

Electronic Supplementary Information

Supramolecular polymers based on pillar[5]arene-fused cryptand: design, fabrication and degradation with fluorescence changing

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1. *Materials and methods*

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **1**,^{S1} **2**,^{S2} **3**,^{S3} **4**,^{S4} **5**,^{S5} **6**^{S3} and **7**^{S6} were prepared according to literature procedure. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. DOSY experiments were performed on a Bruker DPX 600 MHz spectrometers.

2. ^1H NMR spectra of **1**, **5**, and **6**

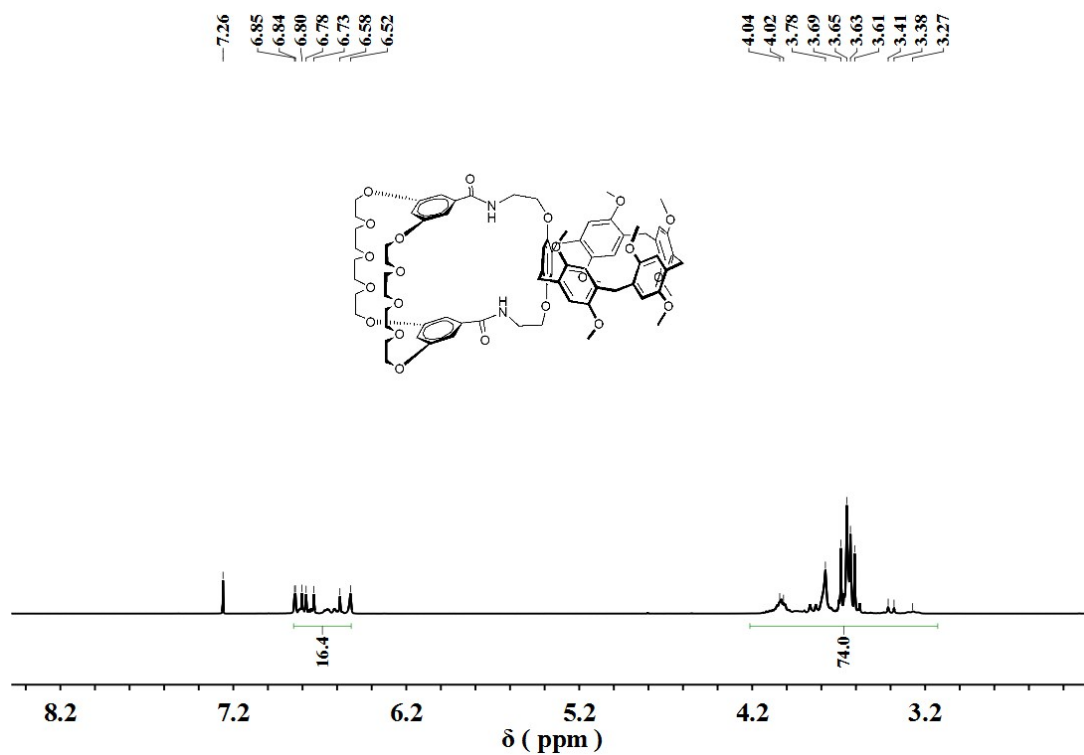


Fig. S1 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **1**.

