

Supporting Information

Unprecedented Cucurbituril-Based Ternary Host-Guest Supramolecular Polymers Mediated through Included Alkyl Chains

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Experimental Section

General Remarks: 4,4'-bipyridine, 1-bromobutane, 1,6-dibromohexane, and 1,8-dibromooctane were purchased from Aldrich. All other reagents and solvents were used as received. Q[8] was prepared according to a published procedure.^[17]

Measurements: ¹H NMR spectra were recorded on a Bruker DPX 400 spectrometer in D₂O and DMSO, while the DOSY spectra recorded only in D₂O. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. 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 EI III. Titration experiments were carried out on a NANO ITC SV. from Ta Inc. at 25°C. DLS data were obtained on a Zeta sizer Nano series at 25°C. SEM images were obtained using a JEOL JSM-6700F field-emission scanning electron microscopy. For SEM imaging, Au (1-2 nm) was sputtered onto the grids to prevent charging effects and to improve the image clarity.

DLS measurements. The sample solution for the DLS measurements was prepared by filtering the solution through a 450 nm millipore filter into a clean scintillation vial. It is worth noting that the aqueous solution of either guest or host Q[8] for the DLS measurements was prepared respectively. Both solutions were then mixed together

and the same DLS measurements were carried out. All the DLS measurements were performed at the scattering angle of 90° on a Zeta sizer Nano series at 25°C.

ITC measurements. Titration experiments were carried out on a NANO ITC SV. from Ta Inc. at 25°C. In the binding assays, the guest solution (1.2 mM) was put in the injection syringe and the host solution {Q[8], 0.10 mM} in the sample cell. Typically 20-30 consecutive injections of 4.0 μ L each were used. The first data point was removed from the data set prior to curve fitting. The data were analyzed with Origin 7.0 software using the independent model.

X-ray crystallographic analysis. Single crystals suitable for X-ray diffraction analysis were grown by the in air slow solvent evaporation of the aqueous reaction mixture of corresponding guest and cucurbituril. Crystal data were determined by X-ray diffraction analysis at 150 K using Oxford Diffraction Gemini E system with $\text{Cu}_{K\alpha}$ radiation $\lambda = 1.5418 \text{ \AA}$, using a ω scan mode with an increment of 1°. Preliminary unit cell parameters were obtained from 30 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for data collecting and processing; ABSPack for absorption correction; and SHELXL for space group and structure determination, refinements, graphics, and structure reporting. CCDC number of 989372 and 981776 for Q[8]@1 and Q[8]@2,

respectively, containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Density functional theory calculations. The DMol³ inputting Q[8]@2 skeleton without hydrogen atoms was obtained from the single crystal structure. The water molecules were added into the DMol³ inputting file according to the isolated oxygen atoms in the cif file of the single crystal structure of Q[8]@2. Optimization of the Q[8]@2 supramolecular system was carried out at the level of PBE-D(Grimme)/DND(3.5)^[18] in DMol³ Software housed at the Mining College of Guizhou University Calculation Centre.

Preparation of 1-butyl-4,4'-bipyridinium bromide. The mixture of 1-bromobutane (1.37 g, 0.010 mol) and 4,4'-bipyridine (4.68 g, 0.030 mol) in CH₃CN (100 mL) was refluxed for 2 h, then cooled to room temperature. The precipitate was filtered and washed thoroughly with diethyl ether, giving the water soluble compound 1-butyl-4,4'-bipyridinium bromide with the yield of 2.64 g, 90%.

Preparation of 1',1''-(hexylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-dium) bromide (1). To a solution of 1-butyl-4,4'-bipyridinium bromide (1.76 g, 0.0060 mol) in DMF (50 mL) was added 1,6-dibromohexane (0.73 g, 0.0030 mol). The mixture was heated to reflux for 3 h and then cooled to room temperature. The precipitate was

filtered and washed thoroughly with diethyl ether, giving the water soluble compound 1',1''-(hexylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-dium)bromide (**1**) with the yield of 2.04 g, 82%. ¹H NMR (400 MHz, D₂O, 25°C): δ 8.96 (d, 8H, *J* = 8.0 Hz), 8.38 (d, 8H, *J* = 8.0 Hz), 4.57 (m, 8H), 1.92 (m, 8H), 1.34 (m, 4H), 1.24 (m, 4H), 0.80 (t, 6H, *J* = 8.0 Hz). Anal. Calcd. for C₃₄H₄₆N₄Br₄: C, 49.18; H, 5.58; N, 6.75; found C, 49.20; H, 5.61; N, 6.71.

Preparation of 1',1''-(octylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-dium)

bromide (2). To a solution of compound 1-butyl-4,4'-bipyridinium bromide (1.76 g, 0.0060 mol) in DMF (50 mL) was added 1,8-dibromooctane (0.82 g, 0.0030 mol). The mixture was heated to reflux for 3 h and then cooled to room temperature. The precipitate was filtered and washed thoroughly with diethyl ether, giving the water soluble compound 1',1''-(octylene-1,4-diyl)bis(1-butyl)-4,4'-bipyridine-1,1'-dium)bromide (**2**) with the yield of 2.05 g, 88%. ¹H NMR (400 MHz, D₂O, 25°C): δ 8.96 (d, 8H, *J* = 8.0 Hz), 8.40 (d, 8H, *J* = 8.0 Hz), 4.59 (m, 8H), 1.93 (m, 8H), 1.26 (m, 12H), 0.82 (t, 6H, *J* = 8.0 Hz). Anal. Calcd. for C₃₆H₅₀N₄Br₄: C, 50.37; H, 5.87; N, 6.53; found C, 50.34; H, 5.89; N, 6.55.

Preparation of supramolecular polymer Q[8]@1. To a solution of **1** (8.30 mg, 0.010 mmol) in deionized water (30 ml), Q[8] (25.56 mg, 0.020 mmol) and zinc chloride (13.6 mg, 0.10 mmol) were added. The resulting reaction mixture was stirred for 30 min at 50°C and filtered. Slow solvent evaporation of the filtrate in air over a

period of about five weeks provided block colorless crystals of the target supramolecular compound Q[8]@1 with the yield of 5.71 mg, 18%.

