Controlled Formation of Supramolecular Polymer Network Driven by Heterometallic Coordination Interactions

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1. Materials and Methods

3-Bromopropyne, sodium azide, 1,10-dibromodecane, CuI, CuSO₄•5H₂O, bis(acetonitrile)dichloropalladium(II), monosodium L-ascorbate, FeCl₂•6H₂O and triphenylphosphine were reagent grade and used as received. 2,6-Bis-(2'-pyridyl)-4-pyridone was synthesized according to the previously reported method. 1H NMR spectra were collected on a Varian Unity INOVA-300 or INOVA-400 spectrometer with TMS as the internal standard. 13C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometer at 100 MHz. The two-dimensional COSY and NOESY experiments were performed on a Varian Unity INOVA-400 MHz spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with an ESI interface and ion trap analyzer. The UV/Vis spectra were recorded on a Beijing Persee TU-1901 UV-Vis spectrometer. Viscosity measurements were carried out with a Ubbelohde semi-micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.37 mm inner diameter) at 25 °C in DMSO.
2. Synthetic route to the target compound 1

![Diagram of synthetic route]

Scheme S1. Synthetic route to the target compound 1.

2.1. Synthesis of compound 5

2,6-Bis-(2'-pyridyl)-4-pyridone (1.03 g, 4.14 mmol) and K₂CO₃ (1.00 g, 7.25 mmol) were placed in a 150 mL round bottomed flask. Then 3-bromopropyne (1.50 g, 12.71 mmol) in DMF (30 mL) was slowly added. The resulting mixture was stirred at 90 °C under N₂ for 24 hours. After the reaction, the solvent was removed with a rotary evaporator and the residue was extracted with H₂O/CH₂Cl₂. After the combined organic extracts were dried over anhydrous Na₂SO₄ and evaporated with a rotary evaporator, the residue was purified by flash column chromatography (CH₂Cl₂ as the eluent) to afford compound 5 as a yellow solid (720 mg, 61%). Mp: 130.3–132.5 °C. The ¹H NMR spectrum of compound 5 is shown in Figure S1.

¹H NMR (300 MHz, CDCl₃, room temperature) δ (ppm): 8.69 (d, J = 4.3 Hz, 2H), 8.61 (d, J = 7.8 Hz, 2H), 8.10 (s, 2H), 7.84 (t, J = 7.7 Hz, 2H), 7.31–7.35 (m, 2H), 4.94 (s, 2H), 2.58 (s, 1H). The ¹³C NMR spectrum of compound 5 is shown in Figure S2. ¹³C NMR (100 MHz, CDCl₃, room temperature) δ (ppm): 160.6, 152.0, 150.7, 143.8, 131.5, 118.6, 116.1, 102.4, 72.4, 71.0, 50.6. ESI–MS m/z: [M + H]⁺ calcd for C₁₈H₁₆N₃O, 288.1137; found, 288.1131; error, 2.1 ppm.
Figure S1. $^1$H NMR spectrum (300 MHz, CDCl$_3$, room temperature) of compound 5.

Figure S2. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound 5.
2.2. Synthesis of compound 4

The compound was synthesized according to a previously reported method.\[S2\] 1,10-Dibromodecane (4.81 g, 16.03 mmol) and NaN₃ (3.12 g, 48.00 mmol) in DMF (80 mL) were heated to 60 °C and stirred for 24 hours. H₂O (300 mL) was then added and the mixture was extracted with CH₂Cl₂ (100 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄. The solvent was removed with a rotary evaporator and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 10 : 1 v/v as the eluent) to provide compound 4 as a colorless oil (3.07 g, 85%). The ¹H NMR spectrum of compound 4 is shown in Figure S4. ¹H NMR (300 MHz, CDCl₃, room temperature) δ (ppm): 3.26 (t, J = 6.9 Hz, 4H), 1.62–1.54 (m, 4H), 1.30 (m, 12H).
2.3. Characterization of compound 1

