

A CB[5] analogue based supramolecular polymer with AIE behaviors

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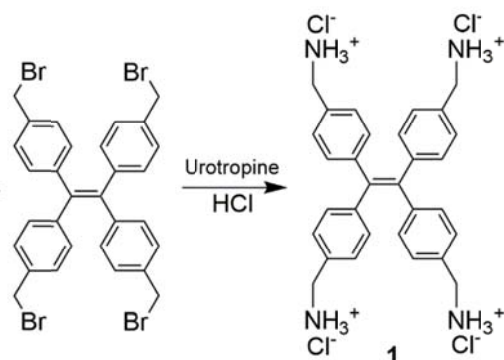
Supporting information

1. Experimental Section

1.1 General Methods

¹H NMR, ¹³C NMR and DOSY spectra were measured on a Brüker AV-400 spectrometer. The molecular mass spectra were recorded on a Waters LCT Premier XE mass spectrometer. DLS were measured on a MALV RN, ZETA SIZER, Model ZEN3600. The UV-Vis absorption spectra were obtained on a Varian Cary 100 spectrometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. The ITC experiments were carried out on a GE MicroCal iTC 200.

Materials: 1,1,2,2-tetrakis(4-(bromomethyl)phenyl)ethene (Scheme S1)^[1] and CyP₅TD[5]^[2] were prepared according the literature. Chemicals were purchased from Adamas, Aldrich and TCI and used as received unless otherwise stated. Solvents were reagent grade, which were dried and distilled prior to use according to standard procedures.



1.2 Synthesis

Scheme S1. The synthetic route of compound **1**.

1.2.1 Synthesis of Compound **1**

1,1,2,2-tetrakis(4-(bromomethyl)phenyl)ethene (1 g, 1.42 mmol) and hexamethylenetetramine (0.83 g, 5.96 mmol) were mixed in chloroform (100 mL) and heated to reflux overnight. The yellow precipitate was removed by filtration and washed with chloroform. The solid was then added to an ethanolic HCl solution (80 mL ethanol and 10 mL conc. HCl) and vigorously refluxed for 48 hours. The flask was cooled to 0° C and the solid was removed by filtration, washed with cold ethanol and dried under high vacuum to give the compound **1** as a white solid (0.52 g, 62% yield); ¹H NMR (400MHz, D₂O) δ(ppm): 7.11 (m, 16H), 3.99 (s, 8H); ¹³C NMR (100 MHz, D₂O) δ(ppm): 143.73, 140.76, 131.65, 131.22, 128.35, 42.66. HRMS (ESI) (m/z) [M-2Cl]²⁺ calcd: 261.1158, Found: 261.1155.

