SUPPORTING INFORMATION

A Cucurbit[5]uril Analogue From Dimethylpropanediurea-Formaldehyde Condensation

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Contents

1. Experimental section:

General: TEM images were recorded on a JEOL JEM-1400 and JEM-2100 apparatus. ^{1}H NMR and ^{13}C NMR spectra were measured on a Brüker AM-400 spectrometer. The molecular mass spectra were recorded on a LCT Premier XE mass spectrometer and a 4800 Plus M-TOF/TOF Analyzer (AB SCIEX, USA). The DLS measurements were carried out on a MALV RN, ZETA SIZER, Model ZEN3600. The ITC experiments were carried out on a MicroCal iTC 200.

Materials: Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures.

2. Synthesis of $Me_{10}TD[5]$:

Paraformaldehyde (0.72 g, 24.0 mmol) was added in a solution of **Me_2TD** [1] (1.84 g, 10.0 mmol) in concentrated HCl (5 ml). The mixture was stirred at room temperature for 1 h, and then heated to 95 °C for 24 h. The resulting solution was cooled to room temperature, and the solid was collected by filtration, and recrystallized in H_2O to afford the desired compound (100 mg, 5%) as a white solid. [2] ^{1}H NMR (400 MHz, D_2O, 298 K): δ 6.53 (d, J = 14.9 Hz, 10H) , 4.89 (s, 10H), 4.20 (d, J = 14.9 Hz , 10H), 1.14 (s, 30H). ^{13}C NMR (100 MHz, D_2O): δ 154.2, 77.5, 62.0, 29.5, 20.1. MALDI-TOF mass m/z 1041 $[M+H]^+$; m/z 1059 $[M+H_2O+H]^+$.

3. Preparation of the single crystal of $Me_{10}TD[5]$ and the polymer:

The single crystal of **$Me_{10}TD[5]$** was formed from a solution of **$Me_{10}TD[5]$** (50 mg, 0.05 mmol), $CaCl_2$ (22 mg, 0.20 mmol) and 3 drops conc. HCl in distilled water (10 mL) which was allowed to stand slow evaporation in air at room temperature, yielding colorless crystals within 2 weeks. The XRD result is shown in Fig. S13a.

The single crystal of the polymer was formed from a solution of **$Me_{10}TD[5]$** (50 mg, 0.05 mmol), **G_2** (10mg, 0.05 mmol) and 6 drops conc. HCl in distilled water (10 mL) which was allowed to stand slow evaporation in air at room temperature, yielding colorless crystals within 4 weeks. The XRD result is shown in Fig. S13b.

4. The solubility measurements of $Me_{10}TD[5]$.

To 500 mg of **Me_{10}TD[5]** was added 30.0 ml of solvent, the mixture was stirred at 298 K for 12h. The insoluble solid was filtered and dried in vacuo at 80° for 24h. The weight (M) of the resulting solid was measured and the solubility of **Me_{10}TD[5]** was then calculated as (500 – M) / (1040 * 0.03) mmol/L.

