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

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1. Materials and methods

4′-Chloro-2,2′:6′,2″-terpyridine, 4-hydroxybenzaldehyde, 1,10-dibromodecane, benzylamine, \( \text{NH}_4\text{PF}_6 \) and zinc triflate \( (\text{Zn(OTf)}_2) \) were purchased from Aldrich and used without further purification.

1D \((1H, 13C)\) and 2D \((^1H–^1H-\text{NOESY})\) 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 \(^1\text{H}\) and 125 MHz for \(^{13}\text{C}\). 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 \( \text{CHCl}_3/\text{CH}_3\text{CN} \) (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.](image)

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

Compound 6 was synthesized according to the literature procedures.\(^{S1}\) \(^1\text{H}\) NMR (500 MHz, \text{CDCl}_3, 293 K) \( \delta \) (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).
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%). ¹H NMR (500 MHz, CDCl₃, 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).¹³C NMR (125 MHz, CDCl₃, 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 Electro spray ionization mass spectrum of monomer 1.

2.3. Synthesis of bisammonium cross-linker 2

Bisammonium cross-linker 2 was synthesized according to the literature procedures.\textsuperscript{52} \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN, 293 K) \(\delta\) (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). \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}CN, 293 K) \(\delta\) (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 \textsuperscript{1}H 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$_3$CN) to a 16.0 μM solution of the monomer 1 in 1:1 CHCl$_3$/CH$_3$CN (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$_3$CN, 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

![2D H-H COSY spectrum](image)

**Fig. S9** Partial 2D H-H COSY spectrum (400 MHz, 1:1 CDCl$_3$/CD$_3$CN, 293K) of supramolecular polymer 3.

3.4. NOESY spectrum of supramolecular polymer network 4 at the monomer concentration of 25.0 mM
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 CHCl₃/CH₃CN, 298 K).

3.6. UV/Vis titrations of 1·Zn²⁺ with different amount of cyclen and 1·Zn²⁺, cyclen with different amount of Zn²⁺

Fig. S12 UV/Vis titration curve of 1·Zn²⁺ with increasing amount of cyclen.
Fig. S13 UV/Vis titration curve of 1·Zn\textsuperscript{2+} with cyclen (32.0 μM), then addition of different amounts of Zn\textsuperscript{2+}.

References:
