Supporting Information

Size-Selective Recognition by a Tubular Assembly of Phenylene–Pyrimidinylene Alternated Macrocycle through Hydrogen-Bonding Interactions

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1. General

Unless otherwise noted, all commercial reagents were used as received. Methallyl dichloride (98%, GC) was purchased from TCI. 3,5-Dibromophenol was prepared according to a reported procedure.[S1] Tetrahydrofuran (THF) was refluxed over a mixture of Na and benzophenone ketyl under argon and distilled just before use. DMF was dried over CaH_2 under argon and freshly distilled prior to use. CH_2Cl_2 was dried over CaH_2 under argon and freshly distilled prior to use. $CHCl_3$ was dried over molecular sieve and freshly distilled under argon before use. ^1H and ^{13}C NMR spectra were recorded on a Bruker model Bruker AV-400 spectrometer, operating at 400 and 100 MHz, respectively. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF mass) was performed on an AB Sciex model AB Sciex 4800 Plus MALDI TOF/TOF Analyzer, using dithranol as a matrix. Gel permeation chromatography (GPC) analyses were performed on JAI model LC-9201 recycling preparative HPLC, using $CHCl_3$ as eluent. Electronic absorption spectra were recorded on a Persee model TU-1901 spectrophotometer, using a quartz cell of 1-cm path length. Fluorescence spectroscopy was conducted using a quartz cell of 1-cm path length on a HORIBA model Fluoromax-4 spectrophotometer. TEM microscopy was recorded on a JEOL model JEM-2100 electron microscope operating at 200 kV. All geometry optimizations were performed with Gaussian 09 (Rev. D. 01) by DFT method using B3LYP functional and the 6-31G basis set.[S2] Atomic force microscopy (AFM) was performed on a SII Nanonavi E-Sweep microscope. Infrared spectra (IR) were recorded on a Varian 640 FT-IR spectrometer.

2. Methods

Determination of the association constant

The association constant K of the complex (**NT_{6mer}⊃G3**) was determined from the following Benesi-Hildebrand equation:[S3]

$$\frac{1}{A-A_0}=\frac{a}{a-b}\left[\frac{1}{K[M]}+1\right]$$

Where K = Association constant;

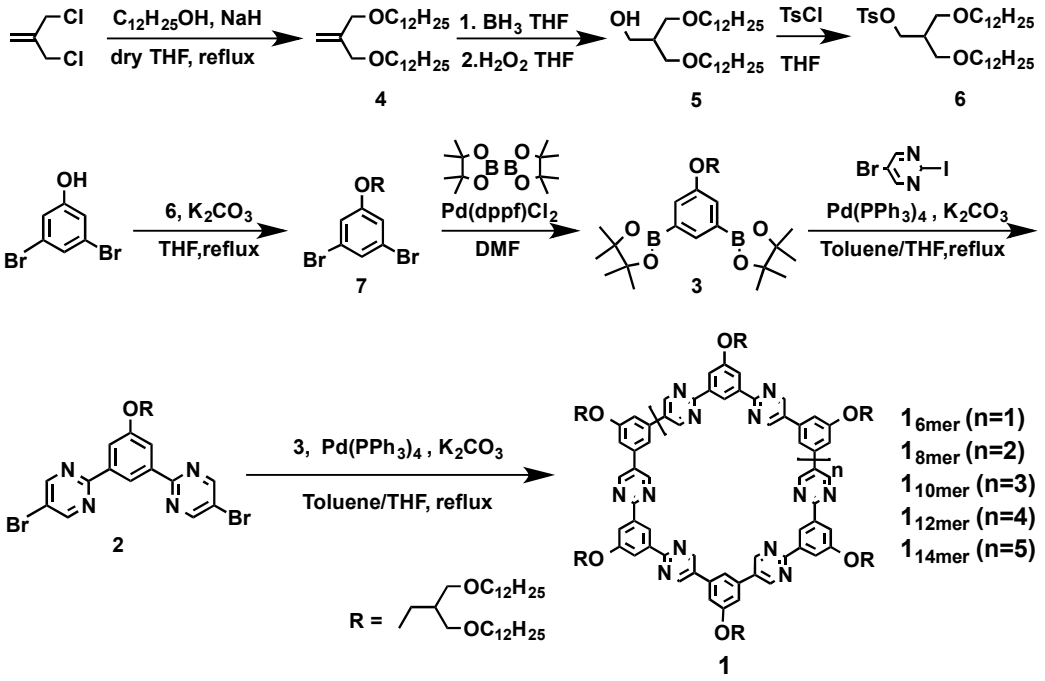
A_0 = The observed absorption in the absence of guest;

A = The observed absorption the guest-added;

[M] = The concentration of the guest-added;

a and b are constants, the association constant value *K* was evaluated graphically by plotting $1/(A-A_0)$ against 1/[M].

3. Synthetic Procedures



Scheme S1. Synthesis of macrocycles **1**

Compound 4. Dry NaH (19.2 g, 0.8 mol), methallyl dichloride (13.5 g, 0.11 mol) and freshly distilled dry THF (200 ml) were placed in a dry round bottomed flask under N_2 atmosphere. To this mixture at room temperature, dodecan-1-ol (42.3g, 0.23 mol) was added dropwise. The mixture was stirred at room temperature for 15 min and then at 65 °C for 12 hours. After cooling to room temperature, the reaction mixture was quenched with water and extracted with DCM. The organic layer was then dried over anhydrous $MgSO_4$ and the solvent was then removed in a rotatory evaporator. Purification of the residue by flash column chromatography on silica gel (eluent: EA/MeOH = 19/1) yielded 32.4 g (75%) of **4** as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.14 (s, 2H), 3.95 (s, 4H), 3.39 (t, J = 6.6 Hz, 4H), 1.62 – 1.48 (m, 4H), 1.25 (s, 36H), 0.87 (t, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.42, 113.13, 77.33, 77.01, 76.70, 71.50, 70.54, 32.10, 31.92, 31.75, 29.94, 29.77, 29.67, 29.64, 29.62, 29.51, 29.35, 26.38, 26.22, 26.04, 22.84, 22.67, 22.49, 14.05. MALDI-TOF mass: calcd. for $C_{28}H_{56}O_2$ $[M + H]^+$: m/z = 425.44; found: 425.20.

Compound 5. Freshly distilled dry THF (100 ml) and compound **4** (8.0 g, 0.02 mmol) were placed in a dry round bottomed flask under N_2 and cooled to 0 °C in an ice bath. To this mixture, BH_3 (1 M, 28 ml) solution in THF was added slowly and the reaction mixture was then allowed to stir at 0 °C for 2 hours. The reaction mixture was then quenched with aqueous NaOH solution (3 M, 28 ml) and allowed to stir for 15 min. This was followed by addition of 30% H_2O_2 aqueous solution (28 ml) and the mixture was stirred at room temperature for 30 min. The reaction mixture was saturated with K_2CO_3 and extracted with DCM. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed in a rotatory evaporator. Purification of the residue by flash column chromatography on silica gel (eluent: EA/MeOH = 19/1) yielded 6.5 g (80%) of **5** as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.78 (dd, *J* = 5.1, 2.4 Hz, 1H), 3.76 (d, *J* = 5.0 Hz, 1H), δ 3.68 (d, *J* = 6.1 Hz, 1H), 3.62– 3.58 (m, 2H), 3.52 (qd, *J* = 9.4, 6.0 Hz, 2H), 3.47 – 3.25 (m, 4H), 2.17 (s, 1H), 1.55 (dd, *J* = 10.2, 3.9 Hz, 4H), 1.46– 1.03 (m, 36H), 0.99 – 0.74 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 77.32, 77.00, 76.68, 71.62, 71.00, 64.84, 41.26, 31.91, 29.83, 29.63, 29.61, 29.59, 29.43, 29.34, 26.15, 22.67, 14.08. MALDI-TOF mass: calcd. for $C_{28}H_{58}O_3$ $[M + Na]^+$: *m/z* = 465.43, found: 465.30.

Compound 6. Compound **5** (3.9 g, 9.57 mmol) and TsCl (9.13 g, 47.9 mmol) were dissolved of dry DCM. Pyridine (11.4 g, 144 mmol) was added under nitrogen. The reaction mixture was stirred at 25 °C under nitrogen for 5 hours. The resulting solution was extracted with DCM and HCl (1 M). DCM solution was then dried over anhydrous $MgSO_4$, and filtered. The solvent was removed in a rotatory evaporator, and the crude product was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to yield 4.6 g (85%) of **6** as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.12 (d, *J* = 5.6 Hz, 2H), 3.46 – 3.23 (m, 8H), 2.47 (s, 3H), 2.20 (q, *J* = 11.5, 5.8 Hz, 1H), 1.54 – 1.40 (m, 4H), 1.37 – 1.17 (m, 36H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.52, 133.14, 129.73, 127.96, 77.35, 77.03, 76.72, 71.35, 68.91, 67.87, 39.73, 29.64, 29.57, 29.35, 26.10, 22.67, 21.58, 14.08. MALDI-TOF mass: calcd for $C_{35}H_{64}O_5S$ $[M + Na]^+$: *m/z* = 619.44, found: 619.20.

Compound 7. 3,5-dibromophenol [S1] (635 mg, 2.54 mmol, 2.5 eq.), **6** (600 mg, 1.01 mmol, 1eq.), an excess of K_2CO_3 (1.38 g, 10 mmol, 10 eq.) and 18-crown-6-ether (13.3 mg, 0.05 mmol, 5% eq.) were added into DMF (20 mL). The mixture was heated at 85 °C for 24 hours. The solution was poured into water and extracted with

DCM. The DCM solution was washed with water, dried over anhydrous $MgSO_4$, and then filtered. Solvent was removed in a rotatory evaporator, and the crude product was then purified by column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1/20) to yield 600 mg (88.23%) of **7** as a colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (s, 1H), 7.01 (d, *J* = 1.5 Hz, 2H), 4.02 (d, *J* = 5.6 Hz, 2H), 3.57 – 3.34 (m, 8H), 2.34 (dd, *J* = 11.6, 5.8 Hz, 1H), 1.55 (dd, *J* = 13.5, 6.6 Hz, 4H), 1.37 – 1.19 (m, 36H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.39, 126.25, 123.04, 117.04, 77.32, 77.01, 76.69, 71.42, 68.61, 66.93, 40.04, 31.94, 29.55, 26.20, 22.70, 14.11. MALDI-TOF mass: calcd. for $C_{34}H_{60}Br_2O_3$ $[M+ Na]^+$: *m/z* = 699.65; found: 699.00.

