Supporting Information

Cucurbit[8]uril-based supramolecular polymers: promoting supramolecular polymerization by metal-coordination

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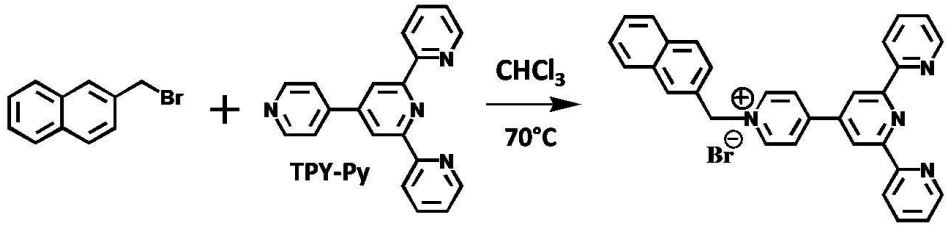
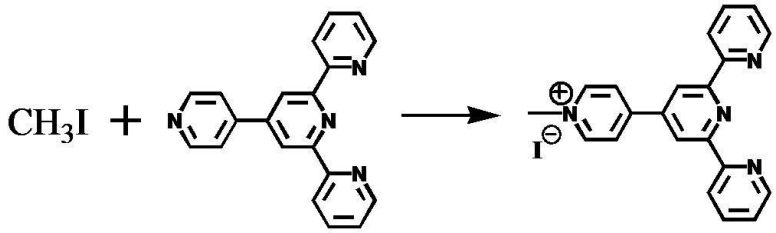
1. Experimental Section

Synthesis of NTPY, MTPY, NAPY and DNPC6

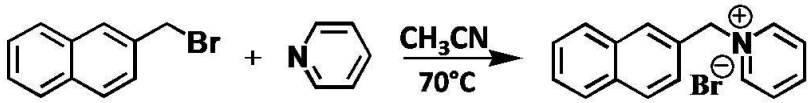
NTPY: TPY-Py and excess of 2-(bromomethyl)naphthalene were heated in $CHCl_3$ at 70 °C for 12 h. The mixture was precipitated in diethyl ether. The green precipitate was collected by filtration and washed with diethyl ether. After vacuum drying, final product was obtained, yielding 98%. ^{1}H NMR (JOEL JNM-ECA300, 300 MHz, DMSO-d_6, 25 °C): δ (ppm) = 9.50 (2 H), 8.93~8.72 (8 H), 8.17~8.10 (6 H), 7.62~7.59 (5H), 6.16 (2 H). ^{13}C NMR δ (ppm) =156.76, 154.60, 153.74, 149.87, 146.07, 144.51, 138.44, 133.48, 133.25, 132.41, 129.60, 128.82, 128.61, 128.28, 127.66, 127.46, 127.00, 126.32, 125.64, 121.85, 119.53, 63.59. MALDI-TOF: *m*/*z* 451.18 [*M*-Br]$^+$.



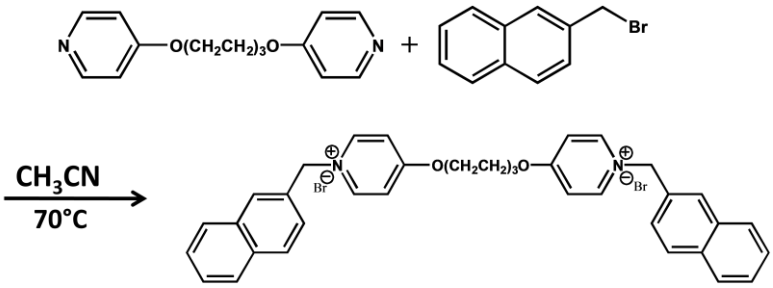
MTPY: TPY-Py and excess of Iodomethane were heated in DMF at 70 °C for 12 h. The mixture was precipitated in diethyl ether. The yellow precipitate was collected by filtration and washed with diethyl ether. After vacuum, final product was obtained, yielding 95%. ^{1}H NMR (JOEL JNM-ECA300, 300 MHz, DMSO-d_6, 25 °C): δ (ppm) = 9.16 (2 H), 8.96~8.64 (8 H), 8.09 (2 H), 7.60 (2 H), 4.45 (3H); ^{13}C NMR δ (ppm) = 156.96, 154.77, 152.77, 149.99, 146.74, 144.37, 138.27, 126.05, 125.58, 121.76, 119.23, 48.13. MALDI-TOF: *m*/*z* 325.12 [*M*-*I*]$^+$.



