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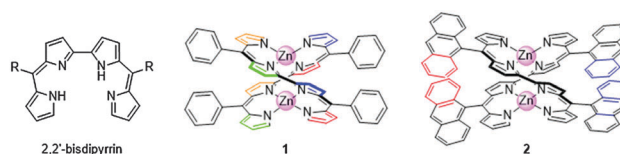
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Pre-organization of clefts for Ag– π interactions in Zn(II) bisdipyrrin helicates for the construction of heterometallic networks†

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Coordination of 2,2'-bisdipyrrin based ligands to Zn(II) cations leads to the formation of binuclear helicates with pre-organized pyrrolic strands as well as peripheral aromatic moieties for Ag– π interactions, thus affording crystalline heterometallic networks upon further interactions with Ag(I) salts without the assistance of additional heteroatom-based coordinating units.

Since it was first hypothesized by Hill and later confirmed by crystallographic investigation,¹ Ag–benzene interaction and more generally Ag– π interactions have been intensely studied,² used for sensing in solution³ and in the field of coordination networks.⁴ Combinations of polyarenes with a variety of silver salts have been particularly explored to generate infinite crystalline architectures. Contrastingly, polypyrrolic ligands have been much less investigated in this context. Studies in solution have demonstrated the ability of these backbones to interact with Ag(I) cations.⁵ Ag– π interactions in the solid state have been recently documented.^{6–8} The large majority of these examples are based on the association of silver salts with metal complexes incorporating bis-pyrrolic dipyrrin⁹ type ligands bearing peripheral coordinating units.⁷ However, a lack of control of this interaction was observed and, in some cases, polymorphism was detected affording, under the same crystallization conditions, extended architectures featuring such a complexation mode and other architectures without.^{7c} In order to promote this interaction, it seemed to be interesting to increase the number of complexation sites and more importantly to pre-organize them in a favourable disposition. In this regard, binuclear helicates resulting from the complexation of Zn(II) cations by tetrapyrrolic 2,2'-bisdipyrrin ligands appeared to be appealing,¹⁰ since they feature four π clefts formed by the pyrrolic rings of the two different strands (Scheme 1). Upon assembling a benzonitrile-appended



Scheme 1 Representation of a 2,2'-bisdipyrrin ligand, and the binuclear Zn(II) helicates **1** and **2** bearing peripheral phenyl or anthracene groups respectively. The π clefts formed by the tetrapyrrolic strands and the anthracene groups are highlighted in colour.

helicate with a series of silver salts, the anticipated complexation of the Ag(I) cations by pyrrolic groups affording tetranuclear Zn_2Ag_2 discrete motifs was observed. The latter further self-assemble into networks, owing to the additional coordination of the nitrile units to silver cations.⁸

Interestingly, the earlier reports on homometallic systems using polyarenes solely took advantage of the pre-organization of Ag– π interaction sites by covalent bonding,^{2,4a} without any stabilizing additional coordination of heteroatom-based units. It would be of interest to form analogous heterometallic networks in a similar manner, using helicates bearing unfunctionalized arene groups. In this respect, it should be noted that, in the binuclear Zn(II) helicates formed by combining 2,2'-bisdipyrrin ligands with Zn(II) cations in a 2/2 ratio, not only are the polypyrrolic strands pre-organized but also the peripheral moieties. Considering that the latter can be extended aromatic moieties, such as anthracene for example, they can also be regarded as a second interaction site for Ag(I). This concept is illustrated herein using phenyl- and anthracene-appended species, **1** and **2** (Scheme 1), allowing the formation of heterometallic networks solely resulting from Ag– π interactions with either the pyrrolic strands or the peripheral aromatic groups and without the assistance of additional binding units.

Helicate **1** was synthesized as described earlier,^{10e} whereas complex **2** was prepared following the synthetic route developed by Scott *et al.* (Fig. 1).¹¹ Upon reaction of Ni(II) complex **3**,¹² with DDQ, compound **4** was obtained in 62% yield. Demetallation by treatment with HCl, followed by NaHCO_3 , afforded the