Compound 3. A mixture of **7** (500 mg, 0.74 mmol, 1 eq.), bis(pinacolato)diboron (473 mg, 1.86 mmol, 2.5 eq.), [$PdCl_2$(dppf)] (54 mg, 0.074mmol, 10% eq.), potassium acetate (478 mg, 4.88 mmol, 6.5 eq.), and DMF (20 mL) was stirred under Ar for 3 h at 80 °C. The solvent was removed in vacuo and the residue was dissolved in acetic ether. The solution was washed with water and dried over $MgSO_4$. The solution was concentrated to dryness, and the residue was purified by flash column chromatography on silica gel (eluent: PE/EA= 20/1), giving the product as a yellow liquid. The obtained liquid was subjected to preparative GPC (gel permeation chromatography, $CHCl_3$ as eluent solution) to purify. Yield: 285 mg (50%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (s, 1H), 7.44 (s, 2H), 4.06 (t, *J* = 5.7 Hz, 2H), 3.57 – 3.51 (m, 4H), 3.40 (t, *J* = 6.6 Hz, 4H), 2.35 (dt, *J* = 11.8, 5.8 Hz, 1H), 1.54 (dd, *J* = 13.9, 6.8 Hz, 4H), 1.33(s, 24H), 1.30 – 1.19 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$):δ (ppm) 158.13, 133.50, 123.41, 83.73, 77.26, 77.00, 76.69, 71.37, 68.92, 66.19, 40.25, 31.92, 29.54, 26.18, 24.86, 22.68, 14.10. MALDI-TOF mass: calcd. for $C_{46}H_{84}B_2O_7$ $[M + Na]^+$: *m/z* =793.78; found: 793.40.

Compound 2. A THF/toluene solution (10 mL/5 mL) of a mixture of **3** (100 mg, 0.13 mmol, 1 eq.) and 5-bromo-2-iodopyrimidine (112.8 mg, 0.40 mmol, 3 eq.) were successively added $Pd(PPh_3)_4$ (32 mg, 0.026 mmol) and an aqueous solution of K_2CO_3 (2 M, 1.5 mL) under argon, and the resulting suspension was refluxed at 80 °C for 2.5 days. After cooling to room temperature, the resulting mixture was extracted with DCM. The organic phase was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (eluent: PE/EA = 20/1), to give **2** as white powder (60 mg) in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.08 (s, 1H), 8.88 (s, 4H), 8.15 (d, *J* = 1.4 Hz,

2H), 4.25 (d, *J* = 5.6 Hz, 2H), 3.62 (d, *J* = 6.0 Hz, 4H), 3.45 (t, *J* = 6.6 Hz, 4H), 2.54 – 2.38 (m, 1H), 1.59 (m, *J* = 14.6, 7.5 Hz, 4H), 1.24 (s, 36H), 0.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.44, 160.23, 157.82, 138.36, 120.47, 118.77, 117.08, 71.53, 68.96, 66.77, 40.33, 32.07, 29.80, 29.69, 29.65, 29.51, 26.34, 22.84, 14.38. MALDI-TOF mass: calcd. for $C_{42}H_{64}Br_2N_4O_3$ $[M + Na]^+$: *m/z* =855.80; found: 855.40.

Macrocycles 1. A THF/toluene solution (5 mL/2.5 mL) of a mixture of **3** (84 mg, 0.1084 mmol, 1 eq.) and **2** (90 mg, 0.1084 mmol, 1 eq.) were successively added $Pd(PPh_3)_4$ (40 mg, 0.0325 mmol, 30% mmol) and an aqueous solution of K_2CO_3 (2 M, 1 mL) under argon, and the resulting suspension was refluxed at 80 °C for 80 h. After cooling to room temperature, the resulting mixture was extracted with chloroform. The organic phase was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was subjected to column chromatography on silica gel (eluent: PE/EA = 3/1), giving the product as a white solid. The solid obtained were subjected to preparative GPC (gel permeation chromatography, $CHCl_3$ as eluent solution) to purify, **1$_{6mer}$-1$_{14mer}$** were given as white solids after several cycles.

1$_{6mer}$: Yield: 12%. ^{1}H NMR (400 MHz, THF): δ (ppm) 9.38 (s, 1H), 9.19 (s, 4H), 8.14 (s, 2H), 7.76 (s, 1H), 7.36 (s, 2H), 4.22 (d, *J* = 5.8 Hz, 2H), 4.18 (d, *J* = 5.8 Hz, 2H), 3.55 (t, *J* = 5.5 Hz, 8H), 3.37 (t, *J* = 6.5 Hz, 8H), 2.35 (d, *J* = 3.1 Hz, 2H), 1.50 (dd, *J* = 13.7, 6.7 Hz, 8H), 1.26 – 1.10 (m, 72H), 0.76 (t, *J* = 6.7 Hz, 12H). MALDI-TOF Mass: calcd. for $C_{228}H_{372}N_{12}O_{18}$ $[M]^+$: *m/z* = 3569.55; found: 3569.64.

1$_{8mer}$: Yield: 9.30%. ^{1}H NMR (400 MHz, THF): δ 9.28 (d, *J* = 25.6 Hz, 1H), 9.05 (dd, *J* = 28.8, 22.0 Hz, 4H), 8.20 (d, *J* = 10.6 Hz, 2H), 7.57 (d, *J* = 39.3 Hz, 1H), 7.31 (d, *J* = 20.6 Hz, 2H), 4.17 (s, 4H), 3.53 (s, 8H), 3.33 (d, *J* = 5.7 Hz, 8H), 2.32 (s, 2H), 1.47 (d, *J* = 6.8 Hz, 8H), 1.16 (s, 72H), 0.75 (s, 12H). MALDI-TOF Mass: calcd. for $C_{304}H_{496}N_{16}O_{24}$ $[M+Na]^+$: *m/z* = 4778.81; found: 4778.70.

1$_{10mer}$: Yield: 8%. ^{1}H NMR (400 MHz, THF): δ (ppm) 9.33 (s, 1H), 9.12 (s, 4H), 8.21 (s, 2H), 7.63 (s, 1H), 7.34 (s, 2H), 4.21 – 4.12 (m, 4H), 3.55 – 3.49 (m, 8H), 3.34 (dd, *J* = 10.4, 6.3 Hz, 8H), 2.32 (s, 2H), 1.46 (d, *J* = 6.0 Hz, 8H), 1.32 – 1.07 (m, 72H), 0.75 (t, *J* = 6.4 Hz, 12H). MALDI-TOF Mass: calcd. for $C_{380}H_{620}N_{20}O_{30}$ $[M+Na]^+$: *m/z* =5967.76; found: 5968.87.

1$_{12mer}$: Yield: 7%. ^{1}H NMR (400 MHz, THF): δ (ppm) 9.31 (s, 1H), 9.11 (d, *J* = 4.0 Hz, 4H), 8.20 (s, 2H), 7.60 (s, 1H), 7.32 (s, 2H), 4.17 (s, 4H), 3.55 – 3.49 (m, 8H), 3.38 – 3.28 (m, 8H), 2.31 (s, 2H), 1.47 (s, 8H), 1.20 (d, *J* = 38.6 Hz, 72H), 0.75 (t, *J* =

6.2 Hz, 12H). MALDI-TOF Mass: calcd. for $C_{456}H_{744}N_{24}O_{36}$ $[M]^+$: m/z = 7139.10; found: 7139.40.

1_{14mer}: Yield: 5%. ^{1}H NMR (400 MHz, THF): δ (ppm) 9.31 (s, 1H), 9.11 (d, J = 4.0 Hz, 4H), 8.20 (s, 2H), 7.60 (s, 1H), 7.32 (s, 2H), 4.17 (s, 4H), 3.55 – 3.49 (m, 8H), 3.38 – 3.28 (m, 8H), 2.31 (s, 2H), 1.47 (s, 8H), 1.20 (d, J = 38.6 Hz, 72H), 0.75 (t, J = 6.2 Hz, 12H). MALDI-TOF Mass: calcd. for $C_{532}H_{868}N_{28}O_{42}$ $[M]^+$: m/z = 8329.10; found: 8333.04.

4. Supporting Reference

(S1) Davidson, J. P.; Sarma, K.; Fishlock, D.; Welch, M.; Sukhtankar, S.; Lee, G. M.; Martin, M.; Cooper, G. F. A Synthesis of 3,5-Disubstituted Phenols. *Org. Process. Res. Dev.* **2010**, *14*, 477.

(S2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

(S3) Benesi, H. A.; Hildebrand, J. H. A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons.*J. Am. Chem. Soc.* **1949**, *71*, 2703.

5. Supporting Figures

5-1. GPC profile

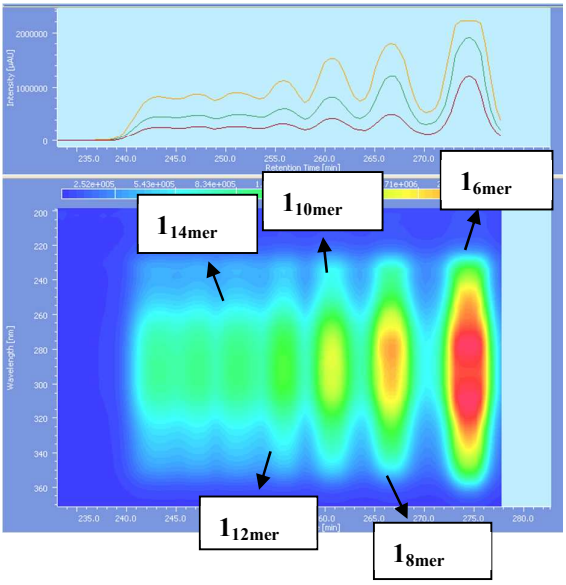


Figure S1. GPC profile of macrocycles **1**.