Preparation of supramolecular polymer Q[8]@2. To a solution of **2** (8.54 mg, 0.010 mmol) in deionized water (30 ml), Q[8] (25.56 mg, 0.020 mmol) and zinc chloride (13.6 mg, 0.10 mmol) were added. The resulting reaction mixture was stirred for 30 min at 50°C and filtered. Slow solvent evaporation of the filtrate in air over a period of about five weeks provided block colorless crystals of the target supramolecular compound Q[8]@2 with the yield of 6.22 mg, 22%

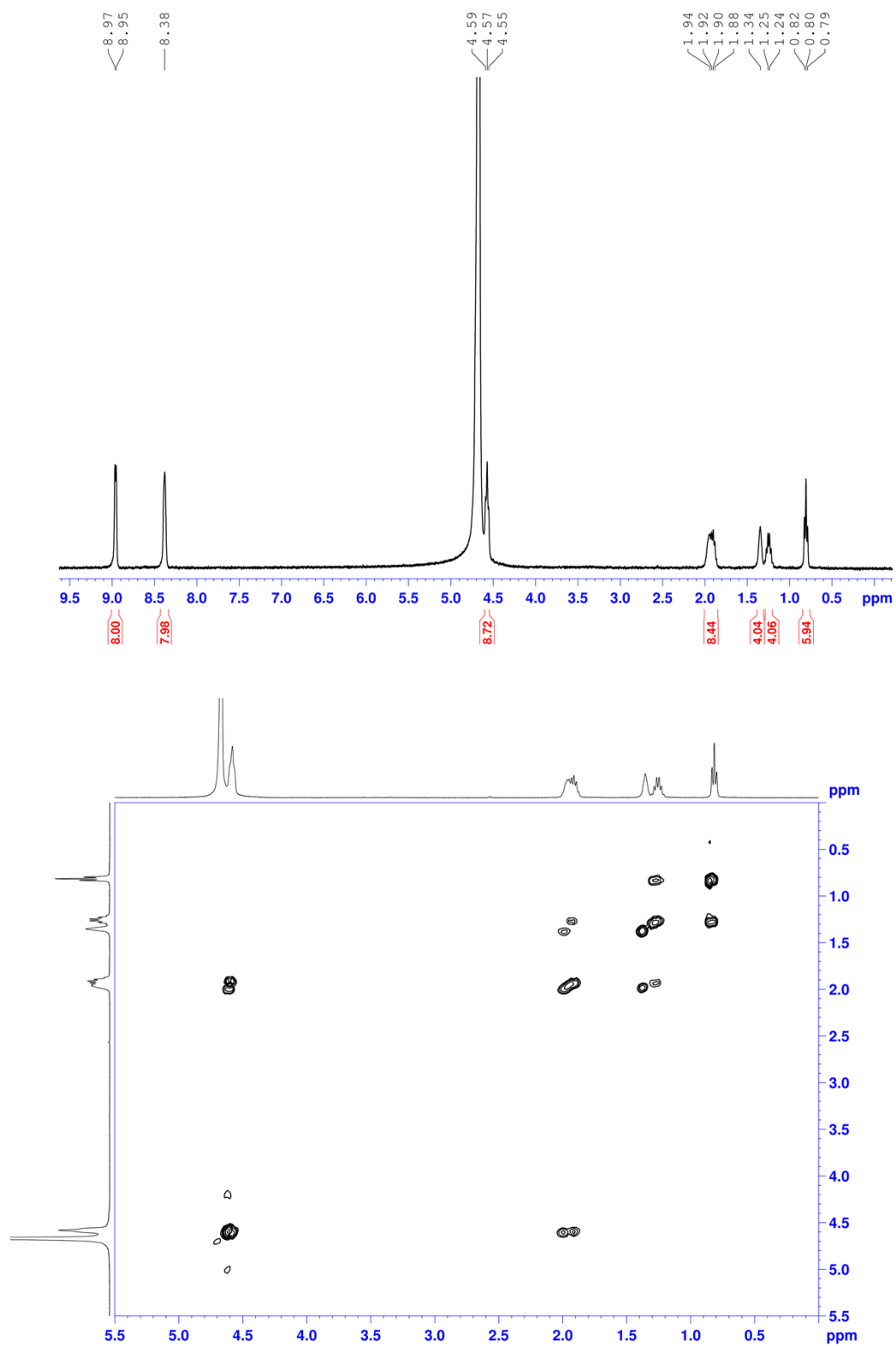


Fig. S1 1H NMR and 1H - 1H COSY spectra of **1** in D_2O .

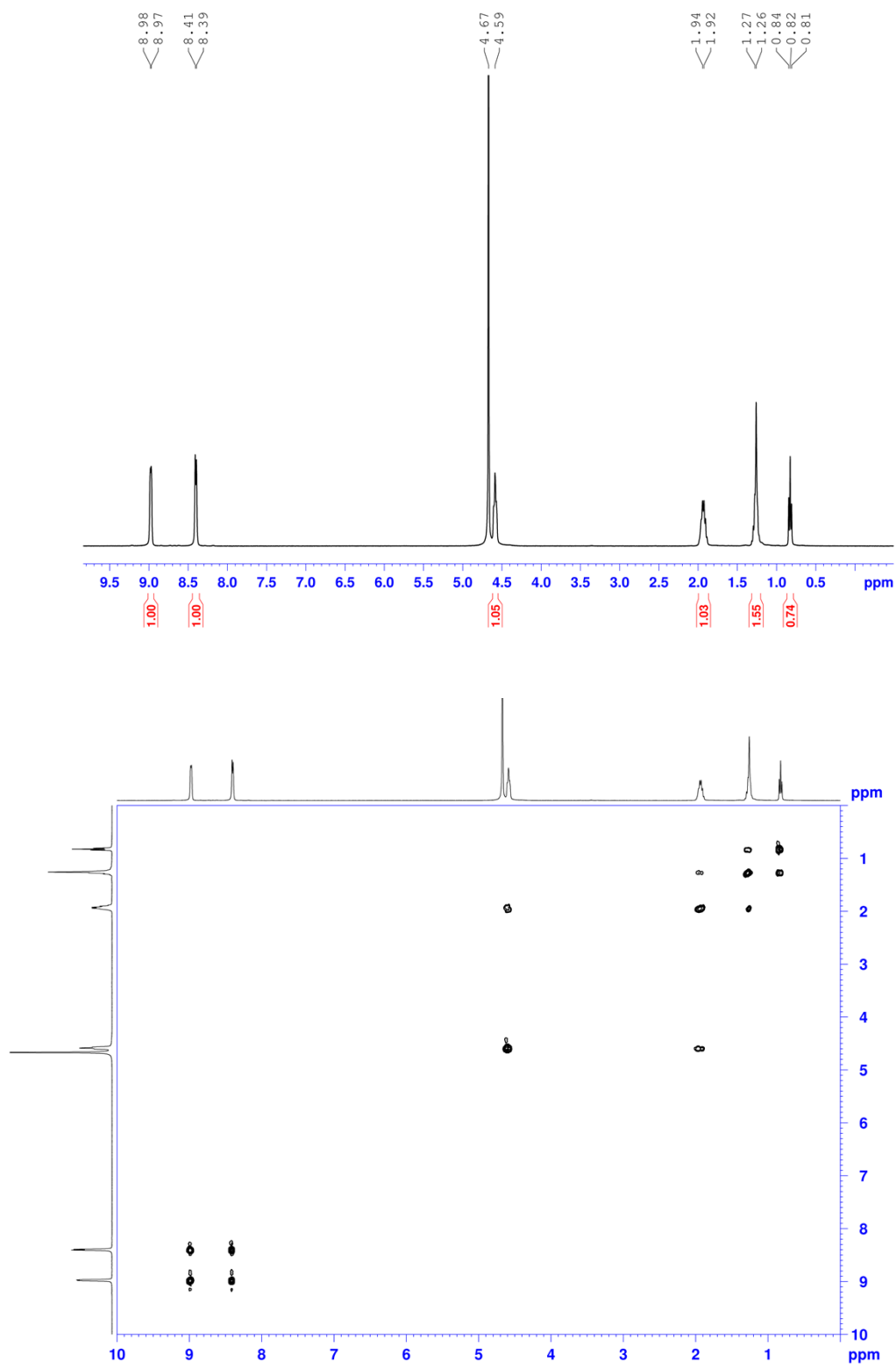


Fig. S2 ¹H NMR and ¹H-¹H COSY spectra of **2** in D₂O.

