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Molecular tectonics: generation of 1-D interdigitated and 2-D interwoven helical silver coordination networks by oligoethylene glycol based tectons bearing two benzonitrile moieties†

Julien Bourlier, Mir Wais Hosseini,* Jean-Marc Planeix and Nathalie Kyritsakas

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Ligands based on oligoethylene glycol units bearing at their extremities benzonitrile groups behave in the crystalline phase as tectons and lead in the presence of silver cation to different coordination networks. Depending on the number of glycol units, 1-D stair type or 1-D interdigitated and 2-D interwoven architectures composed of helical strands are obtained.

Introduction

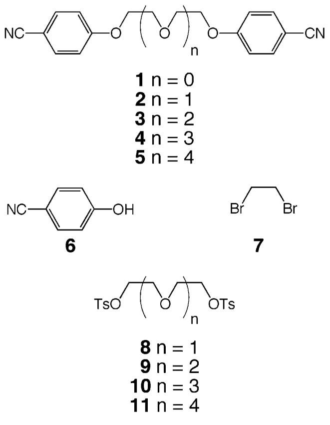
For some time now, we have been active in a domain called molecular tectonics.[1–4] This approach deals with the design and formation of molecular networks and is based on iterative molecular recognition processes between construction units or tectons.[5,6] The concepts and strategies developed in this area may be applied to the design and generation of coordination networks.[3,6,7] The latter, also called coordination polymers,[8] are infinite metallo-organic architectures generated upon mutual bridging between organic tectons and metal centres. These molecular assemblies are usually obtained in the crystalline phase under self-assembly conditions. For *ca.* two decades, this class of architecture has been attracting constant attention and many examples have been reported.[8–19] A major challenge in this area remains the fine understanding, both in terms of connectivity and topology, of the subtle factors governing the formation of these structures. Currently, we are rather far from that level and the majority of cases reported are the result of mixing and observing. In order to get a better insight, we believe that systematic studies based on incremental changes in the structure of the organic ligand and/or in the nature of the metal centre are of prime importance. Pursuing our efforts to better understand the formation of coordination networks and to design and generate new metallo-organic frameworks (for some recent publications see refs. 20–25) we have undertaken a systematic study on the design of construction units combining both primary and secondary coordination sites.[26,27]

In the present contribution we expand on this idea and report on the synthesis of tecton **1–5** as well as on the structural investigations of a variety of 1- and 2-D coordination networks obtained in the solid state in the presence of silver salts.

Results and discussion

Design of the tectons 1–5

In the continuation of our systematic effort to better understand the parameters governing the formation of coordination networks, we have explored the possibility of combining primary and secondary coordination sites within the structure of tectons. For this purpose, tectons **1–5** (Scheme 1) were designed. These molecules are based on oligoethylene glycol fragments bearing at their extremities benzonitrile groups. Concerning the benzonitrile group as coordination site, it is worth noting that in order to increase its coordination ability, the junction between the aryl group and the oligoethylene glycol unit is ensured, at the position 4 with respect to the nitrile moiety, by an ether link. This should indeed increase the electronic density on the nitrile group through electronic delocalisation. Dealing with the oligoethylene glycol connecting fragment, owing to its conformational flexibility, depending on the number of glycol introduced, this spacer may adopt a curved arrangement thus offering a semi circular disposition of oxygen atoms capable of surrounding the metal cation. Thus, one may regard these ligands as construction units offering two nitrile groups as primary coordination sites and oxygen atoms involved in their junctions as secondary binding



Scheme 1

Laboratoire de Chimie de Coordination Organique, UMR CNRS 7140, Université Louis Pasteur, F-67000 Strasbourg, France. E-mail: hosseini@chimie.u-strasbg.fr

† The HTML version of this article has been enhanced with additional colour images.

sites. The designed principle used here is flexible and allows, while keeping the number and nature of the primary sites fixed, to vary the number and location of the secondary interaction sites.

Choice of the metal

Concerning the metal centre, Ag^+ cation was selected because of its spherical nature and thus rather loose coordination requirements both in terms of coordination number and geometry. A further reason why silver cation was chosen is because the formation of Ag–N and Ag–O bonds is reversible and thus well suited for the formation, by self-assembly processes, of periodic architectures in the solid state. Since compounds **1–5** are neutral tectons, the silver cation must be associated with a counter ion in the solid state. In order to avoid binding competition between tectons **1–5** and the anion for silver cation, AsF_6^- and SbF_6^- anions were chosen because of their rather weakly coordination propensity.

Synthesis of tectons 1–5

The preparation of compounds **1–5** was straightforward and based on the condensation of 4-cyanophenol **6** with commercially available 1,2-dibromoethane **7** for the synthesis of **1** or ditosylate derivatives **8–11** for the preparation of **2–5** in refluxing CH_3CN in the presence of K_2CO_3 (see experimental section).

Structural investigations

Crystals of both compounds **1** and **2** were obtained and their solid state structures have been investigated. All five compounds **1–5** have been combined with $AgAsF_6$ and $AgSbF_6$ salts. However, although crystals have been obtained in the case of compounds **1** and **3–5**, for compound **2** no crystalline material could be obtained.