5. Supplementary Figures:

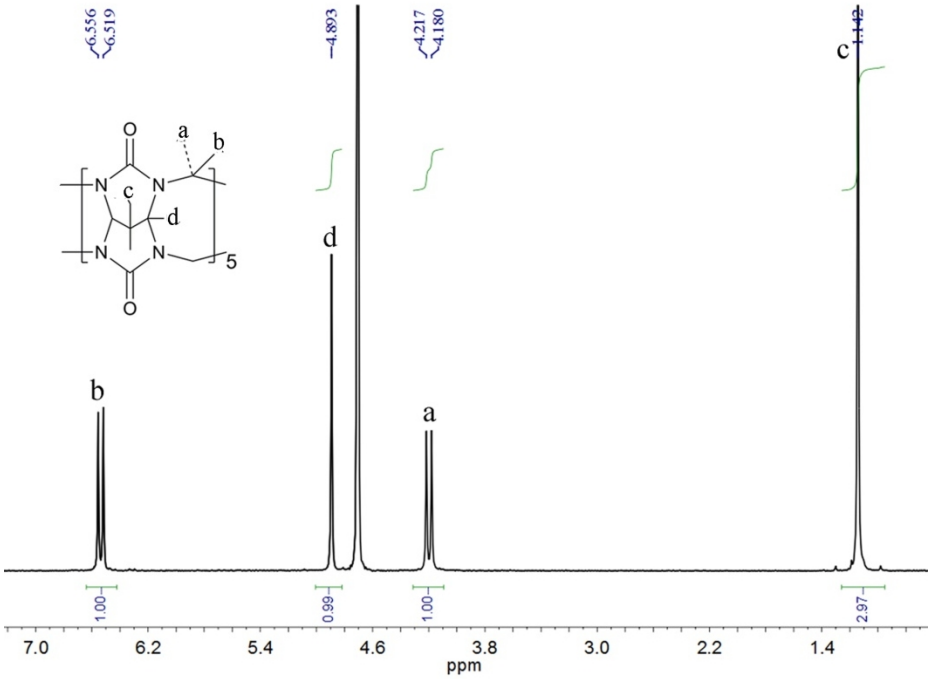

Fig. S1 ^{1}H NMR spectra (400MHz, 99% D_2O, 298 K) of **Me_{10}TD[5]**.

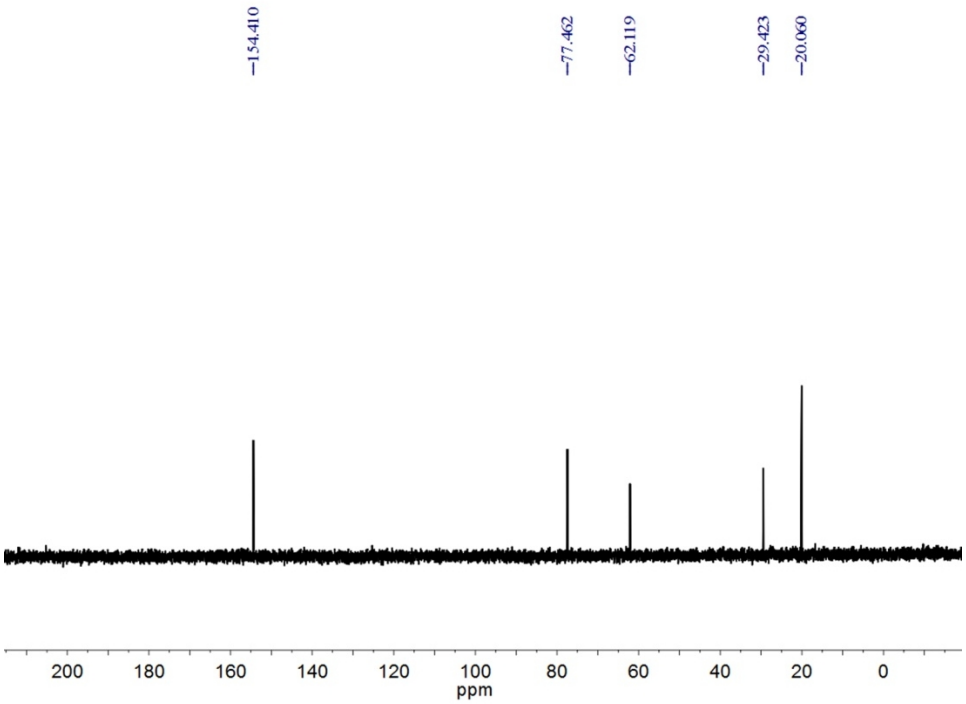

Fig. S2 ^{13}C NMR spectra (100MHz, 99% D_2O, 298 K) of **Me_{10}TD[5]**.