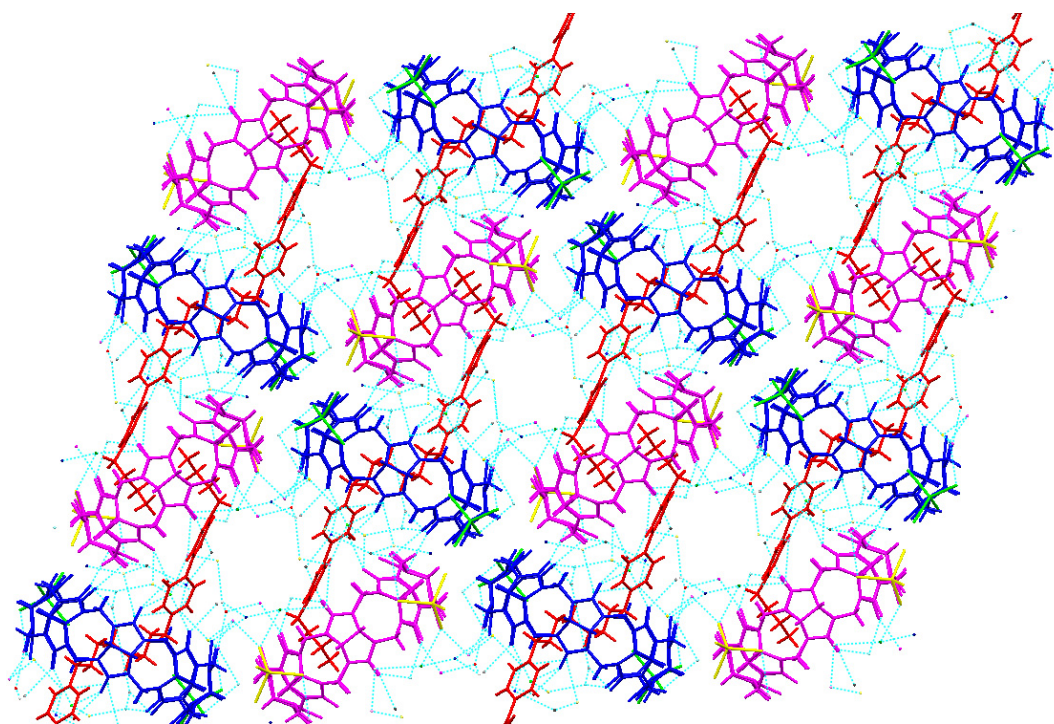


Fig. S3 Two dimensional supramolecular network of supramolecular polymer Q[8]@2.

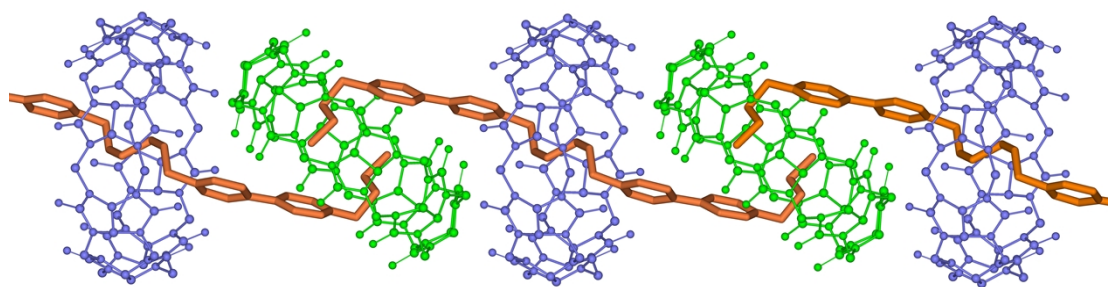


Fig. S4 Crystal structure of supramolecular polymer Q[8]@1 with hydrogen bond and water solvent molecules omitted for clarity.

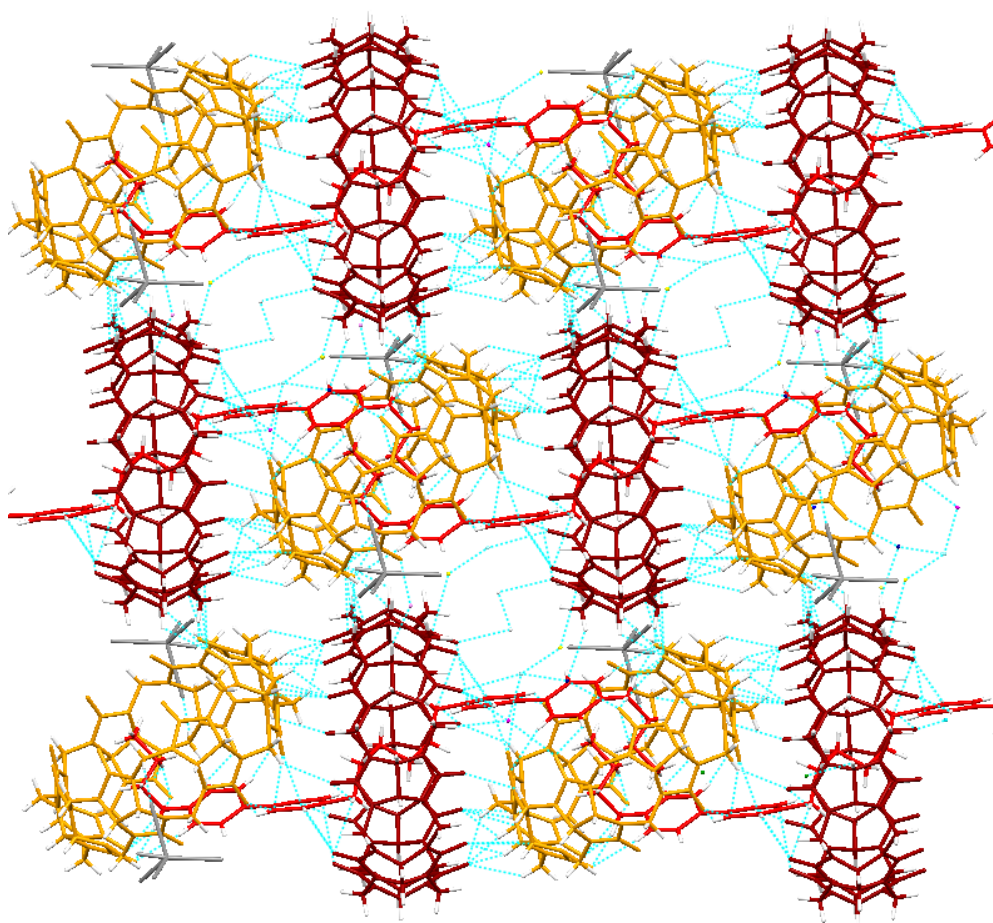


Fig. S5 Two dimensional supramolecular network of supramolecular polymer Q[8]@1.

