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Stimuli-responsive orthogonal supramolecular polymer network formed by metal-ligand and host-guest interactions

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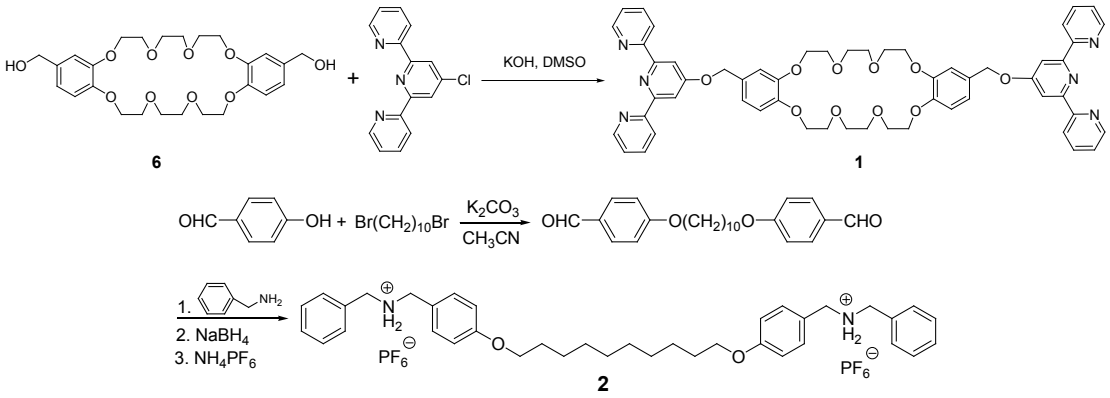
Supporting Information (11 pages)

1. Materials and methods

4'-Chloro-2,2':6',2"-terpyridine, 4-hydroxybenzaldehyde, 1,10-dibromodecane, benzylamine, NH_4PF_6 and zinc triflate ($Zn(OTf)_2$) were purchased from Aldrich and used without further purification.

1D (1H, 13C) and 2D (^1H–^1H-NOESY) nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker Avance 400 or 500 operating at a frequency of 400 or 500 MHz for ^1H and 125 MHz for ^{13}C. Mass spectra were recorded on a Hewlett-Packard 5989 A mass spectrometer (ESI mode). UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 UV/Vis spectrophotometer. Viscosity measurements were carried out with Ubbelohde dilution viscometers (Julabo Technology Corporation visco-170, 0.47 mm inner diameter) in $CHCl_3/CH_3CN$ (1/1, v/v) containing 0.05 mol/L tetrabutylammonium hexafluorophosphate to exclude the polyelectrolyte effect.

*2. Synthesis of compounds **1** and **2***



Scheme S1 Synthetic routes of monomer **1** and bisammonium cross-liker **2**.

*2.1. Synthesis of dibenzo-24-crown-8 diol **6***

Compound **6** was synthesized according to the literature procedures.[S1] ^1H NMR (500 MHz, $CDCl_3$, 293 K) δ (ppm): 6.90 (2H, s), 6.81−6.83 (4H, m), 4.57 (4H, s), 4.12−4.16 (8H, m), 3.89−3.91 (8H, m), 3.81−3.83 (8H, m).

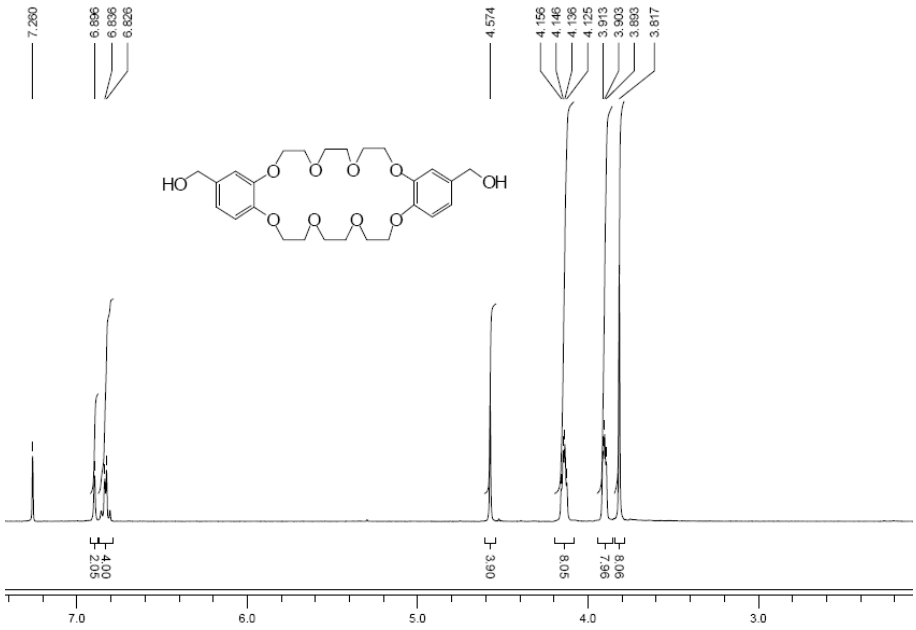


Fig. S1 ^{1}H NMR spectrum of compound **6**.