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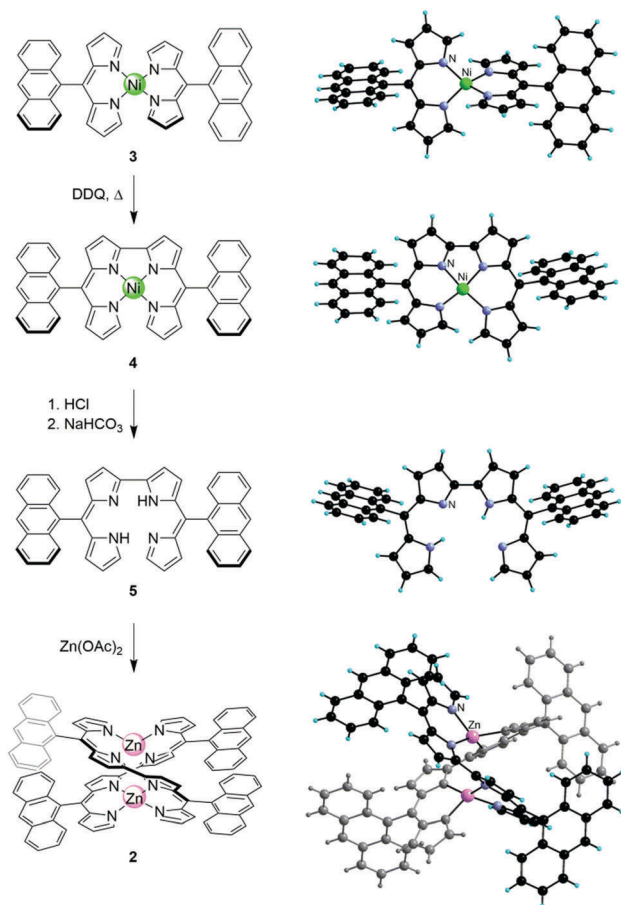


Fig. 1 Synthetic pathway for the preparation of helicate **2** (left) and crystal structures of the intermediates and the final compound (right). Solvent molecules have been omitted for clarity.

2,2'-bis-dipyrin ligand **5** in 91% yield. Subsequent reaction with one equivalent of $\text{Zn}(\text{OAc})_2(\text{H}_2\text{O})_2$ in a $\text{CHCl}_3/\text{MeOH}$ (1/1) mixture led to the formation of the target helicate **2** in 73% yield. All compounds were characterized by ^1H -, ^{13}C -NMR and UV-visible spectroscopies in solution, mass spectrometry and single-crystal X-ray diffraction (see the ESI† for details).

Although the $\text{Ni}(\text{II})$ cation is in a pseudo-tetrahedral environment in **3**, it adopts a distorted square-planar geometry in **4**, as highlighted by the angle between the two dipyrin chelates evolving from 45.3° to 19.2° , with a helical arrangement of the bis-dipyrin ligand around the metal center (Fig. 1). The effect of the bond formation between the two dipyrins is also apparent when comparing the Ni-N distances. They range from 1.885(2) to 1.898(2) Å in **3**, while two are significantly shorter than the others in **4** (1.847(3) and 1.859(3) vs. 1.883(3) and 1.893(3) Å) as previously observed for other reported complexes.^{8,10h,11,13} For the free 2,2'-bisdipyrin ligand **5**, the four pyrrolic rings are coplanar and the two dipyrin chelates are in a *cis* arrangement as reported for other analogous derivatives.^{10h} For helicate **2**, two $\text{Zn}(\text{II})$ cations, separated by 3.326(3) Å, adopt a distorted tetrahedral geometry with the chelates forming an angle of 72.7° . Within a helical strand, the two dipyrin units form an angle of 44.3° . The compound crystallizes in the $P2_1/c$ space group with both

P and *M* helical twists. In all four compounds, the peripheral anthracene group is perpendicular to the bis-pyrrolic backbone, as observed in the structure of the parent dipyrin.¹² In helicate **2**, as anticipated, two aromatic groups face each other with the shortest C–C distance of 3.409 Å (Fig. 1).

The assembly of helicates **1** and **2** with silver salt in the solid state was then investigated. Upon Et_2O vapour diffusion into a toluene solution of a mixture of **1** with an excess of $\text{Ag}(\text{TfO})$, crystals of either network **6** or **7** were obtained after few days and characterized by single-crystal X-ray diffraction. It should be noted that the formation of crystalline materials composed of **6** or **7** was delicate and only a few crystals could be obtained, preventing thus further batch characterization. The formation of network **8**, by Et_2O vapour diffusion into a *o*-xylene solution of a mixture of **2** with an excess of $\text{Ag}(\text{TfO})$, was consistent and produced enough crystals for full characterization (see the ESI† for details). For all three polymers, binuclear $(\text{AgTfO})_2$ units are complexed by the helicates through $\text{Ag}-\pi$ interactions with π -clefts formed by either the pyrrolic strands, in **6** and **7**, or the peripheral anthracene units in **8** (Fig. 2–4).

