Electronic Supplementary Information (ESI)

Fluorescence Enhancement of Coordination Polymeric Gel

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Experimental procedures

**General Considerations:** All starting materials were obtained commercially and used as received. The elemental analyses were performed in the microanalytical laboratory, Department of Chemistry, National University of Singapore. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker ACF 300 spectrometer operating in the quadrature mode at 300 MHz. The infrared spectra (KBr pellet) were recorded using an FTS165 Bio–Rad FTIR spectrophotometer in the range of 400–4000 cm$^{-1}$. ESI mass spectra were recorded on a Finnigan MAT LCQ mass spectrometer using syringe pump method. Solvent present in the compounds was determined using an SDT 2960 TGA thermal analyzer with a heating rate of 5$^\circ$C min$^{-1}$ from room temperature to 600$^\circ$C. Scanning electron microscopy (SEM) images were taken using a Jeol JSM–6700F field emission scanning electron microscope operated at 5 kV and 10 $\mu$A. The UV-vis absorption spectra were obtained using a Varian Cary 50 UV-vis spectrophotometer with a single cell peltier thermostat to control the working temperature in the range of 15 to 70 $^\circ$C. The gel samples were measured in 0.1 mm-path length quartz cuvette. The emission spectra were recorded on a Spex Fluorolog-2 Model F111 fluorescence spectrofluorometer with a Hamamatsu R928 PMT detector. The fluorescence micrograph was obtained with a Leica DM IRB fluorescence microscope using excitation filter BP 340-380 nm.

**X-ray Crystallographic:** The diffraction experiments were carried out on a Bruker AXS SMART CCD diffractometer with Mo K$\alpha$ ($\lambda = 0.71073$ Å) in a sealed tube. The program SMART was used for collecting frames of data, indexing reflections and determining lattice parameters; SAINT$^1$ was used for integration of the intensity of reflections and scaling, SADAB$^2$s was used for absorption correction and SHELXTL$^3$ was used for space group and structure determination and least-squares refinements on $F^2$. All the non-hydrogen atoms were refined anisotropically. All the C–H hydrogen atoms were placed in calculated positions. All the hydrogen atoms of solvent molecule were located and their positional parameters were refined in the least-squares refinements. The disordered positions of lattice water O7 was resolved with occupancy of 0.5.
Mechanical Spectroscopy Measurements on Three-Dimensional Structures: These were carried out on freshly prepared gels using a controlled stress rheometer (AR–1000N, TA Instruments Ltd., New Castle, DE, USA). Parallel plate geometry of 40 mm diameter and 1.5 mm gap was employed throughout. Following loading, the exposed edges of samples were covered with a silicone fluid from BDH (100 cs) to prevent water loss. Dynamic oscillatory work kept a frequency of 1 rad s\(^{-1}\). The following tests were performed: increasing amplitude of oscillation up to 100% apparent strain on shear, time and frequency sweeps at 25°C (60 min and from 0.1 to 10 rad s\(^{-1}\), respectively), and a heating run to 75°C at a scan rate of 1°C min\(^{-1}\). Unidirectional shear routines were performed at 25 °C covering a shear-rate regime between 10\(^{-1}\) and 10\(^{3}\) s\(^{-1}\). Dynamic and steady shear measurements were conducted in triplicate.

Synthesis and Characterization:

Synthesis of H\(_2\)mugly, 1: The ligands are synthesized according to the literature method.\(^4\) A warm solution of 4-methylumbelliferrone (0.881 g, 5 mmol) in ethanol (30 mL) was treated with glycine (0.375 g, 5 mmol) in water (20 mL) and formaldehyde (37%, 370 µL, 5 mmol). The reaction mixture was heated at 90°C for 8 hours. The resulting precipitate was filtered off and recrystallized using 1:1 water:ethanol solution. Yield: 0.72 g (55%). m.p. 268-269°C. Anal Calcd. For C\(_{13}\)H\(_{13}\)NO\(_5\) (263.25): calcd. C 59.31, H 4.98, N 5.32; found C 59.54, H 5.32, N 5.07. IR (cm\(^{-1}\)):\(\nu\)(OH) 3433;\(\nu\)(NH) 3174;\(\nu\)\(_{as}\)(COO\(^{-}\)) 1720;\(\nu\)\(_{as}\)(COO\(^{-}\)) 1598;\(\nu\)\(_s\)(COO\(^{-}\)) 1389. \(^1\)H NMR (300 MHz; D\(_2\)O; ppm): \(\delta\) 7.50 (d, 1H, Ar), 6.65 (d, 1H, Ar), 5.91 (s, 1H, Ar), 4.28 (s, 2H, -CH\(_2\)NH), 3.57 (s, 2H, -NHCH\(_2\)), 2.35 (s, 3H, -ArCH\(_3\)). \(^1\)C NMR (300MHz; D\(_2\)O; ppm): \(\delta\) 173.73 (-COOH), 171.79, 165.08, 157.60, 153.51, 126.03, 118.04, 107.82, 106.85, 104.35 (Ar), 49.16 (-NHCH\(_2\)), 40.66 (-CH\(_2\)NH), 17.84 (-ArCH\(_3\)). EI-MS: m/z 263.1.

