Supporting Information for:	2
1. Experimental Section	2
1.1 Reagents	2
1.2 Instrumentation	2
1.3 Synthetic Procedures	3
1.3.1 Synthetic route of 1	3
1.3.2 Synthetic route of 2	3
1.3.3 Synthetic route of 3	4
1.4 Characterization Data	5
1.4.1 EI-MS (Positive ion mode)	5
1.4.2. 1H NMR spectrum	6
2.Supplementary Figures	8
3. References for supporting information	17

## **Supporting Information for:**

# A Co<sup>2+</sup>-Selective and Chirality-sensitive Supermolecular Metallohydrogel with Nanofiber Networks Skeleton

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#### 1. Experimental Section

### 1.1 Reagents

o,m,p-pyridinecarboxaldehyde, were purchased from Xiensi Reagent (Tianjin, China) L/D- typtophan, sodium borohydride was purchased from Xiya Reagent (Chengdu, China) All other reagents were of analytical grade and deionized water (MillQ, 6.8M $\Omega$ ) was used.

### 1.2 Instrumentation

Field emission scanning electron microscopic (FE-SEM) study: Scanning electron microscope (SEM) images were obtained on a FEI HELIOS NanoLab 600i SEM (America).

Transmission electron microscopy (TEM) study: Transmission electron microscope (TEM) images were carried out on a FEI Titan G2 60-300 TEM (America)

FTIR spectroscopy: FT-IR spectras were recorded with a Perkin Elmer Spectrum One instrument (America). Firstly, KBr crystals baked by infrared light were used as the matrix for sample preparation, and then KBr was mixed with the powdered samples to prepare the thin films.

UV/Vis spectroscopy: were recorded on Shimadzu UV-2450 spectrometer (Japan).

Fluorescence spectroscopy: The samples were detected by using Hitachi F-7000(Japan)

Rheology: The rheological studies were carried out on a rotated rheometer (AR 2000ex, TA Instrument, America).

NMR experiments: The samples were obtained by using AMX-500 (Bruker, Switzerland)

Circular dichroism (CD) study: Circular dichroism spectra of different samples were obtained by using Jasco-815 CD spectrometer (Japan). The samples were detected by using 1mm quartz cell.

#### 1.3 Synthetic Procedures

#### 1.3.1 Synthetic route of 1



Scheme 1 Synthetic route of compound 1

Preparation of compound 1 (named PT) : The compound 1 was prepared following a modified literature procedure.<sup>1</sup> To an aqueous solution (10 mL) of L/D-tryptophan (1g, 5 mmol) containing KOH (0.28 g, 5 mmol), 4-pyridinecarboxaldehyde (0.54 g, 5 mmol) in MeOH (5 mL) was added slowly. The solution was stirred for 2 h at room temperature, and during this period the color of the solution was more and more deep. Then the solution was cooled in an ice bath. NaBH<sub>4</sub> (0.23 g, 6 mmol) was added to the solution slowly. The mixture was stirred for 3 h, and 50% acetic acid was used to neutralize the basic (pH~10) reaction mixture and adjusted the pH to 4.0-5.0. The mixture system was stirred further for 2 h. The resulting solid was filtered off, and washed with methanol and water, dried, and recrystallized from water/methanol (3:1). Yield (compound 1): 0.98g, 66.0%. MS (ESI): calc. for  $C_{17}H_{17}N_3O_2$  295.13; observed 296.04 [M + H]<sup>+</sup>. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, ppm): -CH<sub>2</sub> (2.97, dd, 2H). -CH (3.29, t, *J* = 6.7 Hz, 1H), -CH<sub>2</sub> (3.66, dd, 2H), In-H (6.98-7.13, m, 6H), py-H (7.42, dd, 2H), py-H (8.28, dd, 2H).

