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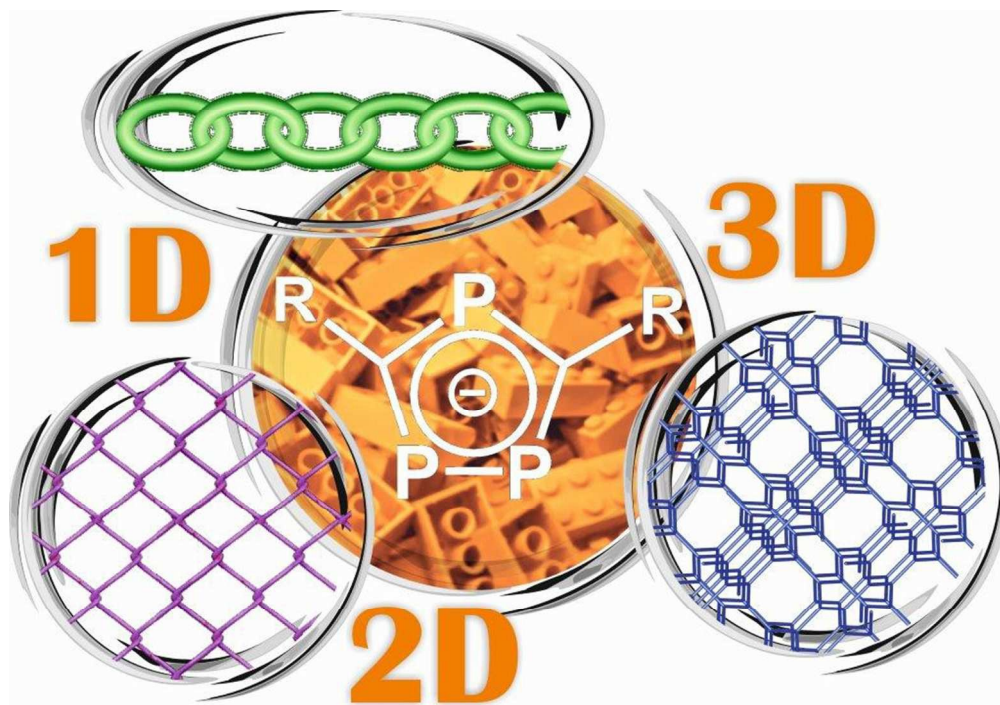
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ARTICLE

1,2,4-Triphospholyl Anions – Versatile Building Blocks for the Formation of 1D, 2D and 3D Assemblies

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The potential of $K[P_3C_2R_2]$ ($R = {}^t\text{Bu}, \text{Mes}$) as building blocks in Metallo-Supramolecular chemistry was investigated and self-assembly processes with Cu(I) halides result in the formation of a large variety of unprecedented one-, two- and even three-dimensional aggregates. The 3D networks show an interesting topological similarity to allotropes of carbon: diamond and the theoretically proposed polybenzene. Furthermore, the negative charge of the phospholyl ligand favours the generation of cationic Cu_aX_b ($a > b$, $X = \text{Cl}, \text{Br}, \text{I}$) assemblies, a challenging area within the well-studied coordination chemistry of CuX units. In addition, the 1D strands were also characterized in solution, revealing that oligomeric units are present.

Introduction

Self-assembly processes and metal-organic frameworks (MOFs) became indispensable principles in Supramolecular and Coordination Chemistry as well as in Crystal Engineering.¹ The spontaneous organization of small building blocks to large assemblies by non-covalent interactions is not only of fundamental interest, but also suited for the development of new materials with defined and tunable properties. Especially the involvement of coordinative bonds in Metallo-Supramolecular Chemistry offers numerous benefits, since they are relatively strong, but often weak enough to show dynamic behaviour. The variety of the used ligands is large, however, the nature of the donor atoms is mostly limited to oxygen, nitrogen or sulphur. So far phosphorus as donor atom played only a minor role, opening a field of broad perspectives. A selection of building blocks based on phosphorus as donor atoms is displayed in Figure 1. Especially phosphaferrrocenes and CuX ($X = \text{Cl}, \text{Br}, \text{I}$) turned out to be a great combination for the construction of monomeric,² oligomeric,³ polymeric^{3,4} and even spherical⁵ coordination compounds. This vast abundance of results can be partially traced back to the variability and flexibility of the coordination behaviour of Cu halides.⁶ Despite this, two aspects still display challenging areas: Firstly, though innumerable neutral and anionic aggregates are reported in literature, cationic Cu_aX_b ($a > b$) assemblies occur only sporadically. Secondly, the formation of 1D strands or 2D networks is well known, though the isolation of 3D

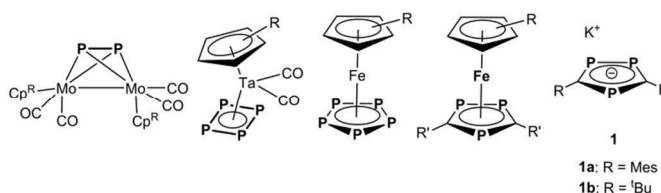


Fig. 1 Selected building blocks for metallo-supramolecular chemistry based on phosphorus as donor atoms.

assemblies with phosphorus as donor atom was only possible in very rare cases. To the best of our knowledge, the only examples of 3D aggregates are built up by inorganic cage molecules⁷ or an organic linker containing a PPh_3 group.⁸ However, especially in view of future usage such as gas storage and catalytic activities, three-dimensional aggregates seem to be the most promising candidates.