*2.2. Synthesis of monomer **1***

Compound **6** (1.02 g, 2.00 mmol) was added to a stirred suspension of powdered KOH (449 mg, 8.00 mmol) in dry DMSO (25.0 mL) at 60 °C. After being stirred for 15 min, 4'-chloro-2,2':6',2"-terpyridine (1.17 g, 4.40 mmol) was added to the mixture and stirred for 24 h at 60 °C. Then the reaction solution was poured into 500 mL of cold water and the resulting precipitate was collected by filtration. The crude product was purified by flash column chromatography (1:1 dichloromethane/ethyl acetate, *v*/*v*) to give compound **1** as a white solid (1.01 g, 50.0%). ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ (ppm): 8.67 (4H, *J* = 4.0 Hz, d), 8.61 (4H, *J* = 7.5 Hz, d), 8.09 (4H, s), 7.82−7.85 (4H, m), 7.30−7.33 (4H, m), 6.99−7.02 (4H, m), 6.87 (2H, *J* = 8.5 Hz, d), 5.21 (4H, s), 4.15−4.20 (8H, m), 3.90−3.93 (8H, m), 3.82−3.83 (8H, m).^{13}C NMR (125 MHz, $CDCl_3$, 293 K), δ (ppm): 166.9, 157.2, 156.1, 149.2, 149.1, 149.0, 136.9, 129.2, 123.9, 121.4, 120.8, 114.0, 113.6, 107.8, 71.4, 70.0, 69.9, 69.6, 69.5. ESI–MS: *m/z* 993.3 $[M+Na]^+$.

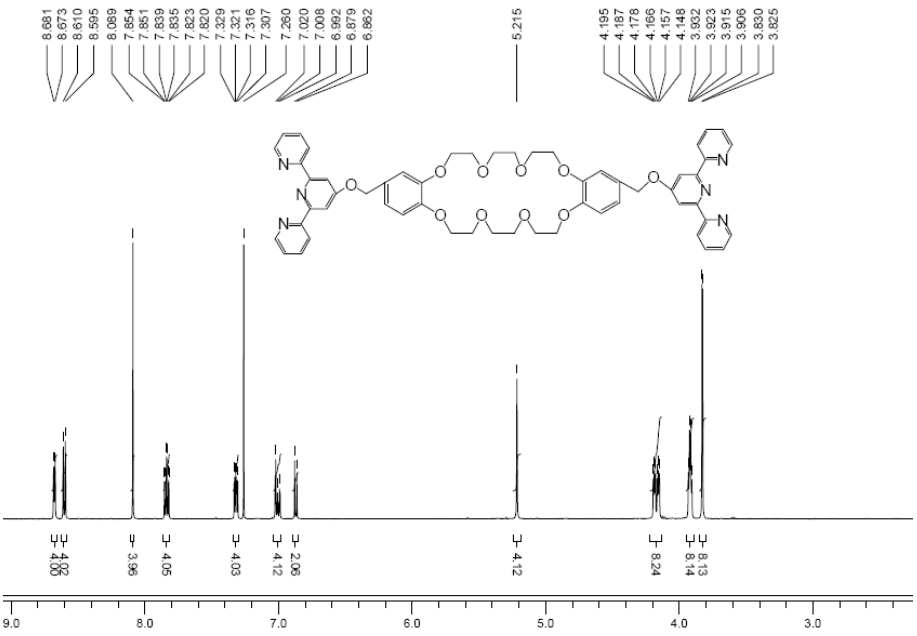


Fig. S2 ^{1}H NMR spectrum of monomer **1**.

