

# Modular nanometer-scale structuring of gel fibres by sequential self-organization

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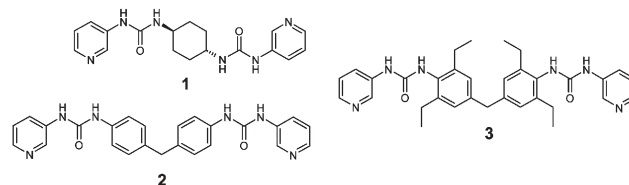
Ag(I) and Cu(II) complexes of a series of simple bis(urea) ligands form soft metallogels. X-ray crystallographic results suggests that the gels' structure is based on hydrogen bonding to counter anions and thus suggests a route to tunable gel rheological properties.

Gels comprise a partially ordered liquid trapped by a highly porous network of fibres resulting in viscoelastic macroscopic properties. As well as being fascinating because of their nanometer-scale structure, recent work has shown that the highly porous, partially ordered network in gels, coupled with their formation by spontaneous self-organization gives them tremendous technological possibilities, for example as selective sorbents or uptake agents,<sup>1–6</sup> in the controlled formation of highly porous polymers,<sup>7</sup> or in the synthesis and support of catalytic nanoparticles.<sup>8–10</sup> The gel host matrix can comprise a wide range of fibrous materials *e.g.* based on organic<sup>11,12</sup> or metal oxide polymers,<sup>13</sup> or on non-covalent assembly of molecular compounds such as cholesterol derivatives, surfactants, elaborated porphyrin and phthalocyanine derivatives, carbohydrates and peptide derivatives, extended bis- and tris(urea) compounds, phenylenevinylene derivatives and oligoamides.<sup>14–19</sup> However, most of the materials reported to date are based on polymers.<sup>11,12</sup> The vast majority of these systems contain long chain alkyl groups in order to arrest full crystallization and limit aggregation to nanometer scale gel fibres.

Gels may be considered to be either hard or soft based on their rheological characteristics. There is significant current technological interest in soft gels that can be readily induced to flow by either a change of temperature or being stressed beyond the yield point.<sup>20</sup>

We now report a simple, readily prepared series of rigid bis(urea) ligands in which gelation occurs to give soft gels *via* a hierarchical series of self-organization steps templated by metal salts. The intrinsic ability of bis(ureas) to aggregate *via* NH $\cdots$ O=C reversible hydrogen bonded interactions<sup>17,18,21</sup> is modulated by, and can be switched by reversible coordination interactions to metal cations and by hydrogen bonding to conjugate anions. The resulting gels and the consequent nanostructuring of metal ions offers interesting technological possibilities.

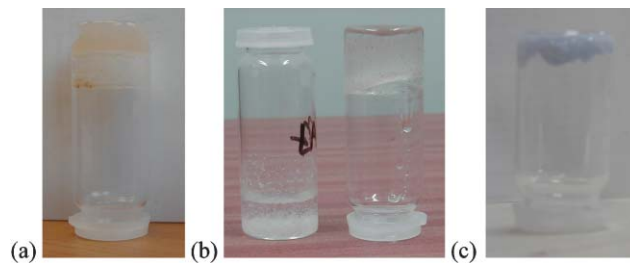
The bis(urea) dipyriddy ligands **1** and **2** are readily prepared in one step by the reaction of commercial diisocyanates with 3-aminopyridine. The strategy is very versatile given the wide availability of commercial isocyanates as industrial intermediates.



Unlike more flexible bis(ureas) containing long alkyl chains, **1** and **2** do not form gels alone in a variety of organic solvents such as tetrahydrofuran, acetonitrile, methanol, chloroform and toluene. However addition of ethyl groups to give **3** does result in the formation of an organogel (Fig. 1a) in chloroform : methanol (50 : 50 v/v) at concentrations of 10 mM, comparable to those for long chain alkyl systems.<sup>15,22,23</sup> The gel was characterized by frequency sweep rheometry. The resultant storage modulus was greater than the loss modulus and frequency independent, both aspects are characteristics of gels.<sup>24</sup> The value of the storage modulus was 16 kPa, implying a weak gel, despite its opacity, which suggests significant structuring and crystallinity.

The gel was dried gently and imaged using SEM and AFM. A representative image is shown in Fig. 2a. The dried xerogel comprises a dense fibrous network with large fibres of up to 500 nm width. On higher magnification the strands are revealed to be collinear fibre bundles with the narrowest fibres measuring *ca.* 60 nm. Addition of Ag(I) salts AgBF<sub>4</sub> and AgNO<sub>3</sub> to **3** again results in gel formation. In the case of AgBF<sub>4</sub> the appearance of the fibres is markedly different with narrower strands showing markedly less bunching, Fig. 2b. Addition of AgNO<sub>3</sub> also dramatically affects the morphology of the gel fibres with both narrow fibres of width *ca.* 35 nm and broader, well-defined, flat ribbons observed.