NAPY: 2-(Bromomethyl)naphthalene was reacted with excess of pyridine in CH_3CN at 70 °C overnight. The mixture was precipitated in diethyl ether and filtrated then dried in vacuum to give final product, yielding 83%. ^{1}H NMR (300 MHz, DMSO-d6, 25 °C): δ (ppm) = 9.25 (2 H), 8.64 (1 H), 8.20 (2 H), 8.09 (1 H), 7.96 (3 H), 7.59 (3 H), 6.03 (2 H); ^{13}C NMR δ (ppm) = 137.26, 136.40, 126.76, 126.56, 125.81, 123.68, 123.21, 122.87, 122.61, 122.12, 121.95, 121.07, 71.09. MALDI-TOF: *m*/*z* 220.08 [*M*-Br]$^+$.



DNPC6: 1,6-dpy was reacted with excessof 2-(Bromomethyl)naphthalene in CH_3CN reflux for 12h. The mixture was precipitated in diethyl ether and filtrated then dried in vacuum to give final product, yielding 90%. ^{1}H NMR (300 MHz, DMSO-d6, 25 °C): δ (ppm) = 9.15~9.01 (4 H), 8.06~7.95 (8 H), 7.68~7.58 (10 H), 5.89 (4 H), 4.37 (4 H), 2.52 (4 H), 1.81 (4 H), 1.48 (4 H); ^{13}C NMR δ (ppm) = 156.53, 137.38, 126.68, 126.58, 126.30, 123.61, 122.80, 122.71, 122.60, 122.01, 121.92, 120.90, 111.64, 77.08, 69.54, 42.66, 40.24. MALDI-TOF: *m*/*z* 413.20 [*M*-$C_{11}H_9$-*Br*]$^+$



ITC studies: ITC was carried out with a Microcal VP-ITC apparatus at 298.15 K.

UV/vis spectra and fluorescence emission spectra: UV-vis spectra were obtained using a HITACHI U-3010 spectrophotometer. Fluorescence spectra were obtained using a HITACHI F-7000 apparatus.
NMR studies: ^{1}H NMR spectra was recorded on a JOEL JNM—ECA300 apparatus (300 MHz). DOSY experiments were carried out with a BRUKER AVANCE 600 NMR Spectrometer.

AFM-based single-molecule force spectroscopy: AFM-based single-molecule force spectroscopy was carried out at room temperature by using commercially available Molecular Force Probe 3D (Asylum Research, Santa Barbara, CA). AFM cantilevers used in experiments were commercially available V-shaped Si_3N_4 cantilevers (Veeco, Santa Barbara, CA) with a spring-constant range of 0.010–0.040 N m^{-1}. A quartz slide was treated with a hot piranha solution (concentrated 98 % H_2SO_4/30 % H_2O_2, 7/3, v/v) for 30 min, and then rinsed thoroughly with deionized water. A solution of 2NTPY-Fe-CB[8] (0.5 mM) was mounted between the AFM tip holder and the freshly cleaned quartz slide. When the slide contacted with the AFM tip due to the movement of the piezo, the supramolecular polymer chains were adsorbed onto the tip and the substrate at the same time, forming a molecular bridge between tip and substrate. When tip and substrate were separated, the molecular bridge was stretched. The force loaded onto the tip and the extension of the molecular bridge were monitored simultaneously, and the force–extension curve was then obtained.