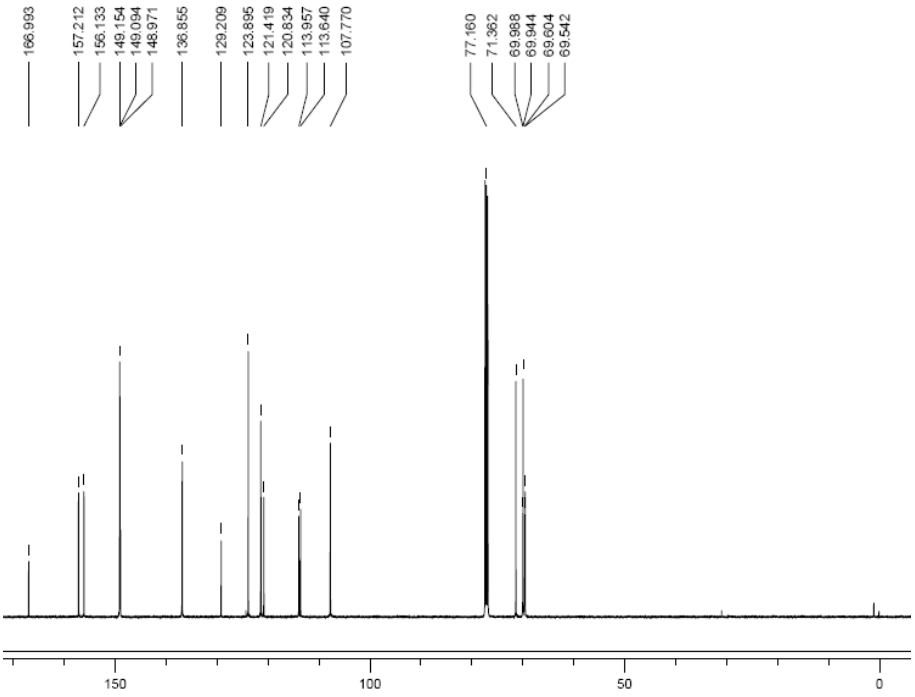


Fig. S3 ^{13}C NMR spectrum of monomer **1**.

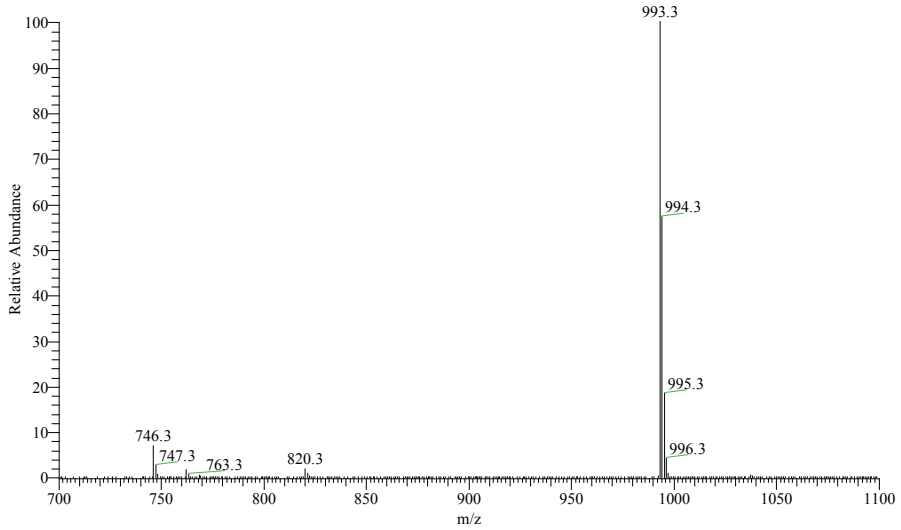


Fig. S4 Electrospray ionization mass spectrum of monomer **1**.

*2.3. Synthesis of bisammonium cross-linker **2***

Bisammonium cross-liker **2** was synthesized according to the literature procedures.[S2] ^{1}H NMR (500 MHz, CD_3CN, 293 K) δ (ppm): 7.46 (10H, s), 7.37 (4H, J = 8.5 Hz, d), 6.96 (4H, J = 8.5 Hz, d), 4.20 (4H, s), 4.17 (4H, s), 3.99 (4H, J = 6.5 Hz, t), 2.10−2.30 (4H, br), 1.72−1.78 (4H, m), 1.42−1.44 (4H, m), 1.32−1.36 (8H, m). ^{13}C NMR (125 MHz, CD_3CN, 293 K) δ (ppm): 161.3, 133.0, 132.8, 131.5, 131.3, 131.1, 130.2, 130.1, 130.0, 123.0, 115.9, 69.1, 52.2, 52.1, 30.3, 30.1, 29.9, 26.7.

