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# Multiple Processing of Metal-Ion Coordination, Anion-Binding, Hydrogen-Bonding- Self-Assembly and $\pi$ - $\pi$ Stacking Subprograms in Silver (I) Coordination Polymers

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*New crystalline coordination-polymers are obtained under conditions in which distinct metal ion coordination, hydrogen-bonding and  $\pi$ - $\pi$  stacking subprograms are involved in independent binding events of ureidopyridyl ligands **1** and **2** by silver hexafluorophosphate or silver triflate. The geometrical information contained in the structure of the ligands **1** and **2** is fully exploited by the silver ion coordination and urea-self assembly or H-bond anion coordination (templating features in an independent way. Describing linear or angular sequences may serve to use the information stored in molecular components that could be read out by synergistic and sequential non-covalent subprograms. It results in linear or tubular supramolecular coordination polymers constructed in a bottom-up strategy.*

*Keywords: Supramolecular chemistry, crystal engineering, hydrogen bonds, pi interactions, self-assembly, silver*

Molecular self-organisation is the basis for the construction of new useful crystalline nanomaterials in a bottom-up strategy. The road taken, from molecular to nano(micro)scale devices, depends both on the nature of its constituents and on the interactions between them. [1-4] Among the noncovalent motifs, metal-ligand coordination [3] hydrogen bonding [4] and  $\pi$ - $\pi$  stacking [5] interactions have been used for the generation of a wide variety of functional nanostructures. One approach to address this issue is to design molecular components built from binding subunits of different types so as to combine within their structure the information required for the processing of distinct programs corresponding to different architectures. [6] Such systems offer the possibility of multiple expressions of the information in molecular systems, which can be expressed in an independent way, [6a] in a mixed fashion [6b] or in a dominant/recessive behaviour [6c] of one distinct subprogram. Metal-directed self-assembly [3, 6] or combined hydrogen-bonding-metal coordination [7] and  $\pi$ - $\pi$  stacking-metal coordination [5, 8] subprograms has been extensively used as a powerful tool for the spontaneous generation of such nanostructures.

Our recent studies have shown that urea-based receptors readily assemble in functional columnar superstructures of interest for polytopic molecular recognition and supramolecular self-organized transport devices. [9] As an extension of these studies, we have recently showed that it would be interesting to combine urea hydrogen-bonding and metal ion-coordination chemistry in order to form mixed metal-ion complexes and anion-urea crystalline networks in which linear and tubular crystalline superstructures are formed (scheme 1) [10].

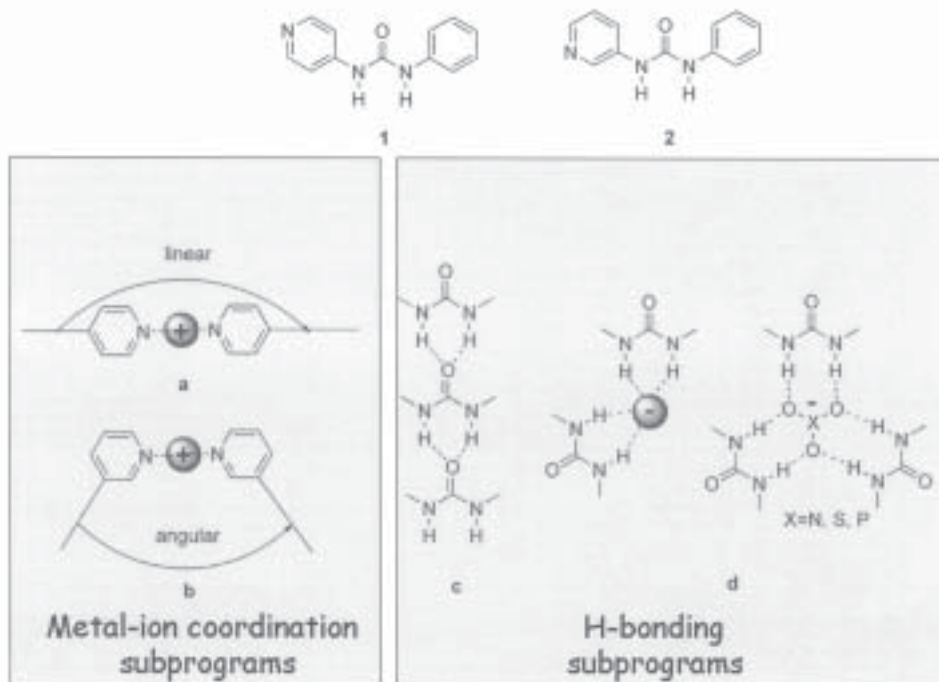
The systems mentioned in this paper operate under conditions in which distinct metal coordination, hydrogen-bonding and  $\pi$ - $\pi$  stacking subprograms were involved in independent binding events. The information contained in the structure of ligands **1** and **2** (scheme 1) was fully

exploited by the metal ions coordination and urea-self assembly [11a] or H-bond-anion coordination (templating) [11b] properties.

