Ag(I)- π interactions with pyrrolic derivatives

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Abstract

Whereas Ag- π interactions with alkenes, alkynes and arenes have been thoroughly explored, assembly with pyrrolic derivatives has been much less investigated. This is surprising given the prominent place that species such as BODIPYs, corroles or porphyrins occupy in chemistry and biology and given that these compounds are actually prone to this mode of complexation of Ag(I) cations in solution as well as in the solid state. Indeed, studies in the liquid phase by NMR, UV-visible and Raman spectroscopy with bis-dipyrin based helicates or systems incorporating porphyrinic units have demonstrated their ability to interact with silver(I) centers. Furthermore, a variety of homo- and hetero-metallic architectures featuring this binding mode, especially with β -pyrrolic carbon atoms, based on a diversity of ligands comprising one, two, three or more pyrrole moieties have been characterized in the crystalline state by X-ray diffraction. Whereas the presence of these interactions is difficult to promote and control a priori, recent work has shown their recurrence with 2,2'-bis-dipyrin based helicates. All these aspects are reviewed in this contribution aiming at highlighting the importance and potential of Ag- π interactions with pyrrolic systems.

Keywords :

Silver; Ag- π interactions; pyrrole; dipyrin; porphyrin; coordination polymers.

Highlights:

- Ag- π interactions with pyrrolic derivatives are reviewed.
- Investigations in solution with helicates and porphyrin-based systems are presented.
- Homo- and hetero-metallic architectures characterized in the crystalline state are detailed.

Abbreviations:

dpm = dipyrin; FOD = 6,6,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato; tfc = tris-(trifluoromethylhydroxymethylene)-(+)-camphorate; TfO⁻ = trifluoromethanesulfonate, triflate; lut = 2,6-lutidine; hfac = hexafluoroacetylacetonate ; salen = N,N'-bis(salicylidene)ethylenediamine; acacpy₂ = 1,3-bis-(4-pyridyl)-1,3-propanedioate.

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1. Introduction

Cation- π interactions have been long recognized as playing an important role in biological and synthetic systems [1-2]. In particular, silver-arene interactions were suggested almost 90 years ago by Hill [3] in the course of investigations on the molecular weight of AgClO_4 in benzene. This was later confirmed by the determination of the crystal structure of this compound [4-5] revealing the formation of one-dimensional coordination chains via complexation of silver cations by bridging aromatic molecules. Following this result, $\text{Ag(I)}-\pi$ interactions have been investigated for a diversity of applications such as for the construction of materials or coordination polymers [6-11], for the elaboration of supramolecular assemblies [12] or for the design of so-called argentivorous molecules [13], for example.

The theoretical background for this type of contact was first elaborated following Mulliken's model based on charge transfer [14]. However, the absence of resolved corresponding absorption bands does not allow an experimental demonstration of this interpretation. An accepted model is the Dewar, Chatt and Duncanson one involving donation of the ligand and metal back-donation, and suggesting a more favourable symmetrical η^2 bonding [15-16]. However, such a pure case is most often not experimentally observed [17] as confirmed by the extensive crystallographic investigations on Ag-arene complexes [18-19] and formalized in a recent theoretical study [20]. Either a η^1 or an unsymmetrical η^2 mode of complexation is usually present in the solid state. In solution, the energy associated with this attractive interaction has been determined to amount to a few kcal/mol, through $^1\text{H-NMR}$ studies using organic derivatives such as molecular torsion balances or clefts [13, 21-24]. Interestingly, while the complexation of silver(I) cations by alkenes, alkynes and arenes has been thoroughly explored and reviewed [6-9], interactions with heterocyclic derivatives such as pyrrole-based compounds have been much less addressed. This is surprising given the prominent place that species such as porphyrins, corroles or open-chain polypyrrolic molecules occupy in chemistry and biology [25] and since these derivatives are actually prone to $\text{Ag(I)}-\pi$ interactions. This contribution aims at reviewing these aspects from earlier studies in solution to more recent work focusing on the crystalline state.

2. Ag- π interactions in solution

The investigations of Ag- π interactions with pyrrolic species in solution were developed with the help of diverse spectroscopic techniques such as NMR, UV-Visible and Raman as well as mass-spectrometry.

2.1. Bis-dipyrin based helicates

Following the seminal work of Furhop on the coordination chemistry of formylbiliverdinate [26], Thompson and Dolphin reported on helicate type complexes obtained by assembly of a series of divalent metal centers with open-chain tetra-pyrrolic ligands [27-28]. The latter organic derivatives comprise two dipyrromethene or dipyrin (dpm) chelate units [29] connected directly by a C-C bond or via a spacer either at α or β positions and are thus named bis-dipyrins (bis-dpm) [30]. The helicate species, particularly studied with Zn(II) cations, are generated in both *P* and *M* forms in equal amount in the absence of asymmetric induction. In order to investigate the helical chirality of these complexes, NMR spectroscopy was employed using AgFOD ($\text{FOD} = 6,6,7,8,8,8\text{-heptafluoro-2,2-dimethyl-3,5-octanedionato}$) in combination with a chiral lanthanide shift agent [31]. Such analytical method, widely used with arenes and alkenes, relies on binding of double bonds to silver cation, via Ag- π interaction, acting as a bridge towards an enantiomerically pure lanthanide moiety, hence leading to chemical shift non-equivalence for diastereotopic nuclei [32]. In their study, Thompson and Dolphin focussed

on the complexation of bis-dpm **1** by Zn(II) affording helicate **2**, the chirality of which was explored (Fig. 1). A signal splitting was observed for this compound upon association with AgFOD and enantiomerically pure Yb(tfc)₃ (tfc = tris-(trifluoromethylhydroxymethylene)-(+)-camphorate) in CDCl₃, as a result of the formation of diastereoisomer pairs [31]. This is further supported by the absence of such splitting when using an achiral lanthanide salt. While this investigation clearly relies on the presence of Ag- π interaction, the actual mode of assembly of the helicate with the silver and ytterbium salts was not further detailed.