Recently we reported on an unexpected fragmentation of the triphosphaferrrocene $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{Mes}_2)]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{Mes} = 2,4,6\text{-trimethylphenyl}$) into $[\text{Cp}^*\text{Fe}]^+$ and $[\text{P}_3\text{C}_2\text{Mes}_2]^-$ moieties, when reacting it with CuX ($X = \text{Cl}, \text{Br}, \text{I}$).⁹ The remaining phospholyl ligands $[\text{P}_3\text{C}_2\text{Mes}_2]^-$ serve as building blocks for a variety of coordination compounds with rare or even novel structural motifs (Figure 2a-c). Due to the negative

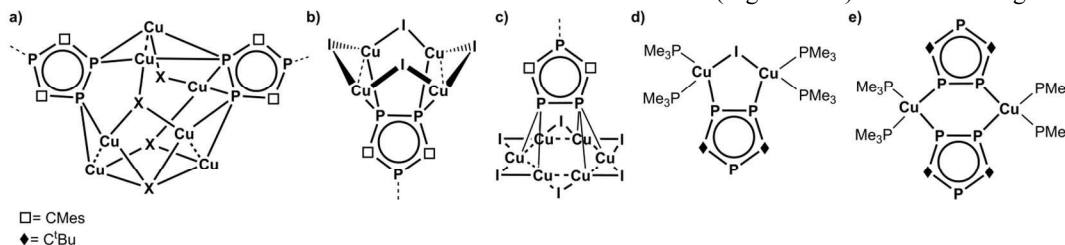
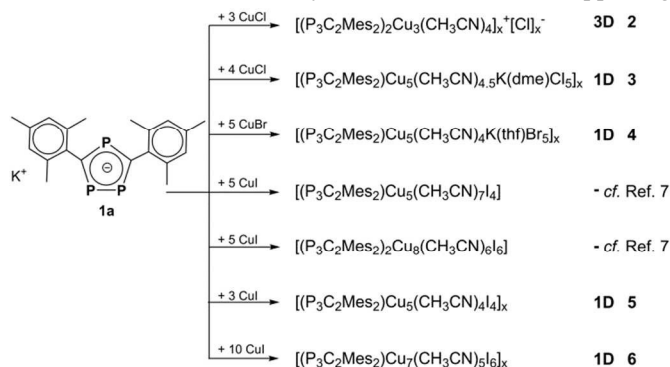


Fig. 2 Selected coordination compounds containing triphospholyl ligands and Cu(I) halides.

charge of this ligand, a buildup of cationic Cu_nX_m aggregates is predetermined. Since the synthesis of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{Mes}_2)]$ starts from $[\text{K}(\text{P}_3\text{C}_2\text{Mes}_2)]$, FeBr_2 and LiCp^* ,¹⁰ the question arose, if the detour of its synthesis and subsequent fragmentation can be avoided. Therefore, we were interested in the use of $[\text{K}(\text{P}_3\text{C}_2\text{Mes}_2)]$ itself as a building block. In the literature, the use of 1,2,4-triphospholyl salts $[\text{Q}(\text{P}_3\text{C}_2\text{R}_2)]$ ($\text{Q} = \text{Li}, \text{K}$; $\text{R} = \text{Mes}, \text{tBu}, \text{Ph}$) was primarily made for the preparation of the sandwich complexes tri- and hexaphosphametalloenes¹¹ or for coupling reactions resulting in phosphorus rich cage compounds.¹² Investigations concerning its coordination chemistry towards coinage metal salts are rare and mostly started not from its potassium or lithium salts, but by its neutral trimethylstannyl-triphosphole derivatives.¹³ Only Nixon *et al.* treated $[\text{K}(\text{P}_3\text{C}_2\text{tBu}_2)]$ with Et_3PAuCl and $\text{Cu}_2\text{I}_2/\text{PMe}_3$, respectively, and obtained monomeric (for Cu see: Figure 2d) or dimeric products (for Cu see: Figure 2e).¹⁴ In these reactions the presence of the ligands PEt_3 and PMe_3 , respectively, impedes further aggregation. Herein we report on the self-assembly process of $[\text{K}(\text{P}_3\text{C}_2\text{Mes}_2)]$ (**1a**) with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) yielding the monomeric compounds $[(\mu, \eta^1: \eta^2: \eta^2\text{-P}_3\text{C}_2\text{Mes}_2)\{\text{Cu}(\text{CH}_3\text{CN})(\mu\text{-I})\}_4\{\text{Cu}(\text{CH}_3\text{CN})\}_3]$ and $[(\mu, \eta^1: \eta^3: \eta^3\text{-P}_3\text{C}_2\text{Mes}_2)_2\{\text{Cu}(\text{CH}_3\text{CN})\}_2\{\text{Cu}(\mu\text{-I})\}_6]$, the 3D network **2** as well as the 1D polymers **3**, **4**, **5**, **6** (Scheme 1). Furthermore, by using the ^tBu derivative $[\text{K}(\text{P}_3\text{C}_2\text{tBu}_2)]$ (**1b**) the 1D polymer **7**, the 3D aggregates **8** and **9** and the 2D network of **10** (Scheme 2) could be isolated.

