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Facile synthesis of one-dimensional organometallic-organic hybrid polymers based on a diphosphorus complex and flexible bipyridyl linkers

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The selective synthesis of a series of new “ladderlike” one-dimensional organometallic-organic hybrid polymers is shown. Those polymers are obtained from the reaction of the diphosphorus ligand complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ with the copper salt $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ in the presence of flexible organic bipyridyl linkers in a high selectivity. This unique behaviour is supported by DFT calculations.

In recent years, coordination polymers have attracted significant attention due to their intriguing network topologies^{1,6} and unique properties.^{2,6} Those coordination polymers are assembled via the coordination of organic ligands usually bearing N, O or S donor atoms to metal ions.³ Yet, the understanding of the supramolecular aggregation processes is still limited, as many factors influence the formation of the final products. Those factors can be external (solvent systems, pH values, temperatures, crystallisation techniques, and template involved)^{4,6} or internal (the geometry or the position of the donor atoms of the ligands and counteranions involved).^{5,6} One way to avoid the low selectivity of the assembling reactions and direct the synthesis towards targeted products is the use of pre-designed precursors.⁷ Another way is to utilise rigid linkers⁸, as the use of flexible linkers often leads to unpredictable frameworks⁹ due to their conformational freedom.¹⁰ Recently, C. Lescop et al. succeeded in the selective synthesis of tetranuclear metallacycles based on mixed rigid and flexible linkers.^{7a} In addition, several groups have synthesized dinuclear metallacycles using flexible ditopic linkers.¹¹ In all these examples, the authors have benefited from the metal-directed self-assembly process to build their targeted inorganic-organic metallacycles. Therefore, the question arises whether it is possible to use flexible organic linkers to control a regular arrangement in the solid state. Obviously, the used interplay of linkers/nodes will then play a decisive role. In this field, our group has previously reported a new approach by using P_n ligand complexes as organometallic connectors between metal centers allowing the formation of one- and two-dimensional

coordination polymers.¹² Moreover, one of those P_n ligand complexes, the tetrahedrane complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ ($\text{Cp} = \text{C}_5\text{H}_5$) (**A**), has been reacted with Ag^+ and Cu^+ salts in the presence of trans-1,2-di(pyridine-4-yl)ethene to give unprecedented organometallic-organic hybrid polymers.¹³ Herein, we present the reaction between the P_2 ligand complex **A**, the $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (**B**), and the flexible ditopic linkers **1-4** (Scheme 1). Due to the different possible arrangements of the flexible linkers¹⁰ and different coordination modes of the P_2 ligand complex¹⁴ towards the Cu^+ cation, a large number of combinations is expected resulting in a large variety of accessible networks. However, those reactions yielded selectively the novel one-dimensional organometallic-organic coordination polymers **5-8** (Scheme 1, Figure 2), where, to the best of our knowledge, no general approach has yet been reported to synthesize selectively coordination polymers based on flexible organic linkers and organometallic nodes.

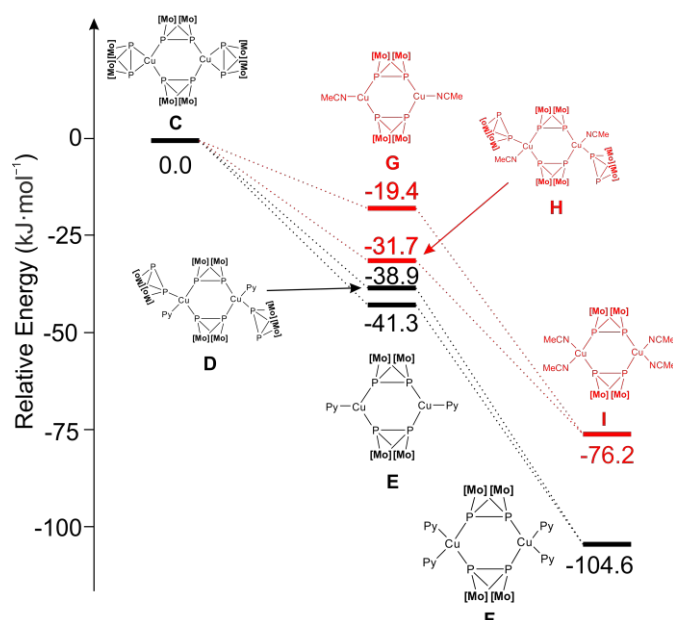


Figure 1. Energy diagram of the reaction of **C** with pyridine and CH_3CN . The positive charges, ligands added or cleaved are not depicted. $[\text{Mo}] = \text{CpMo}(\text{CO})_2$.

