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Gleaned snapshots on the road to coordination polymers: heterometallic architectures based on Cu(I) metallaclips and 2,2'-bis-dipyrrin metalloligands

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Assembly of binuclear Cu(I) metallaclips with 2,2'-bis-dipyrrin based metalloligands gives rise to a diversity of architectures featuring a recurring π -stacked compact tetranuclear metallacycle but differing in their nuclearity and dimensionality depending on the nature of the capping ligands and metal cations.

The rational coordination-driven supramolecular (CDS) synthesis of advanced molecular architectures attracts currently an extensive attention to allow a ready access to metallo-organic assemblies embedding increased structural complexity and new functionalities.¹ Systems based on Pt(II) and Pd(II) metal centers constitute a predominant class of CDS self-assembled structures.² Indeed, the square-planar coordination to these d^8 ions presents high structural rigidity and adequate lability toward a large range of connecting ligands, which are key factors insuring the selectivity in such synthetic procedures. However, over the past few years, alternative and innovative synthetic approaches related to CDS chemistry have been developed, allowing the introduction of a great variety of metal ions in CDS architectures.³ Thus, it was recently highlighted that the pre-assembled $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ Cu(I) fragment (dppm : bis(diphenyl-phosphino)methane) allows versatile adaptive CDS syntheses,⁴ in which the *a priori* disadvantageous highly labile and fluxional coordination spheres of the d^{10} Cu(I) ions can be exploited to afford alternative access to unprecedented supramolecular architectures. In an early study, it was shown that the $[\text{Cu}_2(\mu_2\text{-dppm})_2]^{2+}$ moiety reacts with the linear cyano-capped π -conjugated ditopic linkers **B**₁₋₄ affording one-dimensional coordination polymers (1D-CPs) **C**₁₋₄ in which compact π -stacked metallocyclophanes are connected by ditopic organic linkers (Scheme 1).⁵ In these assemblies, the Cu(I) dimer unit presents an original 'F-shape' geometry with the two metal

Scheme 1: Synthesis of the derivatives **C**₁₋₄,⁵ **D**, **E** and **F**.

ions in either a distorted trigonal planar or tetrahedral coordination sphere. Aiming to explore further the high conformational flexibility exhibited by Cu(I) bimetallic units, it was envisioned to substitute metalloligand linkers for the cyano-capped organic ditopic π -conjugated linkers **B**₁₋₄ and to replace the dppm ligand by the alternative bis(diphenylphosphino)amine dppa (Scheme 1). Recently, metallo-ligands based on pyrrolic dipyrin and 2,2'-bis-dipyrrin derivatives have been reported to form heterometallic architectures such as metallacycles and CPs upon assembly with Ag(I) salts by coordination and Ag- π interactions.⁶ In particular, mononuclear and binuclear helical complexes bearing peripheral nitrile units have been successfully employed for such purposes.⁷ In this context, the 2,2'-bis-dipyrrin Ni(II) and Pd(II) complexes, **Bdp**_{Ni} and **Bdp**_{Pd}, (scheme 1) appeared as appealing nitrile-appended metalloligands for assembly with binuclear Cu(I) fragments as they feature an extension of the π -walls, non-planarity and different degree of helicity that may affect the self-assembly processes. We describe herein the preparation of three new polymetallic assemblies **D-F** (scheme 1) differing in the Cu(I)-dimer bimetallic fragments geometries and the arrangement of the supramolecular and extended intermolecular interaction network.

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Fig. 1. Views of the molecular X-ray structures of derivatives a) **D**, b) **E**, c) **F**; d) "side" views of metallacycle sub-units (anions and solvent molecules have been omitted for clarity).