2. Equilibrium among cyclic species and supramolecular polymers

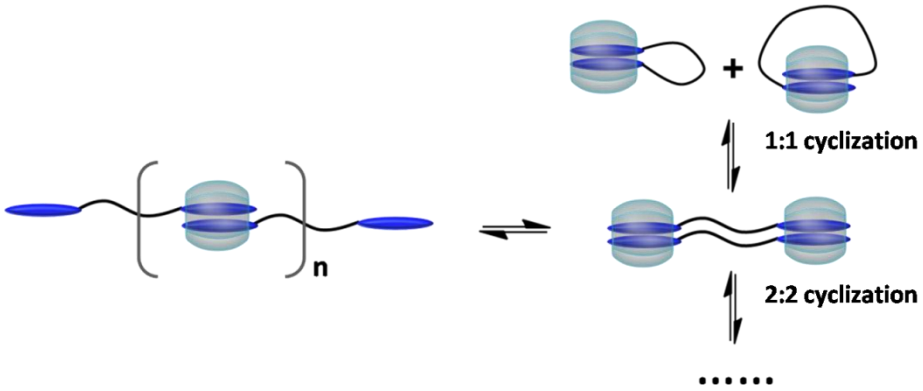


Fig. S1: The formation of small cyclic species always hinder supramolecular polymerization

3. MALDI-TOF data of 2NTPY-Fe complex

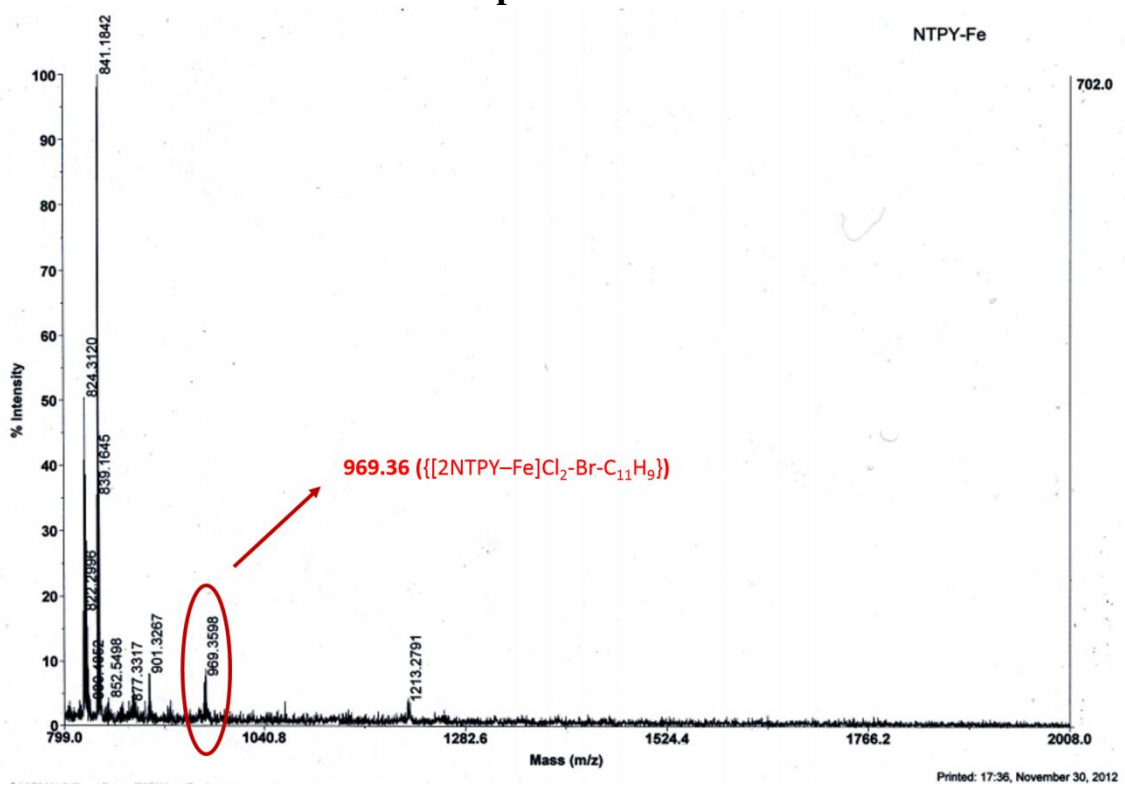
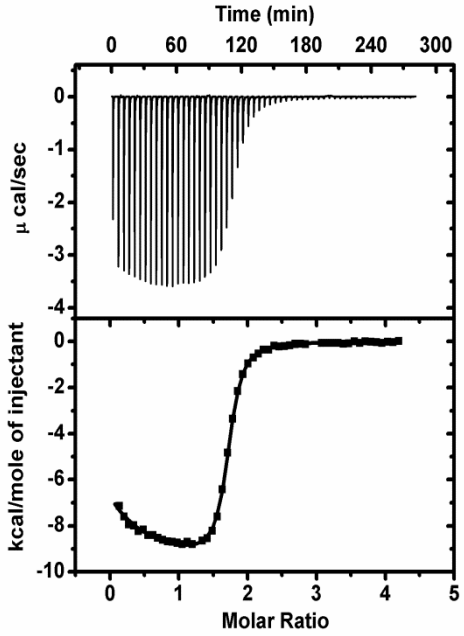


