

Mimicking [2,2]Paracyclophane Topology: Molecular Clips for the Coordination-Driven Cofacial Assembly of π -Conjugated Systems

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The synthesis of π -stacked molecular assemblies is of great importance in understanding the electronic interactions between individual chromophores since π - π interactions play an essential role in biology and in the functions of organic semiconducting materials.¹ One fruitful approach to probe cofacial π - π interactions involves the assembly of chromophore pairs into well-defined [2,2]-paracyclophanes.^{1b,2} These molecules provide incisive insight into bulk properties of conjugated systems and are suitable π -dimer models.² However, straightforward routes to these complex assemblies as well as for tailoring their structure remain a challenge to chemical synthesis. In this paper, we describe a versatile approach using Cu^I dimetallic “clips” that allows a variety of chromophores to be precisely π -stacked into nanosize assemblies using supramolecular coordination-driven chemistry.³

Transition metal complexes are powerful templates for organizing organic chromophores with coordinating termini into well-defined supramolecular assemblies.^{3,4} Following the concepts of the “directional-bonding approach”,³ the construction of metalloparacyclophanes with π -stacked walls requires a bimetallic clip possessing two *cis* coordinatively labile sites that are closely aligned.⁵ This programmed topology is found in the Cu^I dimer **1a**⁶ and its newly prepared analogue **1b** (Figure 1). These compounds possess two Cu^I atoms capped by a 2,5-bis(2-pyridyl)phosphole with a symmetrically bridging trivalent P center, a very rare coordination mode for phosphine ligands.⁷ The coordination sphere of the metal centers is completed by two acetonitrile ligands and by either a P,N (**1a**) or a P,P (**1b**) chelate, two donors with different steric demands (Figure 1). These easily prepared compounds are air-stable and soluble in common organic solvents (CH₂Cl₂, THF, etc.). X-ray diffraction studies revealed that, due to the tetrahedral geometry of the Cu^I atoms, the two acetonitrile ligands have a *cisoid* arrangement (Figure 1). Furthermore, the bridging coordination mode of the phosphole P center imposes a short intermetallic distance [**1a**, 2.555(1) Å; **1b**, 2.667(1) Å] resulting in a close proximity of the two kinetically labile acetonitrile ligands (N \cdots N distances, ca. 3.2 Å).⁸

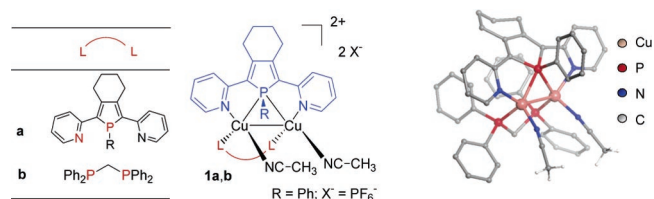
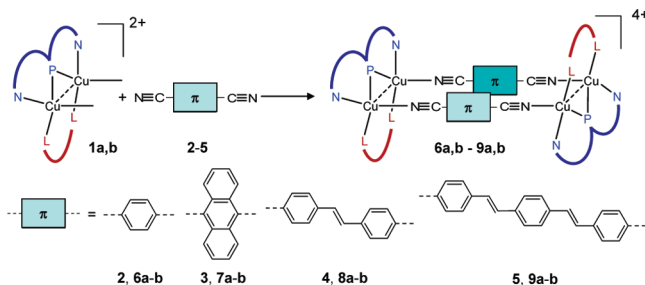


Figure 1. Structure of molecular clips **1a,b**. X-ray crystal structure of **1b** (H atoms of the P ligands have been omitted for clarity).

In a first approach, commonly used cyano-substituted chromophores,³ namely, 1,4-dicyanobenzene **2** and 9,10-dicyanoanthracene **3** (Scheme 1), were selected. They reacted with 1 equiv of the Cu^I dimers **1a,b** in CH₂Cl₂ solution at 40 °C giving rise to the assemblies **6a,b** and **7a,b**, respectively (Scheme 1). These

Scheme 1



compounds were obtained in good yields (ca. 60–70%) as air-stable orange powders soluble in polar solvents (acetone, THF, etc.). Elemental analyses are consistent with the proposed structures, and the upfield ¹H NMR coordination shift of the anthracene moieties of **7b** ($\Delta\delta$, 1.8 ppm), indicating π - π interaction of the ditopic ligands, is consistent with the formation of rectangles. The definitive proof for the structure of derivatives **6a,b** and **7a,b** was given by single-crystal X-ray diffraction studies (Figure 2). All counterions

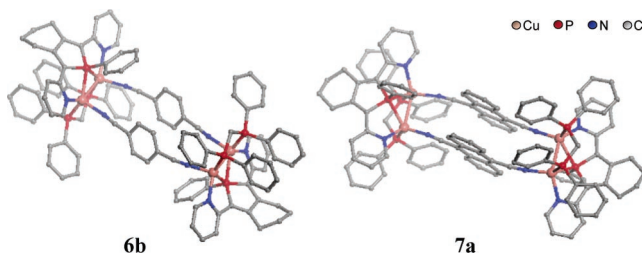


Figure 2. X-ray crystal structures of **6b** and **7a** (H atoms, counterions, and solvents have been omitted for clarity).