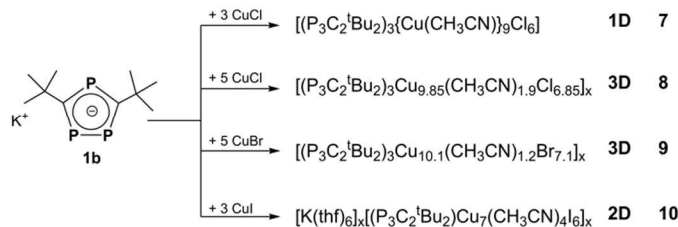
Results and Discussion

Reactions of **1** with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were carried out by two different approaches: a yellow to orange solution of **1** in thf or dme can either be layered with a colourless solution of CuX in CH_3CN or both solutions are stirred together. In all cases an immediate colour change to deep red can be observed. Depending on the presence and amount of CH_3CN , concentration, molar ratio, crystallisation conditions and the R group in the phospholyl ligand ($\text{R} = \text{Mes}, \text{tBu}$), a variety of different products can be isolated (Scheme 1 and Scheme 2), even with the same halide. In these cases the compounds generally crystallize separately and not as mixtures, therefore a selective synthesis is possible in most instances (for detailed conditions see below and the SI). In doing so, the stoichiometric amount of CuX is the most significant factor for a directed synthesis, as it can be seen in Scheme 1 and 2. Furthermore, all crystal structures contain additional solvent molecules, which are only discussed in the supporting



Scheme 1 Reactions of **1a** with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

information in detail. Since several coordination compounds containing **1a** exist due to the fragmentation of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{Mes}_2)]$,⁹ the question arises, if they can also be synthesized using **1a** as starting material. Indeed, with CuI two known products can be obtained. Both are monomeric compounds, the first with a Cu_4I_4 unit forming a crown-like structural motif (Figure 2b), the other with a Cu_6I_6 six-point star-like arrangement, which is coordinated by one phospholyl ligand from each side (Figure 2c). But surprisingly, these two represent the only previously observed examples. In fact, a great pool of novel coordination polymers with different structural motifs is obtained and is described in the following. One common feature among them is the coordination of all three phosphorus atoms of the triphospholyl ring to form polymeric aggregates. Furthermore, CuCl and CuBr tend to form isotypical compounds (*cf.* compound **3** and **4** and **7** and **8**, respectively), whereas CuI -containing frameworks often differ in their structural motif. Another determining factor is the substitution pattern in the phospholyl ligand. The sterically demanding Mes ligand almost exclusively leads to the formation of 1D strands with compound **2** as an exceptional case. In contrast, smaller ^tBu groups allow the aggregation in all directions. In addition, compounds **2-9** show short $\text{X}\cdots\text{H}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) distances ($< \sum_{\text{vdW-radii}}$) with methyl groups of acetonitrile and the R group ($\text{R} = \text{Mes}, \text{tBu}$) and therefore weak interactions within the chain or layer as well as between them are indicated (for pictures see SI). In the following, the obtained products are described in their dimensionality.



Scheme 2 Reactions of **1b** with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

One-dimensional polymers (3-7)

The mesityl group in **1a** exhibits a high steric demand, so that an aggregation in one direction is feasible and preferred. Surprisingly, most of the products (**3-6**) show the structural motif of an eight membered Cu_4X_4 ring. Its distortion and close $\text{Cu}\cdots\text{Cu}$ contacts lead to a crown-like arrangement (Figure 2b and Figure 3, left). This is so far only known for $\text{X} = \text{I}$,¹⁵ and here it is rather unusual, since $(\text{CuI})_4$ units tend to form heterocubanes or ladders.⁶