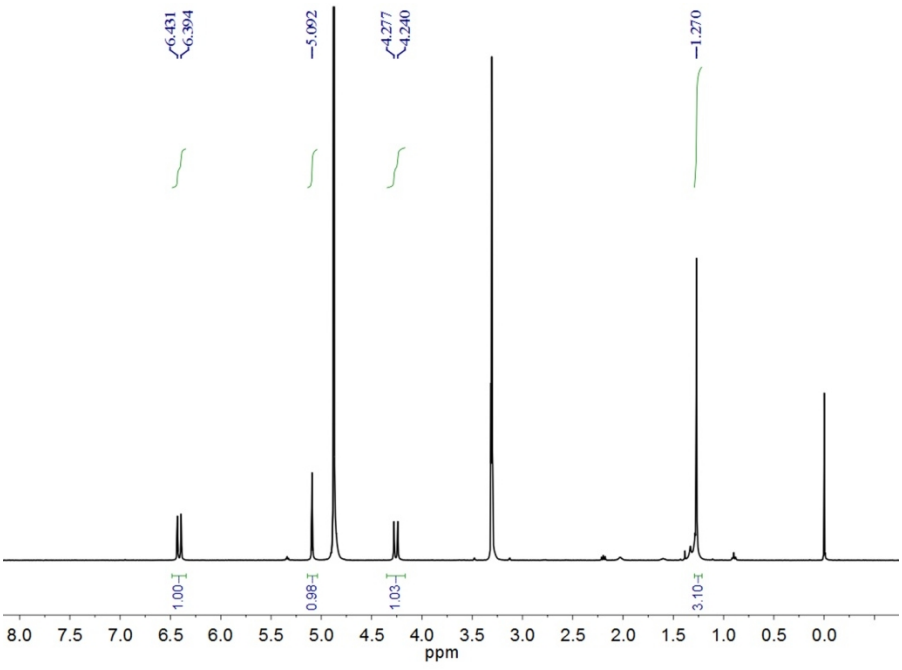

Fig. S3 ^{1}H NMR spectra (400MHz, 99% CD_3OD, 298 K) of **Me_{10}TD[5]**.

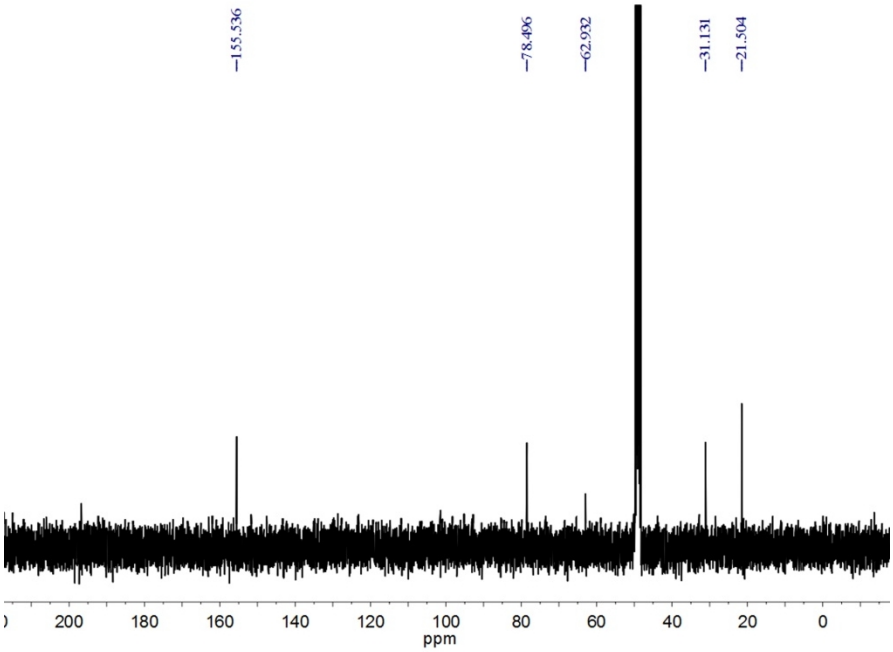

Fig. S4 ^{13}C NMR spectra (100MHz, 99% CD_3OD, 298 K) of **Me_{10}TD[5]**.

