Electronic Supplementary Information

(7 pages)

Polymorphs from supramolecular gels: four crystal forms of the same silver(I) supergelator crystallized directly from its gels.

Dario Braga, Simone d'Agostino, Eros D'Amen, and Fabrizia Grepioni**

---

1. General information

All reactants and reagents were purchased from Alfa-Aesar and used without further purification. Reagent grade solvents were used.

2. Synthesis of the ligand PQ5U

The ligand PQ5U was prepared according to the reported procedure.[1] 5-Aminoquinoline (0.36 g, 2.5 mmol) was dissolved in dry dichloromethane (*ca.* 10 mL); a solution of phenylisocyanate (0.27 mL, 2.5 mmol) in dichloromethane was then added dropwise, and the mixture was stirred at room temperature for 3 h. The product formed was filtered and recrystallized from methanol. PQ5U was identified by X-ray powder diffraction (Figure ESI-1).

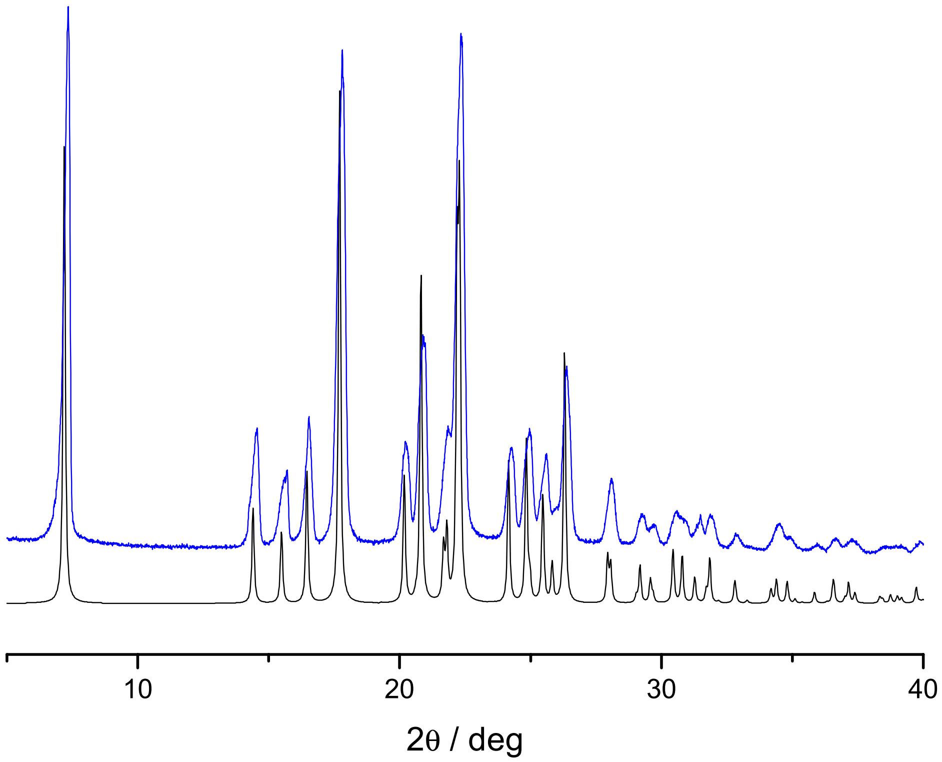


Figure ESI-1. Comparison between the experimental XRPD obtained from polycrystalline PQ5U (blue-line) and that calculated on the basis of the single-crystal structure.

3. Gel preparation, determination of the gel-sol dissociation temperatures and construction of a sol-gel plot

In a typical gelation experiment ca. 10 mg of a finely ground $AgNO_3$:PQ5U mixture in 1:2 or 1:1 molar ratio was suspended in 5 mL of an organic solvent in a 2 cm diameter vial, and the vial was heated until a clear solution was obtained, which was allowed to cool to room temperature. Gelation was complete when the vial could be inverted without liquid flow ("tube inversion test"). Minimum gelation concentration was determined by adding 0.1 mL aliquotes of solvent and repeating the inversion test.

