

Electronic Supplementary Information (ESI)

Reversibly tunable helix inversion in supramolecular gels triggered by Co^{2+}

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Experimental Section

Characterization. The ^1H and ^{13}C NMR spectra were taken on a Bruker DRX 300, and mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. The elemental analysis was performed with a Perkin Elmer 2400 series II instrument.

Preparation of Supramolecular Gel. In a typical gelation study experiment, a solution of Co^{2+} [0.1-1.0 equiv.] in THF was added to solution of L_1 or L_2 in THF in a vial. Each mixture was heated for three minutes to get a homogenous solution. This solution was allowed to cool to ambient temperature gradually to afford gel.

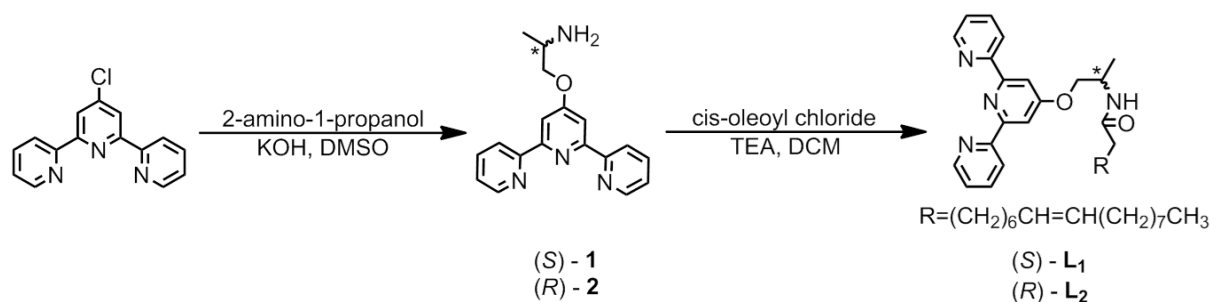
Microscopy Studies. The SEM images were taken with a field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG) using an acceleration voltage of 10–15 kV and an emission current of 10 μA .

Circular Dichroism Studies. The CD spectra were recorded on a Jasco J-815 CD spectrophotometer. CD spectra were determined over the range of 230-700 nm using a quartz cell with 0.1 mm path length. Scans were taken at a rate of 100 nm/min with a sampling interval of 1.0 nm and response time of 1s. The scans were acquired for the gel directly at room temperature in THF. CD spectra of L ([L]=8 mM) were observed in the presence of Co^{2+} (0-1 equiv.).

NMR Studies. The L solution (700 μL , 3.5 μmol , 0.005 M in $\text{THF-}d_8$) was transferred by a micro pipet to an NMR tube. Approximately the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (9 μL , 0.525 μmol , 0.0583 M in $\text{THF-}d_8$) was added *via* Hamilton syringe to an NMR tube and the sample was sealed. The sample was heated to get a homogenous solution and cooled to room temperature. ^1H NMR spectrum was measured with average 1100 scans at ambient temperature. As the cobalt solution (9 μL , 6 μL , 6 μL , 6 μL , 12 μL , and 12 μL) was added stage by stage, the procedure was repeated.

Reversibility of complexes L_1 by NMR and CD. The L_1 solution (450 μL , 2.5 μmol , 1 equiv., 0.0056 M in $\text{THF-}d_8$) and the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (50 μL , 2.5 μmol , 1 equiv, 0.05 M in $\text{THF-}d_8$) were transferred by a micro pipet to an NMR tube. The total concentration of L_1 was 0.005 M. The sample was sealed and heated to get a homogenous solution and cooled to room temperature. ^1H NMR spectrum was measured with average 1100 scans at ambient temperature. As the L_1 solution of 0.005 M (88.2 μL , 245.1 μL , 166.7 μL , 428.6 μL , and 23.1 μL) was added stage by stage, the procedure was repeated. The equivalent of Co^{2+} was reduced to 0.85, 0.60, 0.50, 0.35, and 0.30 equivalents. The total concentration of L_1 was 0.008 M instead of 0.005 M when the CD spectra were performed.

DFT Calculation. We performed density functional theory (DFT) calculations by employing M06-2X functional [Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* 2008, 120, 215.] with LACVP** basis set [Hay, P. J.; Wadt, W. R. J. *Chem. Phys.* 1985, 82, 270.] as implemented in Jaguar 8.2 [Jaguar, version 8.2; Schrodinger, LLC, New York, 2013].



Scheme S1 Synthesis of L_1 and L_2

Synthesis of compound 1 : To a stirred suspension of powdered KOH(1.05 g, 18.7 mmol) in dry DMSO(20 mL) at 60 °C, the (*S*)-(+)-2-amino-1-propanol(0.28 g, 3.7 mmol) was added. After 30min, 4'-chloro-2,2':6',2''-terpyridine(1.00 g, 3.7 mmol) was added and the mixture was stirred for 4 h at 70 °C and then poured into 600 mL of distilled water. The aqueous phase was extracted with CH₂Cl₂ (3×200 mL). The combined organic phases were dried over Na₂SO₄ and evaporated in vacuo, and the residue was recrystallized from ethyl acetate to give 0.72 g (72 %) of **1**. Mp = 118.3 °C, ¹H-NMR(300 MHz, CDCl₃) 8.7(d, 2H, ArH, *J*=4.7 Hz), 8.6(d, 2H, ArH, *J*=7.4 Hz), 8.0(m, 4H, ArH), 7.5(m, 2H, ArH), 4.0(m, 2H, -O-CH₂-CH-), 3.2(dd, 1H, -CH-, *J*=6.3 Hz and *J*=12.5 Hz), 1.7(s, 2H, -NH₂), 1.1(d, 3H, -CH₃, *J*=6.4 Hz). ¹³C-NMR(125MHz, CDCl₃) 160.2, 156.5, 154.2, 148.9, 123.7, 120.8, 105.2, 70.1, 48.1, 21.4. ESI-MS (m/z) calcd. for C₁₈H₁₈N₄O: 306.2; 307.4 [M+H]⁺. Element analysis: calculated for C₁₈H₁₈N₄O : C 70.6, H 5.9, N 18.3 Found: C 70.1, H 5.5, N 17.8.

Synthesis of compound 2 : The synthesis of **2** was performed as described in the synthesis of **1**. The (*R*)-(-)-2-amino-1-propanol was used in place of the (*S*)-(+)-2-amino-1-propanol. Mp = 117.6 °C. ¹H-NMR(300 MHz, CDCl₃) 8.7(d, 2H, ArH, *J*=4.6 Hz), 8.6(d, 2H, ArH, *J*=7.4 Hz), 8.0(m, 4H, ArH), 7.5(m, 2H, ArH), 4.0(m, 2H, -O-CH₂-CH-), 3.2(dd, 1H, -CH-, *J*=6.3 Hz and *J*=12.8 Hz), 1.7(s, 2H, -NH₂), 1.1(d, 3H, -CH₃, *J*=6.2 Hz). ¹³C-NMR(125MHz, CDCl₃) 160.7, 156.5, 155.7, 149.0, 123.7, 121.0, 105.3, 70.1, 48.1, 20.5. ESI-MS (m/z) calcd. for C₁₈H₁₈N₄O: 306.2; 307.1 [M+H]⁺. Element analysis: calculated for C₁₈H₁₈N₄O: C 70.6, H 5.9, N 18.3 Found C 70.2, H 5.5, N 17.9.

