Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Cross-linked Supramolecular Polymer Constructed from Pillar[5]arene and Porphyrine *via* the Host-Guest interactions

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Fig. S9 Electronic absorption spectrum (A) and fluorescence spectrum (B) of TImPor (2×10^{-6} mol/L) upon addition of DMeP5 recorded in $CHCl_3$ with the DMeP5/TImPor molar ratio changing from 0 to 50.

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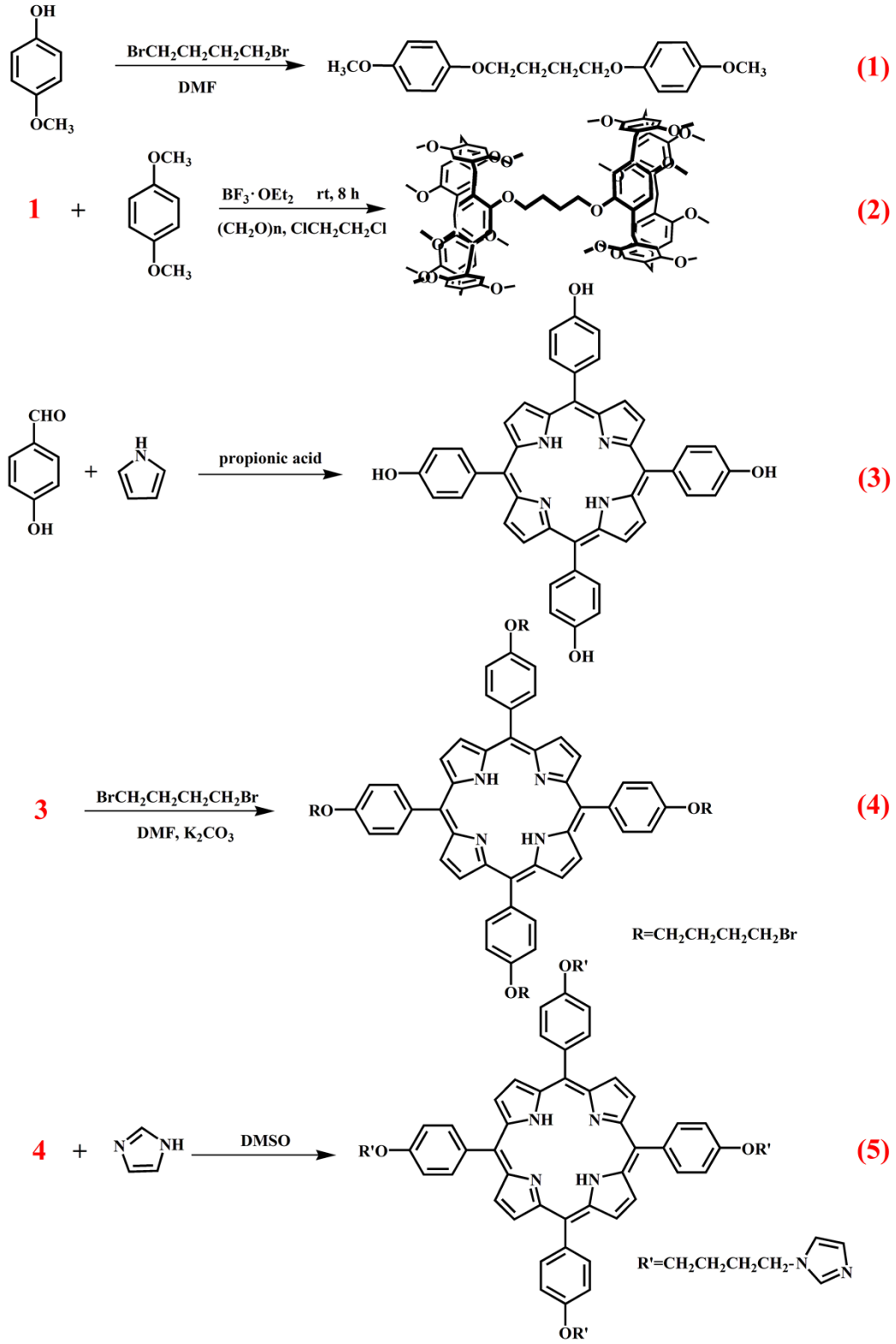
Fig. S12 AFM image of the supramolecular polymer DMeP5@TImPor.

Fig. S13 Diffusion coefficient of DMeP5@TImPor upon addition of 0, 20.0, 40.0, 60.0, 80.0, and 100.0 equiv. competitive guest ADN recorded in $CDCl_3$ at 25 °C.

Fig. S14 DLS data for TImPor with 2.0 equiv. DMeP5 at a fixed concentration of 2.0 mM (A) and adding 100.0 equiv. competitive guest ADN into A (B) recorded in $CHCl_3$ at 25 °C.



Scheme S1. Synthesis of the host DMeP5 and the guest TImPor.

1. General Remarks: All reagents were obtained from commercial sources without further purification. The compounds of **1-5** were prepared according to the literature procedures.[S1-S4]

2. Measurements: ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$ and DMSO-d_6. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Steady-state fluorescence spectroscopic studies were performed on an F4500 (Hitachi). MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio El III. DLS data were obtained on a DynaPro NanoStar at 25 °C. SEM image was obtained using a JEOL JSM-6700F field-emission scanning electron microscopy. TEM image was taken on a JEM-100CX II (JEOL Ltd., Japan) electron microscope operated at 100 kV. AFM image was collected in air under ambient conditions using the tapping mode with a Nanoscope III/Bioscope scanning probe microscope from Digital Instruments.

3. Synthesis procedure: ***Preparation of 1,4-bis(4-methoxyphenoxy)butane (1).***[S1] To a stirred solution of 1,4-dibromobutane (6.5 g, 0.03 mol) in dry DMF (100.0 mL) was added K_2CO_3 (3.0 g, 0.022 mol) and 4-methoxyphenol (1.9 g, 0.015 mol) and the mixture was stirred at 50 °C for 5 d. After the reaction was completed, the solid was removed by filtration and the solvent was removed under reduced pressure to afford 6.81 g of product as a white solid. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 6.83 (s, 4H), 3.98 (s, 2H), 3.77 (s, 3H), 1.94 (s, 2H).