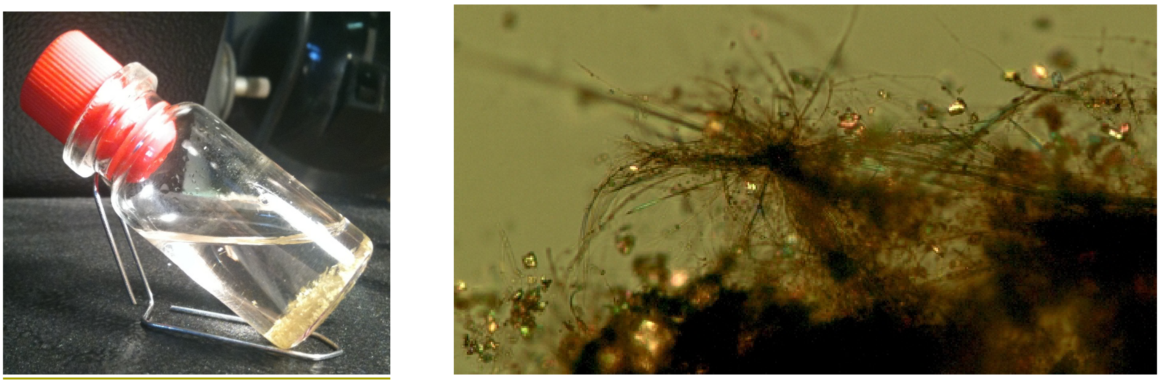
A plot of the gel-sol dissociation temperature (T_{gel}) in EtOH versus the gelator concentration was constructed by using the "dropping ball" method,[3] in which a 0.5 g steel ball was placed on the gel surface in 2 cm diameter vials. The vials were slowly heated in an oil-bath (ca. 1 deg min^{-1}). The temperature at which the steel ball fell to the bottom of the vial was taken as *the gel dissociation temperature* (T_{gel}).

Gels were prepared as follow (data for gel preparation in EtOH): (a) $AgNO_3$ and PQ5U were ground in a 1:2 stoichiometric ratio, then 8 mg, 9 mg, 10 mg, 11 mg, 12 mg and 14 mg of the mixture were suspended in 5 mL of ethanol and boiled for a few minutes until a clear solution was obtained; upon cooling of the solution transparent gels were obtained in all cases.

4. Growth of single crystals from the gels.

Vials containing gels obtained in CH_3CN, EtOH, i-PrOH and MeOH were sealed and left standing at room temperature. After a few days the gels contained in the vials had separated into clear solutions and crystalline materials deposited on the bottom of the vial; Figure ESI-2a, shows the results of the crystallization for the gel obtained from MeOH. The yellow crystals correspond to Form IV.

When the vials are left open in the air at room temperature, a xerogel is formed, which (depending on the laboratory temperature and humidity) may sometimes show the presence of tiny crystals grown on the fibrous material (see Figure ESI-2b: the picture was taken with a polarizing microscope).



(a) (b)

Fig. ESI-2

5. Crystal structure determination and packing features

Single-crystal data for compounds I—IV **(CCDC 801410 – 801413)** were collected on an Oxford X'Calibur S CCD diffractometer equipped with a graphite monochromator (Mo-Kα radiation, $\lambda = 0.71073$Å) and operated at room temperature. Crystal data and details of measurements are summarised in Table ESI-1. All non-hydrogen atoms were refined anisotropically; H_{NH} atoms were directly located; H_{CH} atoms for all compounds were added in calculated positions and refined riding on their respective carbon atoms.

SHELX97[3a] was used for structure solution and refinement on F^2 of **Forms I** to **III**, while **Form III** was solved with SIR2008[3b]; PLATON[3c] and SCHAKAL99[3d] were used for hydrogen bonding analysis and graphical representation of the results, respectively.

X-ray powder diffractograms were collected on a Panalytical X'Pert PRO automated diffractometer equipped with an X'Celerator detector. A Cu anode was used as X-ray source at 40KV and 40 mA.