Molecular compounds **1** and **2** are designed as precursors for the coordination polymeric materials and are based on four encoded features: 1) the pyridil groups could coordinate to  $\text{Ag}^+$  cations upon a linear coordination geometry and their subsequent substitution in  $\gamma$  and  $\beta$  positions might direct to linear and angular (scheme 1a,b) supramolecular polymers, through the simultaneous hydrogen-bonding subprograms; 2) hydrogen-bonding guiding interaction might be the urea head-to-tail motif (Scheme 1c) which could generate H-bond ribbons; 3) the anion binding via H-bonding to urea moiety could generate scaffolds with different binding geometries (Scheme 1d); 4) the  $\pi$ - $\pi$  stacking subprogram involving interactions between the  $\pi$ -donor benzene and the  $\pi$ -acceptor pyridine systems might reinforce and direct the self-assembly of such predefined structural motifs. The two types of urea functionalities (self-assembly subprograms) might be exploited for the specific synthesis of new crystalline networks [11]. The nature of the anion might play a very important role in the urea-urea homomeric and urea-anion heteromeric self-assembly processes. It can interfere within different self-assembly subprograms and few examples are presented when the anion is used as builder component of crystalline networks.

With this in mind, in this paper, we were interested in determining whether the nature of the anion may affect the supramolecular packing of discrete  $[\mathbf{1}_2\text{Ag}]^+\text{X}^-$  and  $[\mathbf{2}_2\text{Ag}]^+\text{X}^-$  complexes in the crystalline coordination polymers, relying on the use of directional information encoded within the metal and ligand precursors. By following the same strategy reported before [10] for  $[\mathbf{1}_2\text{Ag}]^+\text{PF}_6^-$ , **3** and  $[\mathbf{2}_2\text{Ag}]^+\text{PF}_6^-$ , **4** crystalline complexes, we prepared new crystalline complexes  $[\mathbf{1}_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$ , **5** and  $[\mathbf{2}_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$ , **6** by using the triflate,  $\text{CF}_3\text{SO}_3^-$  as a strong

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Scheme 1. Concept and design of molecular precursors **1**, **2**: a) linear and b) angular ion-coordination-directing structure scaffolds; c) urea head-to-tail and d) anion templating hydrogen-bonding supramolecular guiding subprograms

urea H-bonding oxoanion, in order to verify if it can be exploited as a framework builder or if it only assists the framework self-assembly.

### Experimental Part

**General procedure for synthesis of compounds 1 and 2:** **1** and **2** were prepared as previously reported by adding phenyl isocyanate to corresponding  $\gamma$  and  $\beta$ -aminopyridine in benzene and reaction was refluxed under Ar for 5 h [10]. After removal of the solvent, the residue was subjected to crystallization from acetonitrile to afford **1** and **2** as colourless crystals.

$^1\text{H}$  and  $^{13}\text{C}$  NMR, were recorded on an ARX 250 MHz Bruker spectrometer in  $\text{CD}_3\text{CN}$ . Mass spectrometric studies were performed using a quadrupole mass spectrometer (Micromass, Platform II). The microanalyses were carried out at Service de Microanalyses, CNRS, Lyon.

**1-Phenyl-3-pyridine-4-yl-urea, 1** (yield =85%).  $^1\text{H}$  RMN ( $\text{CH}_3\text{CN}$ ):  $\delta = 7.1$  (t,  $J=6.95$  Hz, 1H), 7.28 (m, 6H) 8.1 (s, 1H), 8.4 (d,  $J=6.03$  Hz, 2H), 8.8 (s, 1H);  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ )  $\delta = 113.6, 120.7, 124.6, 129.6, 138.0, 147.7, 150.2, 153.0$ ; ES-MS:  $m/z(\%)$   $[\text{M}+\text{H}^+]$ , 214 (100);  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$  (213.2 g/mol): calcd C 67.59, H 5.20, N, 19.71; found C 67.49, H 5.33, N 19.10.

**1-Phenyl-3-pyridine-3-yl-urea, 2** (yield =80%).  $^1\text{H}$  RMN ( $\text{CH}_3\text{CN}$ ):  $\delta = 7.1$  (t,  $J=6.95$  Hz, 1H) 7.26 (m, 6H), 8.2 (s, 1H), 8.3 (d,  $J=6.03$  Hz, 1H), 8.53 (d,  $J=3.03$  Hz, 1H), 8.9 (s, 1H);  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ )  $\delta = 120.7, 124.6, 129.6, 138.0, 139.4, 147.7, 150.2, 153.0$ ; ES-MS:  $m/z(\%)$   $[\text{M}+\text{H}^+]$ , 214 (100);  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$  (213.2 g/mol): calcd. C 67.59, H 5.20, N, 19.71; found C 66.92, H 5.64, N 20.00.