Free tectons 1 and 2

The solid state structure of the free tecton **1** was investigated by X-ray diffraction on single crystal (monoclinic, space group *P*2(1)/*n*). The structural determination (see Table 1) revealed that for the compound **1** there is an inversion centre at the midpoint of the central C–C bond and the ethylene glycol fragment adopts the *anti* conformation with the OCCO dihedral angle of 180° (Fig. 1). The two benzonitrile groups connected to the ethylene glycol unit through ether junctions ($d_{PhC–O}$ = 1.366 Å, $d_{C–O}$ = 1.432 Å, OCO angle = 117.9°) are perfectly coplanar. The nitrile moiety (d_{CN} = 1.151 Å) is almost linear to the phenyl ring with the CCN angle of 179.2°. The consecutive compounds **1** are arranged parallel to each other with 3.97 Å distance between the phenyl rings centroids.

The solid state structure of the free tecton **2** was investigated by X-ray diffraction on single crystal (monoclinic, space group *C*2/*c*). The structural determination (see Table 1) revealed that for **2** the central oxygen atom lies on a twofold axis with the diethylene glycol fragment adopting the *gauche* conformation (OCCO dihedral angle of −68.0° and −68.2°) (Fig. 2). The two benzonitrile groups connected to the diethylene glycol unit through ether junctions ($d_{PhC–O}$ = 1.359 Å, $d_{C–O}$ = 1.434 Å, OCO angle = 119.7°) are divergently oriented and the com-

Table 1 Data were collected at 173(2) K on a Bruker SMART CCD diffractometer

	1	**1**-AgSbF$_6$	**1**-AgAsF$_6$	**2**	**3**-AgAsF$_6$	**4**-AgSbF$_6$	**4**-AgAsF$_6$	**5**-AgSbF$_6$
Chemical formula	$C_{16}H_{12}N_2O_2$	$C_{24}H_{18}N_3O_3AgSbF_6$	$C_{24}H_{18}N_3O_3AgAsF_6$	$C_{18}H_{16}N_2O_3$	$C_{40}H_{28}N_4O_8Ag_2As_2F_{12}$	$C_{22}H_{24}N_2O_5AgSbF_6$	$C_{22}H_{24}N_2O_5AgAsF_6$	$C_{24}H_{28}N_2O_6AgSbF_6$
Molecular mass	264.28	740.03	693.20	308.33	645.14	740.05	693.22	784.10
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2_12_12_1$
***a*/Å**	3.9740(2)	7.0108(2)	6.9830(2)	15.4963(12)	9.1230(6)	11.96400(10)	11.7680(2)	12.0050(2)
***b*/Å**	13.5340(6)	11.0338(3)	10.9480(3)	4.6033(4)	11.6240(6)	25.7170(4)	25.7570(6)	12.8750(2)
***c*/Å**	11.9280(6)	16.9120(4)	16.7360(5)	22.437(2)	12.4770(9)	8.6320(2)	8.5870(4)	18.8880(3)
***α*/°**	90	93.6370(10)	93.0940(15)	90	62.419(2)	90	90	90
***β*/°**	90.982(3)	95.7360(10)	94.9470(13)	101.678(2)	83.793(2)	97.0780(6)	96.9200(9)	90
***γ*/°**	90	95.7290(10)	95.9610(13)	90	83.386(5)	90	90	90
***V*/Å^3**	641.44(5)	1291.62(6)	1265.25(6)	1567.4	1162.71(13)	2635.64(8)	2538.83(14)	2919.41(8)
***D*$_{calc}$/g cm^{-1}**	1.368	1.903	1.820	1.307	1.843	1.865	1.782	1.784
Z	2	2	2	4	2	4	4	4
Colour	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal size/mm	0.08 × 0.06 × 0.05	0.06 × 0.04 × 0.04	0.10 × 0.06 × 0.05	0.10 × 0.10 × 0.08	0.06 × 0.05 × 0.05	0.14 × 0.12 × 0.10	0.20 × 0.20 × 0.15	0.14 × 0.12 × 0.12
μ(Mo-Kα)/mm^{-1}	0.092	1.879	2.171	0.090	2.356	1.845	2.130	1.674
Data collected	3220	33992	10506	11133	8950	14336	11916	8520
Obsd. data [$I > 2\sigma(I)$]	1867	7529	7340	2292	6759	7709	7520	8520
***R*1**	0.0538	0.0220	0.0388	0.0393	0.0658	0.0464	0.0532	0.334
w*R*2	0.1211	0.0539	0.0753	0.1069	0.1596	0.1151	0.0785	0.0610
GooF	1.050	1.047	1.013	1.015	1.053	1.035	1.000	1.022

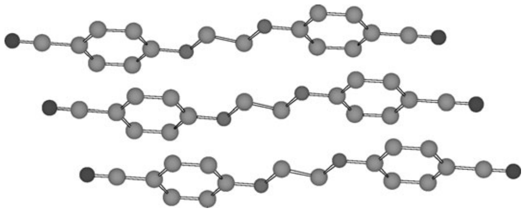


Fig. 1 The solid state structure of **1** showing the *anti* conformation adopted by the ethylene glycol moiety and the packing of consecutive units. For the sake of clarity, H atoms are not represented. For bond distances and angles see text.

