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COMMUNICATION

Highly Interlocked Anion-Bridged Supramolecular Networks from Interrupted Imidazole-Urea Gels

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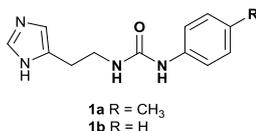
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An imidazole urea displays switchable hydrogelation behaviour that is turned off by metal ion coordination to give anion-bound coordination complex arrays.

The ability of urea derivatives to form supramolecular gels by means of extended hydrogen bonded chains has given rise to a rich field of synthetically and externally tuneable soft materials which has been the subject of intense investigation in recent years.¹ Interruption of the urea α -tape hydrogen bonding pattern by hydrogen bonding to strong acceptors such as anions can weaken and ultimately 'switch off' gelation behaviour.^{1a, 1b, 2} In contrast, metal binding to functionality such as a pyridyl group can 'switch on' gelation by removing the competing urea-pyridyl hydrogen bonding interaction.³ There are now an increasing number of reports of metallo gel formation in which the metal is integral to the gelation behaviour.⁴ Examples of anion-promoted gelation have also been observed⁵ and there is evidence for gel fibre formation being mediated by urea-anion interactions in pyrazole functionalised ureas.⁶ In this work we focus on the imidazole containing urea derivative **1a**, which is conveniently prepared from histamine.



Unlike pyridyl ureas, in which hydrogen bonding to the pyridyl nitrogen atom inhibits gelation, the basic imidazole nitrogen atom in **1a** has the potential to hydrogen bond with the strongly hydrogen bond donating imidazole NH group, leaving the urea moiety free to form the usual hydrogen bonded α -tape motif and hence act as a gelator. This expectation is borne out by the crystal structure of the phenyl derivative **1b** reported by Barboiu and co-workers who demonstrated that compounds of this type favour homomeric association of the urea and imidazole functional groups,⁷ and are interesting in the context

of proton dipolar channel formation.⁸ Compound **1b** crystallises as an acetonitrile solvate showing distinct urea α -tape and imidazole NH \cdots N interactions. Indeed, while less explored than their urea analogues, the ability of imidazole derivatives to form hydrogen bonded chains has been exploited in several supramolecular gel-forming systems.⁹ As well as its self-complementary hydrogen bond donor and acceptor capacity, the basic imidazole group in compounds of type **1** makes them suitable as ligands for transition metal centres,¹⁰ offering the possibility of metal-modulated gelation behaviour and material properties. In comparison to the relatively well studied pyridyl ureas,^{3, 11} the smaller size of the imidazole functionality also potentially results in less steric crowding at the metal centre and hence higher metal:ligand stoichiometry, involving more hydrogen bonded cross linking and hence a more three dimensional topology compared to the pyridyl systems.

While **1a** is a mono(urea) and gelation is generally associated with bis(urea)s,^{1a, 1e, 4c, 12} additional hydrogen bonding from the imidazole group is expected to strengthen the hydrogen bonded chain. Compound **1a** was screened for gel formation in a variety of solvents. Compound **1a** does not gel a range of organic solvents, however it proved to be an effective hydrogelator (see supplementary information Figure S1). Complete dissolution in water requires vigorous heating, but upon cooling at room temperature, a thermoreversible, opaque gel forms in less than three minutes in the range of 0.7-2.0 wt. % yield. Below 0.7 wt. %, weak partial gels or precipitates form, while above 2 wt. % it becomes difficult to completely dissolve the solid. Compound **1a** also forms gels in mixtures of water and other polar solvents such as methanol. For example water/methanol mixtures in ratios of up to 2:1 can be gelled. Brief sonication of the hot aqueous solutions of **1a** results in near-instantaneous gelation. Optical microscopy suggests that gels formed by slow cooling are quite crystalline while the sonication induced gels appear much less crystalline and sonication allows for gelation of considerably lower gelator

concentrations, down to about 0.4 wt. % (SI Figure S2). Ultrasound induced gelation has been observed previously¹³ and the mechanism may well involve instantaneous dissolution and re-precipitation of gelator aggregates from a solid surface under saturation conditions, preventing the formation of long range ordered aggregates. SEM images of the chromium coated xerogels of **1a** prepared thermally show entangled, ribbon-like fibres typically up to about 10 μm in width. Some fibres are short and straight with well-defined edges, which is in keeping with the relative crystalline character of the material observed in optical microscopy. Interestingly, some of the fibres are uniformly twisted into helical structures (Fig. 1). Helical gel fibres are commonly observed for chiral gelators, since chirality is often translated from the molecular level to the nanoscale.¹⁴ However, compound **1a** is not a chiral molecule and both left and right handed helical architectures are observed throughout the non-sonicated xerogel in every sample examined.