Synthesis of compound L₁ : In a two neck flask, **1** (0.40 g, 1.3 mmol) and TEA (0.40 g, 3.9 mmol) were poured into dry CH₂Cl₂(10 mL). The solution was cooled in an ice bath and magnetically stirred after which oleoyl chloride (0.59 g, 2.0 mmol) was added dropwise. The reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure. The crude product thus obtained was purified by column chromatography on Al₂O₃ (eluent: ethyl acetate/*n*-hexane 1/4) to yield 0.43 g (58 %) of **L₁**. Mp = 100.4 °C. ¹H-NMR(300 MHz, DMSO-d₆) 8.7(d, 2H, ArH, *J*=4.6 Hz), 8.6(d, 2H, ArH, *J*=7.9 Hz), 8.0(td, 4H, ArH, *J*=2.4 Hz, *J*=2.4 Hz, and *J*=7.6 Hz), 7.9(d, 1H, -NH, *J*=7.5 Hz), 7.5(dd, 2H, ArH, *J*=4.9 Hz and *J*=6.9 Hz), 5.3(m, 2H, -CH=CH-), 4.2(td, 3H, -O-CH₂-CH-, *J*=5.9 Hz, *J*=5.9 Hz, and *J*=18.3 Hz), 2.1(t, 2H, -CO-CH₂-, *J*=7.0 Hz and *J*=7.0 Hz), 1.9(dd, 4H, -CH₂-CH=CH-, *J*=5.6 Hz and *J*=9.3 Hz), 1.5(d, 2H, -CO-CH₂-CH₂-, *J*=4.9 Hz), 1.2(d, 23H, -O-CH₂-CH-CH₃ and -(CH₂)₄-CH=CH-(CH₂)₆-, *J*=7.1 Hz), 0.8(t, 3H, -CH₃, *J*=6.6 Hz and *J*=6.6 Hz). ¹³C-NMR (125MHz, DMSO-d₆) 171.8, 166.6, 156.6, 154.8, 149.1, 137.2, 129.5, 129.4, 124.4, 120.7, 106.7, 70.4, 43.6, 35.4, 31.2, 29.0, 28.5, 28.4, 26.4, 25.2, 22.0, 17.0, 13.8. ESI-MS (m/z) calcd. for C₃₆H₅₀N₄O₂: 570.4; 571.2 [M+H]⁺. Element analysis: calculated for C₃₆H₅₀N₄O₂ : C 75.8, H 8.8, N 9.8 Found : C 76.2, H 8.5, N 9.5.

Synthesis of compound L₂ : The synthesis of **L₂** was performed as described in the synthesis of **L₁**. The **2** was used in place of **1**. Mp = 100.5 °C. ¹H-NMR(300 MHz, DMSO-d₆) 8.7(d, 2H, ArH, *J*=4.2 Hz), 8.6(d, 2H, ArH, *J*=7.9 Hz), 8.0(m, 4H, ArH), 7.9(d, 1H, -NH, *J*=7.5 Hz), 7.5(dd, 2H, ArH, *J*=5.2 Hz and *J*=6.9 Hz), 5.2(t, 2H, -CH=CH-, *J*=5.8 Hz and 5.8 Hz), 4.2(td, 3H, -O-CH₂-CH-, *J*=5.7 Hz, *J*=5.7 Hz, and *J*=12.3 Hz), 2.1(t, 2H, -CO-CH₂-, *J*=7.0 Hz and *J*=7.0 Hz), 1.9(m, 4H, -CH₂-CH=CH-), 1.5(s, 2H, -CO-CH₂-CH₂-), 1.2(d, 23H, -O-CH₂-CH-CH₃ and -(CH₂)₄-CH=CH-(CH₂)₆-, *J*=10.0 Hz), 0.8(t, 3H, -CH₃, *J*=6.5 Hz and *J*=6.5 Hz). ¹³C-NMR (125MHz, DMSO-d₆) 171.8, 167.3, 156.6, 155.1, 149.3, 137.0, 129.5, 129.5, 124.3, 121.1, 106.4, 71.1, 43.6, 35.3, 31.0, 28.9, 28.3, 28.2, 26.7, 25.9, 22.1, 17.1, 13.7. ESI-MS (m/z) calcd. For C₃₆H₅₀N₄O₂: 570.4; 571.1 [M+H]⁺. Element analysis: calculated for C₃₆H₅₀N₄O₂: C75.8, H 8.8, N 9.8 Found C 76.1, H 8.4, N 9.9.

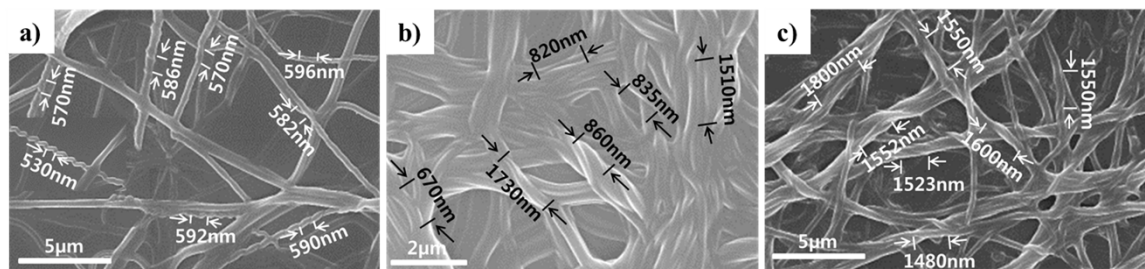
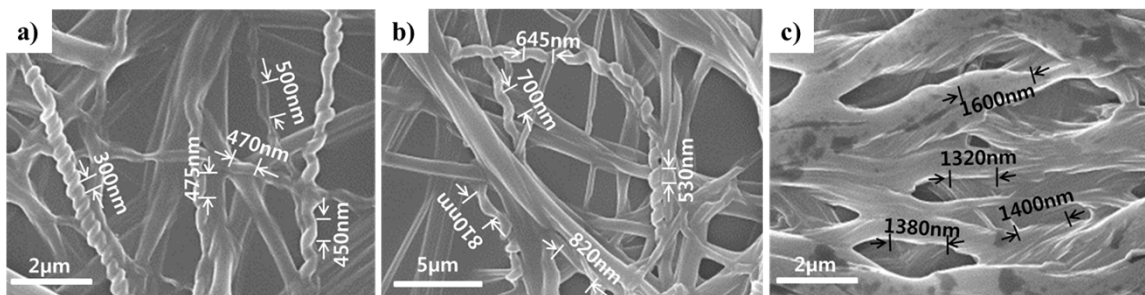
A**B**

Fig. S1 FE-SEM images of the organogel L₁ (A) and L₂ (B) with (a) 0.5, (b) 0.6 and (c) 1.0 equivalents of Co²⁺.

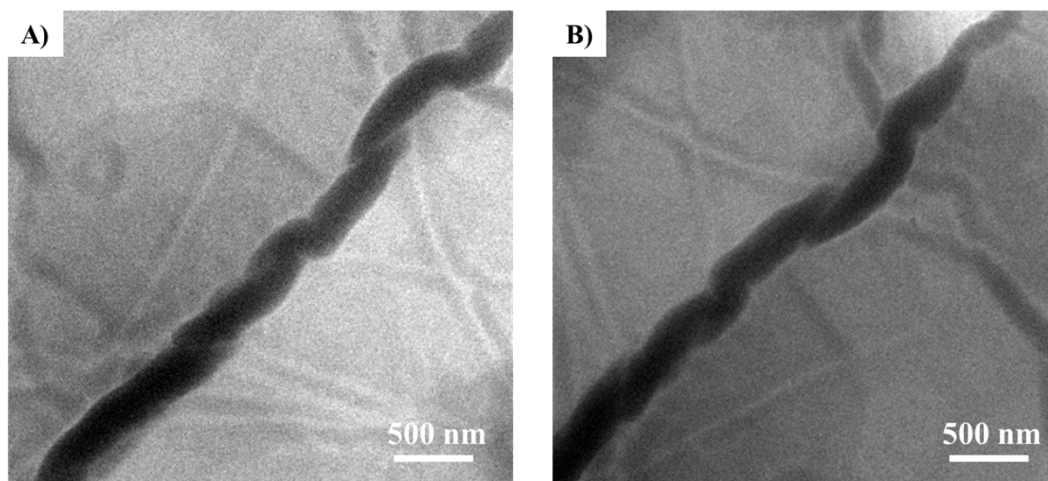


Fig. S2 TEM images of organogels L₁ (A) and L₂ (B) with 1.0 equivalents of Co²⁺.