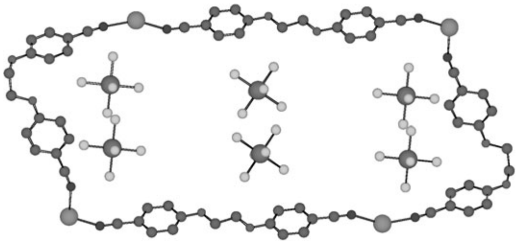


Fig. 3 A portion of the 1-D stair type coordination networks formed between **1** and Ag^+ cation showing the cyclic fragment and the positioning of the anions. For sake of clarity, H atoms are not represented. For bond distances and angles see text.

pound **2** presents a bent type structure. The nitrile moiety (d_{CN} = 1.148 Å) is slightly bent with respect to the phenyl group with the CCN angle of 176.6°. The consecutive compounds **2** are arranged parallel to each other with 4.60 Å distance between the phenyl rings centroids.

Coordination network formed between tecton 1 and silver cation

Upon combining the tecton **1** with $AgAsF_6$ or $AgSbF_6$, crystalline materials were obtained (see experimental section). The X-ray diffraction studies on single crystals revealed that both combinations are *iso*morphous (see Table 1). Thus, here we only describe the structure of **1**-$AgSbF_6$, given that for the other structure only minute differences in bond distances and angles are observed. The crystal (triclinic, $P\bar{1}$) is only composed of the tecton **1**, Ag^+ cation and SbF_6^- anion with a **1**/Ag^+ ratio of 3/2. No solvent molecules are present in the lattice. Concerning the organic tecton **1**, interestingly, the latter adopts two different conformations (Fig. 3). One lying about an inversion centre with the glycol unit ($d_{C–O}$ = 1.432 Å, $d_{C–C}$ = 1.515 Å) in *anti* conformation (OCCO dihedral angle of 180.0°) as in the case of the free compound **1** mentioned above and the other in a general position with the glycol unit ($d_{C–O}$ = 1.400 Å, $d_{C–C}$ = 1.511 Å) adopting the *gauche* conformation (OCCO dihedral angle of 87.6°). The conformer's ratio *anti*/*gauche* is 2/3. Consequently, compound **1** offers two geometrically different tectons (linear for the *anti* conformer and bent for the *gauche* conformer) presenting two sets of two nitrile groups ($d_{C–N}$ = 1.142 Å and 1.147 Å for *anti* and *gauche* conformers, respectively).

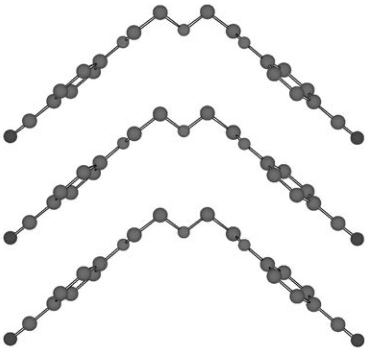


Fig. 2 A portion of the solid state structure of **2** showing the *gauche* conformation adopted by the ethylene glycol moieties and the packing of consecutive units. For sake of clarity, H atoms are not represented. For bond distances and angles see text.

Considering these two construction units and the silver cation offering a coordination number of three with a distorted trigonal geometry, the observed cationic 1-D stair type network may be described in two different manners (Fig. 3–5). The interconnection of both conformers through silver nitrogen bonds (Ag–N distances of 2.186 Å and 2.193 Å, NAgN angle of 152.0°) leads to the formation of a centrosymmetric [4 + 4] metallamacrocycle (Fig. 3 and Fig. 5 left). The interconnection (Fig. 4 and Fig. 5 left), again through Ag–N bonds (Ag–N distances of 2.345 Å and 2.193 Å, NAgN angles of 98.5° and 108.8°) of the metallamacrocycles by the *gauche* conformer leads to the formation of the final architecture. It is worth noting that no interactions between the oxygen atoms of the glycol units and the silver cation is observed implying that the oxygen atoms do not play the role of secondary interaction sites. This might be due to geometric (restricted length of the spacer) and electronic (electronic delocalisation on the nitrile group) reasons.

The other possible way to describe the stair type 1-D network is to consider first the formation of a 1-D zigzag type arrangement resulting from the interconnection of tectons **1** in *gauche* conformation by silver cations (Fig. 5 right) and, in a second step, their interconnection by tectons **1** in *anti* conformation.

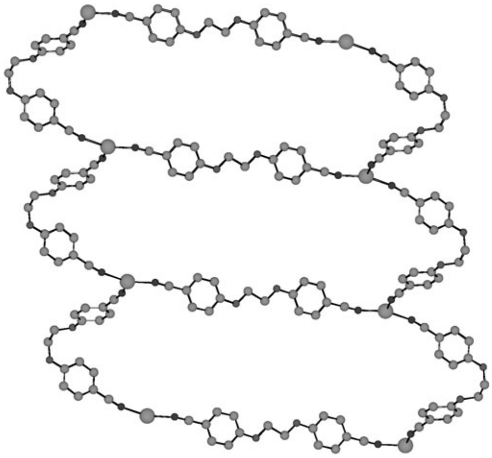


Fig. 4 A portion of the 1-D stair type coordination networks formed between **1** and Ag^+ cation showing the interconnection of the cyclic units by the tecton **1**. For sake of clarity, H atoms and anions are not represented. For bond distances and angles see text.