**General procedure for synthesis and crystallographic data of compounds 3-6**

**Crystal Structure determination:** X-ray diffraction data for the silver complexes **3-6** were collected with monochromatized Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å) on a Xcalibur diffractometer (Oxford Diffraction) equipped with a CCD camera. Data were reduced using the CrysAlis RED

software. The structures were determined using direct methods and refined by full matrix least squares methods (CRYSTALS [12]). All data were used for the refinements except for **6** where only data with  $I > 2\sigma(I)$  were used. Data for the latter compound were particularly weak, due to the size of the selected crystal. Non-hydrogen atoms were refined anisotropically, except for **6**. For this compound the  $\text{PF}_6^-$  counterions was refined as a rigid body. Hydrogen atoms were generally found using Fourier-difference maps and were allowed to ride on their parent atoms. CCDC 215131 (**3**); 215132 (**4**); CCDC 677973 (**5**) and 677974 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

**[1<sub>2</sub>Ag]<sup>+</sup>PF<sub>6</sub><sup>-</sup> 3**, Formation from **1** and  $\text{AgPF}_6$  (2 : 1, mol : mol) in  $\text{CD}_3\text{CN}$  at room temperature.  $^1\text{H}$  RMN ( $\text{CH}_3\text{CN}$ ):  $\delta = 7.1$  (t,  $J=6.95$  Hz, 1H) 7.26 (m, 4H), 8.3 (d,  $J=6.03$  Hz, 2H), 8.53 (d,  $J=6.03$  Hz, 2H), 8.7 (s, 1H), 9.1 (s, 1H), ES-MS:  $m/z(\%)$   $[\text{1}_2\text{Ag}^+]$ , 534.4 (100). X-ray crystallographic data:  $\text{C}_{24}\text{H}_{22}\text{AgF}_6\text{N}_6\text{O}_2\text{P}$ . Crystal dimensions: 0.40 . 0.20 . 0.09 mm. Cell dimensions:  $a = 9.5870(7)$  Å,  $b = 11.7012(8)$  Å,  $c = 12.0765(7)$  Å,  $\alpha = 109.30(1)^\circ$ ,  $\beta = 90.750(8)^\circ$ ,  $\gamma = 89.690(9)^\circ$ ,  $V = 1278.4(2)$  Å<sup>3</sup>, triclinic, space group  $P-1$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.765$  gcm<sup>-3</sup>,  $\mu = 0.931$  mm<sup>-1</sup>. 23558 measured reflections, 14350 unique, 2794 with  $I > 2\sigma(I)$ . Final  $R$  factors  $R_1 = 0.1186$  and  $wR_2 = 0.0759$  ( $R_1 = 0.0347$  and  $wR_2 = 0.0447$  for data  $I > 2\sigma(I)$ ); 361 parameters, maximal residual electron density 1.460 eÅ<sup>-3</sup>.

**[2<sub>2</sub>Ag]<sup>+</sup>PF<sub>6</sub><sup>-</sup> 4**, Formation from **2** and  $\text{AgPF}_6$  (2 : 1, mol : mol) in  $\text{CD}_3\text{CN}$  at room temperature.  $^1\text{H}$  RMN ( $\text{CH}_3\text{CN}$ ):  $\delta = 7.1$  (t,  $J=6.95$  Hz, 1H), 7.26 (m, 4H), 8.3 (d,  $J=6.03$  Hz, 2H), 8.53 (t,  $J=6.03$  Hz, 1H), 8.73 (d,  $J=3.03$  Hz, 1H), 8.9 (s, 1H), 9.2 (s, 1H); ES-MS:  $m/z(\%)$   $[\text{1}_2\text{Ag}^+]$ , 534.4 (100). X-ray crystallographic data:  $\text{C}_{26}\text{H}_{22}\text{AgF}_6\text{N}_7\text{O}_2\text{P}$ . Crystal dimensions: 0.10 . 0.08 . 0.05 mm. Cell dimensions:  $a = 10.907(1)$  Å,  $b = 20.387(1)$  Å,  $c = 13.286(2)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 106.19(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2837.1(6)$  Å<sup>3</sup>, monoclinic, space group  $P2_1/c$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.686$  gcm<sup>-3</sup>,  $\mu = 0.845$  mm<sup>-1</sup>. 53888 measured reflections, 9604 unique, 716 with  $I > 2\sigma(I)$ . Final  $R$  factors

$R_1=0.1171$  and  $wR_2=0.1342$ ; 153 parameters, maximal residual electron density  $1.860 \text{ e}\text{\AA}^{-3}$ .