Hence, **3** and **4** display the first examples for the Cl- and Br-derivative of this structural motif, respectively. Compound **3** can be isolated as yellow-orange prisms in good yields (57%), compound **4** as yellow-orange blocks in very good yields (88%). Compounds **3** and **4** both crystallize as solvates in monoclinic space groups (**3**: $P2_1/n$, **4**: $C2/m$) and display isotypical compounds (Figure 3a-d). The Cu_2 -dimers in the formed crown show a distance of 2.545(1) and 2.553(1) Å for **3** and 2.548(1) Å for **4**. They are coordinated by the adjacent P atoms of **1a** with bond lengths of 2.274(1) – 2.296(1) Å in **3** and 2.280(1) – 2.294(1) Å in **4**, respectively. The halides additionally interact with a potassium centered above the 'crown' ($\text{K}\cdots\text{Cl}$: 3.080(2) – 3.179(2) Å; $\text{K}\cdots\text{Br}$: 3.210(1) – 3.344(1) Å). The coordination sphere is completed by two additional thf (in **3**) or dme (in **4**) molecules. These solvent

ligands exhibit a bridging coordination mode and therefore connect two $[(P_3C_2Mes_2)(Cu_4X_4)]$ units. The aggregation is accomplished by a Cu_2X_2 four-membered ring, which is coordinated by isolated P atoms of **1a** from each side. These four-membered rings are severely disordered over two (in **3**) up to eight (in **4**) positions around the direction of the chain and in some positions the Cu atoms are additionally coordinated by CH_3CN , therefore some of them show a trigonal, some a tetrahedral environment (see SI).

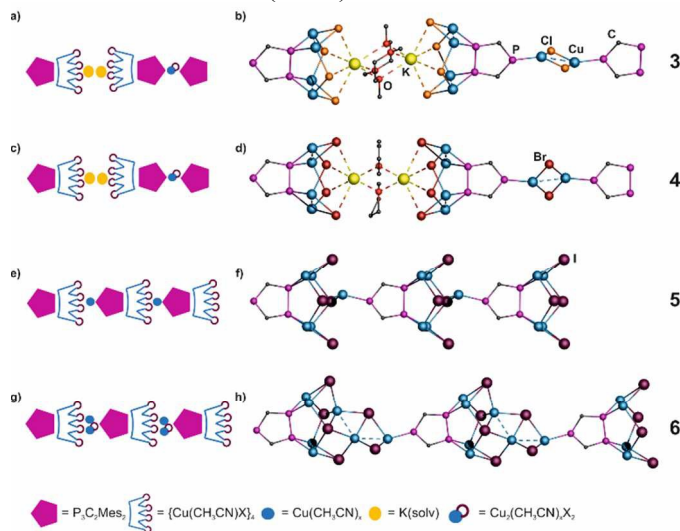


Fig. 3 left: Schematic representations of the structures of a) **3**; c) **4**; e) **5** and g) **6**; right: Sections of the polymeric structures of b) **3**; d) **4**; f) **5** and h) **6**. Mesityl and CH_3CN ligands, H atoms, solvents and minor positions of disordered groups are omitted for clarity.

Using CuI , two slightly different 1D polymers (**5**, **6**) were isolated (Figure 3e-h). Compound **5** crystallizes as red-brown blocks in the tetragonal space group $P4/n$, compound **6** as orange lath-shaped crystals in the triclinic space group $P\bar{1}$. The Cu_4I_4 arrangement is similar to **3** and **4** with close $Cu\cdots Cu$ distances (**5**: 2.541(4) Å; **6**: 2.523(2) Å) and $Cu-P$ bond lengths (**5**: 2.277(5) – 2.319(6) Å; **6**: 2.285(2) Å – 2.319(2) Å). In **5**, this unit is polymerized into a 1D chain by one additional Cu, coordinated by the isolated P atom of **1a** ($P-Cu$ 2.249(6) Å) and two I-tips of the ‘crown’ (Figure 3e, f).

The diffraction pattern of **5** shows quite strong diffuse scattering (see SI) caused by correlated disorder of the $\{Cu_5I_4(CH_3CN)_4(P_3C_2Mes_2)\}$ repeating units within the polymeric chain. Our attempts to model this effect allowed us to suppose that there is the strong negative correlation (alternation of repeating units’ rotations) within the polymeric chains together with the weaker negative correlation between neighboring chains (see SI for details).

In contrast, in **6** a Cu_3I_2 fragment serves as linkage between the top of the crown and the third P atom of the phosphohyl ligand ($P-Cu$ 2.214(2) Å) (Figure 3g, h). The formation of **5** and **6** is remarkable, since the reaction of $[Cp^*Fe(\eta^5-P_3C_2Mes_2)]$ and CuI also gives a 1D polymer containing the same structural motif, but polymerized via a Cu_3I_2 five-membered ring. So, these results again demonstrate the structural variability of the $Cu(I)$ halides, especially of CuI . The orientation of **1a** in **5** and **6** is the same along the chain, while in **3** and **4** they show an alternating orientation. Note, that the Cu_nI_m assembly is positively charged in both polymers, namely $[Cu_5I_4]^+$ in **5** and $[Cu_7I_6]^+$ in **6**. Thus, these examples expand the small and unexplored area of cationic Cu_nX_m clusters. The reason for their formation can most probably be traced back to the use of the

negatively charged triphosphohyl ligand. This approach was also used in two other examples, in which anionic triazolate and tetrazolate linking units were used, respectively.¹⁶

Summing up the results of the reaction of **1a** with CuI , four different coordination compounds are obtained. Fortunately, a selective synthesis can be controlled mainly by stoichiometry. For example, an excess of copper iodide (**1a**: Cu = 1:10) leads to the crystallization of solely compound **6**, which is in agreement with the highest molar ratio of Cu in **6** (**1a**: Cu = 1:7). In contrast, the monomeric compound with the Cu_6 star-like arrangement (Fig. 2c) contains the lowest molar ratio of Cu (**1a**: Cu = 1:4) and can therefore be obtained, when less equivalents of CuI are used. However, not all attempts to reproduce polymer **5** were successful, most likely due to the preferred crystallization of its monomeric derivative (Fig. 2b) with the exact same molar ratio (**1a**: Cu = 1:5). Also the variation of concentration and solvent were not successful in all of the attempts.