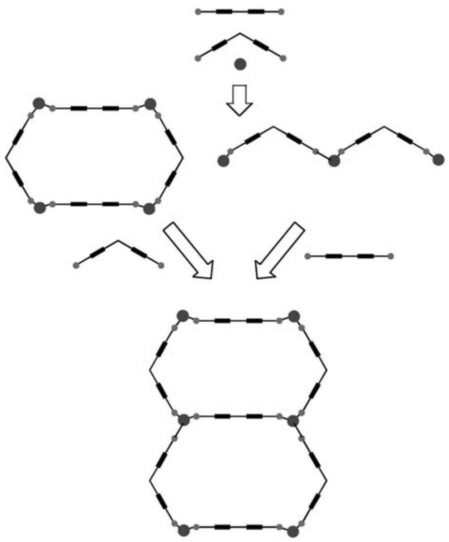


Fig. 5 Schematic representation of the two possible descriptions for the formation of the stair type architecture observed when the tecton **1** was combined with silver cation.

Although the 1-D arrangement presents large cyclic type cavities, the latter are not empty but occupied by SbF_6^- anions for which the Sb cation lies on an inversion centre (Fig. 3). Consequently, no entanglement is observed. No specific interaction between the anions and the cationic part is detected. The 1-D networks are packed in a parallel fashion.

Coordination network formed between tecton 3 and silver cation

The mixing of the tecton **3** with $AgAsF_6$ leads to the formation of crystalline materials (see experimental section) that was analysed by X-ray diffraction on single crystals (see Table 1). The crystal (triclinic, $P\bar{1}$) is composed of compound **3**, Ag^+ cation and AsF_6^- anion with a **3**/Ag^+ ratio of 1/1. No solvent molecules are present in the lattice. Dealing with the organic tecton **3**, among the three ethylene glycol fragments, the two oxygen atoms of the central unit are disordered over two positions. All three ethylene glycol units (C–O distance in the range of 1.422–1.484 Å, C–C distance in the range of 1.487–1.511 Å) adopt the *gauche* conformation. Consequently, the spacer unit connecting the two benzonitrile groups (d_{C-N} = 1.124 Å and 1.150 Å) adopts a helical conformation offering a pocket bearing four oxygen atoms (Fig. 6a). The interconnection, through Ag–N bond (Ag–N distances of 2.225 Å and 2.238 Å) of consecutive tectons **3** by the silver cation (NAgN angle of 133.2°) leads to the formation of a 1-D helical strand (Fig. 6a). The distance between two consecutive silver cations within the same strand is 15.58 Å.

Interestingly, two helical strands of opposite chirality form an achiral double strand 1-D network (Fig. 6b). The driving force for the formation of this peculiar duplex is due to silver oxygen interactions. Indeed, all four oxygen atoms of triethylene glycol units of one strand are involved in interactions with the silver cation belonging to the other strand with two short Ag–O distances of *ca* 2.5 Å for the disordered central unit and two long Ag–O distances (d_{Ag-O} = 2.789 Å and 2.897 Å) for the two peripheral units. Thus, the coordination number for the cation is six and its coordination geometry is a severely distorted octahedron. The distance between two consecutive silver cations belonging to different interconnected strands is 10.106 Å. For the observed duplex architecture, the aryl groups of the two strands are arranged in the parallel fashion with 3.881 Å distance between their centroids (Fig. 6c). It is worth noting that the interconnection of the two helical strands does not lead to formation of an interwoven arrangement but to an interdigitated architecture. Indeed, the two strands do not cross each other (Fig. 7). The 1-D networks are packed in parallel and the empty space is occupied by AsF_6^- anions which were found to be disordered. No specific interactions between the anions and the cationic part of the structure could be detected.

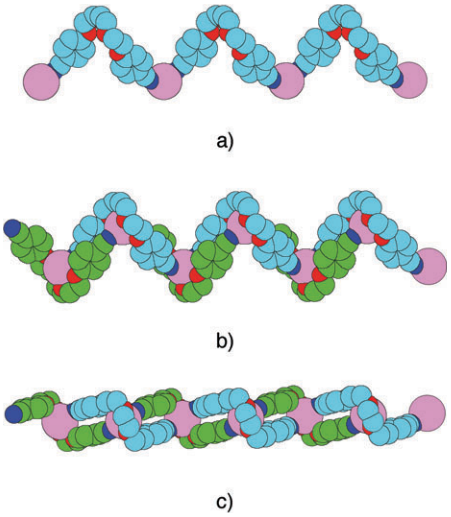


Fig. 6 A portion of the 1-D interdigitated network formed between **3** and Ag^+. The interdigitation between the two helical strands (a) of the opposite handedness is due to the interactions between the oxygen atoms of the triethylene glycol units of the tecton **3** adopting a curved conformation within one strand and metal cations belonging to the other strand (b and c). For sake of clarity, carbon atoms belonging to different strands are differentiated by colour and H atoms and anions are not represented. For bond distances and angles see text.