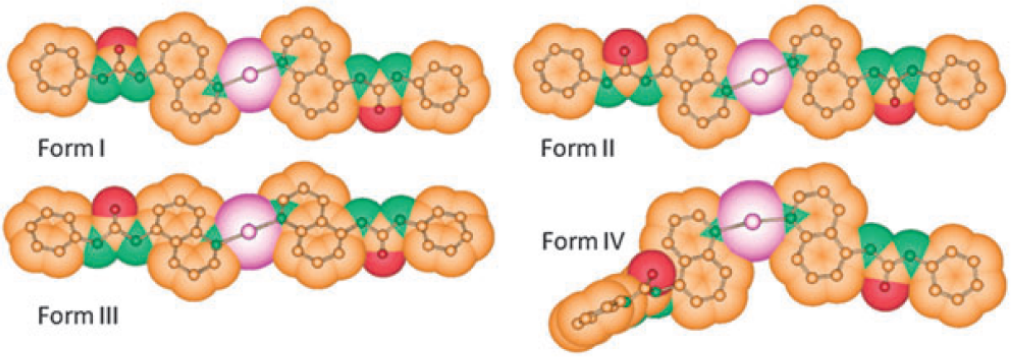


Fig. ESI-3. Comparison of the [Ag(PQ5U)2]+ unit observed in Forms I to IV [H atoms omitted for clarity].

Table ESI-1. Crystal data and structure refinement details for $[Ag(PQ5U)_2]NO_3$ for **Forms I**, **II**, **III** and **IV**.

	I	**II**	**III**	**IV**
Chemical formula	$C_{32}H_{26}N_7O_5Ag$	$C_{32}H_{26}N_7O_5Ag$	$C_{32}H_{26}N_7O_5Ag$	$C_{32}H_{26}N_7O_5Ag$
fw	696.47	696.47	696.47	696.47
Crystal System	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P21/$_n$	C2/c	P-1	P-1
Z	4	4	1	2
Z’	1	0.5	0.5	1
a (Å)	14.9972(7)	13.842(1)	6.2652(2)	7.6870(3)
b (Å)	9.1664(5)	8.3439(7)	7.8792(2)	10.5157(4)
c (Å)	21.561(1)	25.208(2)	15.022(1)	18.9647(8)
α (deg)	90	90	95.156(6)	100.092(3)
β (deg)	101.587(5)	98.141(7)	91.583(6)	101.640(3)
γ (deg)	90	90	94.165(6)	99.170(3)
V ($Å^3$)	2903.6(3)	2882.0(4)	736.1	1447.8(1)
D_{calc} (Mg/m^3)	1.593	1.605	1.571	1.598
μ (mm^{-1})	0.750	0.756	0.740	0.752
n° of collected reflns	12854	6327	5778	10982
n° of indep. reflns	6146	3262	3315	6475
R1[on F_0^2,I>2sigma(I)]	0.0457	0.0415	0.0630	0.0375
wR2 (all data)	0.1098	0.0959	0.2091	0.0485

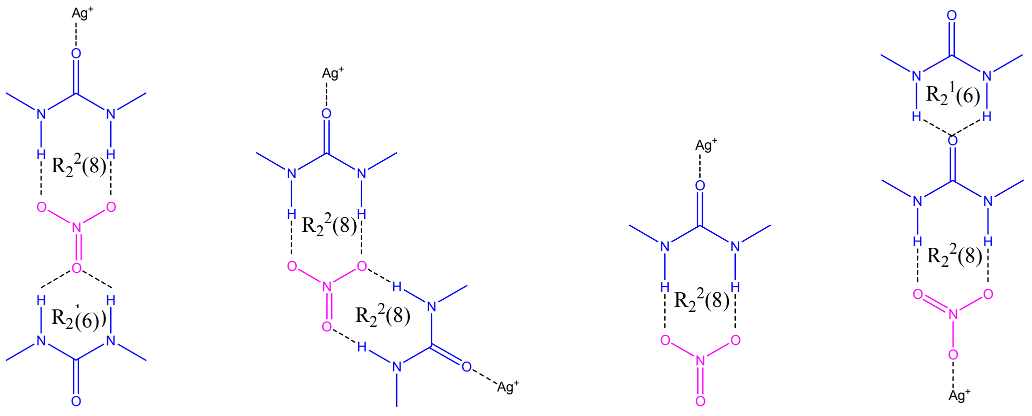
References
[1] D. Kalita, R. Sarma, J. B. Baruah, *CrystEngComm* **2009**, **11**, 803-8 10.
[2] D. K. Smith, in *Organic Nanostructures*, (Eds. J. L. Atwood, J. W. Steed), WILEY-VCH, Weinheim, **2008**, pp. 116-117.
[3] (a) G. M. Sheldrick, *SHELX97*, *Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997; (b) M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna, *J. Appl. Cryst.* **2007**, 40, 609-613 (c) A. L. Speck, *PLATON*; *Acta Crystallogr., Sect. A,* 1990, **46**, C34; (d) E. Keller, *SCHAKAL99*, *Graphical Representation of Molecular Models*; University of Freiburg: Freiburg, Germany, **1999**.