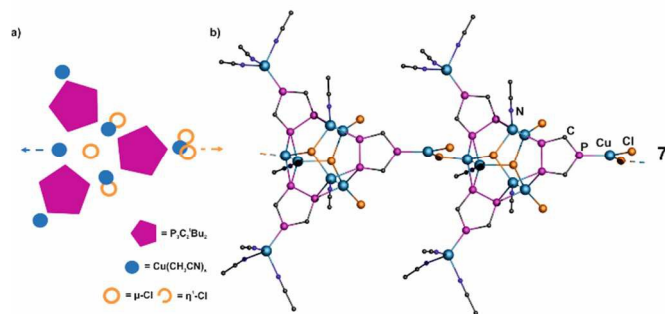


Fig. 4 a) Schematic representation of the structure of **7** b) Section of the polymeric structure of **7**. t Bu ligands, H atoms, solvents and minor positions of disordered CH_3CN are omitted for clarity.

The 1D polymer **7** crystallizes as orange plates in the monoclinic space group $P2_1/m$ and reveals a different structural motif than the other 1D polymers, since it contains **1b** as building block and it also differs by the general structural motif. Due to the lower steric demand of the t Bu group, the arrangement of three phosphohyl rings close to each other is possible. They are connected by three Cu_2 -dimers ($Cu\cdots Cu$ 2.482(1) – 2.496(1) Å), which form a triangular prism ($P-Cu$ 2.325(1) – 2.361(1) Å). The prism is capped by two μ_3-Cl with $\mu_3-Cl-Cu$ 2.390(1) – 2.441(1) Å bond lengths. Each Cu atom additionally coordinates either Cl^- or CH_3CN moieties to reach a tetrahedral environment. Two of these three halides are terminal ($\eta^1-Cl-Cu$ 2.231(1) Å), while the third coordinates another copper atom ($\mu_2-Cl-Cu$ 2.279(2) – 2.300(2) Å), which is in turn bound to an isolated P atom of **1b**. The remaining P atoms of the other two ligands prevent polymerization in other directions by coordination of terminal $Cu(CH_3CN)_3$ units ($Cu-P$ 2.191(2) Å). Therefore, compound **7** displays a 1D polymer. The central assembly with 7 Cu^+ and 6 Cl^- can be regarded as an isomeric unit to the assembly in **6** and is another unprecedented example of a cationic Cu_nX_m unit.

Two-dimensional assembly (**10**)

Starting from **1b** and CuI as building blocks occasionally the 2D network **10** can be isolated. Compound **10** crystallizes as dark red brown blocks in the orthorhombic space group $Pbcn$. In **10**, a central Cu_5 -ring with $Cu\cdots Cu$ distances in the range from 2.540(4) – 2.796(4) Å is coordinated from each side by two units of **1b**, which are perpendicular to each other ($Cu-P$

2.256(5) – 2.564(5) Å (Fig. 5a,b). Four Cu atoms are part of two Cu₃I₂-rings, a building unit, which also occurs in **8** and **9**. The coordination sphere of the remaining Cu is saturated by two μ₂-I ligands (Cu-I 2.483(3) – 2.650(3) Å), hence a tetrahedral environment results for each copper atom. Aggregation takes place by the coordination of the isolated P atom of **1b** to the isolated Cu atom of the perpendicular Cu₃I₂ ring via a relatively short Cu-P bond of 2.215(5) Å. Through the propagation in four directions within the layer a mesh-like structure is formed (Fig. 5c). Furthermore, **10** also displays an unprecedented representative for a cationic copper halide aggregate, since 7 Cu⁺ and 6 I⁻ are present in the repeating unit. In total, the combination with two units of **1b** even leads to an anionic assembly, which is balanced by K(thf)₆⁺ cations embedded in the meshes and separating the layers from each other (for pictures see SI). Together with the ^tBu groups of **1b** the meshes do not provide free space. Due to the alternating arrangement of cationic and anionic ‘layers’ no short I⋯H distances can be found in the crystal structure of **10**.