Coordination network formed between tecton 4 and silver cation

Upon combining the tecton **4** with either $AgAsF_6$ or $AgSbF_6$, again crystalline materials were obtained (see experimental section) and analysed by single crystals X-ray diffraction. As in the case of **1** mentioned above, the structural investigation on both crystals revealed that they are isomorphous (see Table 1). Again here we only describe the structure of **4**-$AgSbF_6$ since for the other structure only small differences in bond distances

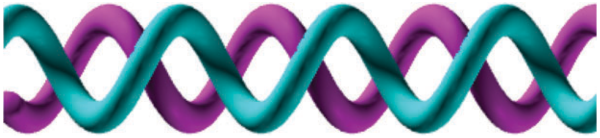


Fig. 7 A schematic representation of the interdigitation of two helical strands with opposite helicity leading to a 1-D achiral architecture.

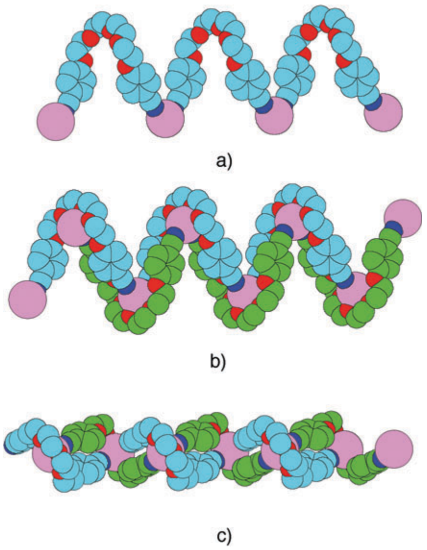


Fig. 8 A portion of the 1-D interdigitated network formed between **4** and Ag^+. The interdigitation between the two helical strands (a) of the opposite handedness is due to the interactions between the O atoms of the tetraethylene glycol units of the tecton **4** adopting a loop type conformation within one strand and metal cations belonging to other strand (b and c). For sake of clarity, carbon atoms belonging to different strands are differentiated by colour and H atoms and anions are not represented. For bond distances and angles see text.

and angles are observed. As in the case of **3** mentioned above, the crystal (monoclinic, $P2(1)/c$) is only composed of compound **4**, Ag^+ cation and SbF_6^- anion with a **4**/Ag^+ ratio of 1/1. In contrast to the previous structure, the tetraethylene glycol moieties of the tecton **4** are not disordered. All glycol units (C–O distance in the range of 1.387–1.436 Å, C–C distance in the range of 1.488–1.502 Å) adopt the *gauche* conformation (OCCO dihedral angles of 58.7°, −63.3°, −76.0° and −79.3°) leading to a helical turn (Fig. 8a) for the tetraethylene glycol spacer connecting the two benzonitrile groups ($d_{C–N}$ = 1.144 Å and 1.148 Å). Once again, the interconnection of consecutive tectons **4** by the silver cation (NAgN angle of 110.3°) through Ag–N bond (Ag–N distances of 2.249 Å and 2.256 Å) leads to the formation of a 1-D helical strand (Fig. 8a). The distance between two consecutive silver cations within the same strand is 13.86 Å.

As in the case of **3**, two helical strands of the opposite chirality form an achiral double strand 1-D network (Fig. 8b). This arrangement also results from silver–oxygen interactions. Among the five oxygen atoms of tetraethylene glycol units of one strand three of them are involved in interactions with the silver cation belonging to the other strand with Ag–O distance in the range of 2.504 Å to 2.607 Å. The Ag–O distances for the remaining two oxygen atoms are 3.252 Å and 3.800 Å. The coordination number for the cation is five and its coordination geometry is a strongly distorted square based pyramidal. The distance between two consecutive silver cations belonging to different interconnected strands is 10.62 Å. The aryl groups of the two strands are again arranged in the parallel fashion with a shorter (3.740 Å) distance between their centroids (Fig. 8c). The interdigitated arrangement of the two helical strands is identical to the one described above for **3** (Fig. 7). The 1-D networks are packed in a parallel fashion and the empty space is occupied by disordered SbF_6^- anions with no specific interactions with the cationic part of the structure.

Coordination network formed between tecton 5 and silver cation

The combination of the tecton **5** with $AgSbF_6$ affords also crystalline material (see experimental section). The structural study by X-ray diffraction on single crystals (see Table 1) revealed that the crystal (orthorhombic, $P2_12_12_1$) is composed of compound **5**, Ag^+ cation and SbF_6^- anion with a **5**/Ag^+ ratio of 1/1. For the tecton **5**, as for compound **4**, the pentaethylene glycol spacer is not disordered. As for tectons **3** and **4**, all ethylene glycol units (C–O distance in the range of 1.400–1.435 Å, C–C distance in the range of 1.475–1.500 Å) adopt the *gauche* conformation (OCCO dihedral angles of −67.2°, −68.8°, 69.3°, −59.0°, −66.9°). The linker between the two benzonitrile groups ($d_{C–N}$ = 1.138 Å and 1.139 Å) adopts a loop type conformation (Fig. 9a). The interconnection of tectons **5** by silver cations (NAgN angle of 128.7°) through Ag–N bond (Ag–N distances of 2.182 Å and 2.192 Å) leads to the formation of a 1-D helical strand (Fig. 9a). Within this strand the distance between two consecutive silver cations is 12.87 Å.