Network **6**, formulated as $[\text{1}(\text{AgTfO})_2]_2(\text{Et}_2\text{O})_3$, crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Fig. 2a). Two $\text{Ag}(\text{I})$ cations are bridged by two TfO^- anions with $\text{Ag}-\text{O}$ distances ranging from 2.351(3) to 2.911(3) Å. For both metal centers, the coordination sphere is completed by interaction with $\text{C}=\text{C}$ bonds of two pyrrolic rings belonging to the two strands of helicate **1** with $\text{Ag}-\text{C}$ distances within the 2.396(4) to 2.539(4) Å range. These distances are in agreement with the ones observed with other mono- and bis-dipyrin complexes.^{7,8} Each helicate binds two silver cations *via* $\text{Ag}-\pi$ interaction in a 1,2-arrangement (Fig. 3a). It is worth noting that the $\text{Zn}-\text{Zn}$ distance (3.186(4) Å) within the helicate is shorter than the one reported for the free compound, 3.243 Å.^{10e} The overall organization is a 1-D polymer with alternating *P* and *M* chirality along the *c* axis (Fig. 2a). In the crystal, these neutral chains are separated by Et_2O solvate molecules.

Interestingly, under the same reaction conditions, crystals of network **7** were also obtained. This compound, formulated as $[\text{1}(\text{AgTfO})_3]$, also crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Fig. 2b). Once again, silver cations form binuclear units owing to the bridging of triflate anions with $\text{Ag}-\text{O}$ distances varying from 2.357(3) to 2.476(3) Å. These neutral $(\text{AgTfO})_2$ cores are complexed by helicate **1** *via* $\text{Ag}-\pi$ interaction with $\text{Ag}-\text{C}$ distances slightly longer than in **6** (2.405(3) to 2.683(3) Å). Each $\text{Zn}(\text{II})$ complex is bound to three $\text{Ag}(\text{I})$ cations, leading to an overall 2-D organization, with alternating *P* and *M* chirality (Fig. 2b). The latter can be described, by analogy with the above mentioned network **6**, as 1-D chains formed by complexation of $(\text{AgTfO})_2$ units by helicate **1** in a 1,2-arrangement along the *b* axis, further connected here by a third binuclear silver based unit (Fig. 2b). The arrangement of the ligands and $\text{Zn}(\text{II})$ cations within helicate **1** itself does not strongly differ from what is observed for **6** (Fig. 3), except again for a shorter $\text{Zn}-\text{Zn}$ distance (3.208(2) Å) compared with the free complex.

Network **8**, formulated as $[\text{2}(\text{AgTfO})_2]_2(\text{o-xylene})(\text{Et}_2\text{O})_5$, crystallizes in the triclinic $P\bar{1}$ space group (Fig. 4). As for the two



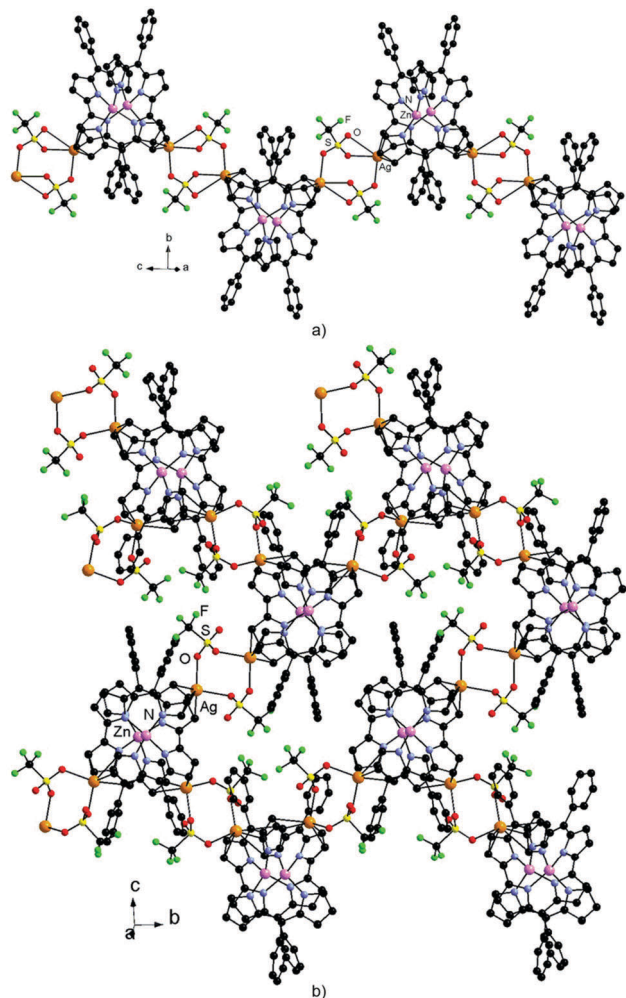


Fig. 2 Portion of the 1D network in the structure of **6** (a) and of the 2D network in the structure of **7** (b). Hydrogen atoms and solvent molecules have been omitted for clarity.

