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Folding of a Supramolecular Framework Based on a Tetrametallic Clip Driven by $\pi-\pi$ Interactions

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Supporting Information

ABSTRACT: Supramolecular extended frameworks based on a rotational molecular clip and having the same "primary structure" can exhibit either an unfolded or a folded framework. This process is driven by intramolecular $\pi-\pi$ interactions, resulting in the formation of an infinite π-stacked column within the folded supramolecular framework.

An important area in inorganic chemistry in the past decade has been the design and structural studies of one-dimensional (1D) coordination polymers (CP) composed of metal ion connectors and linear organic π-conjugated linkers because of their high potential as multifunctional materials.[1] The properties of these 1D CPs are related to their framework topology, which is controlled (i) by the number and orientation of the connector binding sites and (ii) by the supramolecular organization of the 1D chains involving noncovalent interactions (hydrogen-bonding, $\pi-\pi$-stacking, and metallophilic interactions).

In this paper, we describe the use of intramolecular $\pi-\pi$ interactions[2] to control the topology of 1D CP frameworks,[3] offering a new strategy for organization of an isolated π-conjugated molecule into an infinite π-stacked suprastructure.[4] Our approach involves the design of a molecular tetrametallic Cu^I clip[5] that can act as a "swivel pin", affording CPs based on π-stacked metallocyclophane motifs. The CP supramolecular framework exists either as an *unfolded* or as a *folded* structure upon the establishment of cooperative $\pi-\pi$ interactions[2] along the polymer backbone.

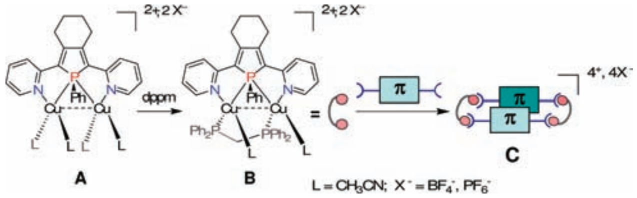

Figure 1. Synthesis and use as a molecular clip of $(Cu^I)_2$ dimer **B**.

1-Phenyl-2,5-bis(2-pyridyl)phosphole has recently emerged as a powerful N,P,N-pincer building block for stabilization of bimetallic complexes,[6] such as the Cu^I dimers **A** and **B** (Figure 1).[6b,c] In these dimers, the P atom adopts a very rare μ-P coordination mode,[7] resulting in short metal—metal distances (~2.6 Å) and a close alignment of the labile *cis*-acetonitrile ligands. These unique structural features make Cu^I dimer **B** a versatile U-shaped molecular clip for the coordination-driven assembly of a wide range of cyano-capped π connectors into π-stacked metallocyclophanes **C** (Figure 1).[8] In order to obtain a supramolecular polymeric scaffold based on metallocyclophane motifs **C**, we designed ligand **1** in which two bis(2-pyridyl)phospholyl (NPN) moieties are linked by a *p*-phenylene fragment (Scheme 1). It is important to note that the P atom of 1-phenylphospholes has considerable pyramidal character.[9] It was thus expected that the *p*-phenylene moiety of **1** will be almost perpendicular to the two coordinating NPN moieties, with free rotation permitted about the P—Ph—P "pin". Derivative **1** was obtained as a yellow solid in 51% yield by the subsequent treatment of 1,8-bis(pyridin-2-yl)octa-1,7-diyne with "zirconocene" and 1,4-bis(dichlorophosphino)benzene.[10] The reaction of **1** with 4 equiv of $[Cu(CH_3CN)_4X]$ ($X^- = BF_4^-$ or PF_6^-) afforded complex **2** as an air-stable derivative (89% yield) that was characterized by both NMR spectroscopy and X-ray diffraction. Its ^{31}P and ^1H NMR data compare well with those of complex **A** (Figure 1), and its solid-state structure confirmed that **2** possesses two $[Cu_2(\mu\text{-NPN})(CH_3CN)_4]$ cores linked by a *p*-phenylene moiety (Scheme 1). As expected, the μ-P atoms of the phosphole rings display a pseudopyramidal geometry with acute C(endocyclic)—P—C(*ipso*-Ph) angles [102.41(17)° and 105.65(18)°] with a distance between the two μ-P centers of about 6.5 Å. The metric parameters of the $[Cu_2(\mu\text{-NPN})]$ fragments of tetrametallic species **2**, including metal—metal and metal—μ-P distances, are similar to those of the dimetallic clip **A** (see Table S3 in the Supporting Information). Therefore, the two $[Cu_2(\mu\text{-NPN})]$ cores of tetrametallic species **2** keep the structural features that make Cu^I dimer **A** a versatile precursor of U-shaped molecular clip **B** for the coordination-driven synthesis of supramolecular π-stacked rectangles **C** (Figure 1).