Recently¹⁵, we have shown that the reaction of the copper salt **B** and the P_2 ligand complex **A** affords a compound **C** that possesses a

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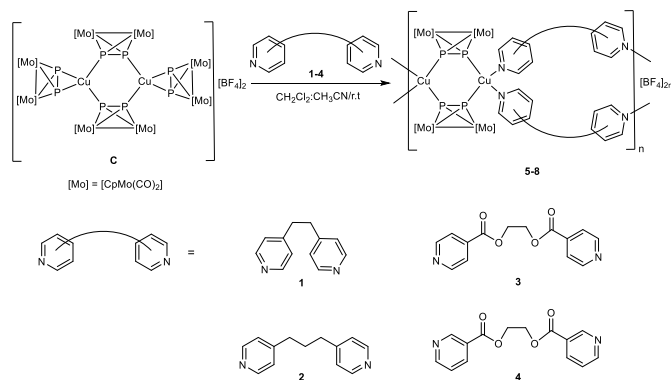
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dimeric $[\text{Cu}_2(\mathbf{A})_4][\text{BF}_4]_2$ structure in the solid state with two $\mu\text{-}\eta^1\text{-}\eta^1$ bridging ligands \mathbf{A} and two ligands \mathbf{A} in η^2 side-on coordination (Figure 1, Scheme 1). In order to study the dimer \mathbf{C} as a suitable precursor for the selective synthesis of organometallic-organic hybrid polymers, DFT calculations have been performed at the B3LYP/def2-TZVP level of theory. Accordingly, the substitution of the terminal ligands \mathbf{A} in the preformed dimeric complex \mathbf{C} by pyridine as a model ligand, leading to \mathbf{F} , is exothermic ($-104.6 \text{ kJ}\cdot\text{mol}^{-1}$) in solution (Figure 1). In contrast, the substitution by dichloromethane (\mathbf{Q}) is endothermic by $87.4 \text{ kJ}\cdot\text{mol}^{-1}$ (Figure S22 in SI). Just like pyridine, acetonitrile can also substitute the terminal ligands \mathbf{A} in \mathbf{C} , but the reaction is less exothermic than in the case of pyridine ($-76.2 \text{ kJ}\cdot\text{mol}^{-1}$; Figure 1). The substitution of the terminal ligands \mathbf{A} in \mathbf{C} leading to \mathbf{D} and \mathbf{H} is more favoured for pyridine than for acetonitrile. This indicates that, starting from the dimer \mathbf{C} , it should be possible to synthesise organometallic-organic hybrid polymers by reacting it with pyridine-based multitopic ligands. In addition, the tuning of the final outcome of the reactions should also be attainable.

Based on this information, complex \mathbf{C} was reacted with the 4,4'-bipyridine ($\mathbf{1-3}$) or 3-3'-bipyridine ($\mathbf{4}$) linkers bearing flexible (C_2H_4 , $\mathbf{1}$), (C_3H_6 , $\mathbf{2}$), ($\text{C}_6\text{H}_4\text{O}_4$, $\mathbf{3}$ and $\mathbf{4}$) linkages in a 1:2 stoichiometry in a mixture of CH_2Cl_2 and CH_3CN at room temperature resulting in the formation of the coordination polymers $\mathbf{5-8}$ as orange or red crystalline solids in good to high (65-94%) yields (Scheme 1). In either case, the same products could also be selectively isolated when all the components were mixed together using different stoichiometries (1 or 3 equivalents) of the organic linker, which

suggest that the products $\mathbf{5-8}$ are thermodynamically favoured, even passing other possible intermediates.