Preparation of DMeP5 (2).[S2] To a solution of **1** (0.30 g, 1.0 mmol), 1,4-dimethoxybenzene (2.2 g, 16.0 mmol), and paraformaldehyde (1.5 g, 50.0 mmol) in dry $ClCH_2CH_2Cl$ (300.0 mL) under N_2 atmosphere for 0.5 h, the anhydrous $FeCl_3$ (0.41 g, 2.5 mmol) was added. The mixture was stirred under N_2 atmosphere for 8 h at room temperature. After the reaction was completed, the solution was diluted with $CHCl_3$ and washed with saturated sodium chloride solution. The organic layer was dried with $MgSO_4$ and solvents removed. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as eluent to afford 0.42 g of product as a white solid. Yield: 28%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 6.78-6.74 (m, 20H), 3.93-3.61 (m, 78H), 2.04 (s, 4H). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 151.04, 150.15, 128.47, 114.33, 114.25, 68.31, 55.92, 31.74, 29.94, 29.55, 26.98, 22.80, 14.26. MS Calcd. for $C_{92}H_{102}O_{20}$: 1527.78; found: m/z 1527.18. Anal. Calcd. for $C_{92}H_{102}O_{20}$: C, 72.33; H, 6.73; found C, 72.37; H, 6.69.

Preparation of TOHPor (3).[S3] 4-Hydroxybenzaldehyde (10.0 g, 82.0 mmol) in propionic acid (500.0 mL) was stirred at 150 °C. To which pyrrole (5.7 mL, 82.0 mmol) dissolved in 50.0 mL propionic acid was added dropwise within 30 min. The reaction mixture was further stirred for 1 h. After the solid was filtered off, the residue was washed by H_2O to afford 5.11 g of product as a dark green solid. Yield: 37%. ^{1}H

NMR (400 MHz, DMSO-d_6, 25 °C) δ (ppm): 8.86 (s, 8H), 8.00 (d, J = 8.0 Hz, 8H), 7.21 (d, J = 8.0 Hz, 8H), -2.89 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C) δ (ppm): 175.14, 157.37, 135.47, 131.90, 119.96, 113.89, 79.14, 48.57, 26.87, 9.06. MS Calcd. for $C_{44}H_{30}N_4O_4$: 678.73; found: m/z 678.33. Anal. Calcd. for $C_{44}H_{30}N_4O_4$: C, 77.86; H, 4.46; N, 8.25; found C, 77.77; H, 4.48; N, 8.31.

Preparation of TBrPor (4).[S1] To a 250 mL flask containing anhydrous potassium carbonate (1.7 g, 12.0 mmol) and **3** (1.4 mg, 2.0 mmol) in dry DMF (100.0 mL), 1,4-dibromobutane (22.0 g, 100.0 mmol) was added under nitrogen atmosphere at 50°C. The reaction mixture was stirred for 5 d. After the solid was filtered off, the solvent was removed. The residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as eluent to afford 202.0 mg of product as a purple solid. Yield: 8%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.86 (s, 8H), 8.12 (d, J = 8.0 Hz, 8H), 4.29 (t, J = 12.0 Hz, 8H), 3.63 (t, J = 12.0 Hz, 8H), 2.28 (m, 8H), 2.18 (m, 8H), -2.76 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 158.86, 135.77, 134.89, 119.88, 112.85, 67.32, 33.71, 29.83, 28.30. MS Calcd. for $C_{60}H_{58}N_4O_4Br_4$: 1218.74; found: m/z 1219.53. Anal. Calcd. for $C_{60}H_{58}N_4O_4Br_4$: C, 59.13; H, 4.80; N, 4.60; found C, 59.21; H, 4.71; N, 4.53.

Preparation of TImPor (5).[S4] 1H-imidazole (82.0 mg, 1.2 mmol), NaOH (48.0 mg, 1.2 mmol), and **4** (70.0 mg, 0.057 mmol) in DMSO (10.0 mL) were stirred at 70 °C for 24 h. The solvent was poured into water. After filtration, the residue was dried by air to afford 64.2 mg of product as a purple solid. Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.85 (s, 8H), 8.12 (d, J = 8.0 Hz, 8H), 7.61 (s, 4H), 7.14 (s, 4H), 7.05 (s, 4H), 4.29 (t, J = 12.0 Hz, 8H), 4.19 (t, J = 12.0 Hz, 8H), 2.20 (m, 8H), 2.00 (m, 8H), -2.77 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 158.74, 137.36, 135.78, 134.99, 129.85, 119.84, 118.97, 112.82, 67.57, 47.03, 31.74, 28.42, 26.68, 22.80, 14.26. MS Calcd. for $C_{72}H_{70}N_{12}O_4$: 1167.40; found: m/z 1166.77. Anal. Calcd. for $C_{72}H_{70}N_{12}O_4$: C, 74.08; H, 6.04; N, 14.40; found C, 74.16; H, 5.98; N, 14.29.