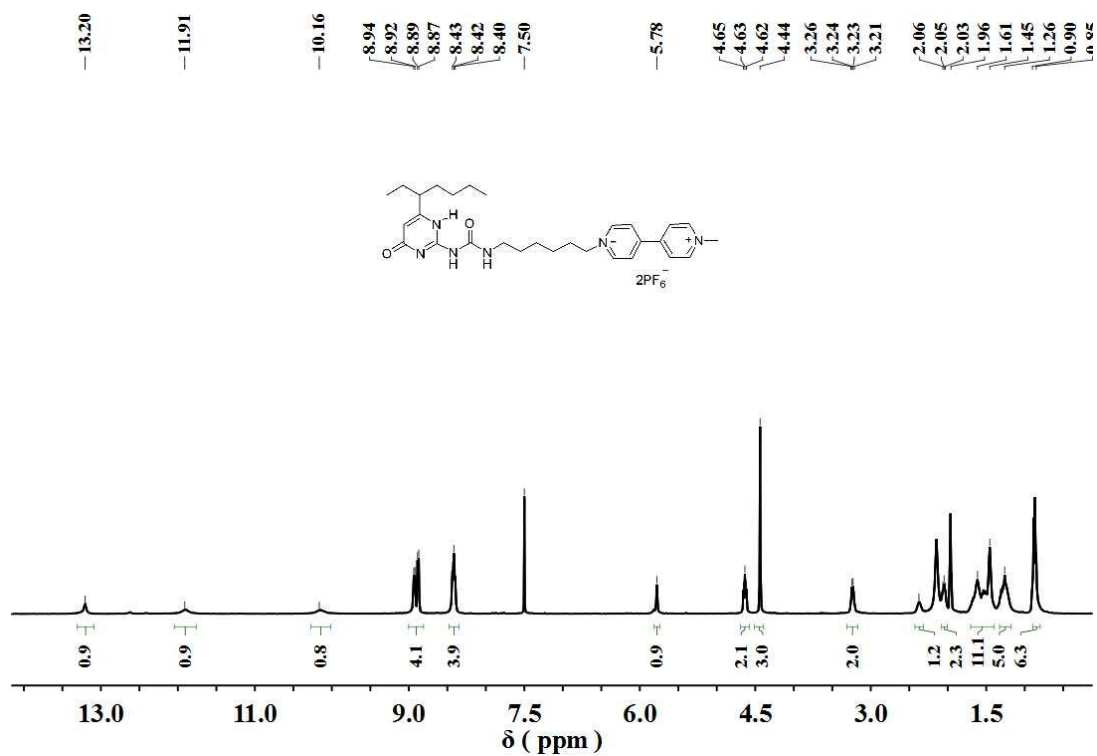


Fig. S2 ^1H NMR spectrum (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 1/1, v/v, 298 K) of **5**.