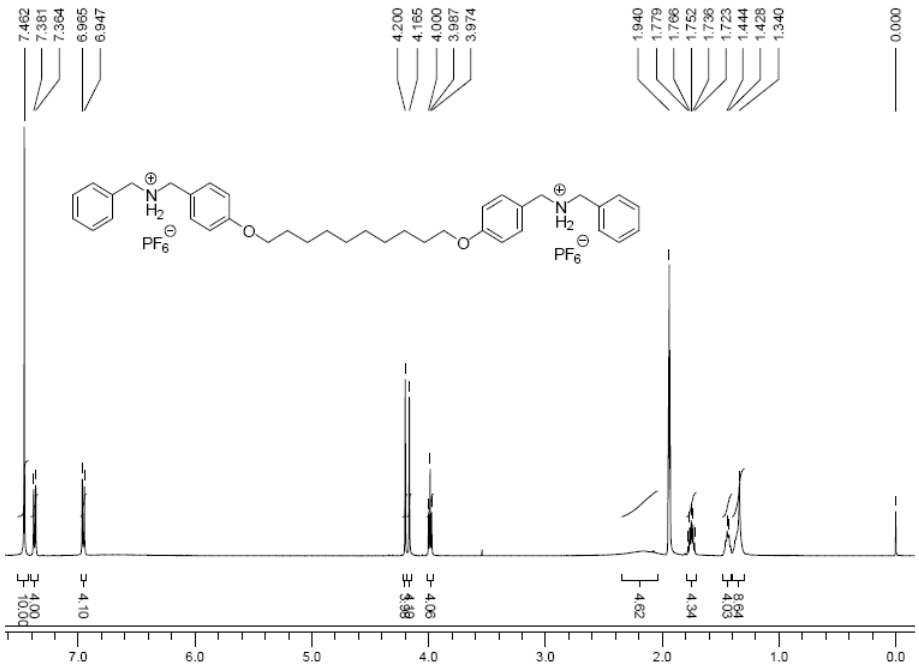


Fig. S5 ^{1}H NMR spectrum of compound **2**.

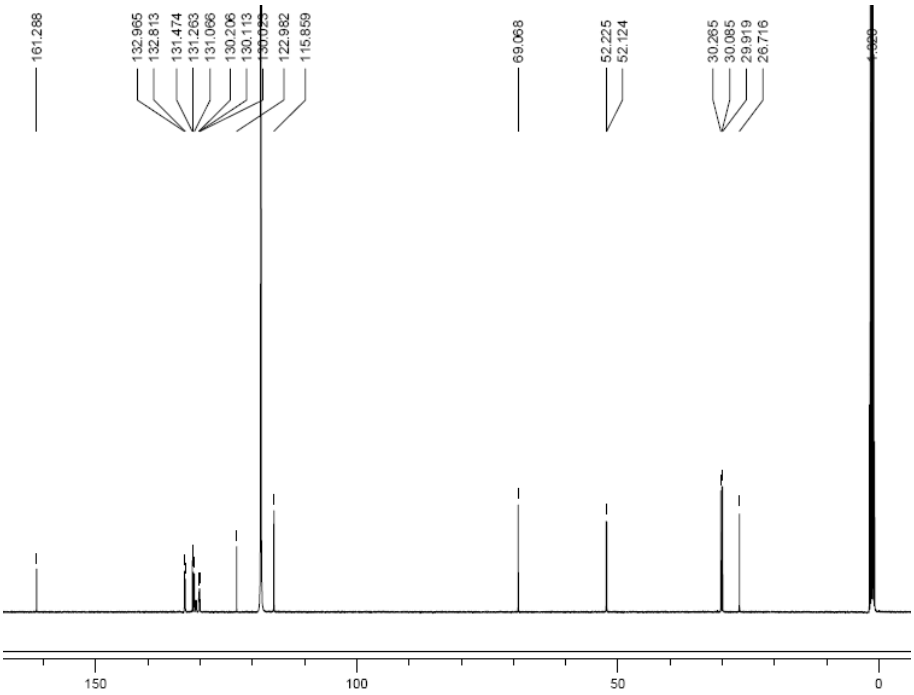


Fig. S6 ^{13}C NMR spectrum of compound **2**.

*3. Characterization of linear supramolecular polymer **3** and supramolecular polymer network **4***

*3.1. UV/Vis titrations between Zn(OTf)$_2$ and monomer **1***

Fig. S7 Shows the UV/Vis titration spectra between $Zn(OTf)_2$ and monomer **1**. It was performed by stepwise addition of $Zn(OTf)_2$ (320 μM in CH_3CN) to a 16.0 μM solution of the monomer **1** in 1:1 $CHCl_3/CH_3CN$ (2.0 mL).