5-2. MALDI-TOF mass spectra

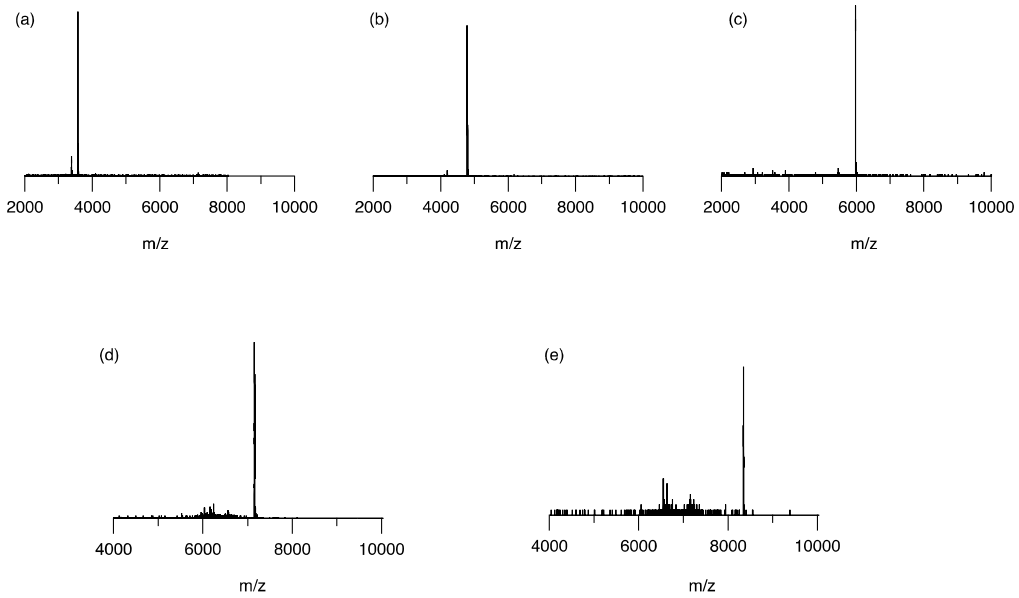


Figure S2. MALDI-TOF mass spectra of macrocycles (a) $\mathbf{1}_{6mer}$, (b) $\mathbf{1}_{8mer}$, (c) $\mathbf{1}_{10mer}$, (d) $\mathbf{1}_{12mer}$ and (f) $\mathbf{1}_{14mer}$.

5-3. Concentration-dependent ^{1}H NMR spectra of NT_{6mer} in CD_2Cl_2

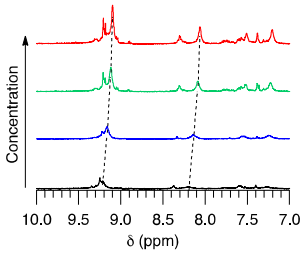


Figure S3. Concentration-dependent ^{1}H NMR spectra of $\mathbf{NT_{6mer}}$ in CD_2Cl_2 at room temperature. [$\mathbf{NT_{6mer}}$] = 0.6×10^{-3} -3×10^{-3} mol/L.

5-4. AFM image of the NT_{6mer}

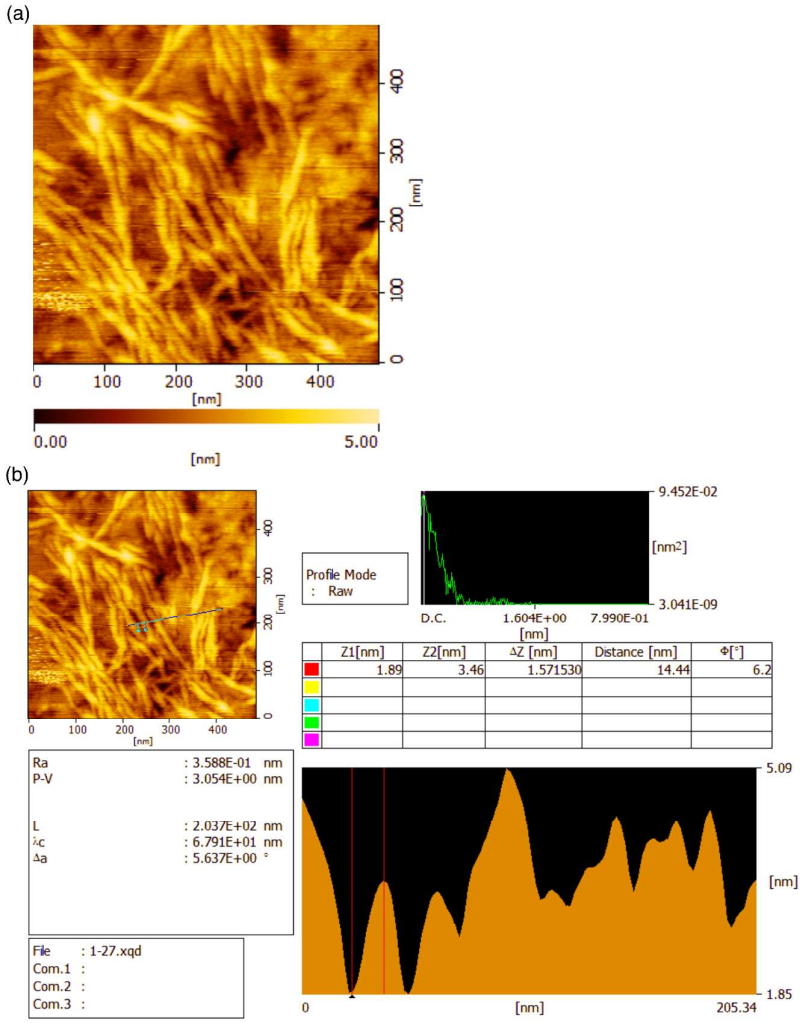


Figure S4. (a) 2D AFM images of nanotubes ($\mathbf{NT_{6mer}}$). (b) The height profiles of nanotubes ($\mathbf{NT_{6mer}}$).

5-5. TEM micrograph of $\mathbf{1_{6mer}}$ from $CHCl_3$ and THF

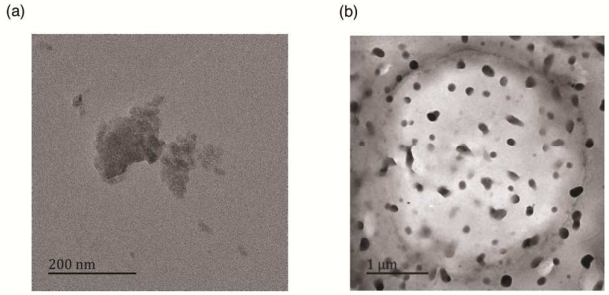


Figure S5. TEM micrograph of drop-cast $\mathbf{1_{6mer}}$ (5×10^{-6} mol/L) from $CHCl_3$ (a) and THF (b) solution.

5-6. TEM micrograph of $\mathbf{1_{8mer}}$ and $\mathbf{1_{10mer}}$ from CH_2Cl_2

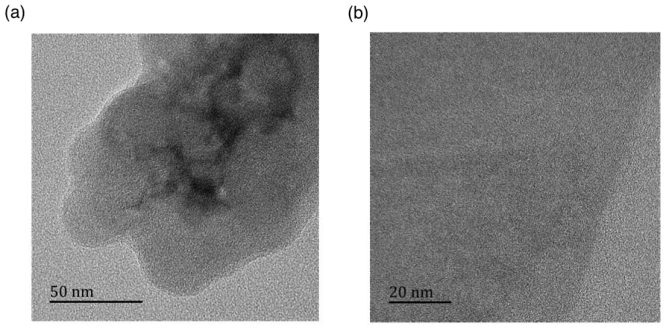


Figure S6. TEM micrograph of drop-cast $\mathbf{1_{8mer}}$ (a, 5×10^{-6} mol/L) and $\mathbf{1_{10mer}}$ (b, 5×10^{-6} mol/L) from CH_2Cl_2.

5-7. Fluorescence spectral changes of $\mathbf{NT_{6mer}}$

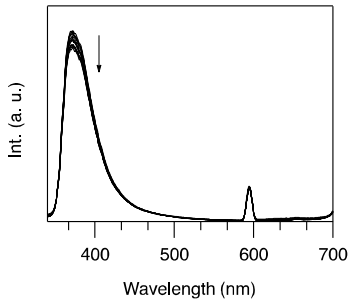


Figure S7. Fluorescence spectral changes of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) in CH_2Cl_2 solution upon addition of **G1** at 25 °C. [**G1**] = 1-50 equiv.

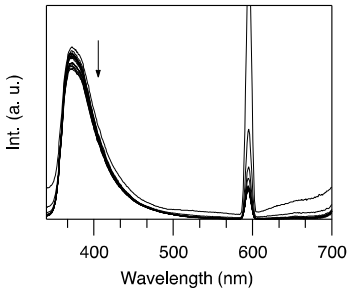


Figure S8. Fluorescence spectral changes of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) in CH_2Cl_2 solution upon addition of **G2** at 25 °C. [**G2**] = 1-100 equiv.

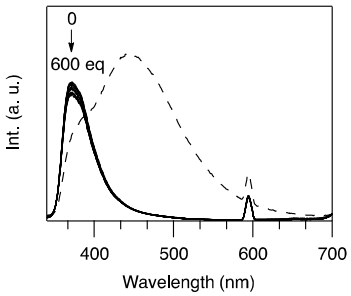


Figure S9. Fluorescence spectral changes of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) in CH_2Cl_2 upon titration with **G1** in the range of 1 equiv. to 600 equiv. (solid line) then **G3** (1 equiv.) sequentially added (dot line).

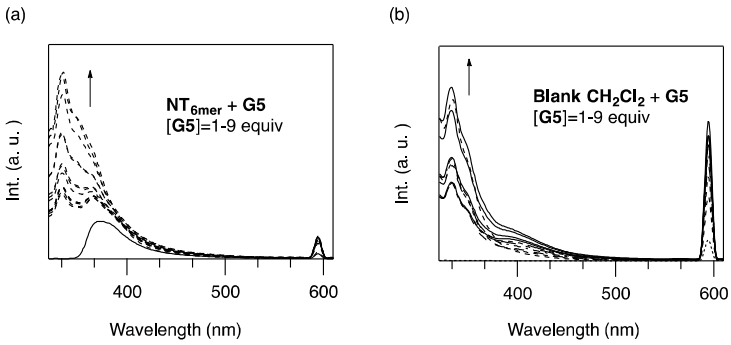


Figure S10. (a) Fluorescence spectra of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) in CH_2Cl_2 solution upon addition of **G5**. (b) Fluorescence spectra of blank CH_2Cl_2 upon addition of **G5**. [**G5**] = 1-9 equiv. Compared (a) with (b), the spectra changes are rose from the increasing concentration of **G5**.

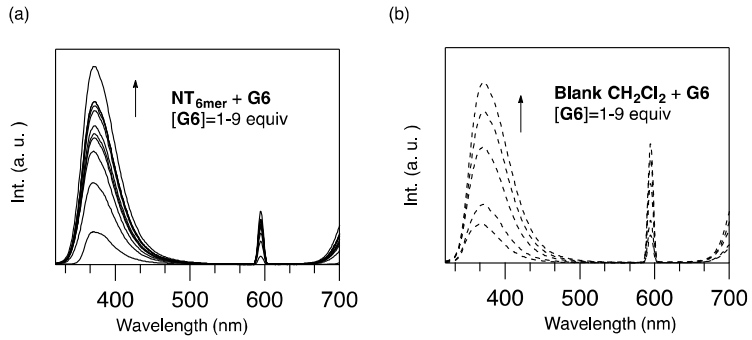


Figure S11. (a) Fluorescence spectra of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) in CH_2Cl_2 solution upon addition of **G6**. (b) Fluorescence spectra of blank CH_2Cl_2 upon addition of **G6.** [**G6**] = 1-9 equiv. Compared (a) with (b), the spectra changes are rose from the increasing concentration of **G6**.