In marked contrast to the other two above discussed structures obtained for tectons **3** and **4**, here, instead of an achiral 1-D duplex arrangement, a chiral 2-D interwoven architecture is obtained (Fig. 9b). Indeed, all consecutive helical strands of the same handedness in the same plane

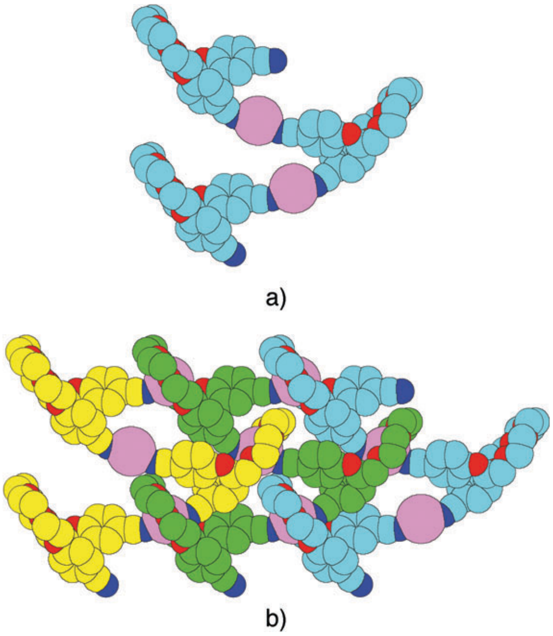


Fig. 9 A portion of the 2-D interwoven chiral network formed between **5** and Ag^+. The entanglement between consecutive helical strands (a) of the same handedness is due to the interactions between the O atoms of the pentaethylene glycol units of **5** adopting a loop type arrangement within each strands and metal cations belonging to consecutive strands (b). For sake of clarity, carbon atoms belonging to different strands are differentiated by colour and H atoms and anions are not represented. For bond distances and angles see text.

Fig. 10 A schematic representation of the entanglement of consecutive helical strands of the same helicity leading to a 2-D interwoven chiral architecture.

interact with each other through silver oxygen interactions. Among the six oxygen atoms of pentaethylene glycol units of one strand, three of them are involved in interactions with the silver cation belonging to the next strand with Ag–O distances of 2.621 Å, 2.667 Å and 2.710 Å. The Ag–O distances for the remaining three oxygen atoms are 3.010 Å, 3.176 Å and 4.871 Å. The coordination number for the silver cation is five. The distance of 7.476 Å between two consecutive silver cations belonging to neighboring strands is considerably shorter than those observed in the case of **3** or **4**. The crystal is chiral ($P2_12_12_1$ space group) and made by packing of homochiral 2-D interwoven networks (Fig. 10). The SbF_6^- anions are not disordered and occupy the empty space between 2-D networks. Once again, no specific interaction between the cationic part of the structure and anions is observed. It is worth noting that although the crystal studied is chiral, it is reasonable to assume that crystals with the opposite chirality must be present in the mixture of crystals (racemic mixture).

Conclusion

Compounds **1** and **3–5** composed of oligoethylene glycol units and two benzonitrile groups behave as tectons when combined with silver cation and lead to the formation of coordination networks in the crystalline phase. The type of architecture obtained is correlated to the number of glycol units connecting the two benzonitrile groups. In the presence of silver cation tecton **1**, based on the ethylene glycol unit, leads mainly to the formation of a stair type 1-D network with no interaction between the oxygen atoms of the glycol unit and the metal cation. This absence of interactions is probably due to geometric (restricted length of the spacer) and electronic (electronic delocalisation on the nitrile group) reasons. In marked contrast and as expected from their design, for tectons **3–5**, based on tri-, tetra- and pentaethylene glycol fragments, respectively, both nitrile groups and oligoethylene fragments act as primary and secondary coordination sites, respectively and participate in the binding of silver cation. All three tectons **3–5** lead to the formation of helical strands. Interestingly, for both tectons **3** and **4** the 1-D network obtained results from the interdigitation of two helical strands of opposite helicity through the interactions of oxygen atoms belonging to one strand with the cation belonging to the other strand. In the case of tecton **5**, consecutive helical strands of the same handedness are interwoven through glycol-metal type interactions. The overall architecture is a chiral 2-D network. Based on the same strategy, the use of other primary and secondary coordination sites as well as other metal cations is currently under investigation.

