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## COMMUNICATION

## Polymorphs from supramolecular gels: four crystal forms of the same silver(1) supergelator crystallized directly from its gels<sup>†</sup>

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A new silver(1) complex with 1-phenyl-3-(quinolin-5-yl)urea has been prepared, acting as a supramolecular supergelator in the presence of polar solvents. In open vials temperature dependent, reversible gel-to-xerogel transition is observed, while in sealed vials direct crystallization of four polymorphs of the same gelling compound is achieved, depending on the gelling solvent.

Gels have become commonplace in everyday life.<sup>1</sup> They can be obtained from small molecules as well as from oligomers and polymers, the vast majority being represented by purely organic gels and by inorganic gels, such as silica gel, *etc.*, but also organometallic and metallo-gels have been reported.<sup>2</sup>

Supramolecular gels are those held together by non-covalent interactions such as hydrogen bonds and metal–ligand interactions. As pointed out by Flory already in 1974<sup>3</sup> and recalled by Dastidar in his recent review<sup>4</sup> "gels are materials that are easier to recognize than to define". Crystallization of a gelator compound is not an easy job especially when crystallization takes place from the very gelling solvent. The examples available in the literature are very few, in particular when small coordination compounds are involved.<sup>5</sup> Steed, Clarke and coworkers have very recently published an exhaustive review on metal- and anion-binding supramolecular gels.<sup>6</sup> Of particular interest are supergelator systems, because they are effective in gel formation at very low concentration, *i.e.* below 1% w/v.<sup>1</sup>

Gels find applications in almost all areas of materials chemistry,<sup>7</sup> and are nowadays been approached with the objective of finding materials suitable for crystallization of new crystal phases.<sup>8</sup> The quest for new crystal forms of molecular species has come to the forefront of solid state chemistry investigations because of the number of potential applications of the different physico-chemical properties of different crystal forms of a same species (polymorphs, co-crystals, hydrates, solvates, salts, *etc.*).<sup>8,9</sup>

In this paper we report (i) the discovery of new supramolecular gels, obtained *via* formation of the silver(I)

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Scheme 1 The ligand 1-phenyl-3-(quinolin-5-yl)urea (PQ5U).

supergelator complex between 1-phenyl-3-(quinolin-5-yl)urea (PQ5U) (Scheme 1) and AgNO<sub>3</sub> in the presence of common organic solvents; (ii) the behaviour of the gels with temperature; and (iii) the four polymorphic modifications of the supergelator obtained by separate crystallizations from MeOH, EtOH, i-PrOH, or CH<sub>3</sub>CN.

We have chosen the ligand  $PQ5U^{10}$  because (i) it is a low weight molecule, and also (ii) in its solid state structure it shows the typical hydrogen bonding urea tape motif; in addition to this, the presence of a nitrogen atom in an accessible position makes it a good candidate for the formation of a discrete metal complex with the silver cation.

The ligand in itself is *not* a gelator, and it is only slightly soluble in polar solvents such as MeOH, EtOH, i-PrOH and CH<sub>3</sub>CN; suspensions are turned into clear solutions upon heating, and slow cooling to room temperature yields the starting solid. Upon addition of AgNO<sub>3</sub> to the PQ5U solutions supramolecular interactions build up between the ligand, the silver cations and the nitrate anions, and thermo-reversible organo-gels are formed.<sup>11</sup>

Gelation is obtained (Fig. 1) when the  $AgNO_3 : PQ5U$  molar ratio is in the range from 1 : 2 to 1 : 1 (see ESI†). Using other nitrates of transition metals such as zinc and cobalt or other salts of silver, such as the acetate and the tetrafluoroborate, does not lead to gel formation. Table 1 lists the gelation properties of the system  $AgNO_3 : PQ5U$  in different organic solvents.



Fig. 1 The clear sol (on the left) and the "tube inversion test" showing gel formation (right).

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<sup>†</sup> Electronic supplementary information (ESI) available: Forms I–IV: synthesis, single crystal data and measurements, packing features, ORTEP plots. CCDC 801410–801413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc10305a

**Table 1** Results of the gelation experiments, in different solvents, for  $AgNO_3 : PQ5U$  stoichiometric ratios of 1 : 2 and 1 : 1 (S = clear solutions; I = insolubility; G = gel formation)

Solvent	Result	Solvent	Result
EtOH	G	THF	I
MeOH	G	1-butanol	G
i-PrOH	G	1-hexanol	S
CH <sub>3</sub> CN	G	Toluene	Ι
(–)Ethyl-lactate	G	Ethyl acetate	Ι
Acetone	Ι	Nitromethane	S
DMF	$\mathbf{X}^{a}$	Dioxane	Ι
Dichloromethane	Ι	Ethanol amine	S
Ethylene glycol	S	t-Butanol	S
Cyclohexane	Ι		
Cyclohexane <sup><i>a</i></sup> Decomposition proc	I duct.		

Upon heating, gel-to-sol transition is observed, due to disruption of the supramolecular interactions that hold the gel-structure together; the solutions revert to the gel state upon cooling.

In order to evaluate the thermal stability of the gel, a plot of the gel–sol dissociation temperature ( $T_{gel}$ ) in EtOH versus the gelator concentration was constructed (see ESI†) by using the "dropping ball" method.<sup>1b</sup> Fig. 2 clearly indicates that  $T_{gel}$ increases with the gelator concentration.<sup>12</sup> The gel–sol–gel interconversion is fully reversible over ten to fifteen cycles of heating and cooling. This means that the assembly of the gelator molecules arises from cooperative non-covalent interactions between the PQ5U molecules, the silver and nitrate ions, and these interactions are broken upon heating the gel.