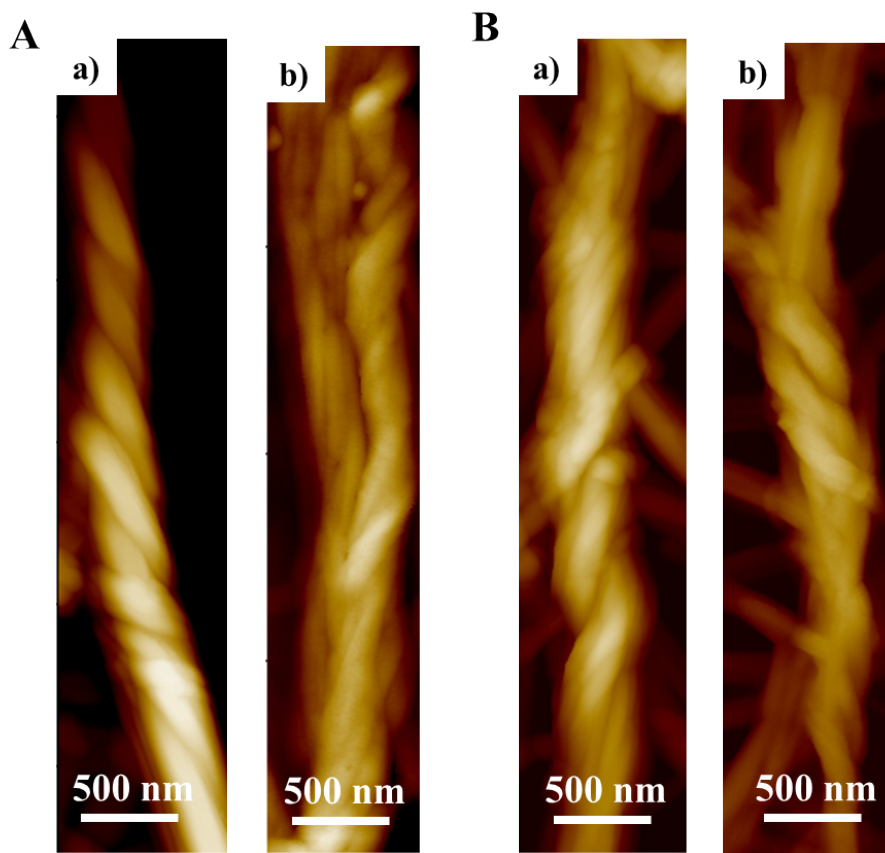


Fig. S3 AFM images of the organogel L_1 (A) and L_2 (B) with (a) 0.5 and (b) 1.0 equivalents of Co^{2+} .

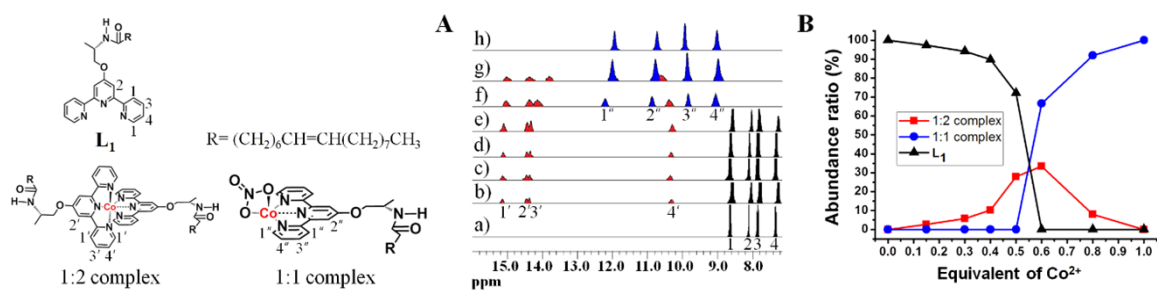


Fig. S4 (A) 1H NMR spectra of the organogel L_1 with (a) 0, (b) 0.15, (c) 0.3, (d) 0.4, (e) 0.5, (f) 0.6, (g) 0.8, and (h) 1.0 equiv. of Co^{2+} in $THF-d_8$. $[L_1] = 5 \times 10^{-3}$ M. (B) Abundance ratio of each species in several equivalents of Co^{2+} in $THF-d_8$ at room temperature. Red and blue colors indicate 1:2 and 1:1 complexes, respectively.

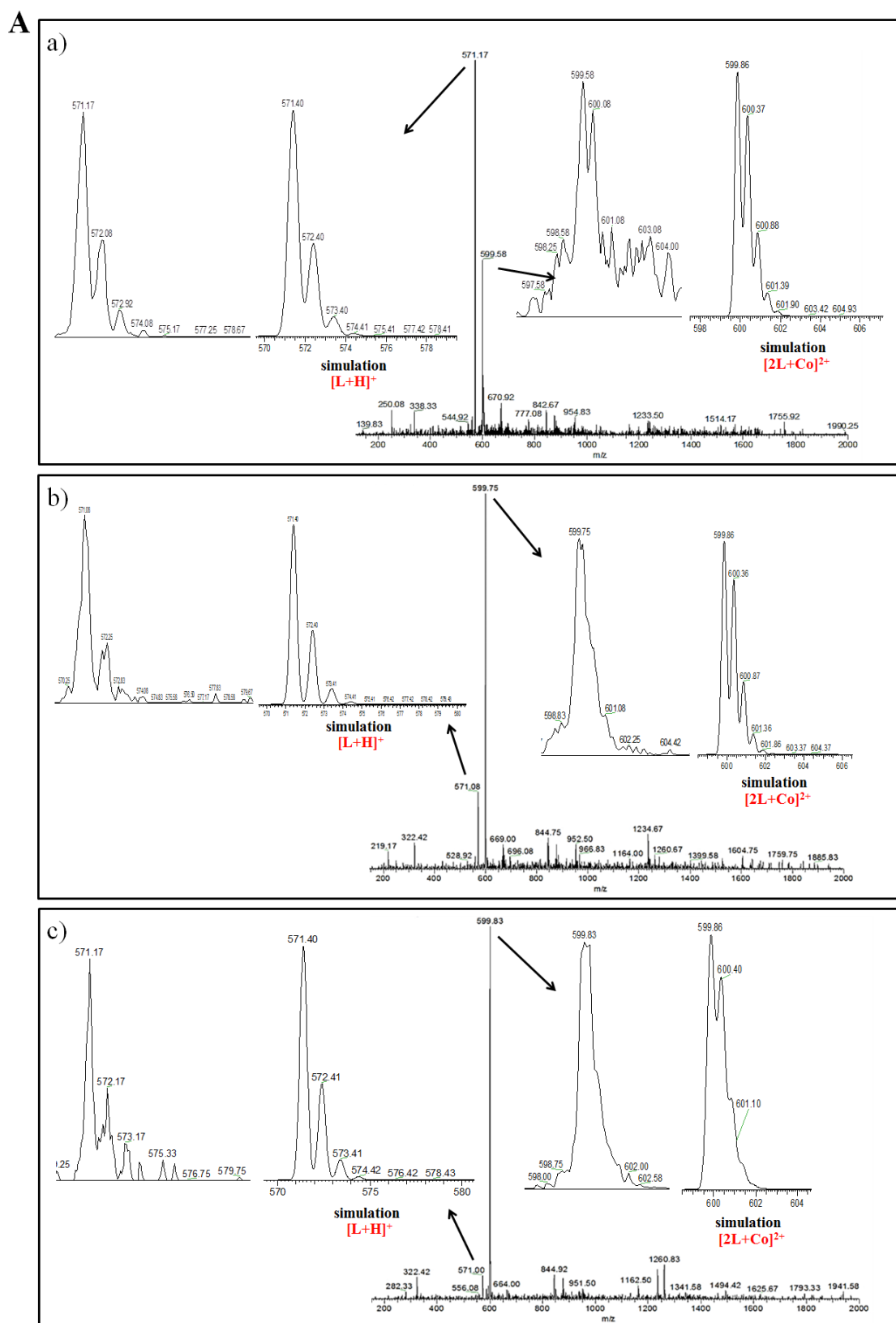


Fig. S5 ESI-mass spectra of organogel L_1 in several equivalents of Co^{2+} . (A) 0.2, 0.4 and 0.5 (a~c) equivalents of Co^{2+} .