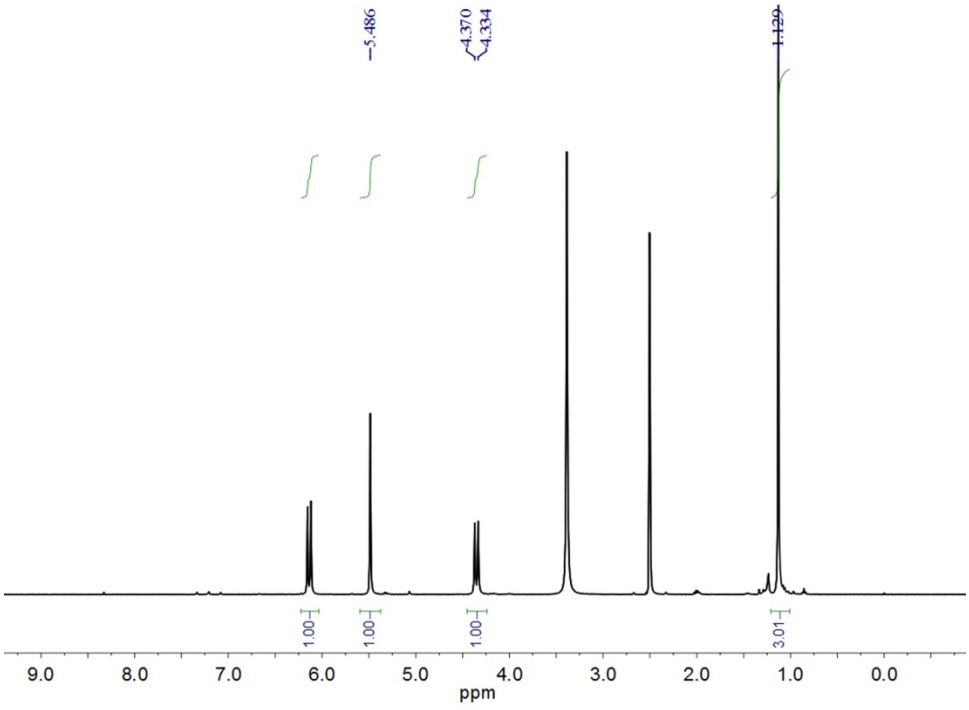

Fig. S5 ^{1}H NMR spectra (400MHz, 99% DMSO-d_6, 298 K) of **Me_{10}TD[5]**.

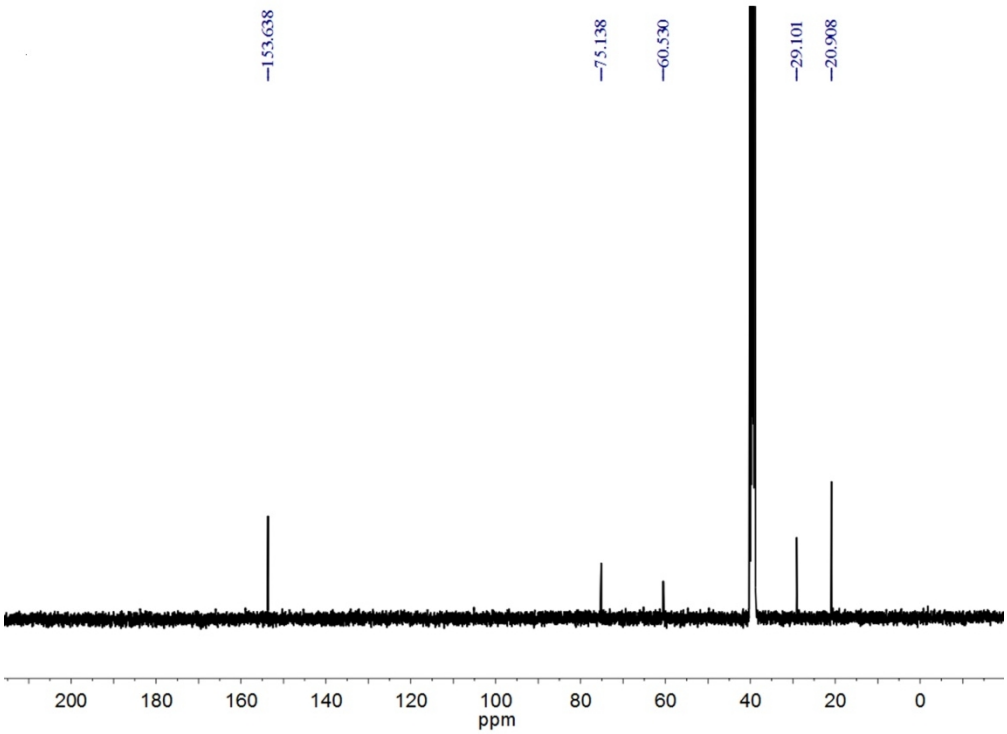

Fig. S6 ^{13}C NMR spectra (100MHz, 99% DMSO-d_6, 298 K) of **Me_{10}TD[5]**.