### 1.3.2 Synthetic route of 2



Scheme 2 Synthetic route of compound 2 (3-PT)

Preparation of compound 2 (3-PT): The ligand 3-PT was prepared following a modified literature procedure. To an aqueous solution (10 mL) of L-tryptophan (1 g, 5 mmol) containing KOH (0.28 g, 5 mmol), 3pyridinecarboxaldehyde (0.54 g, 5 mmol) in MeOH (5 mL) was added slowly. The solution was stirred for 2 h at room temperature, and during this period the color of the solution was more and more deep. Then the solution was cooled in an ice bath. NaBH<sub>4</sub> (0.23 g, 6 mmol) was added to the solution slowly. The mixture was stirred for 3 h, and 50% acetic acid was used to neutralize the basic (pH~10) reaction mixture and adjusted the pH to 4.0-5.0. The mixture system was stirred further for 2 h and then was evaporated until dryness. The solid was extracted by dry and hot MeOH, and was evaporated to thick liquid, then was dried by natural evaporation in the air. The solid obtained was recrystallized by H2O. Yield (compound 2):1.03g, 59%.

MS (ESI): calc. for  $C_{17}H_{17}N_3O_2$  295.13; observed 296.12 [M + H]<sup>+</sup>.

1H NMR (500 MHz, CD<sub>3</sub>OD, ppm): -CH<sub>2</sub> (3.26, m, 2H). -NH(3.52, m, 1H), -CH (3.88, m, 1H), -CH<sub>2</sub> (4.01, dd, 2H), In-H (7.01-7.37, m, 6H), py-H (7.52,d, J = 10 Hz, 1H), py-H (7.64, m, 1H), py-H (8.42, d, 1H), py-H (8.49, dd, J = 5 Hz, 1H).

### 1.3.3 Synthetic route of 3



Scheme 3 Synthetic route of compound 3 (2-PT)

Preparation of compound 3 (2-PT): The ligand 2-PT was prepared following a modified literature procedure. 1 To an aqueous solution (10 mL) of L-tryptophan (1g, 5 mmol) containing KOH (0.28 g, 5 mmol), 2-pyridinecarboxaldehyde (0.54 g, 5 mmol) in MeOH (5 mL) was added slowly. The solution was stirred for 2 h at room temperature, and during this period the color of the solution was more and more deep. Then the solution was cooled in an ice bath. NaBH<sub>4</sub> (0.23 g, 6 mmol) was added to the solution slowly. The mixture was stirred for 3 h, and 50% acetic acid was used to neutralize the basic (pH~10) reaction mixture and adjusted the pH to 4.0-5.0. The mixture system was stirred further for 2 h and then was evaporated until dryness. The solid was extracted by dry and hot MeOH, and was evaporated to thick liquid, then was dried by natural evaporation in the air. The solid obtained was recrystallized by H<sub>2</sub>O. Yield (compound 3):1.03g, 69. 8%.

MS (ESI): calc. for  $C_{17}H_{17}N_3O_2$  295.13; observed 296.12  $[M + H]^+$ .

1H NMR (500 MHz, CD<sub>3</sub>OD, ppm): -CH<sub>2</sub> (3.27, m, 2H). -NH(3.58, m, 1H), -CH (3.90, m, 1H) -CH<sub>2</sub> (4.20, dd, 2H), In-H (6.98-7.25, m, 6H), py-H (7.60,d, J = 10 Hz, 1H), py-H (7.70,t, 1H), py-H (8.18, d, J = 5 Hz, 1H), py-H (8.41, d, J = 5 Hz, 1H).

# 1.4 Characterization Data

# 1.4.1 EI-MS (Positive ion mode)



Fig.S1 Electrospray ionization mass spectra of Compound 1.



Fig.S2 Electrospray ionization mass spectra of Compound 2



Fig.S3 Electrospray ionization mass spectra of Compound 3.

1.4.2. 1H NMR spectrum



Fig.S4 <sup>1</sup>H NMR (500 MHz) Spectra of Compound 1(PT) in  $D_2O$ .





