Molecular tectonics: on the formation of tubular coordination networks†

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Upon combining the organic tecton based on the [1,1,1,1]metacyclophane bearing four pyridine groups with silver cation, a tubular coordination network formed by double bridging of consecutive macrocycles by metal centres is obtained and structurally characterised in the solid state by an X-ray diffraction method. The same tecton when combined with $HgCl_2$ leads to the formation of a doubly interpenetrated 2-D coordination framework.

Introduction

The investigation of strategies allowing the generation of tubular architectures in the solid state is interesting because these types of arrangement may act as predefined channels and thus may permit controlled transport of ions and molecules. In the crystalline phase, such architectures may be obtained under self-assembly conditions using a variety of reversible intermolecular interactions. In particular, it has been demonstrated that tubular arrangements may be formed by chains adopting a helical structure, as observed for polypeptides[1,2] or for helical coordination polymers composed of organic ligands and metal centres.[3,4] The formation of tubular architectures based on the organisation of cyclic units in liquid crystals[5] or using polymeric backbones[6] has been also described. Tubular systems have been also obtained through interconnection of metallamacrocycles formed upon combining silver cation with polydentate ligands.[7,8] Finally, the formation of carbon nanotubes by rolling 2-D graphite sheets has also been demonstrated.[9]

Coordination polymers are metallo-organic architectures formed upon bridging of organic units by metal centres.[10–18] In the crystalline phase, these infinite structures possess translational symmetry and for that reason may be described as molecular networks.[19,20] The dimensionality of these networks is defined by the number of translations operating at the level of the assembling nodes which are based on the coordination of the metal centres by coordinating sites of the organic ligand. In this context, tubular networks, also called metallatubulanes,[21] are 1-D coordination networks.

Pursuing our approach of molecular tectonics,[22–24] we are interested in investigating the possibility of generating tubular architectures based on the formation of reversible coordination bonds. In particular, we have shown that such arrangement may be obtained by combining cyclic units bearing four coordinating sites located in an alternate fashion below and above the plane of the cycle with silver cation offering two coordination sites in linear disposition.[21] In order to further elaborate on this strategy, considering the [1,1,1,1]metacyclophane **1** as a backbone, we designed the tecton **2** (see Scheme 1) and studied its propensity to generate tubular coordination networks.

In the present contribution we report the synthesis of the tecton **2** as well as the structural study of a tubular and a 2-D coordination network obtained in the presence of silver tosylate and mercury dichloride, respectively.

Results and discussion

The [1,1,1,1]metacyclophane is an interesting backbone for the design of tectons because it adopts the 1,3-alternate blocked conformation over a wide range of temperature (see Scheme 2). This conformation was established in the crystalline phase by structural investigations on the compound **1** (Scheme 1)[25] and its mercapto analogue for which all four OH moieties were replaced by SH groups.[26]

Considering this particular 1,3-alternate conformation, we have used this unit as a backbone for the design of a variety of derivatives bearing four coordinating sites located in an alternate fashion below and above the main plane of the macrocycle and thus occupy the apices of a pseudo-tetrahedron (Scheme 2).[27] Examples of disubstituted [1,1,1,1]metacyclophanes bearing two coordinating sites located on the same face of the macrocycle[28] and their use for the formation of metallamacrocycles[29] and 1-D coordination networks[30] have been also reported by us. Using the same strategy, we have also exploited the 1,3-alternate conformation of calix[4]arene derivatives bearing four CN[31] or pyridyl[32] groups for the formation of 1-D coordination networks in the presence of silver cation and quintuple helical braids based on the formation of H-bonds in the presence of H-bond donor moieties, respectively. The formation of a 2-D coordination network between a thiacalix[4]arene derivative blocked in 1,3-alternate conformation and bearing four carboxyl units with silver cation has been also reported.[33]

Design of the tecton 2

The design of the tecton **2** is based on the use of the compound **1** offering a restricted conformational space and the possibility