The **Bdp_{Pd}** metalloligand was prepared by reaction of the free 2,2'-bisdipyrroin ligand with Pd(OAc)₂ and was characterized by ¹H and ¹³C NMR, mass-spectrometry and IR spectroscopy as well as single-crystal X-ray diffraction.⁸ In the crystalline state, while **Bdp_{Pd}** presents a similar organization of the peripheral benzonitrile units with respect to the dipyrroin chelates (torsion angles α , Fig. S6, Table 1) as the previously reported **Bdp_{Ni}** ligand,^{7d} the torsion angle β (Fig. S6) between the two bis-pyrrolic chelates is larger for the Ni complex (Table 1). This is due to shorter M-N distances in **Bdp_{Ni}** leading to a greater strain and repulsion between the hydrogen atoms in the α positions of the end pyrrolic rings and hence a greater helicity (Fig. S4).⁸ The reactions of one equivalent of the in-situ formed [Cu₂(μ_2 -dppm)₂]²⁺ unit with one equivalent of **Bdp_{Pd}** or **Bdp_{Ni}** (Scheme 1) conducted in CH₂Cl₂ at room temperature (RT) under air led to deep dark limpid solutions.^{8,9} Their RT ³¹P{¹H} NMR spectrum shows a broad signal centred at ca. -8.8 ppm for both solutions, suggesting a mixture of species in equilibrium in solution. Yet, upon pentane vapours diffusion into this crude solution, homogeneous batches of air stable deep dark block-shaped crystals of derivatives **D** or **E** (Scheme 1) were isolated in good yields⁸ revealing the selection upon crystallisation of single species among those in dynamic equilibria in solution. Their infrared spectrum shows bands assigned to the dppm ligands and to nitrile groups coordinated on the Cu(I) metal centres ($\nu(\text{C}\equiv\text{N}) = 2232$ and 2229 cm^{-1} for **D** and **E** respectively) together with the absence of coordinated acetonitrile ligands. X-ray diffraction studies⁸ performed at low temperature on single crystals of derivatives **D** or **E** revealed that they both crystallize in the triclinic *P*-1 space group with markedly different unit cells parameters. **D** is a π -stacked compact tetrametallic Cu₄(**Bdp_{Pd}**)₂ metallacycle (Fig. 1a,d) resulting from the connection of two [Cu₂(μ_2 -dppm)₂]²⁺ units by two ditopic connectors **Bdp_{Pd}**. In **D**, the four Cu^I centres lie in the same plane and in the [Cu₂(μ_2 -dppm)₂]²⁺ units, the two metal centers present distorted trigonal planar P₂N₁ coordination sphere resulting from the coordination of one of the phosphorus atoms of the two 1*k*P:2*k*P dppm ligands and of one nitrile group of the ligand **Bdp_{Pd}**. Short intermetallic distances ($d(\text{Cu}-\text{Cu}) = 2.7717(10)\text{ \AA}$) are observed, typical of cuprophilic interactions. Altogether, the other metric parameters of the [Cu₂(μ_2 -dppm)₂]²⁺ units are similar to those

Table 1. Intermetallic distances ($\text{\AA}$) and torsion angles ($^\circ$) in derivatives **Bdp_{Ni}**,^{7d} **Bdp_{Pd}**, **D**, **E** and **F** (see Fig. S6 for a visualisation of the angles α and β).

	Cu...Cu	M(II)...M(II)	$\alpha^{[d]}$	$\beta^{[d]}$
Bdp_{Ni}	-	-	55.6, 58.2	20.5
Bdp_{Pd}	-	-	54.9, 60.2	13.2
D	2.7717(10)	6.66 ^[b]	60.7, 67.6	12.1
E ^[a]	3.262(3)	5.57 ^[b]	51.2, 71.9	18.6
	3.168(3)	5.34 ^[b]	49.6, 74.5	20.5
		4.93 ^[c]	51.5, 55.2	17.4
F			48.1, 54.5	18.3
	3.417(4)	6.05 ^[b]	53.4, 64.9	19.0
		4.70 ^[c]	48.7, 62.7	21.2

