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Neutral two-dimensional organometallic–organic hybrid polymers based on pentaphosphaferrocene, bipyridyl linkers and $\text{CuCl}^\dagger$

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The reaction of the P_n ligand complex $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ (**1**: $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with CuCl in the presence of 4,4'-bipyridine or 1,2-di(4-pyridyl)ethylene leads to the formation of three unprecedented neutral 2D organometallic–organic hybrid networks, the constitutional isomers $[\text{Cu}_2\text{Cl}_2(\text{Cp}^*\text{Fe}(\mu_3, \eta^{5:1:1}\text{-P}_5))(\mu, \eta^{1:1}\text{-C}_{10}\text{H}_8\text{N}_2)]_n$ (**2** and **3**) and the coordination polymer $[(\text{CuCl})_2(\text{Cp}^*\text{Fe}(\mu_3, \eta^{5:1:1}\text{-P}_5))(\mu, \eta^{1:1}\text{-C}_{12}\text{H}_{10}\text{N}_2)]_n$ (**4**) with isomeric square (**2** and **3**) and honeycomb (**4**) layer topologies.

In recent years, coordination polymers (CPs) have received great attention due to their high structural diversity associated with a wide variety of chemical and physical properties.¹ These compounds are generally assembled *via* the coordination of multitopic organic linkers usually bearing N, O or S donor atoms to metal ions or clusters.^{2a–d} Due to the lack of using organometallic building blocks in this field,^{2e–g} our group developed an alternative concept by using organometallic polyphosphorus and polyarsenic ligand complexes with flexible coordination modes as organometallic connectors between metal ions allowing the formation of 1D, 2D and 3D CPs.³ Moreover, one of those polyphosphorus 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**) was reacted with Ag^+ and Cu^+ salts of the weakly coordinating anions (WCA) $\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4^-$, and $\text{FAl}\{\text{OC}(\text{C}_6\text{F}_5)(\text{C}_6\text{F}_{10})\}_3^-$ and the anion BF_4^- , in the presence of bipyridyl linkers to give unprecedented organometallic–organic hybrid CPs.⁴ However, the cavities formed in the polycationic chains of these networks are tightly occupied by anions, making them rather unattractive candidates for possible applications as for instance gas storage purposes.

Otherwise, the pentaphosphaferrocene $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ (**1**: $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)⁵ reacts with Cu^+ halides depending on the reaction conditions to different 1D and 2D polymers,^{3e,h,i} nano-sized fullerene-like spherical aggregates⁶ and a huge organometallic-based capsule.⁷ We therefore became interested in exploring the possibility to establish a novel class of organometallic–organic CPs using the *cyclo*- P_5 ligand complex **1** in combination with metal cations and organic linkers. Moreover, we targeted the synthesis of neutral hybrid networks instead of the already developed synthesis of cationic frameworks from the P_2 ligand complex **A**. Obviously, the Ag^+ or Cu^+ salts of WCA are no suitable candidates for such purposes as the voids in the resulting structures can be occupied by the counterions. Therefore, the use of coordinating anions such as Cl^- could be useful, as they can coordinate much more strongly to the metal centers leading to targeted networks with substantial (non-occupied) porosity. Herein, we report on the synthesis of the first pentaphosphaferrocene-based 2D neutral polymeric compounds. These unprecedented hybrid CPs are obtained from a three-component reaction of the pentaphosphaferrocene **1** in combination with the bipyridyl linkers 4,4'-bipyridine or 1,2-di(4-pyridyl)ethylene and CuCl . To the best of our knowledge, no other neutral organometallic–organic hybrid CPs has been yet reported.