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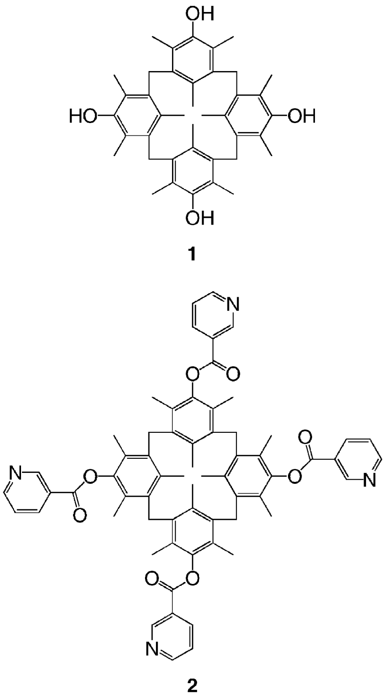
† The HTML version of this article has been enhanced with colour images.



Scheme 1

of anchoring four pyridyl groups as coordinating sites. The junction between the cyclophane backbone and the pyridyl units is ensured by ester groups. The connection point between the pyridine and the backbone is established at the position 3 with respect to the nitrogen atom. Owing to the 1,3-alternate conformation of the tecton **2**, one may either expect a tubular arrangement in the presence of a metal centre offering two coordination sites with a linear or almost linear geometry (Fig. 1 top) or a 2-D network if the connecting metal centre presents two free coordination sites with bent geometry (Fig. 1 bottom).

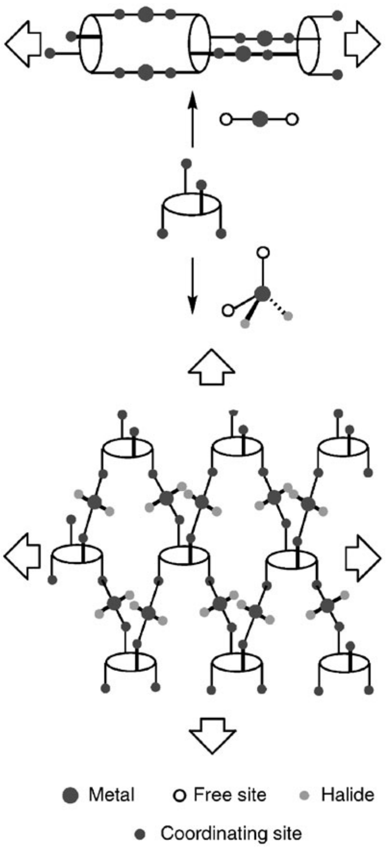
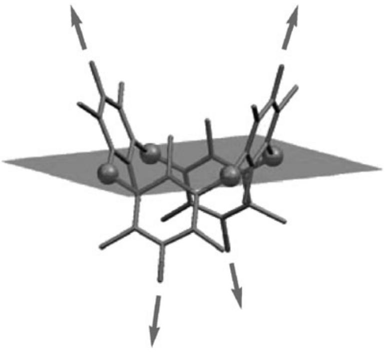


Fig. 1 Schematic representation of the tubular coordination network generated upon combination of a metal centre adopting a linear coordination geometry and a cyclic tecton bearing four coordinating sites arranged in an alternate fashion below and above the ring (top) and of a 2-D network formed with a metal complex offering two coordination sites with a bent geometry (bottom).

Concerning the metal centre, Ag^+ cation was selected because, among various possible geometries, it may adopt linear or T type coordination and because the Ag–N bond formation is reversible and thus well suited for self-assembly processes. However, since the tecton **2** is neutral by nature, the cation must be associated with a counter ion. Although many different silver salts have been used, only in the case of silver tosylate crystalline material was obtained. The other considered metal centre was Hg^{2+}. The latter adopts usually distorted tetrahedral or octahedral coordination geometry. However, in the presence of N donor atoms, the Td geometry is often observed. In order to block two of the four coordination sites and furthermore to neutralize the charge, $HgCl_2$ was used as the connecting unit.



Scheme 2

The synthesis of **2** was straightforward and based on the esterification of the compound **1**, prepared according to a described procedure,[23] by nicotinoyl chloride in dry THF and in the presence of Et_3N (see experimental section).