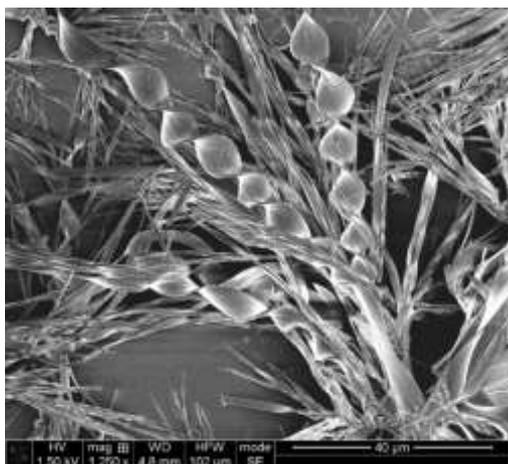


Figure 1 (a). SEM image of a dried 1 wt. % xerogel of **1a** prepared thermally without sonication, showing twisted ribbon-like fibres.

Some materials are known to twist as they crystallise under the right conditions¹⁵ possibly because of variations in mechanical, thermal and/or compositional fields within the crystal growth medium. For example, the process of crystallisation possesses an inherent latent heat which can create localised variations in temperature. Also as crystals form, differences in density and composition increase between the growing crystal and the surrounding solution. Twisting can occur if these field variations are significant on either side of the propagating fibre.¹⁶ In addition, internal and external stresses caused by impurities or surface tension are sometimes thought to be the cause of twisting.

The sonicated **1a** xerogels were also examined using SEM (see SI Figure S3). Likewise these xerogels are fibrous, but on average the ribbon-like fibres tend to be smaller in width than the non-sonicated gels (less than about 5 μm), and are generally longer and more uniform. The twisted structures are also still present but occur less frequently.

The rheological properties of hydrogels of **1a** (prepared thermally) confirm that the material is a true gel. A stress sweep at 1 wt. % shows that at low stresses, G' is almost two orders of magnitude greater than G'' , indicating significant elastic behaviour characteristic of a gel.^{1h} However the marked increase in G'' upon approaching the yield stress is more unusual. This type of behaviour is known as 'weak strain overshoot',¹⁷ and can occur most commonly in particulate

viscoelastic materials as a result of weak structural interactions between large particles or fibres.¹⁸ Such interactions can resist deformation at low stresses, after which they begin to break down resulting in an increase in the loss modulus G'' . The structure is then completely destroyed upon reaching the yield stress and the material begins to flow. This behaviour is consistent with the crystalline nature of **1a**, and the large fibres observed by SEM. Concentration dependency studies show that G' and yield stress increase with concentration up to close to the solubility limit.

Colourless single crystals of **1a** were isolated via slow cooling in acetonitrile and characterised by X-ray crystallography (see SI for crystallographic details). The compound exhibits a typical hydrogen bonded urea α -tape motif between adjacent molecules that aggregate in alternating alignments along the tape axis. This allows for the formation of a second 'zigzag' hydrogen bonded tape between the imidazole nitrogen atoms. The combination of urea $\text{NH}\cdots\text{O}$ and imidazole $\text{NH}\cdots\text{N}$ interactions is clearly sufficiently robust to give rise of fibre formation and hence gelation in an analogous fashion to bis(urea) gelators. The urea $\text{N}\cdots\text{O}$ distances of 2.8937(16) \AA and 2.8787(16) \AA are short and symmetrical which, along with the imidazole $\text{NH}\cdots\text{N}$ distance of 2.9297(18) \AA suggests a robust, unhindered hydrogen bonding pattern (Fig. 2). ¹H NMR spectroscopy of **1a** over the concentration range 0.05 – 5.0 w/v in $\text{DMSO-}d_6$ revealed significant broadening of the imidazole NH resonance into the baseline and a small but consistent chemical shift change $\Delta\delta$ for the urea NH resonances of 0.04 ppm. This data supports the formation of both urea $\text{NH}\cdots\text{O}$ and imidazole $\text{NH}\cdots\text{N}$ interactions in solution.