Table ESI-2. Coordination geometry around the silver ion for **Forms I**, **II**, **III** and **IV** (distances in Å, angles in deg)

	1	**2**	**3**	**4**
Distances				
N—Ag	2.110(3) - 2.122(2)	2.135(3)	2.140(6)	2.188(2) - 2.200(2)
O_{urea}—Ag	2.867(3)	2.866(2)	3.131(4)	-
$O_{nitrate}$—Ag	-	-	-	2.685(2)
Angles				
N—Ag—N	176.4(1)	180.0(1)	180.0(2)	169.98(8)
O_{urea}—Ag—O_{urea}	-	180.0(6)	180	-
$O_{nitrate}$—Ag—N	-	-	-	86.47(2) - 102.39(2)

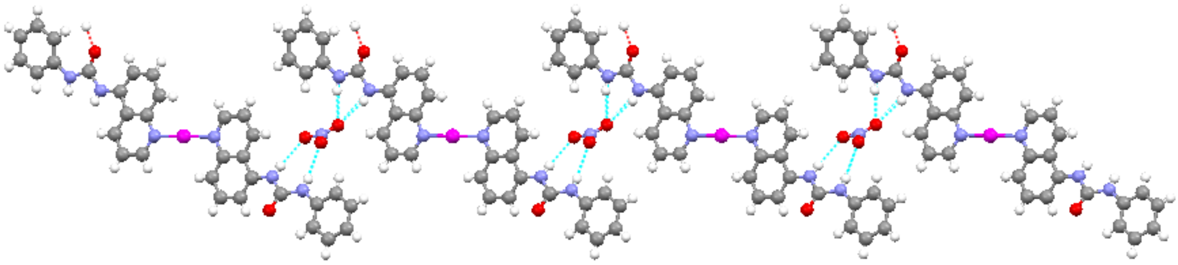
Table ESI-3. N(H)···O hydrogen bond distances (donor-acceptor) for urea-nitrate and urea-urea interactions observed in **Forms I**, **II**, **III** and **IV**.

	Ring motif	**I**	**II**	**III**	**IV**
Urea-nitrate	$R_2^2(8)$	3.006(7)-3.119(7)	2.869(4)-3.283(3)	2.967(8)-3.01(1)	2.883(3)-3.034(4)
Urea-nitrate	$R_2^1(6)$	2.385(6)-2.939(6)	-	-	-
Urea-Urea	$R_2^1(6)$	-	-	-	2.944(3)-3.044(4)