Fig. 1 Representation of helicate **2** obtained by assembly of **1** with Zn(II), investigated by NMR with silver(I)-lanthanide(III) species for the formation of diastereoisomeric pairs. The crystal structure of the binuclear complex is shown as an insert (CSD refcode: MEPZIQ) [33].

The association of Zn(II) helicates and Ag(I) salts was taken advantage of for the characterization of binuclear complexes based on bis-dpm ligands with an enantiopure binol bridge between the two bis-pyrrolic chelate moieties [34]. By ESI-mass spectrometry, only the free base ligand could be detected upon analysing one such compound. Addition of silver salt was used to modify the ionization conditions. This led to the observation of the [helicate/Ag]⁺ ion allowing characterization of the target complex. The authors also indicated that this technique had proven efficient for the analysis by ESI-mass spectrometry of dpm based species in general [34].

2.2 Porphyrin based systems

Shinkai and coworkers have studied the effect of silver ions on Ce(IV) double decker porphyrin systems [35-36]. In a first study, the complex comprising *p*-methoxyphenyl groups in *meso* positions **3** (Fig. 2) was investigated. A bathochromic shift of the Soret absorption band with an isosbestic point was observed upon addition of AgTfO (TfO = trifluoromethanesulfonate, triflate) to a CHCl₃/MeOH (4/1) solution of **3**. Interestingly, a reverse hypsochromic shift was detected upon the introduction of tetra-*n*-butylammonium chloride causing the precipitation of AgCl. Furthermore, this effect was selective for silver since it could not be observed with alkali metal cations. A 1/3 stoichiometry for the adduct **3**/Ag(I) was found and the UV-visible spectroscopy study revealed a positive allosterism. The complexation of a first metal cation allowed the easier binding to a second and then to a third silver cation. Additional NMR studies in CD₂Cl₂/CD₃OD (4/1) suggested that the cooperative binding of Ag(I) by the peripheral π -clefts led to a blocking of the rotational freedom of the *meso* aryl groups. It was inferred that the relative rotation of the porphyrin planes was also limited by complexation, although temperature-dependent NMR analysis could not provide reliable confirmation.

Fig. 2. Representation of Ce(IV) double-decker porphyrin complexes **3-6** investigated for their assembly with Ag(I) salt by Shinkai and coworkers [35-36].

This behaviour was further investigated by using other double-decker systems **4-6** (Fig. 2) [36]. Here again, no shift in the Soret band could be detected in the UV-visible spectrum of these compounds upon addition of sodium, potassium, or thallium ions. In contrast, the complexation of silver was confirmed by observation of the adduct in the corresponding CIS-mass spectra and of a reversible bathochromic/hypsochromic shift in the absorption spectra collected for all species when adding $\text{AgTfO}/(n\text{-Bu}_4\text{N})\text{Cl}$. As for **3**, the sigmoidal shape of the curve of the evolution of the Soret band with respect to increased $[\text{Ag}^+]$ concentration suggested a positive allosterism. It is worth noting that binding is present even with compounds bearing peripheral electron-withdrawing groups such as esters in **4** or fluorine atoms in **5**. This strongly suggests that interaction with the Ag(I) cation operates with the pyrrolic systems rather than with the *meso* aromatic groups and is consistent with the fact that the nature of the latter is known to not strongly modify the basicity of porphyrins and hence their ability to complex metal cations. ^1H -NMR investigation showed that the compounds remained diamagnetic even in the presence of an excess of silver salts, thus excluding a redox process at stake such as reduction to Ce(III) or formation of porphyrin radical. Complexation using compound **6** incorporating two macrocycles functionalized at positions 5 and 15 was studied using variable temperature experiments, since the rate of rotation of the pyrrolic moieties is faster than for tetra-arylporphyrin derivatives. This analysis suggests a mechanism relying on the binding of a first metal cation affecting the relative position and rotation of the two porphyrins within the Ce(IV) complex and hence promoting the interaction with additional silver cations. This was further supported by resonance Raman spectroscopy.

Recently, Ag- π interactions have been used to modify the σ -Lewis acidity of catalysts to allow the activation of ketones and aldehydes [37]. Whereas silver-based π -Lewis acid catalysts have been largely explored [38], their use as σ -Lewis acid catalysts is less common. This is due to the fact that these compounds generally do not feature an available σ -interaction site for the substrate in their design, since it is occupied by a solubilizing ligand such as a phosphine. To circumvent this issue, an alternative strategy based on the use of a π -ligand instead to leave access for the substrate has been proposed. The complexation of AgSbF_6 by Ni(II) porphyrin **7** (Fig. 3) was indeed demonstrated by UV-visible spectroscopy and XANES to take place by interactions with the β -pyrrolic CC bond and partial charge transfer. Such adduct could coordinate 2,6-dimethyl- γ -pyrone as shown by the appearance of a new C=O vibration in the IR spectrum and the disappearance of the one associated with the free molecule. Such behaviour could not be observed using $(\text{Ph}_3\text{P})_2\text{AgSbF}_6$ suggesting the efficient control of the σ -Lewis acidity of the Ag(I) center by π -complexation of porphyrin **7**. This was further supported by Natural Bond Orbital analysis of this system. These calculations indicated that the energy of the interaction of the silver cation with the pyrone was equivalent to the one with the porphyrin that combines charge transfer and π -complexation.

Fig. 3. Modulation of the σ -Lewis acidity of Ag(I) center for interaction with ketones using π -complexing Ni(II) porphyrin **7**, as proposed in [37].