Fig. S2: Signal of m/z = 969.36 in mass spectra was observed, corresponding to {[2NTPY–Fe]Cl_2-Br-$C_{11}H_9$}, which further support the formation of the bifunctional monomer of 2NTPY-Fe complex.

4. ITC Study of the model system of 2NAPY-CB[8]



Data: A20101214NpP_NDH
Model: TwoSites
Chi^2 = 5400

K1	1.64E6 ± 2.31E5 M^{-1}
H1	-1.002E4 ± 231 cal/mol
S1	-5.18 cal/mol/deg
K2	3.93E6 ± 5.32E5 M^{-1}
H2	3.772E4 ± 1.40E5 cal/mol
S2	157 cal/mol/deg

Fig. S3: Fitting ITC data of 2NAPY-CB[8] with two-sites binding model. (Titration of NAPY 2.0 mM into CB[8] 0.1 mM)

5. ^{1}H NMR spectroscopy of 2NAPY-CB[8]

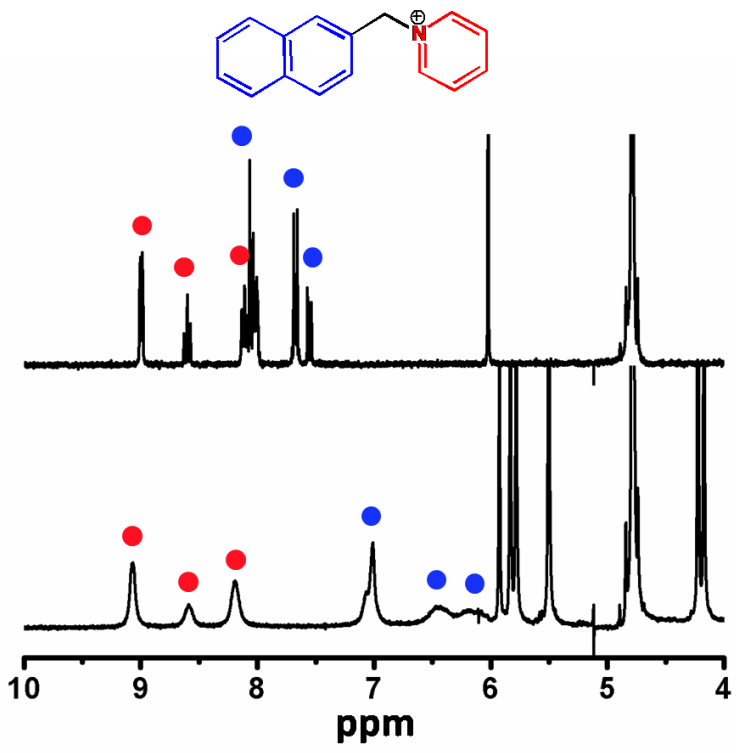


Fig. S4: ^{1}HNMR spectra 2.0 mM NAPY and 1.0 mM 2NAPY-CB[8]. The naphthyl proton peaks are marked with blue dots and the pyridine proton peaks are marked with red dots.

6. ^{1}H NMR spectroscopy of 2MTPY-Fe

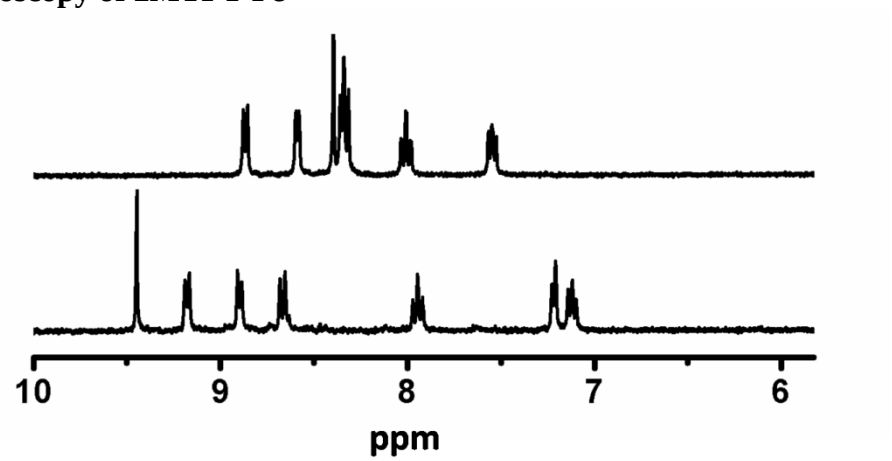


Fig. S5: ^{1}H NMR of MTPY and 2MTPY-Fe in D_2O.

7. ^{1}H NMR spectroscopy of 2NTPY-Fe-CB[8]

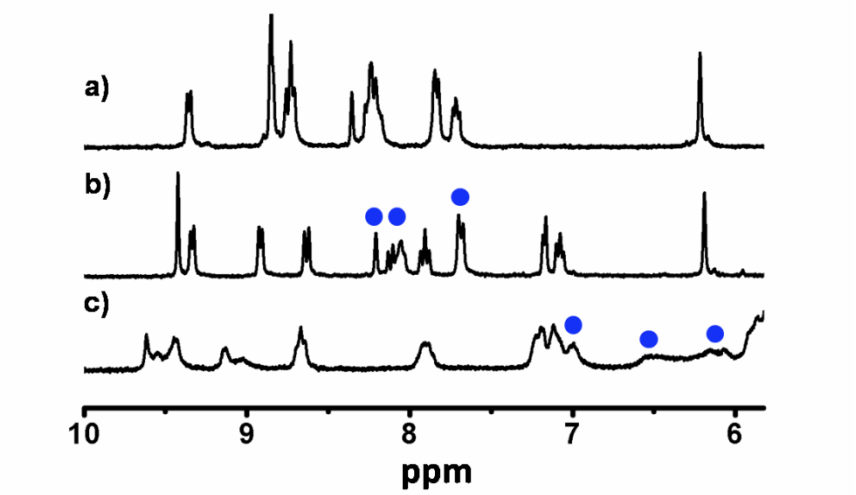


Fig. S6: ^{1}H NMR of a) NTPY in 1:1 DMSO-D_2O; b) 2NTPY-Fe in D_2O; c) 2NTPY-Fe-CB[8] in D_2O. The naphthyl proton peaks of NTPY are marked with blue dots.