Electronic Supplementary Material (ESI)

Platinum (II) Terpyridine-based Supramolecular Polymer Gels with Induced Chirality

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Contents

Methods

General characterization. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker DRX 300. Mass spectroscopy samples were analyzed on a JEOL JMS-700 mass spectrometer. The high resolution mass spectra (HR-MS) were measured by electrospray ionization (ESI) with a micro TOF Focus spectrometer from SYNAPT G2 (Waters, U.K.). A UV-visible spectrophotometer (Jasco V-730) was used to obtain the absorption spectra. IR spectra were observed over the range 500-4000 cm^{-1} with a Thermo Scientific Nicolet iS 10 instrument. Powder X-ray pattern (XRD) was recorded on a Rigaku model NANOPIX X-ray diffractometer with a Cu K_α radiation source.

Circular dichroism studies.

The CD and UV-vis spectra were recorded on a Jasco J-815 CD spectrophotometer. CD spectra were determined over the range of 300-800 nm using a quartz cell with 10 mm path length. Scans were taken at rate of 500 nm/min with a sampling interval of 1 nm and response time of 0.06s. The scans were acquired for the supramolecular nanostructure directly at 25 °C.

Atomic Force Microscopy (AFM) Studies.

AFM measurements were performed by using a XE-100 and a PPP-NCHR 10 M cantilever (Park systems). The AFM samples were prepared by spin-coating (2000 rpm) onto freshly cleaved Muscovite Mica, and images were recorded with the AFM operating in noncontact mode in air at RT with resolution of 1024 × 1024 pixels, using moderate scan rates (0.3 Hz).

Preparation of gel.

1 (5 mg, 0.0046 mmol), various concentrations of dichloro(1,5-cyclooctadiene)platinum(II) (1.0-4.0 equivalent), and the mixture of DMSO/water (v/v, 1:1) 500 μL of solvent was added. The mixture was sonicated to form the metallogel, followed by heating at 383 K for 10 minutes in an oil bath, which was then allowed to cool gradually in the same oil bath to room temperature. Gels were left to stabilize overnight before measurements were performed.

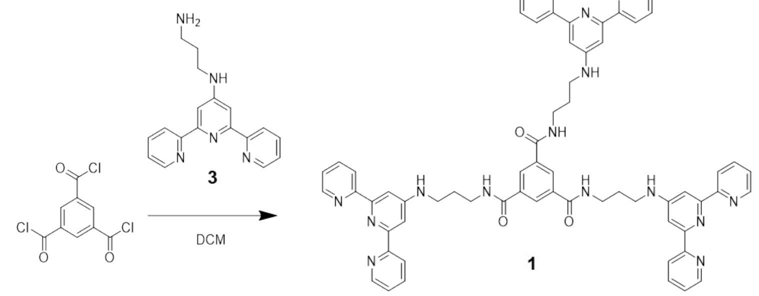
Material synthesis

Synthesis of compound 1.

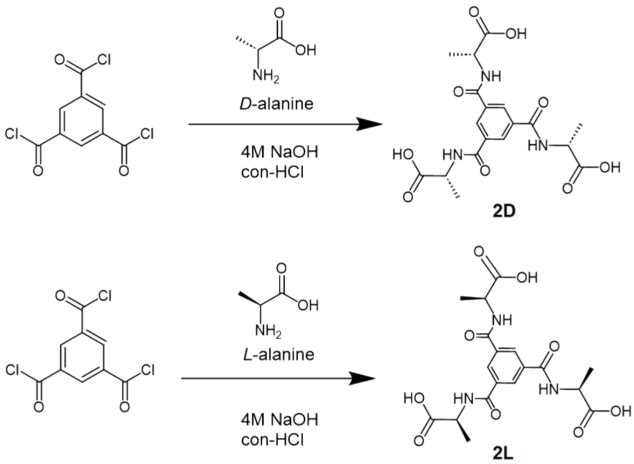
The compound **1** was prepared according to a literature procedure.[3] A solution of **3** (0.4 g, 1.310 mmol) in anhydrous dichloromethane was allowed to cool in an acetone/ice bath for 15 min before adding 1,3,5- benzenetricarbonyl trichloride (0.112 g, 0.042 mmol). A white precipitate was observed, and the reaction mixture was further stirred at room temperature overnight. The solid was then filtered and washed with dichloromethane to yield a beige solid (0.41 g, 90%). mp 230 °C; ^{1}H NMR (300 MHz, CD_3OD) 8.74 (s, 1H, CH_{tpy}), 8.70 (s, 1H, CH_{tpy}), 8.68 (s,1H,$CH_{benzene}$), 8.35 (s, 1H, CH_{tpy}), 8.21−7.85 (3H, CH_{tpy}), 7.64−7.25 (4H, CH_{tpy}), 3.67 (m, 2H, CH_2), 3.63 (m, 2H, CH_2), 2.12 (m, 2H, CH_2); ^{13}C NMR (125 MHz, CD_3OD) 167.22, 160.36, 160.04, 149.99, 146.83, 145.90, 138.54, 138.25, 135.17, 131.91,131.67, 131.17, 129.31, 126.85, 121.73, 121.73,110.65, 106.05, 100.79, 41.30, 37.43, 28.21; IR(KBr, cm^{-1}): 3245, 3094, 3058, 2942, 2871,1637, 1589, 1527, 1464, 1443, 1352, 1297, 1270, 1238, 1159, 1124, 1090, 1034, 993, 908, 867, 785, 736; ESI-MS: m/z 358.25 $[M + 3H]^{3+}/3$, 536.92 $[M + 2H]^{2+}/2$, 1072.58 $[M + H]^+$; Calculated for $C_{63}H_{59}N_{15}O_3$ 1073.4925; found 1073.4930.

Synthesis of Compounds 2D and 2L.