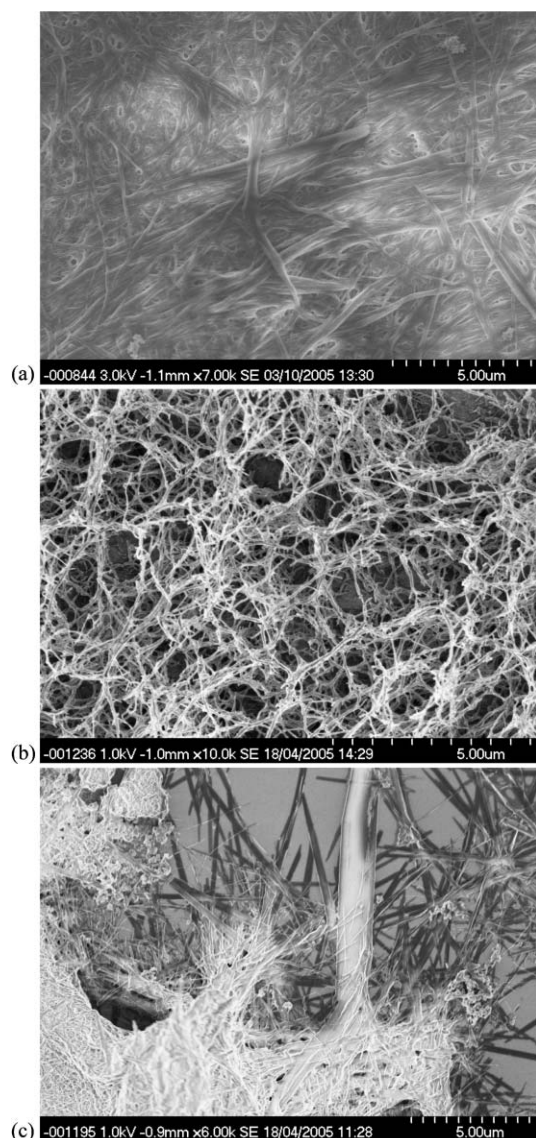
The unalkylated analogue, **2**, alone does not form a gel in thf/water and precipitates as a microcrystalline solid. However,



**Fig. 1** Photographs of (a) organogel of **3** from chloroform/methanol, (b) comparison of solutions of free ligand **2** (left) and **2**/AgBF<sub>4</sub> in thf/water (right) (c) metallogel comprising **1**/Cu(NO<sub>3</sub>)<sub>2</sub> from aqueous methanol.

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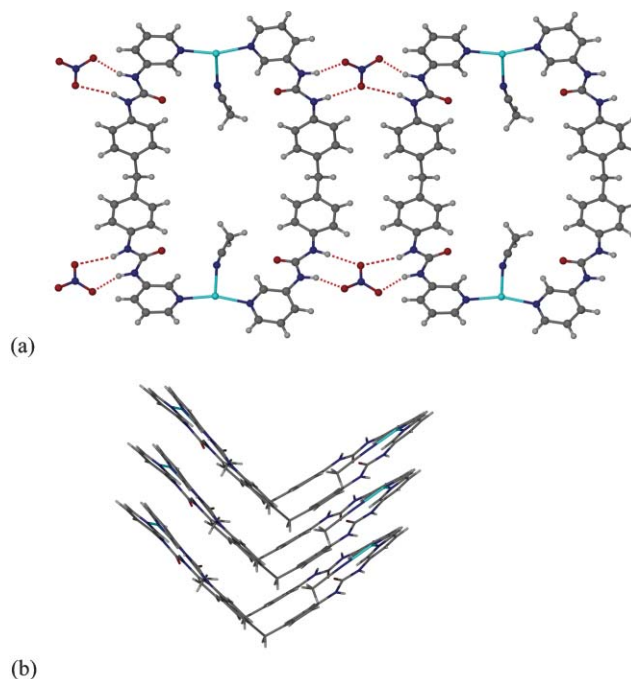
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**Fig. 2** Representative SEM images of dried xerogels (a) **3** alone from chloroform/methanol (50 : 50 v/v) (b) **3** with  $\text{AgBF}_4$  and (c) **3** with  $\text{AgNO}_3$ .