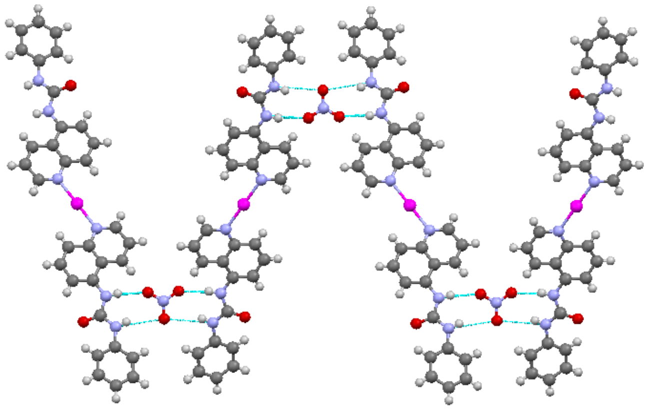


Form I **Form II** **Form III** **Form IV**

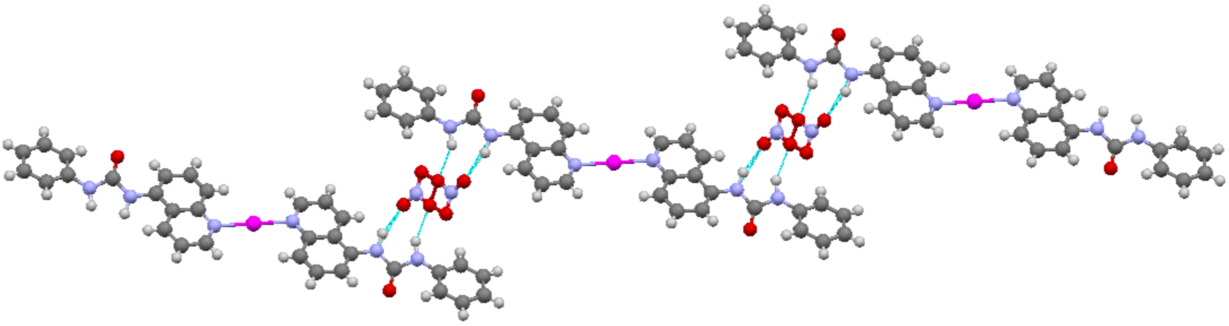
Scheme ESI-1. Hydrogen bonding ring motifs in urea-nitrate and urea-silver interactions observed in **Forms I**, **II**, **III** and **IV**.



Form I

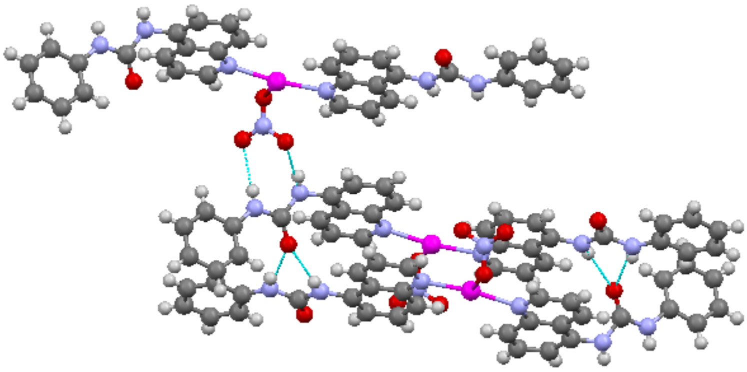


Form II



Form III

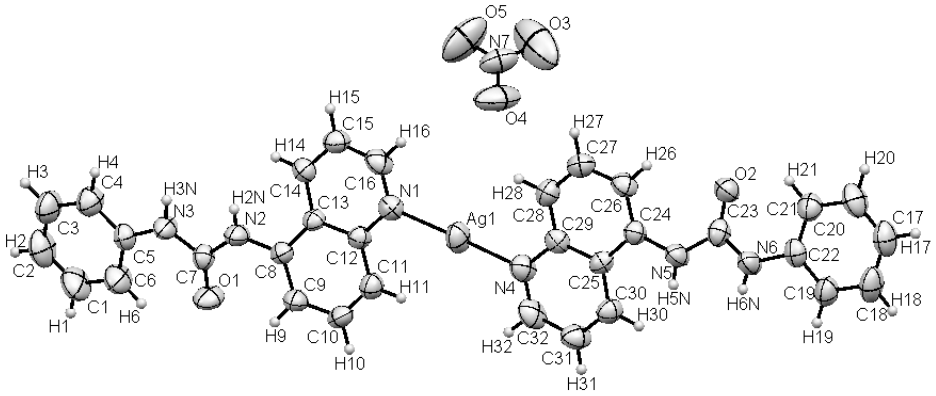
[Note that both disordered positions are shown for each nitrate ion, which is therefore involved in only one hydrogen bonding ring motif at a time.]