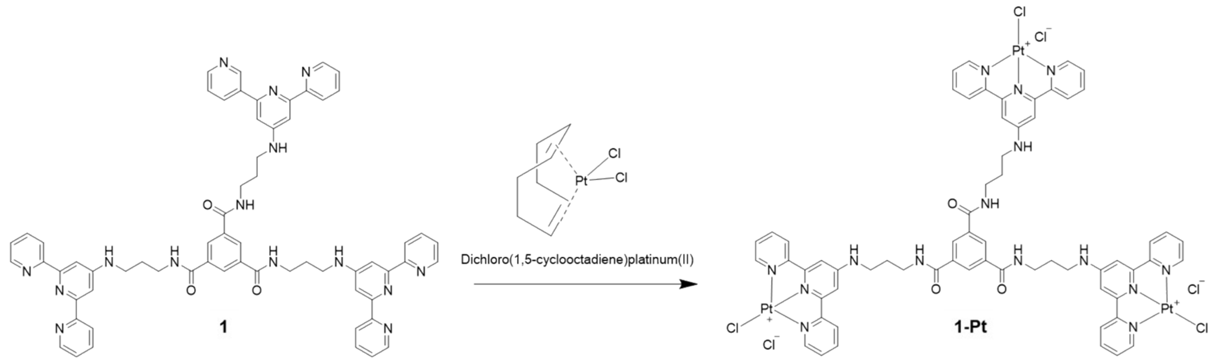
Compounds **2**D and **2**L were prepared according to a literature procedure.[3] A water solution (30 mL) of D- or L-alanine (0.600 g, 6.7 mmol) and NaOH (0.268 g, 6.7 mmol) was also prepared. The freshly prepared 1,3,5-benzenetricarbonyl trichloride and alanine solution were alternatively added slowly in small portions into a round-bottomed flask in an ice-bath, together with the addition of a 4 mol L^{-1} NaOH solution to adjust the pH value to 8.0−9.0. This procedure was finished in an hour. The resulting solution was stirred for another 3 h and then acidified by the addition of a concentrated HCl solution to adjust the pH value at 1−2. Further cooling of the resulting mixture in an ice-bath for several minutes gave a white precipitate, which was separated by filtration and washed by cold water. The crude product was further washed with a 1:1 ethanol and water solution (30 mL), giving a pure product in a yield of 80% after filtration and dryness. m.p.: 216−218 °C; ^{1}H NMR (300 MHz, D_2O) 8.13 (s, 3H, Ar−H), 4.45 (q, 3H, 3J = 7.2 Hz, $-CH(CH_3)COO$), 1.45 (d, 9H, 3J = 7.2 Hz, $-CH_3$); ^{13}C NMR (125 MHz, D_2O) 176.4, 167.9, 133.8, 129.4, 49.4, 15.9. IR (KBr, cm^{-1}): 3366, 3220, 3015, 1727, 1623, 1589, 1535, 1460, 1335, 1309, 1212, 1169, 1118, 912, 807; ESI-MS: m/z 422.00 [M+]; Calculated for C18H21N3O9 [M+] 423.1278; found 423.1254.



Scheme S1. Synthesis of compound **1**.



Scheme S2. Synthesis of **2D** and **2L**.



Scheme S3. Synthesis of **1-Pt**.

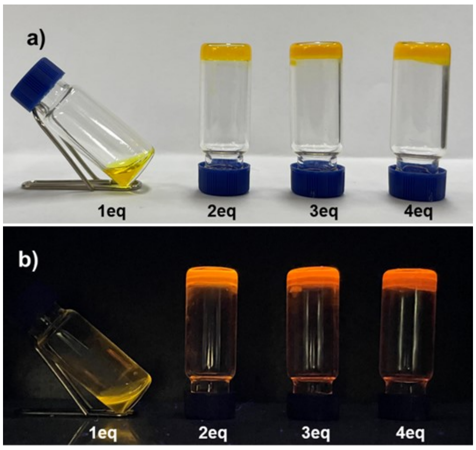


Fig. S1 Photographs of gelation test of **1** (1.0 wt%) with Pt salts at different concentrations (1.0-4.0 equivalent) in a mixture of DMSO/water (v/v, 1:1) (a) taken under ambient light; and (b) taken under UV irradiation (365 nm).