Scheme 1. The reaction of the dimeric complex \mathbf{C} with the flexible organic linkers $\mathbf{1-4}$. Synthesis of the one-dimensional organometallic-organic coordination polymers $\mathbf{5-8}$.

The derivatives $\mathbf{5-8}$ are slightly soluble in donor solvents like CH_3CN , but insoluble in other common organic solvents like CH_2Cl_2 , THF and *n*-pentane. The compounds $\mathbf{5-8}$ were crystallized at room temperature from pentane diffusion into $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solutions of the crude reaction mixtures and characterised by single crystal X-ray structural analysis (Tables S1-S5). Unexpectedly, despite the various lengths of spacers between the pyridyl fragments and the different positions of the donor atoms in the linkers $\mathbf{1-4}$, the

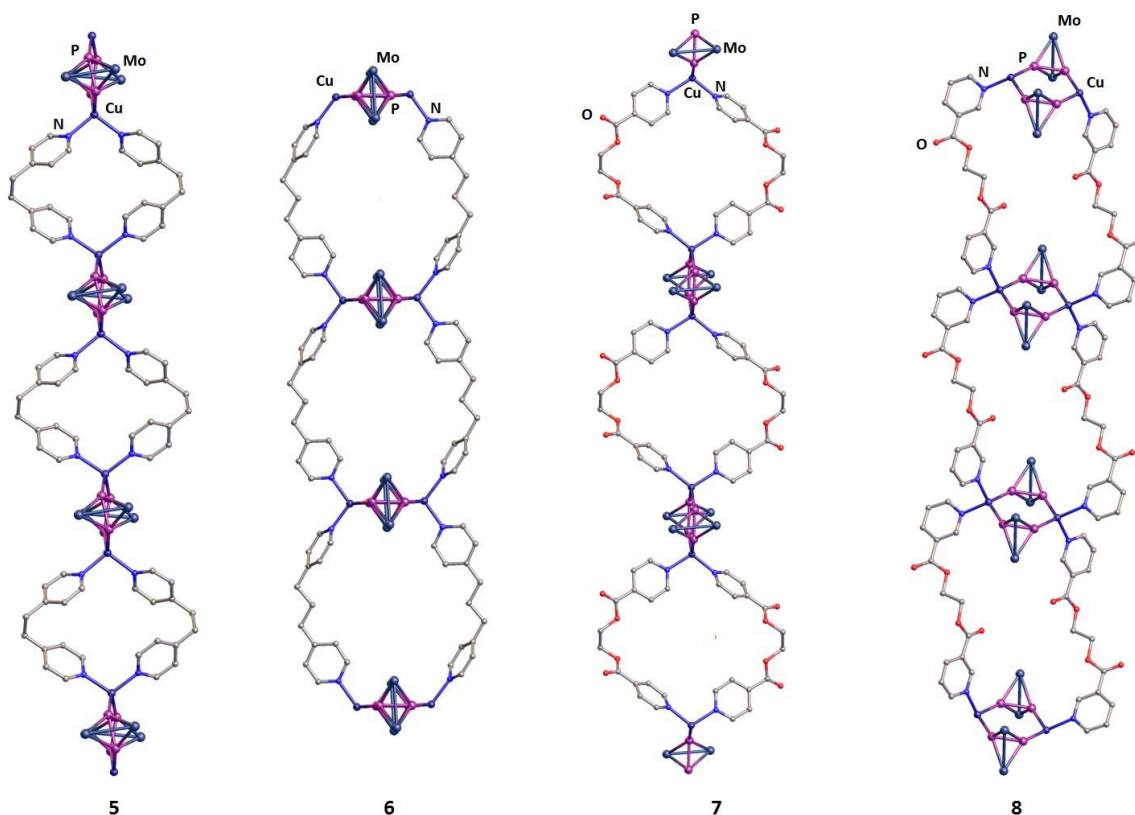


Figure 2. Sections of the 1D coordination polymers $\mathbf{5-8}$. Cp and CO ligands, hydrogen atoms as well as minor parts of the disordered fragments are omitted for clarity.