Structural investigations

The solid state structure of the free tecton **2** was investigated by X-ray diffraction on single crystal (*orthorhombic*, space group *Pban*). The structural determination (see experimental section) revealed that, as expected the tecton **2** adopts the 1,3-alternate conformation (Fig. 2). The four pyridine units connected to the cyclophane backbone through ester junctions ($d_{\mathrm{C=O}} = 1.202$ Å, $d_{\mathrm{CO-O}} = 1.348$ Å, OCO angle = 123.4°) are oriented outwardly with respect to the interior of the backbone. The C=O group is almost coplanar with the pyridine ring (OCCC dihedral angle of 1.8°) and almost perpendicular to the phenyl moiety (CCOC dihedral angle of 94.8°). The

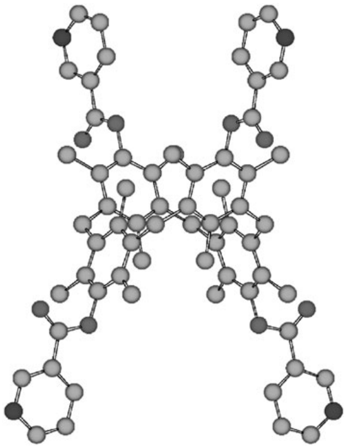


Fig. 2 The solid state structure of **2** showing the 1,3-alternate conformation adopted by the tecton. For the sake of clarity, H atoms are not represented. For bond distances and angles see text.

pyridine units are not perpendicular to the plane of the macrocycle (defined by the four CH_2 groups) but tilted by 110.9°. The distance between the nitrogen atoms of two pyridines located on the same face of the molecule is 14.47 Å.

As stated above, although many silver salts were combined with the tecton **2**, only in the case of silver tosylate were suitable crystals obtained (see experimental section). The single crystal X-ray diffraction study revealed that the crystal (*monoclinic*, space group $C2/c$) was composed of tecton **2**, Ag^+ cation, TsO^- anion, $CHCl_3$ and EtOH solvent molecules.

As expected from the design of the tecton **2** (Fig. 1 top), the mutual interconnection between **2** and Ag^+ cation leads to the formation of a tubular coordination network (Fig. 3).

As expected, the 1,3-alternate conformation of the tecton **2** is maintained. The four pyridine groups attached to the backbone by ester junctions ($d_{C=O}$ in the range of 1.188 Å and 1.196 Å, d_{CO-O} in the range of 1.340 Å and 1.353 Å, OCO angle = 124.5° and 125.0°) are not equivalent but different. Two sets of two pyridines are observed. One set is oriented outwards whereas the other set is oriented towards the interior of the backbone. In contrast with the free tecton **2**, the C=O groups are not coplanar with the pyridine ring but tilted with OCCC dihedral angles of 7.4° for the pyridines oriented outwards and 16.5° for the pyridines oriented inwards. The pyridine rings are almost perpendicular to the phenyl moiety (CCOC dihedral angle of 89.0° and 93.2°). Again, the pyridine units are not perpendicular to the plane of the macrocycle but tilted by 110.1° and 111.6°. These values are close to the one observed for the free tecton **2** (110.9°) demonstrating the rigidity of the backbone. The distance between the nitrogen atoms of two pyridines located on the same face of the molecule of 12.40 Å is shorter than the one observed for the free tecton **2** (14.47 Å).

In the unit cell, two different Ag^+ cations are present. The coordination sphere around the two crystallographically non-equivalent Ag^+ cations is composed of two N atoms and one O atom belonging to a tosylate anion. The coordination geometry around the silver cation is strongly distorted trigonal (almost of the T type) with NAgN angle of 158.4° and NAgO angles of 96.5° and 102.8°. The average N–Ag and Ag–O distances are 2.17 Å and 2.52 and 2.14 Å, respectively. The tosylate anions are not oriented towards the interior of the cavity. Two Ag^+ cations located on the same face of the molecule are separated by *ca.* 12.90 Å.