Synthesis of H\(_2\)muala, 2: H\(_2\)muala is prepared using same procedure. Yield: 0.78 g, (56%). m.p. 296-298°C. Anal. Calcd. For C\(_{14}\)H\(_{15}\)NO\(_5\) (277.28): calcd. C 60.64, H 5.45, N 5.05; found C 60.70, H 5.60, N 5.04. IR (cm\(^{-1}\)):\(\nu\)(OH) 3433;\(\nu\)(NH) 3146;\(\nu\)\(_{as}\)(COO\(^{-}\)) 1721;\(\nu\)\(_{as}\)(COO\(^{-}\)) 1580;\(\nu\)\(_s\)(COO\(^{-}\)) 1392. \(^1\)H NMR (300MHz; D\(_2\)O; ppm): \(\delta\) 7.29 (d, 1H, Ar), 6.52 (d, 3H, -ArCH\(_3\)), 5.91 (s, 1H, Ar), 4.28 (s, 2H, -CH\(_2\)NH), 3.57 (s, 2H, -NHCH\(_2\)), 2.35 (s, 3H, -ArCH\(_3\)).
1H, Ar), 5.68 (s, 1H, Ar), 3.99 (s, 2H, -CH₂NH), 3.54 (q, 1H, -NHCH₂), 2.16 (s, 3H, -ArCH₃), 1.45 (d, 3H, -CH₃). ¹³C NMR (300 MHz; D₂O; ppm): δ 176.08 (-COOH), 171.78, 164.97, 157.62, 153.35, 126.27, 117.97, 107.90, 105.78, 104.46 (Ar), 56.92 (-NHCH), 39.72 (-NHCH₂), 17.86 (-ArCH₃), 15.24 (-CH₃). Ei-MS: m/z 277.1.

**Synthesis of [Zn(mugly)(H₂O)]·0.5H₂O, 3:** To the H₂mugly (26.3 mg, 0.1 mmol) in LiOH (4.8 mg, 0.2 mmol) in water (2 mL), Zn(CH₃COO)₂·2H₂O (22 mg, 0.1 mmol) in water (2 mL) was added. The hydrogel 3 is formed instantly. The crystalline powder of 3 can be obtained by slow evaporation from methanol and DMF solvent mixture. Yield: 21 mg, (60%). Anal. Calcd. For ZnC₁₃H₁₄NO₆.5 (353.65): calcd. C 44.15, H 3.99, N 3.96; found C 44.78, H 4.14, N 3.83. IR (cm⁻¹): υ(OH) 3393; υ(NH) 3256; υ as (COO⁻) 1695; υ as (COO⁻) 1593; υ s (COO⁻) 1390. IR of freeze dried sample (cm⁻¹): υ(OH) 3433; υ(NH) 3247; υ as (COO⁻) 1663; υ s (COO⁻) 1575; υ as (COO⁻) 1395. ¹H NMR (300 MHz; d₆-DMSO; ppm): δ 7.37 (d, 1H, Ar), 6.59 (d, 1H, Ar), 5.84 (s, 1H, Ar), 3.96 (s, 2H, -CH₂NH), 3.56 (s, 2H, -NHCH₂), 2.31 (s, 3H, -ArCH₃), 1.19 (d, 3H, -CH₃). ¹³C NMR (300 MHz; d₆-DMSO; ppm): δ 173.28 (-COOH), 171.66, 160.88, 154.24, 153.55, 124.79, 117.60, 110.27, 105.88, 104.35 (Ar), 51.56 (-NHCH₂), 42.94 (-CH₂NH), 18.26 (-ArCH₃). ESI-MS: 381.7 [Zn(mugly)(H₂O)₃+H⁺]. Weight loss as per TGA: 6.9% (calculated for 1.5 H₂O: 7.6%)