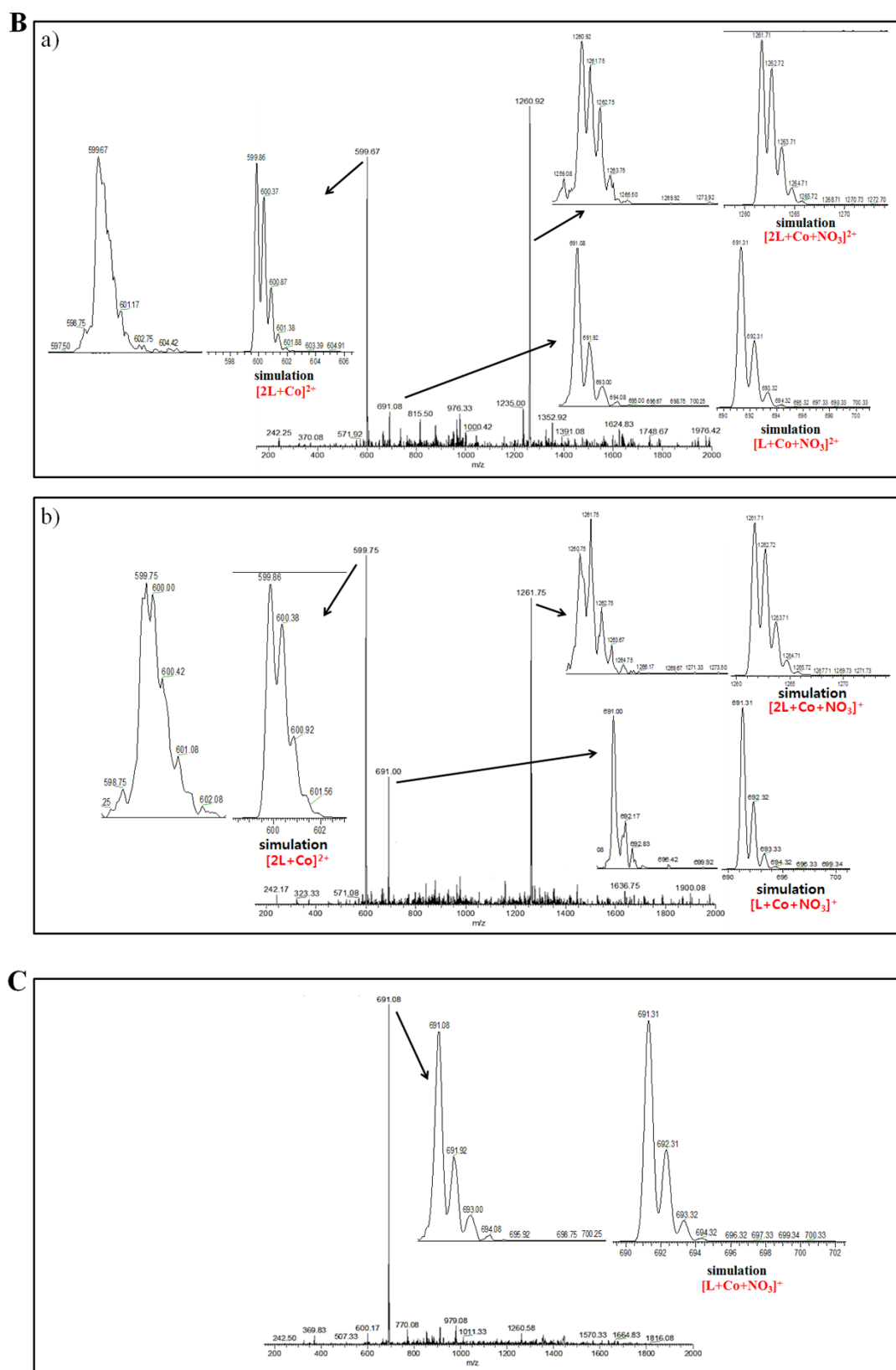


Fig. S5 ESI-mass spectra of organogel L_1 in several equivalents of Co^{2+} . (B) 0.6, 0.8 (a-b), and (C) 1.0 equivalents of Co^{2+} .

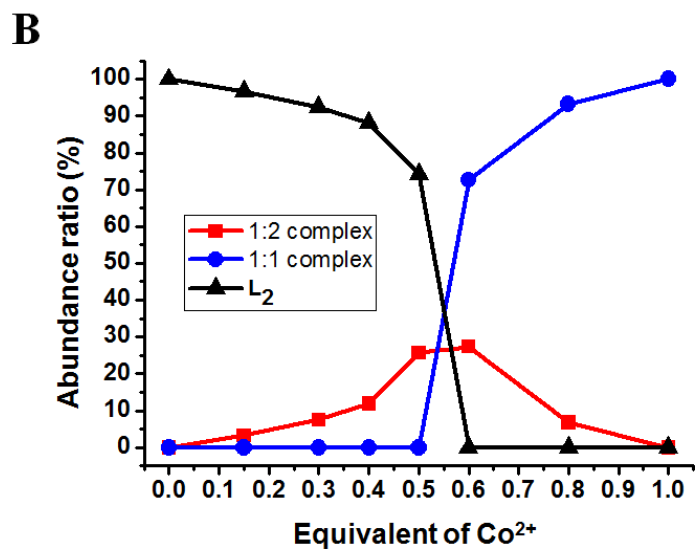
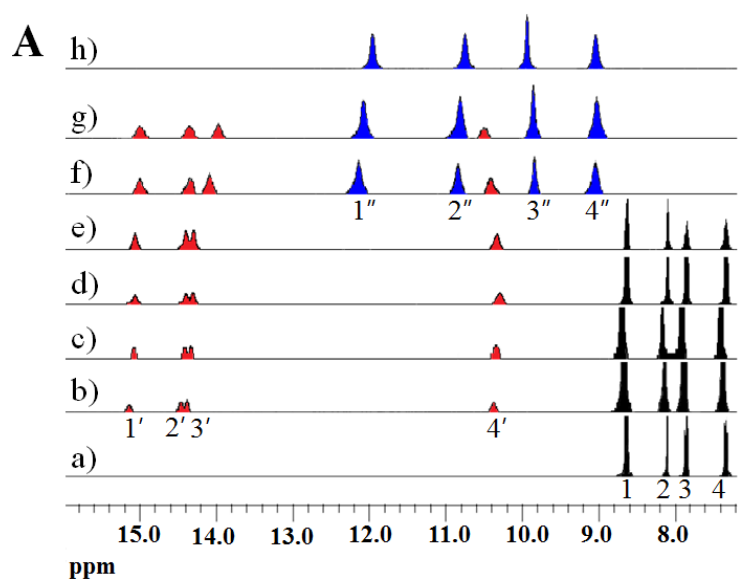
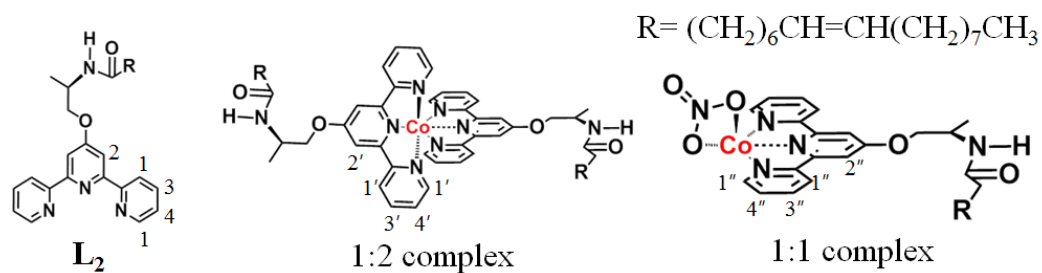


Fig. S6 (A) ¹H NMR spectra of the organogel **L₂** with (a) 0, (b) 0.15, (c) 0.3, (d) 0.4, (e) 0.5, (f) 0.6, (g) 0.8, and (h) 1.0 equivalents of Co²⁺ in THF-*d*₈ at room temperature. [**L₂**] = 5 × 10⁻³ M. (B) Abundance ratio of each species in several equivalents of Co²⁺ in THF-*d*₈ at room temperature.