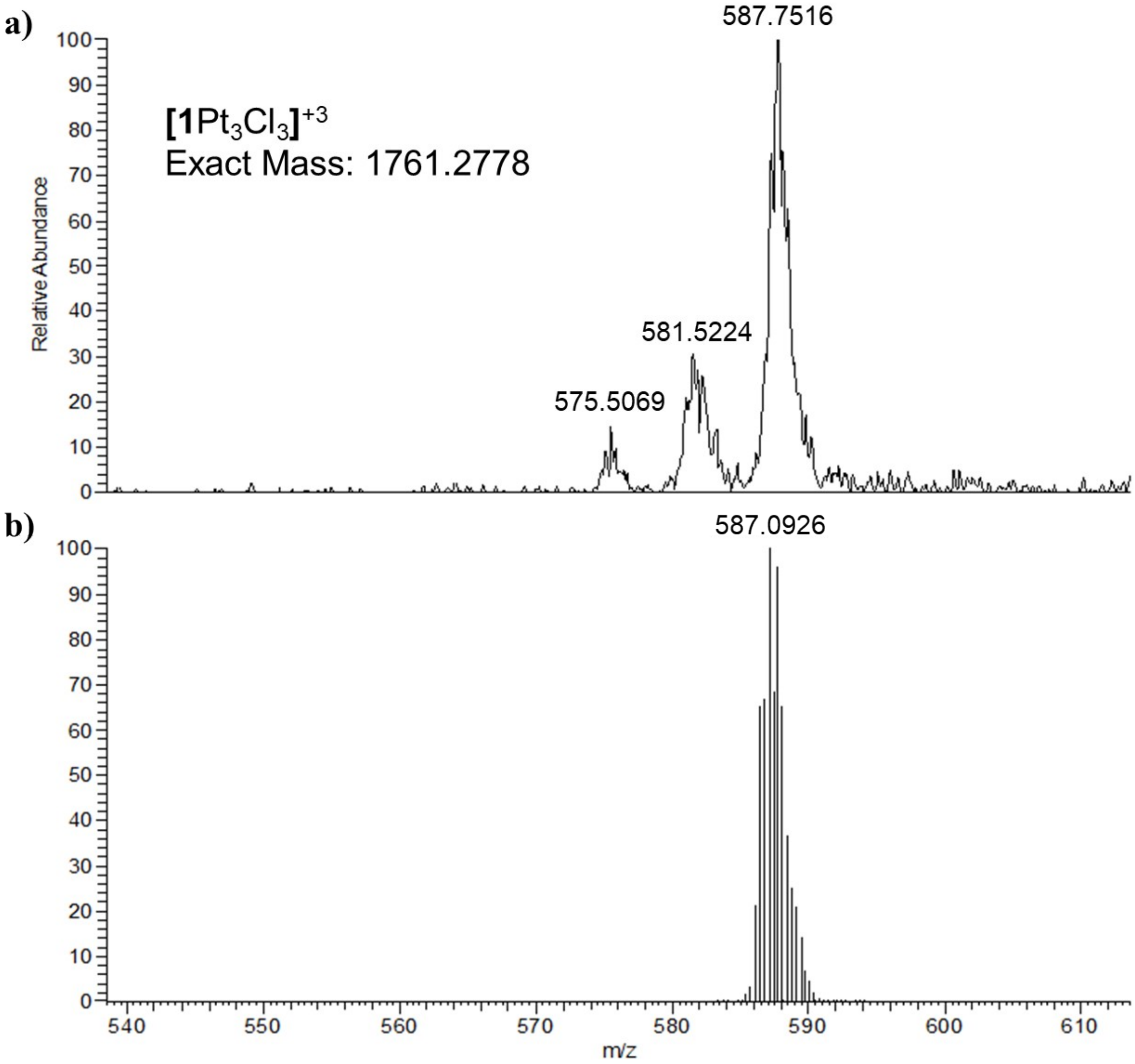


Fig. S2 HR-ESI-mass spectrum of **1-Pt** with (a) experimental and (b) simulated isotopic distribution pattern.

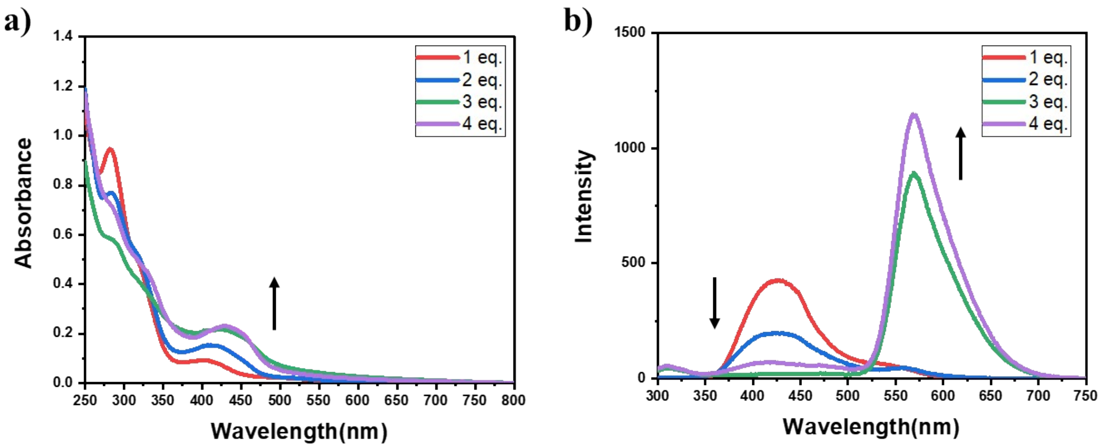


Fig. S3 (a) UV-Vis and (b) emission spectra of **1** (0.1 mM) with Pt salts at different concentrations in a mixture of DMSO/water (v/v, 1:1) (λ_{ex} = 280 nm).