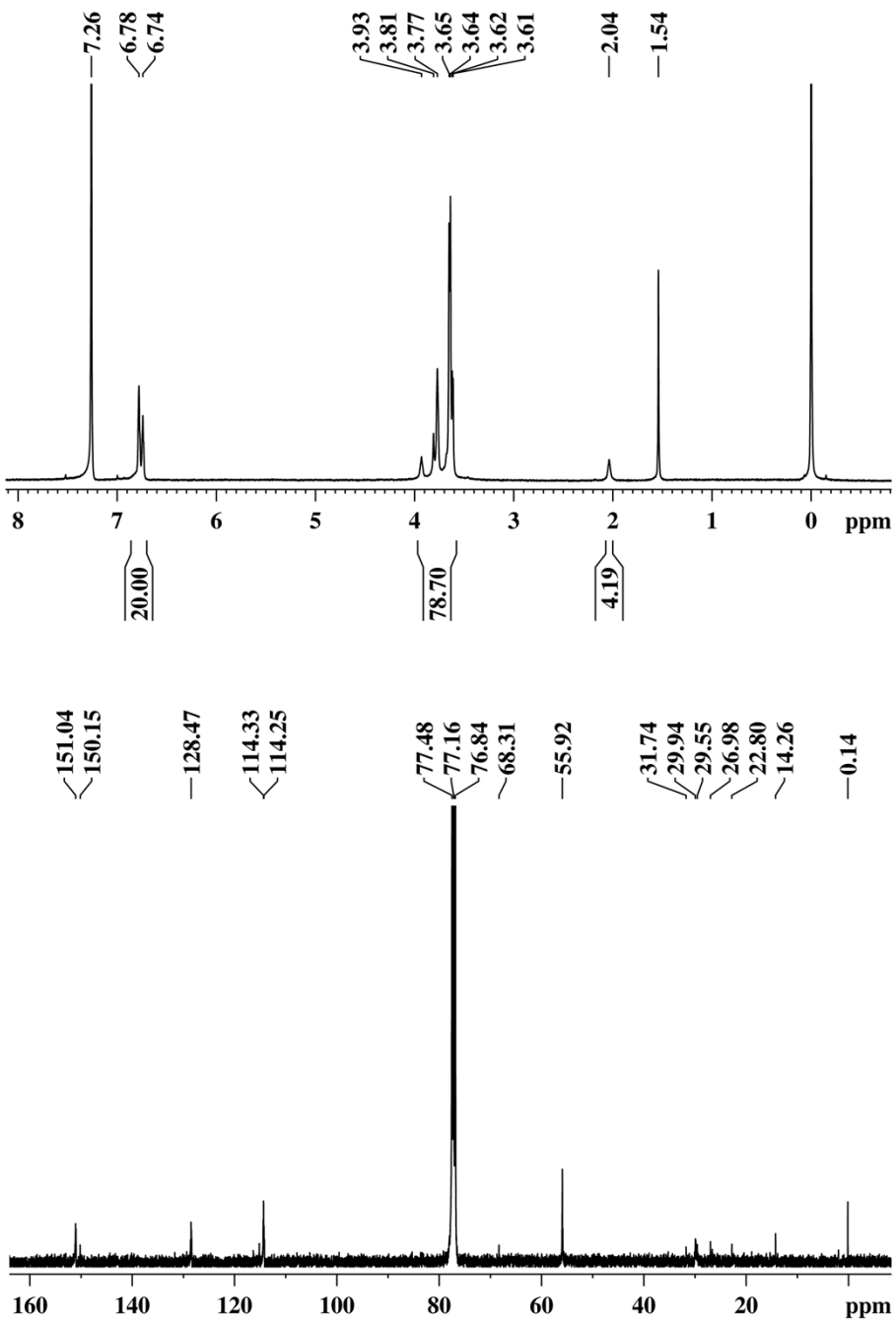


Fig. S1 ^{1}H NMR, ^{13}C NMR spectra of DMeP5 recorded in $CDCl_3$ at 25 °C.

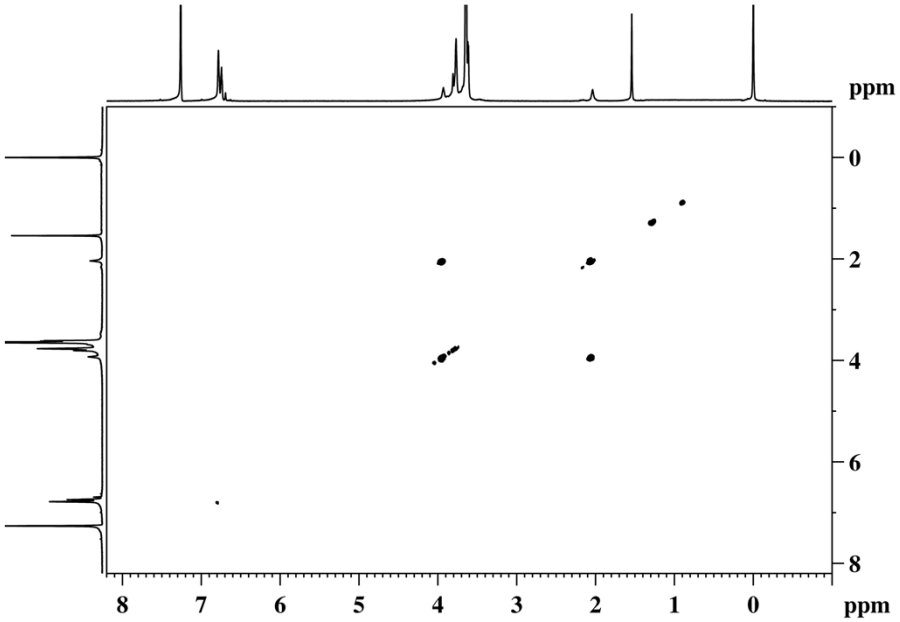


Fig. S2 ^{1}H-^{1}H COSY NMR spectrum of DMeP5 recorded in $CDCl_3$ at 25 °C.

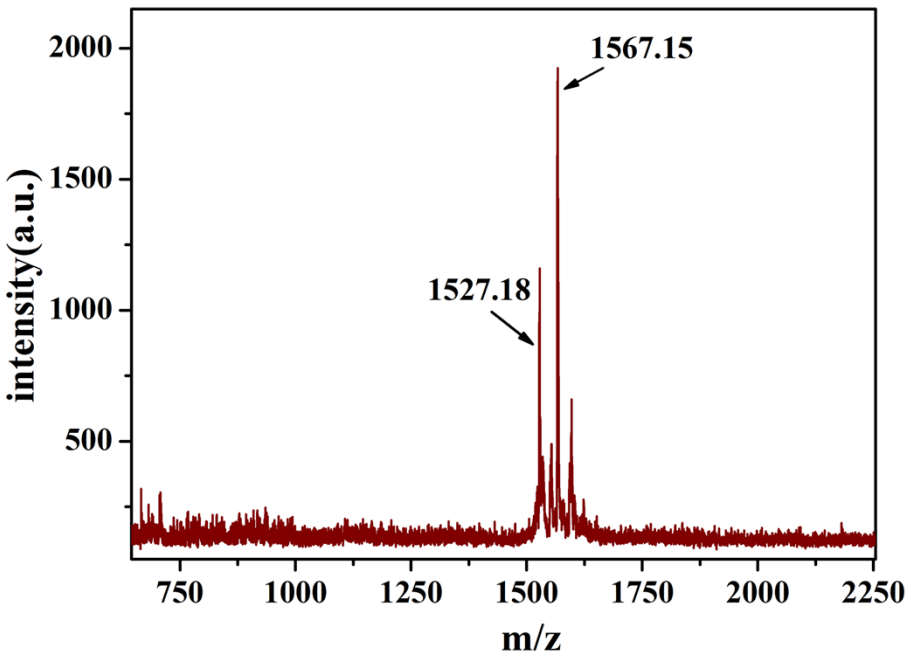


Fig. S3 The MALDI-TOF mass spectrum of DMeP5. The signals at m/z = 1527.18 and 1567.15 correspond to the molecular ion $[M]^+$ and $[M+K^+]^+$, respectively.