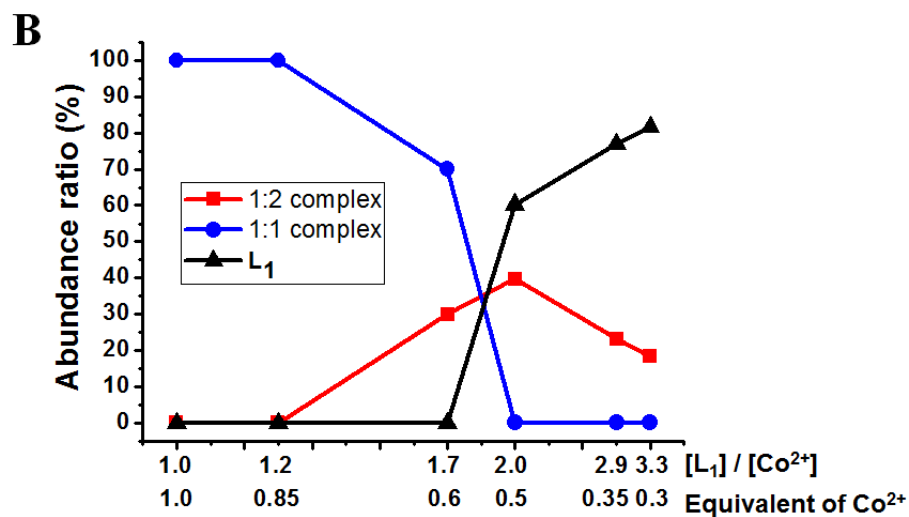
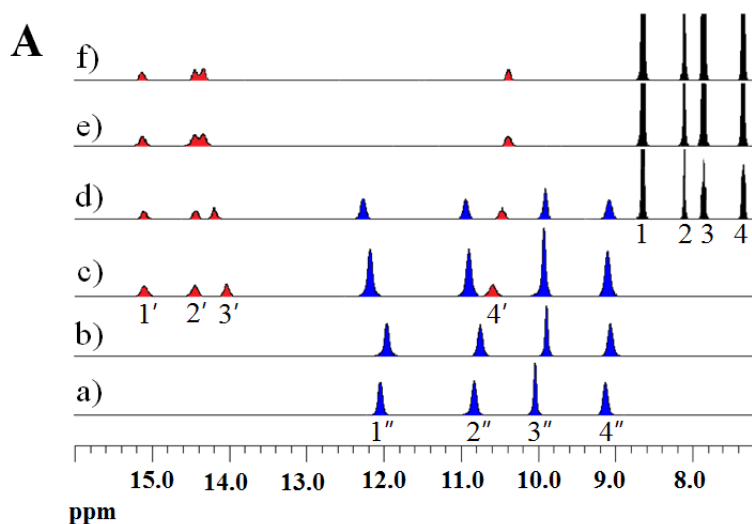
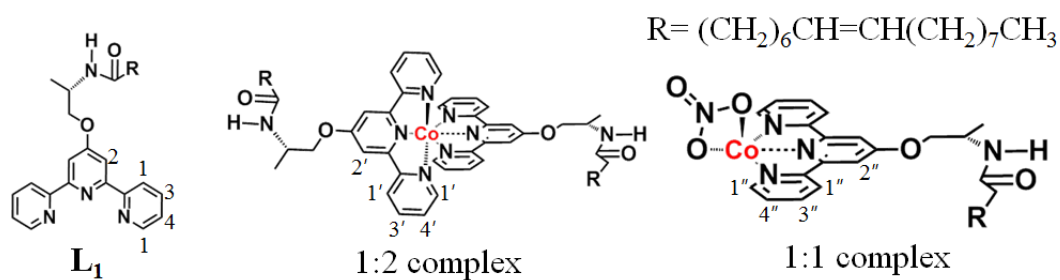


Fig. S7 (A) ¹H NMR spectra of the organogel **L**₁ with (a) 1.0, (b) 0.85, (c) 0.6, (d) 0.5, (e) 0.35, and (f) 0.3 equivalents of Co²⁺ in THF-*d*₈ at room temperature. [**L**₁] = 5 × 10⁻³ M. (B) Abundance ratio of each species in the presence of 1.0 equivalent of Co²⁺ upon addition of **L**₁ in THF-*d*₈ at room temperature. [**L**₁] = 5 × 10⁻³ M.

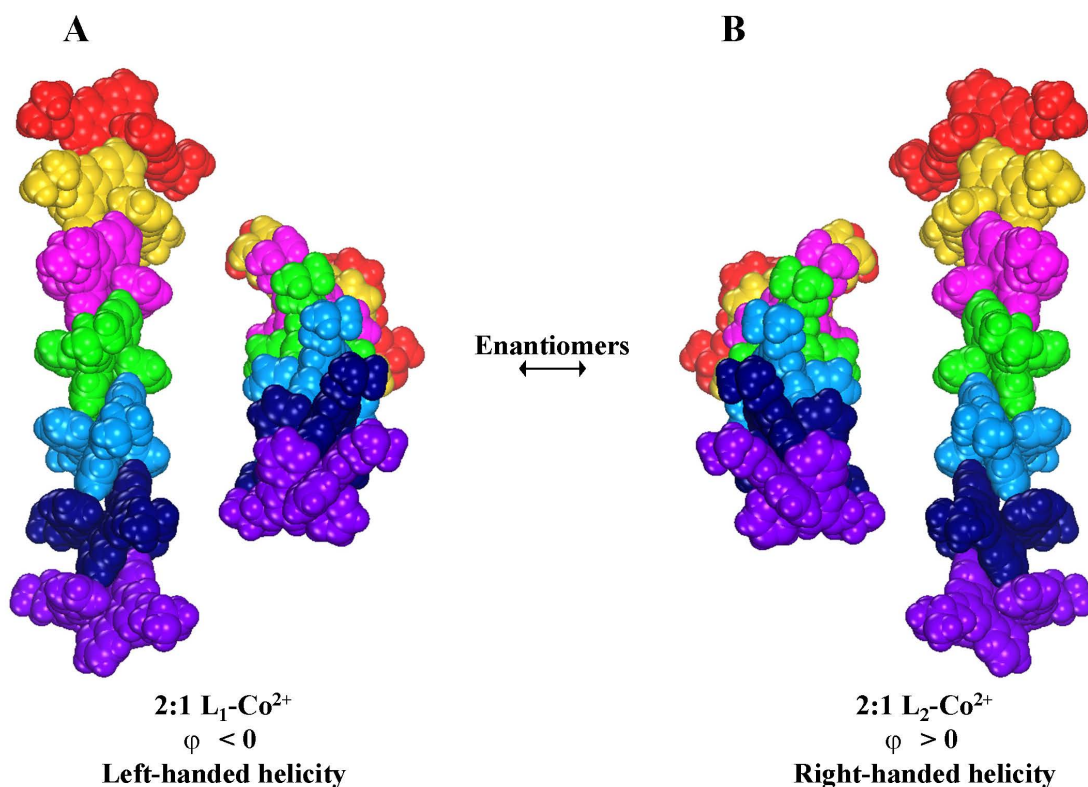


Fig. S8 (A) Left-handed helical fiber and (B) right-handed helical fiber induced by non-coplanar terpyridine ligands. When $\varphi < 0$, left-handed helicity is induced, and when $\varphi > 0$, right-handed one is. To more clearly illustrate how the assembly of Co complexes with non-zero φ induces the overall helical structure, we showed $\varphi = \pm 20^\circ$ cases, which is more exaggerated than the optimized structure from density functional theory (DFT) calculation ($\varphi = \pm 0.5^\circ$).