Owing to the geometry of the tecton **2**, the tubular structure presents two types of cavity. The one defining the tube with an internal diameter of *ca.* 4.39 Å defined by the distance between CH_3 groups belonging to the tecton (Fig. 3 bottom) and lateral cavities resulting from the interconnection of consecutive

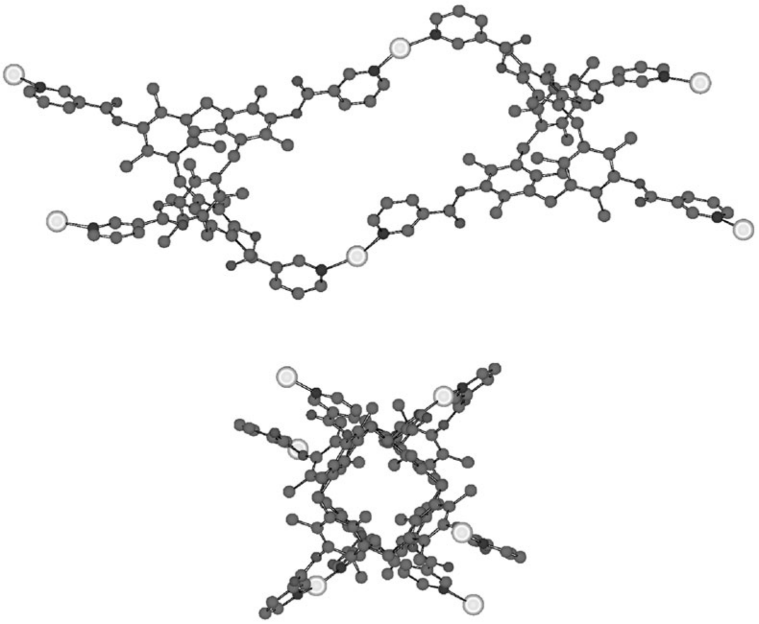


Fig. 3 A portion of the 1-D tubular coordination networks formed between **2** and Ag^+ cation showing views perpendicular (top) and parallel (bottom) to the tube axis. For the sake of clarity, H atoms, tosylate anions and solvent molecules are not represented. For bond distances and angles see text.

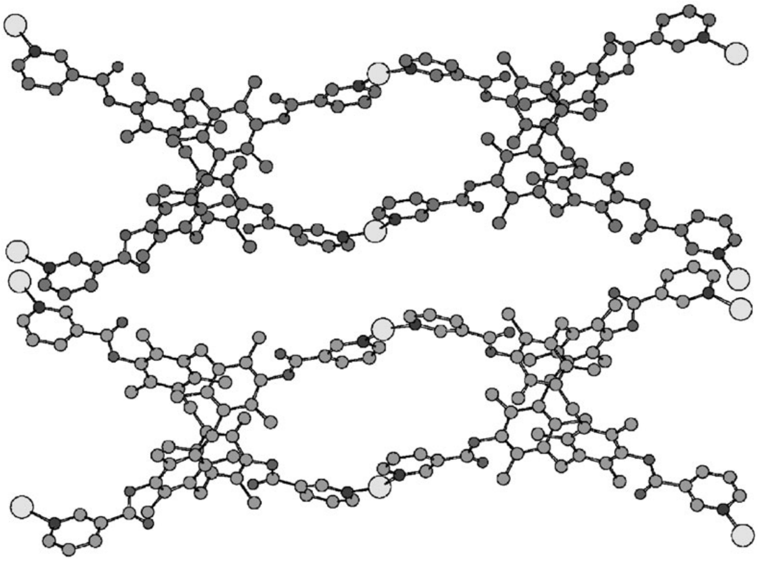


Fig. 4 A portion of the structure showing the parallel packing of 1-D tubular coordination networks formed between **2** and Ag^+ cation and the short metal–metal distance. For the sake of clarity, H atoms, tosylate anions and solvent molecules are not represented. For bond distances and angles see text.

tectons **2** by silver cations (Fig. 3 top). The latter are of rectangular shape and perpendicular to each other in an alternate mode.

The tubular arrangement is not empty but occupied by solvent. However, none of the solvent molecules present are included within the cavity of the cyclophane. Among the chloroform molecules present, two are located within the lateral cavities formed by interconnection of the cyclic units by silver cations. These solvent molecules are held by van der Waals contacts ($d_{Cl–C}$ of 3.41 Å) and by H-bonds ($d_{Cl–H}$ of 2.89 Å) with CH_3 groups of the cyclophane. The other chloroform and ethanol molecules are disordered and located between tubular arrangements.

