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Instantaneous gelation of a new copper(II) metallogel amenable to encapsulation of a luminescent lanthanide cluster†‡

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Combining copper(II) chloride, 4-(1*H*-pyrazol-3-yl)pyridine and triethylamine in dimethylformamide (DMF) results in the instantaneous formation of a metallogel with as little as 0.51 wt% of gelator. The metallogel was found to encapsulate a luminescent lanthanide cluster, yielding a luminescent metallogel.

Molecular gels are self-assembling nanoscale architectures heralded as crucial precursors to a new range of smart materials.[1] Potential applications arising from molecular gels include targeted drug delivery,[2] light harvesting,[3] sensing,[4] catalysis[5] and trace hydrocarbon scavenging.[6] At the forefront of molecular gel research are the metallogels, which are gels formed from gelators containing complexed metals or clusters.[6,7] Metallogels have been shown to be responsive to external stimuli[7f] and make possible a range of spectroscopic, magnetic, catalytic and redox properties that are inherent to the metal ions they contain.[7b,g]

Herein we describe a copper(II) containing discrete metal complex gelator able to gel dimethylformamide (DMF) at 0.51 wt%. Analyses of the gel include *in situ* fourier transform infrared (FTIR) spectroscopy, single crystal X-ray crystallography,§ scanning electron microscopy (SEM) and Raman spectroscopy. Variations to the solvent, cation or anion were found to disrupt the gelation process, typically yielding precipitates (see Supplementary Information‡). By contrast, dissolution of a luminescent europium cluster, $[Eu_5(OH)_5(dbm)_{10}]$ (**1**) (dbm = dibenzoylmethanide), in the DMF solution phase was not found to disrupt gelation, highlighting the potential of this metallogel to encapsulate molecular devices.

A DMF solution containing both 4-(1*H*-pyrazol-3-yl)pyridine[8] (**Hppy**) and triethylamine reacts with a DMF solution of hydrated copper(II) chloride in an equimolar ratio to instantaneously form a metallogel. The pyrazole group is versatile in that it may participate in both metal coordination and hydrogen bonding. Low molecular

weight gelators to contain the pyrazole group are yet to achieve widespread use.[9] To gain greater insight into the self-assembly processes that govern gel formation, the experiment was monitored using *in situ* FTIR spectroscopy. To maximise the information obtained from gelation, the three components were each dissolved in DMF and combined sequentially in order of **Hppy**, copper(II) chloride and triethylamine. In solution, the ligand **Hppy** displays strong bands at 1654 and 1606 cm^{-1} assigned as the C=C and C=N stretches of the pyridine ring.[10] Less intense planar vibrations assigned to the pyrazole ring were observed at 1417, 1400 and 1360 cm^{-1}.[11] The addition of copper(II) chloride in the absence of base results in shifting of both the pyridine and pyrazole bands. The pyridine band at 1606 was seen to shift to 1620 cm^{-1} and the intensity of the band at 1654 cm^{-1} was seen to triple, attributed to dipole polarisation induced by coordination of the metal. The pyrazole band at 992 cm^{-1}, attributed to the γNH vibration, was observed to shift to 1025 cm^{-1} and bands at 1360 and 1417 cm^{-1} were observed to shift to 1365 and 1421 cm^{-1} respectively, which is suggestive of secondary interactions located at the pyrazole ring. The addition of base resulted in gelation, which had little observable effect on the IR spectrum relative to the solution of ligand and metal salt. A broad band at 3183 cm^{-1} assigned to the N–H stretching vibration was seen to decrease in intensity, indicative of deprotonation of the pyrazole. Weak bands attributed to the formation of triethylamine hydrochloride were also observed.

The *in situ* FTIR evidence suggests that the self-assembly process initiates upon combining **Hppy** and copper(II) chloride. Slow evaporation of a concentrated solution of **Hppy** and copper(II) chloride in DMF yielded single crystals after several weeks, which were subsequently investigated by X-ray crystallography (Fig. 1). The copper was found to be coordinated by two chloride anions and two pyridine groups of **Hppy** in a square planar geometry. The two ligands display relatively short Cu–X distances of 2.3126(12) Å and 2.004(4) Å for the chloride and pyridyl groups respectively. Weak axial interactions to Cl ligands in adjoining complexes (Cu(1)···Cl(1) = 3.0003(14) Å), coupled with π–π stacking between **Hppy** ligands (interplanar distance 3.56 Å), induce formation of 1-D chains.

An extended network of hydrogen bonding between the disordered pyrazole ring and the chloride ligands of adjacent 1D chains (Cl(1)···N(3)/C(6) = 3.446(5) Å) orders the structure, promoting crystallinity (Fig. 2).

A sample of the dried gel was then analysed by powder X-ray diffraction and found to have partial crystalline character.