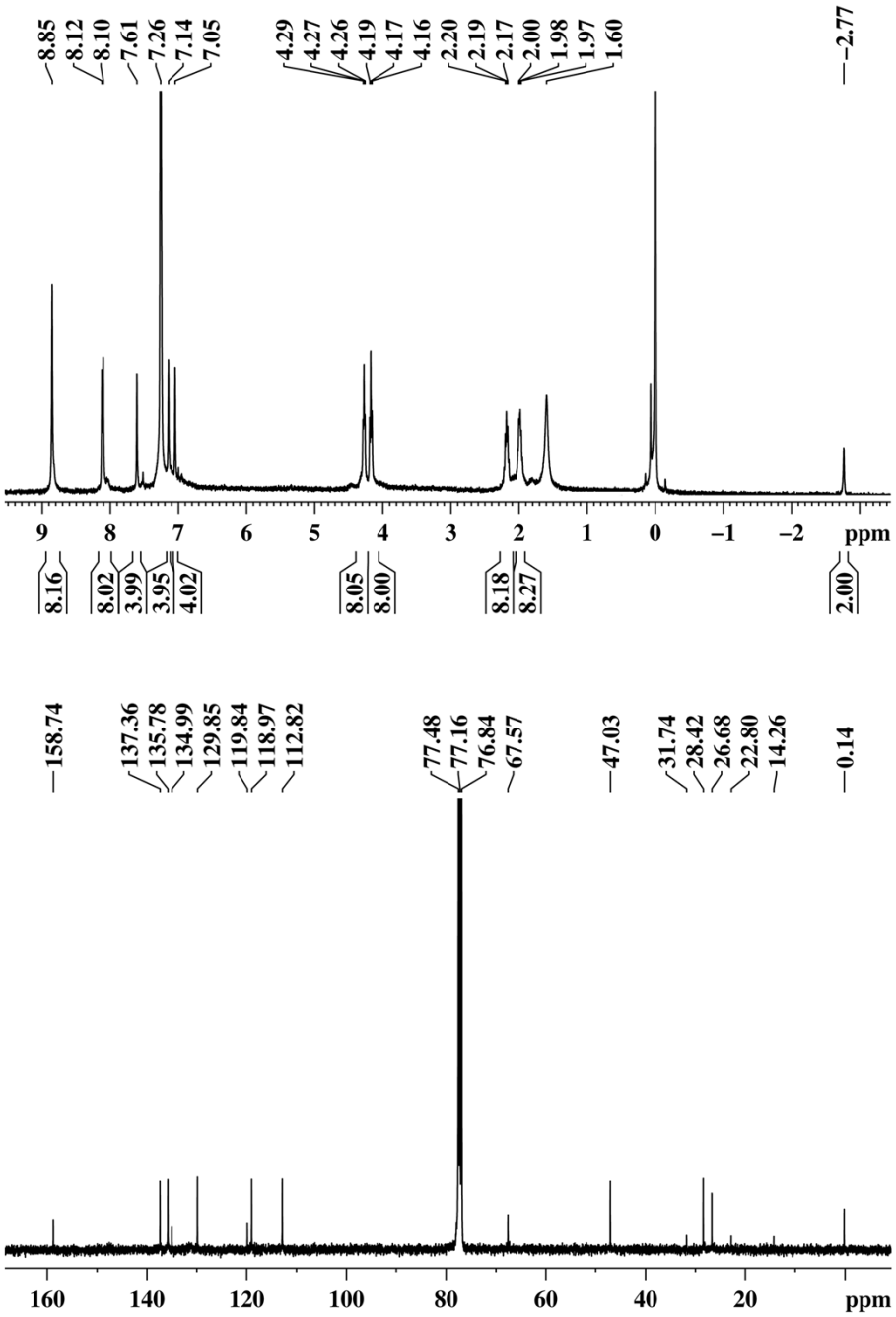


Fig. S4 ^{1}H NMR, ^{13}C NMR spectra of TImPor recorded in $CDCl_3$ at 25 °C.

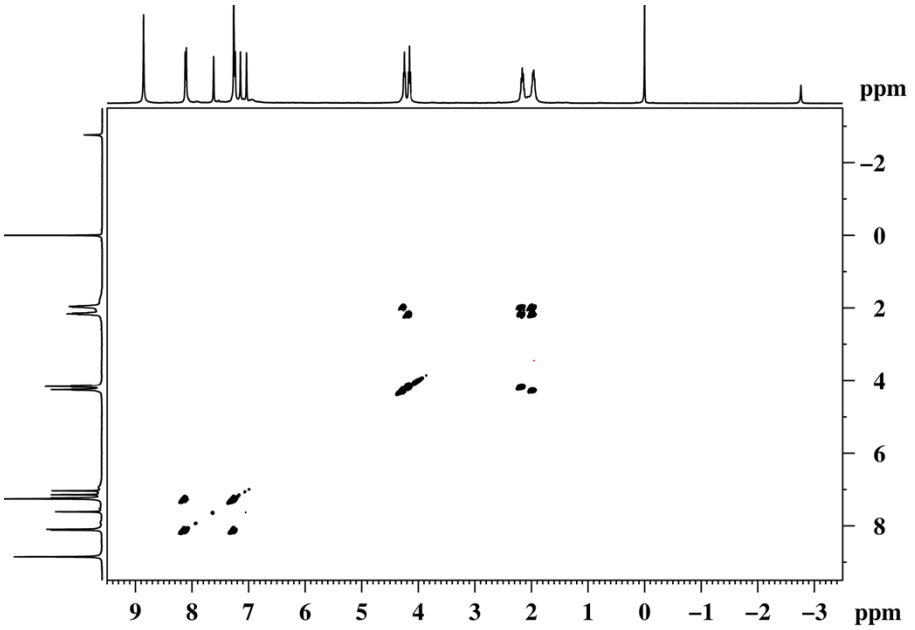


Fig. S5 ^{1}H-^{1}H COSY NMR spectrum of TImPor recorded in $CDCl_3$ at 25 °C.

