Self-Assembly

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Coordination Polymers with π-Stacked Metalloparacyclophane Motifs: F-Shaped Mixed-Coordination Dinuclear Connectors**

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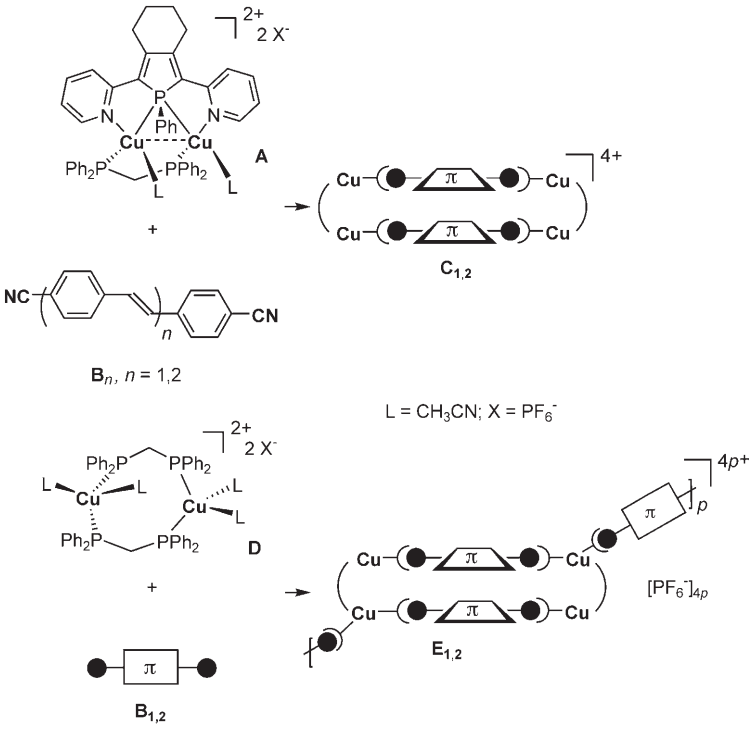
The design and construction of coordination polymers (CPs) composed of metal-ion connectors and linear organic π-conjugated linkers are of great interest, owing to their use as functional materials.[1] One way in which their potential may be expanded is to prepare CPs having new structural motifs. With this idea in mind, face-to-face π-stacked assemblies, such as paracyclophanes, are appealing building blocks for CPs, owing to their unique electronic properties arising from π-orbital overlap.[2] Since the structural motifs of CPs are controlled by the number and orientation of the connector binding sites, the construction of the desired paracyclophane based CP frameworks requires the discovery of connectors with specific coordination characteristics. Herein, we describe a dinuclear connector having an unprecedented F shape, which arises from the close association of isovalent metal atoms with different coordination numbers and geometries. The propagation of the coordination geometry imposed by the "mixed-coordination" connector by using π-conjugated linkers gives CP frameworks with π-stacked metalloparacyclophanes as structural motifs. Furthermore, we show that these complex CP architectures can be obtained directly from their molecular components in a one-pot multicomponent approach, and we propose a mechanism for their construction.



Scheme 1. Synthesis of the CPs $\mathbf{E_{1,2}}$ from well-defined Cu^{I} dimers.

The π-stacked metalloparacyclophanes $\mathbf{C_{1,2}}$ (that is, $\mathbf{C}_n$ with $n = 1$ or 2) can be synthesized by self-assembly of the U-shaped Cu^{I} dimer **A**, which bears a rigid tridentate NPN ligand, with the cyano-capped π-conjugated systems $\mathbf{B_{1,2}}$ (Scheme 1).[3] To prepare CPs having the metalloparacyclophanes $\mathbf{C_{1,2}}$ as repeating units, we investigated the use of the bis(diphenylphosphino)methane (dppm) capped Cu^{I} dimer **D**,[4] which has the U topology of **A**, as well as additional labile coordination sites (Scheme 1). The reaction of **D** with the rigid ditopic linkers $\mathbf{B_{1,2}}$ was conducted in CH_2Cl_2 solution at room temperature with a $\mathbf{D}/\mathbf{B_{1,2}}$ molar ratio of 1:2. After 4–5 h, single crystals grew from the homogeneous solutions (yields > 85%). X-ray diffraction studies[5] revealed that these compounds are the CPs $\mathbf{E_{1,2}}$ (Scheme 1), which are composed of nanosized π-stacked metalloparacyclophane units[6] (lengths 18.3–25.0 Å) connected by the rigid ditopic linkers $\mathbf{B_{1,2}}$ (Figures 1a and 2). These novel CP frameworks are based on $\{Cu_2(\mu_2\text{-dppm})_2\}$ connectors, which have a unique F shape, owing to the close association (Cu···Cu ca. 3.2 Å) of a tricoordinated Cu^{I} center with a trigonal-planar geometry and a tetracoordinated Cu^{I} center with a tetrahedral geometry (Figure 1b). To our knowledge, this type of mixed-coordination dinuclear node is unprecedented in CP skeletons. The Cu–P (2.24–2.25 Å) and Cu–N (1.96–2.08 Å) bond lengths of this $\{Cu_2(\mu_2\text{-dppm})_2\}$ connector are comparable with those of the dimer **D**. Note that no significant differences between the exo- and endocyclic Cu(1)–N bond lengths are observed in the CPs $\mathbf{E_{1,2}}$. The Cu(1)NN and Cu(1)PP planes are perpendicular, as expected for a tetrahedral geometry, and the sums of the angles about the tricoordinated Cu(2) centers are greater than 355° (Figure 1b). These data and the fact that the endocyclic Cu-N-C fragments are nearly linear indicate that