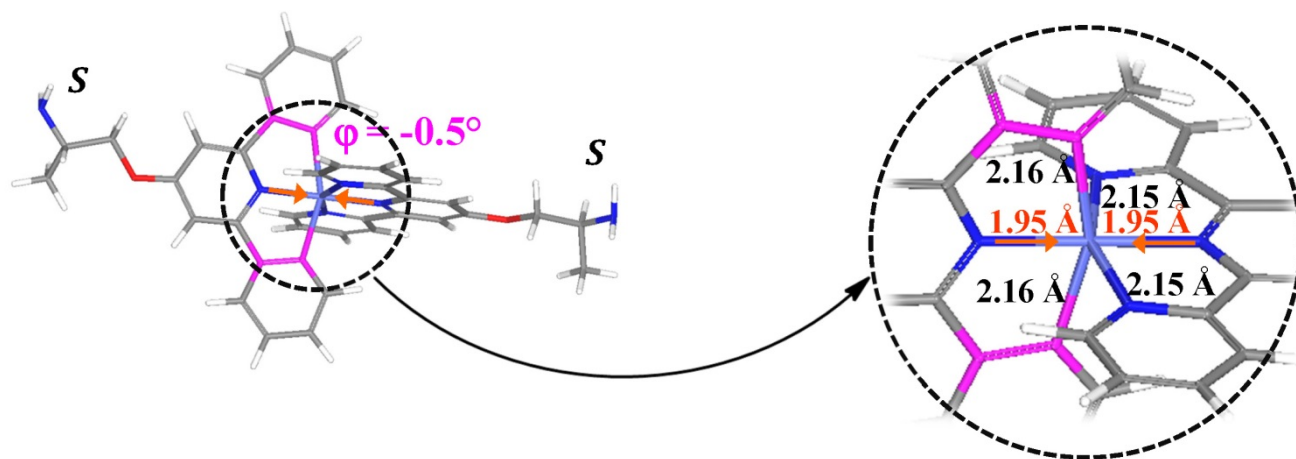


Fig. S9 Co^{2+} coordinated by terpyridines is known as a low-spin d^7 complex. Due to the unevenly occupied e_g orbitals, strong Jahn-Teller effect occurs, yielding two short bonds (1.95 Å) along the axial directions with four long bonds (2.15 Å) along the equatorial directions. Such a local distortion around the Co center causes the twisted terpyridine ligands.

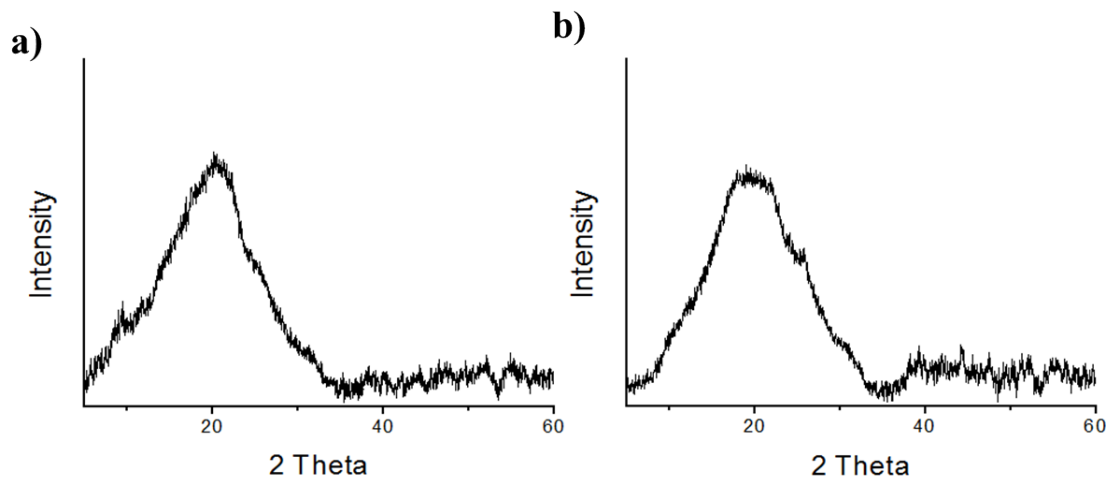


Fig. S10 Powder XRD patterns of xerogels L_1 with a) 0.5 and b) 1.0 equivalent of Co^{2+} .

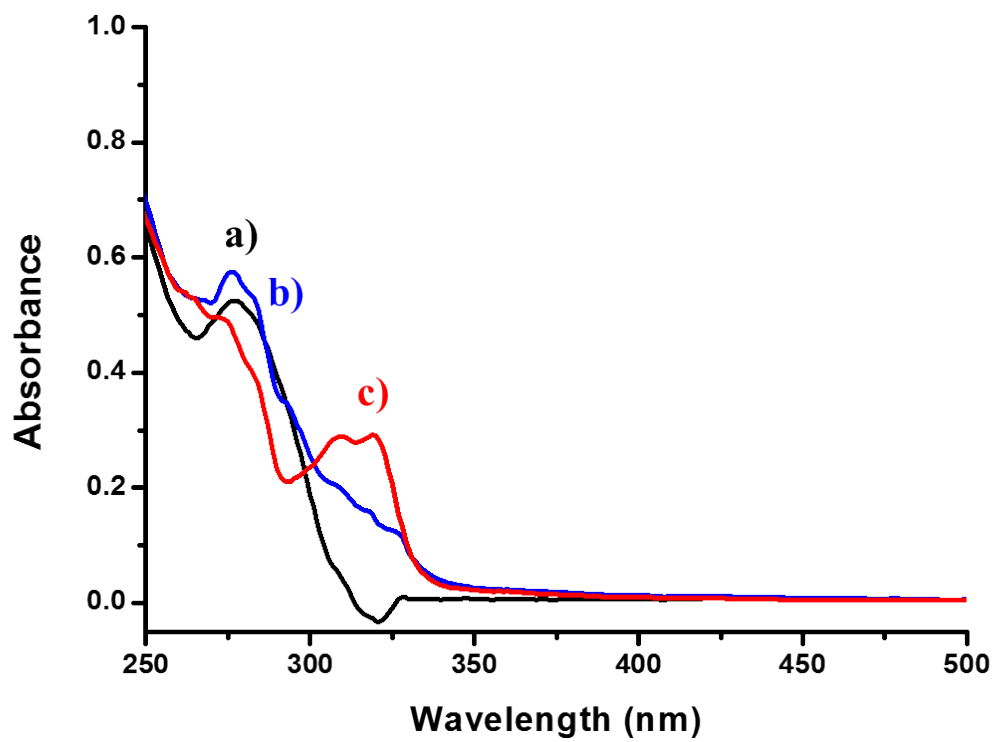


Fig. S11 UV-Vis spectra of L_1 with (a) 0 (black line), (b) 0.5 (blue line) and (c) 1.0 (red line) equivalent of Co^{2+} .