3. Ag- π interactions in the crystalline state

While crystallographic investigations highlighting Ag- π interactions with carbon-based aromatics date back to the 1950s [4, 5], studies on systems with pyrrolic derivatives are much more recent. Both homo- and hetero-metallic systems featuring this mode of complexation have been reported. They are based on a diversity of ligands comprising one, two, three or more pyrrolic rings, conjugated or not. Whereas the first examples are serendipitous, recent attempts at promoting and controlling the interaction have been described.

3.1. Homometallic systems

3.1.1. Mono-pyrrolic ligands

Ghorai and Mani have studied the coordination chemistry of ligand **8H** comprising a central pyrrole moiety and four peripheral 3,5-dimethylpyrazole units bridged by methylene groups [39]. Complexation of Pd(II), Cu(I) as well as Ag(I) has been explored. In particular a tetranuclear compound, $[(\mathbf{8})_2\text{Ag}_4](\text{BF}_4)_2$, has been obtained and structurally characterized (Fig. 4). In this complex, two crystallographically independent Ag(I) cations are present. The first one is coordinated to a pyrazole group and to the deprotonated central pyrrolic unit of **8** in an almost linear fashion. The second one is bound to three pyrazoles. The two metal cations are separated by 3.1150(9) Å, suggesting argentophilic interactions [40]. Within this [2+4] metallamacrocycle, the pyrrolic ring lies above the Ag_2 dimer with Ag-C distances ranging from 2.848(7) to 3.154(6) Å. These distances are below the sum of the van der Waals radii (3.40 Å) [41], yet they are in the higher range for Ag- π interactions characterized in the crystalline state for arenes derivatives [17-19]. Interestingly, the silver cations are weakly interacting with both the α and β pyrrolic carbon atoms. These weak interactions appear secondary and to be resulting from the arrangement of the macrocycle driven by Ag-N coordination.

Fig. 4. Schematic representation of ligand **8H** and crystal structure of the tetranuclear complex $[(\mathbf{8})_2\text{Ag}_4]^{2+}$ (CSD refcode: POFCUK). The Ag- π interactions are highlighted in purple dash line and Ag-Ag ones in black dash line, one of the ligand molecules is shown in grey and hydrogen atoms have been omitted for clarity.

The coordination chemistry of ligand **9**, analogue of **8H** bearing only 3,5-dimethylpyrazole units at the α -positions of the pyrrolic ring has been studied by Jana and Mani [42]. Whereas

the deprotonated version of the ligand affords a discrete trinuclear Ag(I) complex not featuring Ag- π interactions, assembly of the native ligand with AgTfO yields a one-dimensional coordination polymer of interest. In this compound formulated $[(\mathbf{9})\text{Ag}](\text{TfO})(\text{CH}_2\text{Cl}_2)$, the silver center is bridging two molecules of **9** by coordination to the pyrazolyl groups (Fig. 5a). The environment of the metal cation is completed by weak coordination to the triflate anion as well as interactions with carbon atoms of the central pyrrole with Ag-C distances of 2.741 and 2.937 Å. These distances are shorter than in the previous case comprising a tetrafunctionalized ligand.

Fig. 5. Schematic representation of ligand **9** and crystal structure of the 1D chain $[(\mathbf{9})\text{Ag}](\text{TfO})(\text{CH}_2\text{Cl}_2)$ (a). Representation of dipyrromethane ligand **10** and crystal structure of the 1D chain $[(\mathbf{10})\text{Ag}](\text{BF}_4)$ (b) (CSD refcodes: GEBFAX, TUKLIW). The Ag- π interactions are highlighted in purple dash line and CH hydrogen atoms as well as solvent molecules and anions have been omitted for clarity.

3.1.2 Bis-pyrrolic ligands

Increasing the pyrrole/3,5-dimethylpyrazole ratio, Mani and coworkers reported dipyrromethane derivatives bearing the pyrazole based units in α positions and either a cyclohexyl or two ethyl groups at the *meso* positions and their assembly with Pd(II), Cu(I) and Ag(I) salts [43]. In particular, ligand **10**, featuring a *meso* cyclohexyl unit, and AgBF₄ formed a 1D polymer owing to the coordination of the metal cations by the pyrazolyl units (Fig. 5b). Within these 1D chains, both crystallographically independent silver cations also interact with β pyrrolic carbon atoms of two neighbouring dipyrromethane moieties in a η^1 fashion with Ag-C distances ranging from 2.597(9) to 2.758(8) Å in analogy with the mono-pyrrolic ligand **9**. As in the previous example, the pyrrole remained protonated at the nitrogen acting here as a hydrogen bond donor for the tetrafluoroborate anions.

Ma and coworkers have studied the assembly of ligand **11**, a bis-pyrrole hydrazone, with AgNO₃ (Fig. 6) [44]. A 2D network formulated $[(\mathbf{11})(\text{AgNO}_3)_2]$ has been obtained and characterized by single-crystal X-Ray diffraction, IR and Raman spectroscopies. In this compound, the silver cation is coordinated to a nitrogen atom of the central hydrazone group and to two bridging nitrate anions. In addition, the metal center lies above a CN bond of the pyrrolic ring with Ag-C and Ag-N distances of 2.690 and 2.631 Å respectively suggesting Ag-

π interactions. This structure is unique as it represents the first and only example of η^2 -coordination of Ag(I) by a pyrrolic CN bond. Given that almost all the other structures show complexation at the CC bonds, this result is rather surprising and a re-examination of the association of ligand **11** with AgNO₃ as well as other Ag(I) salts may be of interest to determine whether this mode of organization pertains to this derivative/salt combination or can be generalized.