[a] two symmetrically independent molecules in the unit cell; [b] intramolecular distances; [c] intermolecular distances; [d] values in italic measured for the **Bdp_{Ni}** ligands that are not involved in the π -stacked metallacycle sub-units.

observed usually for such a fragment.^{4,5} The Cu-cyano bond lengths are typical ($1.965(5)$ and $1.981(5)\text{ \AA}$) and the Cu...(N=C-) angles vary from $170.3(5)$ to $178.7(5)^\circ$, revealing little steric stress within the metallacycles at the level of the bimetallic Cu(I) fragments. Conversely, compared to the X-ray structure of the free ligand **Bdp_{Pd}**, the phenyl rings of the ditopic linkers in **D** present a *cis*-orientation toward the mean plane of the bis-dipyrroin moiety (Fig. 1d) with α angles being slightly increased (Table 1). The two parallel-displaced bis-dipyrroin units are more planar (smaller β angles, table 1) within the assembly **D** than in the free **Bdp_{Pd}**. These variations can very likely be assigned to the maximisation of the strong stabilizing interlinker π - π intramolecular (shortest interlinker intramolecular distances, ca. $3.0\text{ \AA}$) observed between the two parallel displaced bis-dipyrroin units, leading to a intramolecular distance between the two Pd(II) cations of $6.66\text{ \AA}$. Whereas the structure of **D** is based on a 1:1 ratio between the [Cu₂(μ_2 -dppm)₂]²⁺ units and the metalloligand, the molecular structure of **E** exhibits a 1:2 ratio, as it features a π -stacked compact metallacycle sub-unit with, surprisingly, two additional pendant **Bdp_{Ni}** ligands coordinated (Fig. 1b,d).¹⁰ Similarly to the organization observed in **D**, the compact metallacycle in **E** is based on two [Cu₂(μ_2 -dppm)₂]²⁺ units associated by two homoditopic connectors **Bdp_{Ni}**. One of the Cu(I) ions of each [Cu₂(μ_2 -dppm)₂]²⁺ fragment presents a distorted trigonal planar P₂N₁ coordination sphere as in **D** but the second Cu(I)

ion is also coordinated to another **Bdp_{Ni}** ligand and has a distorted tetragonal P_2N_2 coordination sphere. Consequently, the $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ unit in **E** presents a 'F-shape' geometry, as observed in the structure of the 1D-CPs **C₁₋₄** (Scheme 1).⁵ Nevertheless, here, no CP is formed since the second nitrile group of the pendant **Bdp_{Ni}** ligand remains uncoordinated, affording an unexpected discrete $Cu_4(Bdp_{Ni})_4$ assembly. In the compact metallacycle sub-unit of **E**, the intermetallic distances ($d(Cu-Cu)$, 3.168(3) and 3.262(3) Å)¹⁰ are larger than observed in **D**, but similar to those observed in the 1D-CPs **C₁₋₄**.⁵ Regarding **Bdp_{Ni}** ligands, those embedded in the metallacyclic units of **E** present significantly different α angles (Table 1), while those of terminal **Bdp_{Ni}** ligands are similar to the α angles of the free metalloligand.⁸ All bis-dipyrrin fragments in the whole assembly present β angles (Table 1) analogous to the free **Bdp_{Ni}** complex. Finally, the bis-dipyrrin fragments within the compact metallacycle sub-unit present parallel-displaced organisation associated with strong π - π interactions (shortest interlinker intramolecular distances, ca. 3.0 Å), and a distance between the Ni(II) centers of 5.337-5.563 Å shorter than what is observed in the Pd based compound **D** (Table 1). Thus, reactions of the two sterically demanding ditopic metalloligands **Bdp_{Pd}** and **Bdp_{Ni}** with the flexible $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ units afford two different discrete supramolecular scaffolds **D** and **E** that also vary from the 1D-CPs **C₁₋₄** obtained with the **B₁₋₄** organic linkers (Scheme 1). While the architecture exhibited by **E** has never been characterized so far, the isolated compact π -stacked metallacycle **D** resembles a series of analogous compact supramolecular tetrametallic Cu(I) assemblies obtained from reacting 'U-shape' rigid Cu(I) dimers stabilized by the bridging phosphane N,P,N bis(2-pyridyl)phosphole ligand with a variety of cyano-capped π -conjugated ditopic ligands.¹¹ The variability of the CDS structures obtained using the $[Cu_2(\mu_2\text{-dppm})_2]^{2+}$ fragment confirms the interest of using precursors offering conformational flexibility to access original and various supramolecular organizations. The increased steric demand associated with the presence of the helical bis-dipyrrin group in the metalloligands **Bdp_{Pd}** and **Bdp_{Ni}** compared to the linear π -conjugated ligands **B₁₋₄** very likely induces constraints interfering with the formation of extended network of type **C₁₋₄** (Scheme 1).¹² Interestingly, derivatives **D** and **E** can formally be considered as oligomeric intermediates backbones representing "frozen" self-association steps along the formation of the 1D-CPs **C₁₋₄**. Therefore, one can envision that applying a molecular design on the inner cores of the ditopic