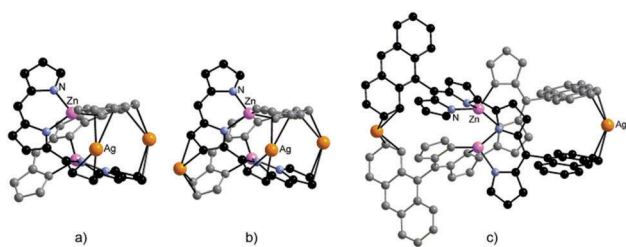


Fig. 3 Details of the Zn₂Ag_x cores ($x = 2, 3$) in **6** (a), **7** (b) and **8** (c). The peripheral phenyl groups have been omitted for clarity in (a) and (b).

previous extended architectures, silver cations form binuclear units bridged by TfO[−] anions with Ag–O distances between 2.358(3) and 2.436(3) Å. The units are complexed by helicate **2** via Ag– π interaction with pairs of peripheral anthracene groups (Fig. 3c and 4), leading to a 1D network with alternating *P* and *M* helices. The Ag–C distances range from 2.411(4) to 2.567(4) Å. In networks **6** and **7**, the Ag(I) cations interact consistently with the same C=C bond of the pyrrolic ring, whereas the situation is different in the structure of **8**. Indeed, one Ag(I) center

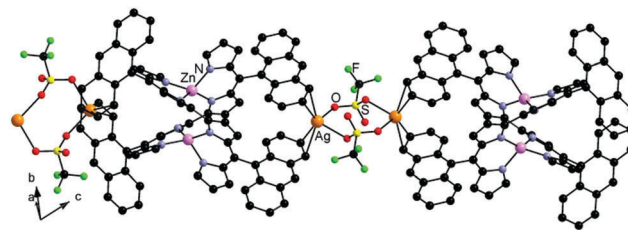


Fig. 4 Portion of the 1D network in the structure of compound **8**. Hydrogen atoms and solvent molecules have been omitted for clarity.

interacts with the outer C=C bonds of the anthracene groups, while the other cation is complexed by inner ones (Fig. 3b). This is in agreement with what has been reported for Ag(I) complexation by stilbenoid type ligands.^{2d} The penetration of the cation in the π cleft is more pronounced (complexation by inner C=C bonds), when the two aromatic groups form a wider angle (55.1 vs. 18.5° here). As observed for the two previous compounds, the Zn–Zn distance (3.288(2) Å) is slightly shorter than in the free helicate. X-ray powder diffraction study on network **8** confirmed that a single phase is obtained, although a slight loss of crystallinity of the material upon removal from the mother liquor was observed (Fig. S7, ESI†).

Mononuclear Zn(II) dipyrin complexes have been described to be emissive in the crystalline state by us¹⁴ and others.^{12d} In light of these observations and of the reported luminescence of bis-dipyrin Zn(II) helicates in solution,¹⁰ a preliminary investigation of the emission of helicates **1** and **2** as well as network **8** in the solid state was performed. While **2** shows a weak emission at 854 nm upon excitation at 720 nm, no emission could be detected up to 900 nm for **1**. Upon complexation of Ag(I) cations, this emission seems to be quenched, since no luminescence could be detected for network **8**.

In conclusion, the coordination of 2,2′-bisdipyrin strands around two Zn(II) cations affords helicates with two distinct pre-organized sites for Ag– π interaction: the pyrrolic and the peripheral ones in the case of larger aromatic units. This was exploited for the formation of three heterometallic networks obtained upon combinations of Ag(TfO) with either phenyl or anthracene peripherally appended helicates. With the former, both a 1- and a 2-D network have been obtained showing the complexation of binuclear (AgTfO)₂ units via Ag– π interactions with the pyrrolic rings. Contrastingly, with the latter, Ag– π interaction takes place with the peripheral anthracene groups. It should be noted that the formation of these networks does not require the assistance of additional hetero-atom based coordinating units but relies solely on complexation of the (AgTfO)₂ motifs by the pre-organized carbon based groups. Future work will focus on extending this strategy to other helicates as well as to Cu(I) cations.

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