Fig. 6. Representation of ligand **11** and crystal structure of the 2D coordination polymer $[(\mathbf{11})(\text{AgNO}_3)_2]$ (CSD refcode: BEPWOJ). The Ag- π interactions are highlighted in purple and CH hydrogen atoms have been omitted for clarity.

3.1.3. Tris-pyrrolic ligand

The coordination chemistry of benziporphodimethenes comprising a tris-pyrrolic tripyrrin fragment [30] and an aromatic moiety bridged by sp^3 carbon atoms has been explored by Hung and coworkers using Zn(II), Cd(II), Hg(II) and Ag(I) salts [45]. In particular, derivative **12H** (Fig. 7) afforded two different complexes upon reaction with AgNO₃ in the presence of 2,6-lutidine (lut). The procedures to obtain either species differ in the work-up stage. While water extraction of the crude product provides a binuclear $[(\mathbf{12})\text{Ag}]_2$ complex, a tetranuclear compound formulated $[(\mathbf{12})\text{Ag}_2\text{NO}_3(\text{lut})]_2$ could be isolated in the absence of this treatment (Fig. 7). In the earlier complex, the silver cation is coordinated to the tridentate mono-anionic deprotonated tripyrrinato moiety forming a neutral $[(\mathbf{12})\text{Ag}]$ unit that self-assembles into a head-to-tail dimer, owing to Ag- π interaction with the β pyrrolic C=C bond of the central pyrrolic ring with Ag-C distances of 2.476(3) and 2.579(3) Å (Fig. 7a). It is worth noting that the metal center also interacts with the phenyl ring of the ligand within the $[(\mathbf{12})\text{Ag}]$ unit with an Ag-C distance of 2.646(3) Å. The tetranuclear complex can be described as having the same binuclear core capped on each face by a $[\text{AgNO}_3(\text{lut})]$ fragment (Fig. 7b). The central pyrrolic nitrogen atom of the tripyrrin core is thus coordinating two different metal centers and an argentophilic interaction is also present ($d_{\text{Ag-Ag}} = 3.1886(4)$ Å). The environment of the central Ag(I) cation within the dimer is similar to the one observed in the binuclear complex albeit with slightly longer Ag-C distances ($d_{\text{Ag-Cpyrrole}} = 2.514(3)$ and $2.614(3)$ Å; $d_{\text{Ag-Cphenyl}} = 2.645(3)$ Å). Interestingly, the stability of both compounds in solution has been investigated by ¹H NMR spectroscopy in CDCl₃. Focusing on the chemical shift of the central β -pyrrolic protons, it was shown that $[(\mathbf{12})\text{Ag}]_2$ is in equilibrium with the monomeric unit with an association constant of

26.8. This value tends to indicate that the Ag- π interactions are not retained in CDCl_3 solution. The same applies to the tetranuclear species. However, it was demonstrated that the capping $[\text{AgNO}_3(\text{lut})]$ remained coordinated to the monomeric unit in solution.

Fig. 7. Ligand **12H** and crystal structure of dimeric complex $[(\mathbf{12})\text{Ag}]_2$ (a) and $[(\mathbf{12})\text{Ag}_2\text{NO}_3(\text{lut})]_2$ (b) (CSD refcode: ICAJAZ, ICAJED). The Ag- π interactions are highlighted in purple dash line and Ag-Ag ones in black dash line, one of the ligand molecules is shown in grey and hydrogen atoms have been omitted for clarity.

3.1.4. Oligo-pyrrolic ligand

Wojaczynski, Maciołek and Chmielewski have developed ligand **13H₅** consisting in a bis-pyrrolic dipyrryn unit bearing two N-confused porphyrins [46-47] at the α positions and have studied its assembly with silver salts [48]. Upon reaction with AgOAc , a neutral binuclear Ag(III) complex was obtained, $[(\mathbf{13H})\text{Ag}_2]$. Coordination takes place at the two macrocyclic units with the metal cations bound to three nitrogen atoms and a carbon atom belonging to the inverted pyrrole ring. This compound thus contains four nitrogen atoms available for further complexation: the ones of the dipyrryn moiety and the outer one of each of the two N-confused porphyrins. This has been taken advantage of for the assembly with AgBF_4 leading to the octanuclear mixed-valent species $\{[(\mathbf{13})\text{Ag}^{\text{III}}_2]\text{Ag}^{\text{I}}_2\}_2^{2+}$ (Fig. 8). Interestingly, this compound can also be directly obtained by reaction of **13H₅** with AgBF_4 . As shown by X-Ray diffraction, two $[(\mathbf{13H})\text{Ag}_2]$ units, deprotonated at the dipyrryn site, are coordinating two pairs of Ag(I) centres formed via argentophilic interactions ($d_{\text{Ag-Ag}} = 2.8757(9)\text{-}2.8699(9) \text{ \AA}$). Each of the silver(I) cations is coordinated to one nitrogen atom of the dipyrrynato moiety and to the outer nitrogen of the N-confused porphyrin. Furthermore, within each pair, one metal center is also interacting via Ag- π interaction with a β -pyrrolic carbon atom of the dipyrrynato fragment with Ag-C distances of $2.539(9)\text{-}2.568(9) \text{ \AA}$ (Fig. 8). This interaction is also apparent in the splitting of the peak corresponding to this pyrrolic carbon in ^{13}C NMR owing to $^{107,109}\text{Ag}\text{-}^{13}\text{C}$ spin-spin coupling. This also supports the stability of the octanuclear complex in CDCl_3 solution.

Fig. 8. Two paths for the synthesis of $\{[(13)Ag^{III}_2]Ag^I_2\}^{2+}$ and its crystal structure (CSD refcode: MAVGUO). The Ag- π interactions are highlighted in purple dash line and Ag-Ag ones in black dash line. One of the ligand molecules **13** is shown in grey. Hydrogen atoms and *meso* aromatic groups have been omitted for clarity.