Fig.S6 <sup>1</sup>H NMR (500 MHz) Spectra of Compound 3 in  $CD_4OD$ .

2.Supplementary Figures



Fig.S7 Scanning electron microscope (SEM) and Transmission electronmicroscope (TEM) images of PT (The concentration is 0.1M).



**Fig.S8** Digital photos of different concentrations (from left to right: 0.04M, 0.06M, 0.08M, 0.10M, 0.2M) of PT-Co metallohydrogels.



**Fig.S9** SEM images of the  $Co^{2+}$  complex gels with A)CoCl<sub>2</sub>, B) CoSO<sub>4</sub>, C) Co(OAc)<sub>2</sub>, D) Co(NO<sub>3</sub>)<sub>2</sub>. SEM images of the complex gels gained by using different anions showed fibril structures with diameters in the 20-80 nm range (Fig S9 †), suggesting that the anions of Co(II)-salts exhibited little influence on the morphologies of metallohydrogels.



**Fig.S10** Digital images of a) the metallohydrogel formed by PT and  $Co^{2+}$ , b) the precipitation formed by compound 2 and  $Co^{2+}$  c) the viscous solution formed by compound 3 and  $Co^{2+}$ .



**Fig.S11** Scanning electron microscope Images (SEM) of A) PT-Co gel B) 3-PT-Co viscous solution C) 2-PT-Co precipitation D) addition EDTA to PT-Co gel.



**Fig.S12** The concentrate-dependent Fluorescence spectrum of the mixture of the compound 1(PT) (5 mM) in water with increasing proportion of  $Co^{2+}$ .



**Fig.S13** CD signals for A) L-PT, and L-PT-Co, B) 2-PT(compound 3), and 2-PT-Co, and B) 3-PT(compound 2), and 3-PT-Co, respectively (The concentration of all solutions is 20 mM).

From Circular dichroism spectra (CD) spectra (Fig. S13<sup>†</sup>), we observed that the strength of CD signals increase between 240 nm and 300 nm when  $Co^{2+}$  was added to the ligand solution, especially, PT-Co, which indicated that  $\pi-\pi$  interactions strengthen. New CD signals appear due to the cobalt complexes chromophores in near ultraviolet area among the three systems, amazingly, only PT-Co has CD signal in the visible light region. These results showed the evident differences between PT-Co and its isomeric systems in intensity and peak position.



Fig.S14 DFS experiments at different gel concentrations (strain = 0.1%).

A frequency sweep experiment was performed at constant strain 0.1%. At different gelator concentrations, the values of G' were higher than  $10^4$  Pa, exhibiting the excellent mechanical strength of these metallohydrogels.



**Fig.S15** DTS experiment was carried out at constant strain at 0.1% and frequency constant at 1 Hz (fresh hydrogel prepared at the CGC) in order to detect the mechanical stability of the hydrogel. The values of G' and G'' kept almost invariable during the measure process, which shows that the gel gained is of excellent temporal stability.



Fig.S16 DSS experiments at constant frequency of 1 Hz ( fresh hydrogel was prepared at the CGC).



**Fig.S17** The step strain experimental data obtained from the PT-Co metallohydrogel at strain = 0.1%. The concentration was maintained at 0.1 M and the ratio of PT and Co<sup>2+</sup> was 2:1.