The tubular networks are packed in a parallel fashion (Fig. 4). Among the four silver cations coordinated by the tecton **2**, two are engaged in lateral argentophilic interactions between consecutive 1-D networks with the $Ag^+–Ag^+$ distance of 3.39 Å. The other two silver cations are distant by 14.44 Å.

Upon slow diffusion of a chlorobenzene solution containing the tecton **2** into a EtOH solution of $HgCl_2$ crystalline material was obtained after *ca* two weeks. The analysis of a single-crystal by X-ray crystallography (see experimental section)

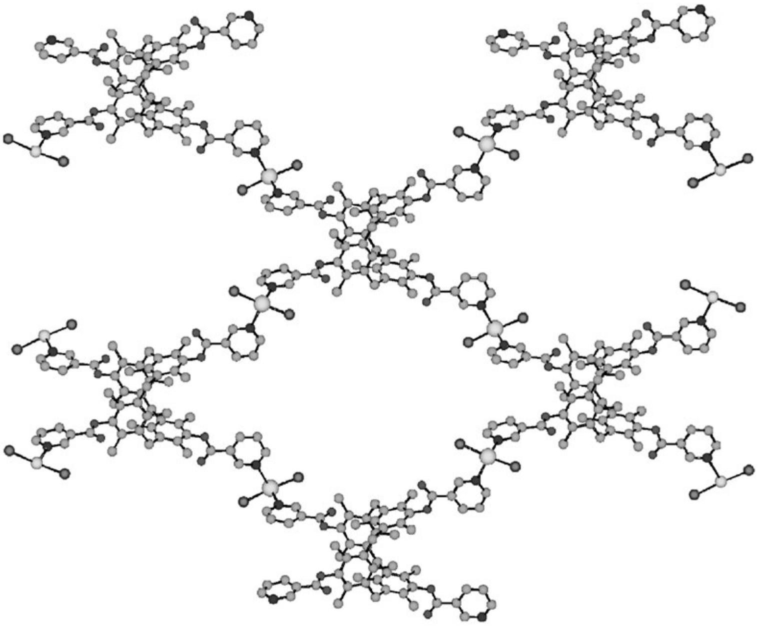


Fig. 5 A portion of the 2-D coordination networks formed between **2** and $HgCl_2$. For the sake of clarity, H atoms and solvent molecules are not represented. For bond distances and angles see text.

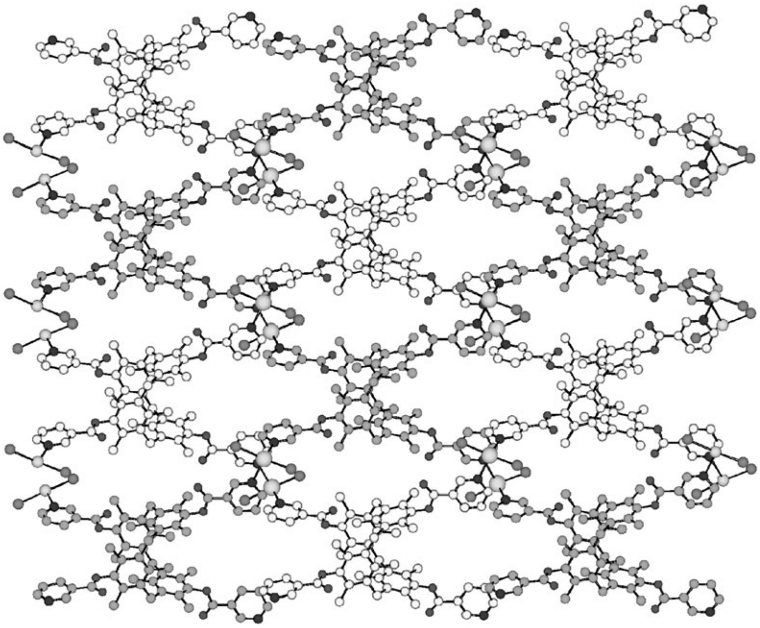


Fig. 6 A portion of the doubly interpenetrated 2-D coordination networks formed between **2** and $HgCl_2$. For the sake of clarity, carbon atoms belonging to two 2-D networks involved in the interpenetration are differentiated by colour and H atoms and solvent molecules are not represented.