According to the *Directional Bonding Approach* depicted in Figure 1, "bis-clip" **2** was reacted with 1,1-bis(diphenylphosphanyl)methane (dppm), acting as a blocking ligand, and fumaronitrile **3** (1:2:2 molar ratio in CH_2Cl_2; Scheme 1). Following pentane vapor diffusion at room temperature into this CH_2Cl_2 solution, a homogeneous batch of yellow single crystals of derivative **4** was obtained (53% isolated yield). An X-ray diffraction study revealed that derivative **4** is a CP based on metallocyclophane motifs formed upon the assembly of two ditopic linkers **3** on U-shaped $[Cu_2(NPN)(dppm)]$ subunits (Figure 2a). The $[Cu_2(\mu\text{-NPN})]$ moieties of the "bis-clip" have an anti conformation with respect to the *p*-phenylene pivot (Figure 2a, green fragment; distance between the two μ-P centers, 6.4 Å), resulting in a 1D zigzag supramolecular framework **D** (Figure 2b). In the metallocyclophane subunits, the Cu atoms lie in the same plane defining a rectangle (intermetallic distances: 2.64 and 9.94 Å), and the two ethylene moieties of linker **3** have an almost face-to-face arrangement with a separation of 3.2 Å,

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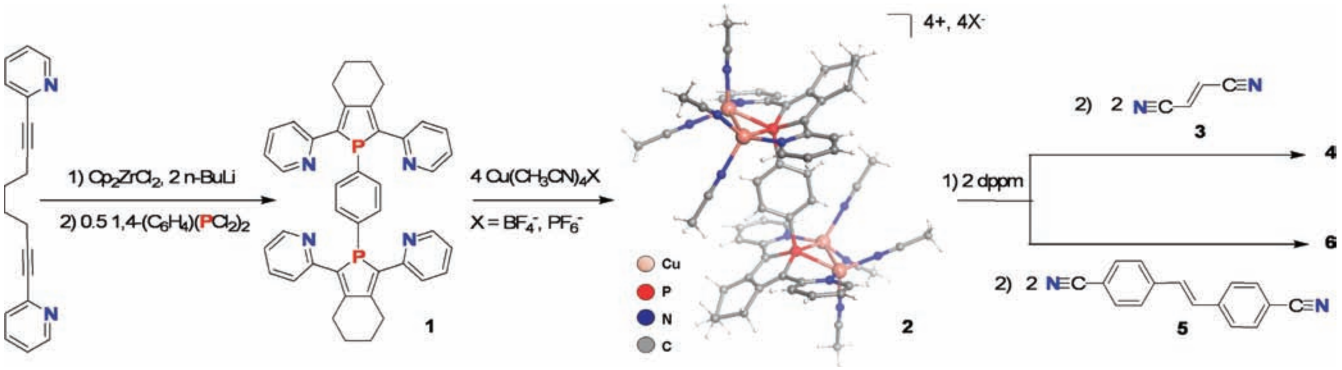
Scheme 1. Synthesis of Ligand 1, of the Corresponding $(Cu^I)_4$ Complex 2 (View of the X-ray Crystallographic Structure), and of the CPs 4 and 6