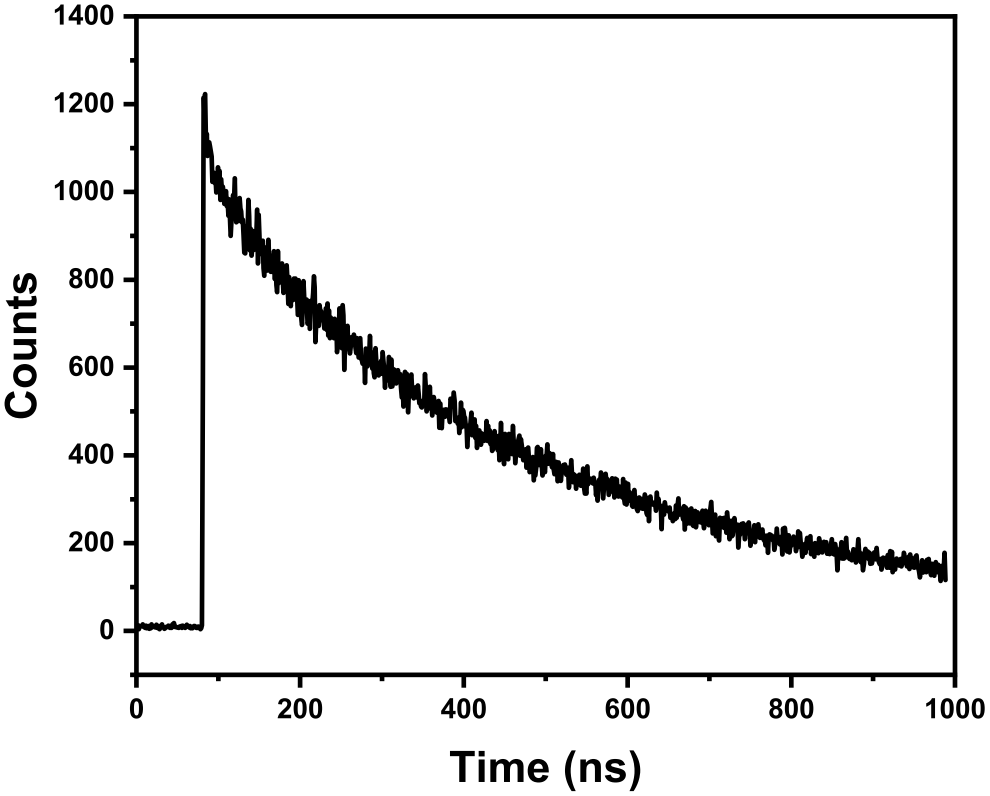


Fig. S4 Lifetime of **1-Pt** (1.0 mM) in a mixture of DMSO/water (v/v, 1:1).

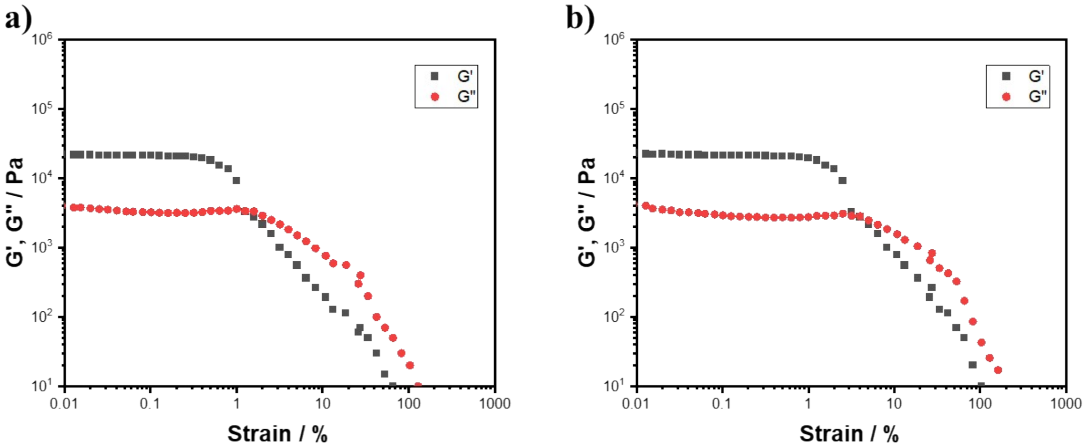


Fig. S5 Rheometer data of (a) **1**-Pt and (b) **1-Pt** with **2D** (1.0 equiv.) (1.0 wt%).

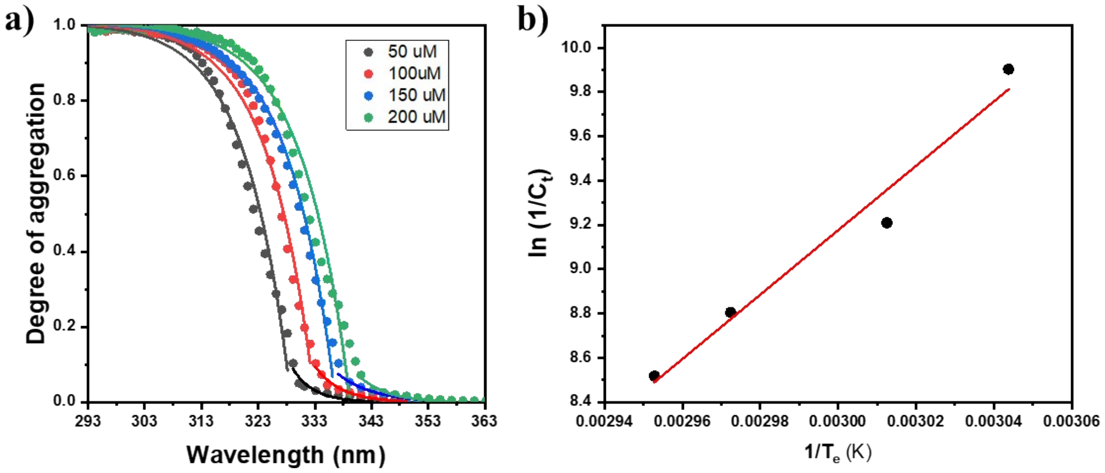


Fig. S6 Temperature-dependent degree of **1-Pt** obtained from the apparent absorption coefficients at λ = 450 nm at different total concentrations in a mixture of DMSO/water (v/v, 1:1) during the heating process. The curves show the resulting fits to the cooperative model proposed by Meijer and co-workers[2,3]. (b) Plot of natural logarithm of the reciprocal c_T as a function of the reciprocal T_e (Correlation coefficient of 0.985), from which the standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) for the assembled **1**-Pt were determined by using van't Hoff Equation: $\Delta H° = -120$ kJ mol^{-1} and $\Delta S° = -286$ J mol^{-1} K^{-1}.

Table S1. Thermodynamic parameters were obtained by fitting the temperature-dependent degree of aggregation (**1-Pt**) in a mixture of DMSO/water (v/v, 1:1) to the cooperative model.