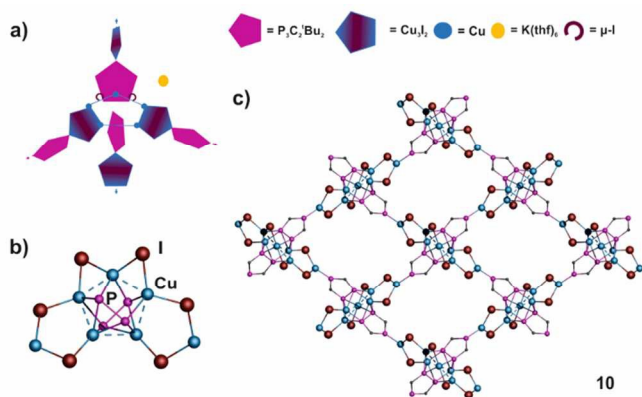


Fig. 5 a) Schematic representation of the structure of **10** b) Core motif of **10** c) Section of the 4-connected anionic polymer network of **10**. ^tBu and CH₃CN ligands, H atoms, solvents and counterions are omitted for clarity.

Three-dimensional networks (**2**, **8**, **9**)

Surprisingly, from the reaction of **1a** with CuCl as a second product also the 3D polymer **2** can be isolated, despite the sterically demanding Mes group. Since they differ significantly in their Cu content, a directed synthesis is enabled by using different stoichiometry. More than three equivalents CuCl lead to the formation of **3** (**1a**:Cu = 1:5), whereas three or less equivalents of CuCl result in the crystallisation of **2** (**1a**:Cu = 1:1.5).

Compound **2** crystallizes as red blocks in the tetragonal space group *I*4₂*d* (see also SI). The repeating unit contains four phospholyl ligands **1a**, whose adjacent P atoms are connected via two Cu₂ dimers (Cu⋯Cu 2.555(2) Å; P-Cu 2.181(4) – 2.503(5) Å) (Fig. 6a-c). Hence, this is the only assembly, whose central core structure does not include a halide and is built up only by **1a** and Cu units. The linkage of the remaining P atoms of the phospholyl rings by Cu(CH₃CN)₂ leads to a polymeric structure. Charge balance is afforded by the presence of an uncoordinated Cl⁻ per repeating unit (4 **1a**⁻, 5 Cu⁺, 1 Cl⁻). In addition, this core acts as a tetrahedral node and induces a propagation in the other two dimensions, resulting in a 3D network (Fig. 6e-f). Its net topology can be assigned to the **dia**

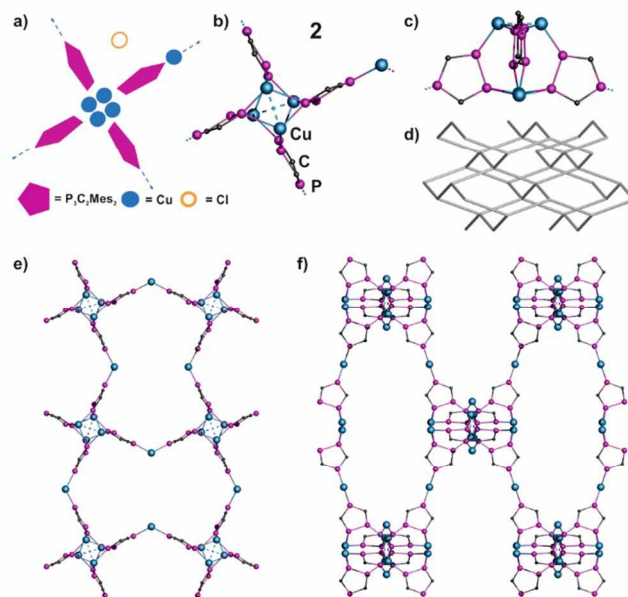


Fig. 6 a) Schematic representation of the structure of **2** b) Central structural motif of **2** (top view) c) Central motif of **2** (lateral view) illustrating the tetrahedral nodes d) fragment of the **dia** net e) Sections of the cationic polymer network of **2**. View along the e) c-axis, f) a-axis. Mes and CH₃CN ligands, H atoms, counterions and solvents are omitted for clarity.

type (Fig. 6d).¹⁷ Hence, it shows topological similarity with diamond, which gives this net its name.

Also with R = ^tBu in **1b** the formation of three dimensional networks is observed. When a solution of **1b** in dme is layered with a solution of CuX (X = Cl, Br), at the phase boundary the formation of big dark red blocks of **8** (X = Cl) and **9** (X = Br), respectively, can be observed already after one day. Both compounds are isotypical and crystallize in the cubic space group *F*4₃*c*. However, their core structures turned out to be severely disordered. The crystal structure of **9** is more ordered (see SI for details), therefore it will be described first. The central structural motif of **9** contains three Cu₂-dimers and the adjacent P atoms of three units of **1b**, which are arranged according to a distorted hexagonal P₆Cu₆ prism (Cu⋯Cu 2.694(1) – 2.783(2) Å; Cu-P 2.298(2) – 2.620(2) Å) (Fig. 7a-c). This prism is capped by copper on one side and by a CuBr unit on the other one. In addition, each Cu₂-dimer is a component of a Cu₃Br₂ five-membered ring (similarly to **10**). This description is the case for 87% of **9**, whereas in its minor part (13%) the μ₃-Br coordinates an additional Cu(CH₃CN)₃ unit, and some Br positions are replaced by acetonitrile ligands (cf. SI). In **8**, the disorder is similar and the major part remains the same as in **9**. However, different occupation factors and additional Cu deficiencies make its description more complicated and are explained in detail in the SI. In total, the differences in the occupation factors of the disordered fragments for **8** and **9** and the requirement of a charge balance lead to the sum formulae [(P₃C₂^tBu₂)₃Cu_{9.85}Cl_{6.85}(CH₃CN)_{1.9}]_x for **8** and [(P₃C₂^tBu₂)₃Cu_{10.1}Br_{7.1}(CH₃CN)_{1.2}]_x for **9**.