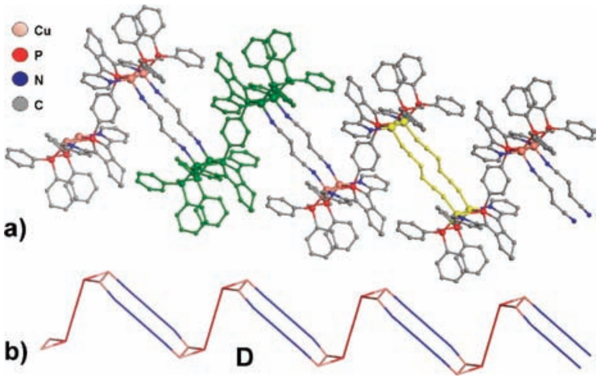


Figure 2. (a) X-ray crystal structure of CP **4** (H atoms, counteranions, and solvents have been omitted for clarity; a metallocyclophane fragment is highlighted in yellow and one "bis clip" in green). (b) **D**: representation of the underlying network connectivity of framework **4**..

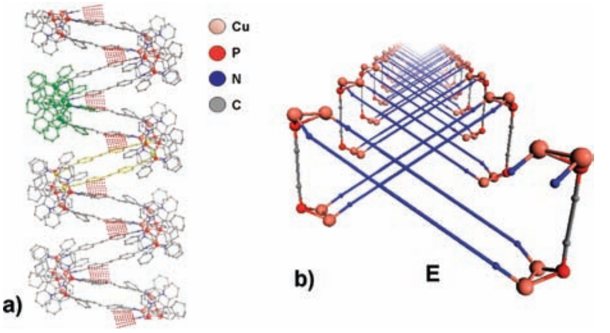


Figure 3. (a) X-ray crystal structure of CP **6** (H atoms, counteranions, and solvents have been omitted for clarity; a metallocyclophane fragment is highlighted in yellow and one "bis-clip" in green; local $\pi-\pi$ interactions between neighboring metallacyclophanes are shown with red dots). (b) **E**: representation of the underlying network connectivity of framework **6**.

revealing $\pi-\pi$ interactions (Figure 2a, yellow fragment). The BF_4^- counteranions and molecules of cocrystallized solvent are located outside the self-assembled structure. Indeed, the self-sorting processes leading to discrete π-stacked metallacyclophanes **C** previously observed with the bimetallic clip **A** also takes place with the tetrametallic clip 2.

The comparison of the solid-state structures of "bis-clip" **2** (Scheme 1) and CP **4** (Figure 2a) clearly shows that this coordination-driven process involving the linear linker **3** follows the rules of the *Directional Bonding Approach*[5] because the topology of the CP framework **D** (Figure 2b) is imposed by the shape of the $(Cu^I)_4$ molecular clip (compound **2**, Scheme 1).

One appealing property of discrete metallacyclophanes **C** (Figure 1) is their ability to self-organize into infinite π-stacked columns via intermolecular $\pi-\pi$ interactions, provided that the homoditopic conjugated linker *trans*-1,2-bis-(4-cyanophenyl)-ethylene (**5**; Scheme 1), or longer homologues, is used.[8] It was thus interesting to investigate whether the use of linker **5** could implement weak secondary $\pi-\pi$ interactions between the metallacyclophane units of framework **D** (Figure 2b), resulting in conformation changes along the CP strand.