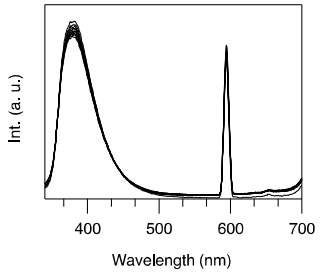


Figure S12. Fluorescence spectral changes of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) in CH_2Cl_2 upon titration with **G3** in the presence of DMSO. [**G3**] = 1-9 equiv.

5-8. Fluorescence spectral changes of $\mathbf{1_{8mer}}$ and $\mathbf{1_{10mer}}$ in CH_2Cl_2 upon addition of G3

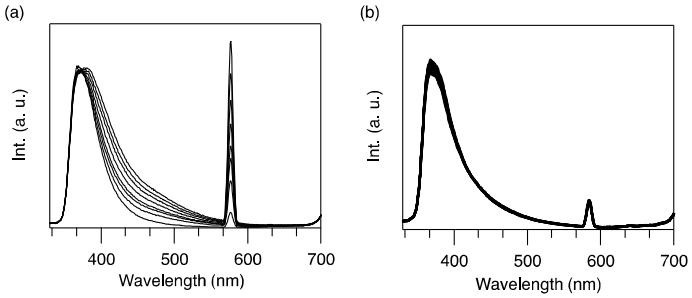


Figure S13. Fluorescence spectral changes of $\mathbf{1_{8mer}}$ (a, 5×10^{-6} mol/L) and $\mathbf{1_{10mer}}$ (b, 5×10^{-6} mol/L) in CH_2Cl_2 solution upon addition of **G3**. [**G3**] = 1-12 equiv. The fluorescence spectra of $\mathbf{1_{8mer}}$ and $\mathbf{1_{10mer}}$ showed little changes in their intensity or wavelength.

5-9. Benesi-Hildebrand analysis

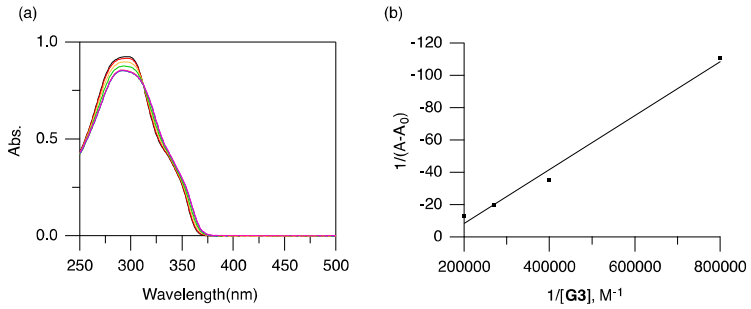


Figure S14. (a) Electronic absorption spectral changes of $\mathbf{NT_{6mer}}$ (5×10^{-6} mol/L) upon titration with **G3** in CH_2Cl_2 at 25 °C, [**G3**] = 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2 equiv. (b) Benesi-Hildebrand analysis of $\mathbf{NT_{6mer}}$ with **G3** based on the absorption intensity of $\mathbf{NT_{6mer}}$ at 297 nm upon titration with **G3**, [**G3**] = 0, 0.25, 0.5, 0.75 and 1 equiv.

$Y = A + B \cdot X$

Parameter	Value	Error
A	25.069	6.22
B	-0.00016723	1.3e-5
R: 0.99399		

$K_a = A/B = (25.069/16.723) \times 10^5 = 1.499 \times 10^5$

$\Delta K_a = \ | \Delta A/A - \Delta B/B | \times Ka = 0.255 \times 10^5$

$K = Ka + \Delta K_a = (1.499 \pm 0.255) \times 10^5$

5-10. Infrared spectra

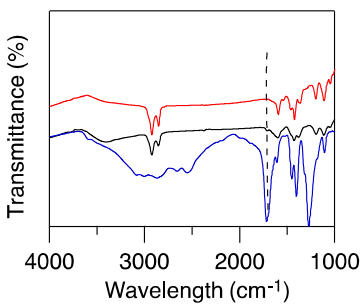


Figure S15. Infrared spectra (KBr) of **NT_{6mer}**(red), **G3**(blue), and **$NT_{6mer}\supset$G3**(black).

5-11. Fluorescence spectrum of $NT_{6mer}\supset$G3 in the presence of DMSO

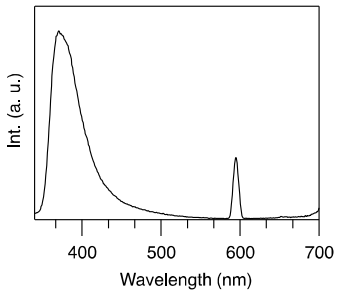


Figure S16. Fluorescence spectrum of **$NT_{6mer}\supset$G3** in CH_2Cl_2 after addition of a drop of DMSO.

5-12. TEM micrograph of $NT_{6mer}\supset$G3 in the presence of DMSO

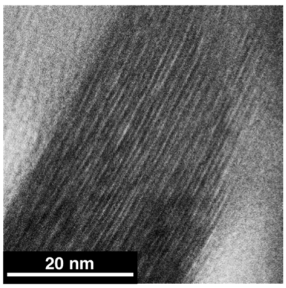


Figure S17. TEM micrograph of an air-dried CH_2Cl_2 solution of **$NT_{6mer}\supset$G3** after addition of a drop of DMSO.

5-13. DFT profiles

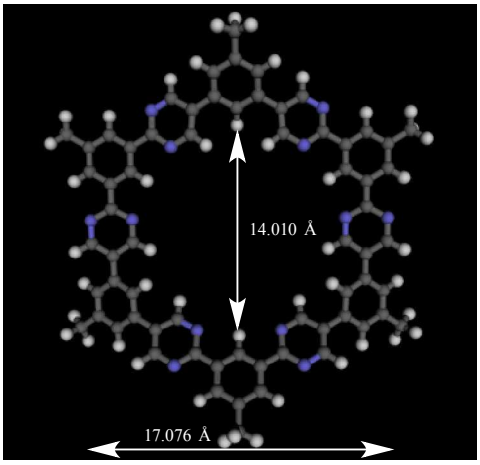


Figure S18. Optimized model structure of $\mathbf{1}_{\mathbf{6mer}}$.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.584378	3.568609	-0.460568
2	6	0	-7.377905	2.847555	-0.423168
3	6	0	-6.162395	3.537087	-0.307345
4	6	0	-6.150858	4.936688	-0.230810
5	6	0	-7.364395	5.645378	-0.294215
6	6	0	-8.588105	4.970570	-0.409292
7	6	0	-7.378442	1.375215	-0.496865
8	6	0	-4.872658	5.649976	-0.054914
9	7	0	-8.561955	0.713456	-0.412762
10	6	0	-8.538473	-0.630142	-0.460641
11	6	0	-7.351853	-1.371457	-0.617045
12	6	0	-6.181467	-0.593873	-0.718661
13	7	0	-6.184525	0.744919	-0.648082
14	7	0	-4.868791	7.008197	-0.085077
15	6	0	-3.698758	7.640721	0.111681
16	6	0	-2.493124	6.960013	0.366055
17	6	0	-2.597895	5.555296	0.365835
18	7	0	-3.752666	4.908751	0.151165
19	6	0	1.194649	-8.848929	1.618338
20	6	0	1.204472	-7.587893	0.994445
21	6	0	-0.009729	-6.960132	0.685580
22	6	0	-1.226596	-7.585488	0.993702
23	6	0	-1.220536	-8.845547	1.616896
24	6	0	-0.013229	-9.485442	1.936994

25	6	0	2.475959	-6.922435	0.656353
26	6	0	-2.496058	-6.916306	0.654636
27	7	0	3.645494	-7.548776	0.949609
28	6	0	4.793736	-6.922669	0.634641
29	6	0	4.829555	-5.661542	0.011924
30	6	0	3.567868	-5.097144	-0.257654
31	7	0	2.415260	-5.703514	0.058768
32	7	0	-2.431423	-5.697540	0.057319
33	6	0	-3.582130	-5.087650	-0.259553
34	6	0	-4.845559	-5.648312	0.009424
35	6	0	-4.813789	-6.909772	0.631760
36	7	0	-3.667565	-7.539304	0.947123
37	6	0	-6.095807	-4.949353	-0.359469
38	6	0	-6.169885	-3.549061	-0.269588
39	6	0	-7.318570	-2.849624	-0.678918
40	6	0	-8.417498	-3.587574	-1.158689
41	6	0	-8.384434	-4.988123	-1.225877
42	6	0	-7.215324	-5.657048	-0.833504
43	6	0	7.380416	5.624616	-0.295830
44	6	0	6.164947	4.919292	-0.231921
45	6	0	6.172630	3.519637	-0.307983
46	6	0	7.386211	2.826723	-0.423795
47	6	0	8.594657	3.544442	-0.461694
48	6	0	8.602238	4.946403	-0.410944
49	6	0	4.888764	5.636149	-0.055923
50	6	0	7.382666	1.354356	-0.496914
51	7	0	4.888688	6.994378	-0.086278
52	6	0	3.720483	7.630200	0.110670
53	6	0	2.513004	6.952902	0.365389
54	6	0	2.613813	5.547897	0.365207
55	7	0	3.766727	4.898093	0.150390
56	7	0	6.187003	0.727347	-0.647917
57	6	0	6.180194	-0.611467	-0.717872
58	6	0	7.348376	-1.392285	-0.615745
59	6	0	8.537063	-0.654224	-0.459596
60	7	0	8.564318	0.689329	-0.412380
61	6	0	1.236393	7.646626	0.645102
62	6	0	7.310912	-2.870382	-0.676881
63	6	0	6.160114	-3.566311	-0.267546
64	6	0	6.081980	-4.966431	-0.356821
65	6	0	7.199592	-5.677562	-0.830203
66	6	0	8.370754	-5.012193	-1.222534
67	6	0	8.407850	-3.611717	-1.156000
68	6	0	1.219692	8.901463	1.282990