The X-ray crystal structure of the closely related phenyl derivative 1-[2-(1H-imidazol-4-yl)ethyl]-3-phenylurea (**1b**) was reported by the Barboiu group in 2008.⁷ Compound **1b** crystallises as an acetonitrile solvate. The solvate structure also exhibits both a hydrogen bonded urea α -tape and an imidazole chain motif, although the overall crystal packing arrangement is quite different. As with **1a**, molecules are arranged in an anti-parallel fashion. However in the case of **1a**, the urea and imidazole hydrogen bonded tape motifs each lie along a single plane. For **1b** on the other hand, each molecule in the urea tape is offset from the two molecules either side of it by approximately 60° , allowing for $\text{CH}\cdots\pi$ interactions between the imidazole and the phenyl ring.

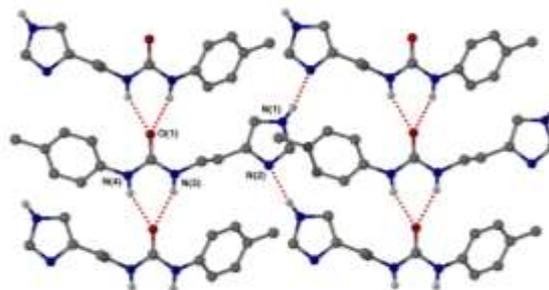


Figure 2. Crystal packing in **1a**. Selected hydrogen bond lengths (\AA): urea $\text{N3}\cdots\text{O1}$ 2.8937(16) \AA , $\text{N4}\cdots\text{O1}$ 2.8787(16) \AA , imidazole $\text{N1}\cdots\text{N2}$ 2.9297(18) \AA .

Compound **1b** was re-synthesised and screened for gelation behaviour in an analogous fashion to **1a**. Unlike **1a** however, compound **1b** does not act as a hydrogelator, instead precipitating out of hot solution upon cooling or sonication. It is possible that the presence of the methyl group allows a faster-growing, more compact structure in comparison to the solvate-forming **1b**. Consistent with this hypothesis is the fact that the

hydrogen bonded distances in the urea α -tape in **1b** are significantly longer at 2.92 and 3.03 Å, whereas the imidazole NH \cdots N interaction is markedly shorter at 2.75 Å. The presence of the methyl group may also substantially affect the aqueous solubility of **1a**.

There is considerable interest in the use of metal ions and anions to tune gelation behaviour and gel material properties.^{1h, 4a, 4g} In order to probe the importance of the imidazole NH \cdots N interaction in the gelation behaviour of **1a** we examined its gelation formation properties in the presence of copper(II) and zinc(II); metal ions likely to be strongly bound by the imidazole nitrogen atom. Such complexation would interrupt the NH \cdots N hydrogen bonding seen in the structure of **1a**, while the interactions of the urea functionality to counter anions is expected to disrupt the urea α -tape formation, since inorganic anions are significantly stronger hydrogen bond bases than the urea carbonyl oxygen atom.^{1a} Rheological experiments were conducted on hydrogels of **1a** in the presence of Cu(NO₃)₂ and ZnCl₂ (0.1 eq.), using the same method as for the pure **1a** gels. The gelator was dissolved in warm water, and an aqueous solution of the metal compound added to give an overall 1 wt. % solution of gelator with further heating to dissolve the resulting precipitate. Fig. 3 shows stress sweep rheometry data for these metallogels after cooling to room temperature in comparison to a 1 wt. % pure compound **1a** hydrogel. In both cases, the presence of the metal salt dramatically lowers the storage modulus G' by at least an order of magnitude compared to the pure **1a** hydrogel. The yield point also drops from 44.7 Pa for the pure gel to 3.9 and 1.2 Pa in the presence of Zn(II) and Cu(II), respectively. Evidently coordination of **1a** to a metal centre substantially weakens the gel, in accordance with the hypothesis that the imidazole hydrogen bonding is required for gelation. Further addition of metal compound (> *ca.* 0.2 molar equivalent) prevents gelation completely, and amorphous precipitates instantly form from the hot solution.

