Electronic Supporting Information

Fluorescent hydrogel formation from carboxyphenyl-terpyridine†

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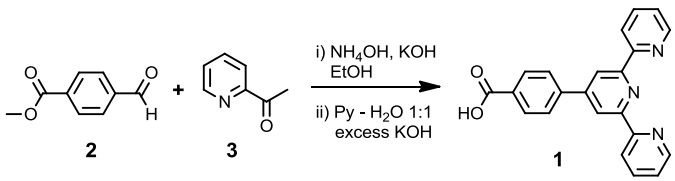
1. Materials

All starting materials were obtained from Sigma Aldrich UK and used as received. Solvents and metal salts or bases were obtained from Fisher Scientific UK. Deuterated DMSO was obtained from Apollo Scientific UK and silver tetrafluoroborate was obtained from Acros UK.

2. Characterisation Methods and Equipment

NMR Spectra (^{1}H, ^{13}C and COSY experiments) were recorded on Bruker DPX400, operating on 400MHz for proton and 101MHz for carbon NMR spectra. Mass Spectrometry was performed on a Waters 2700 Sample Manager. UV-Vis spectra were collected using a Varian Cary Bio 300 with 3 mM concentration in a 0.0125 M aqueous sodium hydroxide solution. Fluorescence spectra were taken on Varian Eclipse, showing emission at 376 nm in the gel and solution state, and an extra peak at 528nm in the gel state. Individual spectra were recorded at 300-900 nm going from 20 °C to 70 °C and back down to 20 °C at 10 °C intervals, by setting the temperature and scanning after ten minutes equilibration time. Melting curves were taken with variable rate of the temperature increase at 1 °C, 0.5 °C and 0.2 °C per minute. The settings used to collect the data were: excitation: 275 nm (excitation slit: 5 nm), emission: 376 nm and 528 nm (emission slit: 5 nm), averaging time: 1 s. All scanning electron micrographs (SEM) were taken using a Phillips XL30 ESEM, samples were prepared on the substrate dried under high-vacuum overnight.

3. Synthesis of Terpy-Ph-CO_2K



Methyl-4-formal-benzoate **2** (2.46g, 15mmol) was dissolved in ethanol (250mL) and 2-acetylpyridine **3** (3.4mL, 30mmol) was added. Aqueous ammonia solution (35% v/v, 3mL, 45mmol) and potassium hydroxide (2.56g, 45mmol) were added to the reaction mixture. The reaction was left to stir overnight, and the reaction mixture had turned an opaque brown colour. Another portion of ammonia was added (35% v/v, 2mL, 30mmol) and after approximately 3 hours, the reaction mixture had turned an opaque orange. A TLC of the reaction showed formation of one product. The mixture was filtered, giving a white-pink coloured solid. Crystallisation from boiling methanol gave the intermediate ester. MS-ESI (+ve)($C_{23}H_{17}N_3O_2$): Mass calcd. 367.132; Found mass 385.3 [M+NH3]. Rf (10% ammonia in methanol): 0.88.

Terpy-Ph-CO_2Me was dissolved in a pyridine-water mixture (1:1 ratio, 100mL total). Potassium hydroxide (2.43g) was added and the reaction was heated to reflux overnight. The potassium hydroxide was neutralised with hydrochloric acid (35% v/v, 5mL). As the acid was added a white precipitate was observed, this was collected by filtration and washed with approximately 70mL of water. Yield: 874.6mg (310mmol, 77%). ^{1}H NMR (400 MHz, DMSO-d^6): δ ppm 7.55 (ddd, J=6.9, 5.7, 1.0 Hz, 2 H, **2**); 8.06 (m, J=7.6, 1.5 Hz, 4 H, **3 & 10**); 8.16 (d, J=8.6 Hz, 2 H, **11**); 8.70 (d, J=8.1 Hz, 2 H, **4**); 8.77 (s, 2 H, **7**); 8.78 (d, J=4.0 Hz, 1 H, **1**); 13.07 - 13.24

(s, 1 H, **14**). ^{13}C NMR (101 MHz, DMSO-d^6): δ ppm 118.44 (CH, **1 or 7**); 121.12 (CH, **4**); 125.04 (CH, **2**); 127.55 (CH, **3**); 130.61 (CH, **11**); 137.92 (CH, **10**); 148.85 (C, **5, 6, 8, 9, 12 or 13**); 149.60 (CH, **1 or 7**); 155.07 (C, **5, 6, 8, 9, 12 or 13**); 156.25 (C, **5, 6, 8, 9, 12 or 13**); 167.18 (C, **5, 6, 8, 9, 12 or 13**). R_f (10% ammonia in methanol): 0.84. UV-Vis: (1.25M NaOH in water, 30μM): λ_{max} 275nm. Emission: λ_{em} (relative intenisty) - 376nm (1), 528nm (0.4).