3.2. Heterometallic assemblies

The examples presented so far are homometallic assemblies, resulting from the association of an organic derivative with a silver salt. Interestingly, Ag- π interactions have been also observed in heterometallic architectures prepared following a stepwise approach [49-54] consisting in the synthesis of a metal complex bearing peripheral binding sites, so-called metalloligand, followed by subsequent reaction with Ag(I) salts.

3.2.1. Dipyrrin based systems

Dipyrrins form under mild basic conditions an anionic chelate and can be readily functionalized at the pyrrolic and *meso* positions [29]. These features have made them attractive ligands for the formation of luminescent complexes and supramolecular assemblies [55-57] and have been taken advantage of for the sequential formation of heterometallic coordination networks, in particular with silver salts.

3.2.1.1. Metal complexes

Ligand **14H** (Fig. 9) incorporating a dipyrrin unit unfunctionalized at the α and β positions and equipped with a 3,5-dicyanophenyl group at the *meso* position has been developed by our group and used for the elaboration of heterometallic coordination polymers [58]. In particular,

complex $(\mathbf{14})_2\text{Zn}$ formed a crystalline material upon association with silver triflate in benzene, $\{[(\mathbf{14})_2\text{Zn}]\text{Ag}_2(\text{TfO})_2\}(\text{C}_6\text{H}_6)_{2.5}$. In the structure of this two-dimensional compound, binuclear triflate-bridged $\text{Ag}_2(\text{TfO})_2$ units are coordinated to the peripheral nitrile groups of the $(\mathbf{14})_2\text{Zn}$ metalloligand. In addition, the $\text{Ag}(\text{I})$ cations also interact in an unsymmetrical η^2 fashion with the β -carbon atoms of the dipyrinato moiety with $\text{Ag}-\text{C}$ distances ranging from 2.397(4) to 2.583(4) Å (Fig. 9). These distances are shorter than what has been observed in the homometallic system based on the N-confused porphyrin appended ligand described above (Fig. 8).

Fig. 9. Representation of dipyrin **14H** and its complex $(\mathbf{14})_2\text{Zn}$ and crystal structure of the 2D heterometallic network $\{[(\mathbf{14})_2\text{Zn}]\text{Ag}_2(\text{TfO})_2\}(\text{C}_6\text{H}_6)_{2.5}$ (CSD refcode: ODOCOA). The $\text{Ag}-\pi$ interactions are highlighted in purple. Hydrogen atoms as well as benzene solvate molecules have been omitted for clarity.

Following this result, the formation of heterometallic architectures based on dipyrin **15H** bearing a benzonitrile has been investigated (Fig. 10) [58–59]. The homoleptic complex $(\mathbf{15})_2\text{Cu}$ reported earlier by Cohen and coworkers [60] was assembled with AgTfO yielding a crystalline 1D coordination network $\{[(\mathbf{15})_2\text{Cu}]\text{Ag}_2(\text{TfO})_2(\text{H}_2\text{O})\}$ (Fig. 10a) [58]. As in the previous case, the silver cations are coordinated to peripheral nitrile groups and triflate anions but also interact with β -carbon atoms of the dipyrinato moiety of neighbouring metalloligands in a η^2 fashion. Interestingly, one of the two crystallographically independent cations interacts with two different bis-pyrrolic chelates, whereas the other forms $\text{Ag}-\pi$ interaction with only one dipyrinato moiety and sees its coordination sphere completed by a water molecule. The $\text{Ag}-\text{C}$ distances range from 2.515(9) to 2.68(1) Å and are longer than what has been observed with the above-mentioned Zn complex. With the heteroleptic analogue $[(\mathbf{15})(\text{hfac})\text{Cu}]$ (hfac = hexafluoroacetylacetonate), a 2D polymer was obtained, $\{[(\mathbf{15})(\text{hfac})\text{Cu}]\text{AgTfO}\}(\text{C}_6\text{H}_6)_{1.5}$. The coordination environment is similar to the one described with the homoleptic metalloligands since the $\text{Ag}(\text{I})$ cation is bound to a nitrile group, a triflate anion and interacts with β -pyrrolic carbon atoms of two different chelate units in either a η^1 or η^2 fashion ($d_{\text{Ag}-\text{C}}$ = 2.382(5)–2.703(5) Å) (Fig. 10b). With another heteroleptic complex $[(\mathbf{15})(\text{salen})\text{Co}]$ (salen = N,N'-

bis(salicylidene)ethylenediamine), a discrete heterometallic species was isolated with AgSbF_6 (Fig. 10c). In this [2+2] metallamacrocycle $\{[(\mathbf{15})(\text{salen})\text{Co}]\text{Ag}(\text{H}_2\text{O})(\text{MeCN})\}_2(\text{SbF}_6)_2$, the $\text{Ag}(\text{I})$ cation is coordinated to an acetonitrile and a water molecule as well as to the nitrile unit of a metalloligand and the β -pyrrolic C=C bond of another complex with Ag-C distances of 2.449(4) and 2.614(4) Å.

Fig. 10. Representation of dipyrin **15H** and associated metalloligands $[(\mathbf{15})_2\text{Cu}]$, $[(\mathbf{15})(\text{hfac})\text{Cu}]$, $[(\mathbf{15})(\text{salen})\text{Co}]$ and crystal structures of networks $\{[(\mathbf{15})_2\text{Cu}]\text{Ag}_2(\text{TfO})_2(\text{H}_2\text{O})\}$ (a) and $\{[(\mathbf{15})(\text{hfac})\text{Cu}]\text{AgTfO}\}(\text{C}_6\text{H}_6)_{1.5}$ (b) and metallamacrocycles $\{[(\mathbf{15})(\text{salen})\text{Co}]\text{Ag}(\text{H}_2\text{O})(\text{MeCN})\}_2^{2+}$ (c) and $[(\mathbf{15H})\text{Ag}]_2^{2+}$ (d) (CSD refcodes: ODOCUG, ODOCIU, TIXMAP, TIXLOC). The Ag- π interactions are highlighted in purple dash-line. Anions, solvent molecules and CH hydrogen atoms have been omitted for clarity.