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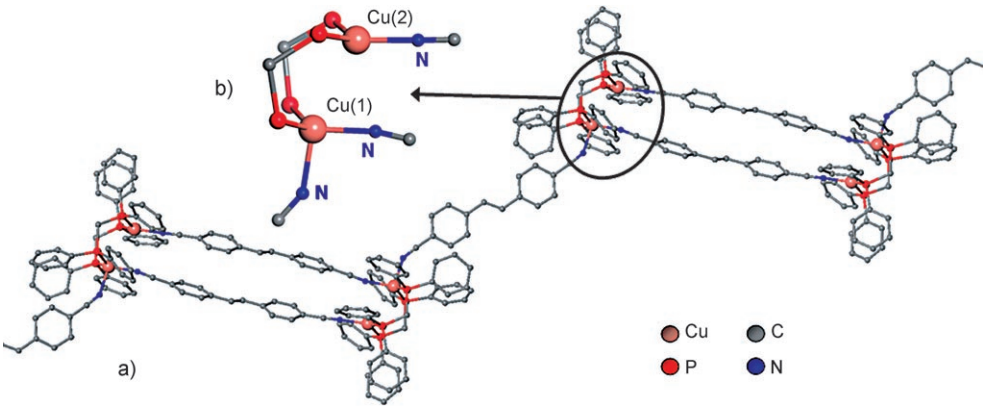


Figure 1. a) A cationic chain of the CP $\mathbf{E_1}$ (H atoms are omitted for clarity). b) Enlargement of an F-shaped node (phenyl rings on P atoms are omitted for clarity).

The F-shaped connectors based on coordinatively saturated and unsaturated Cu^I centers are particularly striking (Figure 1b). The formation of CPs based on these intriguing nodes is extremely favored, as revealed by the following experiments. All the basic molecular constituents of the CPs $\mathbf{E_{1,2}}$ (Cu^I/dppm/$\mathbf{B_{1,2}}$ in a molar ratio of 4:4:3) were dissolved in a CH_2Cl_2 solution at room temperature (Scheme 2). Note that

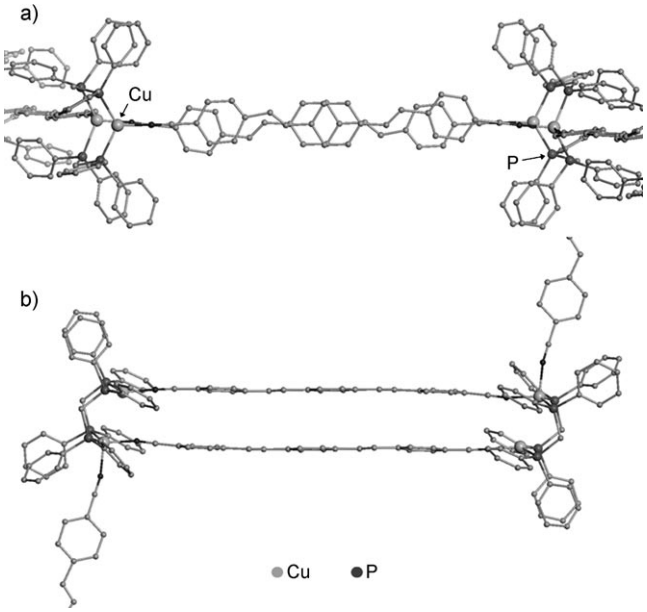
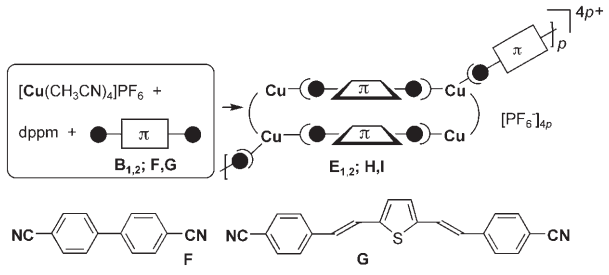


Figure 2. a) Top and b) side views of a metallocyclophane unit of the CP $\mathbf{E_2}$ (H atoms are omitted for clarity).



