1.4 Hz, 2H), 7.31 (d, J = 9.4 Hz, 2H), 6.30 (d, J = 1.4 Hz, 1H), 5.28 (s, 1H), 4.22 (m, , 4H), 3.43 (t, J = 6.9 Hz, 2H), 2.48 (t, J = 2.6 Hz, 2H), 1.87 (m, 6H), 1.56 (m, 6H), 1.37 – 1.25 (m, 12H), 1.02 (t, J = 7.4 Hz, 3H).

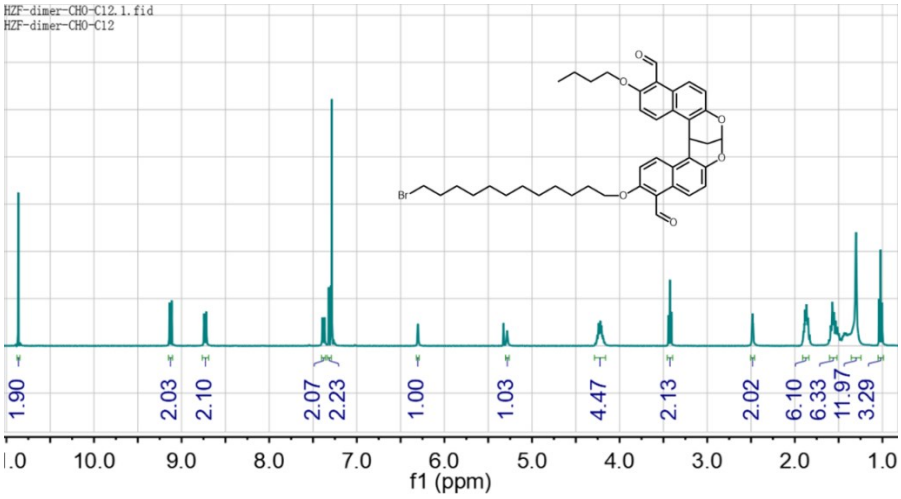


Fig. S12. ^{1}H-NMR spectrum of Compound 4 (400 MHz, $CDCl_3$, 298 K).

BB1-DABCO:

Compound 4 (81 mg, 0.11 mmol) in acetonitrile (MeCN) was added dropwise into DABCO (2, 2'-Diazabicyclo [2.2.2] octane) (123 mg, 1.1 mmol) in MeCN at 80 °C, and was stirred overnight. After cooling down to room temperature, the solution was concentrated in a vacuum, and was recrystallized by ethyl ether several times, and the BB1-DABCO was obtained. (77 mg, 95%). ^{1}H NMR (400 MHz, Acetonitrile-d3): ppm= 10.80 (s, 2H), 9.00 (d, J = 9.4 Hz, 2H), 8.94 – 8.89 (m, 2H), 7.57 (dd, J = 9.6, 2.0 Hz, 2H), 7.28 (d, J = 9.4 Hz, 2H), 6.33 (d, J = 1.4 Hz, 1H), 5.50 (s, 1H), 4.35 – 4.21 (m, 4H), 3.13 (d, J = 11.3 Hz, 12H), 3.07 – 3.01 (m, 2H), 2.53 (t, J = 2.7 Hz, 2H), 1.89 – 1.82 (m, 4H), 1.54 (m, 4H), 1.40 – 1.13 (m, 14H), 1.01 (t, J = 7.4 Hz, 3H).

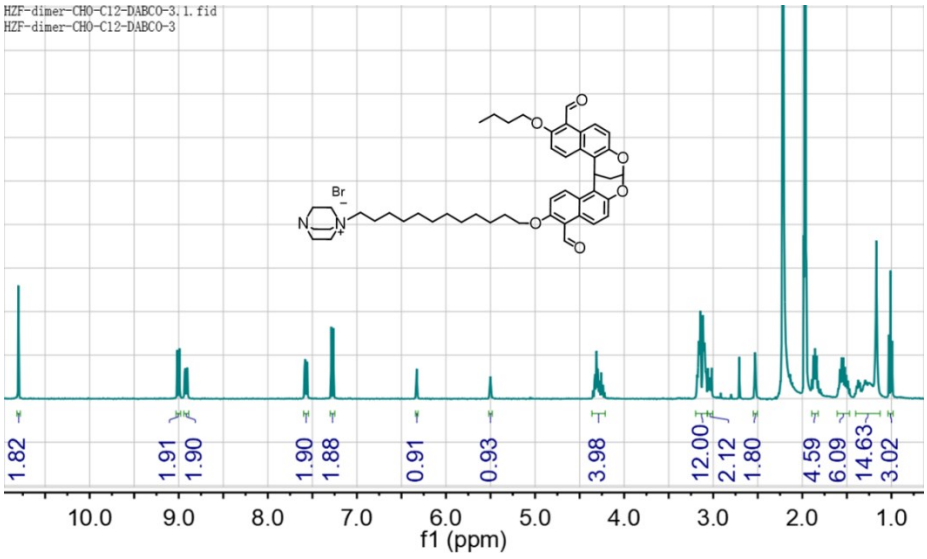
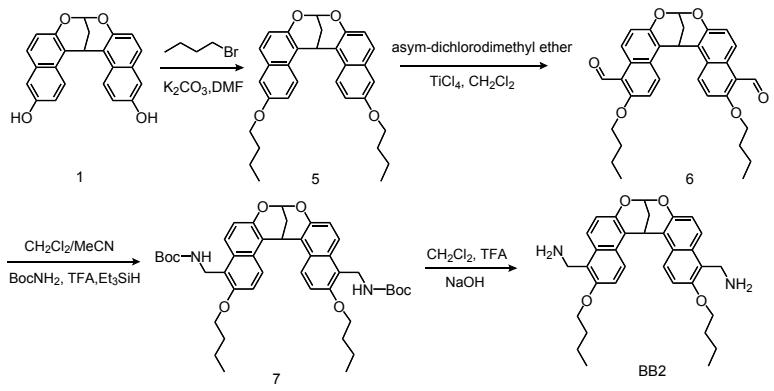


Fig. S13. ^{1}H-NMR spectrum of compound BB1-DABCO (400 MHz, CD_3CN, 298 K).