$[1_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$  **5**, Formation from **1** and  $\text{AgCF}_3\text{SO}_3$  (2 : 1, mol : mol) in  $\text{CD}_3\text{CN}$  at room temperature.  $^1\text{H}$  RMN ( $\text{CH}_3\text{CN}$ ):  $\delta = 7.1$  (t,  $J=6.95$  Hz, 1H) 7.26 (m, 4H), , 8.3 (d,  $J=6.03$  Hz, 2H), 8.53 (d,  $J=6.03$  Hz, 2H), 8.9 (s, 1H), 9.2 (s, 1H); ES-MS : m/z(%)  $[1_2\text{Ag}]^+$ , 534.4 (100). X-ray crystallographic data:  $\text{C}_{26}\text{H}_{26}\text{AgF}_3\text{N}_6\text{O}_5\text{S}$ . Crystal dimensions:  $0.40 \times 0.20 \times 0.09$  mm. Cell dimensions:  $a=10.1222$  (7)  $\text{\AA}$ ,  $b=11.8593$  (7)  $\text{\AA}$ ,  $c=12.7508$  (7)  $\text{\AA}$ ,  $\alpha=94.132$  (5)°,  $\beta=110.273$  (6)°,  $\gamma=99.597$  (5)°,  $V=1401.7$  (2)  $\text{\AA}^3$ , triclinic, space group  $P\bar{1}$ ,  $Z=2$ ,  $\rho_{\text{calc}}=1.695$   $\text{gcm}^{-3}$ ,  $\mu=0.843$   $\text{mm}^{-1}$ . 24218 measured reflections, 15071 unique, 11622 with  $I > 2\sigma(I)$ . Final  $R$  factors  $R_1=0.0544$  and  $wR_2=0.0550$  ( $R_1=0.0412$  and  $wR_2=0.0519$  for data  $I > 2\sigma(I)$ ); 388 parameters, maximal residual electron density  $1.35 \text{ e}\text{\AA}^{-3}$ .

$[2_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$  **6**, Formation from **2** and  $\text{AgCF}_3\text{SO}_3$  (2 : 1, mol : mol) in  $\text{CD}_3\text{CN}$  at room temperature.  $^1\text{H}$  RMN ( $\text{CH}_3\text{CN}$ ):  $\delta = 7.1$  (t,  $J=6.95$  Hz, 1H) 7.26 (m, 4H), 8.3 (d,  $J=6.03$  Hz, 2H), 8.53 (t,  $J=6.03$  Hz, 1H), 8.73 (d,  $J=3.03$  Hz, 1H), 8.9 (s, 1H), 9.2 (s, 1H); ES-MS : m/z(%)  $[1_2\text{Ag}]^+$ , 534.4 (100). X-ray crystallographic data:  $\text{C}_{27}\text{H}_{26}\text{AgF}_3\text{N}_7\text{O}_5\text{S}$ . Crystal dimensions:  $0.48 \times 0.46 \times 0.23$  mm. Cell dimensions:  $a=10.9587$  (5)  $\text{\AA}$ ,  $b=20.2847$  (9)  $\text{\AA}$ ,  $c=13.5558$  (8)  $\text{\AA}$ ,  $\alpha=90^\circ$ ,  $\beta=106.621$  (5)°,  $\gamma=90^\circ$ ,  $V=2887.5$  (3)  $\text{\AA}^3$ , monoclinic, space group  $P2_1/c$ ,  $Z=4$ ,  $\rho_{\text{calc}}=1.666$   $\text{gcm}^{-3}$ ,  $\mu=0.841$   $\text{mm}^{-1}$ . 53753 measured reflections, 9514 unique, 5556 with  $I > 2\sigma(I)$ . Final  $R$  factors  $R_1=0.0851$  and  $wR_2=0.0660$  ( $R_1=0.0490$  and  $wR_2=0.0625$  for data  $I > 2\sigma(I)$ ); 397 parameters, maximal residual electron density  $1.48 \text{ e}\text{\AA}^{-3}$ .

## Results and Discussions

*Synthetic comparative study of solid state structures of  $[1_2\text{Ag}]^+\text{PF}_6^-$  **3**,  $[2_2\text{Ag}]^+\text{PF}_6^-$  **4**,  $[1_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$  **5** and  $[2_2\text{Ag}]^+\text{PF}_6^-$  **6** crystalline complexes:*

The ligands **1** and **2** were prepared as previously reported from phenyl isocyanate and 4- and 3-aminopyridine, respectively. Complexation studies revealed that the addition of  $\text{AgPF}_6$  and of  $\text{AgCF}_3\text{SO}_3$  salts to acetonitrile suspensions of **1** or **2** (2 : 1, mol : mol) caused a rapid dissolution of the ligand to give colourless solutions. Crystals of  $[1_2\text{Ag}]^+\text{PF}_6^-$  **3**,  $[2_2\text{Ag}]^+\text{PF}_6^-$  **4**,  $[1_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$  **5** and  $[2_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$  **6** complexes were obtained from acetonitrile/ isopropylether (1/5) solutions at room temperature. The  $^1\text{H}$  NMR spectra of the complexes **3-6** were very sharp, indicating the formation of discrete metal complexes. They showed a deshielding of the pyridine protons due to the silver complexation and of the N-H urea protons due to the anion complexation. The ESI mass spectra of the complexes **3-6** showed peaks for polymeric species at 534.4 for  $[\text{L}_n\text{Ag}_n]^{n+}$   $n=1-3$  (the charge state were determined by isotopic profile simulations).

