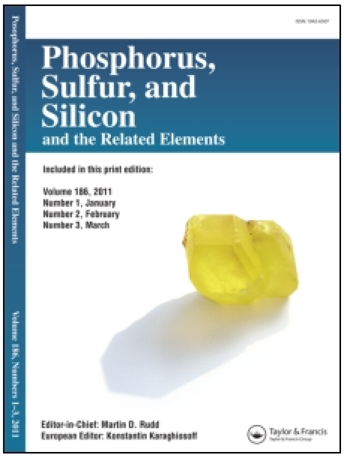

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Organophosphorus-Conjugated Materials for Optoelectronic Applications

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Organophosphorus-Conjugated Materials for Optoelectronic Applications

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The supramolecular organization of nano-size π-conjugated systems within metalloparacyclophanes and coordination polymers synthesis is described.

Keywords π-conjugated systems; coordination polymers; phosphole

INTRODUCTION

π-Conjugated oligomers and polymers have emerged as promising materials for application in flexible, lightweight, and low-cost electronic devices such as organic light-emitting diodes (OLEDs), field-effect transistors (FETs), plastic lasers, and photovoltaic cells.[1] One of the most appealing attributes of these types of molecular material is their aptitude for exhibiting multifunctional properties, something that is nicely illustrated by their use in the fabrication of high-performance OLEDs, which are employed as devices for flat-panel displays in a host of commercial products (e.g., cell phones, digital cameras, etc.).[2] The performance of organic devices is mainly determined by the chemical structure of the conjugated chains and their supramolecular organization.[1] Varying the chemical composition of conjugated systems is a major concern to further optimize organic materials. We have recently shown that the incorporation of phosphole moieties into the conjugated framework is a fruitful strategy to diversify the structure of π-conjugated molecular materials.[3] One appealing property of these P building blocks is

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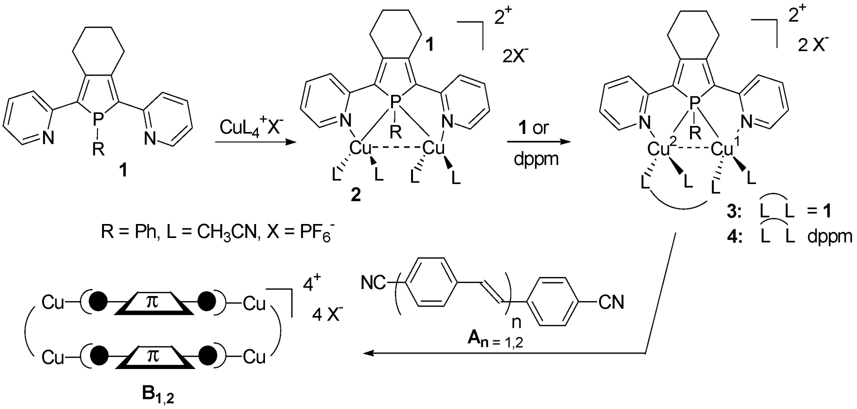
that they possess reactive phosphorus centers allowing direct access to a range of novel π-conjugated systems. These chemical modifications of the phosphorus atoms allow a fine tuning of the optical and electrochemical properties of phosphole-based π-conjugated systems. This unique way of tailoring π-conjugated systems has been exploited for the optimization of phosphole-based materials as emissive materials for OLEDs[3a,b] or selective sensors.[3c] In this article, we focus on the use of phosphorus chemistry, especially the aptitude of specific P-ligands to stabilize bimetallic complexes, in order to control the supramolecular organization of π-conjugated systems in the solid state. Two strategies leading to molecular metalloparacyclophanes and coordination polymers based on π-stacked conjugated systems are described.

RESULTS AND DISCUSSION

One fruitful approach to probe co-facial π-π interactions involves the assembly of chromophore pairs into well defined [2,2]paracyclophanes.[4] However, straightforward routes to these complex assemblies, as well as tailoring their structure, remain a challenge to chemical synthesis. Transition metal complexes are powerful templates for organizing organic chromophores with coordinating termini into well-defined supramolecular assemblies.[5] We have thus designed bimetallic clips possessing two *cis* coordinatively labile sites that are closely aligned for the construction of metalloparacyclophanes with π-stacked walls. This programmed *U*-topology was obtained in Cu^I-dimers using the unique ability of di(2-pyridyl)phosphole ligand **1** (Scheme 1) to stabilize metal dimers.[6] Indeed, the reaction of **1** with $Cu(CH_3CN)_4PF_6$(1:2



SCHEME 1

ratio) in CH_2Cl_2 at room temperature gives the dimetallated complex **2** in 95% yield (Scheme 1). An X-ray diffraction study revealed that the two Cu^I atoms are capped by a 2,5-bis(2-pyridyl)phosphole ligand **1** acting as a 6-electron μ-1kN:1,2kP:2kN donor. Two acetonitrile ligands of **2** can be displaced by one equivalent of phosphole **1** or dppm leading to complexes **3** and **4**, respectively. X-Ray diffraction studies confirmed that these compounds possess two Cu^I atoms capped by a 2,5-bis(2-pyridyl)phosphole with a symmetrically-bridging trivalent P-center and two acetonitrile ligands having a *cisoid* arrangement. Furthermore, the bridging coordination mode of the phosphole P-center imposes a short intermetallic distance [**3**, 2.555(1) Å; **4**, 2.667(1) Å] resulting in a close proximity of the two kinetically labile acetonitrile ligands (N—N distances, *ca*. 3.2 Å).