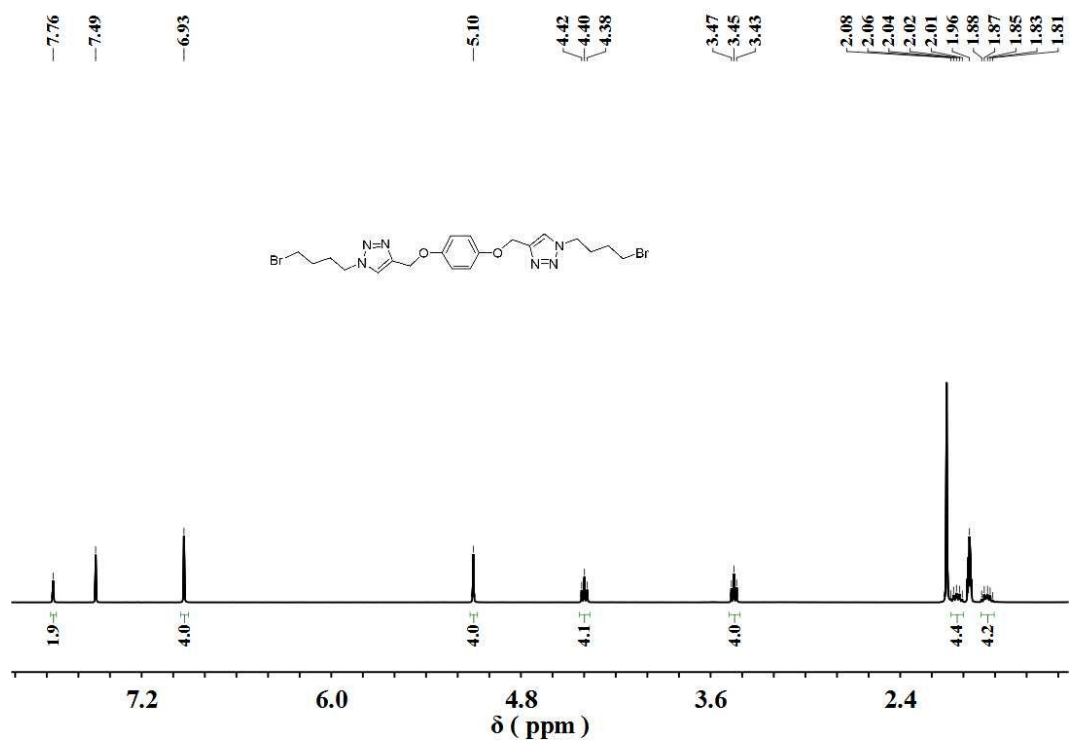


Fig. S3 ^1H NMR spectrum (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 1/1, v/v, 298 K) of **6**.

3. ^1H NMR spectra of **1** \rightarrow **2**, **1** \rightarrow **3**, and **2** \rightarrow **1** \rightarrow **3** in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (v/v=1/1)

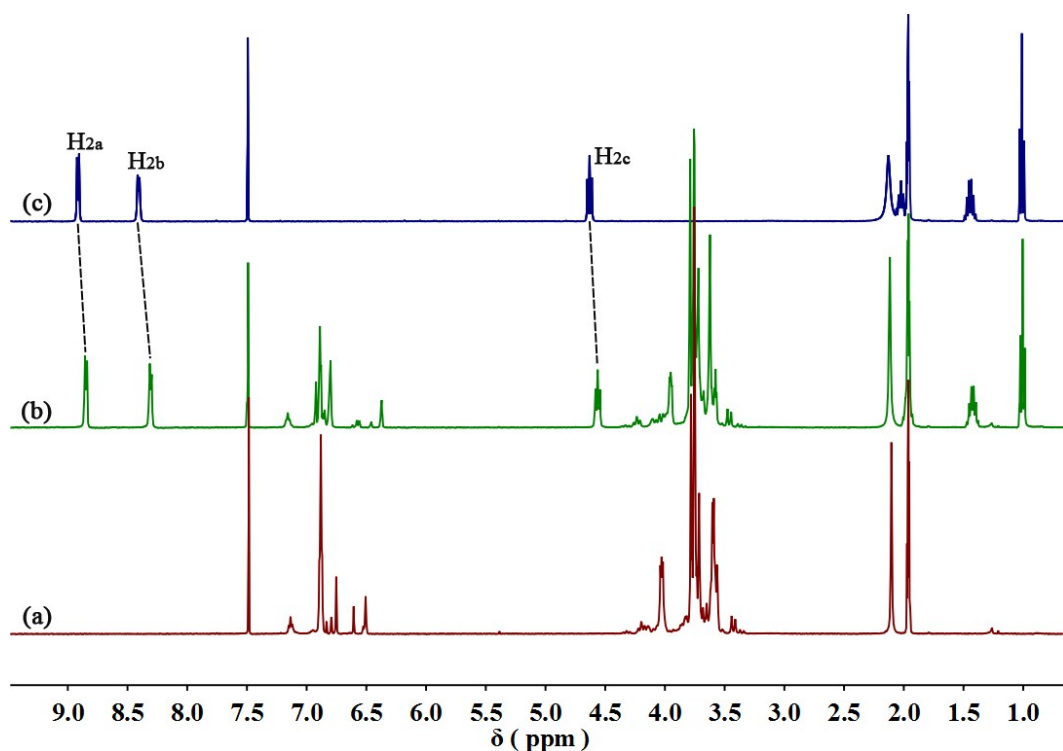


Fig. S4 Partial ^1H NMR spectra (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 1/1, v/v, 298 K): (a) **1**; (b) 4.00 mM **1** and 4.00 mM **2**; (c) **2**.