The crystal structure of  $\text{Ag}^+$  complexes **3-6** revealed that these crystals are based on linear (Figure 1a,c) and angular (fig. 1b,d) elementary scaffolds in which the  $\text{Ag}^+$  ion is coordinated by two pyridine units situated on the same plane (the averaged Ag-N bond lengths is 2.15  $\text{\AA}$ ), presenting a linear coordination geometry. Subsequent substitution of pyridine moieties in  $\gamma$  and  $\beta$  positions induced a linear or an angular (inner angle between nitrogen mean lines of about  $165^\circ$  and  $85^\circ$ , respectively) relative disposition of secondary phenylurea H-bond-directing moieties. This results in the emergence of quasi-rigidly preorganised linear and angular respectively building blocks of **3**, **5** and respectively **4**, **6**.

The  $\text{PF}_6^-$  counteranion was chosen for their F...H-N H-bonding and their hydrophobic properties. [4, 6] In both **3**

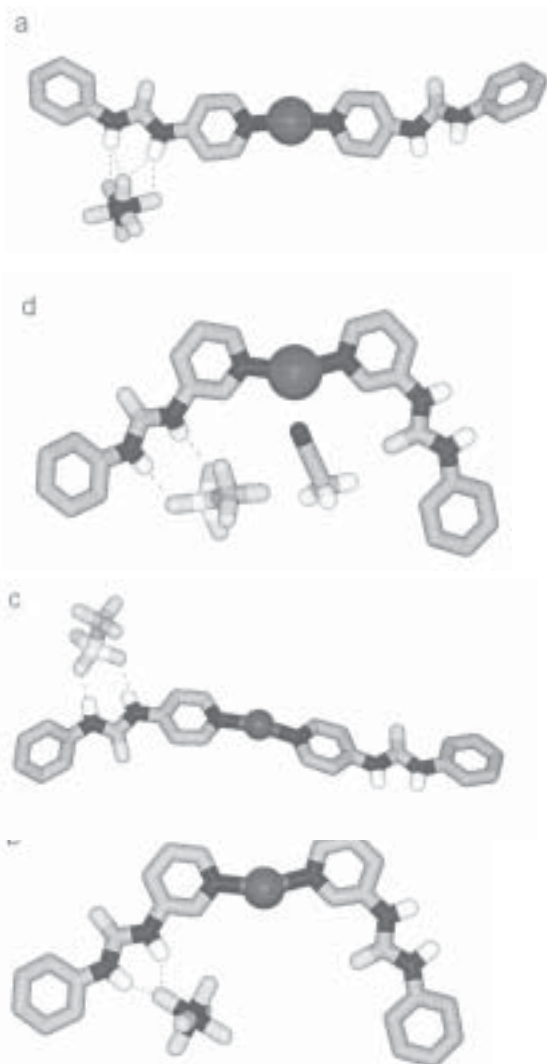
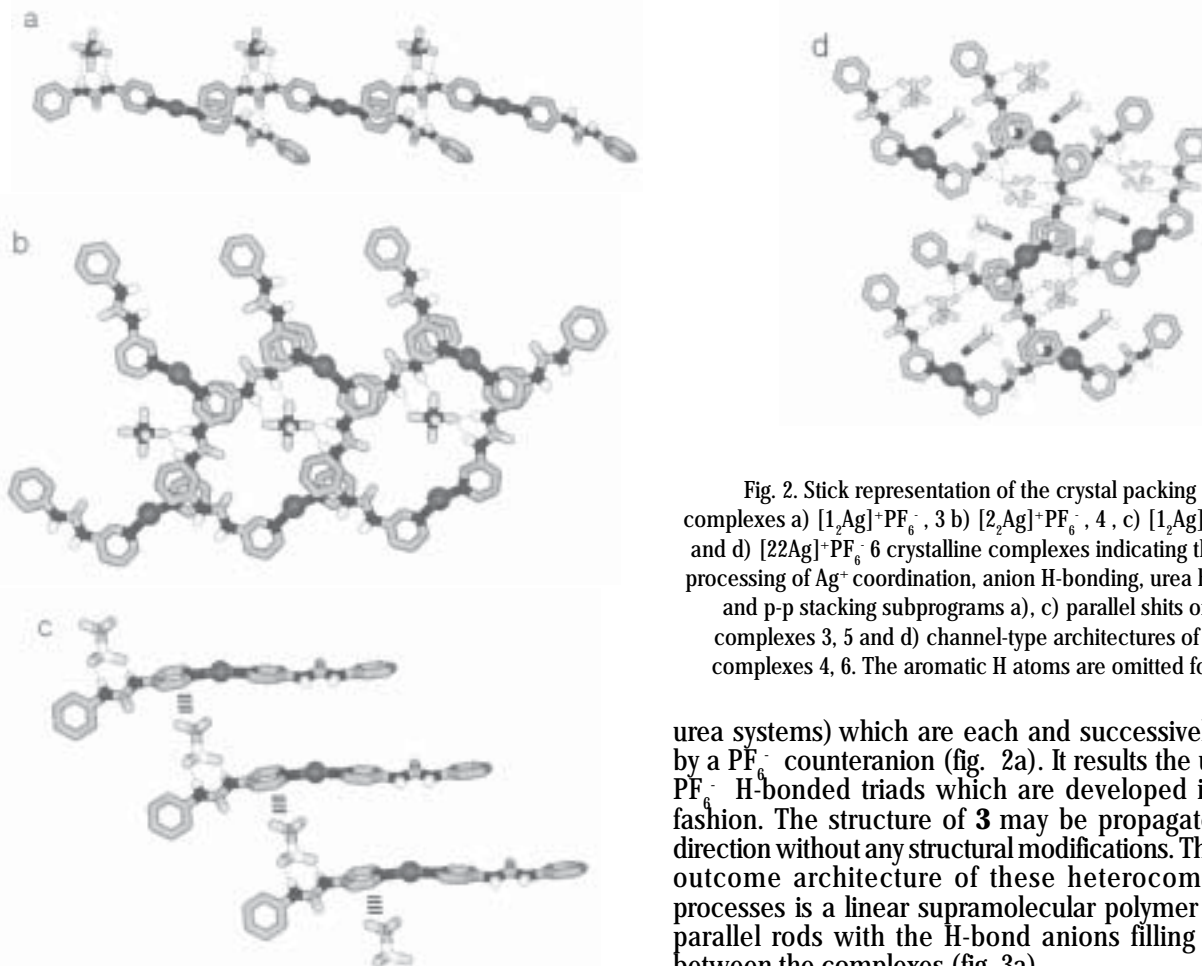