XRPD patterns of fresh gels, obtained directly in the sample holder, were measured for the gels obtained from MeOH, i-PrOH, CH<sub>3</sub>CN and EtOH (Fig. 3). All samples show a broad peak at  $2\theta$  between 3° and 4°, which corresponds to a *d* spacing of ~2.5 nm; for gels obtained from ethanol and acetonitrile this peak is sharper than those obtained from methanol and i-propanol.

If the gels are dried in open vials xerogels are formed: XRPD patterns of the air-dried samples (xerogels) were also recorded (see Fig. 4): as it can be seen, the low angle peak is



Fig. 2 Effect of the concentration<sup>12</sup> (expressed in % w/v) on the gel–sol transition temperature in different solvents for an AgNO<sub>3</sub> : PQ5U molar ratio of 1 : 2.



Fig. 3 XRPD patterns of fresh gels  $(AgNO_3 : PQ5U = 1 : 2)$  obtained from acetonitrile, methanol, i-propanol and ethanol.



Fig. 4 XRPD patterns of the xerogels  $(AgNO_3 : PQ5U = 1 : 2)$  obtained from EtOH, MeOH, CH<sub>3</sub>CN and i-PrOH.



**Fig. 5** (a) SEM image of the xerogels obtained by drying in the air the 1:2 AgNO<sub>3</sub>: PQ5U gel from EtOH. The fibrous nature of the xerogel can be appreciated. The white spots indicate the presence of silver(1) (Courtesy of Prof. Giuseppe Falini). (b) Crystallization of Form IV as obtained by drying in a sealed vial the 1:2 AgNO<sub>3</sub>: PQ5U gel from MeOH.

maintained for all samples, but more and different peaks are observed at a higher angle.

The same patterns can be observed if  $AgNO_3$  and PQ5U are ground together in the stoichiometric ratio 1 : 2 in the presence of a small quantity of solvent (kneading). A SEM image (see Fig. 5a), of the xerogel obtained by air-drying the



**Fig. 6** Images of the single crystals for the four polymorphs of the complex [Ag(PQ5U)<sub>2</sub>]NO<sub>3</sub>, as obtained from CH<sub>3</sub>CN, Form I, EtOH, Form II, i-PrOH, Form III and MeOH, Form IV.

ethanol containing gel, reveals the presence of a 3D network of branched and entangled fibres, which must be effective in trapping the solvent molecules in the gel phase.

Crystallizing a gelator complex system is normally a difficult task,<sup>6,10a,13</sup> and more so if crystallization is attempted from the gelling solvent. If our gels are dried in sealed vials, phase separation takes place, resulting in clear solution and single crystals (see Fig. 5b and ESI<sup>†</sup>). Interestingly and—to the best of our knowledge—unprecedentedly, different crystal forms are obtained from different gelling solvents. We report here the polymorphs of the complex of formula [Ag(PQ5U)<sub>2</sub>]NO<sub>3</sub> (see Fig. 6) obtained from CH<sub>3</sub>CN, Form I, EtOH, Form II, i-PrOH, Form III and MeOH, Form IV, which were characterized by single-crystal X-ray diffraction (see ESI<sup>†</sup>).

In terms of gross structural features the  $[Ag(PQ5U)_2]^+$  units (see ESI<sup>†</sup>) for Forms I–III are very similar, consisting of linearly coordinated ligand–Ag<sup>+</sup> systems, while Form IV contains a nitrate anion participating in the coordination sphere of the Ag<sup>+</sup> cation to which it is directly bound.

Since the relative ligand conformation in Forms I to III (transoid) and that in Form IV (cisoid) is different, one might be tempted to consider this latter compound as a different isomer of the complex. However, we reckon that these examples lend further support to the idea that the difference



**Fig. 7** The first coordination sphere around the  $Ag^+$  ion in Forms I to IV. In Form IV the  $NO_3^-$  anion directly interacts with the silver cation, and two  $(C-H)\cdots Ag^+$  interactions can also be observed [Portions of the PQ5U ligands in Forms I and IV and most H atoms omitted for clarity].

between molecular isomers and "crystal isomers", *e.g.* polymorphs,<sup>9,14</sup> can be semantic and depends on the compromise between minimization of crystal energy and of molecular energy.

Fig. 7 shows the first coordination sphere around the  $Ag^+$  ion, which is completed by an  $O_{urea}$  atom and a silver cation in Form I, by two  $O_{urea}$  atoms in Forms II and III and by a nitrate anion and two C–H groups of adjacent ligands in Form IV.

In conclusion, four different crystal forms of the same gelator could be obtained from four different gelling solvents, indicating that crystallization from gels is a viable route to obtain new crystal forms; work is in progress to extend this method to the preparation of polymorphs of co-crystals, and to investigate (i) the combined effect of gel and solvent on the formation of polymorphs; (ii) crystallizations of the complex from solvents that do not form gels with it and (iii) the relative stability of the four polymorphic forms.

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- 10 (a) D. Kalita, R. Sarma and J. B. Baruah, *CrystEngComm*, 2009, **11**, 803–810; (b) We have also tested the 1-phenyl-3-(quinolin-8-yl)urea molecule,  $^{10a}$  but no gel formation/complexation with Ag<sup>+</sup> has been observed.
- 11 Work is in progress to photochemically characterize the luminescence properties of these gels, as both solid PQ5U, its solutions and the organo-gels described in the present communication show a blue luminescence (471 nm) at an excitation wavelength of 400 nm.
- 12 Critical gelator concentrations (% w/v) are 0.08, 0.16, 0.20, 0.30 and 0.36 for 1-butanol, ethanol, i-propanol, methanol and acetonitrile, respectively. The gel–sol transition for CH<sub>3</sub>CN is at room temperature, irrespective of the gelator concentration. For this reason the corresponding plot was not included in Fig. 1.
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