Scheme 2. One-pot synthesis of the CPs $\mathbf{E_{1,2}}$, **H**, and **I**.

the metalloparacyclophane units are strain-free, probably because of the flexibility of the dppm-capped Cu^I nodes. The coordinated N atoms of the organic linkers lie almost in the Cu_4 plane (N-Cu-Cu-N 3.5–6.9°). The fully planar aromatic moieties are parallel (Figures 1a and 2b) with interplane distances of 3.6–3.7 Å, revealing π–π interactions.[2] The four Cu atoms connected by the two linkers define a rhombus (endocyclic N-Cu-Cu 65.4–66.7, 115.5–116.2°), and the two π systems adopt a parallel-displaced arrangement (lateral offset 1.4–1.5 Å; Figure 2a), which is an energetically favored stacking.[2c] This organization differs notably from the face-to-face π stacking imposed by the rigid Cu^I clips in the discrete rectangles $\mathbf{C_{1,2}}$ (Scheme 1). In fact, the flexible mixed-coordination $\{Cu_2(\mu_2\text{-dppm})_2\}$ connector can adapt its structure (that is, shape and Cu···Cu distance) to maximize weak π–π interactions.[7]

the counteranion used in this one-pot procedure is PF_6^-, as was the case in the experiments involving the precursor **D** (Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of the homogeneous crude reaction mixtures showed one broad signal at −8.0 ppm, a chemical shift typical for Cu^I–phosphine complexes (for free dppm, $\delta = -21.1$). This signal, which is not due to the Cu^I dimer **D** (sharp singlet at $\delta = -8.4$ ppm), splits into two broad singlets ($\delta = -6.3$, -9.1 ppm) at 5°C. These data indicate that the crude reaction mixtures contain several Cu^I complexes in equilibrium at room temperature, owing to multiple and reversible Cu^I–ligand (dppm, $\mathbf{B_{1,2}}$) exchanges.[8] After 4–5 h, single crystals grew from the solutions, and X-ray diffraction studies revealed that the obtained compounds were the CPs $\mathbf{E_{1,2}}$ (yields > 75%; Scheme 2). It is remarkable that the spontaneous self-organization of these sets of elemental building blocks leads to the same supramolecular structures as obtained by using the well-defined and preorganized molecular clip **D** (Scheme 1). Note that the CPs $\mathbf{E_{1,2}}$ are obtained in excellent yields with different original Cu^I/dppm/$\mathbf{B_{1,2}}$ ratios.[9] Hence, the three simple building blocks Cu^I, dppm, and $\mathbf{B_{1,2}}$ can self-assemble into large and complex CP architectures from a library of interconverting Cu^I complexes, irrespective of the original stoichiometry.

An evaluation of the scope of this straightforward one-pot synthetic method for the formation of CPs having π-stacked metallocyclophane motifs was then undertaken. The cyano-capped π-conjugated building blocks **F** and **G**, which have a biphenyl core or a 2,5-distyrylthiophene core, respectively (Scheme 2), were selected, since their structures differ markedly from those of the *para*-phenylene vinylene based

linkers $\mathbf{B_{1,2}}$. These compounds were used in the one-pot procedure (Cu^{I}/dppm/**F**,**G** in a molar ratio of 4:4:3) and afforded single crystals of the CPs **H**,**I** (yield 77–82%; Scheme 2), which have a gross structure similar to that of $\mathbf{E_{1,2}}$ (Figure 3).[5] The metalloparacyclophane units of the CPs

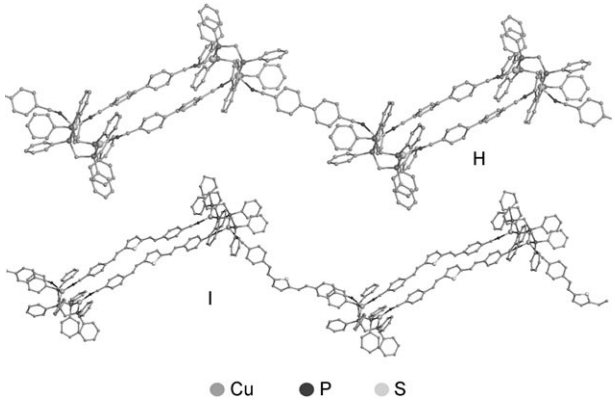


Figure 3. Cationic chains of the CPs **H** and **I** (H atoms are omitted for clarity).