2. Supplementary Figures

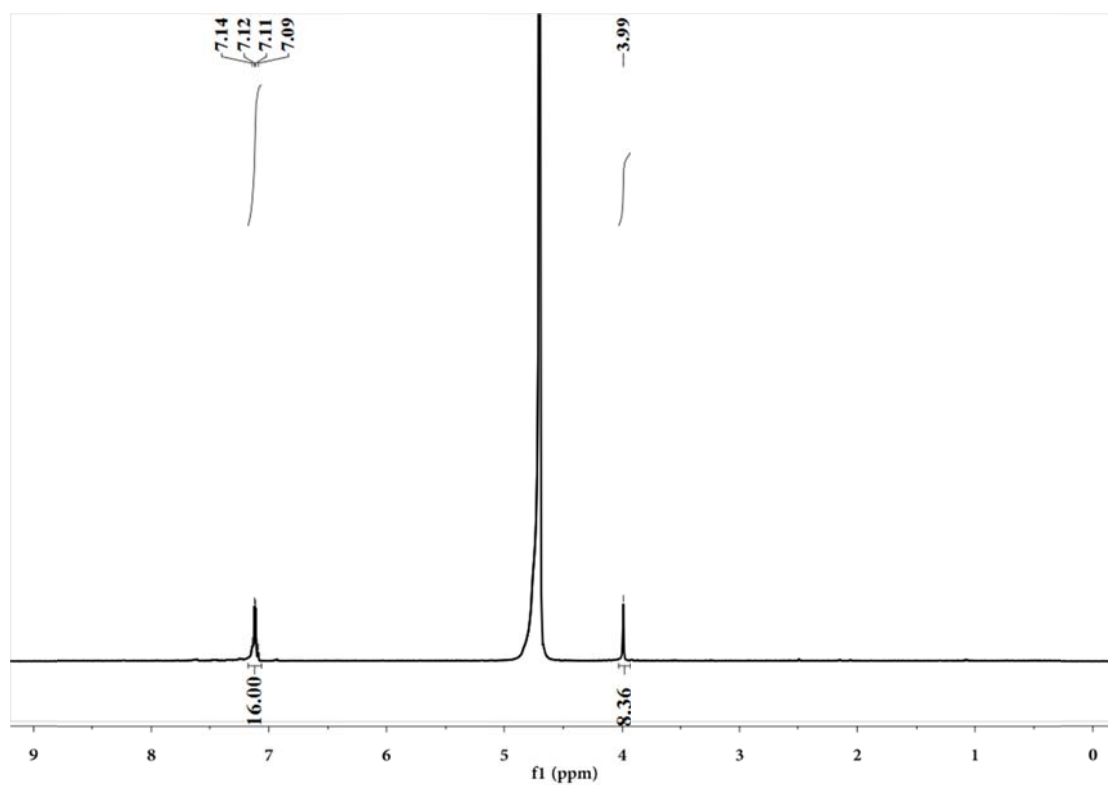


Fig. S1 ¹H NMR spectra (400MHz, 99% D₂O, 298 K) of **1**.

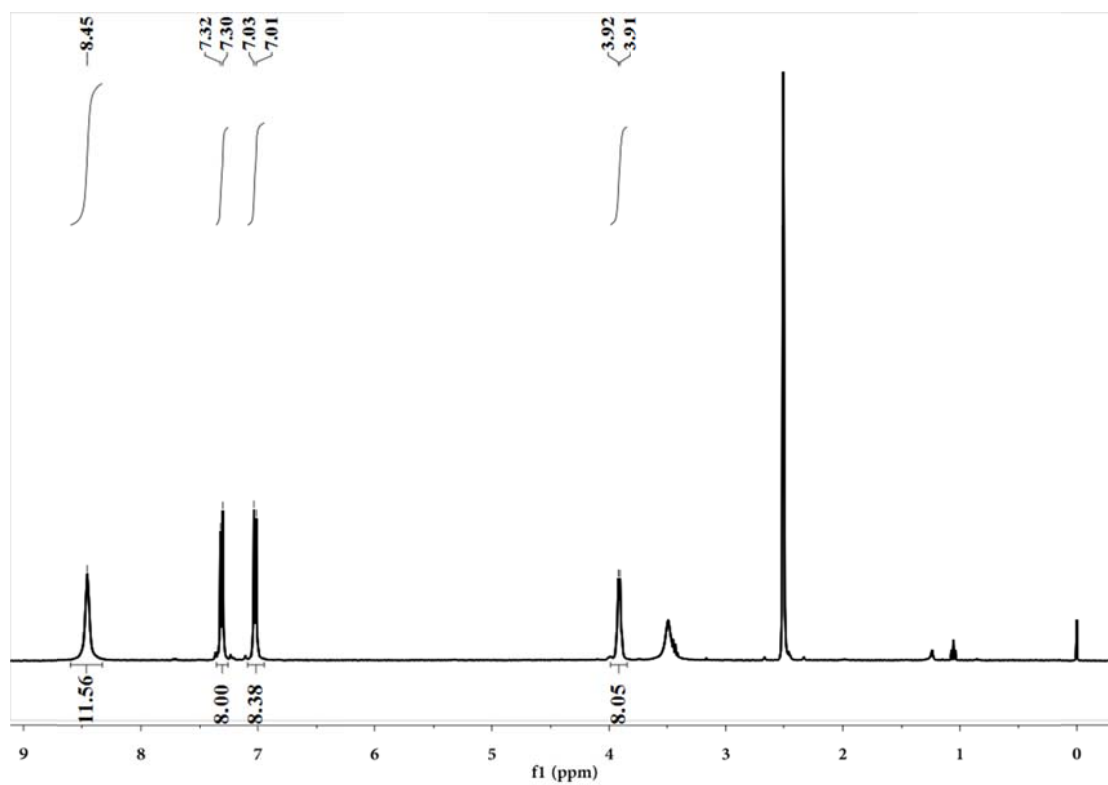


Fig. S2 ¹H NMR spectra (400MHz, 99% DMSO-d₆, 298 K) of **1**.