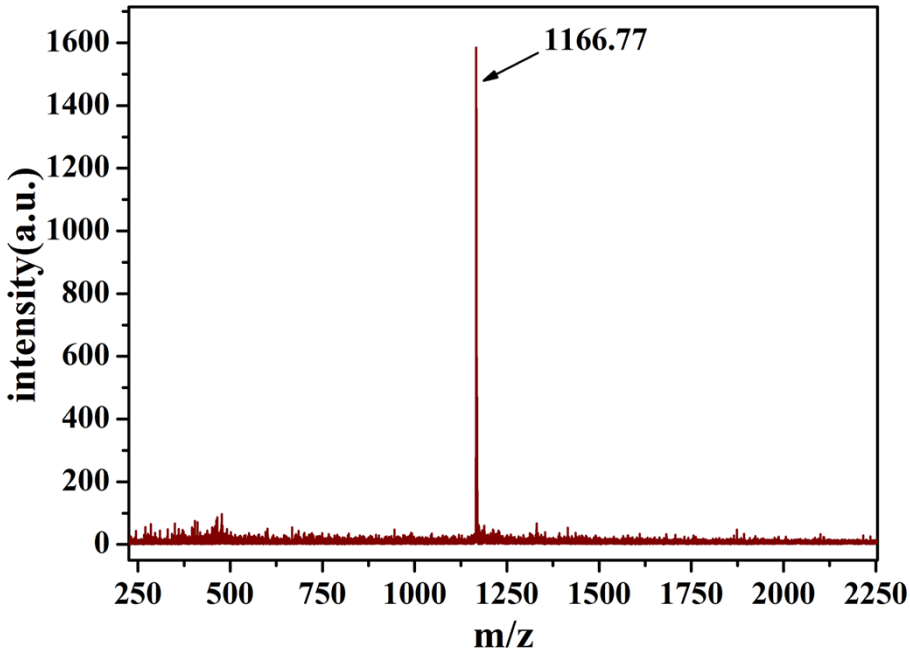


Fig. S6 The MALDI-TOF mass spectrum of TImPor. The signal at m/z = 1166.77 corresponds to the molecular ion $[M]^+$ (calculated 1167.40).

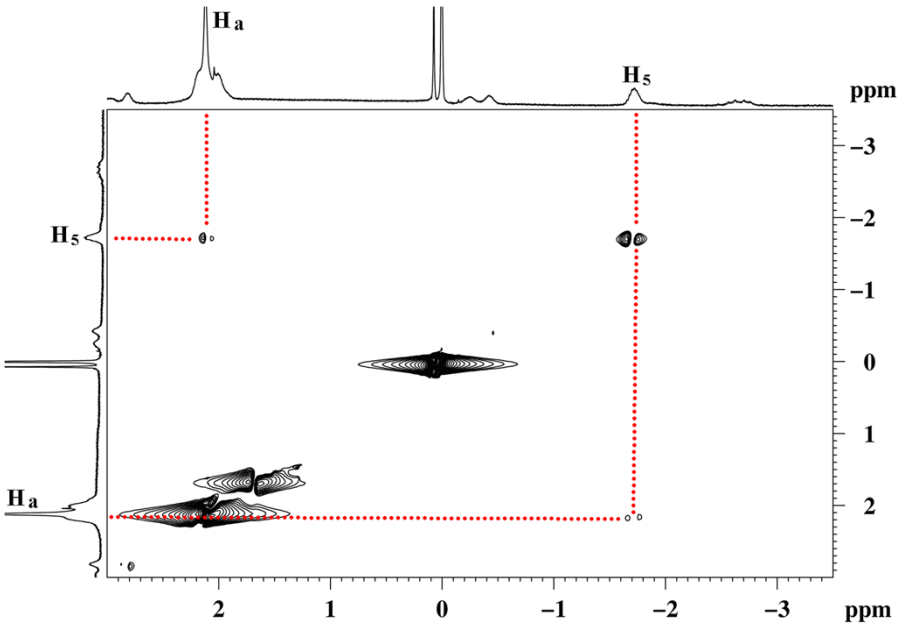


Fig. S7 Partial NOESY NMR spectrum of the complex DMeP5@TImPor recorded in $CDCl_3$ at 25 °C.