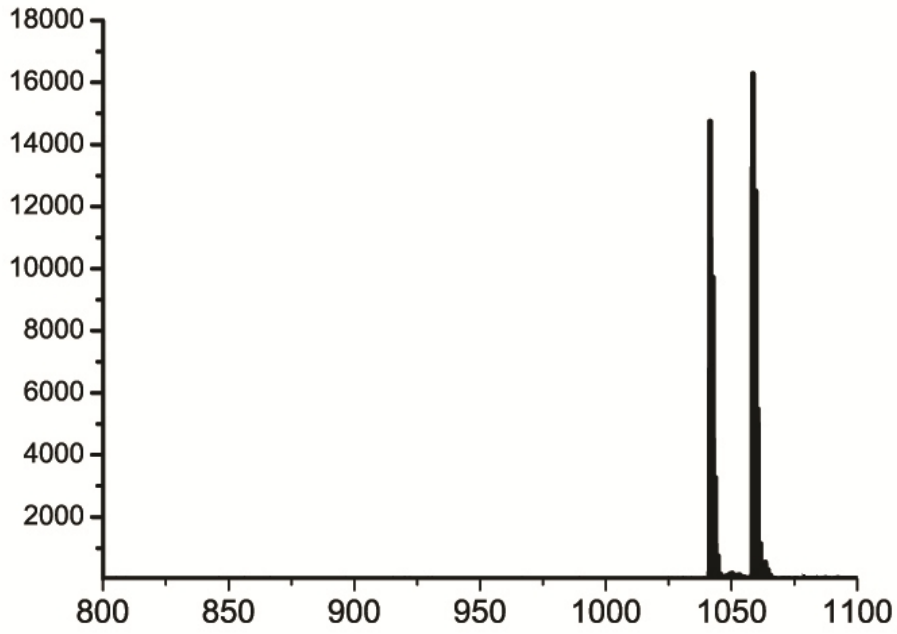

Fig. S7. MALDI-TOF of **Me_{10}TD[5]**: m/z 1041 $[M+H]^+$; m/z 1059 $[M+H_2O+H]^+$.