**Synthesis of [Zn(muala)(H₂O)]·0.5H₂O, 4.** To the H₂muala (27.7 mg, 0.1 mmol) in LiOH (4.8 mg, 0.2 mmol) in methanol (10 mL), Zn(CH₃COO)₂·2H₂O (22 mg, 0.1 mmol) in DMF (10 mL) was added. The reaction was stirred for 30 min and filtered. Colourless crystals suitable for X-ray crystallographic analysis were obtained after 2 weeks. Yield: 19 mg, (50%). Anal. Calcd. For ZnC₁₄H₁₆NO₆.5 (367.65): calcd. C 45.73, H 4.39, N 3.81; found C 46.21, H 4.61, N 3.88. IR (cm⁻¹): υ(OH) 3447; υ(NH) 3265; υ as (COO⁻) 1656; υ as (COO⁻) 1584; υ s (COO⁻) 1394. IR for freeze dried sample (cm⁻¹): υ(OH) 3437; υ(NH) 3266; υ as (COO⁻) 1656; υ as (COO⁻) 1580; υ s (COO⁻) 1415. ¹H NMR (300MHz; d₆-DMSO; ppm): δ 7.38 (d, 1H, Ar), 6.57 (d, 1H, Ar), 5.85 (s, 1H, Ar), 3.98 (d, 2H, -CH₂NH), -NHCH₂ (not detected due to overlapping with water), 2.31 (s, 3H, -ArCH₃), 1.19 (d, 3H, -CH₃). ¹³C NMR (300 MHz; d₆-DMSO; ppm): δ 176.63 (-COOH), 171.00, 160.94, 154.27, 153.40, 124.77, 117.55, 110.56, 107.81, 106.21 (Ar), 58.85 (-NHCH), 42.23 (-NHCH₂), 22.71 (-ArCH₃), 20.19 (-CH₃).
18.30 (-CH$_3$). ESI-MS: 397.9 [Zn(mual)(H$_2$O)$_3$+H]$. Weight loss as per TGA: 4.9% (calculated for 1 H$_2$O: 5.0%).

**Figure S1.** (a) A ball and stick diagram of 4; (b) A portion of the 1D coordination polymer of 4; (c) Packing of 4 viewed from the c-axis; (d) Packing of 4 viewed down the b-axis.
Figure S2. UV-vis spectral traces of 1 upon Zn$^{2+}$ binding in H$_2$O in the presence of two equivalents of LiOH ([1] = 9.12 × 10$^{-5}$ M).

Figure S3. Job’s plot for 1:1 binding of 1 with Zn$^{2+}$ in H$_2$O, with the absorbance at 360 nm monitored (χ$_{\text{host}}$ = [1]/[1]+[Zn$^{2+}$] and ΔA is the change in absorbance at 360 nm).
Figure S4. UV-vis absorption spectra of 1 ([1] = 9.3 × 10^{-5} M) in the presence of one equivalent of Zn^{2+} at various pH in buffer solutions.

Figure S5. UV-vis absorption spectra of hydrogel 3 ([3] = 25 mM) in 0.1 mm-path length quartz cuvette at various temperatures from 15 °C to 70 °C.
**Figure S6.** UV-vis absorption spectra of $1 + \text{Co}^{2+}$, $1 + \text{Ni}^{2+}$ in H$_2$O, and hydrogel 3 ([1] and [3] = 25 mM).

**Figure S7.** Emission spectra of 1 upon addition of Zn$^{2+}$ in H$_2$O in the presence of two equivalents LiOH upon excitation at $\lambda = 352$ nm.
Figure S8. Emission spectra of (a) hydrogel 3 and 1 + Co$^{2+}$ upon excitation at 318 nm, and (b) hydrogel 3 and 1 + Ni$^{2+}$ upon excitation at 310 nm.

Figure S9. Emission spectra of hydrogel 3 before and after pH response upon excitation at $\lambda = 340$ nm.
**Figure S10.** Dynamic oscillation strain sweep of $G'$ and $G''$ for hydrogel 3 at frequency of 1 rad s$^{-1}$ and 25 °C.

**Figure S11.** Dynamic oscillation time sweep of $G'$ and $G''$ for hydrogel 3 at strain of 0.5 %, frequency of 1 rad s$^{-1}$ and 25 °C.
References: