Neutral two-dimensional organometallic–organic hybrid polymers based on pentaphosphaferrocene, bipyridyl linkers and CuCl†

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The reaction of the P₅ ligand complex [Cp*Fe(η⁵-P₅)] (1: Cp* = η⁵-C₅Me₅) 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 [Cu₂Cl₂(Cp*Fe(μ-η⁵-P₅))(μ-η⁵-C₅H₅N₂)]ₙ (2 and 3) and the coordination polymer [[CuCl₂(Cp*Fe(μ-η⁵-P₅))(μ-η⁵-C₅H₅N₂)]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 multioptic organic linkers usually bearing N, O or S donor atoms to metal ions or clusters.2e–g Due to the lack of using organometallic building blocks in this field,3–e our group developed an alternative concept by using organometallic phosphorus and polysericn 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 polysphosphorus ligand complexes, the tetrahedrane complex [Cp₂Mo₂(CO)₂(η⁵-P₅)] (Cp = C₅H₅) (A) was reacted with AgI and CuI salts of the weakly coordinating anions (WCA) Al[OC(CF₃)₃]₄−, and FaL[OC(C₆F₅)(C₆F₁₀)]₃− and the anion BF₄−, 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.

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metallic–organic hybrid polymers with the general formula \([\text{Cu}_2\text{Cl}_2\{\text{Cp}^*\text{Fe}[\mu_3-\eta^1-3\text{C}_10\text{H}_8\text{N}_2]\}_0]\) (Fig. 1).

Interestingly, the polymers 2 and 3 are constitutional isomers with a planar layered constitution providing different types of rings in the 2D polymeric arrangements (Fig. 1). Small (with a maximum dimension of 1.14 nm)\(^8\) and large (with a maximum dimension of 1.51 nm)\(^8\) rectangular rings in 2 and one-type trapezoidal rings (with a maximum dimension 1.34 nm)\(^8\) in 3 appear, depending on the coordination of the 4,4′-bipyridine linkers to one or the other Cu ion of the \([\text{Cu}_2\text{Cl}_2]\) dimer. In both kinds of these isomeric square \(\{\text{squ}\}\) layers 2 and 3, two \([\text{Cu}_2\text{Cl}_2]\) four-membered rings are bridged by a pentaphosphaferrocene molecule with the cyclo-P\(_5\) ligand adopting the 1,3-bridging mode and forming infinite chains. These chains are in turn connected via the 4,4′-bipyridine linkers coordinated to the copper atoms to give the final 2D structures. Consequently, each copper ion in 2 and 3 possesses a distorted tetrahedral coordination geometry \((2\text{Cl} + 1\text{P} + 1\text{N})\). The 4,4′-bipyridine linkers in the polymers 2 and 3 are well separated from each other (from \(\sim 7.9\ \text{Å}\) in 2 up to \(\sim 11.8\ \text{Å}\) in 3) and therefore do not show any intramolecular \(\pi\)–\(\pi\) stacking interactions. The P–P bond lengths in 2 and 3 are in the range between 2.101(3) and 2.120(5) Å, which is essentially consistent with those of the non-coordinated complex 1 (2.117 Å).\(^9\)

The Cu–P bond lengths in 2 and 3 are in the range between 2.173(5) and 2.184(5) Å.

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–\(\pi\) interactions between the methylene hydrogens of the \(n\)-pentane molecules and the \(\pi\) clouds of the pyridyl moieties of the 4,4′-bipyridine linker (CH–\(\pi\) (pyridyl centroid) distances are 3.318(4)–3.498(2) Å).

These results motivated us to expand these investigations by using the slightly longer linker 1,2-di(4-pyridyl)ethylene. The reaction of 1 with CuCl and 1,2-di(4-pyridyl)ethylene in a 1 : 2 : 1 stoichiometry leads to the formation of compound 4 as brown blocks in moderate yield (40%, see the ESI†) suitable for single crystal X-ray structure analysis. Compound 4 is a novel neutral 2D organometallic–organic hybrid polymer of the formula \([\{\text{CuCl}_2\}(\text{Cp}^*\text{Fe}[\mu_3-\eta^1-3\text{P}_5])_2(\mu_3-\eta^1-3\text{C}_12\text{H}_{10}\text{N}_2)]_0\). The stoichiometry of the building blocks in the resulting polymer 4 is different from that of the used starting materials. Polymer 4 is also obtained in a similar yield upon using a 2 : 2 : 1 stoichiometric ratio of 1, CuCl and 1,2-di(4-pyridyl)ethylene. In 4, the \([\text{CuCl}_2]\) units are connected by the organic linkers in contrast to the \([\text{Cu}_2\text{Cl}_2]\) rings in 2 and 3 and therefore give honeycomb layers (hcb topology) (Fig. 2). Owing to the doubled stoichiometric amount of pentaphosphaferroocene spacers in 4 as compared to 2 and 3, larger rings are formed with a maximum dimension of 2.24 nm, which are left empty in this solvent-free structure.\(^8\) As a result, \(\pi\)–\(\pi\) stacking occurs between the almost parallel \(\text{Cp}^*\) ligands of 1 and the planar 1,2-di(4-pyridyl)ethylene linkers with interplanar distances of 3.47–3.54 Å (cf. ESI†), in contrast to the polymers 2 and 3 where no such \(\pi\)–\(\pi\) stacking is observed.

The P–P bond lengths in 4 are in the range between 2.105 (2) and 2.115(8) Å, comparable to those of the non-coordinated ligand 1 and the polymers 2 and 3. The Cu–P bond in 4 (2.210 (9) Å) is slightly elongated compared to those in 2 and 3.

The compounds 2–4 are only very slightly soluble in donor solvents such as CH\(_2\)CN but completely insoluble in other common organic solvents such as CH\(_2\)Cl\(_2\), THF and \(n\)-pentane. Their room temperature \(^31\text{P}(^1\text{H})\) NMR spectra in CD\(_2\)CN exhibit single signals at ca. 151 ppm, which are very similar to that of the free ligand complex 1 (152.2 ppm)\(^{10}\), revealing a degradation of the polymeric structure in solution.
Conclusions

In conclusion, we have shown the possibility of using the pentaphosphorous ferrocene 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 P₅ 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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Notes and references


8 Calculated from the largest distance between the Cu⁺ ions minus the doubled ionic radius of Cu⁺ for the coordination number 4 (0.74 Å).