H,**I** contain F-shaped mixed-coordination $\{Cu_2(\mu^2\text{-dppm})_2\}$ nodes. The four Cu atoms connected by two linkers define a nanoscale rhombus. The biphenyl cores of **H** are twisted (23.9–24.9°), and the distances between the aromatic fragments are at the upper accepted limits for π stacking (ca. 3.8 Å). In contrast, the fully planar 2,5-distyrylthiophene moieties of **I** lie in parallel planes separated by only 3.6 Å, and as observed for $\mathbf{E_{1,2}}$, they adopt a displaced arrangement (lateral offset 1.4 Å).

These results highlight the simplicity and versatility of our approach to CPs based on π-stacked metallocyclophane motifs. The formation of these complex CP frameworks in the one-pot method clearly involves multilevel self-assembly processes. A plausible scenario can be proposed, following an experiment conducted with the biphenyl based linker **F** and $[Cu(CH_3CN)_4]BF_4$ in place of $[Cu(CH_3CN)_4]PF_6$. This change in the counteranion affects the solubility of the Cu^{I} species: $[Cu(CH_3CN)_4]PF_6$ gives polymer **H** (Scheme 2, Figure 3), while $[Cu(CH_3CN)_4]BF_4$ affords the discrete metalloparacyclophane **J**, which was characterized by an X-ray diffraction study (Figure 4). The rhombohedral metalloparacyclophane **J** features mixed-coordination $\{Cu_2(\mu^2\text{-dppm})_2\}$ connectors in which the remaining coordination site of the tetracoordinated Cu^{I} atoms is occupied by a labile acetonitrile ligand. The tetracationic derivative **J** is, thus, the metallocyclophane repeat unit of the polymer **H** (Figure 3) obtained using the $[Cu(CH_3CN)_4]PF_6$ salt (Scheme 2). The isolation of this potential intermediate supports the following mechanism for the construction of the metallocyclophane based CPs. The first step is very probably the self-assembly of the mixed-coordination Cu^{I} dimers and the organic linkers into metalloparacyclophanes of type **J** (primary structure). Then, these nanosized rhombohedra self-assemble into CP networks (secondary structure) through the stepwise displacement of the acetonitrile ligands by the ditopic organic linkers. In other words, the CPs described herein are obtained by the self-assembly of self-assembled nanostructures.

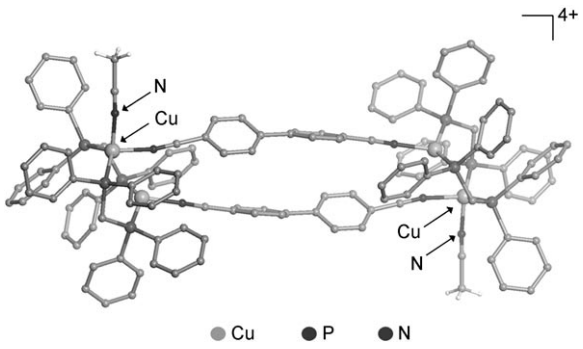


Figure 4. The discrete tetracationic metalloparacyclophane **J**, which bears two acetonitrile ligands (H atoms are omitted for clarity, with the exception of those of the CH_3CN ligands).

In conclusion, we have shown that nodes having an unprecedented topology can be obtained by associating two isovalent metal centers with different coordination geometries. These mixed-coordination Cu^{I} connectors organize nanosized π-conjugated systems into CPs having π-stacked metallocyclophane motifs. The potential functionalities afforded by the presence of paracyclophane like motifs and unsaturated Cu^{I} centers in these CPs are under active investigation.

Experimental Section

$\mathbf{E_2}$: $[Cu(CH_3CN)_4]PF_6$ (0.040 g, 0.107 mmol), dppm (0.041 g, 0.107 mmol), and the linker $\mathbf{B_2}$ (0.047 g, 0.080 mmol) were introduced into a Schlenk tube as solids. CH_2Cl_2 (60 mL) was then added, and the solution was stirred for 10 min at room temperature. Yellow single crystals of $\mathbf{E_2}$ appeared from the homogeneous solution after 4–5 h. The crystals were collected, washed with Et_2O (3 × 10 mL), and dried under vacuum for 48 h at 40 °C (0.067 g, 75% yield).