Concentration (μM)	**Te (K)**	**ΔH_e (KJ mol^{-1})**	**K_a**
200	328.5	114	2.0 x 10^{-3}
150	331.9	133	3.1 x 10^{-3}
100	336.4	110	3.9 x 10^{-3}
50	338.6	112	2.9 x 10^{-3}

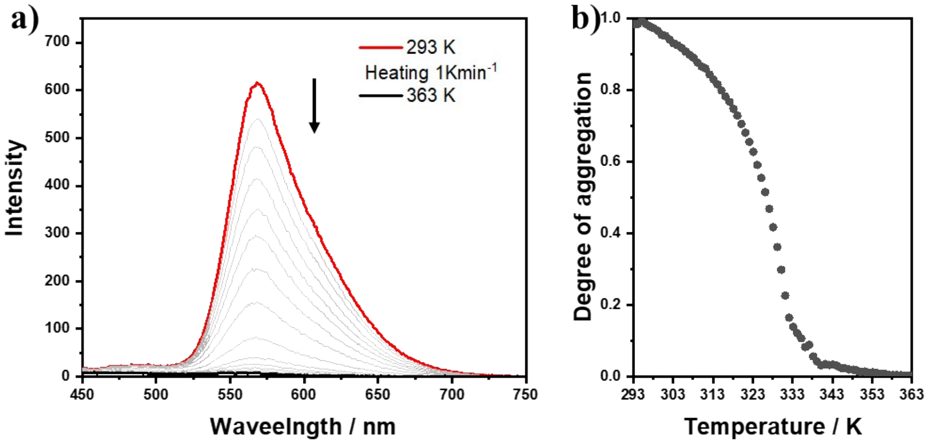


Fig. S7 (a) Temperature-dependent emission spectra changes of **1-Pt** (0.1 mM, λ_{ex} = 280 nm) in a mixture of DMSO/water (v/v, 1:1). (b) Heating curve of **1-Pt**, monitoring the intensity at 568 nm.

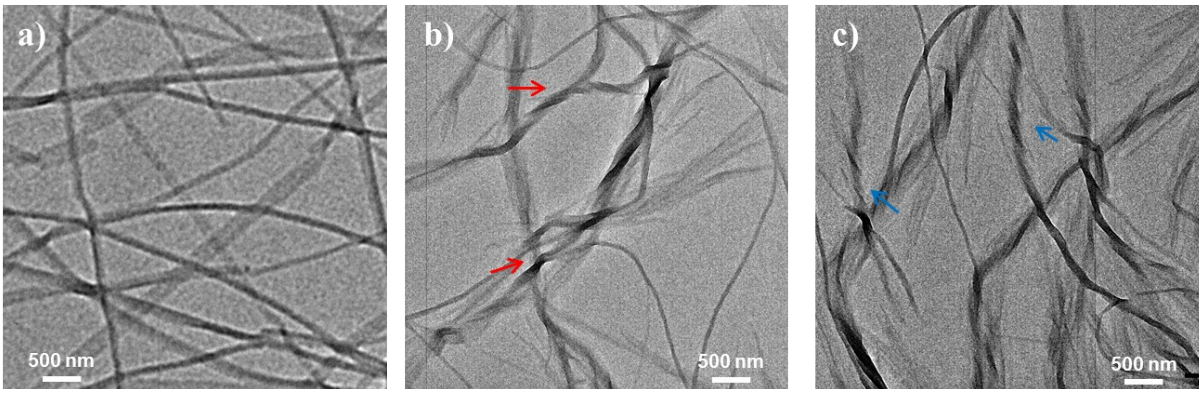


Fig. S8 *TEM images of (a)* ***1-Pt*** *and* ***1-Pt*** *with (b)* ***2D*** *(1.0 equiv.) and (c)* ***2L*** *(1.0 equiv.) The red and blue arrows indicate right- and left-handed structures, respectively.*

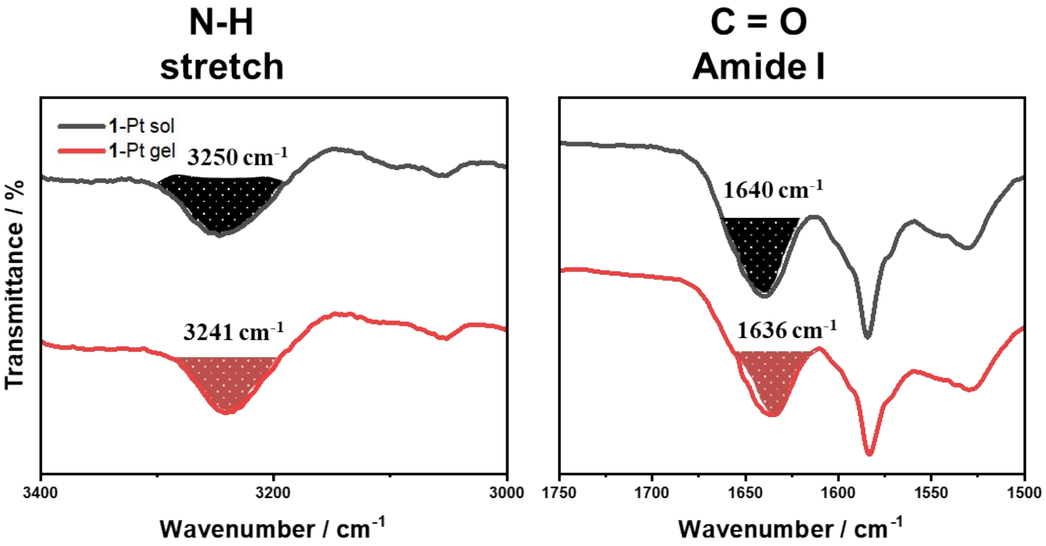


Fig. S9 FT-IR spectra of **1-Pt** in sol (black line, DMSO) and gel (red line, DMSO/water) states.