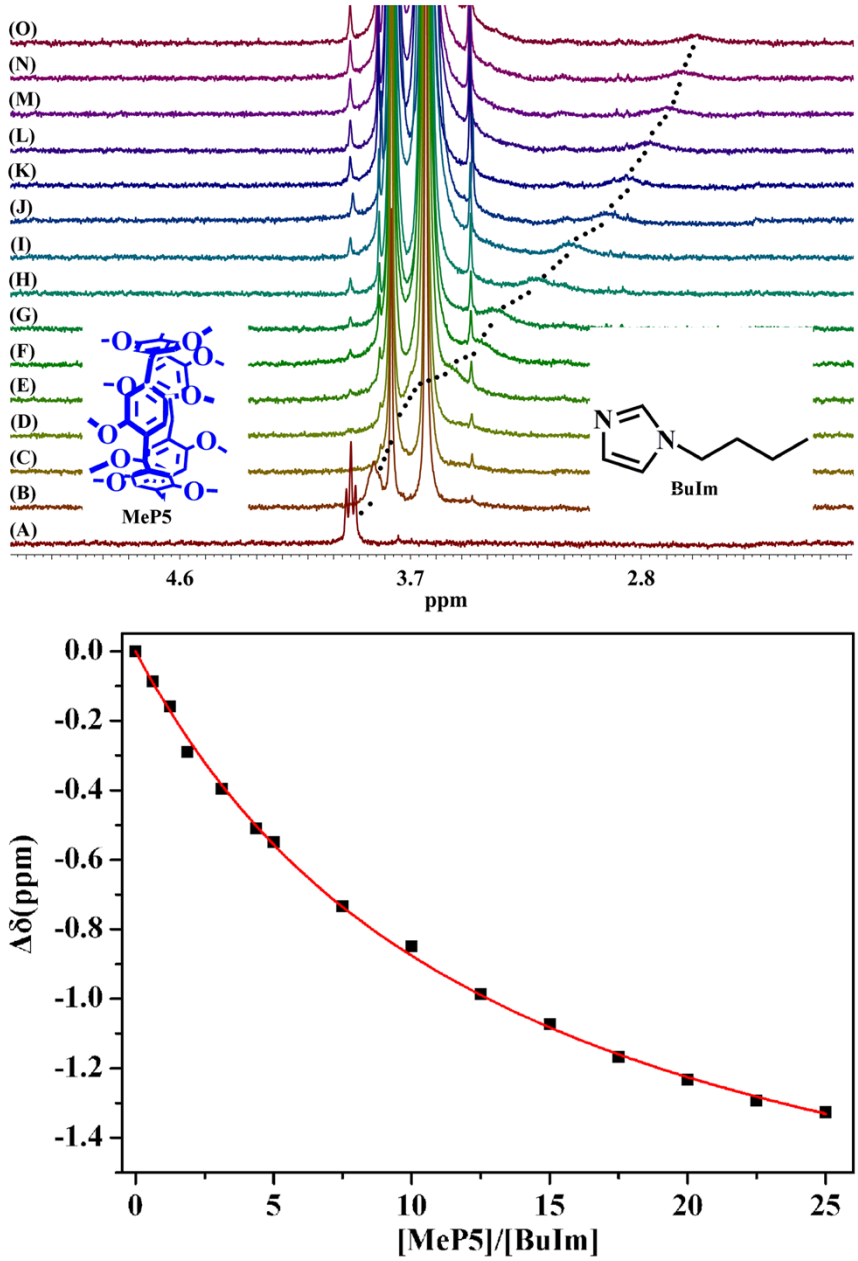


Fig. S8 (Top) Partial ^{1}H NMR spectra and (Bottom) the non-linear curve-fitting of BuIm (0.5 mM) upon addition of MeP5 recorded in $CDCl_3$ at 25 °C with the MeP5/BuIm molar ratio: 0 (A), 0.625 (B), 1.25 (C), 1.875 (D), 3.125 (E), 4.375 (F), 5 (G), 7.5 (H), 10 (I), 12.5 (J), 15 (K), 17.5 (L), 20 (M), 22.5 (N), and 25 (O). To investigate the binding affinity of DMeP5 with TImPor, 1,4-dimethoxypillar[5]arene (MeP5) and 1-Butylimidazole (BuIm) were chosen as the model compounds.[8e] ^{1}H NMR titrations were performed with a constant concentration of BuIm (0.5 mM) and varying molar ratio of MeP5/BuIm in the range of 0-25, Fig. S8. According to previous report, [8a] the stoichiometry of the complex MeP5@BuIm was determined to be 1:1. By a non-linear curve-fitting method,[8a,8e] the association constant (K_a) of MeP5 with BuIm was estimated to be 1.62×10^2 M^{-1}.

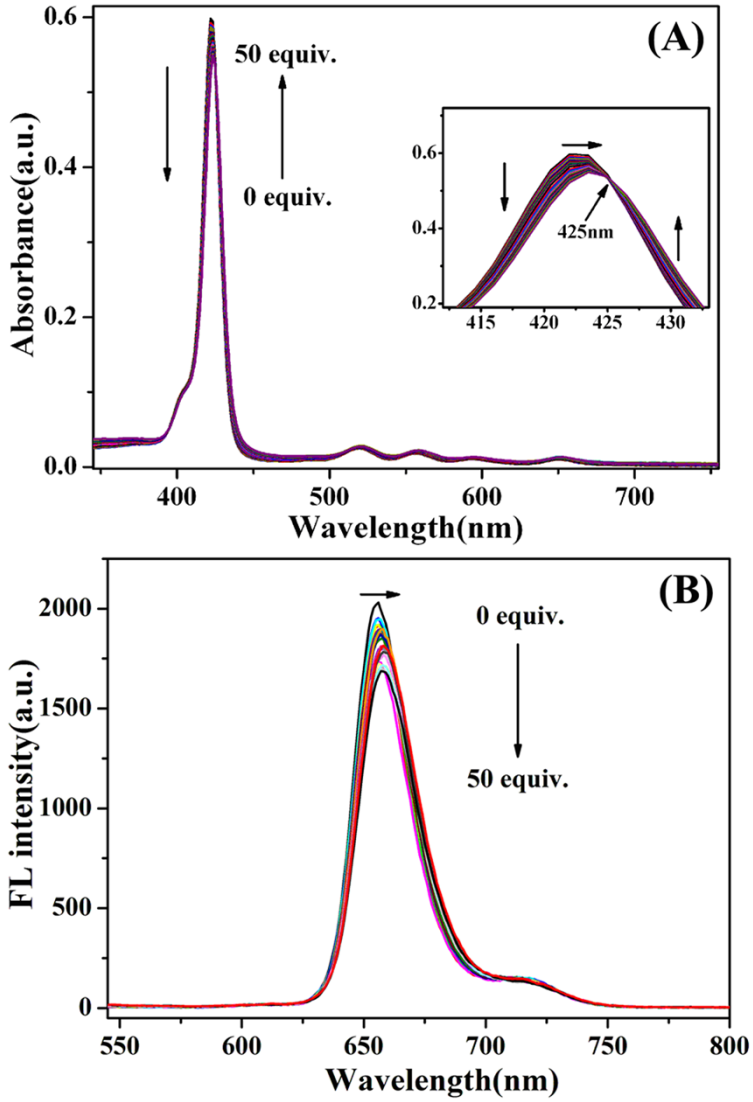


Fig. S9 Electronic absorption spectrum (A) and fluorescence spectrum (B) of TImPor (2×10^{-6} mol/L) upon addition of DMeP5 recorded in $CHCl_3$ with the DMeP5/TImPor molar ratio changing from 0 to 50.