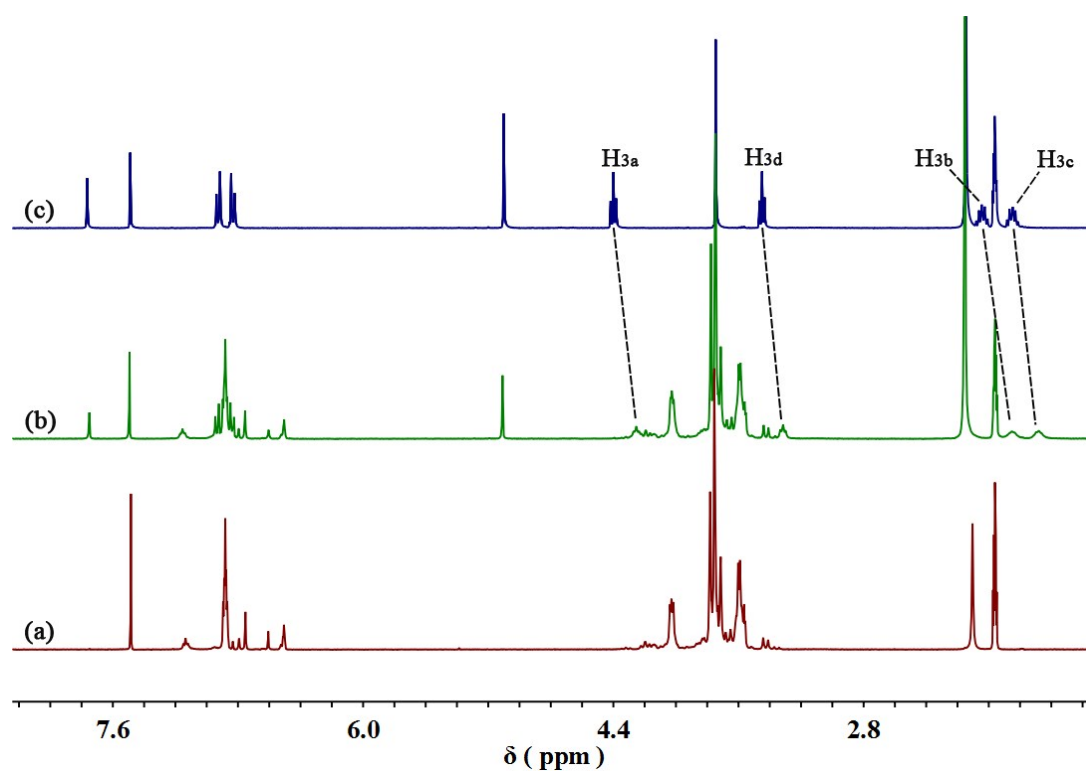


Fig. S5 Partial ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN, 1/1, v/v, 298 K): (a) **1**; (b) 4.00 mM **1** and 4.00 mM **3**; (c) **3**.