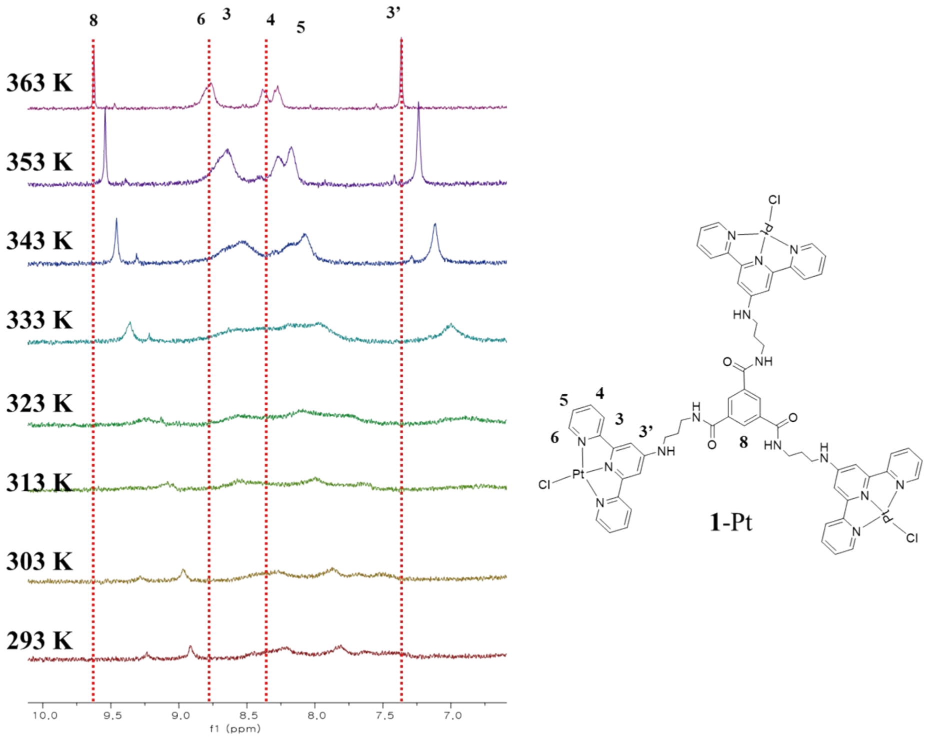


Fig. S10 Temperature-dependent ^{1}H NMR spectra of **1-Pt** (1.0 mM) in a mixture of DMSO-d_6/D_2O (v/v, 1:1)

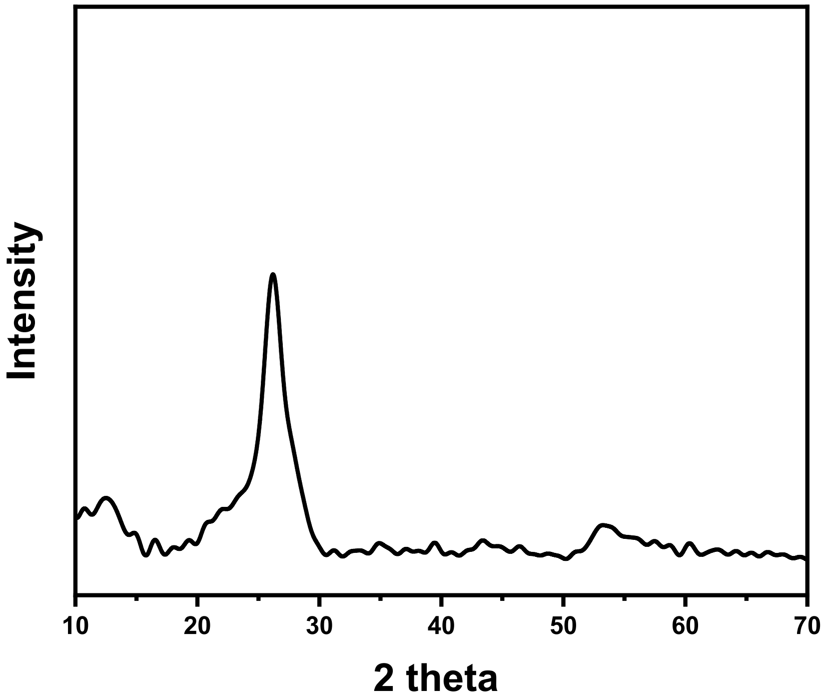


Fig. S11 Wide-angle X-ray diffraction pattern of **1-Pt**.

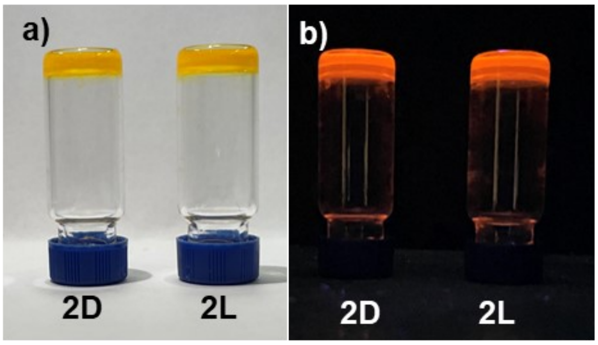


Fig. S12 Photographs of gelation test of **1-Pt** (1.0 wt%) with **2D** and **2L** (1.0 equivalent) in a mixture of DMSO/water (v/v, 1:1) (a) taken under ambient light; and (b) taken under UV irradiation (365 nm).