4. Gelation experiments

Gelation in Methanol

The appropriate weight of Terpy-Ph-CO_2H **1** was measured into a 3.5mL sample vial, and 0.5mL of the appropriate concentration of sodium hydroxide in methanol was added. The vials were then heated to 70°C in a water bath for fifteen minutes to ensure all the material dissolved. No gel formation was observed.

Sample Name	Weight of 1 /mg	Concentration of NaOH / M	Solvent
A1	2	1	Methanol
A2	3	1	Methanol
A3	5	1	Methanol
A4	3	2	Methanol
A5	5	1.5	Methanol

Gelation in Water/NaOH

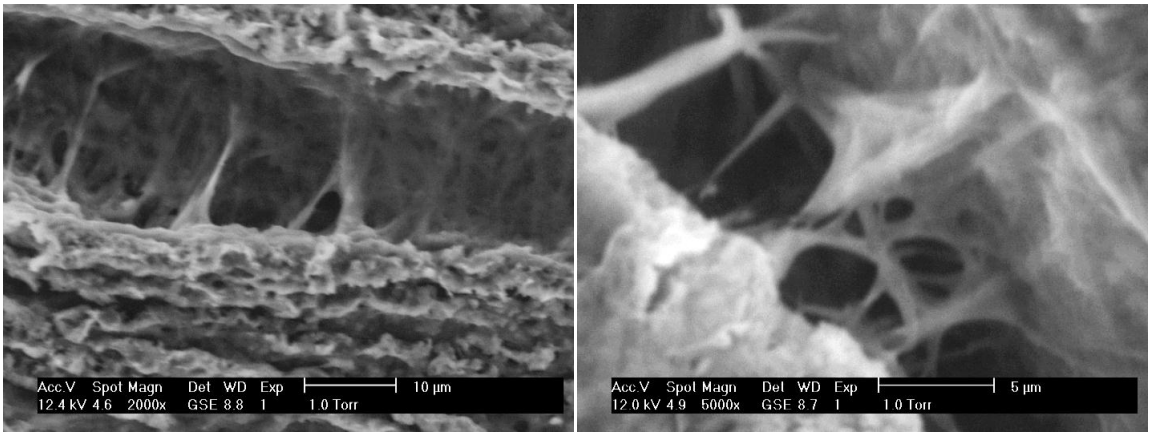
The appropriate weight of Terpy-Ph-CO_2H **1** was measured into a 3.5mL sample vial, and the appropriate concentration of sodium hydroxide (0.5mL) in water was added. The vials were then heated above 70°C in a water bath for fifteen minutes to ensure all the material dissolved.

Sample Name	Weight of 1 /mg	Concentration of NaOH / M	Solvent
B1	2	1	Water
B2	3	1	Water
B3	5	1	Water
B4	3	2	Water
B5	5	1.5	Water
B6	3	0.25	Water
B7	3	0.5	Water
B8	5	0.25	Water
B9	5	0.5	Water
B10	5	2	Water
B11	4	0.25	Water
B12	4	0.5	Water
B13	4	0.75	Water
B14	5	0.75	Water
B15	6	0.5	Water

B16	7	0.5	Water
B17	4	1	Water
B18	8	0.5	Water
B19	9	0.5	Water
B20	6	1	Water
B21	7	1	Water
B22	7	1.25	Water
B23	6	0.75	Water
B24	7	0.75	Water
B25	8	0.75	Water
B26	9	0.75	Water
B27	10	0.5	Water
B28	10	0.75	Water
B29	5	1.25	Water
B30	7	0.25	Water
B31	8	0.25	Water
B32	9	0.25	Water

Selected SEM pictures of gels.

B9 fresh:



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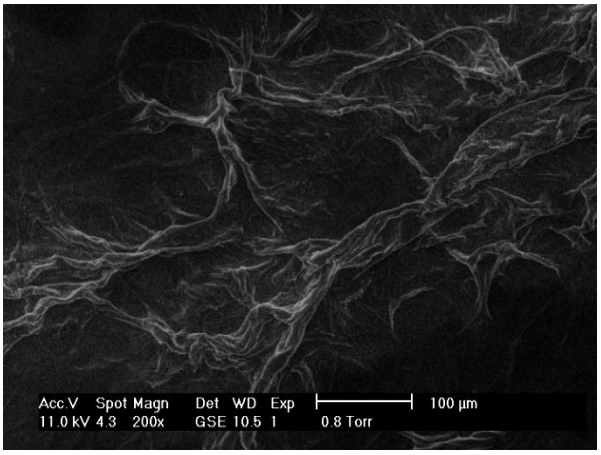
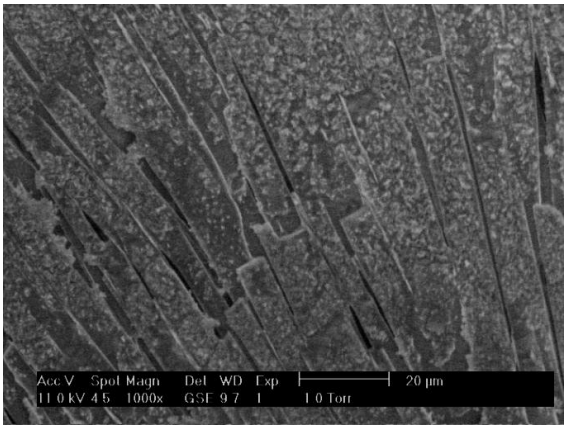