According to the procedure used to prepare supramolecular assembly **4**, the "bis-clip" **2** was treated at room temperature in CH_2Cl_2 with 2 equiv of dppm and 2 equiv of the ditopic linker **5** (Scheme 1). Pentane vapor diffusion into this CH_2Cl_2 solution afforded very tiny yellow single crystals of derivative **6** (54% yield). An X-ray diffraction study revealed that the scaffold of **6** is a CP consisting of metallocyclophane motifs (intermetallic distances: 2.70 and 18.29 Å and 2.68 and 18.43 Å)[11] linked by P–Ph–P moieties (Figure 3; distance between the two μ-P centers, 6.4 Å). The four Cu^I atoms of the metallocyclophane motifs lie again in the same plane, and the BF_4^- counteranions and cocrystallized solvent molecules are located outside the self-assembled structure. The π walls of the metallocyclophane motifs participate in endocyclic $\pi-\pi$ interactions (distances, 3.4 Å) with an almost face-to-face arrangement (lateral offset, 1.5 Å). These structural data are similar to those encountered in the discrete metallocyclophane **C** based on linker **5** (Figure 1; $\pi-\pi$ distances, 3.4 Å; lateral offset, 1.1 Å).[8] Remarkably, in assembly **6**, the $[Cu_2(\mu\text{-NPN})]$ moieties of the "bis-clip" have a syn arrangement (Cu1–P–P–Cu2, 58–60°; Figure 4a), a conformation that is found neither in the tetrametallic precursor **2** nor in the CP **4** (anti arrangement of the $[Cu_2(\mu\text{-NPN})]$ moieties; Cu1–P–P–Cu2, 180°; Scheme 1 and Figure 4b). During the self-sorting process leading to derivative **6** (Scheme 1), a rotation about the P–Ph–P pivot of the "bis-clip" **2** occurred. This syn arrangement, along with the fact that two consecutive "bis-clips" present a "clockwise" and an "anticlockwise" rotation with respect to the P–Ph–P pins, affords supramolecular assembly **6** with a zigzag folded structure (Figure 3b). Therefore, supramolecular assemblies **4** and **6**, which display the same 1D

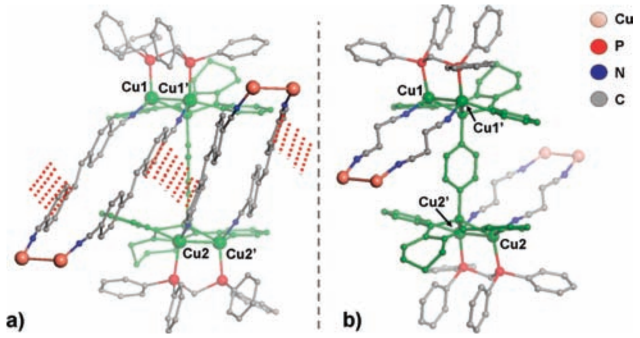


Figure 4. Focus on "bis-clip" fragments (in green) of (a) folded CP **6** (local $\pi-\pi$ interactions between neighboring metallacyclophanes are shown with red dots) and (b) nonfolded CP **4**.

"primary structure", exhibit completely different "secondary structures": derivative **4** possesses a linear framework **D** (Figure 2b), while that of assembly **6** is folded (**E**, Figure 3b).

Although steric factors cannot be totally excluded, it is very likely that the increased polarizable π surface of the metallocyclophane π system (**3** → **5**, Scheme 1) drives this behavior. Indeed, because of the "clockwise"–"anticlockwise" rotation occurring all along its framework, the π walls of two neighboring metallocyclophane motifs of CP **6** are engaged in $\pi-\pi$ interactions ($\pi-\pi$ distances *between* the metallocyclophanes, 3.4 Å; Figure 4a).

This structure results in the formation of an infinite π-stacked column within the core **E** of CP **6** (Figure 3b). Therefore, the driving force for the rotation around the swiveling P–Ph–P pivot is very probably the establishment of these cooperative $\pi-\pi$ interactions within the folded π-stacked supramolecular framework **E**. This result highlights that the sum of the cooperative weak $\pi-\pi$ interactions is sufficient to drive the self-sorting processes in which rotational molecular clips are involved, affording folded supramolecular frameworks.

In conclusion, the design of the tetrametallic molecular clip **2** based on bis-N,P,N ligand **1** bearing a molecular "swivel pin" allowed the straightforward synthesis of a folded supramolecular framework following two hierarchical programmed self-assembly processes based, respectively, on the *Directional Bonding Approach*, to construct the primary structure, and nondirectional weak $\pi-\pi$ interactions, to stabilize the folded secondary structure. The scope of this straightforward approach toward π-stacked assemblies, which mimics the complex hierarchical self-assembly found in nature, is under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data including crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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