The aptitude of Cu^I-dimers **3**,**4** to give supramolecular rectangles was investigated using the cyano-substituted (*para*-phenylenevinylene)-based chromophores $\mathbf{A}_n$. Indeed, these ditopic linkers reacted with one equivalent of the Cu^I-dimers **3**,**4** in CH_2Cl_2 giving rise to the assemblies $\mathbf{B}_{1,2}$ (Scheme 1). These compounds were obtained in good yields (ca., 60–70%) as air-stable orange powders soluble in polar solvents (acetone, THF...) and were characterized by single-crystal X-ray diffraction studies. The four Cu-atoms lie in the same plane defining a rectangle with lengths on the nano scale (>20 Å).[7] The metric data of the dimetallic clips do not change significantly upon their incorporation into the self-assembled structures demonstrating the conformation rigidity of the Cu^I-based subunits. The aromatic moieties of the chromophores are parallel as a result of hindered rotation and, due to the short Cu-Cu distances in the dimer clips (ca., 2.6 Å), they participate in face-to-face π-interactions (phenyl centroid-centroid distances: 3.4–3.5 Å). These results show that the programmed molecular dimers **3**,**4** having a *U*-shape are powerful molecular clips to organize π-conjugated systems within metalloparacyclophanes. Remarkably, these rectangles have a parallel-displaced arrangement along the *a*-axes with short intermolecular distances (ca., 3.6 Å)[6] (Figure 1). The substantial gain in dispersion interactions that results from the contact of such large polarizable surfaces probably favors these intermolecular interactions.

In order to prepare coordination polymers (CPs) having metalloparacyclophanes $\mathbf{B}_{1,2}$ as repeating units, we have investigated the use of dppm-capped Cu^I-dimer **5** (Scheme 2) having the *U*-topology of **3**,**4** but additional labile coordination sites. The reaction of **5** with the rigid ditopic linkers $\mathbf{A}_{1,2}$ afforded CPs $\mathbf{C}_{1,2}$ (Scheme 2) composed of nanosize π-stacked metalloparacyclophane units (lengths > 18.3–25.0 Å), an

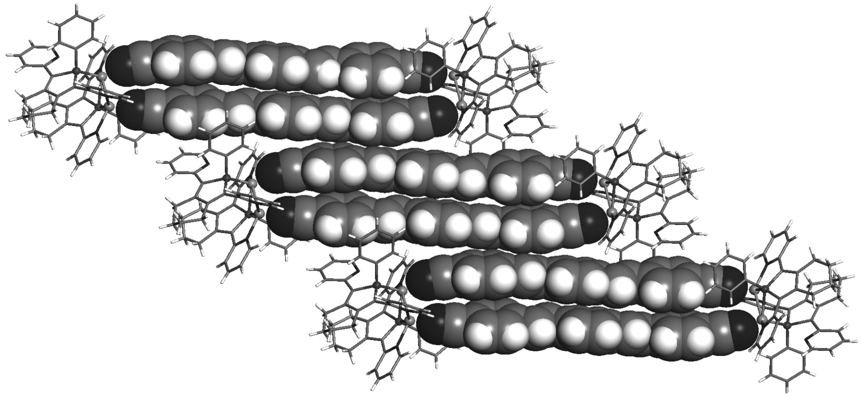
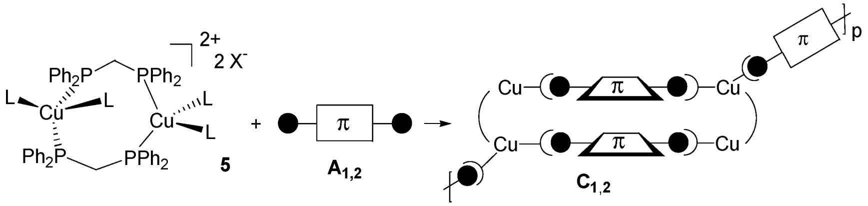


FIGURE 1 View illustrating the supramolecular arrangement of metallaparacyclophanes $\mathbf{B_2}$ along the a-axes.



$X^- = PF_6^-$; $L = CH_3CN$

SCHEME 2

extremely rare motif for CPs [7], connected by rigid ditopic linkers $\mathbf{A}_{1,2}$. This unexpected framework is based on $Cu_2(\mu^2\text{-dppm})_2$ connectors having a unique *F*-shape due to the close association (Cu···Cu distances, ca. 3.2 Å) of one tricoordinated trigonal planar and one tetracoordinated tetrahedral Cu^I-centers. The fully planar aromatic moieties are parallel with interplanar distances between of 3.6–3.7 Å revealing $\pi - \pi$ interactions. The four Cu-atoms define rhombus and the two π-systems adopt a parallel-displaced arrangement, which is an energetically favored stacking.

CONCLUSION

In conclusion, we have described the synthesis of Cu^I-dimers that react with nanosized π-conjugated systems to π-stacked metalloparacyclophanes. Varying the structure of the Cu^I-dimers allows obtaining novel coordination polymers having π-stacked metalloparacyclophanes as repetitive motifs. These very simple synthetic methodologies, which use the concepts of molecular self-assembly, can be applied to virtually any cyano-capped chromophores.

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