Interestingly, the core of both compounds **8** and **9** is preceded stellar-like to give a 6-connected 3D network (Fig. 7a,b). It demonstrates the topological similarity with one of the theoretically possible allotropes of carbon, so-called polybenzene or cubic graphite (Fig. 7e). The polybenzene

structure can be derived from a benzene molecule if every hydrogen atom is replaced by a phenyl ring, in which every hydrogen atom is in turn replaced by a phenyl ring, *etc* (Fig. 7e).^{18,19} This structure was first predicted by Gibson *et al.* in 1946.²⁰ The calculations based on first-principles molecular dynamics showed that this carbon allotrope should be quite stable, but so far no synthetic approach was found.¹⁹

If one treats the phenyl ring as a ‘node’ of the framework, the resulting 6-connected 3D net belongs to the **h_{xg}** topological type (Fig. 7d),²¹ the same as the found 3D framework in **8** and **9** irrespective of any disorder. Eight other crystal structures of coordination polymers retain the same topological type (see SI). In these complexes the $\{M_3(\mu_3-O)\}^{4+}$ or $\{M_3(\mu_3-OH)\}^{5+}$ units ($M^{2+} = Cu^{2+}, Ni^{2+}$) joint to each other by N-heterocyclic bridging ligands like 1,2,4-triazolate,²² 5-(4-pyridyl)tetrazolate,²³ or pyrazole-4-carboxylate.²⁴ Interestingly, all structures crystallize or are described in cubic space groups, $Fd\bar{3}c$ ($\{M_3(\mu_3-O)\}$ - or $\{M_3(\mu_3-OH)\}$ -based polymers), $Pn\bar{3}m$ (polybenzene) and $F\bar{4}3c$ (**8** and **9**).

Whereas crystals of **2** decompose rapidly in air, the crystals of **8** and **9** turned out to be extremely stable. They were kept in air during two years, intriguingly without losing crystallinity. An repeated elemental analysis of **9** and X-ray diffraction experiments of **8** and **9**, respectively, proved the identical composition and excluded oxidation.

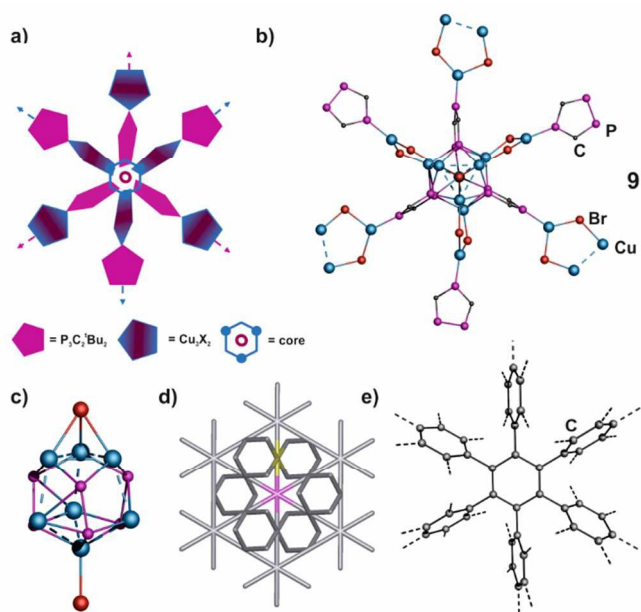


Fig. 7 a) Schematic representation of the structure of **8** and **9**. b) Section of the polymeric structure of **9**. ^tBu and CH₃CN ligands, H atoms, solvents and minor positions of disordered fragments are omitted for clarity. c) Major part of the central core motif in **9** (87%) d) Fragment of the **h_{xg}** net with mutually tilted 6-connected nodes marked in magenta and yellow e) Section of the polymeric structure of polybenzene (simulated).

Since the combination of CuCl and **1b** leads to two different compounds (**7** and **8**), the conditions of a directed synthesis were investigated. In this case the used method turned out to be of importance. Since **7** is soluble, it can be isolated from stirring experiments, while diffusion methods exclusively lead to the crystallization of the completely insoluble polymer **8** at the phase boundary. As a supporting factor, a higher molar ratio is used for the synthesis of **8** (**1b**:Cu = 1:5).