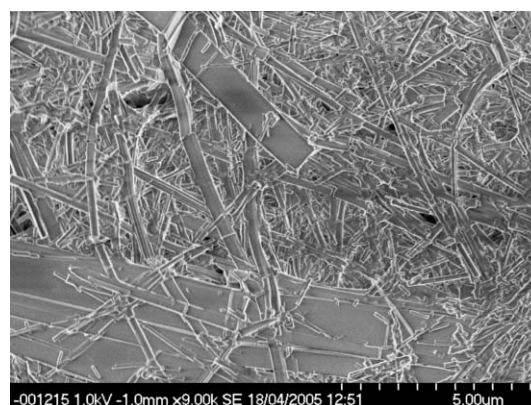
reaction of **2** with  $\text{AgBF}_4$  in the same medium thf/water (2 : 1 v/v) results in the formation of a semi-transparent, weak gel, thus the presence of the labile metal salt promotes gel formation, Fig. 1b. Reaction of **2** with  $\text{AgNO}_3$  in a variety of solvent mixtures (**2** in either thf/water, chloroform/methanol or toluene/methanol;  $\text{AgNO}_3$  in MeCN) again does not result in gel formation but allows the isolation of a crystalline product of formula  $[\{\text{Ag}(\text{2})(\text{MeCN})\}_2(\text{NO}_3)_2 \cdot 2\text{CHCl}_3 \cdot 1.5\text{H}_2\text{O}]$  **4**. The complex was characterized by X-ray crystallography† (Fig. 3) and suggests some insight into the aggregation process of **2** and **3** with Ag(I) salts and, by inference, the structure of the metallo gels formed by **2** and **3** with  $\text{AgBF}_4$ , and **3** with both  $\text{AgBF}_4$  and  $\text{AgNO}_3$ .

Complex **4** comprises a discrete 2 + 2 metallomacrocycle with approximately linear coordination at the Ag(I) centres ( $\text{N}-\text{Ag}-\text{N} = 163.41(14)^\circ$ ) and four externally directed urea groups hydrogen bonding to  $\text{NO}_3^-$  anions. The anions bridge between adjacent macrocycles *via* unsymmetrical pairwise  $\text{R}_2^2(8)$  hydrogen bonded<sup>25</sup> rings (Fig. 3a), supported by  $\text{CH} \cdots \text{O}$  interactions similar to the



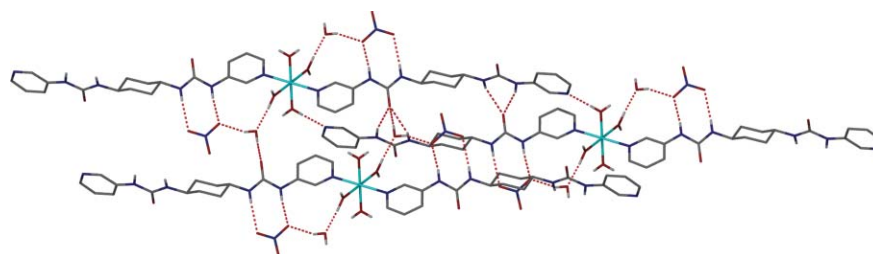
**Fig. 3** (a) X-ray structure of the metallomacrocycle  $[\{\text{Ag}(\text{2})(\text{MeCN})\}_2(\text{NO}_3)_2]$  in **4** (two repeats). Each chain interacts with its neighbours *via*  $\text{NH} \cdots \text{anion}$  hydrogen bonds. (b) Polar  $\pi$ -stacked chains of macrocycles. Ag (cyan), O (red), N (blue), C (grey), H (light grey).

discrete nitrate sandwich complex formed by the monodentate, *p*-tolyl analogue of **2**.<sup>26,27</sup> The interior of the macrocycle is occupied by two acetonitrile molecules interacting weakly with the Ag(I) centre ( $\text{Ag}-\text{NCMe} = 2.556(5)$  Å) to give a very unusual T-shape geometry. The acetonitrile molecules are situated slightly off-centre, apparently maximising van der Waals interactions with the ligand. In order to aid in understanding gel formation it is interesting to look at the solid-state packing of the macrocycles. In addition to being linked by hydrogen bonding to nitrate ions, the macrocycles also form polar stacks in the solid state (Fig. 3b). It is possible that the stronger hydrogen bonding to nitrate results in the crystallization of **4** while in the case of the reaction of **2** with  $\text{AgBF}_4$  the complex is more soluble allowing gel formation. Additional ethyl groups, as in complexes with **3**, renders the whole system more soluble again promoting gel formation and reducing