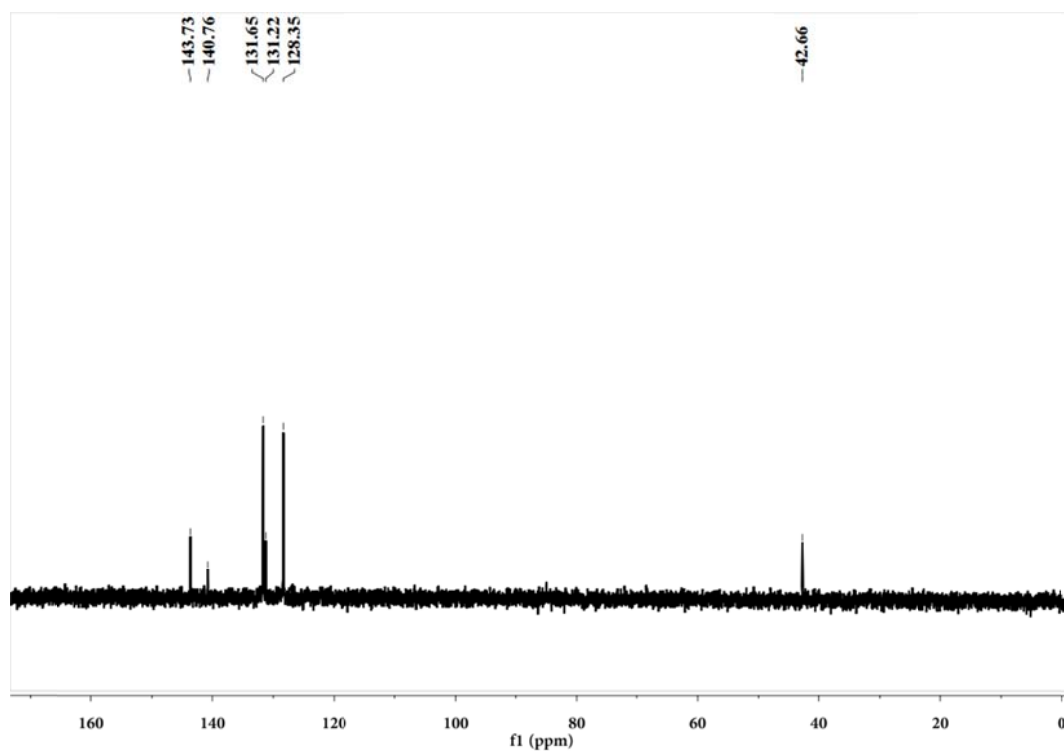


Fig. S3 ^{13}C NMR spectra (100MHz, 99% D_2O , 298 K) of **1**.

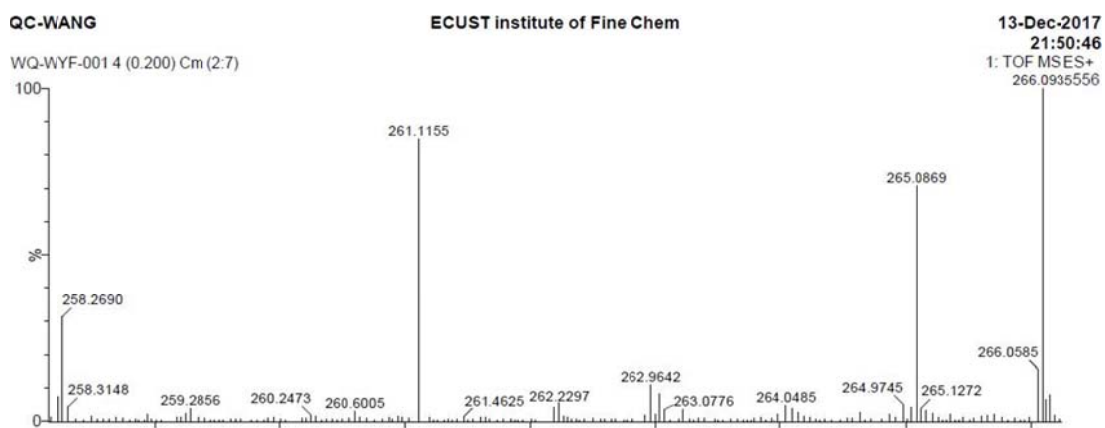


Fig. S4 ESI-MS of **1** : m/z 261.1155 $[\text{M}-2\text{Cl}]^{2+}$.