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[1] a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; b) O. M. Yaghi, M. O'Keeffe, N. W. Ocking, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; c) G. S. Papaefstathiou, L. R. MacGillivray, *Coord. Chem. Rev.* **2003**, *246*, 169–184; d) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217–225; e) C. A. Mirkin, B. J. Hollidays, *Angew. Chem.* **2001**, *113*, 2076–2097; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043; f) C. A. Wheaton, M. C. Jennings, R. Puddephatt, *J. Am. Chem. Soc.* **2006**, *128*, 15370–15371; g) M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem.* **2006**, *118*, 5818–5822; *Angew. Chem. Int. Ed.* **2006**, *45*, 5689–5693; h) J. J. Zhang, H. J. Zhou, A. Lachgar, *Angew. Chem.* **2007**, *119*, 5083–5086; *Angew. Chem. Int. Ed.* **2007**, *46*, 4995–4998.

[2] a) Y. Morisakim, Y. Chujo, *Angew. Chem.* **2006**, *118*, 6580–6587; *Angew. Chem. Int. Ed.* **2006**, *45*, 6430–6437; b) *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH,

Weinheim, **2004**; c) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244 – 1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210 – 1250; d) G. P. Bartholomew, G. C. Bazan, *Acc. Chem. Res.* **2001**, *34*, 30 – 39; e) F. J. M. Hoeben, P. Jonkheijm, P. W. Meijer, A. P. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546.

[3] a) B. Nohra, S. Graule, C. Lescop, R. Réau, *J. Am. Chem. Soc.* **2006**, *128*, 3520 – 3521. For an approach to π-stacked assemblies using H bonds, see: b) A. N. Sokolov, T. Friscic, L. R. MacGillivray, *J. Am. Chem. Soc.* **2006**, *128*, 2806 – 2807; c) A. N. Sokolov, T. Friscic, S. Blais, J. A. Ripmeester, L. R. MacGillivray, *Cryst. Growth Des.* **2006**, *6*, 2427 – 2428.

[4] M. M. Wu, L. Y. Zhang, Y. H. Qin, Z. N. Chen, *Acta Crystallogr. Sect. E* **2003**, *59*, m195 – m196.

[5] CCDC-638863 (**E_1**), CCDC-638864 (**H**), CCDC-638865 (**E_2**), CCDC-641183 (**I**), and CCDC-643159 (**J**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Complete experimental details can be found in the Supporting Information.

[6] CPs based on metallocyclophanes are extremely rare and possess very different structures: a) M. Munakata, G. L. Ning, Y. Suenaga, T. Kuroda-Sowa, M. Maekawa, T. Ohta, *Angew. Chem.* **2000**, *112*, 4729 – 4731; *Angew. Chem. Int. Ed.* **2000**, *39*, 4555 – 4557; b) S. Q. Liu, T. Kuroda-Sowa, H. Konaka, Y. Suenaga, M. Maekawa, T. Mizutani, G. L. Ning, M. Munakata, *Inorg. Chem.* **2005**, *44*, 1031 – 1036; c) G. S. Papaefstathiou, I. G. Georggiev, T. Friscic, L. R. MacGillivray, *Chem. Commun.* **2005**, 3974 – 3976.

[7] The different rigidity/flexibility of the two Cu^I-dimer clips is illustrated by the fact that the Cu···Cu separation in clip **A** and assemblies **$C_{1,2}$** are identical, whereas this distance decreases by more than 0.52 Å in **$E_{1,2}$** compared to **D**.

[8] The formation of kinetically labile Cu^I complexes is corroborated by the fact that the detection of the ^{31}P NMR signal of free dppm in a CH_2Cl_2 solution containing $[Cu(CH_3CN)_4]^+$ and **E_1** (1:1.5 molar ratio) requires a Cu^I/dppm molar ratio greater than 14:1.

[9] Experiments were conducted with Cu^I/dppm/**$B_{1,2}$** molar ratios of 4:8:3 and 4:4:6. Such a situation, in which the creation of a mixture of diverse products in equilibrium is combined with an irreversible event (selective crystallization), can be defined as pseudodynamic combinatorial chemistry: P. T. Corbett, J. Leclaire, L. Vial, K. R. West, J.-L. Wietor, J. K. M. Sander, S. Otto, *Chem. Rev.* **2006**, *106*, 3652 – 3711.