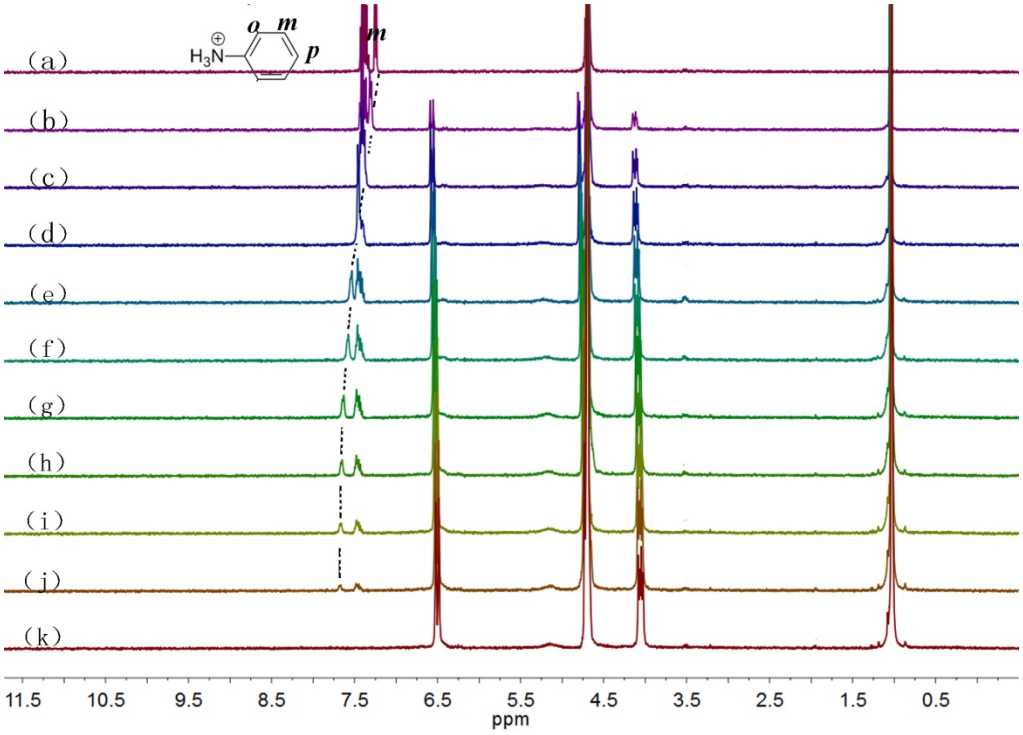

Fig. S8. ^{1}H NMR Job plots experiments in D_2O for **Me_{10}TD[5]** and aniline hydrochloride. (a) **Me_{10}TD[5]** : aniline hydrochloride = 0 : 1. (b) 0.1 : 0.9 (c) 0.2 : 0.8 (d) 0.3 : 0.7 (e) 0.35 : 0.65 (f) 0.5 : 0.5. (g) 0.6 : 0.4. (h) 0.7 : 0.3. (i) 0.8 : 0.2. (j) 0.9 : 0.1 (k) 1 : 0. The total concentration was 4.0 mM.

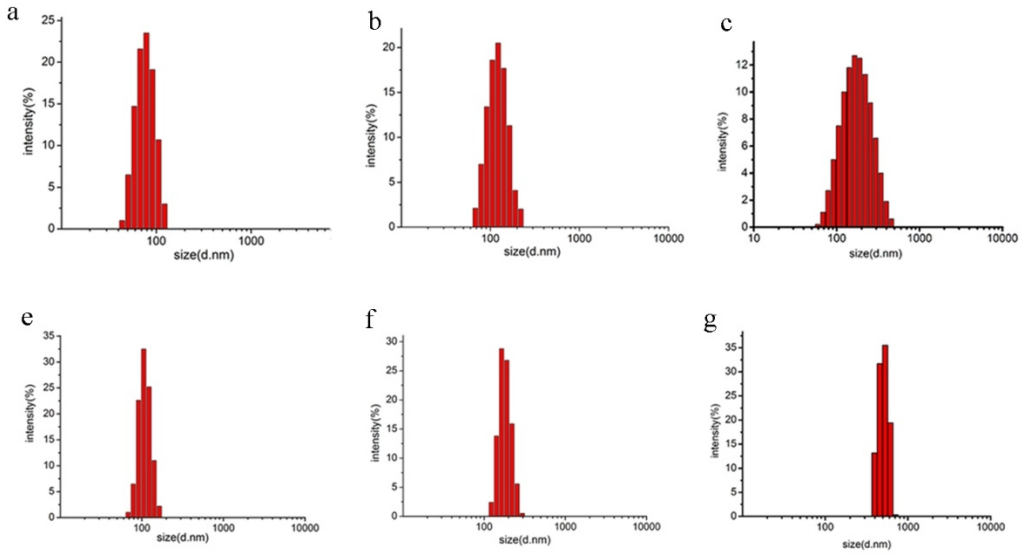

Fig. S9. Dynamic Light Scattering results: (a) **G_1** + **Me_{10}TD[5]** (***C***= 5×10^{-5} M), the peak is at 78 nm in aqueous solution. (b) **G_1** + **Me_{10}TD[5]** (***C***= 1×10^{-4} M), the peak is at 122 nm in aqueous solution. (c) **G_1** + **Me_{10}TD[5]** (***C***= 2×10^{-4} M), the peak is at 190 nm in aqueous solution. (d) **G_2** + **Me_{10}TD[5]** (***C***= 5×10^{-5} M), the peak is at 105 nm in aqueous solution. (e) **G_2** + **Me_{10}TD[5]** (***C***= 1×10^{-4} M), the peak is at 164 nm in aqueous solution. (f) **G_2** + **Me_{10}TD[5]** (***C***= 2×10^{-4} M), the peak is at 295 nm in aqueous solution.