69	6	0	0.013787	9.546905	1.591845
70	6	0	-1.194044	8.904871	1.283335
71	6	0	-1.214475	7.650113	0.645437
72	6	0	0.010061	7.044562	0.313759
73	6	0	-9.889065	5.739650	-0.494559
74	6	0	-9.585485	-5.764056	-1.721040
75	6	0	-0.018815	-10.830176	2.632032
76	6	0	9.569662	-5.791865	-1.717023
77	6	0	9.905275	5.711886	-0.496859
78	6	0	0.015769	10.905231	2.258590
79	1	0	-9.516022	3.018274	-0.532645
80	1	0	-5.232526	2.987387	-0.265891
81	1	0	-7.336399	6.727997	-0.241214
82	1	0	-9.497973	-1.125798	-0.351385
83	1	0	-5.214130	-1.057337	-0.882695
84	1	0	-3.726556	8.724154	0.049371
85	1	0	-1.734399	4.930530	0.570459
86	1	0	2.142752	-9.322235	1.847897
87	1	0	-0.008585	-5.992717	0.203600
88	1	0	-2.170382	-9.316397	1.845343
89	1	0	5.710540	-7.437849	0.905348
90	1	0	3.483279	-4.140344	-0.763546
91	1	0	-3.494442	-4.131004	-0.765194
92	1	0	-5.732255	-7.422286	0.901888
93	1	0	-5.335139	-3.004438	0.156718
94	1	0	-9.301922	-3.066925	-1.512582
95	1	0	-7.164559	-6.737347	-0.931689
96	1	0	7.355416	6.707326	-0.243192
97	1	0	5.241267	2.972502	-0.266157
98	1	0	9.524773	2.991525	-0.533752
99	1	0	3.751295	8.713545	0.048254
100	1	0	1.748601	4.925577	0.570040
101	1	0	5.211573	-1.072290	-0.881759
102	1	0	9.495154	-1.152527	-0.350016
103	1	0	5.326829	-3.019086	0.158285
104	1	0	7.145724	-6.757753	-0.927939
105	1	0	9.293863	-3.093786	-1.509903
106	1	0	2.155146	9.367774	1.576276
107	1	0	-2.128091	9.373812	1.576914
108	1	0	0.008648	6.108334	-0.232553
109	1	0	-10.190285	5.897224	-1.539189
110	1	0	-10.704532	5.201429	0.000600
111	1	0	-9.800530	6.726277	-0.028243
112	1	0	-10.246096	-6.043873	-0.889297

113	1	0	-9.285074	-6.689432	-2.223353
114	1	0	-10.180591	-5.174232	-2.425744
115	1	0	0.939085	-11.345645	2.509735
116	1	0	-0.807398	-11.480883	2.237963
117	1	0	-0.197831	-10.720274	3.710178
118	1	0	9.266586	-6.715702	-2.220577
119	1	0	10.228291	-6.074816	-0.884770
120	1	0	10.167660	-5.203466	-2.420462
121	1	0	10.719294	5.171870	-0.001270
122	1	0	10.206910	5.867784	-1.541622
123	1	0	9.819414	6.699130	-0.031352
124	1	0	0.902860	11.042448	2.885471
125	1	0	0.014827	11.711637	1.512811
126	1	0	-0.868868	11.043450	2.888730

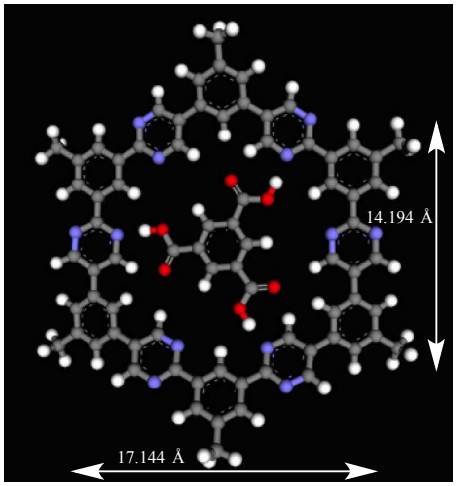


Figure S19. Optimized model structure of $\mathbf{1}_{\mathbf{6mer}}\supset\mathbf{G3}$. Caclulated the distances by DFT between three carboxylic acid of TMA and nitrogen atoms of pyrimidine are 1.65338, 1.65199 and 1.66286 Å, respectively, suggesting possible formation of multiple hydrogen bonds.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.389389	0.160032	-0.157771
2	1	0	2.460001	0.295056	-0.071744
3	6	0	0.850632	-1.128369	-0.282935
4	6	0	-0.532938	-1.303721	-0.400611
5	1	0	-0.948026	-2.299360	-0.490690

6	6	0	-1.380624	-0.186545	-0.402004
7	6	0	-0.848312	1.100212	-0.260169
8	1	0	-1.504544	1.961081	-0.245977
9	6	0	0.538037	1.270904	-0.133503
10	6	0	1.071029	2.642139	0.035054
11	6	0	1.772950	-2.287004	-0.284790
12	6	0	-2.838172	-0.406538	-0.544585
13	8	0	0.320512	3.644210	0.115559
14	8	0	2.413271	2.705364	0.105788
15	8	0	3.019718	-2.151451	-0.288622
16	8	0	1.151406	-3.481034	-0.286750
17	1	0	1.742830	-4.323021	-0.216824
18	8	0	-3.330778	-1.555402	-0.649128
19	8	0	-3.568659	0.723965	-0.556912
20	1	0	2.847089	3.639107	0.183244
21	1	0	-4.594862	0.627674	-0.598419
22	6	0	-8.651659	3.102673	-0.311550
23	6	0	-7.406762	2.442514	-0.267700
24	6	0	-6.225633	3.200214	-0.206857
25	6	0	-6.293249	4.604039	-0.199019
26	6	0	-7.543898	5.240681	-0.268540
27	6	0	-8.732588	4.499128	-0.323736
28	6	0	-7.390103	0.967231	-0.286358
29	6	0	-5.064481	5.418545	-0.093191
30	7	0	-8.564959	0.311517	-0.100661
31	6	0	-8.575904	-1.034325	-0.102691
32	6	0	-7.417616	-1.798891	-0.322682
33	6	0	-6.254818	-1.048001	-0.545847
34	7	0	-6.221813	0.297270	-0.502778
35	7	0	-5.181940	6.768983	-0.176108
36	6	0	-4.068488	7.508449	-0.036989
37	6	0	-2.801308	6.947919	0.207586
38	6	0	-2.774810	5.536626	0.251800
39	7	0	-3.880352	4.785627	0.097989
40	6	0	1.648983	-8.834037	1.275557
41	6	0	1.589771	-7.529623	0.742788
42	6	0	0.338035	-6.936142	0.512193
43	6	0	-0.839907	-7.641181	0.813520
44	6	0	-0.756895	-8.939181	1.343638
45	6	0	0.484990	-9.547756	1.578299
46	6	0	2.853118	-6.827628	0.445292
47	6	0	-2.164241	-7.027777	0.578782
48	7	0	4.021071	-7.479306	0.682960
49	6	0	5.186850	-6.849065	0.447812

50	6	0	5.247899	-5.542625	-0.064991
51	6	0	4.001930	-4.955305	-0.324085
52	7	0	2.829944	-5.557784	-0.051999
53	7	0	-2.215085	-5.770460	0.072556
54	6	0	-3.422918	-5.220395	-0.145537
55	6	0	-4.628325	-5.898047	0.137867
56	6	0	-4.472511	-7.190820	0.670037
57	7	0	-3.270799	-7.753495	0.884429
58	6	0	-5.955025	-5.288328	-0.113292
59	6	0	-6.112179	-3.896601	-0.032423
60	6	0	-7.340327	-3.277334	-0.331049
61	6	0	-8.440009	-4.085838	-0.667179
62	6	0	-8.321648	-5.483711	-0.720553
63	6	0	-7.074248	-6.070369	-0.458965
64	6	0	7.020570	5.930150	-0.071993
65	6	0	5.828157	5.177610	-0.049174
66	6	0	5.896756	3.775749	-0.102240
67	6	0	7.147314	3.136429	-0.158408
68	6	0	8.322538	3.905846	-0.158950
69	6	0	8.271484	5.306998	-0.123347
70	6	0	4.542815	5.895232	0.050965
71	6	0	7.238857	1.662398	-0.219983
72	7	0	4.557345	7.251519	-0.019379
73	6	0	3.400630	7.930853	0.090844
74	6	0	2.167846	7.292697	0.309249
75	6	0	2.239569	5.894739	0.384627
76	7	0	3.382635	5.201149	0.232837
77	7	0	6.096364	0.945460	-0.360546
78	6	0	6.191170	-0.394079	-0.445571
79	6	0	7.426178	-1.075600	-0.375183
80	6	0	8.549972	-0.245948	-0.203941
81	7	0	8.469296	1.093676	-0.137738
82	6	0	0.855636	7.959243	0.469756
83	6	0	7.529355	-2.550984	-0.481087
84	6	0	6.427228	-3.360939	-0.164943
85	6	0	6.478676	-4.759455	-0.313155
86	6	0	7.678660	-5.356311	-0.734808
87	6	0	8.806182	-4.574112	-1.030149
88	6	0	8.712785	-3.178684	-0.918649
89	6	0	0.737033	9.265634	0.974642
90	6	0	-0.522801	9.841664	1.200591
91	6	0	-1.673049	9.079743	0.946695
92	6	0	-1.588895	7.771480	0.430341
93	6	0	-0.316490	7.239188	0.171425