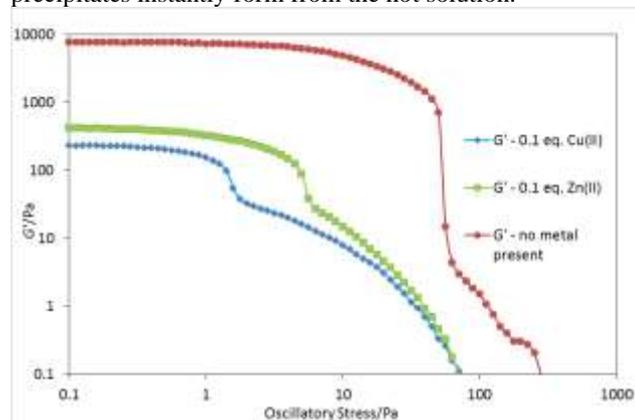


Figure 3. Stress sweep rheometry data for a 1 wt. % hydrogen of compound **1a** in the presence of Cu(NO₃)₂ and ZnCl₂ compared to the pure compound.

Examination of a hydrogel formed in the presence of 0.1 eq. Cu(NO₃)₂·2.5H₂O using SEM revealed a plate shaped crystalline morphology, which is a significant deviation from the fibrous morphologies of the pure compound **1a** hydrogels (see SI, Figure S5).

In order to probe the interaction mode of the metal salts with gelator **1a**, single crystal X-ray crystal structures were determined for two complexes derived from the reaction of copper(II) salts with **1a**. The blue complexes were prepared by vapour diffusion of diethyl ether into a solution of **1a** in methanol containing 0.25 equivalents of CuCl₂·2H₂O, or on

standing of a methanol solution of **1a** containing 0.15 equivalents of Cu(NO₃)₂·2.5H₂O. Elemental analysis of the crystalline products gave the formulations [Cu(**1a**)₄Cl]Cl (**2**) and [Cu(**1a**)₆](NO₃)₂·2MeOH (**3**), confirmed by X-ray crystallographic analysis. Both structures exhibit unidentate coordination of the imidazole moieties to the metal centres accompanied by hydrogen bonding of the pendant urea groups to the counter anions. While it has not been established that these crystalline complexes isolated from methanol are identical to those formed upon addition of copper(II) salts to the hydrogels, they nevertheless provide a highly plausible mechanism by which the NH \cdots O and NH \cdots N hydrogen bonding observed in the structure of **1a** can be interrupted by metal coordination and anion hydrogen bonding.

In the structure of **2** the Cu(II) centre is 5-coordinate, and forms an elongated square based pyramid. The four **1a** ligands coordinate through the N1 imidazole nitrogen atom and sit in the slightly distorted equatorial positions, with Cu-N bond lengths of 1.9970(17) Å. The axial position is occupied by a chloride anion, Cu-Cl distance 2.6410(12) Å. The four organic ligands form a concave 'bowl' and these bowl-shaped structures form a one dimensional stack *via* hydrogen bonds between the imidazole NH group and the urea oxygen atoms of an adjacent complex, to give an infinite hydrogen bonded polymer (Fig. 4) with short N \cdots O distances of 2.735(2) Å. Each stack interacts with three other adjacent stacks *via* four hydrogen bonds from the urea NH to the uncoordinated chloride anions, N \cdots Cl distance 3.2983(18) Å.

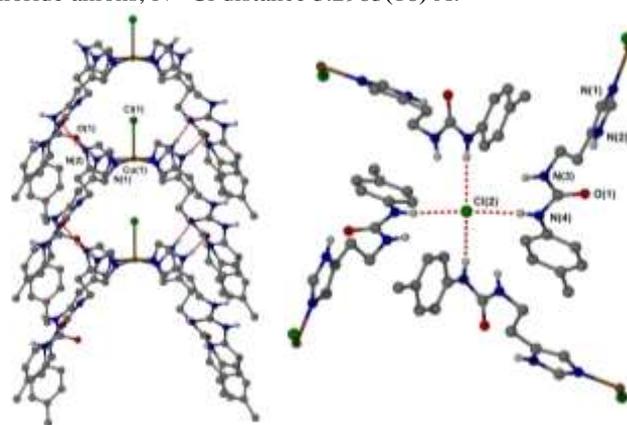


Figure 4. X-ray crystal structure of **2** (a) stacking *via* imidazole NH \cdots O hydrogen bonding, (b) hydrogen bonding of four urea moieties to the non-coordinated chloride anion. Selected hydrogen bond lengths (Å): N(2) \cdots O(1) 2.735(2), N(4) \cdots Cl(2) 3.2983(18) Å.