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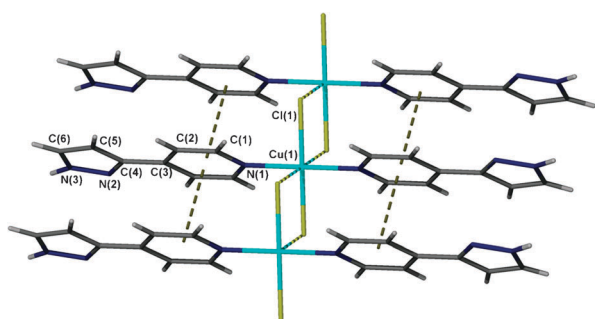**Fig. 1** Crystal structure of [CuCl$_2$(**Hppy**)$_2$] highlighting the π–π stacking and weak Cu–Cl interactions in the solid-state. Only one position of the disordered pyrazoles is shown.

Although weak, the bulk of the observed peaks were consistent with those predicted from the crystal structure of [CuCl$_2$(**Hppy**)$_2$] (see Supplementary Information‡).

The IR evidence suggests that similar square planar complexes are formed in solution and aggregate into discrete 1D chains held together by weak Cu⋯Cl and π–π interactions, as observed in the crystalline state. The self-assembly of the 1D nanostructure is shown in Scheme 1 (Step 1). The addition of triethylamine initiates an equilibrium that imparts a minor degree of deprotonation to the pyrazole functionalities, which are postulated to then displace chloride bridges on adjoining fibres, reversibly linking the fibres together, stopping crystal growth, and forming the 3D nanostructure of the gel (Scheme 1, Step 2). This behaviour is rationalised by comparing the pK_a values of the pyrazole group (12.0) and triethylammonium chloride[12] (10.2) relative to the pH of the metallogel (9.32). The relative proximity of the pK_a values for protonated triethylamine and the pyrazole ligand suggest that in equilibrium these species may overlap, however at pH 9.3, as determined for the gel, the equilibrium will strongly favour protonated pyrazole ligand and deprotonated triethylamine. Furthermore, a decrease in the N–H stretching vibration and a band at 225 cm^{-1} that correlates with the δ(Cu–Cl) vibration of a coordinated copper centre in the Raman spectrum are consistent with the proposed structure.[13]

The nanoscale morphology of the dried gel was next investigated by SEM, which confirmed the presence of rod-like nano-fibres (Fig. 3). The average diameter of the nanofibers was found to be approximately 40 nm. Energy-dispersive X-ray (EDX) spectroscopy was performed on the nanofibres which determined the elemental composition to comprise copper, chlorine, nitrogen,
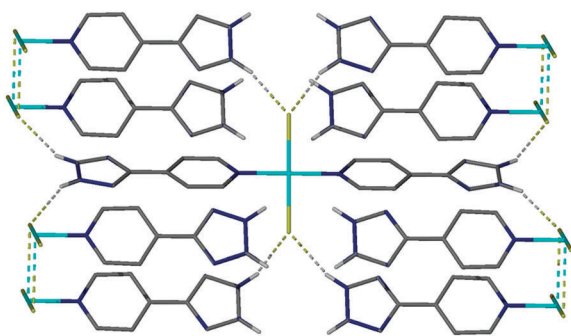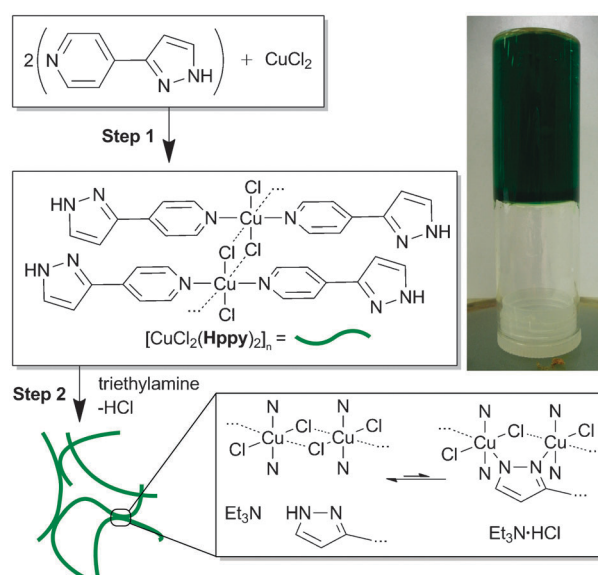

Scheme 1 Postulated self-assembly of the copper(II) metallogel (top right) as evidenced by vibrational spectroscopy.

and carbon. The absence of oxygen negates the possibility of 1-D chain formation as a result of chloride displacement by residual water present in the DMF post addition of triethylamine. Raman measurements also gave no evidence of a Cu–OH–Cu vibration in the region of 290–370 cm^{-1}.[14]