revealed that in addition to **2** and $HgCl_2$, disordered EtOH, H_2O and chlorobenzene solvent molecules are also present in the lattice. The crystal (*orthorhombic*, space group *P*2*(1)*2*(1)*2) is composed of 2-D neutral coordination networks and solvent molecules. The 2-D network (Fig. 5), formed by the bridging of consecutive tectons **2** by $HgCl_2$ units, is of the type described in Fig. 1 (bottom).

Concerning the tecton **2**, the bond distances and angles observed for the ester junction connecting the pyridine groups to the backbone ($d_{C=O}$ in the range of 1.200 Å and 1.203 Å, d_{CO-O} in the range of 1.324 Å and 1.342 Å, OCO angle = 123.8° and 125.3°) are close to those observed for the free tecton **2** and for the tubular arrangement obtained with silver cation. In marked contrast to the case of tubular structure described above, all four pyridine groups are oriented outwards thus allowing the formation of the sheet type structure (Fig. 5). In contrast to the tubular architecture but in agreement with the free tecton **2**, the C=O groups are almost coplanar with the pyridine ring (OCCC dihedral angle of *ca.* −2.8°). The pyridine rings remain almost perpendicular to the phenyl moiety (CCOC dihedral angle of −88.7° and −93.9°). As for the other two structures described above, the pyridine units are not perpendicular to the plane of the macrocycle but tilted by 106.5° and 107.4°. These values are close to the one observed for the free tecton **2** (110.9°) demonstrating again the rigidity of the backbone. Distances between the nitrogen atoms of two pyridines located on the same face of the molecule of 12.49 Å and 13.77 Å are shorter than the one observed for the free tecton **2** (14.47 Å).

Dealing with the mercury centre connecting the organic tectons, its coordination sphere is composed of two nitrogen atoms (d_{HgN} of 2.43 Å and 2.44 Å) belonging to consecutive tectons **2** and two chloride ligands (d_{HgCl} of 2.34 Å and 2.36 Å). The coordination geometry around the metal is a strongly distorted tetrahedral with ClHgCl and NHgN angles of 154.7° and 95.1°, respectively.

Because of the size of the tecton **2** and the divergent orientation of the pyridine groups, their interconnection by mercury centres leads to the formation of large cavities (Fig. 5). Consequently, a double interpenetration is observed for packing reasons (Fig. 6). However, the doubly interpenetrated structure is not fully compact and offers space for the accommodation of chlorobenzene molecules. Within a 2-D sheet, the chlorobenzene molecules are disposed in the *syn*-parallel fashion thus leading to a polar arrangement. However, the consecutive planes are packed in an *anti*-parallel mode leading thus to an apolar arrangement.

Conclusion

The functionalisation of the [1,1,1,1]metacyclophane backbone which adopts the 1,3-alternate conformation by four pyridine units leads to the tecton **2**. The latter offers four monodentate coordinating sites located below and above the main plane of the macrocycle in an alternate fashion. The combination of **2** with of silver adopting an almost linear coordination geometry leads, as expected, to the formation of a 1-D tubular metalloorganic architecture. The same tecton in the presence of mercury, adopting distorted tetrahedral coordination geometry, forms a doubly interpenetrated 2-D network. The use of analogues of **2** bearing other types of coordinating sites for the generation of coordination polymers is currently under investigation.