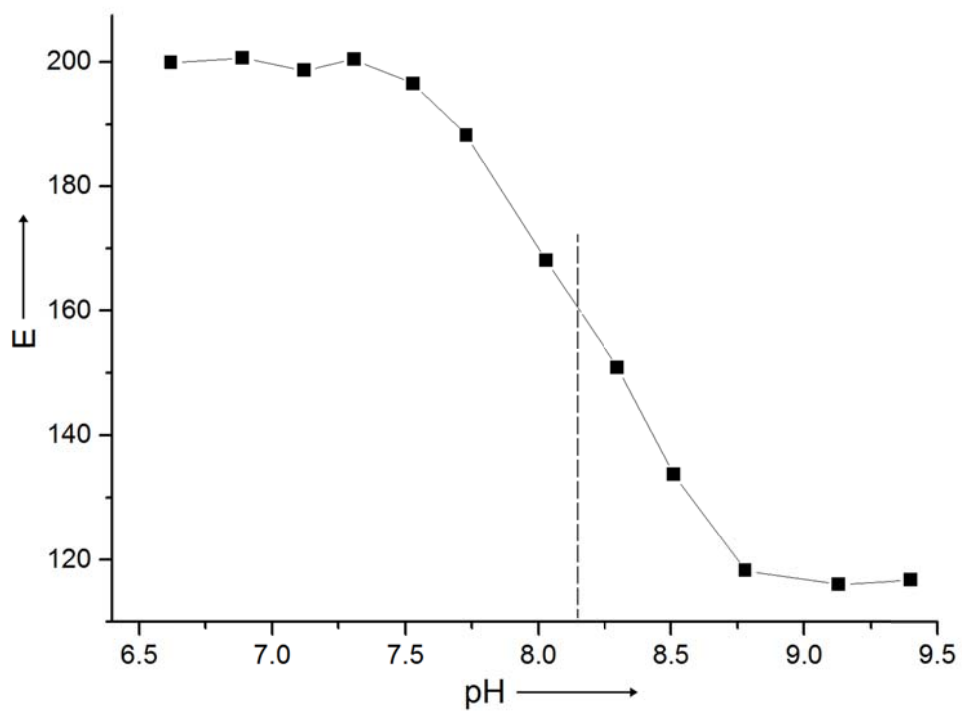


Fig. S5 pKa of ammonium group of guest **1** (10 μ M) monitored through the emission change at $\lambda=480$ nm upon pH variation in H₂O with the excitation of 330 nm. (The pKa value of **1** is 8.15.)