94	6	0	-10.071870	5.198798	-0.408043
95	6	0	-9.518571	-6.343079	-1.065990
96	6	0	0.556393	-10.948980	2.145805
97	6	0	10.098870	-5.224620	-1.473236
98	6	0	9.546877	6.121560	-0.139375
99	6	0	-0.638238	11.255655	1.727497
100	1	0	-9.552409	2.501051	-0.339283
101	1	0	-5.252939	2.729413	-0.149110
102	1	0	-7.569442	6.324499	-0.268929
103	1	0	-9.536615	-1.500313	0.093432
104	1	0	-5.304434	-1.522729	-0.759212
105	1	0	-4.196813	8.581413	-0.139844
106	1	0	-1.854839	4.987320	0.425413
107	1	0	2.623255	-9.275343	1.447842
108	1	0	0.250203	-5.937740	0.105445
109	1	0	-1.679326	-9.462128	1.569871
110	1	0	6.086795	-7.402293	0.698947
111	1	0	3.929341	-3.950634	-0.719453
112	1	0	-3.418517	-4.217884	-0.562344
113	1	0	-5.334814	-7.786865	0.952692
114	1	0	-5.269194	-3.292193	0.278142
115	1	0	-9.390693	-3.627911	-0.924335
116	1	0	-6.969887	-7.146605	-0.557720
117	1	0	6.947053	7.010619	-0.041607
118	1	0	5.004537	3.163640	-0.102518
119	1	0	9.274989	3.388827	-0.191175
120	1	0	3.472633	9.009075	-0.013469
121	1	0	1.355938	5.291936	0.552633
122	1	0	5.252915	-0.922633	-0.582165
123	1	0	9.545879	-0.664199	-0.098321
124	1	0	5.520314	-2.902963	0.210398
125	1	0	7.728346	-6.432556	-0.873293
126	1	0	9.569223	-2.577109	-1.206055
127	1	0	1.628172	9.829702	1.233856
128	1	0	-2.642699	9.503588	1.188251
129	1	0	-0.238737	6.253435	-0.269331
130	1	0	-10.244421	5.607583	-1.412558
131	1	0	-10.894368	4.511896	-0.185675
132	1	0	-10.130153	6.036778	0.295915
133	1	0	-10.094098	-6.600408	-0.166501
134	1	0	-9.213744	-7.282850	-1.537711
135	1	0	-10.198958	-5.826120	-1.750793
136	1	0	1.592266	-11.253806	2.322776
137	1	0	0.104789	-11.679342	1.462475

138	1	0	0.016642	-11.021738	3.097898
139	1	0	9.913110	-6.160412	-2.010604
140	1	0	10.737444	-5.463696	-0.612078
141	1	0	10.673634	-4.565194	-2.131728
142	1	0	10.196703	5.862160	0.705587
143	1	0	10.122987	5.942812	-1.055964
144	1	0	9.334156	7.193350	-0.082196
145	1	0	0.216746	11.519433	2.358743
146	1	0	-0.673580	11.982912	0.905087
147	1	0	-1.549499	11.389227	2.319568

5-14. ^{1}H NMR spectra profiles of $\mathbf{1}_{\mathbf{6mer\text{-}14mer}}$

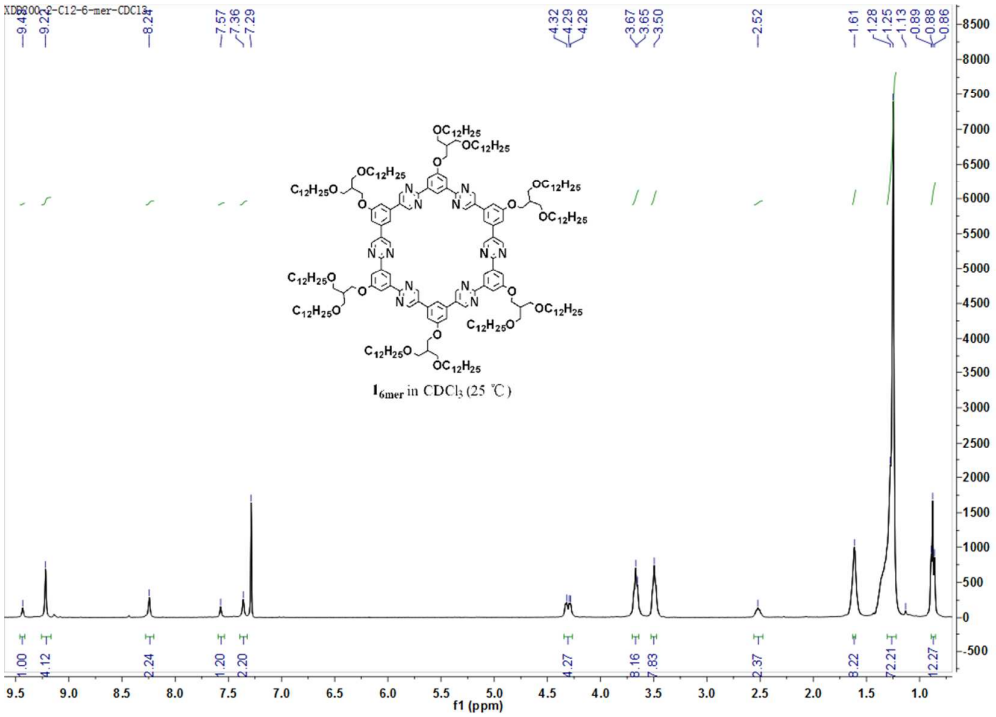
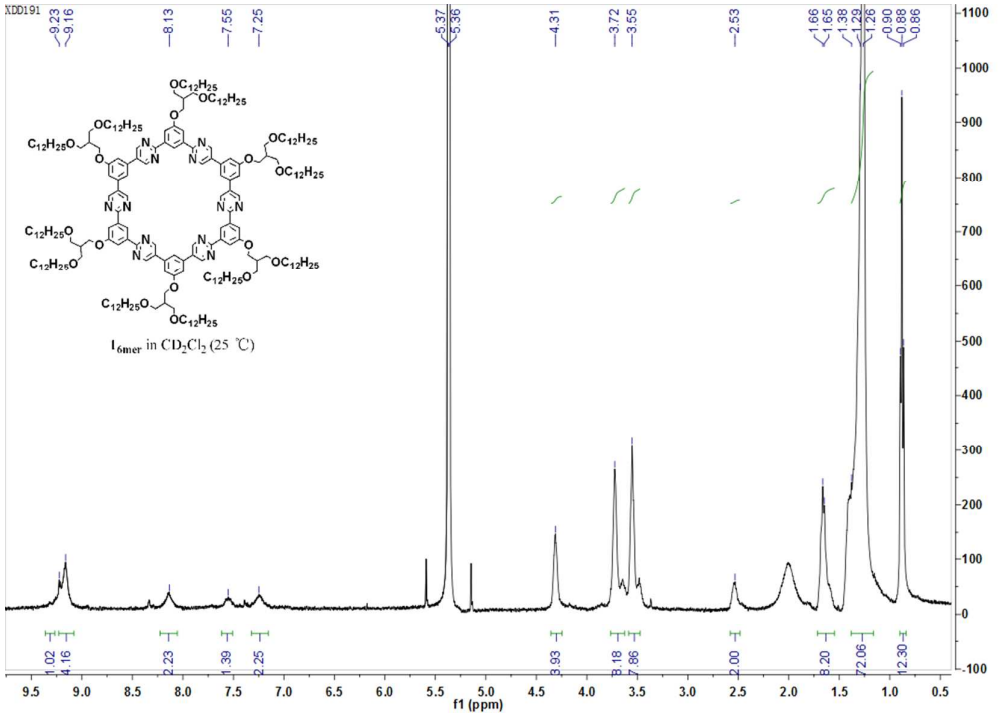
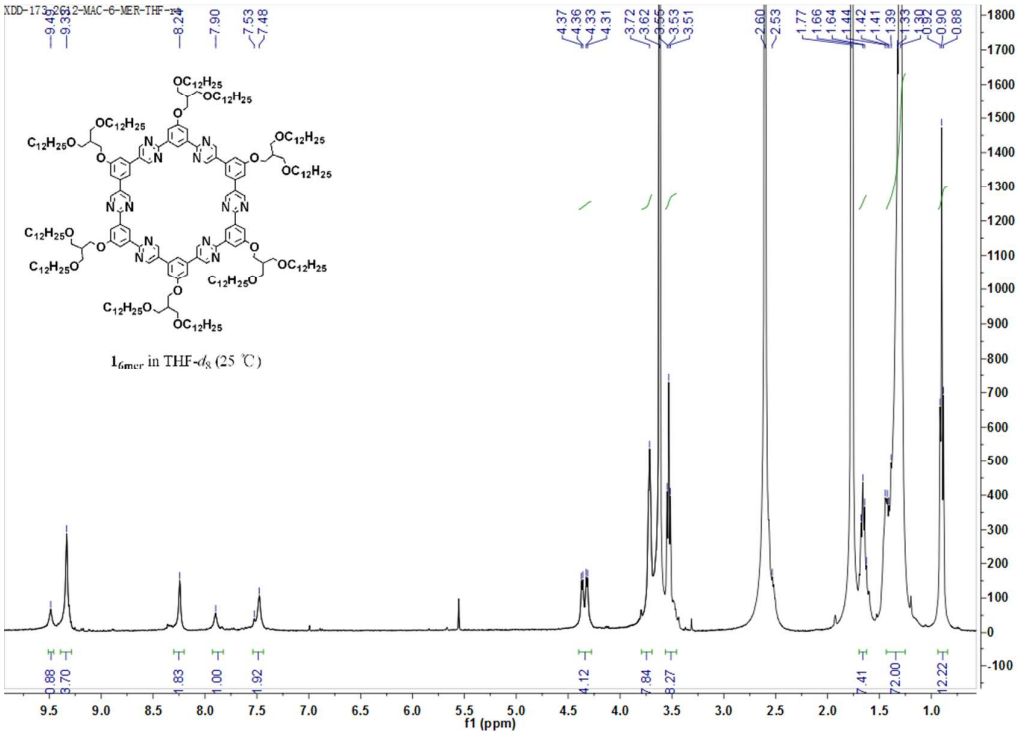


Figure S20.



I_{6mer} in CD_2Cl_2 (25 ℃)

Figure S21.



I_{6mer} in THF-d_8 (25 ℃)

Figure S22.