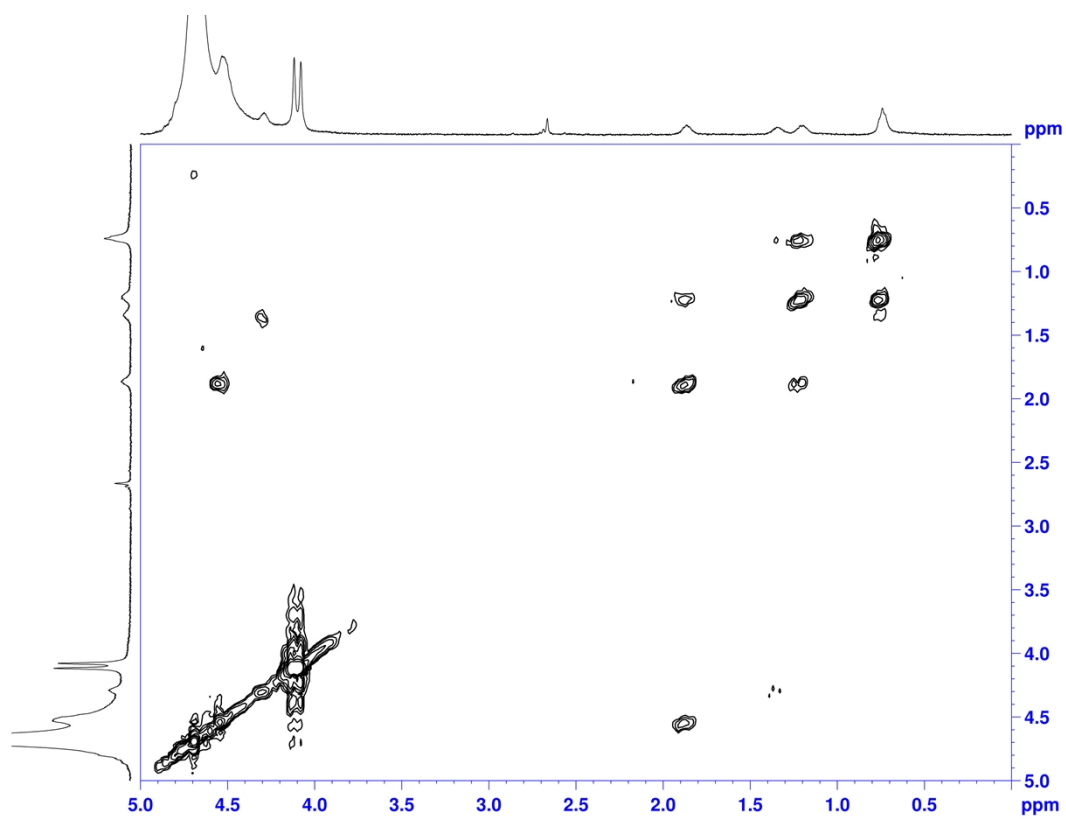
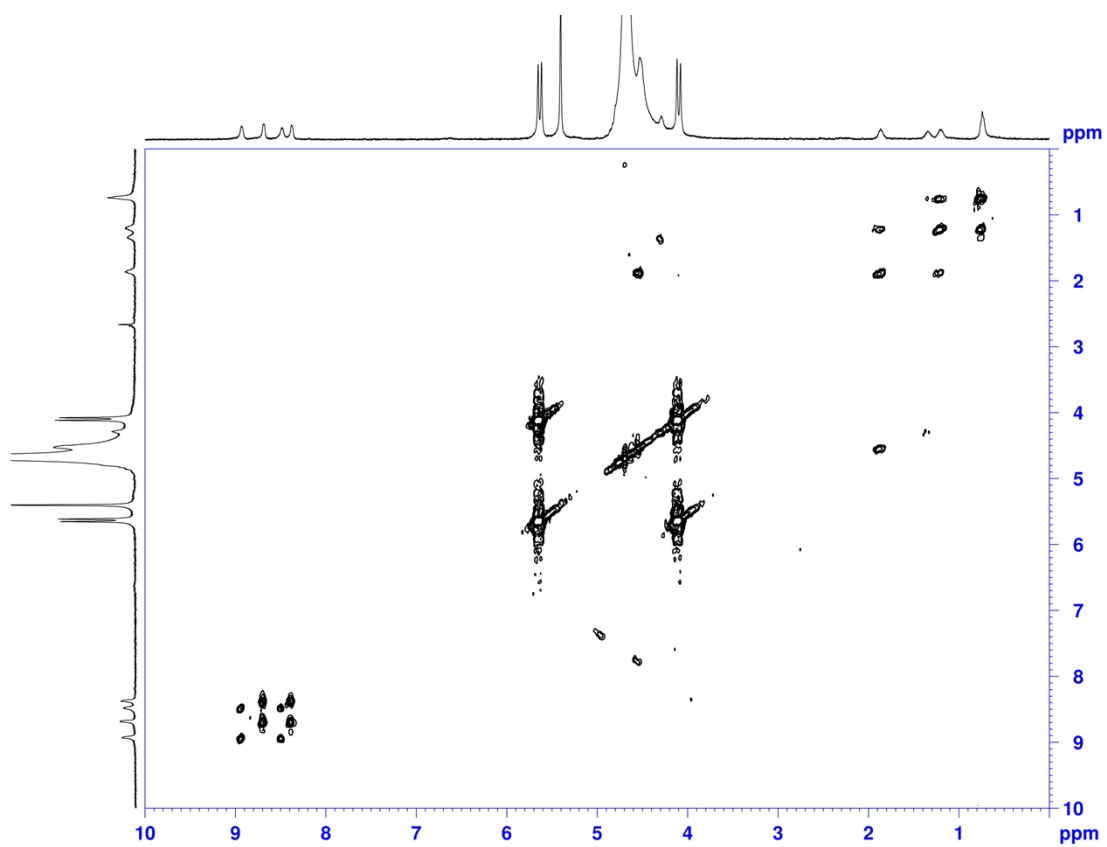


Fig. S6 COSY spectrum of **1** and Q[8] in the ratio of 1:2 in D₂O at 298.15 K.