BB2:



Scheme S2. Synthetic procedures of mono-functionalized amine bis-naphthalene cleft BB2.[1]

Compound 1 (4.00 g, 11.22 mmol), 1-bromobutane (0.76 g, 5.60 mmol), and K_2CO_3 (1.56 g, 11.22 mmol) were mixed in dry DMF (60 mL). The mixture was stirred for 24 h at room temperature under an argon protection. The solution was poured into H_2O (150 mL). The suspension was filtered off. The filter cake was re-dissolved in CH_2Cl_2, and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under a reduced pressure. The crude product was subjected to column chromatography (SiO_2, petroleum ether: CH_2Cl_2 = 1:1) to give compound 5 as a white solid (2.2 g, 43 %).

To the solution of compound 5 (420 mg, 0.9 mmol) in dry CH_2Cl_2 (9 mL) at 0 °C, α,α-dichloromethyl methyl ether (0.33 mL, 3.6 mmol) was added. It was followed by the slow addition of $TiCl_4$ (690 mg, 3.6 mmol) via syringe. After stirring at 0 ℃ for 1 h, the mixture was warmed to room temperature and stirred for another 2.5 h. The solution was then poured into saturated aqueous $NaHCO_3$. The resulting suspension was extracted with CH_2Cl_2 (50 mL×3). The combined organic phase was washed consecutively with saturated aqueous $NaHCO_3$ (100 mL) and H_2O (150 mL), was then dried over anhydrous Na_2SO_4. After filtration, the crude product was obtained by removing the solvent under reduced pressure. Pure compound 6 as a yellow solid (406 mg, 86%) was afforded after column chromatography (SiO_2, cyclohexane : CH_2Cl_2 = 1: 1).

To the solution of compound 6 (240 mg, 0.44 mmol) and t-Butyl carbamate (324 mg, 2.76 mmol) in the mixture of MeCN (6 mL) and CH_2Cl_2 (12 mL), triethylsilane (0.44 mL, 2.84 mmol) and TFA (0.36 mL, 2.21 mmol were added. The resulting mixture was stirred overnight at room temperature. Following the addition of saturated aqueous $NaHCO_3$ (4 mL), the mixture was extracted with CH_2Cl_2 (60 mL×4). The combined organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the remaining residue was purified by column chromatography (SiO_2, cyclohexane : CH_2Cl_2 = 8: 1) to give compound 7 as a white solid (243 mg, 76 %), which was used directly in the next step. Compound 7 (3.00 g, 5.7 mmol) was dissolved in TFA (40 mL) and CH_2Cl_2 (80 mL). The resulting solution was stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure at room temperature. The remaining solid was suspended in CH_2Cl_2 (200 mL), and then washed with aqueous solution of NaOH (1.0 mM, 60 mL×2) and then H_2O (60 mL×2). The organic phase was dried over anhydrous Na_2SO_4 and then filtered. The organic solvent was removed in vacuum at room temperature to give pure BB2 as a yellow solid (1.79 g, 58%). ^1H NMR (400 MHz, $CDCl_3$, 300 K): ppm = 8.47 (d, J = 9.2, 2H), 7.81 (d, J = 9.2, 2H), 7.32 (d, J = 9.2, 2H), 7.19 (d, J = 9.2, 2H), 6.25 (s, 1H), 5.29 (s, 1H), 4.18 (s, 4H), 4.15 – 4.02 (m, 4H), 2.47 – 2.35 (m, 2H), 1.88 – 1.79 (m, 4H), 1.62 – 1.47 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H).

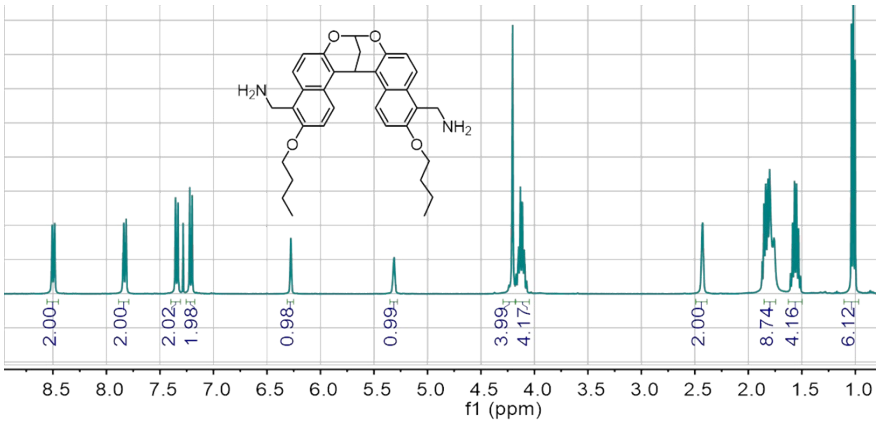


Fig. S14. ^{1}H-NMR spectrum of compound BB2 (400 MHz, $CDCl_3$, 298 K).

4. References

1. Z. He, G. Ye, W. Jiang, *Chem. Eur. J*, **2015**, 21, 3005 – 3012.

2. Z. He, X. Yang, W. Jiang, *Org. Lett.*, **2015**, 17, 3880−3883.