Experimental section

Synthesis

Compound 1. 4-Cyanophenol **6** (2.76 g, 23.2 mmol) and K_2CO_3 in excess (6.41 g, 46.4 mmol) were dissolved in acetonitrile (150 mL). The mixture was stirred before 1,2-dibromoethane **7** (2.18 g, 11.6 mmol) was added. The mixture was refluxed overnight. The solvent was removed under reduced pressure. A saturated aqueous potassium carbonate (50 mL) solution was added to the residue and the organic mixture was extracted with CH_2Cl_2 (3 × 50 mL). Organic layers were combined and the solvent was removed. The residue thus obtained was purified by column chromatography (ethyl acetate/cyclohexane: 40/60). The pure compound **1** was obtained as a white solid in 76% yield. Mp = 204 °C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 4.39 (s, 4H, CH_2), 7.00 (d, 4H, arom, J = 9 Hz), 7.61 (d, 4H, arom, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 69.9, 104.1, 115.1, 119.3, 134.1, 161.8. Calculated for $C_{16}H_{12}N_2O_2$ (264.28): C 72.72, H 4.58, N 10.60; found C 72.20, H 4.59, N 10.19%.

Compound 2. 4-Cyanophenol **6** (2 g, 16.7 mmol) and K_2CO_3 (4.64 g, 33.4 mmol) were dissolved in acetonitrile (150 mL). To the stirred mixture, compound **8** (3.47 g, 8,39 mmol) was added. The solution was heated to reflux overnight. Solvent was removed under reduced pressure. A saturated aqueous potassium carbonate (50 mL) solution was added to the residue and the organic mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and the solvent was removed. The residue was purified by column chromatography (ethyl acetate/cyclohexane: 40/60). The pure compound **2** was obtained as a white solid in 74% yield. Mp = 135 °C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.94 (t, 4H, CH_2, J = 4.8 Hz), 4.19 (t, 4H, CH_2, J = 4.8 Hz), 6.95 (d, 4H, arom, J = 9 Hz), 7.57 (d, 4H, arom, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 67.7, 69.7, 104.3, 115.3, 119.1, 134.0, 161.9. Calculated for $C_{18}H_{16}N_2O_3$ (308.33): C 70.12, H 5.23, N 9.09; found C 69.85, H 5.205, N 8.98%.

Compound 3. 4-Cyanophenol **6** (2 g, 16.7 mmol) and K_2CO_3 (4.64 g, 33.4 mmol) were dissolved in acetonitrile (150 mL). The mixture was stirred before compound **9** (3.84 g, 8.39 mmol) was added. The solution was refluxed overnight. Solvent was removed under vacuum. The residue was suspended in CH_2Cl_2 (50 mL) and stirred before the solid was removed by filtration. This operation was repeated twice. The solvent was evaporated affording the compound **3** as a light yellow solid in 84% yield. Mp = 119 °C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.74 (s, 4H, CH_2), 3.87 (t, 4H, CH_2, J = 4.8 Hz), 4.16 (t, 4H, CH_2, J = 4.8 Hz), 6.95 (d, 4H, arom, J = 9 Hz), 7.57 (d, 4H, arom, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 67.7, 69.5, 70.9, 104.2, 115.3, 119.1, 134.0, 162.0. Calculated for $C_{20}H_{20}N_2O_4$ (352.38): C 68.17, H 5.72, N 7.95; found C 68.02, H 5.69, N 7.87%.

Compound 4. 4-Cyanophenol **6** (597 mg, 5.01 mmol) and K_2CO_3 (1.4 g, 10.1 mmol) were dissolved in acetonitrile

(50 mL). The mixture was stirred and compound **10** (1.26 g, 2.51 mmol) was added. The solution was heated to reflux overnight. Solvent was removed under reduced pressure. The residue was suspended in CH_2Cl_2 (25 mL) and stirred before the solid was removed by filtration. This operation was repeated twice. The solvent was evaporated to dryness affording the desired compound **4** as a white solid in obtained in 93% yield. Mp = 52 °C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.68 (m, 8H, CH_2), 3.85 (t, 4H, CH_2, J = 4.8 Hz), 4.15 (t, 4H, CH_2, J = 4.8 Hz), 6.95 (d, 4H, arom, J = 9 Hz), 7.56 (d, 4H, arom, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 67.8, 69.4, 70.7, 70.9, 104.1, 115.3, 119.2, 134.0, 162.1. Calculated for $C_{22}H_{24}N_2O_5$ (396.44): C 66.65, H 6.10, N 7.07; found C 66.85, H 6.25, N 6.93%.

Compound 5. 4-Cyanophenol **6** (435 mg, 3.65 mmol) and K_2CO_3 (1 g, 7.24 mmol) were dissolved in acetonitrile (50 mL). The mixture was stirred and compound **11** (1 g, 1.83 mmol) was added. The solution was refluxed overnight. Solvent was removed under vacuum. The residue was suspended in CH_2Cl_2 (25 mL) and stirred before the solid was removed by filtration. This operation was repeated twice. The solvent was evaporated to dryness leaving the pure compound **5** as a white solid in 82% yield. Mp = 44 °C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.61–3.73 (m, 12H, CH_2), 3.85 (t, 4H, CH_2, J = 4.8 Hz), 4.15 (t, 4H, CH_2, J = 4.8 Hz), 6.94 (d, 4H, arom, J = 9 Hz), 7.56 (d, 4H, arom, J = 9 Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 67.8, 69.4, 70.6, 70.9, 104.1, 115.3, 119.2, 134.0, 162.1. Calculated for $C_{24}H_{28}N_2O_6$ (440.49): C 65.44, H 6.41, N 6.36; found C 65.18, H 6.29, N 6.33%.