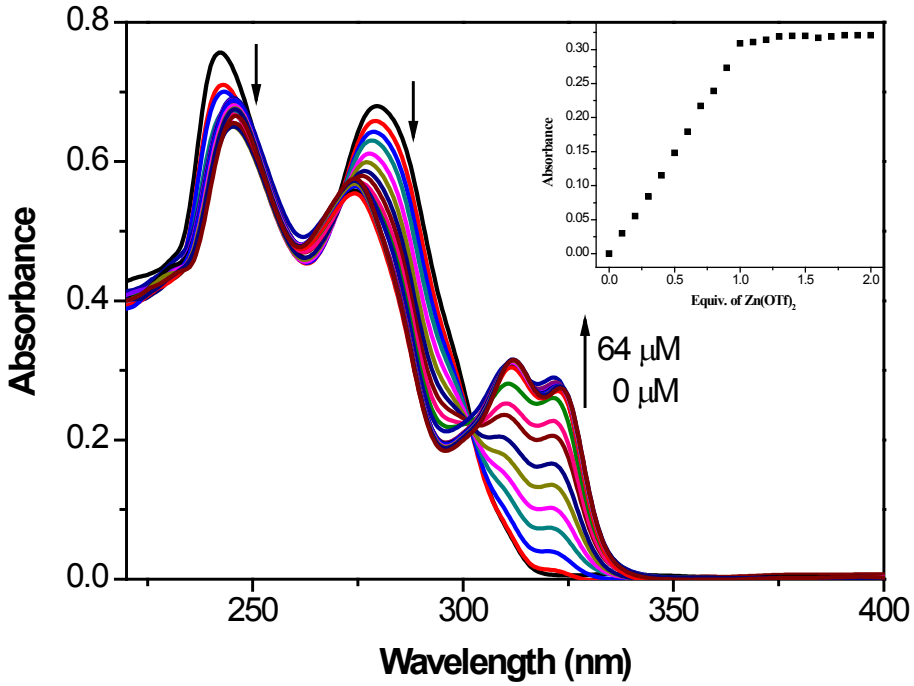


Fig. S7 UV/Vis titration curve of monomer **1** with increasing amount of $Zn(OTf)_2$; Inset: Plot of the absorbance intensity at 312 nm *versus* the amount of $Zn(OTf)_2$.

*3.2. ^{1}H NMR spectra of supramolecular polymer **3** at the monomer concentration of 25.0 mM*

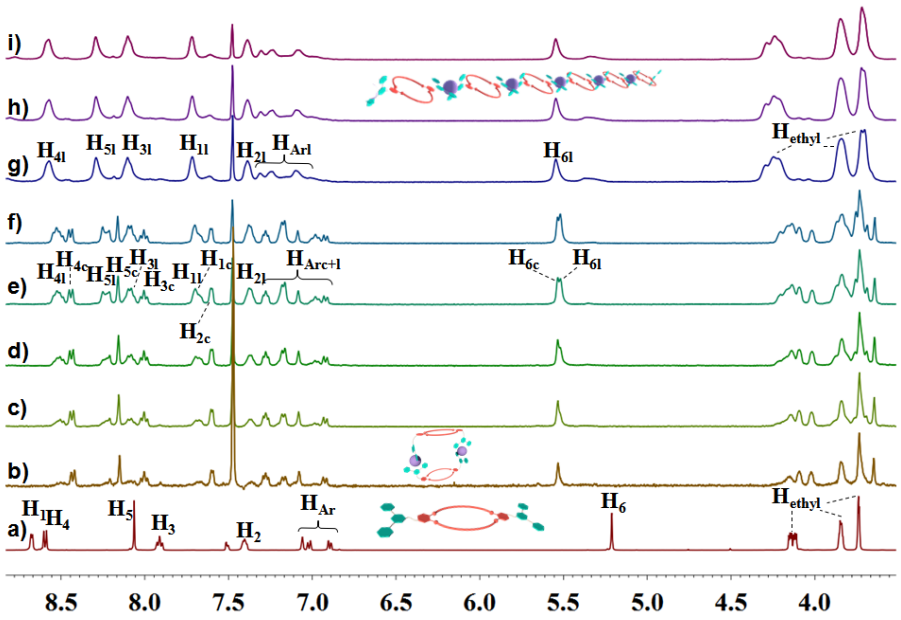


Fig. S8 ^{1}H NMR spectra (500 MHz, 1:1 $CDCl_3/CD_3CN$, 293K) of (a) monomer **1** and supramolecular polymer **3** constructed by mixing equimolar $Zn(OTf)_2$ and **1** at different concentrations: (b) 1.00; (c) 3.00; (d) 5.00; (e) 8.00; (f) 10.0; (g) 15.0; (h)

20.0; (i) 25.0 mM. Here "l" and "c" denote the linear and cyclic species, respectively.