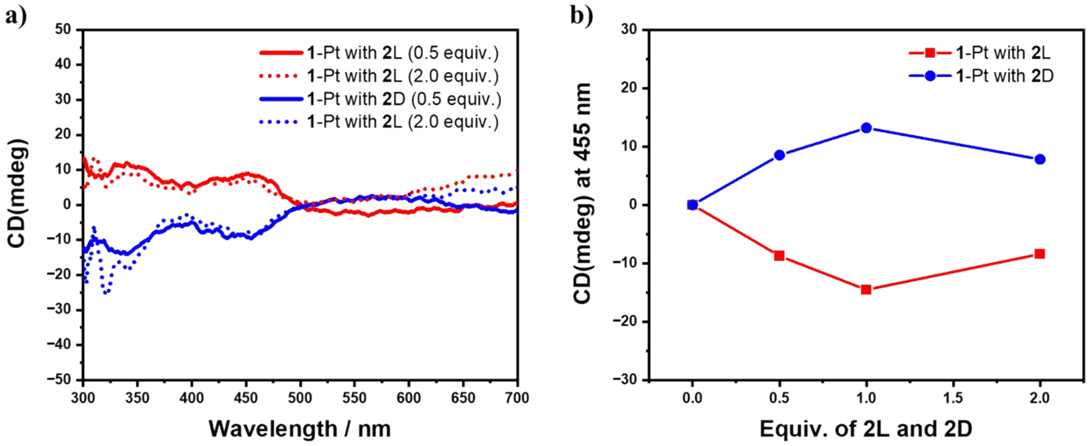


Fig. S13 (a) CD spectra of **1-Pt** (0.1 mM) with **2D** (blue line) and **2L** (red line) in DMSO/water (v/v, 1:1). (b) The plot of CD spectra at 455 nm reveals relative enhancement when using various molar equivalents of **2D** (blue line) and **2L** (red line) added to **1-Pt**.

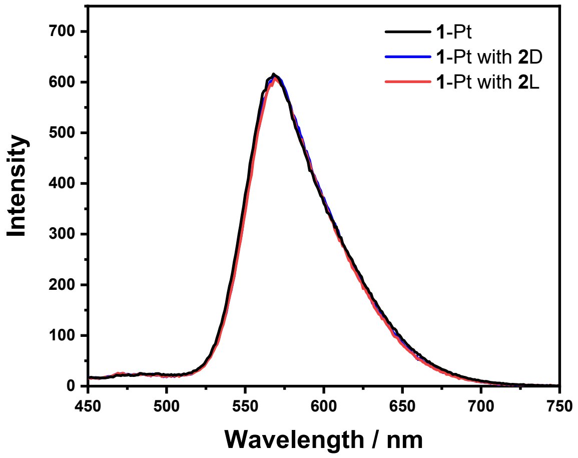


Fig. S14 Emission spectra changes of **1-Pt** (0.1 mM) (black line) and **1-Pt** with **2D** (blue line) and **2L** (red line) in a mixture of DMSO/water (v/v, 1:1).

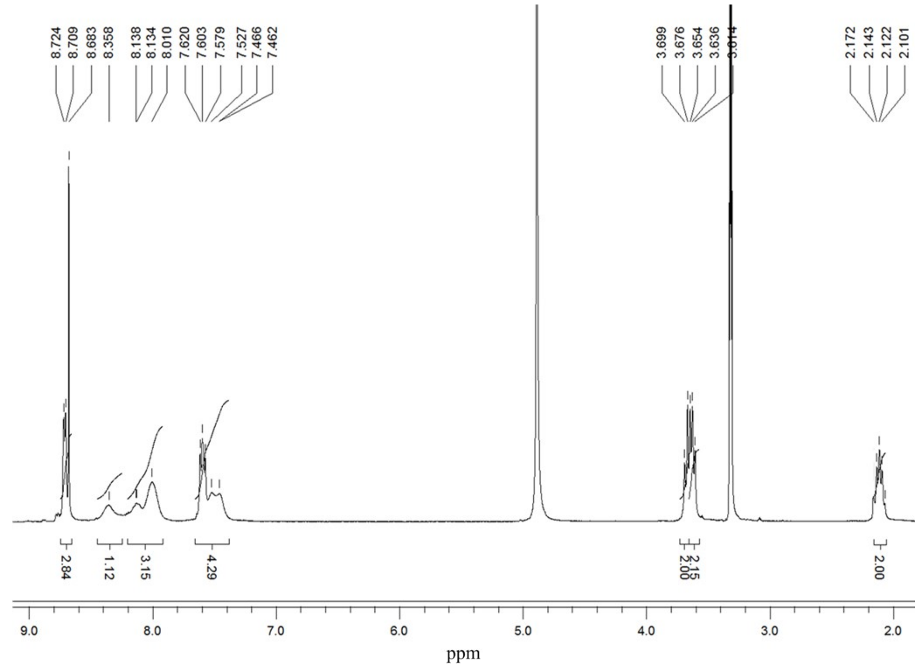


Fig. S15 ${}^{1}H$ NMR spectrum of **1** (300 MHz, CD_3OD).