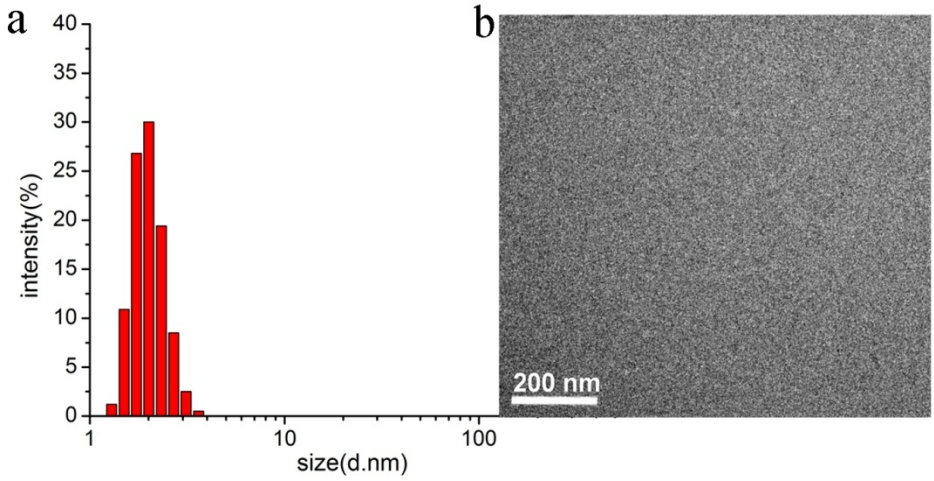

Fig. S10 (a) Dynamic Light Scattering result for **Me_{10}TD[5]** (***C***= 2×10^{-4} M), the peak is at 2 nm in aqueous solution. (b) TEM images of **Me_{10}TD[5]** (***C***= 2×10^{-4} M).

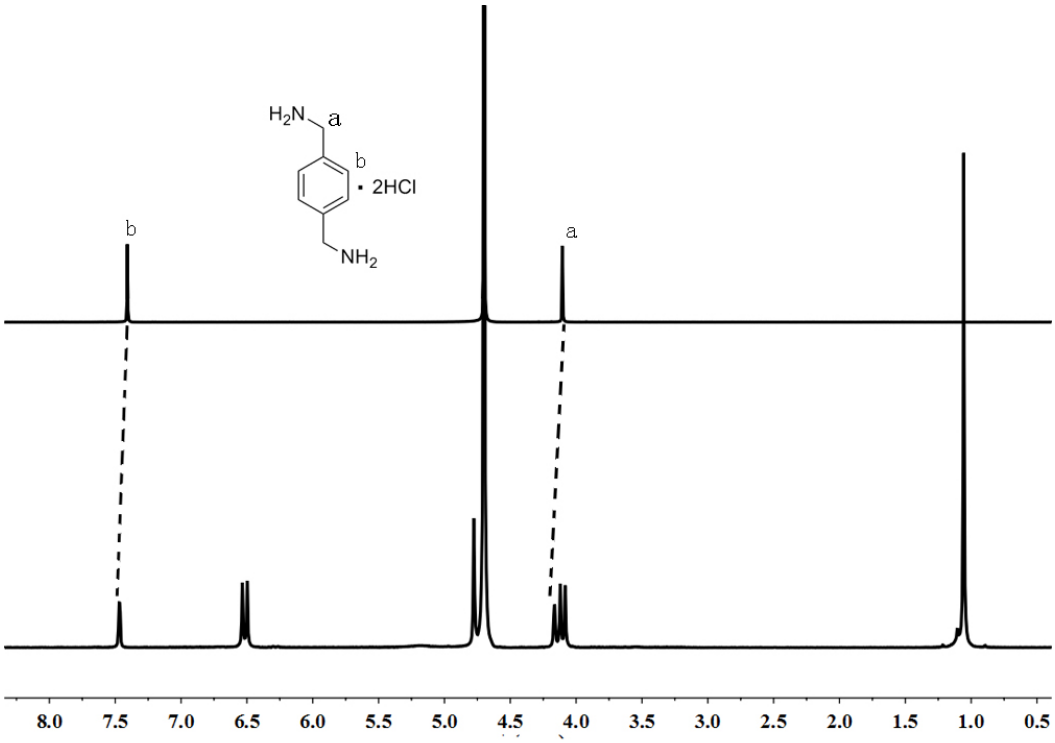

Fig. S11. ^{1}H NMR spectra of 1,4-xylylene diamine dihydrochloride (up) in D_2O and the addition of **Me_{10}TD[5]** (bottom). (both 1 :1, 2.0 mM).