Experimental section

Synthesis

Compound 1 was prepared according to a published procedure[25]. Compound **2**: Under argon and at room temperature, to a solution of compound **1** (100 mg, 0.17 mmol) and Et_3N (0.5 mL, 3.80 mmol) in dry THF (30 ml) a solution of nicotinoyl chloride (240 mg, 1.35 mmol) in dry THF (10 ml) was added. The mixture was refluxed under argon overnight. After cooling to room temperature, the volatiles were removed under reduced pressure and to the residue CH_2Cl_2 (30 ml) was added. The organic layer was washed with saturated aqueous $NaHCO_3$ solution (3 × 30 ml) and dried over $MgSO_4$ before it was evaporated to dryness. The slightly coloured solid residue thus obtained was dissolved in CH_2Cl_2 (30 ml) and MeOH was added and the mixture was cooled in an ice bath overnight. The pure compound **2** was obtained in 70% yield (120 mg) as a white crystalline powder. Mwt = 1013.18 g mol^{-1} ($C_{64}H_{60}O_8N_4$), Mp > 300 °C, ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C, ppm) δ: 1.30 (s, 12H, *p*-CH_3), 2.24 (s, 24H, *o*-CH_3), 4.05 (s, 8H, Ar-CH_2-Ar), 7.40 (t, 4H, J = 4.8 Hz, H-Py), 8.52 (d, 4H, J = 7.8 Hz, H-Py), 8.90 (s, 4H, H-Py), 9.49 (s, 4H, H-Py); ^{13}C-RMN ($CDCl_3$, 75 MHz, 25 °C, ppm) δ: 4.2, 18.6, 32.6, 123.6, 125.3, 125.8, 133.9, 137.7, 138.2, 146.1, 151.3, 154.1, 163.6. Calculated for $C_{64}H_{60}O_8N_4 \cdot 1.5CHCl_3$:% C 65.93, H 5.16, N 4.70; found: % C 65.96, H 5.25, N 4.56.

Crystallisation conditions

Compound 2. Crystals were obtained at room temperature in a crystallisation tube (height = 15 cm, diameter = 0.4 cm), upon slow diffusion of *n*-hexane (1 ml) into a CH_2Cl_2 solution (0.5 ml) containing the compound **2**.

[2-AgTsO]$_n$. In a crystallisation tube (height = 15 cm, diameter = 0.4 cm), at room temperature and in the dark a $CHCl_3$ solution (0.5 ml) of **2** (3.0 mg) was layered with a EtOH (1 ml) solution of silver tosylate (3.3 mg). The tube was sealed with a stopper and kept in the dark at room temperature avoiding vibrations. After *ca.* 1 week, colourless crystals were obtained.

[2-HgCl$_2$]$_n$. In a crystallisation tube (height = 15 cm, diameter = 0.4 cm), at room temperature a solution of **2** (3.0 mg) in chlorobenzene (0.5 ml) was layered with a EtOH (1 ml) solution of mercury chloride (3.3 mg). The tube was sealed with a stopper and kept at room temperature avoiding vibrations. After *ca.* 2 week, 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 (λ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC reference numbers 616017–616019. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607982m.

Crystallographic data for 2. $C_{70}H_{60}N_4O_{9.5}$, M = 1109.22, *orthorhombic*, a = 17.0505(6), b = 17.6067(6), c = 12.0448(5) Å, U = 3615.9(2) Å^3, Space group *Pban*, Z = 2, Refls measured: 43812, Independent Refls: 5262, Final R indices [I > 2sigma(I)]: R_1 = 0.1117, wR_2 = 0.2533.

Crystallographic data for [2-AgTsO]$_n$. $C_{85}H_{80}Ag_2Cl_{18}N_4O_{15}S_2$, M = 2315.49, *monoclinic*, a = 11.609(2), b = 23.520(5), c = 35.590(7) Å, β = 95.59(3)°, U = 9672(3) Å^3, Space group $C2/c$, Z = 4, Refls measured: 58562, Independent Refls: 11092, Final R indices [I > 2sigma(I)]: R_1 = 0.0759, wR_2 = 0.2230.

Crystallographic data for [2-HgCl$_2$]$_n$. $C_{71}H_{60}C_{14.5}Hg_2N_4O_{11}$, M = 1705.94, *orthorhombic*, a = 22.5845(10), b = 12.3139(5), c = 17.2598(6) Å, U = 4800.0(3) Å^3, Space group *P*2*(1)*2*(1)*2, Z = 2, Refls measured: 45965, Independent Refls: 10976, Final R indices [I > 2sigma(I)]: R_1 = 0.0938, wR_2 = 0.2468.

Acknowledgements

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