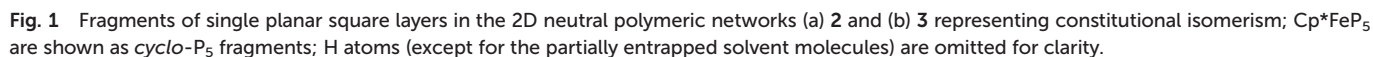
In a first approach, the *cyclo*- P_5 ligand complex **1** was reacted with CuCl and 4,4'-bipyridine in a 1 : 2 : 1 stoichiometry. This reaction afforded the products **2** or **3** as brown crystals in excellent yields (84% and 75%, respectively, see the ESI[†]), depending on the used solvent mixture. Compound **2** is obtained when a CH_2Cl_2 solution of **1** is slowly added to a $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2$ (1 : 1) solution mixture of CuCl and 4,4'-bipyridine, while compound **3** is isolated when a toluene solution of **1** is added to a $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2$ (1 : 1) solution mixture of CuCl and 4,4'-bipyridine. The compounds **2** and **3**, respectively, crystallize at room temperature from *n*-pentane (**2**) or toluene (**3**) diffusion into the solutions of the crude reaction mixtures, and their structures were examined by X-ray crystallography (see the ESI[†]). Their crystal structures reveal that the assemblies **2** and **3** represent unprecedented neutral 2D organo-

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In the crystal structure of network **2**, one *n*-pentane molecule is embedded in each of the small cavities of the rings and only partially occupies these cavities. These guest molecules are stabilized by CH $\cdots\pi$ interactions between the methylene hydrogens of the *n*-pentane molecules and the π clouds of the pyridyl moieties of the 4,4'-bipyridine linker (CH $\cdots\pi$ (pyridyl centroid) distance is 3.097(9) Å). Similarly, one CH₂Cl₂ molecule is partially embedded in each of the cavities of the rings of **3**. These CH₂Cl₂ molecules are stabilized by the Cl $\cdots\pi$ interactions between the chlorine atoms of the CH₂Cl₂ molecules and the π

The compounds 2-4 are only very slightly soluble in donor solvents such as CH₃CN but completely insoluble in other common organic solvents such as CH₂Cl₂, THF and *n*-pentane. Their room temperature ³¹P{¹H} NMR spectra in CD₃CN exhibit single signals at *ca.* 151 ppm, which are very similar to that of the free ligand complex **1** (152.2 ppm)^{3d} revealing a degradation of the polymeric structure in solution.

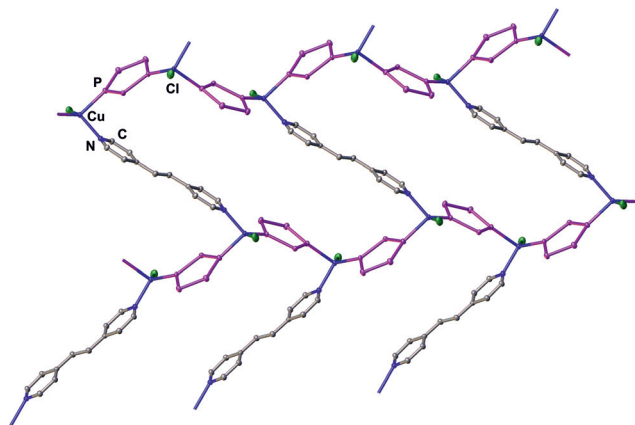


Fig. 2 Fragment of a single layer in the neutral 2D polymeric network **4**; Cp*FeP₅ are represented as *cyclo*-P₅ fragments; H atoms are omitted for clarity.

Conclusions

In conclusion, we have shown the possibility of using the pentaphosphaferrocene ligand complex (1) in a three-component reaction with CuCl and the bipyridyl linkers 4,4'-bipyridine or 1,2-di(4-pyridyl)ethylene to synthesize a new class of hybrid CPs. This new reaction allows the synthesis of three unique neutral 2D organometallic-organic hybrid CPs with different layer topologies. These results show the importance of this novel method using P_n ligand complexes for the synthesis of a new class of hybrid CPs. For the first time, the use of CuCl allows the approach to unprecedented neutral organometallic-organic hybrid CPs in which the meshes are only occupied by solvent molecules, in contrast to previously obtained cationic hybrid CPs with the anions in the voids. This finding opens up a new chapter in this chemistry. Current investigations involve the use of multitopic pyridine-based linkers to synthesize neutral 3D organometallic-organic hybrid networks as an analogy to the very well-studied class of neutral 3D metal organic frameworks (MOFs).

Conflicts of interest

There are no conflicts to declare.

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