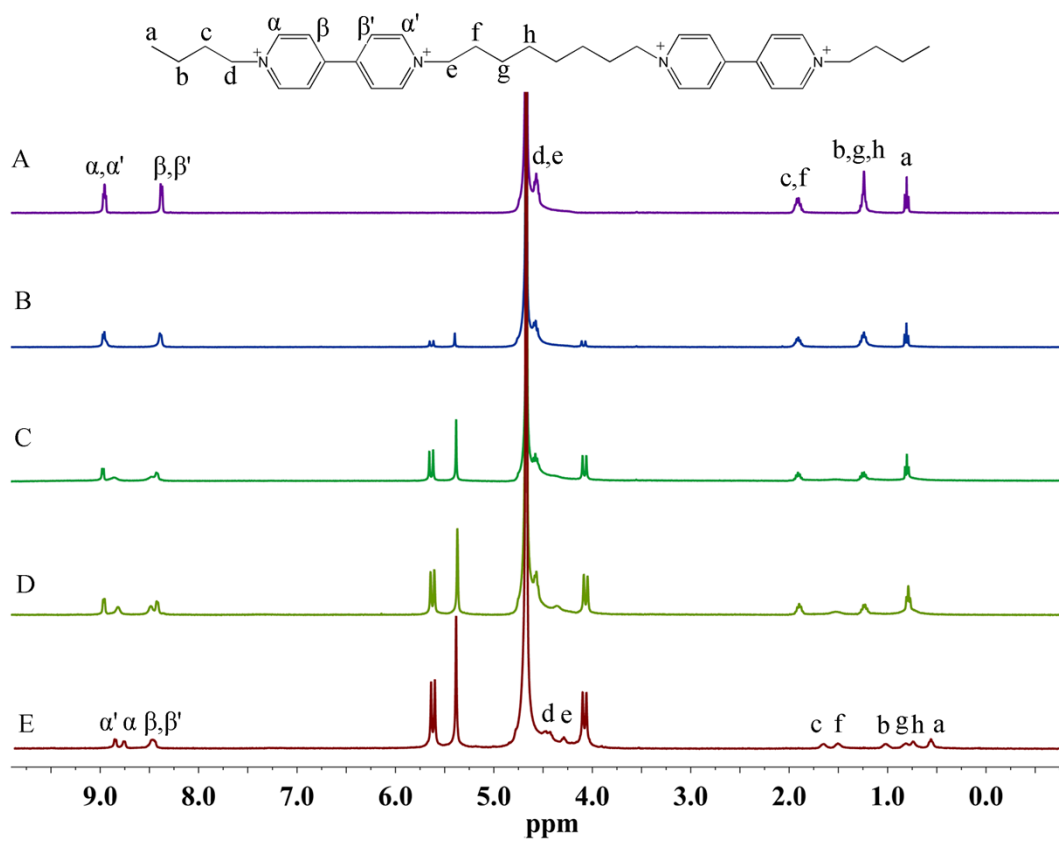


Fig. S7 ^1H NMR spectra of **2** (A), **2** and Q[8] in the ratio of 0.25(B), 1.0 (C), 1.5 (D), and 2.0 (E) in D_2O .

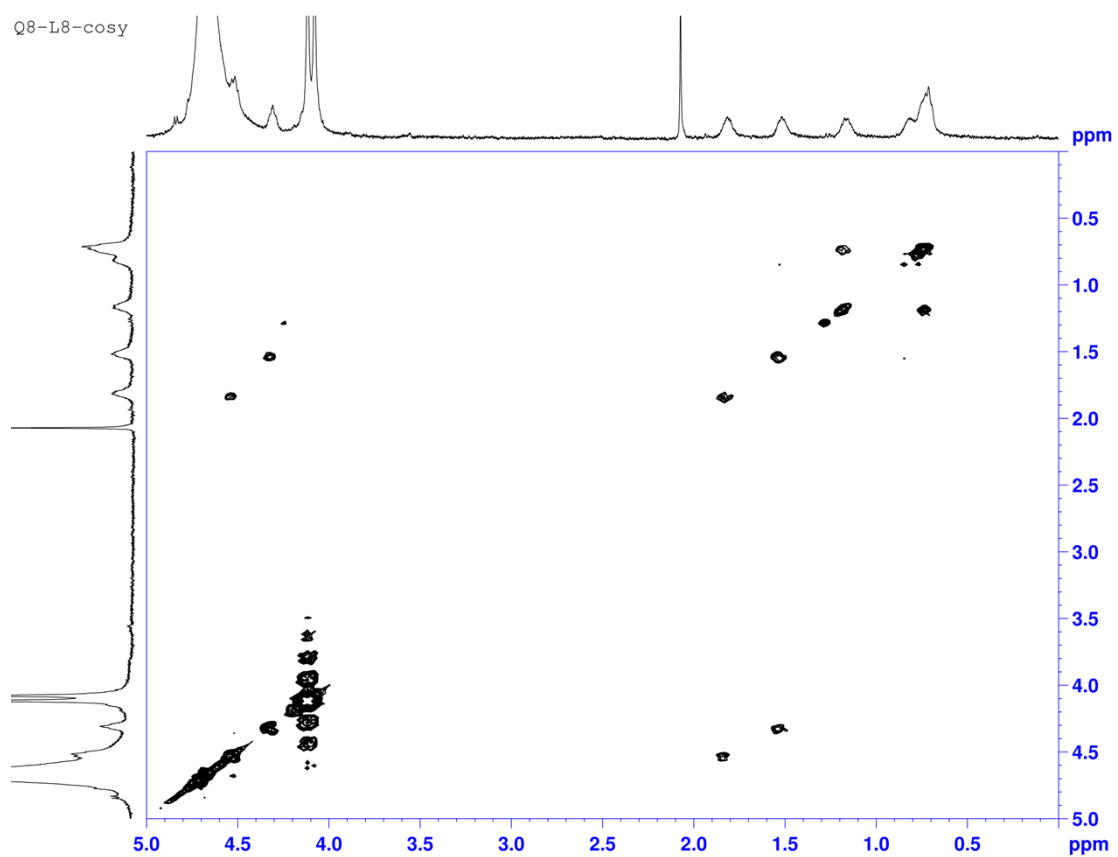
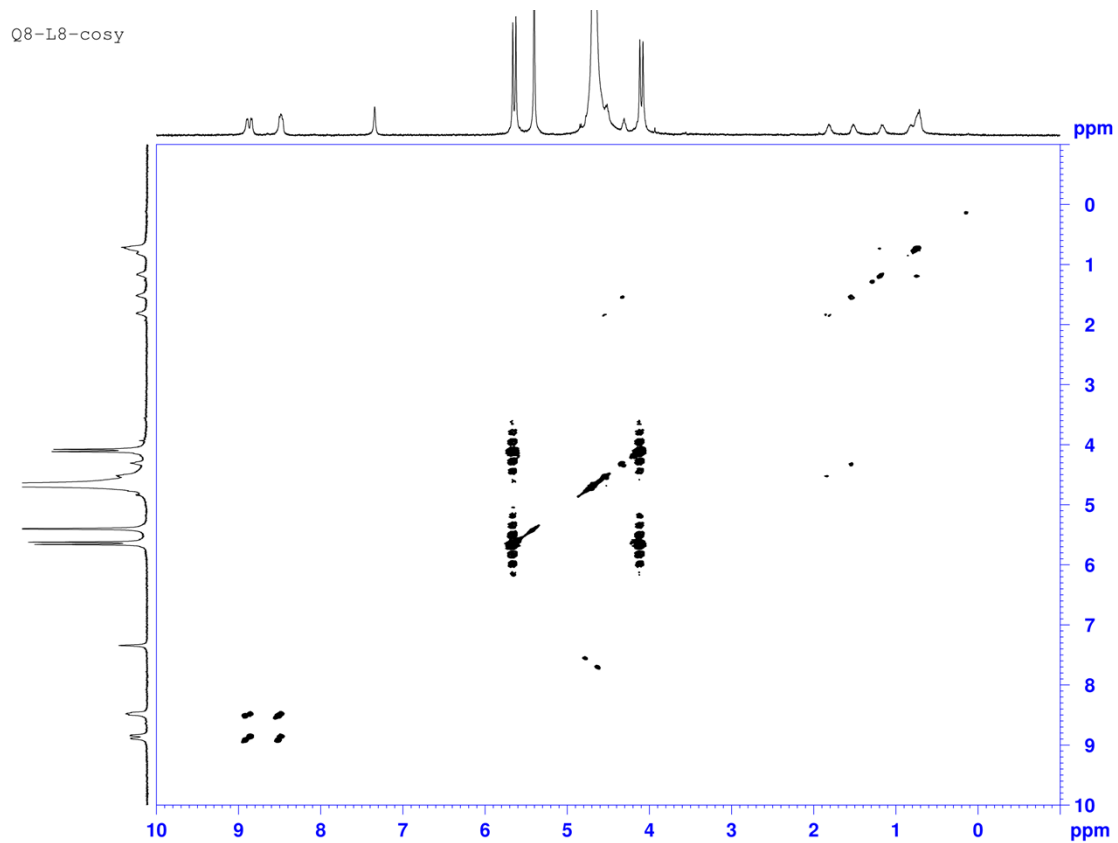


Fig. S8 COSY spectrum of **2** and Q[8] in the ratio of 1 : 2.2 in D₂O at 298.15 K.