Fig. 1. Stick representation of the crystal structure of silver complexes a)  $[1_2\text{Ag}]^+\text{PF}_6^-$  **3** b)  $[2_2\text{Ag}]^+\text{PF}_6^-$  **4** , c)  $[1_2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$  **5** and d)  $[2_2\text{Ag}]^+\text{PF}_6^-$  **6** crystalline complexes indicating a linear or an angular relative disposition of the ligands and the specific H-bonding of the  $\text{PF}_6^-$  and  $\text{CF}_3\text{SO}_3^-$  anions. The aromatic H atoms are omitted for clarity

and **4** complexes the  $\text{PF}_6^-$  counteranion in H-bonded to one urea moiety and the F...H-N H-bond lengths fall within the ranges 2.04-2.28  $\text{\AA}$  (Figure 1a,b). In the case of the complexes **5** and **6** the triflate anion was chosen as a strong H-bonding complexant and in both complexes, it is strongly bonded to the urea moiety via two short H-bonds (the d<sub>O-H</sub> bond lengths fall within the ranges 1.80-2.20  $\text{\AA}$ ) (fig. 1c,d).

The two H-bonding subprograms can in principle yield a set of interconverting complexes [13] and to lead to a preferential expression of a specific member of the equilibrating set of complexes resulted from urea head-to-tail motif or anion-template formation of specific architectures. The two independent H-bond subprograms are expressed in an independent way in the structure of the linear complex **3** (fig. 2a). In this case the  $\text{PF}_6^-$  complexation and urea head-to tail subprograms are processed independently in parallel fashion and are assisted by favourable  $\pi$ - $\pi$  stacking interactions between neighbouring  $\pi$ -donor benzene and the  $\pi$ -acceptor pyridine rings (centroid-centroid distance of 3.98  $\text{\AA}$ , corresponding to van der Waals contact). The urea moiety of the linear building block is connected by head-to-tail hydrogen bonds with one urea moiety of two neighbouring molecules of **1** (average N—H—O distance is 3.01  $\text{\AA}$ , consistent with other



urea systems) which are each and successively bonded by a  $\text{PF}_6^-$  counteranion (fig. 2a). It results the urea-urea- $\text{PF}_6^-$  H-bonded triads which are developed in parallel fashion. The structure of **3** may be propagated in one direction without any structural modifications. The resulted outcome architecture of these heterocomplexation processes is a linear supramolecular polymer of infinite parallel rods with the H-bond anions filling the voids between the complexes (fig. 3a).