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assemblies **5-8** are 1D coordination polymers (Figure 2). In the derivatives **5-8**, each *side-on* coordinating ligand **A** present in the parent dimer **C** is substituted by the pyridine functions of two linker molecules. As a consequence, 1D polymers are formed with $\text{Cu}_2(\text{A})_2$ repeating units, which are linked together via the organic connectors (Figure 2). Within those repeating units, each copper ion comprises a distorted tetrahedral environment of two P and two N atoms. Interestingly, in the polymeric chains of **5** and **7**, each of the Cu centers of the Cu_2P_4 six-membered rings participates in a different metallacyclic fragment, while they participate in similar metallacyclic repeating units in the derivatives **6** and **8**. In other words, the derivatives **5** and **7** can be described as infinite dinuclear metallacyclic chains formed by $\text{Cu}_2(\text{5})_2$ metallacycles connected to each other via Mo_2P_2 ligands, while the derivatives **6** and **8** are infinite tetranuclear metallacyclic chains where the Mo_2P_2 ligands are a part of the metallacycles. The P-P bond lengths in the derivatives **5-8** are in the range between 2.072(2) and 2.086(2) Å, comparable to those of the non-coordinated ligand **A** (2.079(6) Å) and slightly shortened compared to that of the complex **C** (2.094(2)-2.159(2) Å). The Cu-P bonds of the derivatives **5-8** vary in a wider range (2.261(1)-2.307(1) Å) and are also shortened as compared to those of the parent dimer **C** (2.260(2)-2.385(2) Å). The Cu_2P_4 six-membered rings in all derivatives **5-8** are nearly planar, with folding angles of (4.4-7.9°). In the assemblies **5-8**, the central flexible linkages have an *anti*-“antiperiplanar” and *gauche*-“synperiplanar” and conformations for the linkers **1-3** and **4**, respectively (Figure 2). The coordination polymers possess virtual porosity, with cavities having “circular” (**5-7**) and “rectangular” (**8**) meshes of maximum diameters ranging between 1.02 and 1.47 nm and minimum diameters ranging between 0.32 and 0.73 nm.

The room temperature ^{31}P NMR spectra in CD_3CN of the complexes **5-8** show broad signals centered at -51.5 (**5**), -53.4 (**6**) and -48.2 (**7** and **8**) ppm, which are upfield shifted as compared to the free P_2 ligand complex **A** (-43.2 ppm) and comparable to the signal of the dimer **C** (-49.1 ppm, Table S6). Their room temperature ^1H NMR spectra (Figures S9-S12) present simple sets of signals with a 1:1 ratio of **A**:**L** (**L**= **1-4**), which suggest the formation of supramolecular assemblies with $\text{Cu}_2(\text{A})_2\text{L}_2$ repeating units. The ^{13}C NMR spectra show also typical sets of signals corresponding to the bipyridine linkers and the **A** ligands (Figures S13-S16). The ^{19}F NMR spectra of all complexes are featured by two signals centered at ca. -150.5, and -151.8 ppm, which correspond to the BF_4 counteranions (Table S6). The IR spectra exhibit two strong bands at ca. $\nu(\text{CO}) \approx 1920$ and 1980 cm^{-1} , which can be attributed to the carbonyl groups of the **A** moieties.

The results obtained demonstrate a new approach for the selective synthesis of novel 1D organometallic-organic hybrid polymers **5-8** based on the reaction of the organometallic P_2 -ligand complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ (**A**), the copper salt $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (**B**) and the flexible pyridine-based linkers **1-**

4. This is possible due to the lability of the η^2 -coordinated P_2 units, which could be easily substituted by the pyridine-based organic linkers **1-4**. In these aggregation reactions, the flexibility of the linkers **1-4** plays a “positive role” instead of the usual “destructive role” in directing the synthesis towards selective product formation since those linkers can easily adopt their backbones to afford the thermodynamically favored polymers. Current investigations focus on the use of rigid linkers with defined lengths and functionalities. The reactions of those linkers with the P_2 -based dimer precursor **C** are expected to be directionally leading to selective products with the possibility of a fine tuning and control of the sizes of the cavities formed. In addition, the incorporated functionalities could play a role in the host-guest chemistry of defined host molecules.

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