**Fig. 4** SEM image of metallo gel derived from **1** and copper(II) nitrate.





**Fig. 5** X-ray crystal structure of  $[\text{Co}(\mathbf{1})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  **5** showing hydrogen bonding interactions. CH hydrogen atoms omitted for clarity.

crystallinity. The structure of **4** also suggests a reason why the gels should be relatively free-flowing despite their highly structured nature. If gel aggregation is *via* hydrogen bonding to anions then the gel rheological properties will be linked to the strength of the (relatively weak) hydrogen bonds and to the  $\pi$ -stacking. The van der Waals dimensions of the metallomacrocyclic-nitrate unit are *ca.*  $2 \times 1.5$  nm and hence the smallest fibres would comprise *ca.* 10–15 molecules in width. This aggregation mode contrasts to the  $\text{NH} \cdots \text{O}=\text{C}$  hydrogen bonding proposed for other bis(urea) gels which do not contain metals.<sup>23</sup>

Analogous gelation behaviour was also observed for ligand **1** in the presence of copper(II) nitrate, the incorporation of the metal being readily apparent from the blue coloration of the decanted material (Fig. 1c). The copper nitrate gel proved to be crystalline and adopted a structure involving well-defined ribbons of highly variable width, somewhat related to the morphology of the fibres seen for **3**/ $\text{AgNO}_3$  (Fig. 4, *cf.* Fig. 3c). Under similar conditions (methanol : water 12 : 1 v/v) with cobalt(II) nitrate, crystals of a 2 : 1 complex  $[\text{Co}(\mathbf{1})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  **5** were isolated, fig. 5. The metal centre is coordinated by two mutually *trans* ligands **1** bound by only one pyridyl nitrogen atom each. The urea groups closest to the coordinated pyridyl units hydrogen bond to nitrate as with **4** however, bridging to the next molecule is *via* included water. End-to-end interactions are *via* hydrogen bonding from coordinated water to the uncoordinated pyridyl groups and conventional urea  $\text{R}_1(6)$  urea hydrogen bonds are also observed. Thus the structure of **5** retains the anion-mediated intermolecular interactions observed in **4**. This key aspect suggests that systematic variation of anion identity and urea hydrogen bond acidity (*e.g.* *via* peripheral substitution) could lead to gels with systematically tailored rheological properties and well-defined structure.

In conclusion we report a general approach to a variety of well-defined self-assembling metallogels subject to facile variation.

## Notes and references

† Crystal data for **4**:  $\text{C}_{28}\text{H}_{26}\text{Ag}_1\text{Cl}_3\text{N}_8\text{O}_{5.74}$ ,  $M = 780.66$ , orthorhombic, space group  $Pmn2_1$  (No. 31),  $a = 43.826(4)$ ,  $b = 5.2608(5)$ ,  $c = 14.0960(14)$  Å,  $V = 3250.0(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.595$  g cm<sup>-3</sup>,  $F_{000} = 1575.730$ , Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 120$  K,  $2\theta_{\text{max}} = 55.6^\circ$ , 27657 reflections collected, 2787 unique ( $R_{\text{int}} = 0.02$ ). Final  $\text{Goof} = 0.8655$ ,  $R1 = 0.0473$ ,  $wR2 = 0.1110$ ,  $R$  indices based on 6271 reflections with  $I > 3.00\sigma(I)$  (refinement on  $F^2$ ), 419 parameters, 7 restraints. Lp and absorption corrections applied,  $\mu = 0.920$  mm<sup>-1</sup>. Absolute structure parameter = 0.55(3). **5**:  $\text{C}_{36}\text{H}_{56}\text{CoN}_{14}\text{O}_{16}$ ,  $M = 999.88$ , triclinic, space group  $P\bar{1}$  (No. 2),  $a = 9.3380(6)$ ,  $b = 11.3324(7)$ ,  $c = 11.4099(7)$  Å,  $\alpha = 74.1670(10)$ ,  $\beta = 71.2920(10)$ ,  $\gamma = 80.3580(10)^\circ$ ,  $V = 1095.99(12)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.515$  g cm<sup>-3</sup>,  $F_{000} = 525$ , Mo $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 120(2)$  K,  $2\theta_{\text{max}} = 61.0^\circ$ , 14659 reflections collected, 6590 unique ( $R_{\text{int}} = 0.0205$ ). Final  $\text{Goof} = 1.092$ ,  $R1 = 0.0436$ ,  $wR2 = 0.1027$ ,  $R$

indices based on 5923 reflections with  $I > 2\sigma(I)$  (refined on  $F^2$ ), 335 parameters. Lp and absorption corrections applied,  $\mu = 0.479$  mm<sup>-1</sup>. CCDC 281274 & 281275. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511259a.

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