linkers can be a tool to control the extend of supramolecular self-assembly processes governing the association of flexible Cu(I) polymetallic building blocks.

Considering the discrepancy observed in the structures of **D** and **E** in spite of a priori minor differences in the ditopic linker used, this study was extended in a second step to probing the impact of a slight variation in the structure of the diphosphane assembling ligand. The dppa ligand was selected, in which the central $-\text{CH}_2-$ methylene moiety lying between the phosphorus centers of the dppm ligand is formally replaced by a $-\text{NH}-$ secondary amino group. The same reaction conditions as applied for the formation of **D** and **E** were employed, replacing the dppm ligand by the dppa ligand. While the experiment involving the ligand **Bdp_{Pd}** afforded unidentified dark oily residue, dark crystals of the new derivative **F** were grown selectively from the reaction conducted with the **Bdp_{Ni}** ligand. X-ray diffraction studies⁵ revealed that **F** crystallizes in the triclinic *P*-1 space group and presents an original ladder-type 1D-CP framework comprising compact metallacyclic sub-units (Fig. 1c,d). The derivative **F** is based on a repetition unit bearing a 1:2 ratio between of $[Cu_2(\mu^2\text{-dppa})_2]$ units and the **Bdp_{Ni}** ligands. Both Cu(I) centers of the $[Cu_2(\mu^2\text{-dppa})_2]$ moieties of **F** present a distorted tetragonal P_2N_2 coordination sphere due to the coordination of two P-atoms of the two 1 κ P:2 κ P dppa ligands and of the nitrile group of two ditopic **Bdp_{Ni}** ligands. The intermetallic distance ($d(Cu-Cu)$ = 3.417(4) Å) in **F** is notably increased compared to the values observed in **D** and **E**. The other metric data of the $[Cu_2(\mu^2\text{-dppa})_2]$ units in **F** are otherwise very similar to those observed in the $[Cu_2(\mu_2\text{-dppm})_2]$ fragments of **D** and **E**. In the backbone of the 1D-CP **F**, the bimetallic units present an original 'II – shape' geometry bearing two parallel-displaced "inner" linkers involved in π - π interactions (shortest interlinker intramolecular distances, ca. 2.9 Å) within compact π -stacked metallacycle sub-units and two "outer" linkers connecting these $Cu_4(Bdp_{Ni})_2$ fragments (Fig. 1c). As a result, the original scaffold of a 1D-ladder including π -stacked metallacycle is formed (Fig. 1c,d). The two symmetrically independent **Bdp_{Ni}** ligands in **F** present very similar metric data (including angles α and β , see Table 1) that range among the values observed in **E**, albeit with a slightly longer Ni-Ni distance (Table 1) in **F** within the π -stacked metallacycle backbone. The characterization of this new supramolecular assembly bearing an alternative geometry compared to those of **C₁₋₄**, **D** and **E** confirms the large impact of the conformational flexibility of Cu(I) dimers stabilized by 1 κ P:2 κ P diphosphane P-X-P ligands (X = CH_2 , NH), giving access