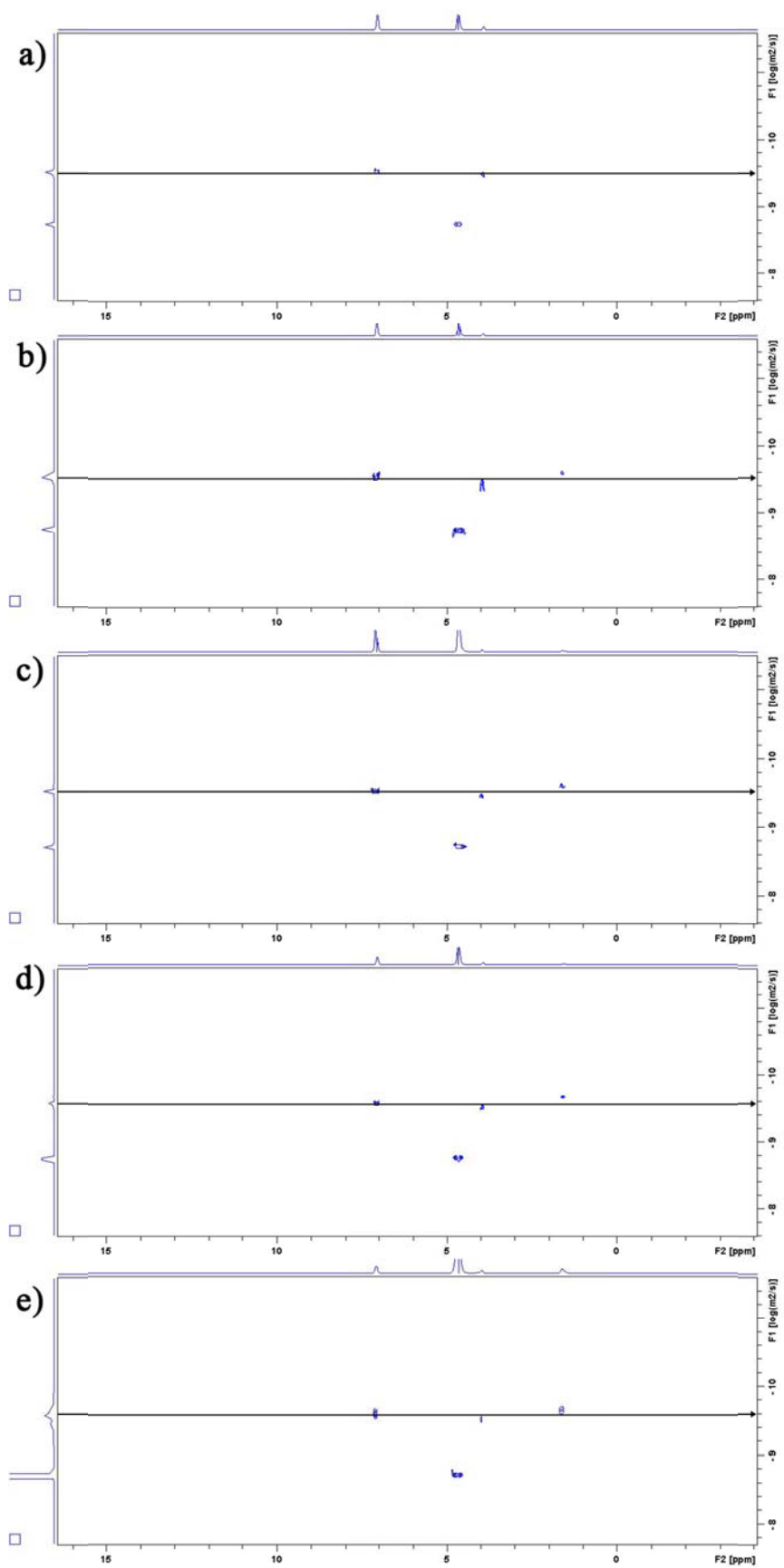


Fig.S6 DOSY of a) **1**, b) **1**+0.25 CyP₅TD[5], c) **1**+0.5 CyP₅TD[5], d) **1**+0.75 CyP₅TD[5] and e) **1**+1 CyP₅TD[5]. (3 mM)