*3.3. 2D H-H COSY spectrum of supramolecular polymer **3** at the monomer concentration of 25.0 mM*

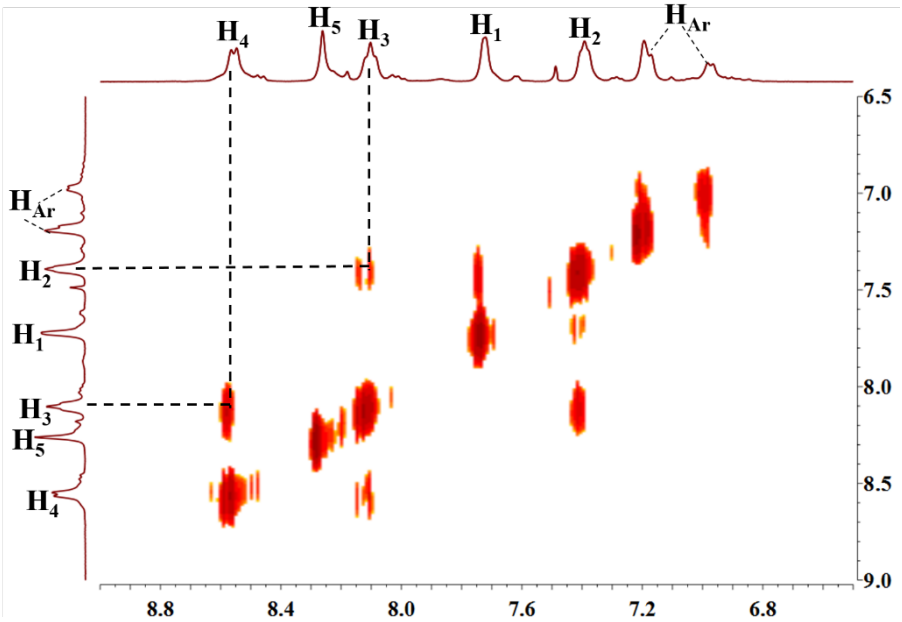


Fig. S9 Partial 2D H-H COSY spectrum (400 MHz, 1:1 $CDCl_3/CD_3CN$, 293K) of supramolecular polymer **3**.

*3.4. NOESY spectrum of supramolecular polymer network **4** at the monomer concentration of 25.0 mM*