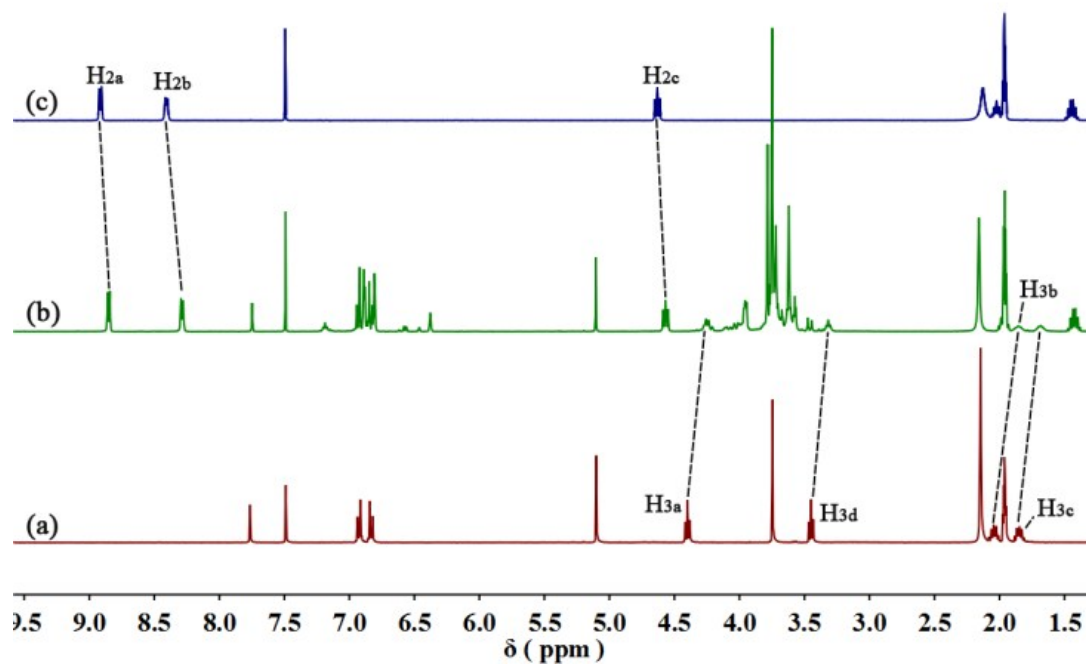


Fig. S6 Partial ¹H NMR spectra (400 MHz, CDCl₃/CD₃CN, 1/1, v/v, 298 K): (a) **3**; (b) mixtures of 4.00 mM **1**, 4.00 mM **2** and 4.00 mM **3**; (c) **2**.

4. Concentration-dependent ^1H NMR spectra

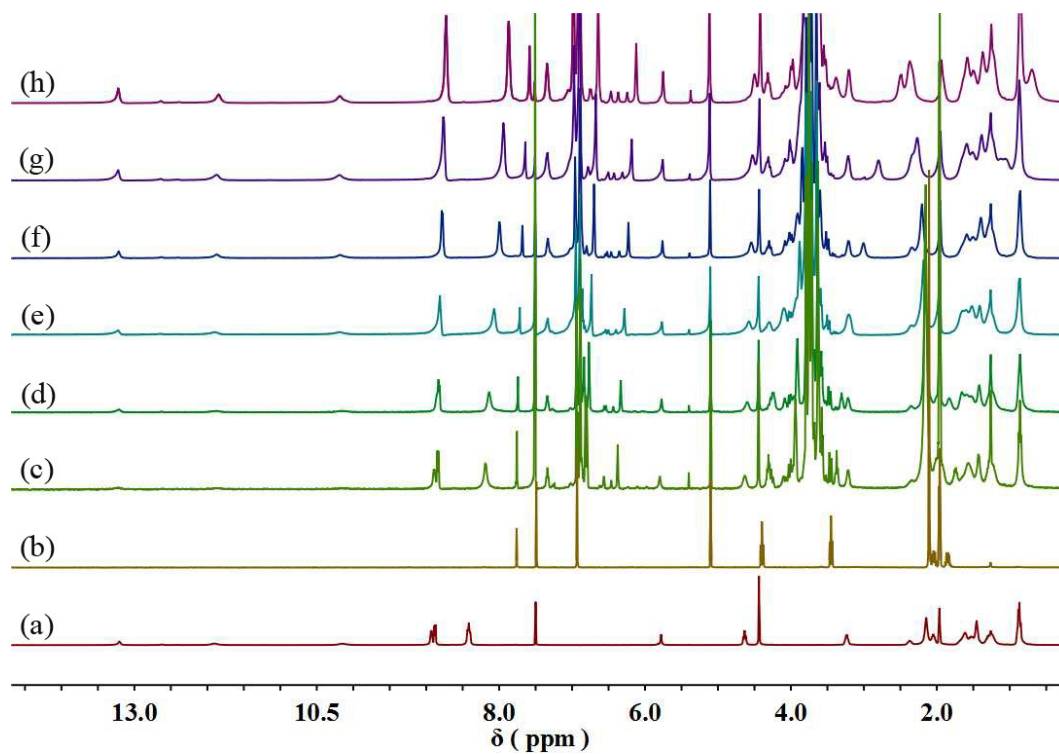


Fig. S7 ^1H NMR spectra (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 1/1, v/v, 298 K) of (a) individual **5**; (b) individual **6**; mixtures of **1**, **5** and **6** in a 2:2:1 molar ratio at different **1** concentrations: (c) 2, (d) 4, (e) 8, (f) 16, (g) 32 and (h) 64 mM.