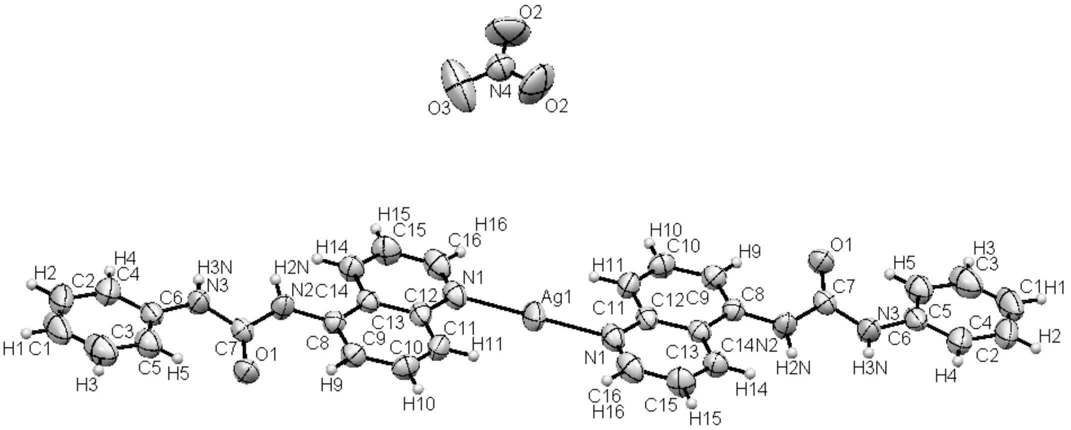
Form IV

Figure ESI-4. Hydrogen bonding ring motifs in **Forms I**, **II**, **III** and **IV** involving urea groups, nitrate ions and silver cations, as represented in Scheme S1.

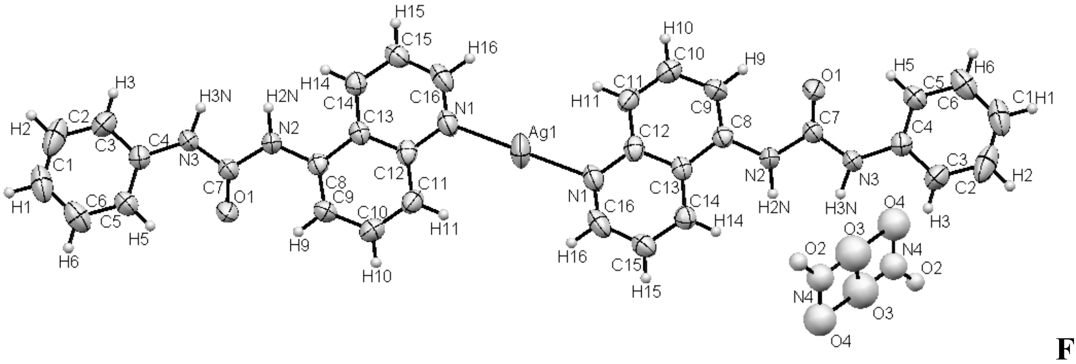
6. ORTEP drawings for Forms **I**, **II**, **III** and **IV**



Form I

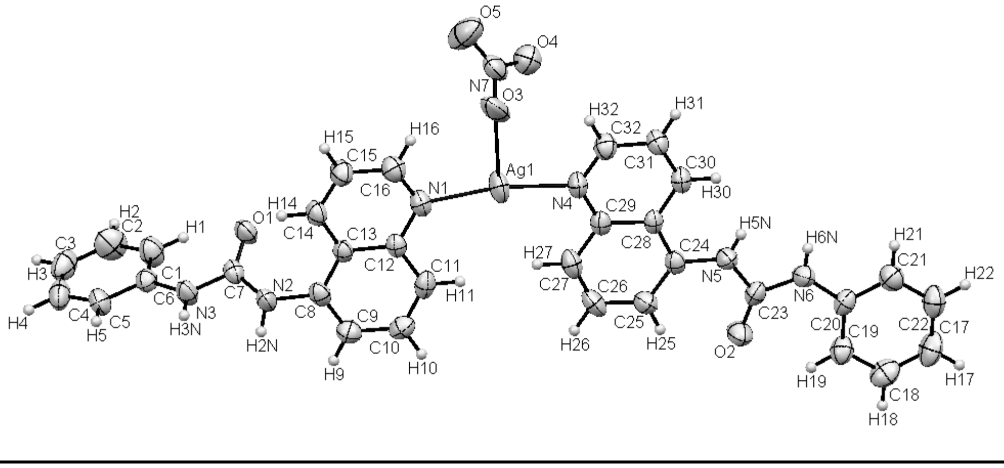


Form II



Form III

(Note that both disordered positions are shown for the nitrate ion)



Form IV