B11 aged three weeks:



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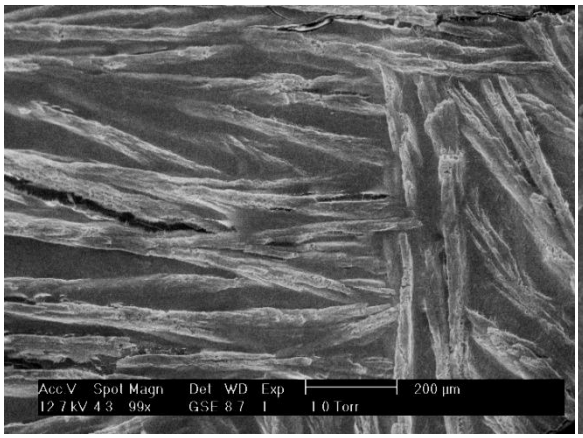

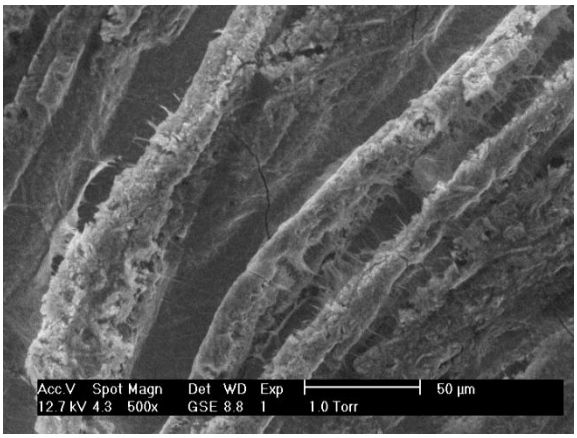

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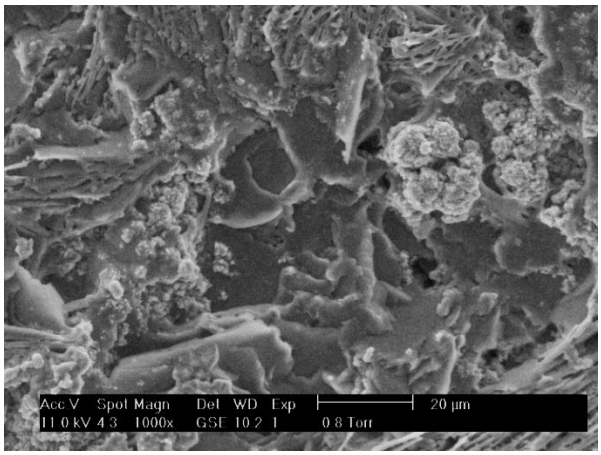
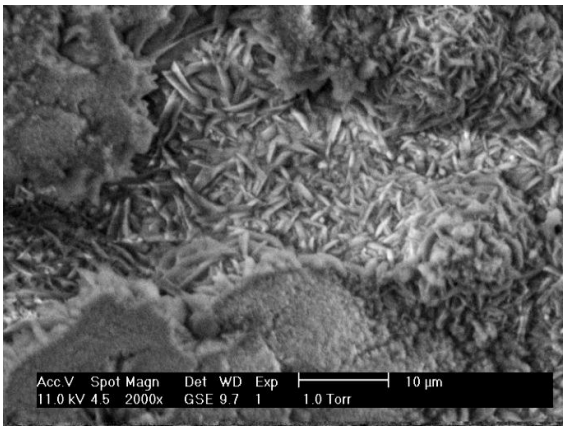


B11 aged three weeks:



Gelation with Water/Ammonia

The appropriate weight of Terpy-Ph-CO_2H **1** was measured into a 3.5mL sample vial, and the appropriate concentration of ammonium solution (0.5mL) was added. No gel formation was observed.