The thixotropic property of the hydrogel was tested by shaking-resting test. Upon violently shaking by hand, the gel transferred to a turbid liquid. This turbid liquid quickly restored to a self-supported gel within several seconds, illustrating a rapid thixotropic responsiveness. Meanwhile,A time dependent step-strain rheological experiment<sup>2</sup> was performed in three steps. Firstly, the metallohydrogel was conducted with a constant strain of 0.1% (step 1). Then the strain was changed from 0.1% to 30% and remained for several minutes at 30% to damage gels completely (step 2). Then the strain was reduced from 30% to 0.1% again and remained for several minutes at 0.1% to observe whether the gel can restore (step 3). The angular frequency remained constant at 1 Hz during the whole experiment. The storage modulus (G<sup>2</sup>) was higher than the loss modulus values (G<sup>2</sup>) at the constant strain 0.1%, indicating a gel nature. Nevertheless, at constant strain 30%, the value of G<sup>2</sup> was larger than G<sup>2</sup>, which confirmed the gel to sol transformation. After removing of 30% strain, the gel immediately restored 95% of its original mechanical strength and recovered to 100% in several seconds. The excellent thixotropic properties of this gel indicated a prospective application as an injectable soft materials applied in drug delivery system.



**Fig.S18** Plot of Tgel of PT-Co metallohydrogels with different concentrations(0.04M, 0.05M, 0.08M, 0.10M, 0.2M).



**Fig.S19** Scanning electron microscope Imagines (SEM) (A) Suspension (B) Clear solution (Sample preparation method: Rapid freeze-drying) (C) Clear solution (Sample preparation method: slow volatilization) by dropping HCl to the metallohydrogel (D)Local amplification of C.



Fig.S20 UV/Vis spectra of (A) diluted PT-Co hydrogel and (B) dissolved PT-Co-HCl solid.



Fig.S21 The time-dependent UV-Vis study of the PT-Co hydrogels.

To identify the dynamic gelation behavior of PT–Co gel, we conducted time-dependent UV– vis absorption investigations; the results are shown in Fig. S21<sup>+</sup> and suggest that the coordination reaction between PT and Co<sup>2+</sup> is a rapid process.



**Fig.S22** Thermogravimetric analysis (TGA) thermogram of PT-Co. Thermal analysis system in a dynamic nitrogen atmosphere (heating rate: 10°C/min, PT-Co, mass 1-3 mg, temperature range from room temperature up to 800°C).

The thermogravimetric analysis experiment on the xerogel of the metallohydrogel suggested the strong binding forces between PT and  $Co^{2+}$  (Fig. S22†). The first drop in the curve (around 100 °C) represents water loss. The second drop (starting at around 280 °C and ending at about 450 °C) was ascribed to the loss of organic compound. Notably, this mixture still maintained more than 60% of its original weight after heating to 450 °C and undergoing two degradation steps, indicating that PT–Co had perfect thermal stability.<sup>3</sup>



Fig.S23 A)UV-Vis study of Drug release of PT-Co metallohydrogel B)Drug release curves of PT-Co metallohydrogel.

Adding 5 uL 10 mM aromatic dye methylene blue (MB) to 2 mL metallohydrogel had insignificant effect on PT-Co metallohydrogel except the color change (from pink to blue). The MB-loaded metallohydrogel was covered with water on the surface of gel in an incubator. A few minutes later, the water layer gradually turned blue. Kinetic-release study was conducted, a small amount of the water solution were taken out every once in a while, and their UV spectra (Fig S23A <sup>†</sup>) were measured to note the value of absorbance at 664 nm. The whole

release process remained 48h and a percentage release figure was obtained, (Fig S23B <sup>†</sup>) suggesting that the metallohydrogel has enough space to incorporate molecules, and so indicating it has future promise for being applied to drug releasing medium.



**Fig.S24** TEM images of A) L-PT–Co gel, B) D-PT–Co gel, C) racemic mixtures, and D) collapsed L-PT–Co gel after being heated.

When the metallohydrogel PT-Co is heated, the molecular thermal motion is accelerated, and non-covalent forces between the molecules has weakened. The result is that the gel collapsed and turned into viscous suspension. From TEM image(Fig. S24D), it was observed that original 3D network structure of the gel has been destroyed and the fiber has become disorderly. When the temperature goes down to room temperature, the perfect 3D network structure is formed again due to slow self-assembly of PT-Co molecules.

# 3. Reference for supporting information

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