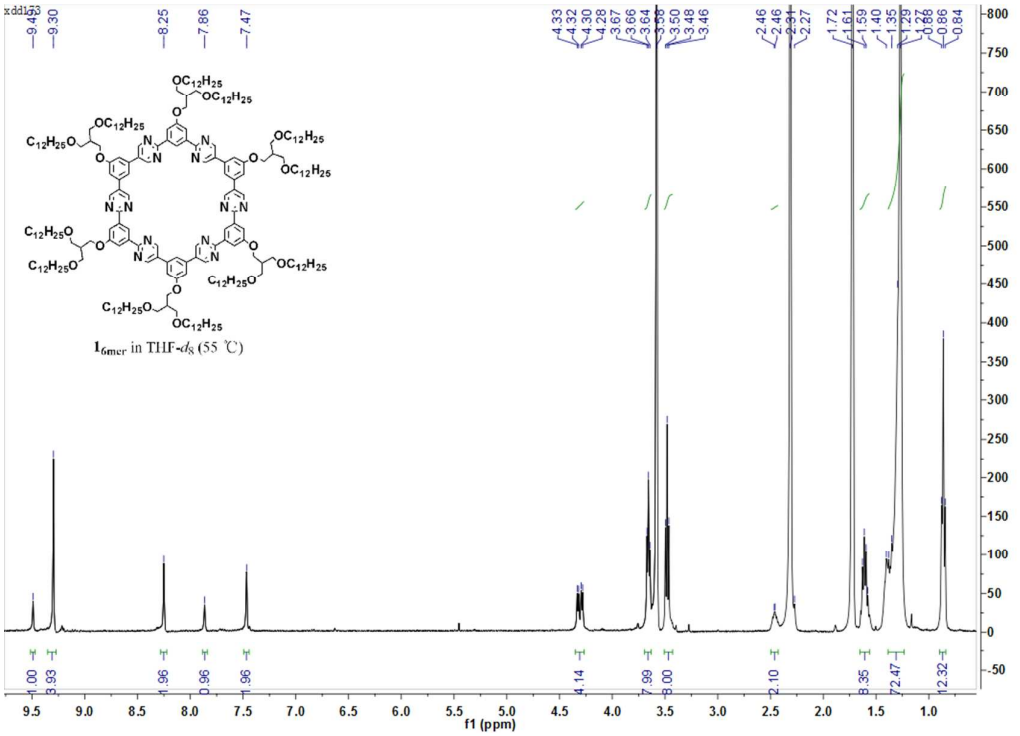


Figure S23.

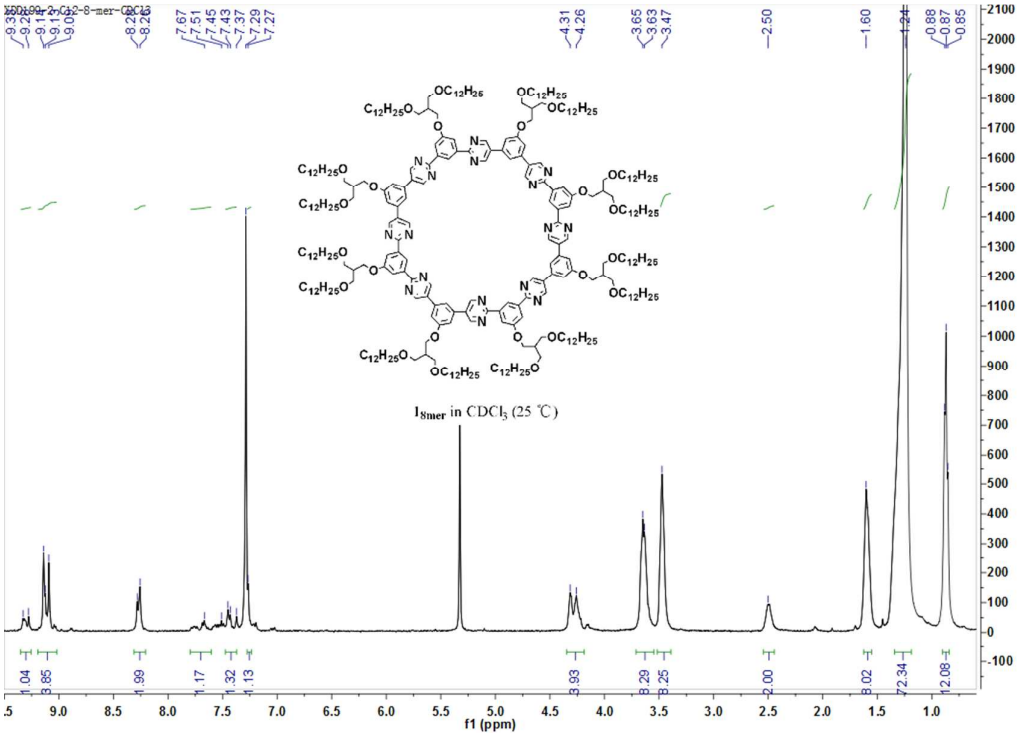


Figure S24.

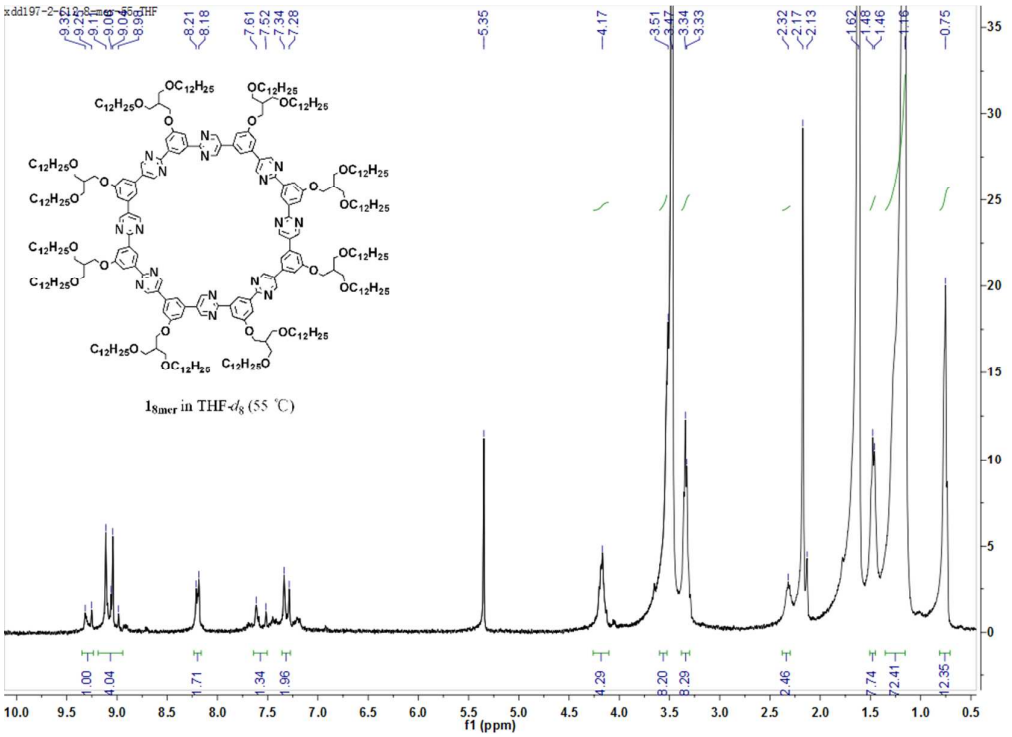


Figure S25.

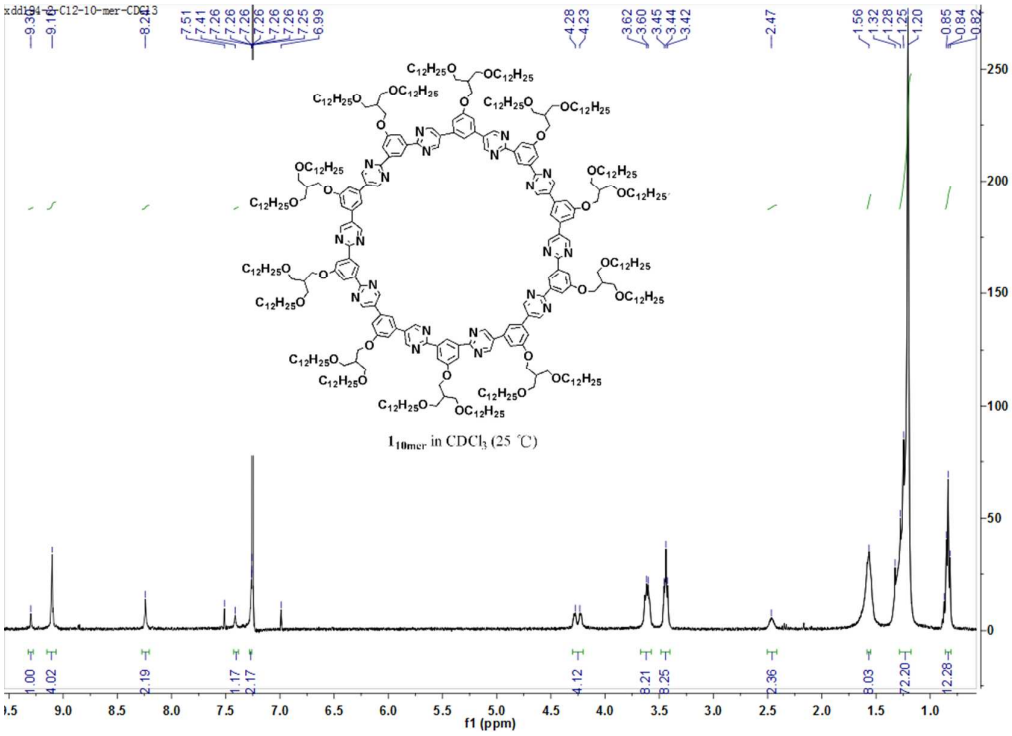


Figure S26.

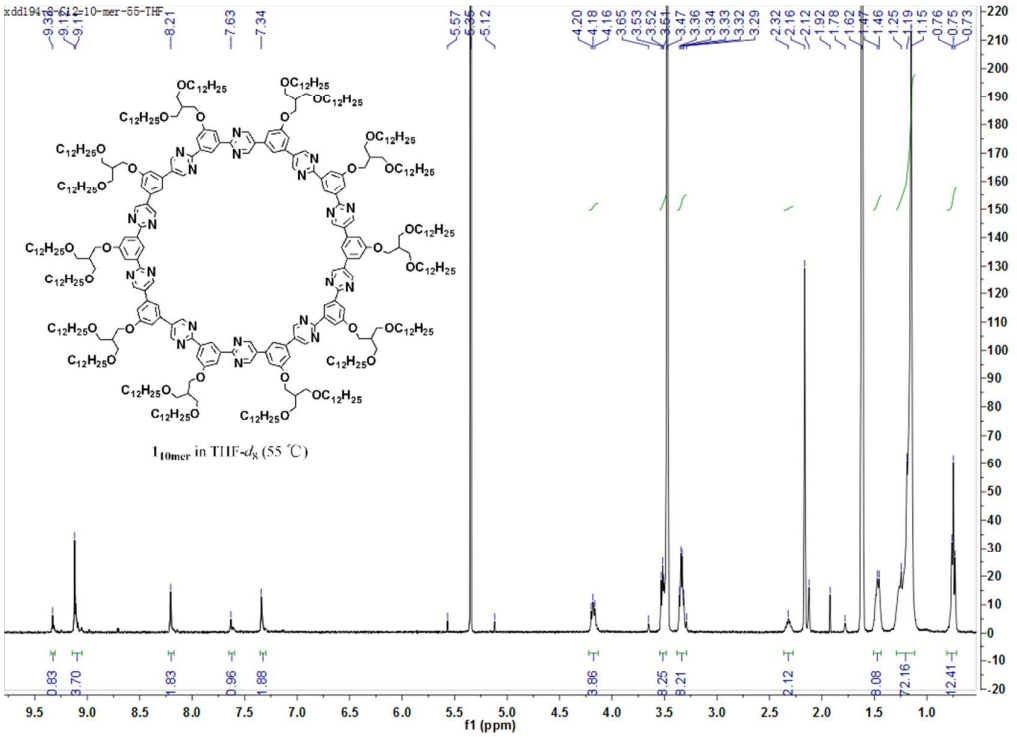


Figure S27.