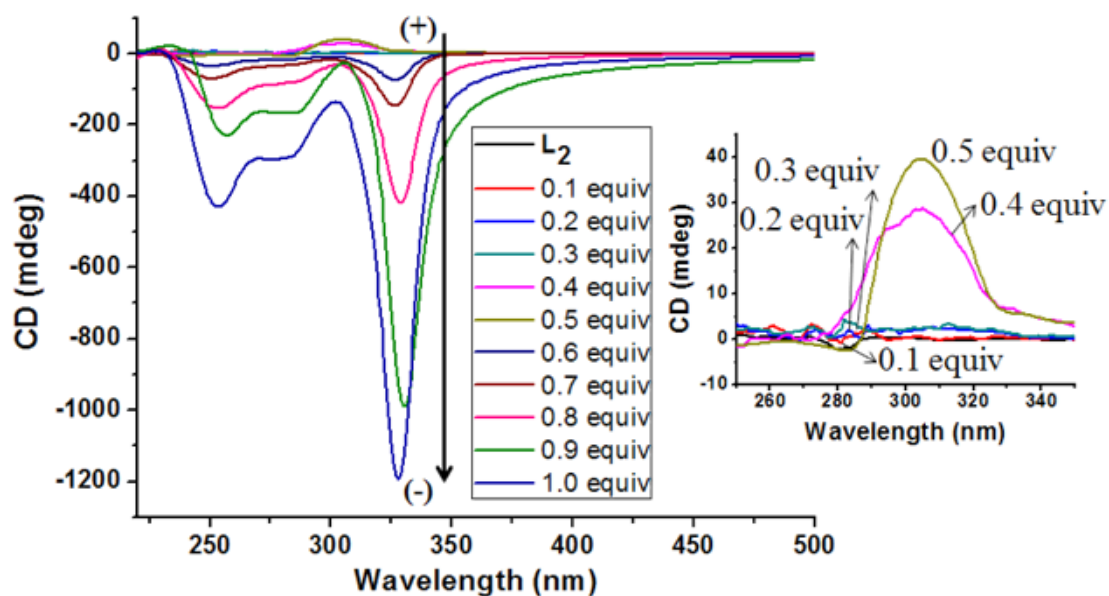


Fig. S12 CD spectral changes of organogel L_2 in several equivalents of Co^{2+} at room temperature. $L_2=8 \times 10^{-3}$ M, 1.0 mm cuvette.

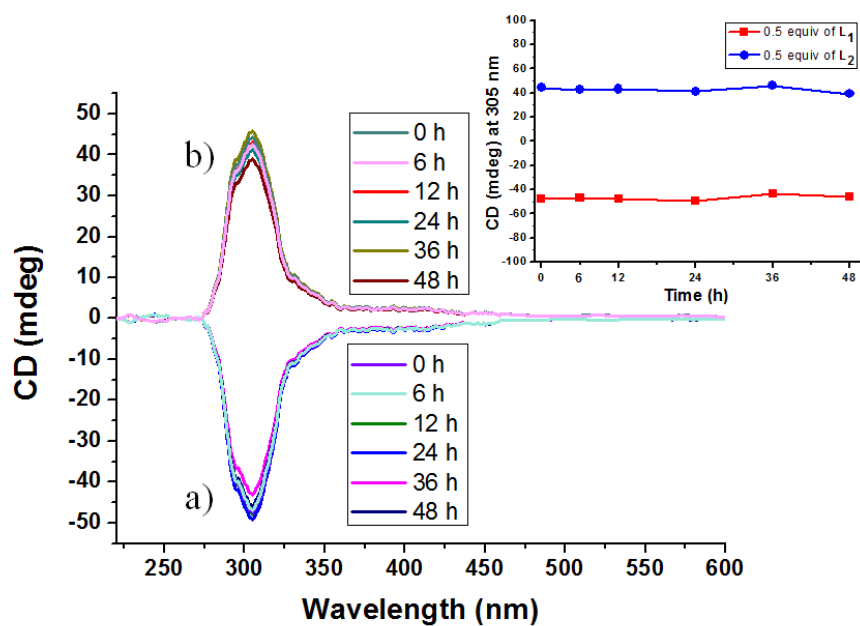


Fig. S13 Time-independent CD spectral changes of organogel (a) L_1 and (b) L_2 with 0.5 equivalents of Co^{2+} in THF at room temperature. Inset: plot of the CD amplitude at 305 nm versus time. $[L_1] = [L_2] = 8 \times 10^{-3}$ M, 1.0 mm cuvette.

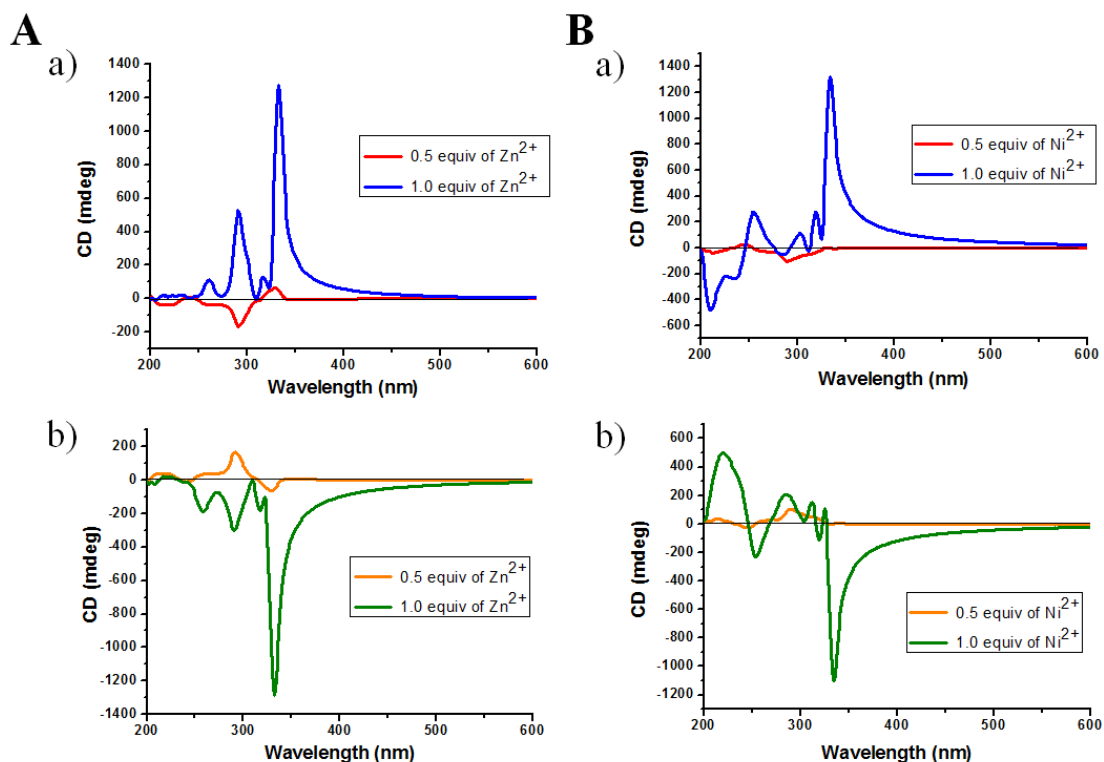


Fig. S14 CD spectral changes of organogel (a) L_1 and (b) L_2 with 0.5, and 1.0 equivalents of (A) Zn^{2+} and (B) Ni^{2+} at room temperature. $[L_1] = [L_2] = 8 \times 10^{-3}$ M, 1.0 mm cuvette.