The incorporation of luminescent lanthanide metals into gels has become a focus of attention, due to tuneable emission profiles and amenable doping characteristics of gels.[15] Lanthanide clusters have similarly garnered increasing attention over recent decades owing to a host of interesting properties that promote their application as molecular devices. In particular, their unique spectroscopic and magnetic properties suggest important future applications as luminescent probes[16] and single molecule magnetic species.[17] As a reflection of the interest surrounding lanthanoid clusters, we chose the luminescent pentanuclear europium species [Eu$_5$(OH)$_5$(dbm)$_{10}$] (**1**) (dbm = dibenzoylmethanide) to demonstrate encapsulation of such a cluster by the copper metallogel.[18]

Ultraviolet irradiation of the gel induced a characteristic red glow at the gel's surface. Subsequent phosphorescence spectroscopy performed on a thin film yielded the excitation and emission spectrum shown in Fig. 3. The phosphorescence lifetime was determined to be *ca* 1 ms. The phosphorescence profile is typical of metal-based europium emission of the ^{5}D$_0$ excited

Fig. 2 Solid-state hydrogen bonding network of [CuCl$_2$(**Hppy**)$_2$]. Hydrogen atoms not participating in hydrogen-bonding have been omitted, and the pyrazole group is disordered over two positions.
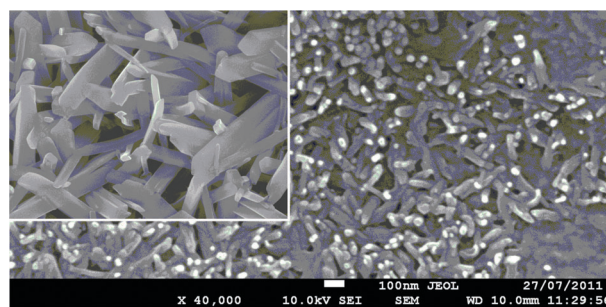

Fig. 3 SEM image of the dried chloride containing gel highlighting the thin interconnecting rod-like morphology. The inset image displays the rods under greater magnification.
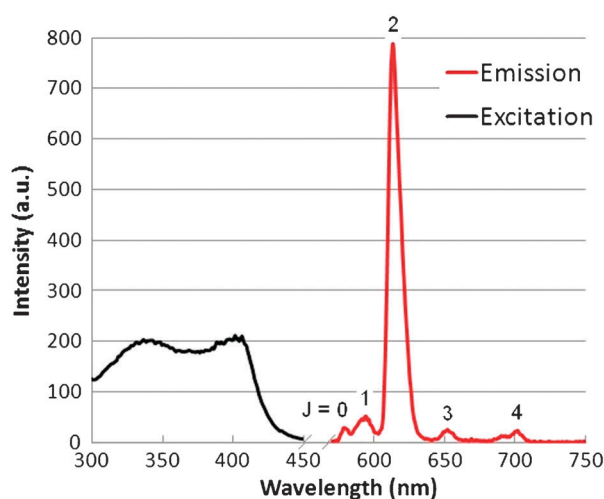
Fig. 4 Emission spectrum of a dried sample of copper gel encapsulating pentanuclear europium cluster **1** using an excitation wavelength of 340 nm.

state to a suitable ground state ($J = 0$–6).[16] The highest intensity initial five transitions ($^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4)) are shown in Fig. 4.

Retention of the cluster motif within the gel was evidenced by Raman spectroscopy, whereby low-intensity bands located at 406, 529, 619, 679, 685, 706, 793 and 818 cm^{-1} were found to correspond well with the known vibrational 'fingerprint' of the cluster.[18] Other vibrations were lost under more intense bands generated by the copper fibres within the gel.

In summary, we have synthesised a new copper(II) metallogel derived from the [CuCl$_2$(**Hppy**)$_2$] complex and thoroughly investigated the gel's mode of self-assembly. We have classed this material as a discrete metal complex gelator capable of immobilising DMF at 0.51 wt%. The amenability of the gel towards encapsulation of a europium cluster has been demonstrated with a phosphorescent profile obtained from the gel matching that of the cluster.

Notes and references

§ *Single-crystal studies*: Data for [CuCl$_2$(**Hppy**)$_2$] was collected at 123(2) K at the MX2 beamline of the Australian Synchrotron. The data collection and integration were performed within Blu-Ice[19] and XDS[20] software programs. Structural solution and refinement was carried out using SHELXL-97.[21]

Crystal data for [CuCl$_2$(**Hppy**)$_2$]: crystal size: $0.03 \times 0.01 \times 0.01$ mm^3, orthorhombic, space group *Pnnm*, $a = 3.7720(8)$, $b = 10.381(2)$, $c = 20.876(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90$ Å, $V = 817.4(3)$ Å^3, $Z = 2$, Least-squares refinement of 56 parameters without restraints for 1136 reflections with $I > 2\sigma(I)$ out of 13606 reflections gave residual factors $R_1 = 0.0623$, w$R_2 = 0.1617$, and GOF = 1.108.

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