Fig. 2. Solid-state organisation of the derivatives (a) **E** and (b) **F** (the dotted lines represent directions of propagations of the different ladder-backbones represented).

to a large variety of supramolecular assemblies' organisations. One can stress that the discrete assembly **E** (based on 'F-shape' $[\text{Cu}_2(\mu^2\text{-dppm})_2]$ units) and the ladder-type 1D-CP framework of **F** (based on 'II-shape' $[\text{Cu}_2(\mu^2\text{-dppa})_2]$ nodes) can be formally related. Indeed, the **F**-type scaffold could be obtained via a further step in the self-assembling processes in which the coordination of the free nitrile function of the pendant **Bdp_{Ni}** ligands of **E** would occur on the distorted trigonal planar Cu(I) metals centers of its $[\text{Cu}_2(\mu^2\text{-dppm})_2]$ units.

A typical feature observed with the discrete π -stacked compact tetrametallic metallacycles obtained from the 'U-shape' rigid Cu(I) dimers stabilized by the N,P,N bis(2-pyridyl)phosphole ligand lies in their ability to self-aggregate in the solid state via intermolecular π - π interactions, affording π -stacks of various dimensionalities.¹¹ Beside the structuring role these interactions can play in the bulk, they also give an access to molecular solids in which increased charge-carrier mobility can be reached.¹³ Yet, the discrete π -stacked compact tetrametallic metallacycle **D** do not present any π - π intermolecular interactions in the solid state. This shows that the alteration of the backbones of the π -conjugates can also impact the bulk supramolecular organisation of these compact metallacycles. Conversely, derivatives **E** and **F** present very specific solid state intermolecular extended networks. On one hand, in the solid-state packing of **E**, intermolecular π - π interactions (interlinker intermolecular distances, ca. 3.0 Å) are observed between the π -walls of bis-dipyrrin moieties of neighbouring pendant **Bdp_{Ni}** ligands. It induces the formation of a non-covalent 1D network (Fig.2a) that resembles the 1D-CP organisation of derivatives **C₁₋₄** (Scheme 1). On the other hand, considering **F**, intermolecular π - π interactions (interlinker intermolecular distances, ca. 3.0 Å) between the π -walls of the π -stacked compact metallacycle of one ladder 1D-CP and the bis-dipyrrin moieties of the connecting ditopic **Bdp_{Ni}** linkers of the neighbours CPs are observed. It results in discrete stacks of four bis-dipyrrin moieties (Fig.2b). Importantly, the intermolecular Ni(II)-Ni(II) distances in **E** and **F** (Table 1) are significantly shorter in these π -stacks than those intramolecular, observed within the π -stacked metallacyclic sub-units. This suggests that such π - π intermolecular interactions may play an important role in the selection and the stabilization of the new species **E** and **F**, and complement the versatility already offered by the configurationally highly flexible Cu(I) bimetallic units.

This set of results shows that, by applying small variations on the structure of the building blocks employed in adaptive CDS processes based on Cu(I) bimetallic precursors, it is possible to operate a rich harvest among the various CDS structures that can be isolated via crystallisation selection among the species lying in solution equilibria. This very versatile and rich synthetic approach using polymetallic Cu(I) flexible precursors may be very attractive regarding the current attention paid to the preparation and the study of advanced multifunctional solid-state luminescent Cu^I complexes.¹⁴ It also highlights that dipyrrin based metalloligands can be assembled with metallic

systems other than Ag(I) ones,⁷ thus opening the door to a whole diversity of supramolecular assemblies.

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Conflicts of interest

There are no conflicts to declare.

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