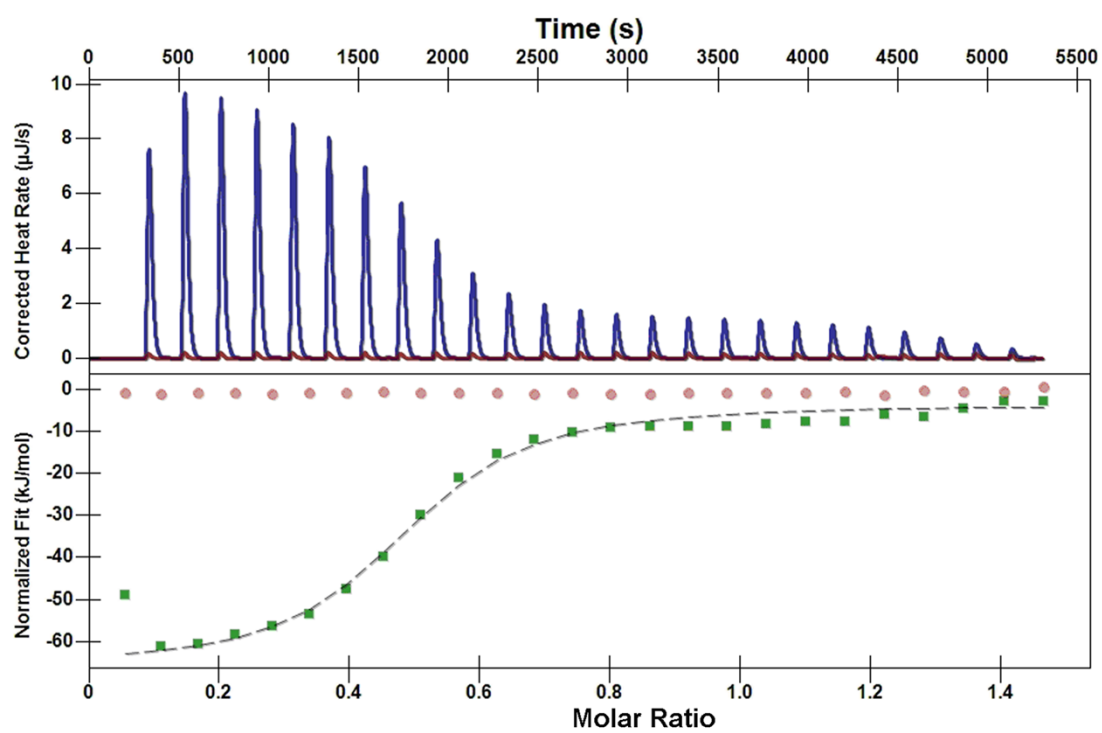


Fig. S9 ITC data for the binding of Q[8] with **2** in aqueous solution at 25°C.

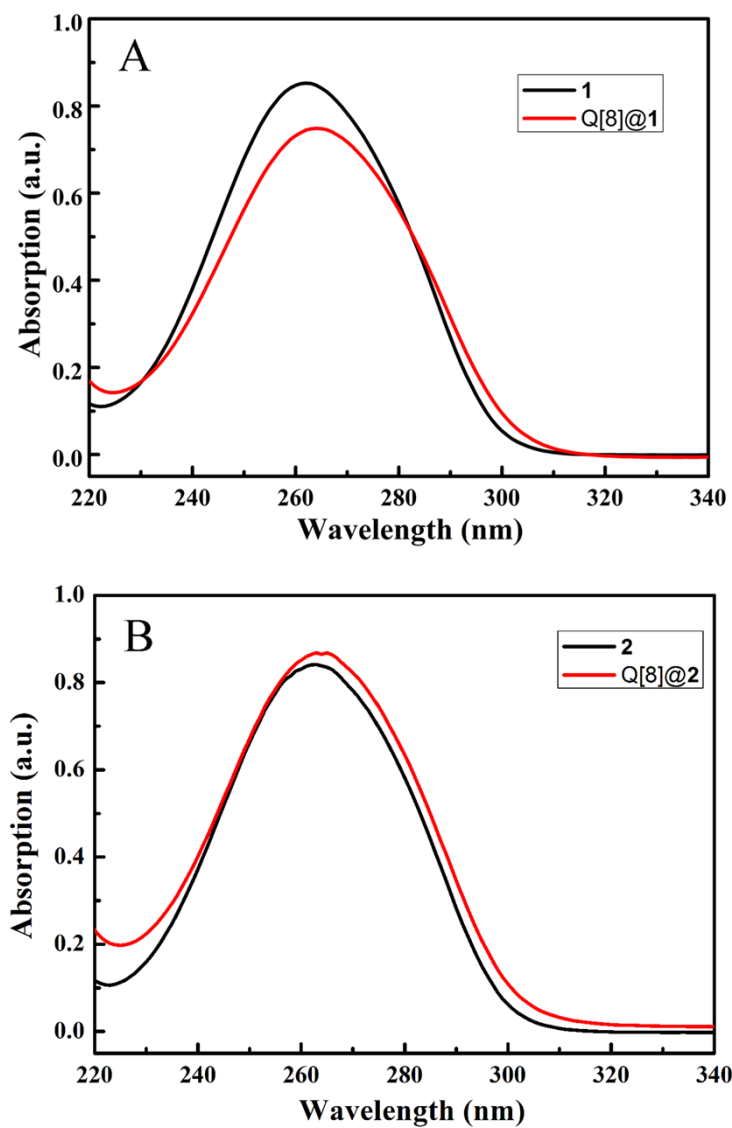


Fig. S10 Electronic absorption spectra of Q[8]@1 (A) and Q[8]@2 (B).