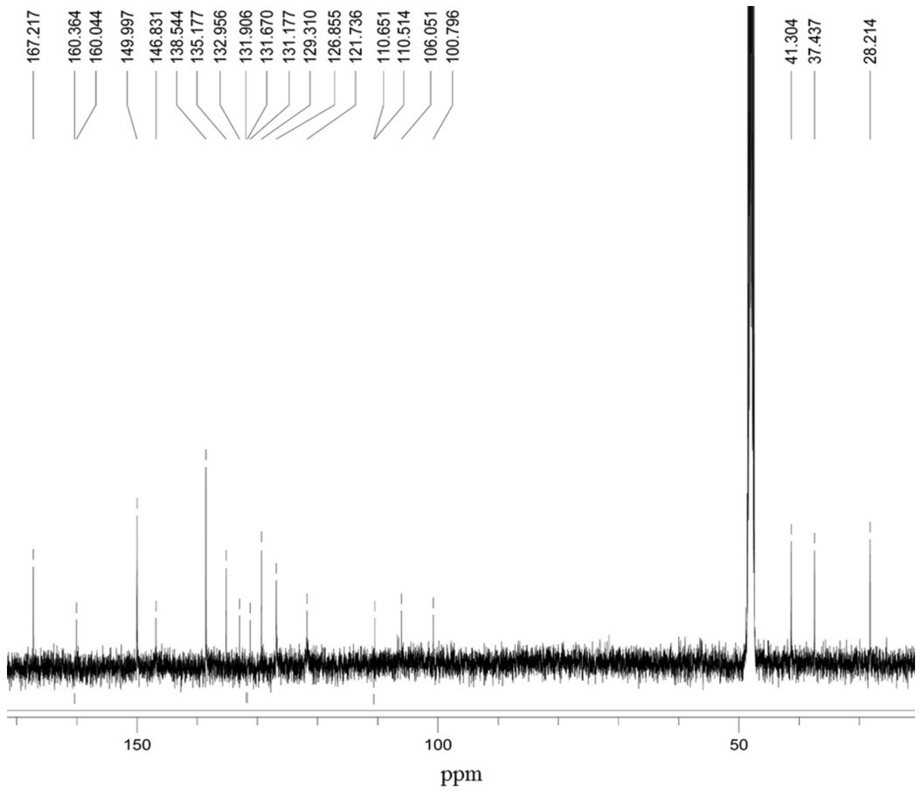


Fig. S16 ${}^{13}C$ NMR spectrum (125 MHz) of **1** (300 MHz, CD_3OD).

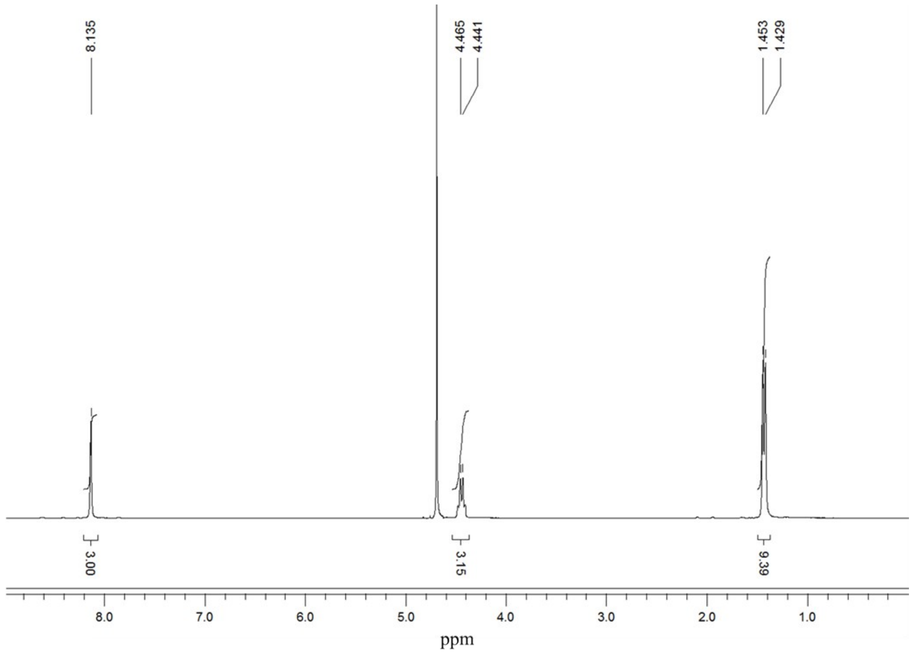


Fig. S17 ^{1}H NMR spectrum of **2D** (300 MHz, D_2O).

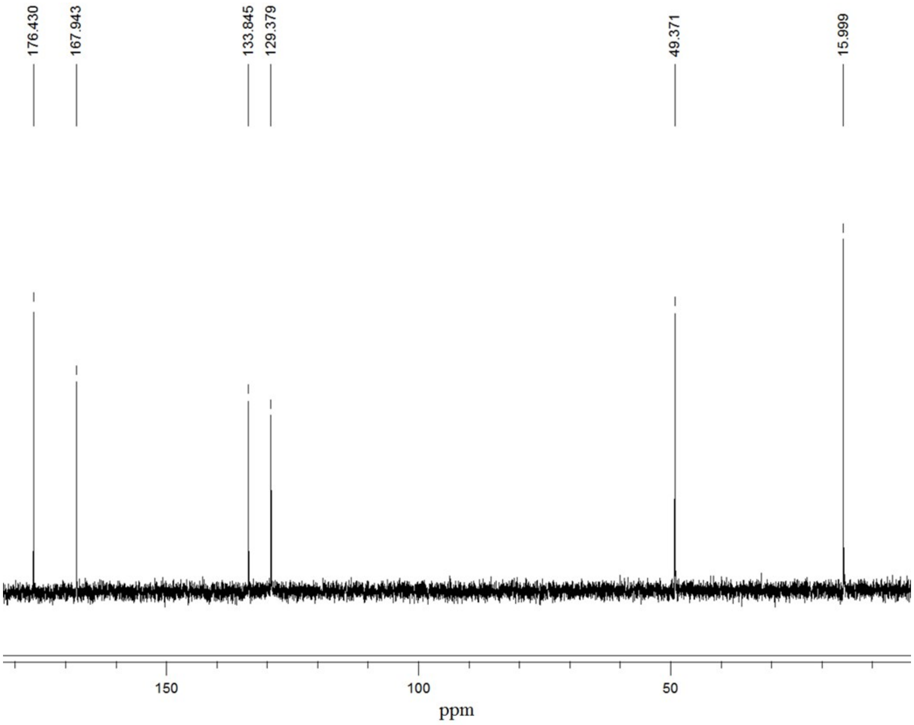


Fig. S18 ^{13}C NMR spectrum of **2D** (125 MHz, D_2O).

References

1. S. H. Jung, J. Jeon, H. Kim, J. Jaworski and J. H. Jung, *J. Am. Chem. Soc.*, 2014, **136**, 6446–6452.
2. M. M. J. Smulders, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* 2008, **130**, 606–611.
3. P. Jonkheijm, P. van der Schoot, A.P.H.J. Schenning, E.W. Meijer, *Science* 2006, **313**, 80–83.