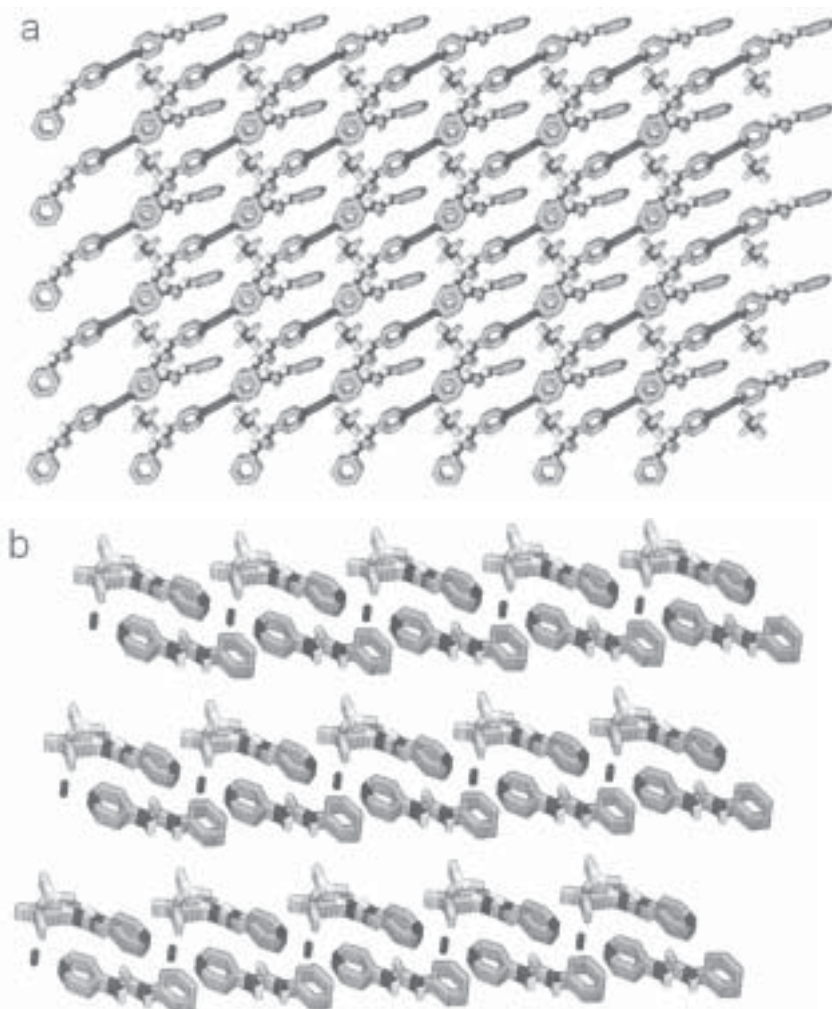


Fig. 3. a) Crystal packing of linear supramolecular rods of silver complexes a)  $[1/2\text{Ag}]^+\text{PF}_6^-$ ; **3** and b)  $[1/2\text{Ag}]^+\text{CF}_3\text{SO}_3^-$ ; **5**. The aromatic H atoms are omitted for clarity