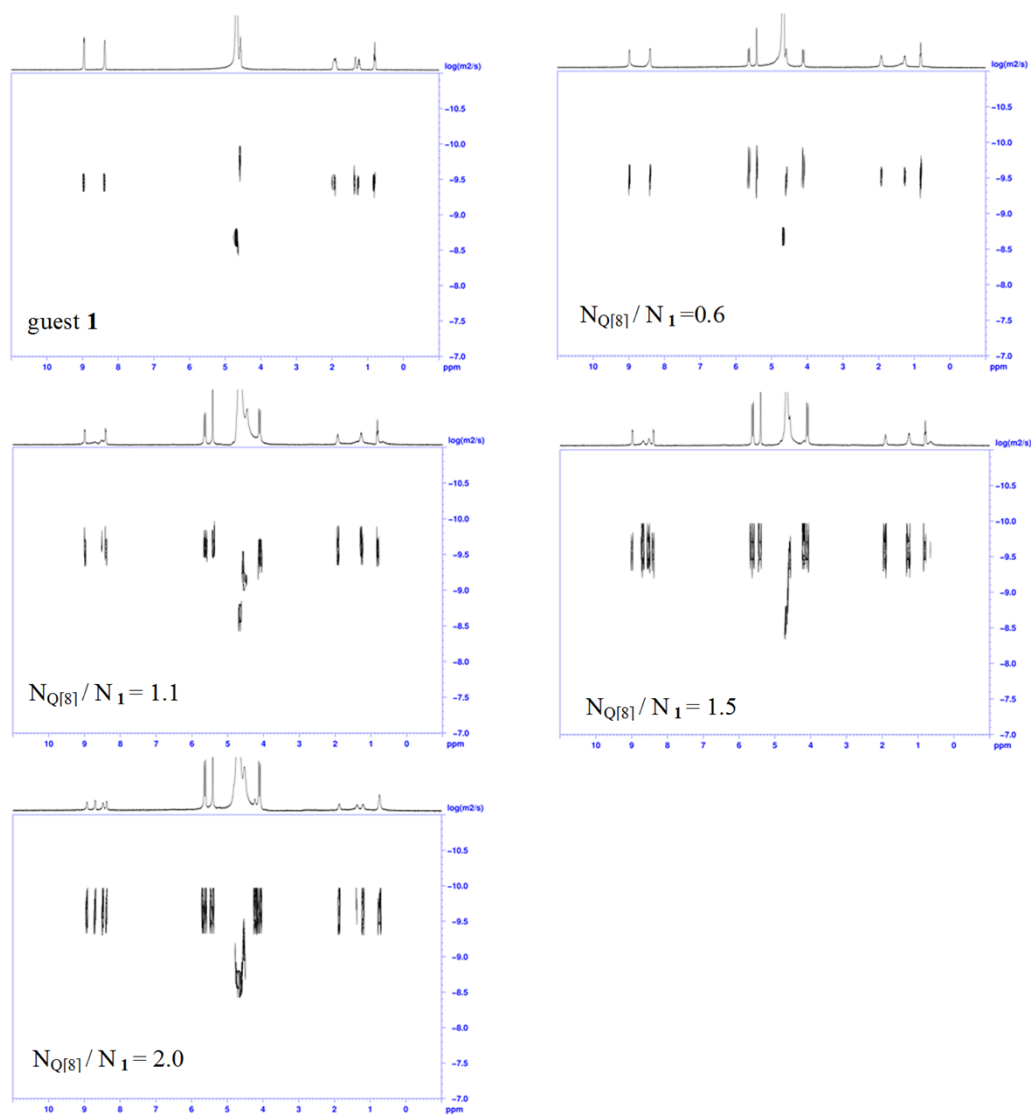


Fig. S11 DOSY spectra for **1** with different ratios of Q[8], along with the increase of the ratio of Q[8] to **1**, the average diffusion coefficients of the complexes get decreased. Therefore, the supramolecular polymerization can be adjusted by tuning the ratio of guest **1** and Q[8].

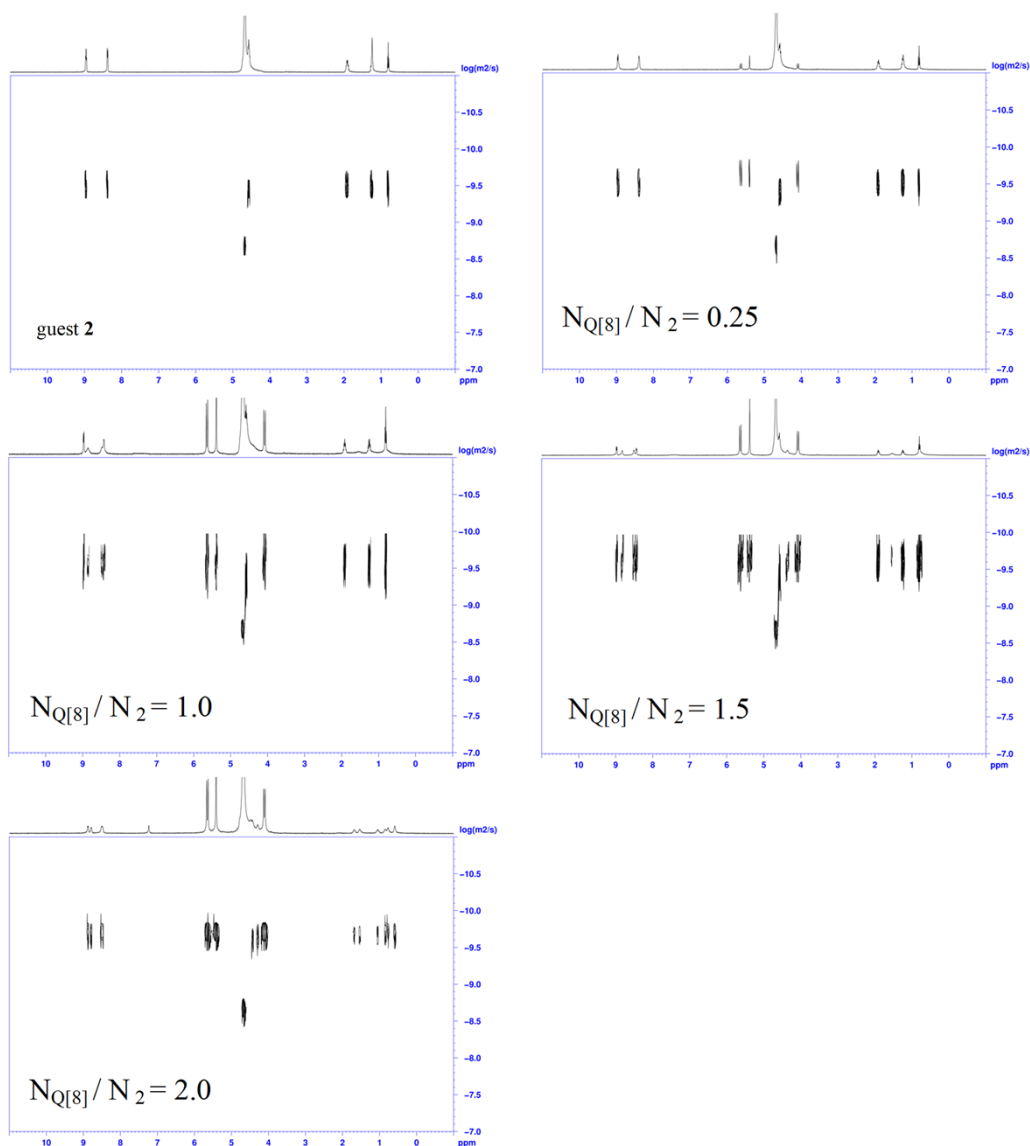


Fig. S12 DOSY spectra for **2** with different ratios of Q[8], along with the increase of the ratio of Q[8] to **2**, the average diffusion coefficients of the complexes get decreased. Therefore, the supramolecular polymerization can be adjusted by tuning the ratio of guest **2** and Q[8].