5. SEM and TEM studies of the supramolecular polymers

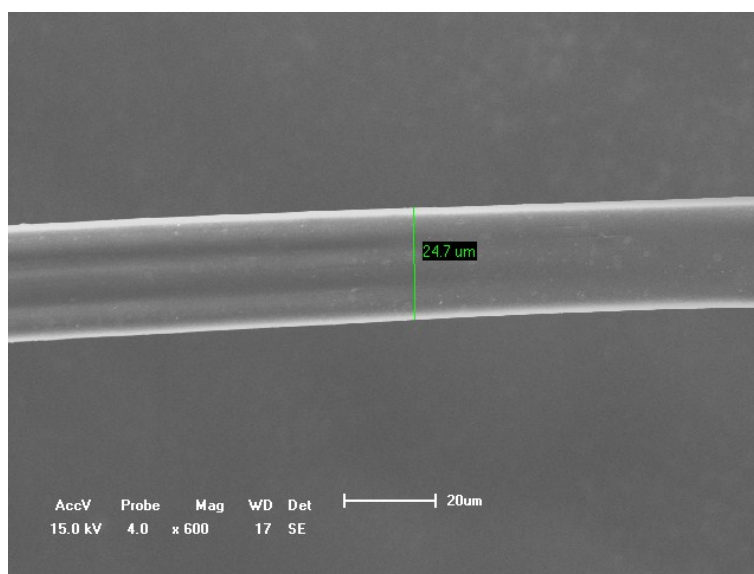


Fig. S8 SEM micrograph (gold coated) of a fiber drawn from a very concentrated mixed solution of **1**, **5** and **6**.

SEM: Long thin rod-like fibers with regular diameter about 24.7 μm were directly pulled from a very concentrated mixed solution of **1**, **5** and **6** and observed by SEM (gold coated), which gave visual physical evidence for the formation of large molecular weight supramolecular polymer because a polymeric structure of high molecular weight was necessary for the fiber formation.^{S7}

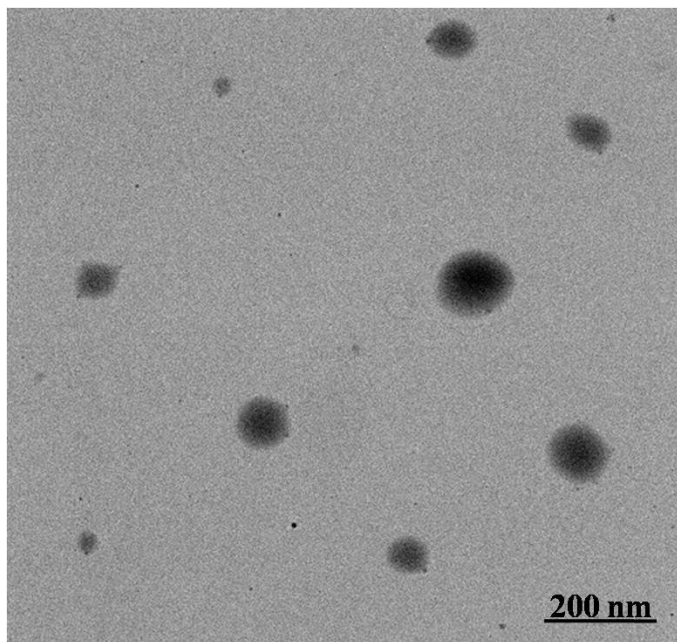


Fig. S9 TEM image of the supramolecular polymers (carbon-coated copper grid).

TEM: A drop of the solution of the sample (mixtures of **6** ($[\mathbf{6}] = 1 \times 10^{-3} \text{ M}$) with 2.0 equiv. of **1** and **5** in $\text{CHCl}_3/\text{CH}_3\text{CN}$) was placed on a carbon-coated copper grid. After the excess of solvent was evaporated, TEM images were taken. As shown from the representative TEM image (Fig. S9), globular aggregates were distinctly visualized, which presumably originated from the winding of the linear supramolecular polymers.^{S8} Similar results from linear supramolecular polymers were also reported previously.^{S9}

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