It is worth noting that the homoleptic species $[(\mathbf{15})_3\text{Co}]$ incorporating the same ligand forms a coordination polymer also with AgTfO however solely based on coordination of the silver cation to the peripheral nitrile groups, thus not featuring any Ag- π interactions [61]. Additionally, association of free dipyrin **15H** with AgBF_4 has been shown to yield to a [2+2] metallamacrocycle by coordination of the metal center to the nitrile group and a pyrrolic nitrogen atom (Fig. 10d) [59]. Interestingly, this tendency to form this type of macrocycles

exempt of Ag- π interactions has been also reported with a variety of α,β -unsubstituted dipyrins bearing a peripheral binding unit such as a pyridine or an imidazole [62].

Fig. 11. Representation of dipyrin **16H** and heteroleptic metalloligand $[(16)(acacpy_2)Cu]$ and top and side views of the crystal structure of the heterometallic network formed with $AgBF_4$ (a) and $AgTfO$ (b) (CSD refcodes: FEBHAX, FEBHEB). The Ag- π interactions are highlighted in purple dash-line. Anions, solvent molecules and hydrogen atoms have been omitted for clarity.

The pyridyl appended analogue **16H** has been employed by us and others for the preparation of several Cu(II), Co(III), Fe(III), In(III) and Ga(III) metalloligands used for the construction of heterometallic networks with silver salts. While almost all them have led to architectures where no Ag- π interactions can be observed in the crystalline state [63-66], this complexation mode could be detected with heteroleptic complexes $[(\mathbf{16})(\text{acacpy}_2)\text{Cu}]$ and $[(\mathbf{16})_2(\text{acacpy}_2)\text{Co}]$ ($\text{acacpy}_2 = 1,3\text{-bis-(4-pyridyl)-1,3-propanedioate}$) (Figs. 11 and 12) [67].

Metalloligand $[(\mathbf{16})(\text{acacpy}_2)\text{Cu}]$ was associated with AgBF_4 and AgTfO affording 2- and 3-D networks $\{[(\mathbf{16})(\text{acacpy}_2)\text{Cu}]\text{Ag}\}_4(\text{BF}_4)_4(\text{H}_2\text{O})$ and $\{[(\mathbf{16})(\text{acacpy}_2)\text{Cu}]\text{Ag}\}(\text{TfO})$, respectively (Fig. 11). In both compounds, the silver cation is coordinated to three pyridyl groups belonging to three neighbouring Cu complexes, leading to the formation of 2D sheets. While the latter are flat with the tetrafluoroborate anion, they are ruffled in the triflate case. In addition, the Ag(I) centers interact with the β -pyrrolic carbon atoms of dipyrinato moieties belonging to another sheet with Ag-C distances ranging from 2.639(6) to 2.869(6) Å and 2.601(8) to 2.808(7) Å, for the BF_4^- and TfO^- based materials respectively (Fig. 11). This is slightly longer than with the benzonitrile functionalized dipyrin described above.

Fig. 12. Representation of metalloligand $[(\mathbf{16})_2(\text{acacpy}_2)\text{Co}]$ and crystal structure of the two heterometallic networks obtained upon assembly with AgTfO showing the presence (a) or absence (b) of $\text{Ag}-\pi$ interactions (highlighted in purple dash-line) (CSD refcodes: FEBHOL, FEBHUR). Triflate anions, solvate molecules and hydrogen atoms have been omitted for clarity.

The heteroleptic metalloligand $[(\mathbf{16})_2(\text{acacpy}_2)\text{Co}]$ was assembled with AgTfO leading, in the same crystallization batch, to the formation of two different heterometallic architectures formulated $\{[(\mathbf{16})_2(\text{acacpy}_2)\text{Co}]\text{Ag}(\text{MeCN})\}_2(\text{TfO})_2(\text{MeCN})_4(\text{C}_6\text{H}_6)$ and

{[(**16**)₂(acacpy)₂Co]Ag(MeCN)}(TfO)(C₆H₆) (Fig. 12). In the two networks, the silver center is coordinated to an acetonitrile molecule and peripheral pyridyl groups of the metalloligands. Interestingly, while they have been prepared under the same conditions, only the earlier compound features weak Ag- π interaction with one β -pyrrolic carbon atom in a η^1 fashion with an Ag-C distance of 2.767(8) Å (Fig. 12a). This illustrates the fine balance between the different interactions at stake in the construction of these crystalline solids that can lead to the presence or absence of Ag- π contacts in the networks isolated.