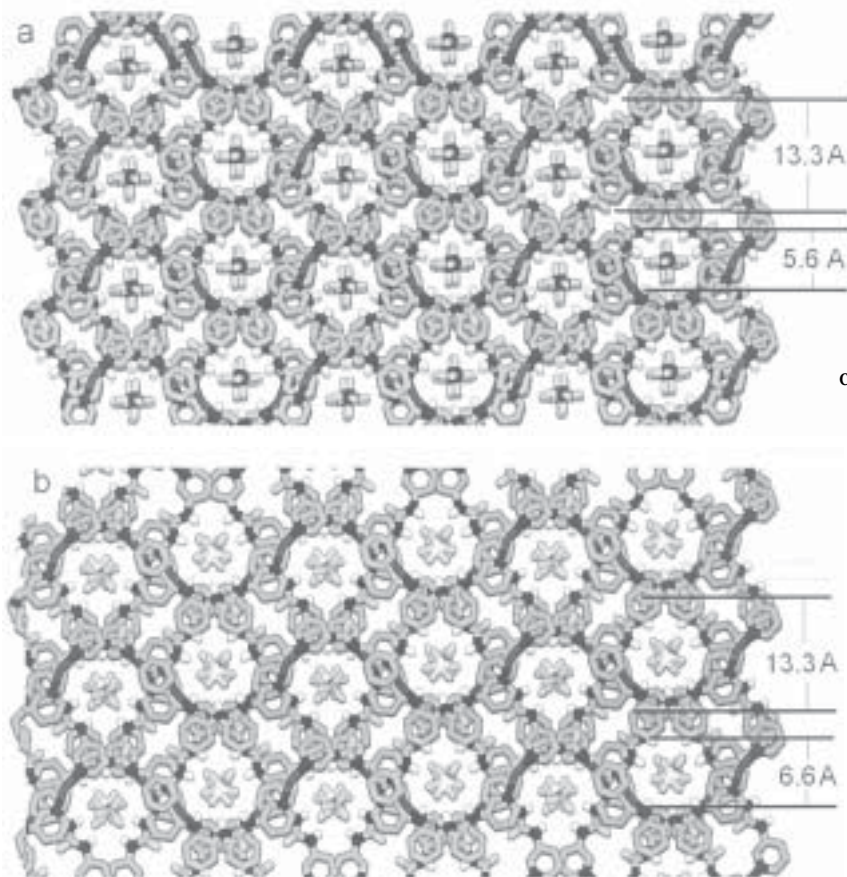


Fig. 4. a) Crystal packing of tubular bundles of complex a) 4. and b) 6. The aromatic H atoms are omitted for clarity.

In the case of the linear complex **5**, the strong H-bonding of the triflate anion represents a dominant behaviour compared to the head-to-tail urea-urea H-bonding processes. It results in the disruption of such H-bonding events with the total complexation of the triflate anions by the urea moieties and the generation of parallel sheets of linear complexes. These layers are in close contact and are connected by the cooperative triflate urea H-bonding at and weak F- $\pi$  (F- $\pi$  distance of 3.3 Å) [14a] and C-H-F interactions (the F-H distance of 2.42 Å) between the CF<sub>3</sub> group of the triflate anion and a vicinal pyridine moiety from a neighbouring layer (fig. 3c, fig. 4b) [14b].

The relative output expression of angular isostructural complexes **4** and **6** containing the angular building blocks is different from previously presented complexes and deserves some comment. As shown in figures 2b,d the dominant anion hydrogen bonding (for both PF<sub>6</sub><sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) is favoured to urea-urea homo-association and is independent to the nature of the anion. The relative angular disposition of donor urea moieties allowed considerable overlap between all aromatic pyridine-benzene pairs with an average  $\pi$ - $\pi$  stacking centroid-centroid distance of 3.65 Å.

Accordingly, tubular arrays of  $\pi$ - $\pi$  stacked columnar devices of about 13.3 Å external diameter, are generated in the solid state by the self-organization process (fig. 4a,b). The anions are completely H-bonded to urea groups pointing the inner part of the tube. The synergistic effect of the metal ion binding, of the anion H-bond templating and of the large stacking interactions results in the formation of a regulated tubular bundle-type device in which the anions are arranged into an approximately linear array, tightly fitting into polar N-H surrounded central cavity of about 5.60-6.60 Å diameter. One may point out that the role of the stacking interaction in the present tubular superstructures is related to that in previously described organic nanotubes [15] and artificial helices [8].

## Conclusion

In summary, studies of H-bond mediated self-assembly of compounds **1** and **2** have established that two modes of H-bonding are possible in the solid state, depending on the nature of the anions used and on the relative position of the H-bond units. The heteroditopic ureidopyridyl ligands present some flexibility due to the conformational rotation around the central urea moiety. The simultaneous complexation of the silver (I) cation by two pyridine moieties and of the PF<sub>6</sub><sup>-</sup> and the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> counteranions by the urea moiety results in the formation of discrete complexes **3-6**, presenting restricted rotation around the central urea functionality. The geometrical information contained in the structure of the ligands **1** and **2** and the heteroditopic complexation of silver hexafluorophosphate and of silver triflate are fully exploited in an independent way resulting in the emergence of quasi-rigidly preorganised linear and angular respectively building blocks of **3** and **5** and respectively **4** and **6**. The triflate anion, a strong complexant oxoanion, determines the disruption of urea-urea homomeric association in the case of linear complexes derived from ligand **1** and induces a different bridging feature of the parallel layers in the solid state of **5**.

The relative angular disposition of donor urea moieties in **4** and **6** allowed considerable overlap between all aromatic pyridine-benzene pairs and these additional  $\pi$ - $\pi$  stacking contacts reinforce and direct the self-assembly of above combined structural motifs in the solid state. Accordingly very robust tubular arrays of  $\pi$ - $\pi$  stacked architectures insensitive to the complexation behavior of the anion are generated in the solid state by synergistic and sequential metal ion complexation, hydrogen bonding and  $\pi$ - $\pi$  stacking interactions.

Finally, the present results show that by using rationally heteroditopic ligands it is possible to control through metal-ion and anion binding (templating) the constitutional shape

of the functional output supramolecular device. Described linear or orthogonal sequences may serve to use the information stored in molecular components that could be read out by synergistic and sequential metal ion complexation, hydrogen bonding and  $\pi$ - $\pi$  stacking interactions. It results linear or tubular supramolecular polymers constructed in a bottom-up strategy.

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