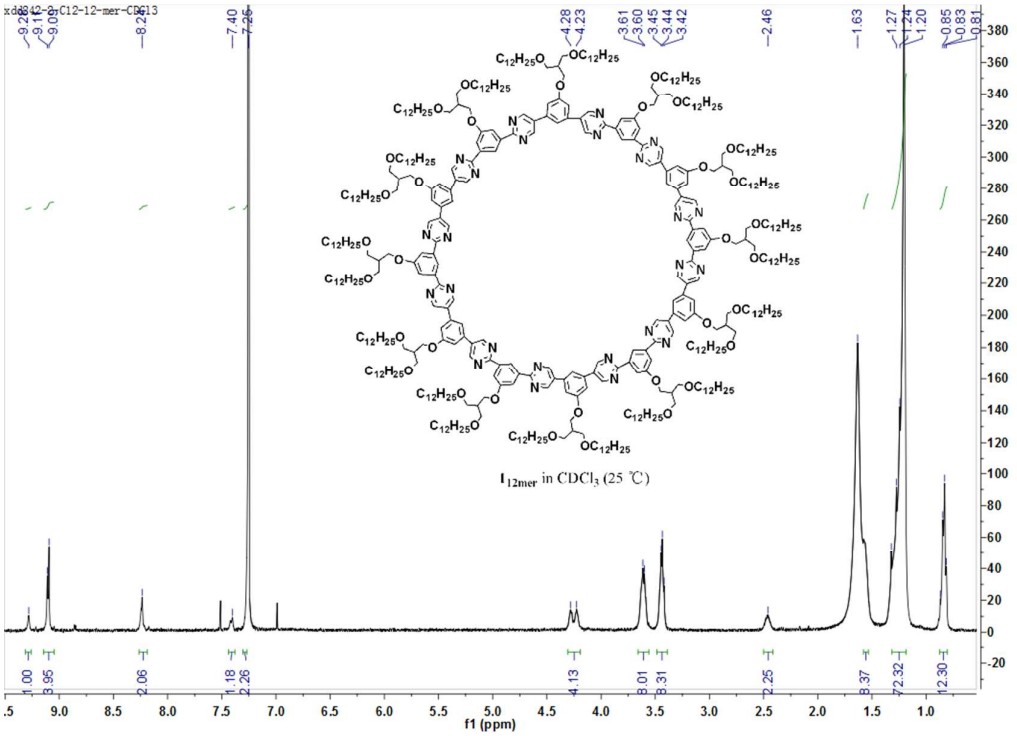


Figure S28.

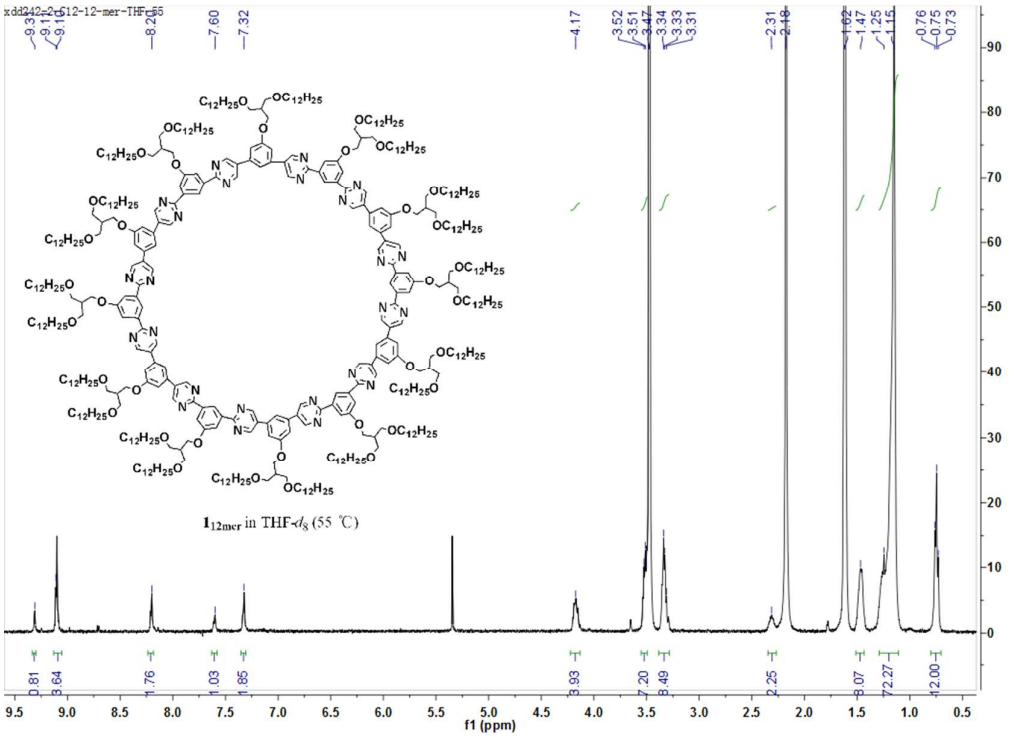


Figure S29.

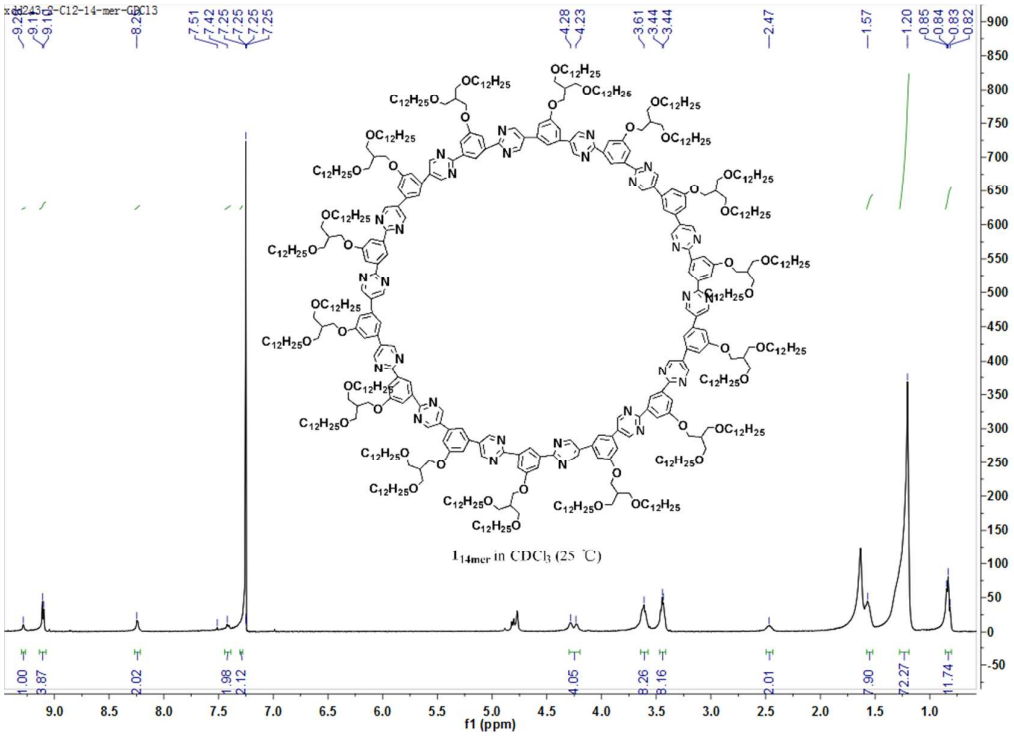


Figure S30.

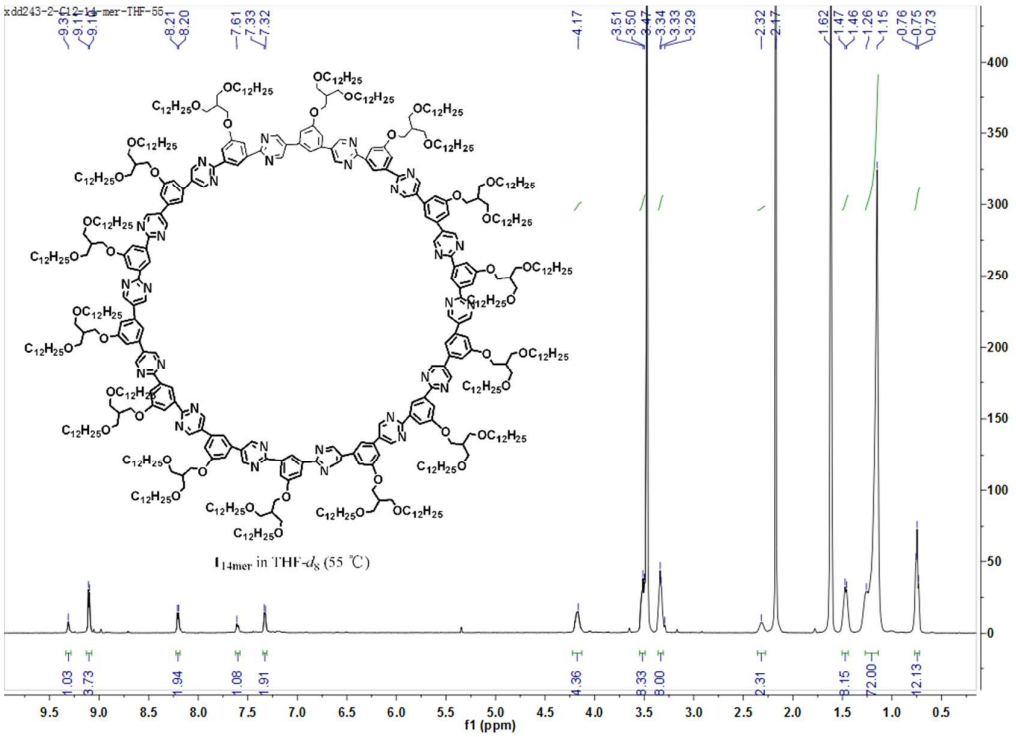


Figure S31.