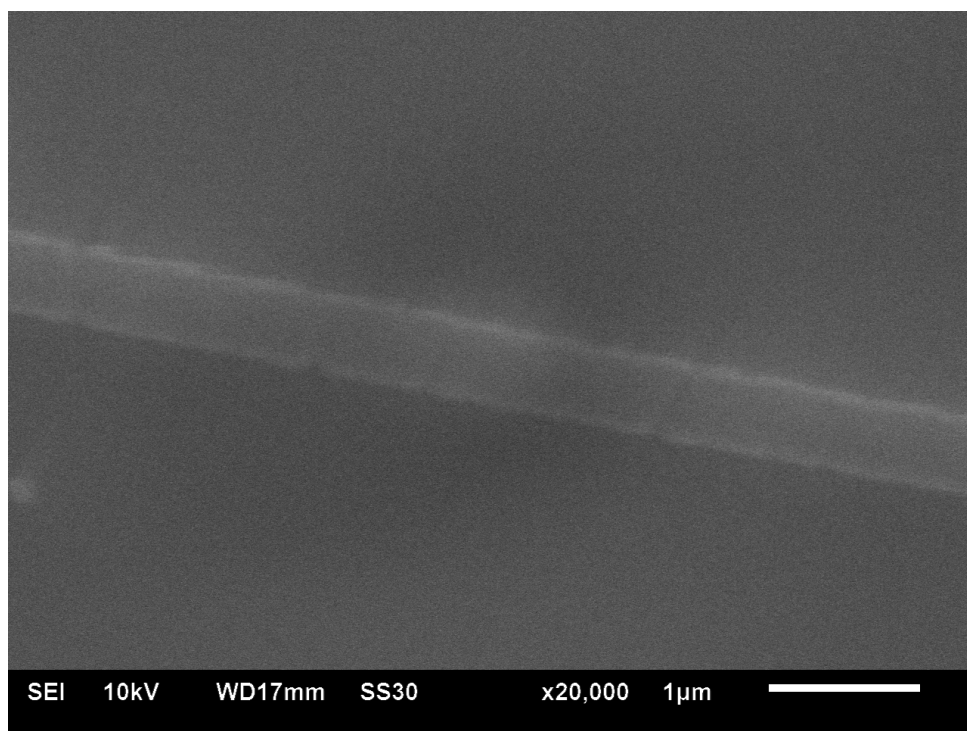


Fig. S13 The SEM image of supramolecular polymer Q[8]@2.

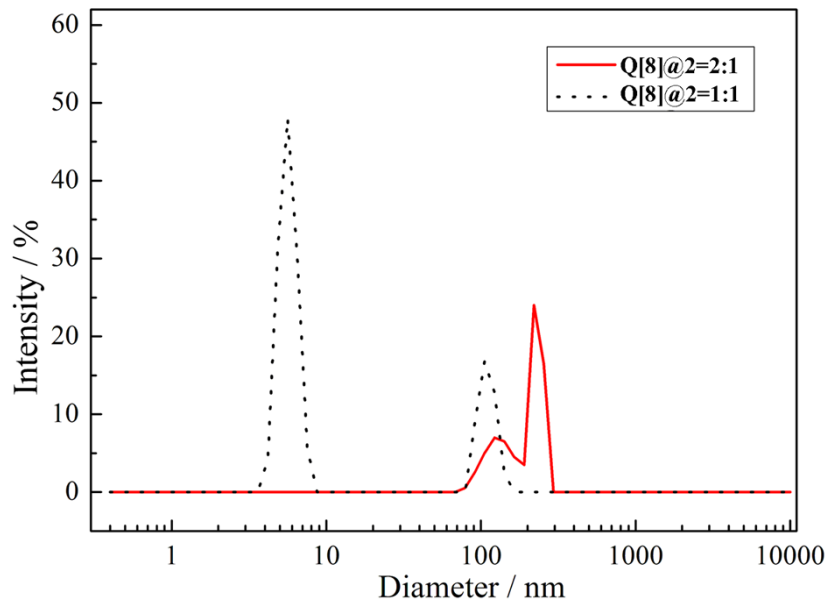


Fig. S14 DLS data of Q[8]@2.

Table S1. Chemical shifts of the protons of bound guests in comparison with the free guests at the molar ratio of 2.0 between Q[8] and guest.

Complex	$\Delta\delta$ (ppm)												
	α	α'	β	β'	a	b	c	d	e	f	g	h	
Q[8]@1	Upfield	Upfield	No change	Downfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield	-
	0.27	0.03		0.10	0.06	0.07	0.05	0.04	0.28	0.57	0.60		
Q[8]@2	Upfield	Upfield	Downfield	Downfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield	Upfield
	0.25	0.14	0.08	0.08	0.23	0.24	0.26	0.13	0.28	0.38	0.46	0.23	

Table S2. Complex stability constant (K_a), enthalpy (ΔH°), and entropy changes ($T\Delta S^\circ$) for Q[8]@1 and Q[8]@2.

Complex	K_a (M^{-1})	ΔH° ($kJ\ mol^{-1}$)	$T\Delta S^\circ$ ($kJ\ mol^{-1}$)
Q[8]@1	$(4.87 \pm 0.23) \times 10^5$	-62.69	-30.17
Q[8]@2	$(8.49 \pm 0.17) \times 10^5$	-55.58	-24.41

Table S3 Diffusion coefficients obtained from DOSY spectroscopy for **Q[8]@1**.

Molar ratio of Q[8]@1	D_{avg} (10⁻¹⁰ m² s⁻¹)
0	3.09
0.6	2.53
1.1	2.42
1.5	2.19
2.0	1.21

Table S4 Diffusion coefficients obtained from DOSY spectroscopy for **Q[8]@2**.

Molar ratio of Q[8]@2	D_{avg} (10⁻¹⁰ m² s⁻¹)
0	3.05
0.25	2.67
1.0	2.40
1.5	2.21
2.0	1.07

Table S5 Crystal data and structure refinements of Q[8]@1 and Q[8]@2.

compound	Q[8]@1	Q[8]@2
Formula	C ₆₅ H ₇₁ Cl ₄ N ₃₄ O ₂₉ Zn	C ₁₃₂ H ₁₄₂ Cl ₂₀ N ₆₈ O ₈₉ Zn ₄
F.W.	1999.75	5075.70
system	triclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2/ <i>n</i>
<i>a</i> /Å	17.6178(9)	23.2417(11)
<i>b</i> /Å	18.0031(10)	17.5255(6)
<i>c</i> /Å	18.3649(10)	30.5983(11)
α /deg	88.054(2)	90
β /deg	64.192(2)	108.234(4)
γ /deg	73.825(2)	90
<i>Z</i>	2	2
volume/Å ³	5010.6(5)	11837.5(9)
<i>D</i> _{calc} /g cm ⁻³	1.326	1.424
<i>F</i> 000	2058.0	5164.0
parameters	1173	1410
Independent reflns	10556[R _{int} = 0.0734]	7687[R _{int} = 0.1238]
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.1745	0.1126
w <i>R</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.2327	0.2533
<i>S</i>	1.809	0.990