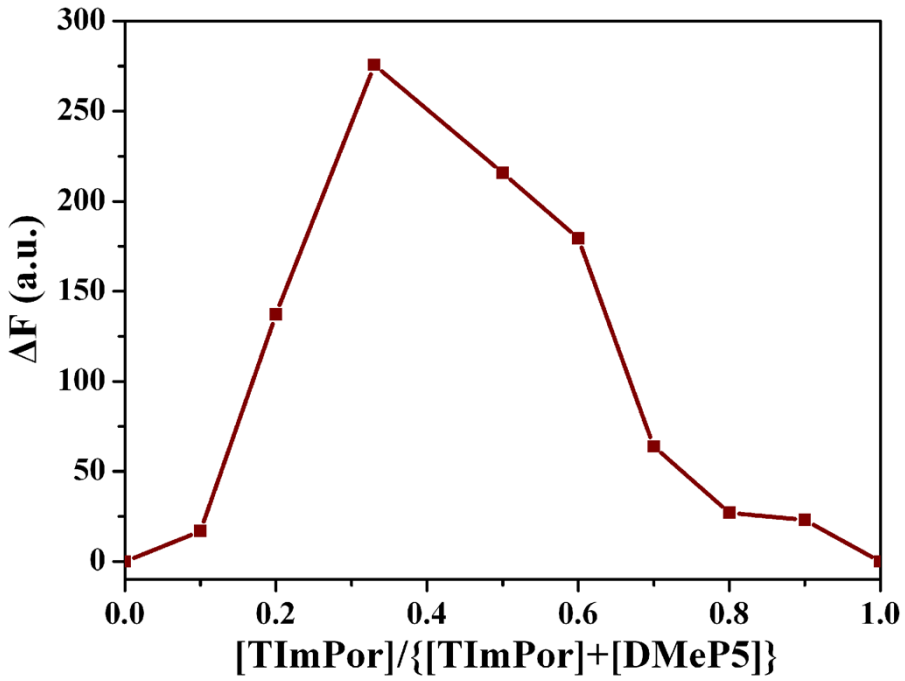


Fig. S10 Job's plot of ΔF in fluorescence intensity of guest TImPor *versus* the molar ratio of [TImPor]/{[DMeP5] + [TImPor]}. To investigate the stoichiometry of the complex between DMeP5 and TImPor, the Job's plot experiment was carried out. Fig. S10 indicates the stoichiometry of the complex between DMeP5 and TImPor is 2:1 in $CHCl_3$.

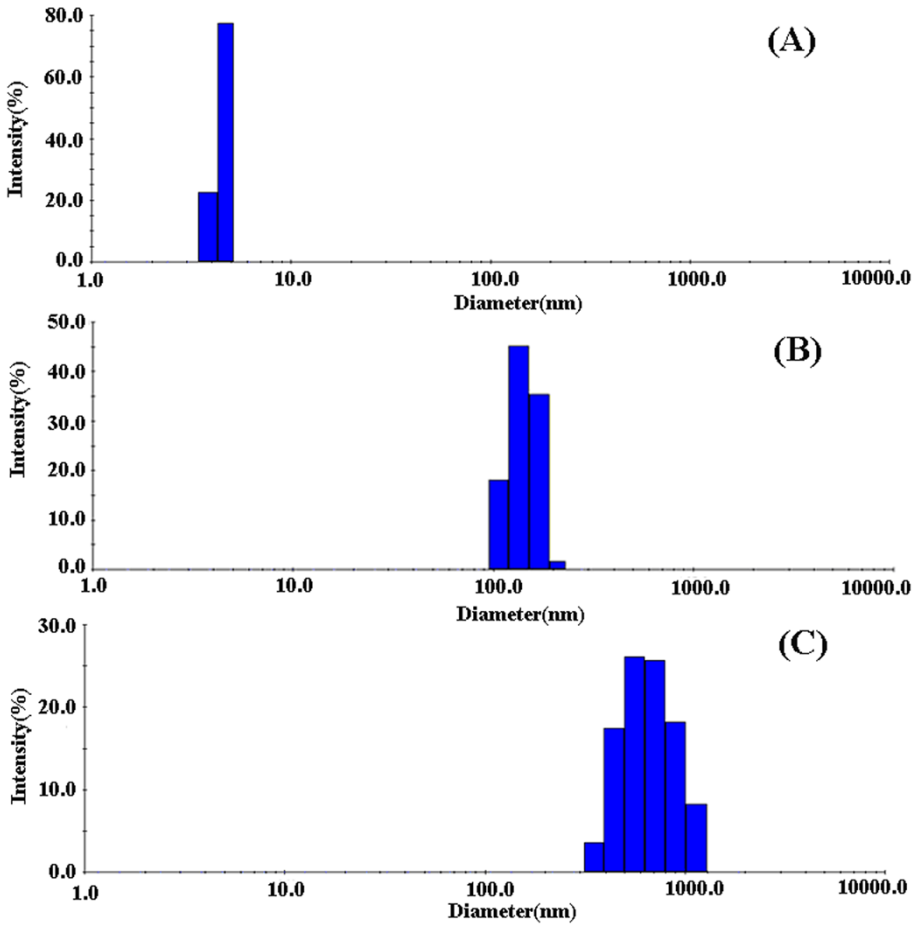


Fig. S11 DLS data for TImPor (A), TImPor with 1.0 equiv. DMeP5 (B), and TImPor with 2.0 equiv. DMeP5 (C) at a fixed concentration of 2.0 mM recorded in $CHCl_3$ at 25 °C. As can be seen in Fig. S11, the observation of a diameter distribution centered at 5 nm should be ascribed to TImPor. Along with mixing DMeP5 and TImPor at the molar ratio of 1:1, a diameter distribution centered at 144 nm was observed due to the formation of the low degree of polymerization. When the molar ratio between DMeP5 and TImPor was changed to 2:1, a new diameter distribution centered at 690 nm was observed, which is higher than those of A and B, indicating the formation of large supramolecular assemblies with high molecular weight.

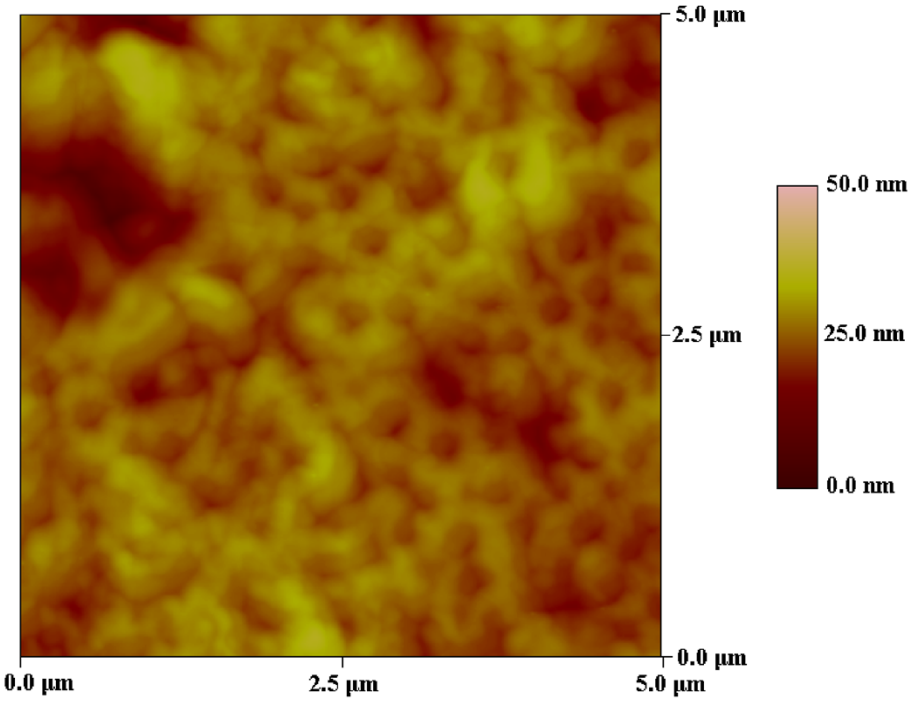


Fig. S12 AFM image of the supramolecular polymer DMeP5@TImPor.