Sample Name	Weight of 1 /mg	Concentration of ammonia / M	Solvent
C1	4	1.5	Water
C2	4	2	Water
C3	4	2.5	Water
C4	6	1.5	Water
C5	6	2	Water
C6	6	2.5	Water
C7	7	15	Water
C8	7	11.25	Water
C9	7	7.5	Water
C10	7	3.75	Water

Gelation with Water/LiOH

Terpy-Ph-CO_2H **1** (5mg) was measured into a 3.5mL sample vial, and the appropriate concentration of lithium hydroxide in water (0.5mL) was added. The vials were then sonicated in a water bath for thirty minutes to ensure all the material dissolved. No gel formation was observed.

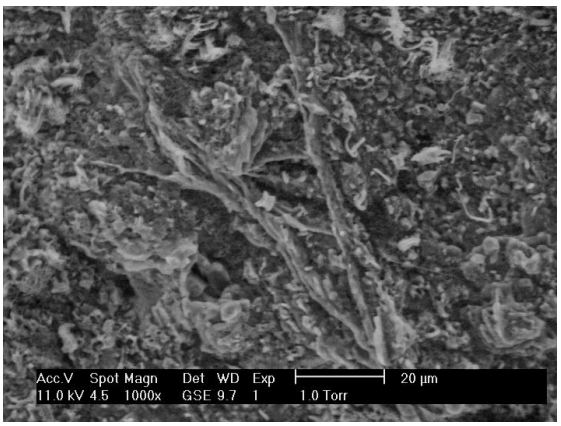
Sample Name	Weight of 1 /mg	Concentration of LiOH / M	Solvent
D1	5	0.25	Water
D2	5	0.5	Water
D3	5	0.75	Water
D4	5	1	Water

Gelation with Water/KOH

Terpy-Ph-CO_2H **1** (5mg) was measured into a 3.5mL sample vial, and the appropriate concentration of potassium hydroxide in water (0.5mL) was added. The vials were then sonicated in a water bath for thirty minutes to ensure all the material dissolved. Gel formation was only observed at 4 °C.

Sample Name	Weight of Terpy-Ph-CO_2H /mg	Concentration of KOH /M	Solvent
E1	2	0.25	Water
E2	3	0.5	Water
E3	5	0.75	Water
E4	3	1	Water
E5	5	1.5	Water

E3 fresh:

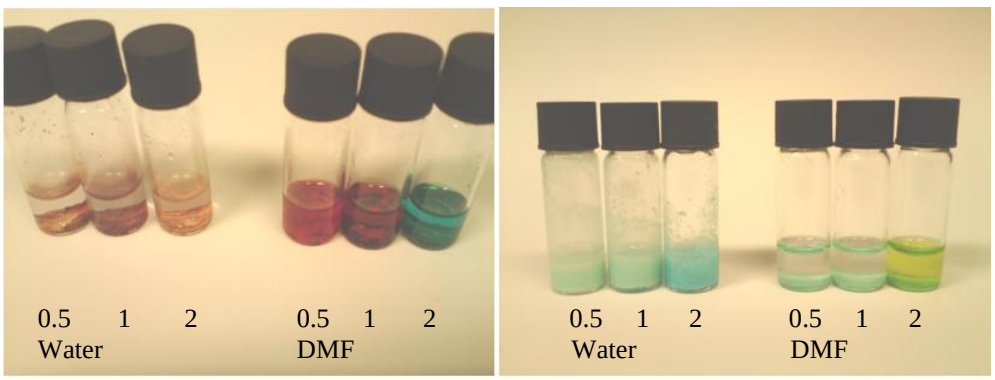


Gelation Experiments with metallated Terpy-Ph-CO_2H

Metallation with Cobalt and Copper

Stock solutions of 11.4, 22.8 and 45.6mM of copper (II)and cobalt (II) chloride (giving 0.5:1, 1:1 and 2:1 ratios of metal chloride to **1** respectively) were made up in two different solvents, water and dimethyl formamide. Compound **1** (4mg) was weighed out into sample vials and the metal chloride solution (0.5mL) with appropriate solvent was added. The vials were heated to 120°C for fifteen minutes. No gel formation was observed.

Sample Name	Weight of 1 /mg	Metal Ion (2+)	Ratio of metal ion to 1	Solvent
F1	4	Co	0.5	DMF
F2	4	Co	1	DMF
F3	4	Co	2	DMF
F4	4	Co	0.5	Water
F5	4	Co	1	Water
F6	4	Co	2	Water
G1	4	Cu	0.5	DMF
G2	4	Cu	1	DMF
G3	4	Cu	2	DMF
G4	4	Cu	0.5	Water
G5	4	Cu	1	Water
G6	4	Cu	2	Water



F4 F5 F6 F1 F2 F3 G4 G5 G6 G1 G2 G3

5 Water Absorption and 18-crown-6 Experiments

A B13 sample gel and a B16 sample gel (see above) were prepared in 5mL vials. They were heated at 75°C for fifteen minutes and left to cool to room temperature; water (0.25mL) was placed on top of the gels and the vials were left to rest on a flat surface.