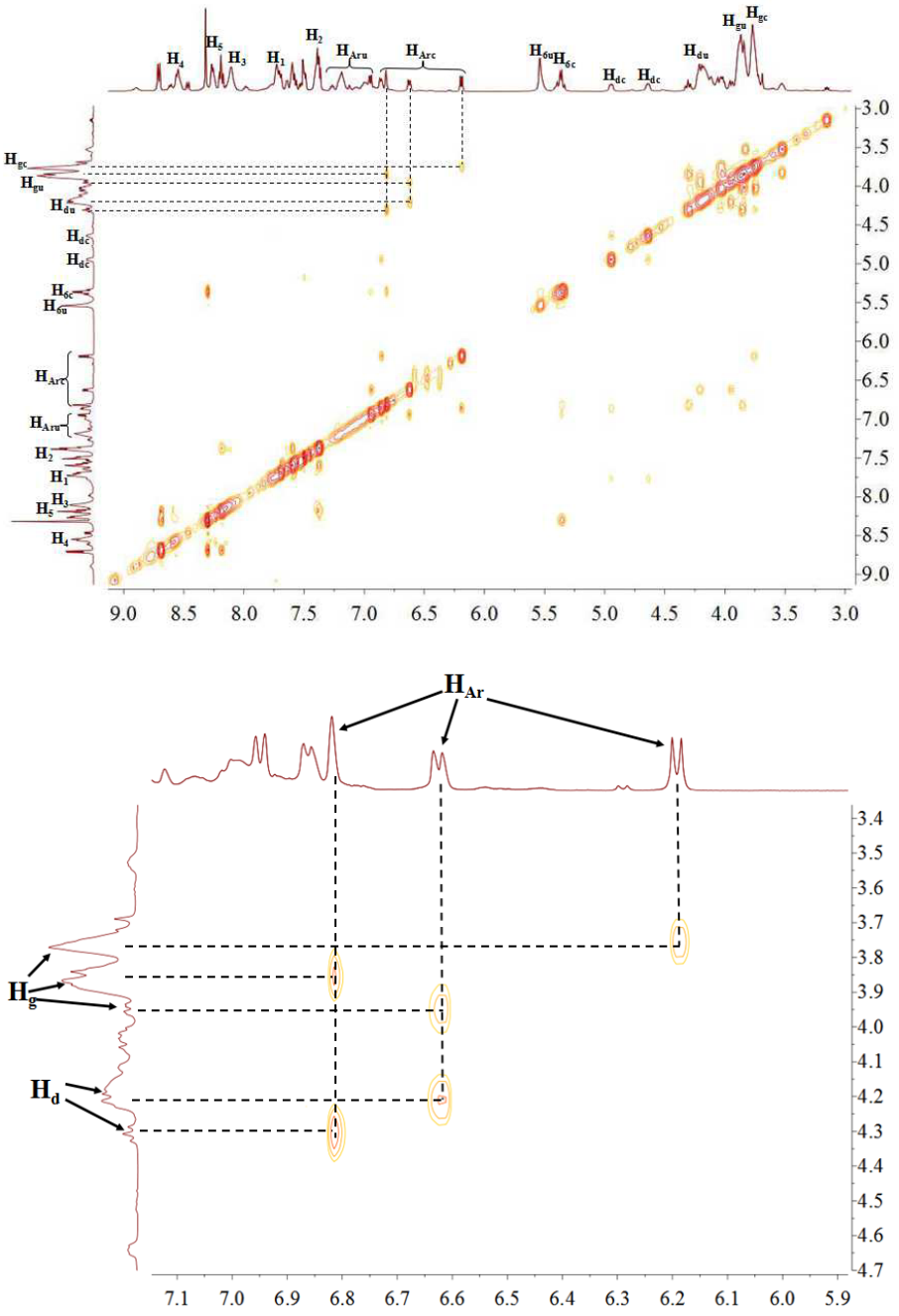


Fig. S10 NOESY spectrum (500 MHz, 1:1 $CDCl_3/CD_3CN$, 293K) of supramolecular polymer network **4**.

*3.5 The effect of the content of cross-linker **2** on reduced viscosity of supramolecular polymer network **4***

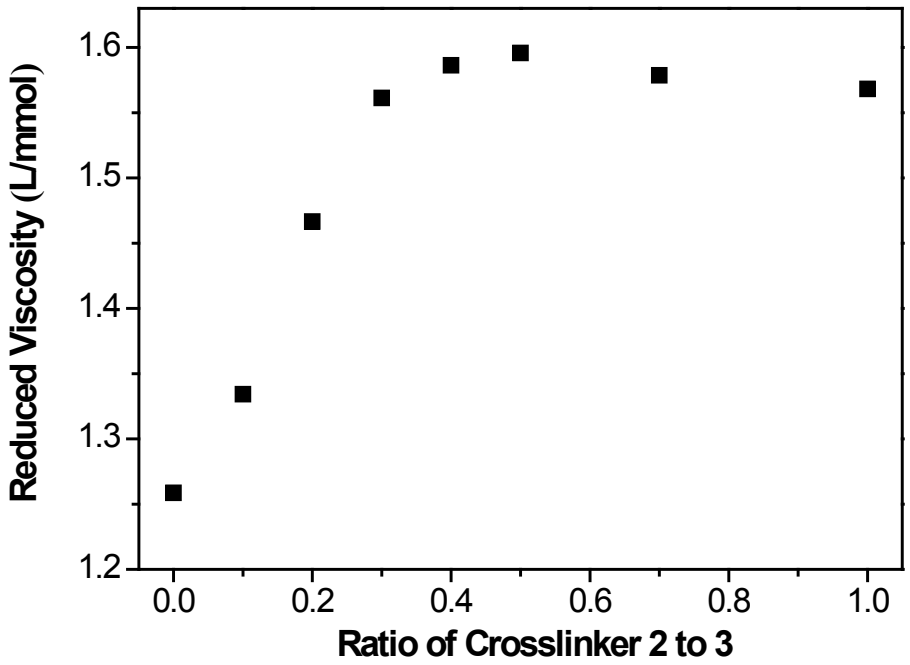


Fig. S11 Reduced viscosity of supramolecular polymer network **4** (25.0 mM linear supramolecular polymer **3** with different ratio of cross-linker **2**) (1:1 $CHCl_3/CH_3CN$, 298 K).

3.6. UV/Vis titrations of ***1***·Zn^{2+} *with different amount of cyclen and* ***1***·Zn^{2+}*, cyclen with different amount of* Zn^{2+}

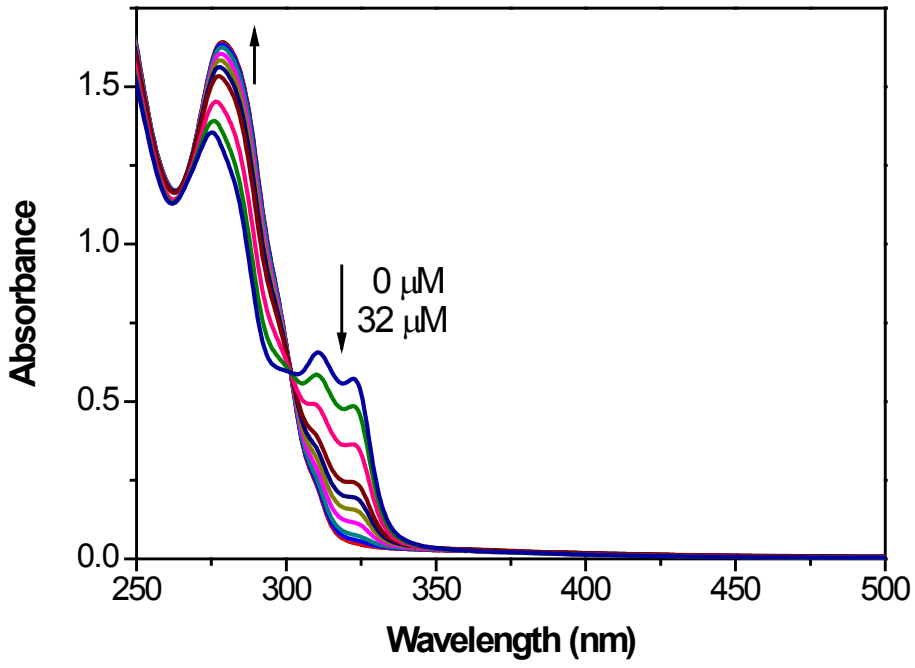


Fig. S12 UV/Vis titration curve of **1**·Zn^{2+} with increasing amount of cyclen.

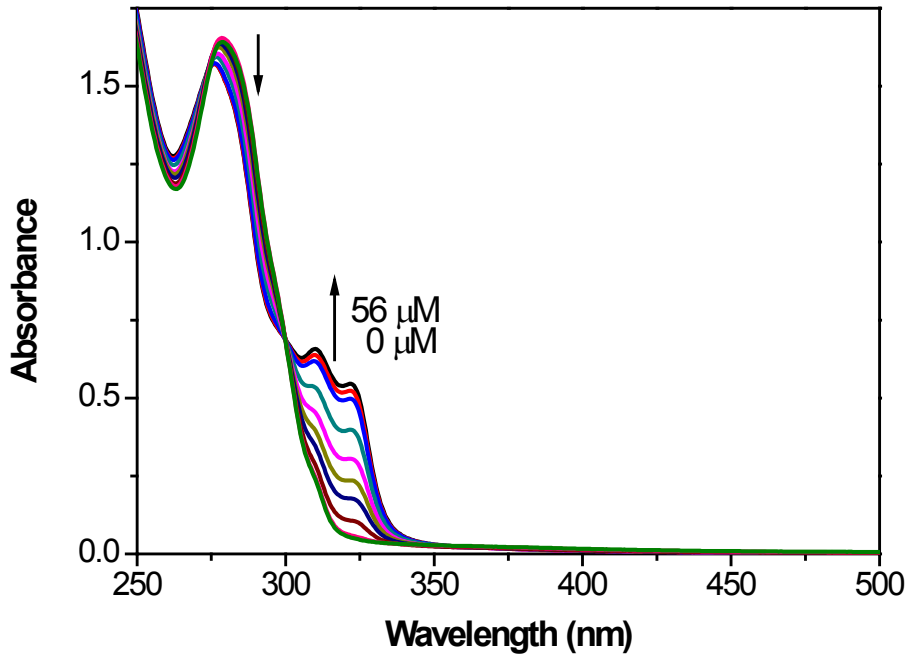


Fig. S13 UV/Vis titration curve of **1**·Zn^{2+} with cyclen (32.0 μM), then addition of different amounts of Zn^{2+}.

References:

S1. H. W. Gibson, H. Wang, C. Slebodnick, J. Merola, W. S. Kasse and A. L. Rheingold, *J. Org. Chem.* 2007, **72**, 3381.

S2. H. W. Gibson, N. Yamaguchi and J. W. Jones, *J. Am. Chem. Soc.* 2003, **125**, 3522.