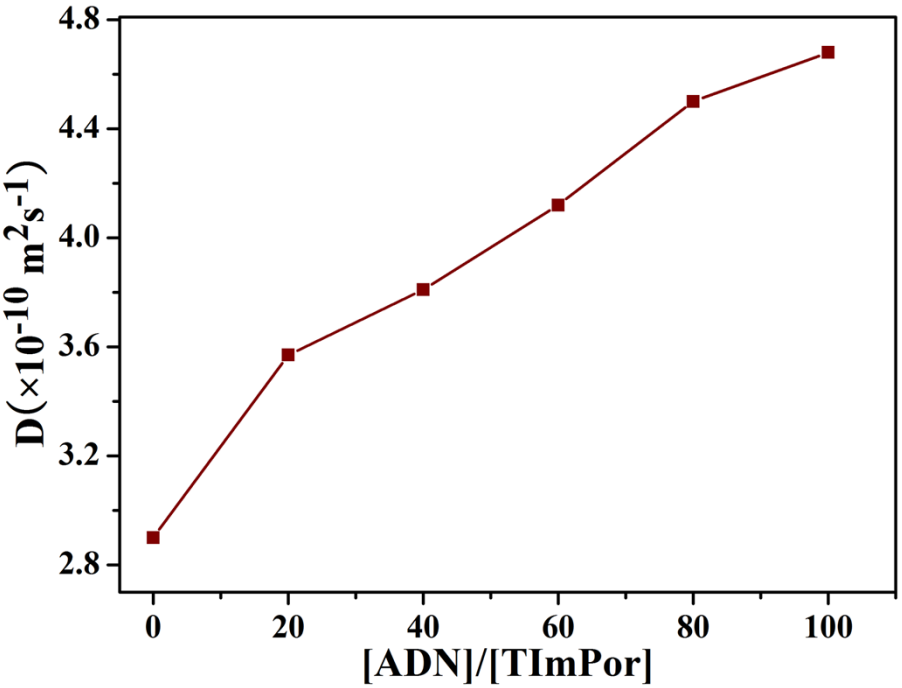


Fig. S13 Diffusion coefficient of DMeP5@TImPor upon addition of 0, 20.0, 40.0, 60.0, 80.0, and 100.0 equiv. of competitive guest ADN recorded in $CDCl_3$ at 25 °C. As shown in Fig. S13, upon addition of 100.0 equiv. of competitive guest ADN to the $CDCl_3$ solution of the supramolecular polymer DMeP5@TImPor, the average diffusion coefficient of the supramolecular assemblies increased pronouncedly from 2.90×10^{-10} to 4.68×10^{-10} m^2s^{-1}, which indicated the disassembly of cross-linked supramolecular polymer network and the formation of new inclusion complex between DMeP5 and ADN.

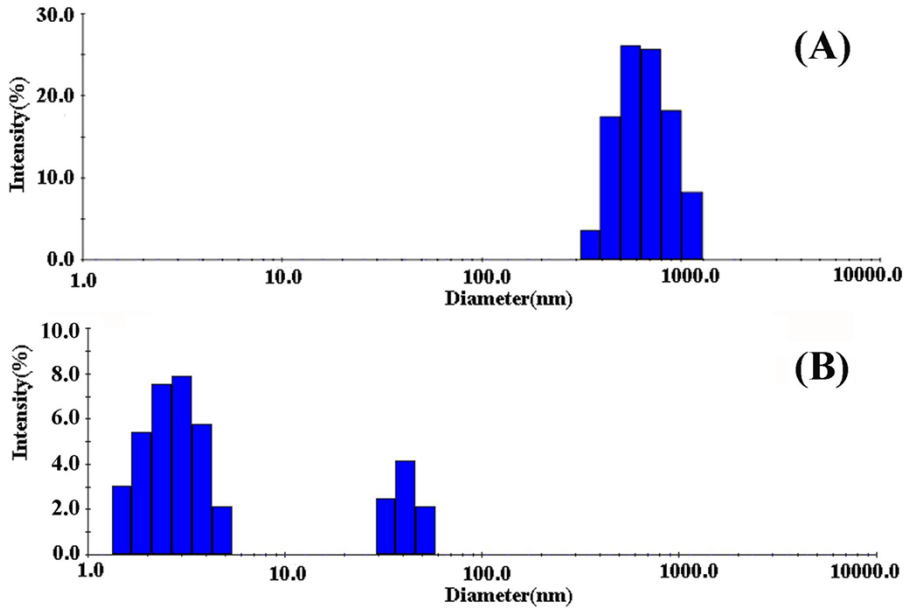


Fig. S14. DLS data for TImPor with 2.0 equiv. DMeP5 at a fixed concentration of 2.0 mM (A) and adding 100.0 equiv. competitive guest ADN into A (B) recorded in $CHCl_3$ at 25 °C.

S1 C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 4360.
S2 (a) T. Ogoshi, K. Kitajima, T. Aoki, S. H. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2010, **75**, 3268; (b) L. Gao, C. Han, B. Zheng, S. Dong and F. Huang, *Chem. Commun.*, 2013, **49**, 472.
S3 J. Sun, Y. Chen, L. Zhao, Y. Chen, D. Qi, K. Choi, D. Shin and J. Jiang, *Chem.-Eur. J.*, 2013, **19**, 12613.
S4 K. Han, Y. Zhang, J. Li, Y. Yu, X. Jia and C. Li, *Eur. J. Org. Chem.*, 2013, 2057.