and cocrystallization solvent molecules are located outside the self-assembled molecules. The four Cu atoms lie in the same plane defining a rectangle with lengths on the nanoscale (ca. 11.8 Å). The metric data of the dimetallic clips **1a,b** do not change significantly upon their incorporation into the self-assembled structures, demonstrating the conformational rigidity of the Cu^I-based subunits. For example, the values of the directing N–Cu–Cu–N angles range from 28.0 to 36.1° for **6a** and **7a** (**1a**, 34.1°) and from 7.3 to 10.5° for **6b** and **7b** (**1b**, 5.7°). The aromatic moieties of the chromophores are parallel as a result of hindered rotation (Figure 2), and due to the short Cu–Cu distances in the dimer clips (2.562–2.745 Å), they participate in face-to-face π -interactions (phenyl centroid–centroid distances: 3.4–3.5 Å). Notably the lateral offsets of the π -ligands vary with the nature of the clip (**6a,7a**, 1.8 Å; **6b,7b**, 0.3 Å), probably as a result of the different steric demands of the P,N and P,P chelating ligands. These results show that, despite the repulsive interactions between the closed-shell π -clouds, molecular clips **1a,b** can force face-to-face π -stacking of aromatic derivatives upon coordination into well-defined supramolecular

metalloparacyclophanes. Hence, due to their rigidity and topology, complexes **1a,b** are unique building blocks for the synthesis of π -stacked molecular assemblies having a [2.2]paracyclophane-like topology.

To extend the scope of our approach and to evaluate the size limit of the self-assemblies attainable using clips **1a,b**, longer rigid ditopic chromophores were investigated. Derivatives **4** and **5** (Scheme 1) were selected since (*para*-phenylenevinylene)-based chromophores are among the most widely studied π -conjugated organic materials.^{1c,9} The self-assembly processes involving the Cu^I dimers **1a,b** and the ligands **4** or **5** (1/1 ratio) were conducted in CH₂Cl₂ solution at 40 °C for up to 15 h (Scheme 1). The four novel derivatives **8a,b** and **9a,b** were isolated as air-stable powders, and single crystals were obtained for **8a,b** and **9a** (Scheme 1). As observed for the smaller assemblies **6a,b** and **7a,b**, the bridging P atoms impose short Cu–Cu distances (2.661–2.723 Å), and the four Cu atoms of **8a,b** and **9a** define a rectangle (Figure 3). The

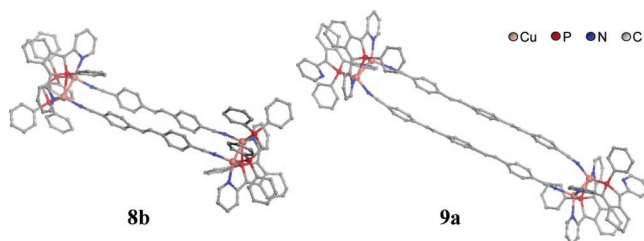


Figure 3. X-ray crystal structures of **8b** and **9a** (H atoms, counteranions, and solvent molecules have been omitted for clarity).

length of these rectangles (Cu–Cu distances) is fixed by the size of the ditopic ligands and reach 18.1 Å for **8a,b** and 25.2 Å for **9a**. Note that the overall dimension of **9a** is about 39 Å in length. The (*para*-phenylenevinylene)-based π -ligands are almost planar, the twist angles in **9a** being below 15.1° (Figure 3), and the bond lengths and valence angles of **4** and **5** are similar in the free state and in the assembly **8a,b** and **9a**, respectively. The (*para*-phenylenevinylene)-based chromophores in **8a,b** and **9a** have a face-to-face arrangement with short intramolecular interplanar distances (ca. 3.5 Å) revealing cofacial π – π interactions. It is worth noting that these distances are identical to those recorded for **6a,b** and **7a,b** incorporating shorter ligands. The fact that the cofacial distances in these arrays are maintained using connectors with lengths varying from 7.9 to 21.4 Å clearly demonstrates that their structures are predetermined by the nature of the programmed Cu^I clips **1a,b** and more precisely by the short Cu^I–Cu^I distance and the rigidity of these scaffolds.

A last remarkable feature is the stacking pattern of metalloparacyclophanes **8a,b** and **9a** in the solid state. The cationic parts of the rectangles have a parallel-displaced arrangement along the *a*-axes with short intermolecular distances (ca. 3.6 Å) (Figure 4). The substantial gain in dispersion interactions that results from the contact of such large polarizable surfaces probably favors these intermolecular interactions.^{1a} Hence, a unique infinite columnar stack resulting from intra- and intermolecular π – π interactions of (*para*-phenylenevinylene)-based chromophores is observed with these novel metalloparacyclophanes (Figure 4).

In conclusion, we have described a rational and straightforward synthetic approach to a variety of nanoscale π -stacked metalloparacyclophanes utilizing the power and simplicity of molecular self-assembly.¹⁰ This synthetic methodology can be applied to virtually any cyano-capped chromophores, and its extension to other types of π -conjugated systems as well as the elucidation of the electronic properties of these novel π -stacked molecular assemblies is under active investigations.

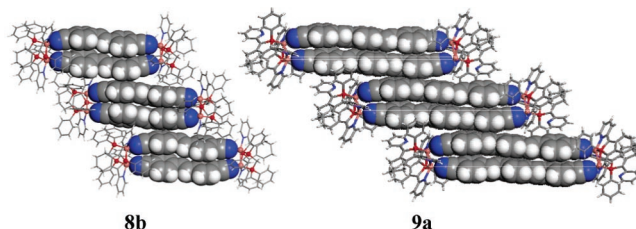


Figure 4. Views of the packing of **8b** and **9a** along the *a*-axes (H atoms, counteranions, and solvent molecules have been omitted for clarity).

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Supporting Information Available: Representative synthetic procedures; CIF files, tables of crystal data, ORTEP views for compounds **1b**, **4**, **5**, **6a,b**–**8a,b**, and **9a** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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