3.2.1.2. BODIPY and azaBODIPY

Owing to their unique photophysical properties, BODIPY dyes have been widely investigated over the past decades for diverse applications [68-70]. They have also been employed for the preparation of luminescent metal-organic frameworks [54]. However, to the best of our knowledge, only a single report has so far described the assembly of such compound with silver salts [71]. BODIPY **17** bearing a mesityl group at the *meso* position and benzonitrile moieties at the α positions has been shown to form a series of [2+2] metallamacrocycles with AgX salts ($X^- = \text{AsF}_6^-, \text{BF}_4^-, \text{ClO}_4^-$) (Fig. 13) [71]. In these assemblies, the silver center is coordinated in an almost linear fashion to a nitrile group of each of two BODIPYs. The coordination sphere is completed by anion or solvent molecules depending on the crystallization conditions. Furthermore, in [(**17**)Ag]₂(BF₄)₂(CHCl₃)₂ and [(**17**)AgClO₄]₂(CHCl₃)₂, Ag- π interactions between neighbouring macrocycles are present. In the earlier compound shown in Fig. 13, long Ag-C distances of 2.871(4) and 2.983(4) Å are observed between the metal cation and two β -pyrrolic carbon atoms. This leads to a 3D organization. For the perchlorate-based system, similar interactions can be seen ($d_{\text{Ag-C}} = 2.605(4)$ - $2.916(4)$ Å) with the dipyrinato fragment but also with peripheral benzonitrile carbon atoms ($d_{\text{Ag-C}} = 2.837(5)$ - $3.050(5)$ Å). These distances are rather long compared with the other examples presented so far. However, these compounds represent, with the tetranuclear complex based on **8H**, rare examples to feature Ag- π interactions with a β -functionalized pyrrole derivative. Furthermore, it can be noted that these species are luminescent with emission in the crystalline state between 750 and 800 nm upon excitation at 530 nm.

Fig. 13. Representation of BODIPY **17** and crystal structure of metallamacrocycle [(**17**)Ag]₂(BF₄)₂(CHCl₃)₂ (CSD refcode: XAWRUL). The Ag- π interactions are highlighted in purple dash-line. Anions, solvent molecules and hydrogen atoms have been omitted for clarity.

AzaBODIPYs are analogues of BODIPYs incorporating a nitrogen atom at the *meso* position and featuring absorption and emission at longer wavelengths [68-70]. Our group has recently reported the association of such compounds with silver salts [72]. In particular, azaBODIPY **18** bearing *o*-methoxyphenyl and *p*-benzonitrile groups at the α and β positions respectively has been shown to form a 2D coordination polymer with Ag(BF₄), [(**18**)AgBF₄] (Fig. 14). In this material, the silver cation is coordinated to the nitrile group of two azaBODIPY derivatives and

to a tetrafluoroborate anion, forming 1D chains. Furthermore, weak Ag- π interactions are present between neighbouring chains ($d_{\text{Ag-C}} = 2.709(6)$ - $2.846(6)$ Å) affording an overall 2D organization. It should be noted however that these interactions do not involve pyrrolic carbon atoms but the one of peripheral *o*-methoxyphenyl groups.

Fig. 14. Representation of azaBODIPY **18** and crystal structure of the two-dimensional network $[(\mathbf{18})\text{AgBF}_4]$ with Ag- π interactions in purple dash-line (CSD refcode: BAMLUZ). Anions and hydrogen atoms have been omitted for clarity.

3.2.2. 2,2'-bis-dipyrin based helicates

The ability to anticipate the presence/absence of Ag- π interactions is limited, owing to the weakness of this complexation mode and to the fine balance of interactions at stake in the construction of the solids. Analysis *a posteriori* upon determination of the crystal structure of the assemblies reveals whether or not this mode of binding is operating in the crystal, limiting potential design of these assemblies. Aiming at addressing this issue, our group has attempted to develop pyrrolic metalloligands prone to Ag- π interactions in a consistent fashion [73-74]. Inspired by the studies performed in solution showing that compounds comprising several pyrrolic units facing each other such as double decker porphyrin complexes or helicates where prone to π -bind Ag(I) cation (see section 3.1.), we have been interested in helicates formed by coordination of 2,2'-bis-dpm ligands to Zn(II) [26, 29, 75, 76, 77]. These species feature pyrrolic moieties organized as π -clefts *a priori* likely to bite Ag(I) cations. In this context, complex **19** based on a 2,2'-bis-dpm ligand bearing peripheral benzonitrile groups has been prepared and assembled with AgX salts ($\text{X}^- = \text{TfO}^-$, SbF_6^- , BF_4^-). Discrete, one-, two- and three-dimensional architectures have been obtained and characterized by X-ray diffraction (Fig. 15). In tetranuclear complex $\{(\mathbf{19})[\text{AgTfO}(\text{THF})]_2\}(\text{CHCl}_3)_2$, two Ag(I) cations bind β -pyrrolic carbon atoms of two different strands of the helicate in a bis- η^2 fashion with Ag-C distances ranging from 2.469(3) to 2.58(3) Å (Fig. 15a). These distances are in the same range as what has been observed with metalloligands based on mono-dipyrin **15H** (Fig. 10). In addition, the coordination sphere of the metal centers is completed by a THF molecule and a triflate anion. Upon modification of the crystallization conditions, the coordination environment and hence the dimensionality of the assembly could be altered, while maintaining the Ag- π interactions. AcOEt and CH_2Cl_2 were substituted for THF and CHCl_3 , respectively, as solvents leading to two different networks. In $\{(\mathbf{19})[\text{AgTfO}]_2\}(\text{CH}_2\text{Cl}_2)_3$, two Ag(I) cations, interact with the pyrrolic π -clefts ($d_{\text{Ag-C}} = 2.393(3)$ - $2.692(3)$ Å) and are organized on the same side of the helicate, as in the case of the discrete complex (Fig. 15b). Their coordination sphere is completed by a bridging anion and either a terminal triflate or a peripheral nitrile of a neighbouring helicate leading to an overall 1D arrangement. Under the same conditions,

$\{(\mathbf{19})\text{Ag}_2\}(\text{TfO})_2(\text{CH}_2\text{Cl}_2)$ was also isolated. In this compound, again two Ag(I) ions interact with β -pyrrolic carbon atoms ($d_{\text{Ag-C}} = 2.421(4)\text{--}2.687(4)$ Å) (Fig. 15c). However, they are located on opposite sides of the helicate and are not coordinated to the triflate anion but to the peripheral nitrile groups of neighbouring metalloligands leading to a 2D network. The assembly of **19** with AgX salts with non-coordinating anions such as SbF_6^- and BF_4^- led to 3D networks $\{(\mathbf{19})\text{Ag}_2\}(\text{X})_2$ featuring the same isomer of the tetranuclear Zn_2Ag_2 core formed by Ag- π interaction ($d_{\text{Ag-C}} = 2.465(3)\text{--}2.668(3)$ Å) bridged by nitrile coordination (Fig. 15d).