Compound 5 (300 mg, 1.05 mmol) and 4 (70.0 mg, 0.31 mmol) were dissolved in DMF (15 mL). Then an aqueous solution (5 mL) of monosodium L-ascorbate (200 mg, 1.01 mmol) and CuSO₄•5H₂O (25 mg, 0.10 mmol) was added. The resulting mixture was heated at 60 °C and stirred for 24 hours. The solvent was then removed with a rotary evaporator and the residue was extracted with H₂O/CH₂Cl₂. The combined organic extracts were dried over anhydrous Na₂SO₄ and removed with a rotary evaporator. The crude product was purified by flash column chromatography (CH₂Cl₂/CH₃OH, 40 : 1 v/v as the eluent) to afford compound 1 as a pale yellow solid (210 mg, 84%). Mp: 165.7–168.1 °C. The ¹H NMR spectrum of
compound 1 is shown in Figure S5. $^1$H NMR (300 MHz, $d_6$-DMSO, room temperature) $\delta$ (ppm): 8.71 (d, $J = 4.6$ Hz, 4H), 8.60 (d, $J = 7.9$ Hz, 4H), 8.26 (s, 2H), 8.07 (s, 4H), 7.99 (m, 4H), 7.49 (m, 4H), 7.45 (s, 4H), 4.35 (t, $J = 7.0$ Hz, 4H), 1.85–1.68 (m, 4H), 1.22–1.00 (m, 12H). The $^{13}$C NMR spectrum of compound 1 is shown in Figure S6. $^{13}$C NMR (100 MHz, CDCl$_3$, room temperature) $\delta$ (ppm): 166.5, 157.3, 156.0, 149.1, 143.4, 136.8, 123.9, 122.6, 121.3, 107.5, 62.2, 50.5, 30.2, 29.1, 28.8, 26.4. ESI–MS m/z: [M + H]$^+$ calcd for C$_{46}$H$_{47}$N$_{12}$O$_2$, 799.3945; found, 799.3948; error, 0.4 ppm.

Figure S5. $^1$H NMR spectrum (300 MHz, $d_6$-DMSO, room temperature) of compound 1.
Figure S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound 1.

Figure S7. Electrospray ionization mass spectrum of compound 1.
3. Characterization of the supramolecular polymer network

3.1. UV/Vis titration between FeCl₂ and terpyridine

Figure S8a shows the UV/Vis titration spectra for the model system comprising FeCl₂ and terpyridine. It was carried out by stepwise addition of FeCl₂ (0.67 mM in DMSO) to a 0.064 mM solution of terpyridine in DMSO (2.3 mL). The immediate formation of metal–ligand complex was directly evidenced by the color change of the solution (from colorless to purple), which could further confirmed by the appearance of MLCT band (\(\lambda_{\text{max}} = 558\) nm). After the achievement of maximum absorbance at the FeCl₂/terpyridine molar ratio of 0.5, the absorption band has no significant change upon further addition (Figure S8b), confirming the 1 : 2 molar ratio for Fe²⁺ and terpyridine.

![Figure S8a](image)

**Figure S8.** Change in the UV/Vis absorption spectra of terpyridine upon the addition of FeCl₂. a) UV/Vis absorption spectra. b) The normalized absorbance at 558 nm.

3.2. UV/Vis titrations between FeCl₂ and monomer 1

Figure S9 shows the UV/Vis titration spectra between FeCl₂ and monomer 1. It was performed by stepwise addition of FeCl₂ (0.72 mM in DMSO) to a 0.027 mM solution of the monomer 1 in DMSO (2.2 mL). The formation of metal–ligand complex was directly confirmed by the appearance of MLCT band located at 563 nm, further confirming the 1 : 1 stoichiometry for the complexation between monomer 1 and FeCl₂.
**Figure S9.** Change in the UV/Vis absorption spectra of monomer 1 upon addition of FeCl₂.

### 3.3. COSY and NOESY spectra of the linear supramolecular polymer 2 at monomer concentrations of 10.0 mM

The two-dimensional COSY NMR spectrum of the linear supramolecular polymer 2 was recorded at monomer concentrations of 10.0 mM (Figure S10). Strong correlations could be seen between the protons H₆ and the neighbouring protons H₅₋₇ on the terpyridine unit. Based on the two-dimensional NOESY NMR spectrum (Figure S11), the NOEs were clearly observed for the linear species (H₆l with H₅₋₇l), and cyclic species (H₆c with H₅₋₇c). Moreover, the correlations between H₁ and H₃, as well as those between H² and H⁴ also exist, benefiting for the proton assignments after the Fe²⁺-terpyridine complexation.
**Figure S10.** H-H COSY spectrum (400 MHz, DMSO-$d_6$, room temperature) of the linear supramolecular polymer 2.

**Figure S11.** NOESY spectrum (400 MHz, DMSO-$d_6$, room temperature) of the linear supramolecular polymer 2.
3.4. **COSY spectrum of the supramolecular polymer network 3 at monomer concentrations of 10.0 mM**

The two-dimensional COSY NMR spectrum of the supramolecular polymer network 3 was recorded at the monomer concentration of 10.0 mM (Figure S12). Strong correlations could be observed between the protons H₆ and the neighbouring protons H₅–₇ on the terpyridine unit. Such phenomena were similar to that observed in linear supramolecular polymer 2, hence demonstrating the preferential complexation between Pd²⁺ and the 1,2,3-triazole ligand without the participation of terpyridine unit.

![H-H COSY spectrum (400 MHz, DMSO-d₆, room temperature) of the supramolecular polymer network 3.](image)

**Figure S12.** H-H COSY spectrum (400 MHz, DMSO-d₆, room temperature) of the supramolecular polymer network 3.

**References:**