Crystallisation conditions

Compound 1. Crystals of **1** were obtained upon slow evaporation of a $CHCl_3$ solution of **1** at room temperature.

Compound 2. In a crystallisation tube (height = 15 cm, diameter = 0.4 cm), at room temperature upon slow evaporation of a $CHCl_3$ solution (1 mL) of **2** (5 mg) colourless crystals were obtained after two days.

1-AgAsF$_6$ and 1-AgSbF$_6$. In a crystallisation tube (height = 15 cm, diameter = 4 mm) a 1,2-dichloroethane solution (0.75 mL) containing the compound **1** (3.75 mg) was layered with a 50/50 1,2-dichloroethane/EtOH mixture (0.75 mL) before a EtOH solution (0.75 mL) of silver salt was added ($AgSbF_6$: 4.8 mg; $AgAsF_6$: 3.75 mg). The tubes were sealed with a stopper and kept in the dark at rt. After one week, colourless crystals were obtained.

3-AgSbF$_6$. In crystallisation tube (height = 15 cm, diameter = 4 mm) a 1,2-dichloroethane solution (0.75 mL) of **3** (3.75 mg) was layered with a 50/50 1,2-dichloroethane/EtOH mixture (0.75 mL) before an EtOH solution (0.75 mL) of $AgSbF_6$ (3.75 mg) was added. The tube was sealed with a stopper and kept in the dark at rt. After two months, colourless crystals were obtained.

4-AgAsF$_6$ and 4-AgSbF$_6$. In a crystallisation tube (height = 15 cm, diameter = 4 mm) a 1,2-dichloroethane solution (0.75 mL) of **4** (3.75 mg) was layered with a 50/50 1,2-dichloroethane/EtOH solution (0.75 mL) before an EtOH solution (0.75 mL) of silver salt was added ($AgSbF_6$: 3.75 mg; $AgAsF_6$ 3.75 mg). The tubes were sealed with a stopper and kept in the dark at rt. After two weeks, colourless crystals were obtained.

5-AgSbF$_6$. In a crystallisation tube (height = 15 cm, diameter = 4 mm) a 1,2-dichloroethane solution (0.75 mL) of **5** (3.75 mg) was layered with a 50/50 1,2-dichloroethane/EtOH solution (0.75 mL) before an EtOH solution (0.75 mL) of $AgSbF_6$ (3.75 mg) was added. The tube was sealed with a stopper and kept in the dark at rt. After two weeks, colourless crystals were obtained.

Crystallography. Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo Kα radiation (see Table 1). For all structures, diffraction data were corrected for absorption and structural determination was achieved using SHELXS-97. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC 624584–624587 contains the supplementary crystallographic data for this paper. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611415f

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References

1 J. D. Wuest, *Chem. Commun.*, 2005, 5830.
2 S. Mann, *Nature*, 1993, **365**, 499.
3 M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313.
4 M. W. Hosseini, *Chem. Commun.*, 2005, 5825.
5 M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696.
6 M. W. Hosseini, *CrystEngComm*, 2004, **6**, 318.
7 M. W. Hosseini, in *NATO ASI Series*, ed. D. Braga, F. Grepiono and G. Orpen, Ser. c, Kluwer, Dordrecht, Netherlands, 1999, vol. 538, p. 181.
8 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
9 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **193**, 117.
10 G. F. Swiergers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.
11 B. Moulton and M. J. Zawortko, *Chem. Rev.*, 2001, **101**, 1629.
12 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
13 K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96.
14 C. Janiak, *Dalton Trans.*, 2003, 2781.
15 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
16 S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2434.
17 G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 218.
18 D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273.
19 M. Fujita, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. Mac Nicol, F. Vögtle, J. P. Sauvage and M. W. Hosseini, Elsevier, Oxford, 1996, vol. 9, pp. 253–282.

20 E. Deiters, V. Bulach and M. W. Hosseini, *Chem. Commun.*, 2005, 3906.

21 E. Graf, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *New J. Chem.*, 2005, **29**, 343.

22 D. Pocic, J.-M. Planeix, N. Kyritsakas, A. Jouaiti and M. W. Hosseini, *CrystEngComm*, 2005, **7**, 624.

23 J. Pansanel, A. Jouaiti, S. Ferlay, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *New J. Chem.*, 2006, **30**, 683.

24 A. Jouaiti, M. W. Hosseini, N. Kyritsakas, P. Grosshans and J.-M. Planeix, *Chem. Commun.*, 2006, 3078.

25 J. Pansanel, A. Jouaiti, S. Ferlay, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *New J. Chem.*, 2006, **30**, 71.

26 B. Schmaltz, A. Jouaiti, M. W. Hosseini and A. De Cian, *Chem. Commun.*, 2001, 1242.

27 A. Jouaiti, M. W. Hosseini and N. Kyritsakas, *Chem. Commun.*, 2003, 472.