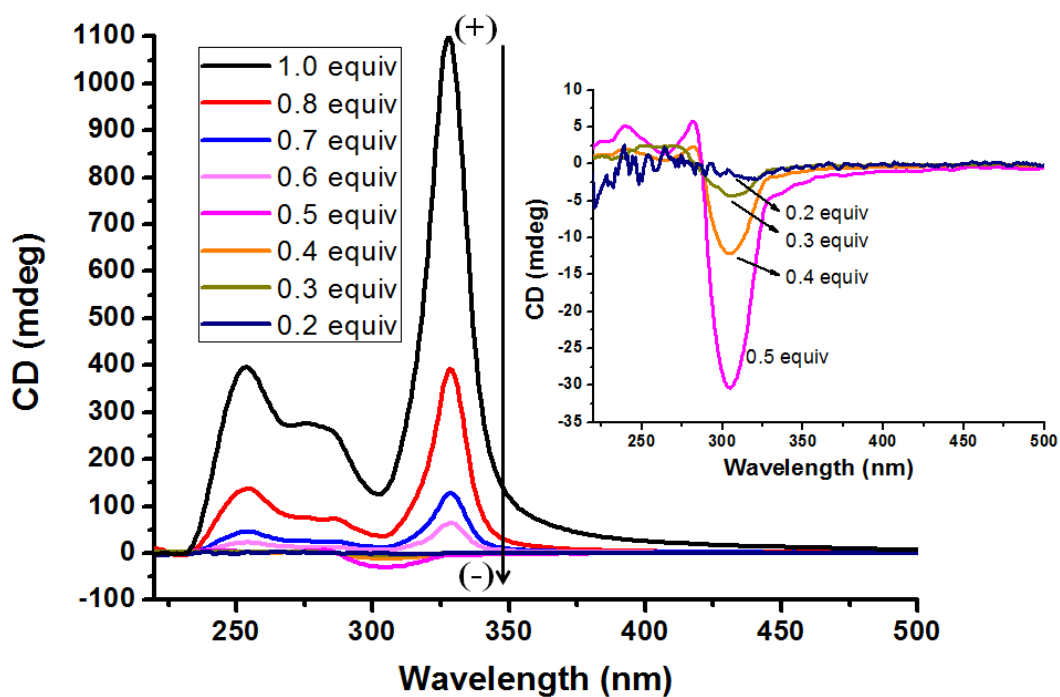


Fig. S15 CD spectra changes of organogel L_1 in the presence of 1.0 equivalents of Co^{2+} upon addition of L_1 in THF at room temperature. $[L_1] = 8 \times 10^{-3}$ M.

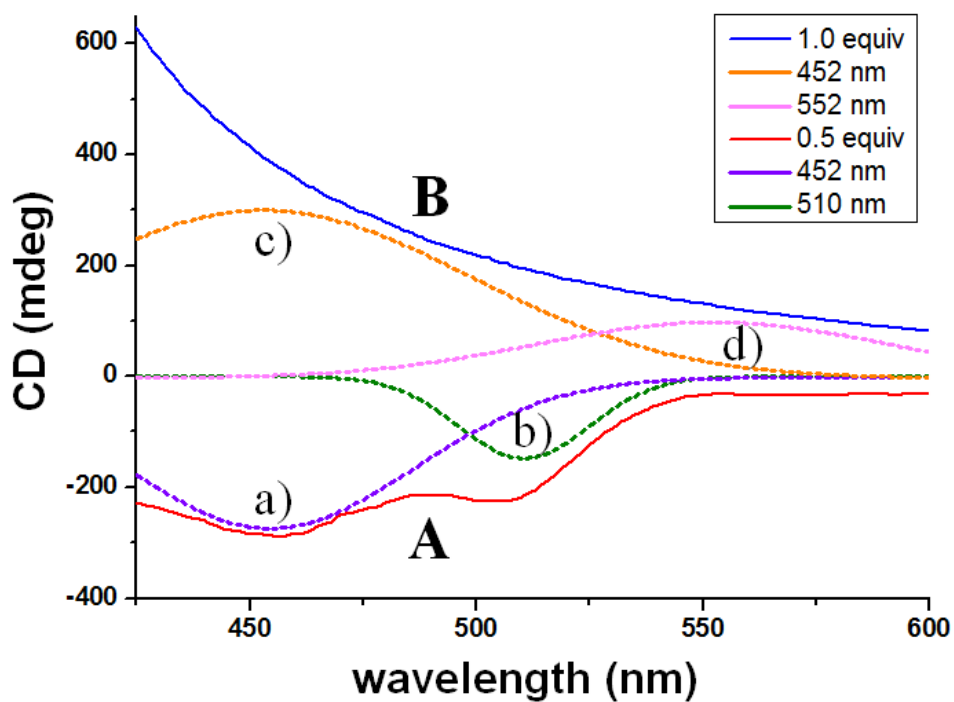


Fig. S16 CD spectra of organogel L_1 with (A) 0.5 and (B) 1.0 equivalents of Co^{2+} at room temperature. (a and b, c and d) CD spectra obtained from curve-fitting of spectrum (A, B). $[L_1] = 1 \times 10^{-1}$ M, 1.0 mm cuvette.

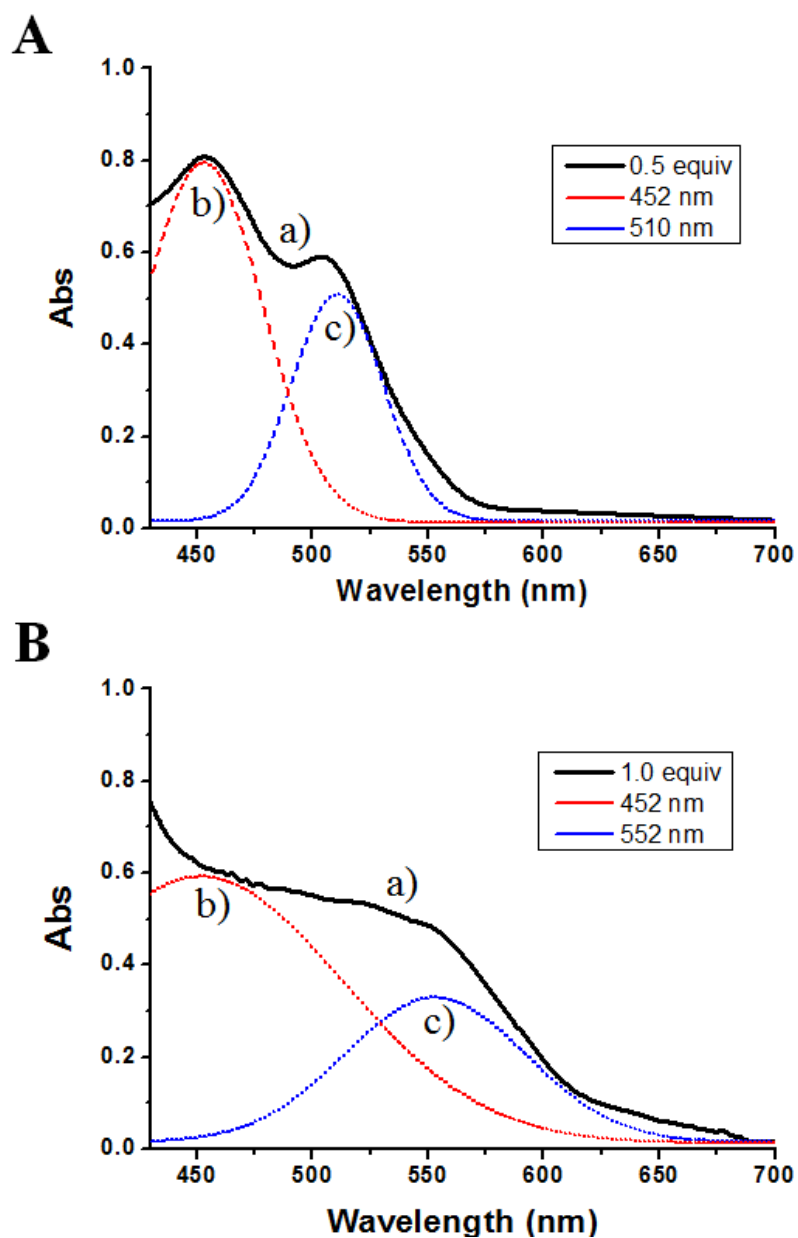


Fig. S17 UV-vis absorption spectra of organogel L_1 with (A) 0.5 and (B) 1.0 equivalents of Co^{2+} at room temperature. (b and c) UV-vis absorption spectra obtained from curve-fitting of spectrum (a). $[L_1] = 1 \times 10^{-1}$ M, 1.0 mm cuvette.