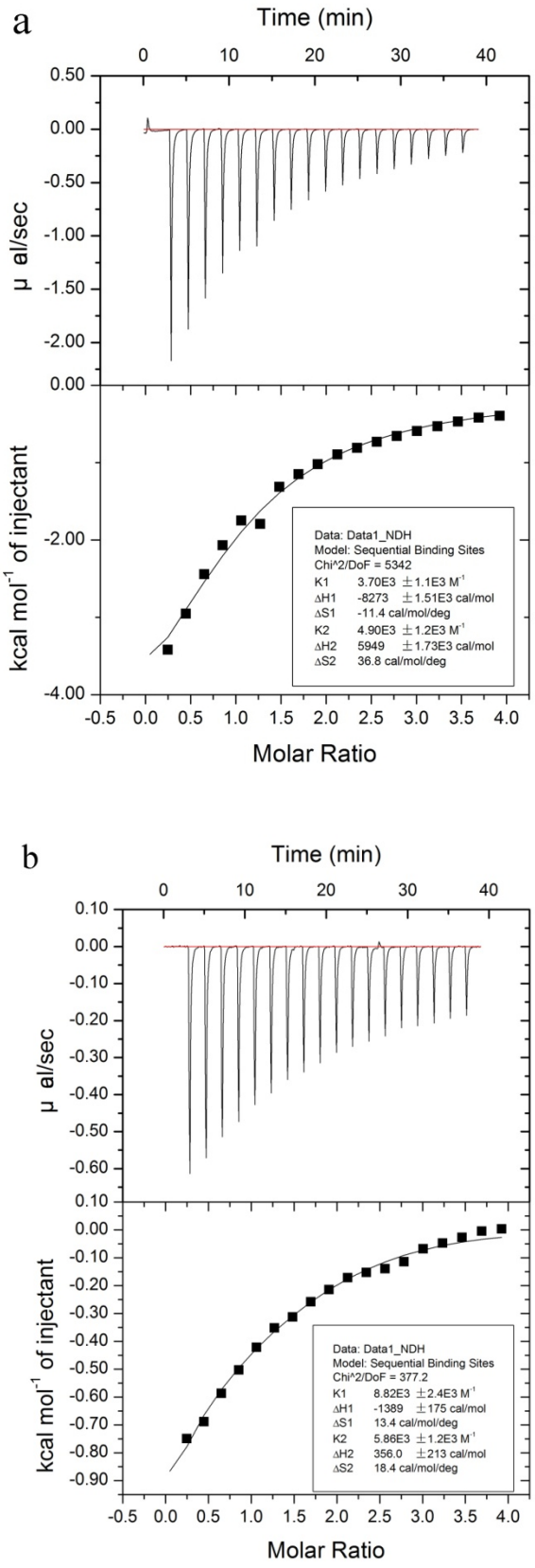

Fig. S12. ITC results for the complexation of (a) **Me_{10}TD[5]** with aniline hydrochloride, and (b) **Me_{10}TD[5]** with benzyl amine hydrochloride, both at 25˚C.

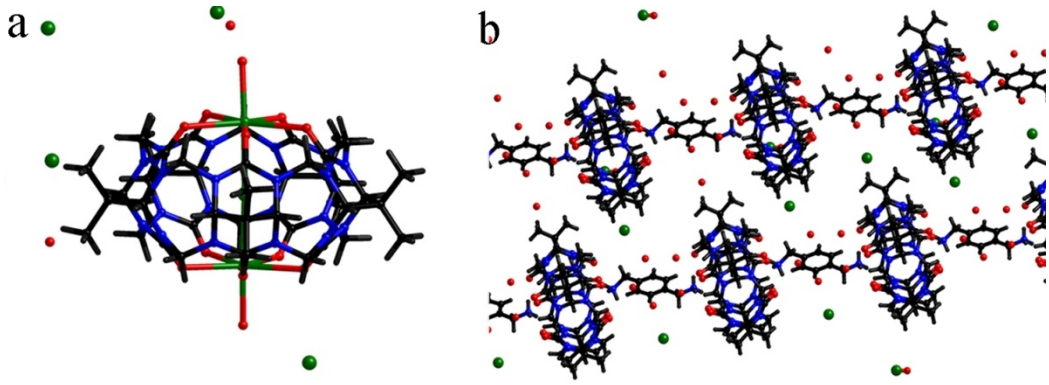

Fig. S13. The single crystal structures of **Me_{10}TD[5]-$CaCl_2$** (a) and the polymer **Me_{10}TD[5]-G_2** (b).

Reference:

[1] E. A. Bugnet, T. D. Nixon, C. A. Kilner, R. Greatrex and T. P. Kee, *Tetrahedron Lett.,* 2003, **44**, 5491.

[2] A. I. Day, A. P. Arnold and R. J. Blanch, *J. Org. Chem.,* 2001, **66**, 8094.