The structure of **3** is based on a Jahn-Teller distorted octahedral copper(II) centre with three crystallographically unique Cu-N bonds to the six **1a** ligands; 2.049(2), 2.072(2) and 2.402(2) Å. Each imidazole group NH forms hydrogen bonds with the urea oxygen atom of an adjacent ligand coordinated to a separate Cu(II) centre. Donor-acceptor N \cdots O distances are short and fairly symmetrical at 2.819(3), 2.890(3) and 2.894(3) Å. The net result is an array of hydrogen bonded 'cages' containing a **back-to-back stacked pair of nitrate anions mutually offset by about 0.4 Å**, made up of six ligands, each coordinated to independent Cu(II) centres (Fig. 5). The N-N distance between the pair of nitrate anions is very short at 3.010(5) Å. The nitrate anions are situated to facilitate bifurcated hydrogen bonds between the inward-facing urea NH groups and the nitrate oxygen atoms with N \cdots O in the range 2.925(3)-3.248(3) Å. It is surprising to observe this nitrate

'stacking' since it might be assumed to be electrostatically unfavourable for two anions to be in close proximity and urea-nitrate hydrogen bonding must overcome the nitrate-nitrate repulsion. Bowman-James and co-workers have reported the encapsulation of two nitrate anions in a bicyclic cryptand cage.¹⁹ In this example the nitrate anions are also stabilised through NH-nitrate hydrogen bonding, and similarly found to stack on top of each other, although in an eclipsed rather than staggered conformation. The nitrate-nitrate N-N distance is 3.34 Å, *i.e.* significantly greater than the distance of 3.01 Å in the present case.

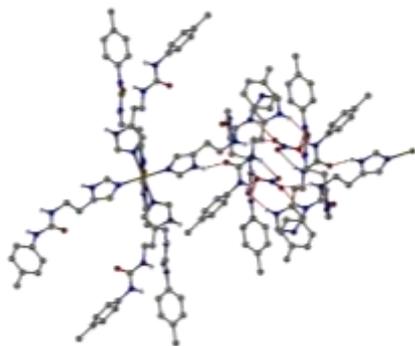


Figure 5. X-ray crystal structure of **3** showing the distorted octahedral Cu(II) centre and urea hydrogen bonded nitrate anion pair.

Conclusions

This work has demonstrated that imidazole ureas represent a viable alternative to bis(urea) low molecular weight hydrogelators. Like bis(urea)s, compounds of type **1** can form two independent, co-directional hydrogen bonded chains; however, the contrast between **1a** and **1b** demonstrates that this factor alone is insufficient for gelation behaviour and gelation is also unpredictably dependent on substituents. The well-known propensity of imidazoles to coordinate to metal centres and ureas to hydrogen bond to anions provides a facile means to 'turn off' gelation behaviour by addition of even very small (sub-stoichiometric) amounts of metal salt. This behaviour contrasts to that of pyridyl-terminated bis(urea)s, in which gelation is frequently facilitated by metal coordination because binding the pyridyl group to a metal centre removes non-gel-forming urea-pyridyl hydrogen bonding interactions.^{3a} The sterically relatively unhindered nature of the imidazole group allows a single metal centre to bind up to six imidazole derived ligands. Hence, a small amount of metal cation is highly effective at sequestering imidazole ureas and hence disrupting gel formation.

Notes and references

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Electronic Supplementary Information (ESI) available: Crystallographic information in CIF format for the structures of **1a**, **2** and **3**, and experimental details covering synthesis of new compounds, gel rheology and SEM analysis. CCDC 1016071-1016073. See DOI: 10.1039/c000000x/

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Graphical Abstract

Hydrogels from a combination of imidazole and urea hydrogen bonding interactions are turned off by metal complexation and anion binding.