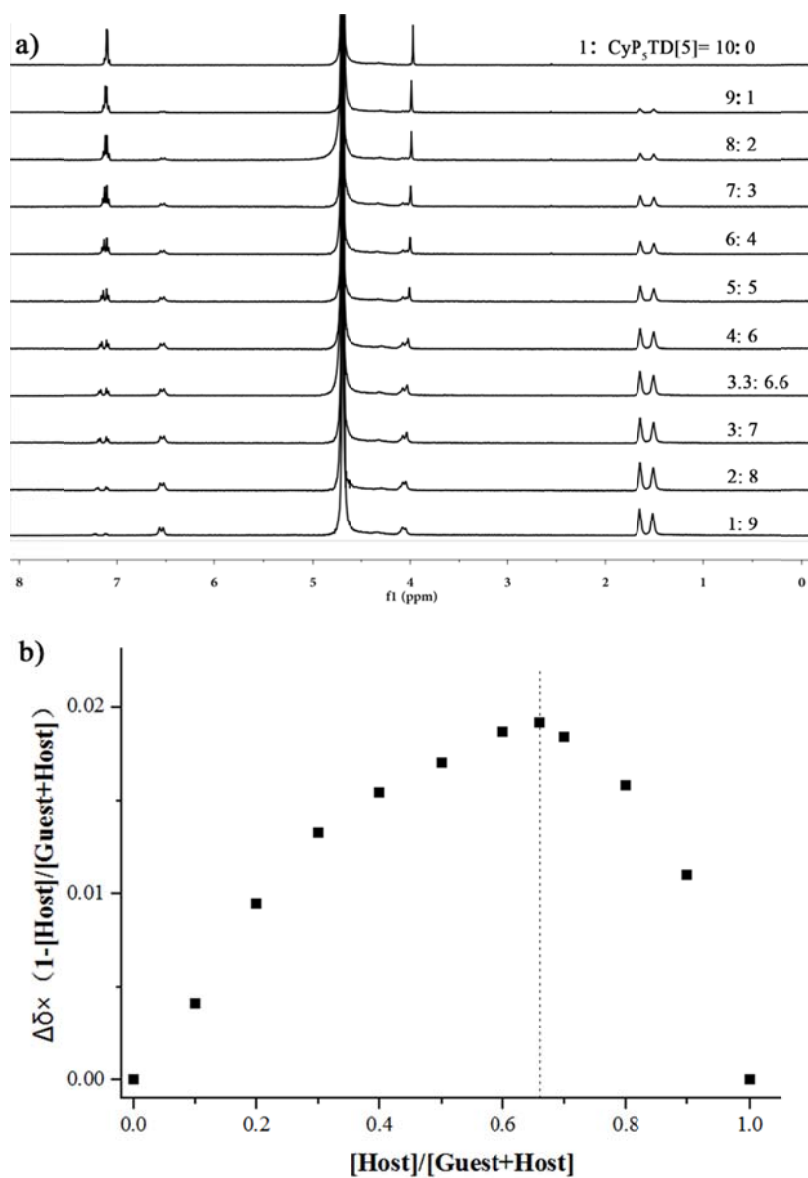


Fig. S7 a) ¹H NMR Job's plot experiments in D₂O for **1** and CyP₅TD[5]. The total concentration was 0.87 mM. b) Job's plot for the complexation of **1** and CyP₅TD[5]. The stoichiometry of **1** and CyP₅TD[5] is determined as 1: 2.

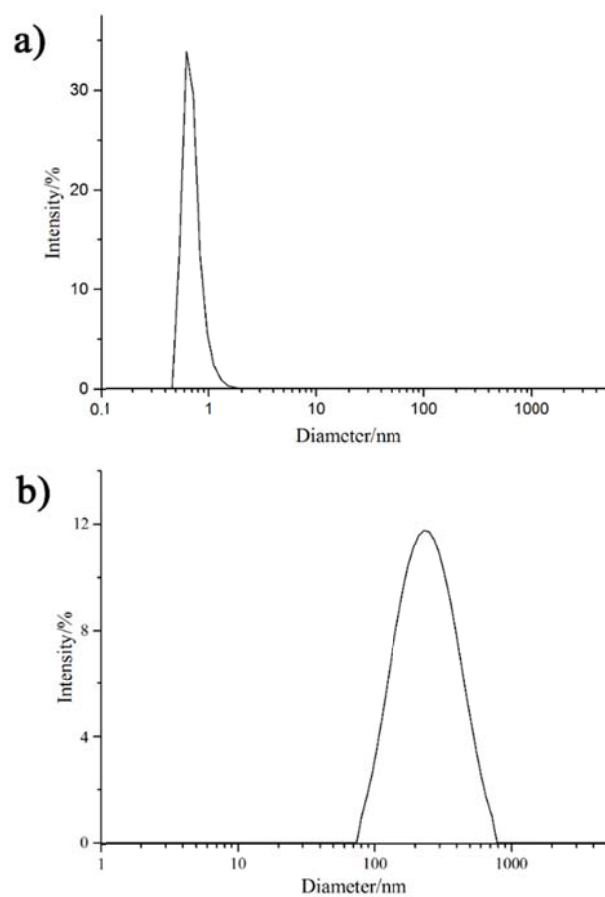


Fig. S8 DLS data of a) 0.05mM **1** and b) 0.05mM [**1**-2CyP₅TD[5]]; the DLS data are shown as the size probability distribution obtained by a CONTIN analysis.

3 References

- [1] Y.-X. Zhu, Z.-W. Wei, M. Pan, H.-P. Wang, J.-Y. Zhang and H.-Y. Su, *Dalton Trans.*, 2016, **45**, 943–950.
- [2] Y. Wu, L. Xu, Y. Shen, Y. Wang and Q. Wang, *New J. Chem.*, 2017. **41**, 6991