Characterization in solution

All received compounds are insoluble in common solvents like hexane, toluene, Et₂O, thf, dme and CH₂Cl₂. Only the 1D polymers (**3-7**) are soluble in CH₃CN to give yellow to deep red solutions. If a coordination to Cu (nuclear spin I = 3/2) is still present in solution one would expect two broad signals in the corresponding ³¹P{¹H} NMR spectra. This is the case for **6** and **7**. The signals of **6** appear at δ = 136 and 222 ppm with the integral ratio of 2:1 for the adjacent and the isolated P atoms of the phospholyl ring, respectively. In comparison with the salt **1a** (δ = 261.7 ppm (t, 1P) and 266.4 ppm (d, 2P)), both signals are shifted to higher field. Interestingly, the adjacent phosphorus atoms show a much more intensive shift (130 ppm) than the isolated one (40 ppm) so that the order of the signals is inverted. In contrast, the signals of the adjacent P atoms of **1b** (δ = 246.3 ppm (d)) are shifted to higher field than the isolated one (δ = 254.9 ppm (t)), which is reversed in comparison with **1a**. However, in **7** this trend does not occur and the signals of **7** (δ = 137 (2P) and 264 (1P) ppm) appear in the same order like in the spectra of **1a** and **6**. Hence, the signal of the isolated phosphorus shows a slight downfield shift of 11 ppm, whereas the signal of the adjacent P atoms is strongly upfield shifted by 109 ppm.

In contrast, the ³¹P{¹H} NMR spectrum of **3** shows only one small broad signal at 205 ppm, so Cu remains coordinated to the phospholyl ligand in solution. The lack of a second signal might be a hint of the equivalence of the P atoms. However, a more likely reason is the disappearance of the other signal below the noise floor due to its broadness, since the quality of the spectrum is due to the bad solubility already quite poor.

Surprisingly, the ³¹P{¹H} NMR spectrum of the isotypical compound **4** shows three signals. Due to the identical shift the signal at δ = 138 ppm it can be assigned to the isolated P atom of the phospholyl ligand. The other two signals appear at 204 and 217 ppm, respectively. This indicates the presence of two different species in the ratio of 3:1. The signals might be attributed to a smaller, monomeric and a larger, oligomeric unit, like it was observed for other phospholyl-based polymers.⁹

The size of the aggregate in solution cannot be derived from the NMR spectra, though hints for at least oligomeric units are also given by mass spectrometry. The corresponding cationic ESI mass spectra show fragments up to [(P₃C₂Mes₂)₄Cu₁₁Cl₆]⁺, [(P₃C₂Mes₂)₄Cu₁₀Br₅]⁺, [(P₃C₂Mes₂)₄Cu₁₀I₅]⁺ and [(P₃C₂^tBu₂)₇Cu₁₆Cl₈]⁺, respectively.

The 2D and 3D networks are insoluble even in CH₃CN. However, its analysis by ESI mass spectrometry was able for **2** and **9** after sonication, which leads to a degradation of the 3D network. The corresponding spectra look almost the same like the above mentioned ones with [(P₃C₂Mes₂)₅Cu₈Cl₂]⁺ as the biggest fragment for **2** and [(P₃C₂^tBu₂)₇Cu₁₇Br₉]⁺ for **9**.

Furthermore, solutions of the polymeric compounds **2**, **4**, **7-9** as well as the monomeric assembly [(P₃C₂Mes₂)₄{Cu(CH₃CN)(μ₂-I)}₄{Cu(CH₃CN)₃}] in CH₃CN were analysed by UV-vis spectroscopy, revealing partially overlapping absorption bands (for details and spectra see SI). However, a dependency of the dimensionality of the network or the halide cannot be deduced. In the contrary, a relation between the R group is indicated, since all solutions of the mesityl derivatives are red in colour with an absorption band at λ = 532 nm, whereas the ^tBu substituted assemblies give yellow solutions. Moreover, these results are in agreement with the above discussed depolymerisation behaviour of the products in donor solvents like CH₃CN.

Conclusions

In summary, the triphospholyl ligands **1a** and **1b** were introduced as building blocks in Supramolecular Chemistry. The self-assembly processes with CuX (X = Cl, Br, I) lead to the formation of unprecedented polymeric networks. The negative charge of the cyclic ligand favours the aggregation of cationic Cu_aX_b (a > b) assemblies, which were so far only rarely known. The 1D strands in **3-6** show a rather uncommon crown-like arrangement. The 2D network of **10** is comparable with a wire-mesh. Even the selective synthesis of three dimensional aggregates is possible, all of them with an interesting structure. The net of **2** reveals tetrahedral nodes and a resulting **dia**-topology and is therefore related to diamond. Furthermore, the star-like build-up of compounds **8** and **9** can be assigned to the **hxxg**-topology, hence it shows structural analogy to 'polybenzene'. This allotrope of carbon is proposed to be quite stable, however could not be synthesized so far. The results nicely demonstrate the potential of the triphospholyl ligands in Supramolecular Chemistry, especially for the formation of MOF-like assemblies.

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