Fig. 15. Representation of benzonitrile appended binuclear Zn(II) helicate **19** and crystal structures of discrete complex $\{(\mathbf{19})[\text{AgTfO}(\text{THF})]_2\}(\text{CHCl}_3)_2$ (a), 1D network $\{(\mathbf{19})[\text{AgTfO}]_2\}(\text{CH}_2\text{Cl}_2)_3$ (b), 2D network $\{(\mathbf{19})\text{Ag}_2\}(\text{TfO})_2(\text{CH}_2\text{Cl}_2)$ (c) and 3D network $\{(\mathbf{19})\text{Ag}_2\}(\text{X})_2$ ($\text{X}^- = \text{SbF}_6^-$, BF_4^-) (d) (CSD refcodes: GIVMUV, GIVNAC, GIVNEG, GIVNIK). Ag- π interactions are shown in purple dash-line. Hydrogen atoms and non-coordinated solvent molecules and anions have been omitted for clarity.

Helicate **19** thus assembles recurrently via Ag- π interactions with different AgX salts under various solvent conditions. Following these results, our group has investigated the possibility to build networks solely using this complexation mode without relying on the assistance of peripheral coordinating groups [74]. Metalloligand **20** [75] based on a phenyl-appended 2,2'-bis-dpm ligand was reacted with AgTfO to afford two different heterometallic networks $\{(\mathbf{20})[\text{AgTfO}]_2\}_2(\text{Et}_2\text{O})_3$ and $\{(\mathbf{20})[\text{AgTfO}]_3\}$ (Fig. 16). In both compounds, the silver cations organize in dimers bridged by triflate anions and are complexed by the pyrrolic π -clefts of the helicate in a bis- η^2 fashion with Ag-C distances ranging respectively from 2.396(4) to 2.539(4) Å and from 2.405(3) to 2.683(3) Å. While, in the first material, each helicate is complexing two

silver centers yielding a 1D chain (Fig. 16a), the metalloligand is interacting with three different Ag(I) cations to afford a 2D arrangement in the second network (Fig. 16b).

Fig. 16. Representation of binuclear Zn helicate **20** and crystal structure of 1D chain in $\{(\mathbf{20})[\text{AgTfO}]_2\}_2(\text{Et}_2\text{O})_3$ (a) and 2D network in $\{(\mathbf{20})[\text{AgTfO}]_3\}$ (b) (CSD refcodes: OWUZOX, OWUZUD). Ag- π interactions are shown in purple dash-line. Hydrogen atoms, peripheral phenyl groups and solvent molecules have been omitted for clarity.

This example illustrates that the coordination of 2,2'-bis-dpm ligand to Zn(II) cations pre-organizes the tetra-pyrrolic strands to form π -clefs prone to the complexation of Ag(I) cations. It is worth noting that this process also determines the relative organization of the peripheral groups. This was taken advantage of using Zn(II) helicate **21** based on a 2,2'-bis-dpm ligand bearing anthracenyl groups at the *meso* positions (Fig. 17). In this compound, there exist two types of π -clefs: the pyrrolic and the arene ones. Interestingly, upon assembly with AgTfO, 1D network $\{(\mathbf{21})[\text{AgTfO}]_2\}(\text{o-xylene})(\text{Et}_2\text{O})_5$ is formed as a result of the complexation of $[\text{AgTfO}]_2$ dimer by pairs of anthracenyl groups with Ag-C distances ranging from 2.411(4) to 2.567(4) Å. The pyrrolic strands are not involved in the silver cation binding.

Fig. 17. Representation of binuclear Zn helicate **21** and crystal structure of a 1D chain in $\{(\mathbf{21})[\text{AgTfO}]_2\}(\text{o-xylene})(\text{Et}_2\text{O})_5$ (CSD refcode: OXABAS). Ag- π interactions are shown in purple dash-line. Hydrogen atoms and solvent molecules have been omitted for clarity.

Conclusion

Silver-arene interactions were postulated almost a century ago and have been the object of intense research. Ag(I)- π interactions with pyrrolic derivatives represent a more recent field. Yet, investigations in solution and in the crystalline state have demonstrated that this type of compounds is also prone to this mode of complexation of Ag(I) cation, as illustrated in this contribution. Studies by NMR, UV-Visible, Raman spectroscopy and mass-spectrometry have shown that, albeit weak, it is operating in solution with bis-dpm complexes and porphyrin double deckers. This binding mode has been taken advantage of for the modulation of the reactivity of silver-based catalysts. Investigations in the crystalline phase are more abundant and several structures featuring Ag- π interactions have been reported based on various ligands incorporating one, two or more pyrrolic moieties. In a large majority of assemblies, the complexation takes place with the β -pyrrolic C=C bonds, whereas few cases of contact with α -carbon atoms and a single occurrence of binding to a CN bond have been described. Owing to the weakness of this complexation mode and to the fine balance of interactions at stake in the construction of the solids, different assemblies can be isolated under the same crystallization conditions. This makes our ability to possibly control or promote these interactions in a designed fashion difficult. However, recently it has been shown that assemblies based on 2,2'-bis-dpm Zn(II) binuclear helicates and silver salts feature consistently this mode of complexation. While these results appear promising, further investigations on these interactions will be of interest to be able to fully exploit them in catalysis, surface deposition [78] or for the construction of metal-organic frameworks with specific adsorption properties [79] for example thus opening the way to potential applications.

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