



Cite this: *Dalton Trans.*, 2018, **47**, 1014

Received 13th November 2017,

Accepted 8th December 2017

DOI: 10.1039/c7dt04286h

rsc.li/dalton

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

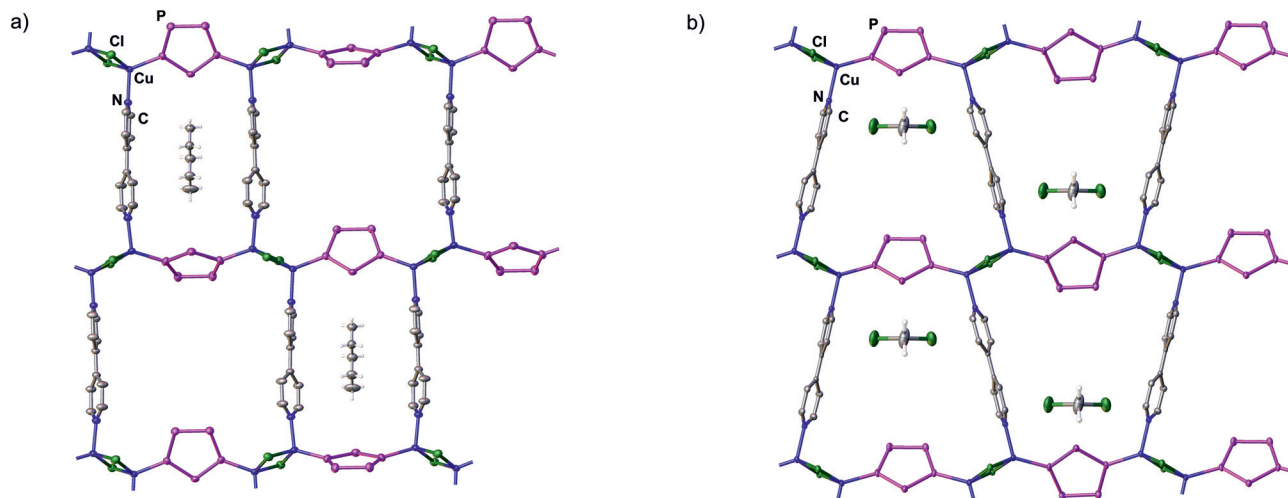
In a first approach, the *cyclo*- P_5 ligand complex **1** was reacted with CuCl and 4,4'-bipyridine in a 1 : 2 : 1 stoichiometry. This reaction afforded the products **2** or **3** as brown crystals in excellent yields (84% and 75%, respectively, see the ESI[†]), depending on the used solvent mixture. 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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[†]Electronic supplementary information (ESI) available: Details of syntheses, characterization and X-ray crystallography. CCDC 1583104–1583106. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt04286h



metallic-organic hybrid polymers with the general formula $[\text{Cu}_2\text{Cl}_2\{\text{Cp}^*\text{Fe}(\mu_3, \eta^{5:1:1}\text{-P}_5)\}(\mu, \eta^{1:1}\text{-C}_{10}\text{H}_8\text{N}_2)]_n$ (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 Cu₂Cl₂ dimer. In both kinds of these isomeric square (**sql**) layers 2 and 3, two [Cu₂Cl₂] four-membered rings are bridged by a pentaphosphaferrocene molecule with the *cyclo*-P₅ 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 Cl + 1 P + 1 N). The 4,4'-bipyridine linkers in the polymers 2 and 3 are well separated from each other (from ~7.9 Å in 2 up to ~11.8 Å in 3) and therefore do not show any intramolecular π - π 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 $\cdots\pi$ 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

clouds of the pyridyl moieties of the 4,4'-bipyridine linker (Cl... π (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 $[(\text{CuCl})_2\{\text{Cp}^*\text{Fe}(\mu_3, \eta^{5:1:1}\text{-P}_5)\}_2(\mu, \eta^{1:1}\text{-C}_{12}\text{H}_{10}\text{N}_2)]_n$. 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 [CuCl] 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 pentaphosphaferrocene 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, π - π stacking occurs between the almost parallel 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 π - π 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 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.

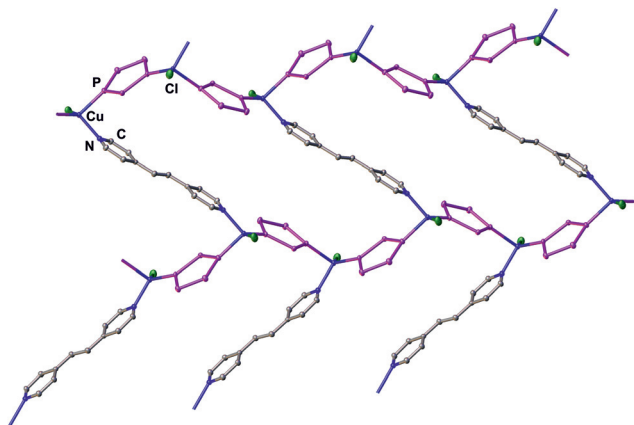


Fig. 2 Fragment of a single layer in the neutral 2D polymeric network 4; Cp*FeP₅ are represented as *cyclo*-P₅ fragments; H atoms are omitted for clarity.

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.

Acknowledgements

This work was comprehensively supported by the European Research Council by Grant ERC-2013-AdG 339072. The COST action CM 1302 (SIPs) is gratefully acknowledged.

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