

## Supramolecules

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## An Icosidodecahedral Supramolecule Based on Pentaphosphaferrocene: From a Disordered Average Structure to Individual Isomers

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Dedicated to Professor Karl Wieghardt on the occasion of his 75th birthday

**Abstract:** Pentaphosphaferrocenes [ $\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)$ ] (**1**) and  $\text{Cu}^I$  halides are excellent building blocks for the formation of discrete supramolecules. Herein, we demonstrate the potential of  $\text{Cu}(\text{CF}_3\text{SO}_3)$  for the construction of the novel 2D polymer  $[[\text{Cp}^*\text{Fe}(\mu_4, \eta^{5:1:1:1}\text{-P}_5)]\{\text{Cu}(\text{CF}_3\text{SO}_3)\}]_n$  (**2**) and the unprecedented nanosphere  $(\text{CH}_2\text{Cl}_2)_{1.4} @ [[\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)]_{12}/\text{Cu}(\text{CF}_3\text{SO}_3)]_{19.6}$  (**3**). The supramolecule **3** has a unique scaffold beyond the fullerene topology, with 20 copper atoms statistically distributed over the 30 vertices of an icosidodecahedron. Combinatorics was used to interpret the average disordered structure of the supramolecules. In this case, only two pairs of enantiomers with  $D_5$  and  $D_2$  symmetry are possible for bidentate bridging coordination of the triflate ligands. DFT calculations showed that differences in the energies of the isomers are negligible. The benzyl ligands enhance the solubility of **3**, enabling NMR-spectroscopic and mass-spectrometric investigations.

Although supramolecular chemistry is based on nature, it has become an indispensable and fascinating field for the directed synthesis of certain assemblies. Among these, discrete spherical supramolecules are particularly surprising as they can reach large dimensions, approaching the size of small proteins, and often provide defined inner cavities suitable for guest enclosure,<sup>[1]</sup> in addition to an unprecedented molecular symmetry and challenging solid-state chemistry, including crystallography. For their synthesis by self-assembly, non-covalent bonds in particular provide many advantages, such as the combination of strength and reversibility. As the

donor–acceptor bonding is directional, rational design becomes possible by variation of the symmetry and geometry of the corresponding building blocks.<sup>[2]</sup> In contrast to sixfold-symmetric building blocks, which form 2D layers, the use of pentatopic nodes allows for bending and leads to unique spherical aggregates. Aside from our approach based on using the planar fivefold-symmetric *cyclo*- $\text{P}_5$  ligand in [ $\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)$ ] (**1**;  $\text{Cp}^R = \text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$  (**1a**);  $\text{Cp}^{\text{Bn}} = \eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5$  (**1b**);  $\text{Cp}^{\text{BIG}} = \eta^5\text{-C}_5(4\text{-nBuC}_6\text{H}_4)_5$  (**1c**); Figure 1 a), others, such as the Williams and Wright groups, also made use of such fivefold-symmetric starting materials, such as the pentakis(4-pyridyl)cyclopentadienide (Figure 1 b)<sup>[3]</sup> and the pentakis(1-methylpyrazole)cyclopentadienide ligands (Figure 1 c),<sup>[4]</sup> as well as [ $\text{C}_5(\text{CN})_5$ ]<sup>−</sup> (Figure 1 d), respectively.<sup>[5]</sup> In contrast to **1**, all of these ligands contain nitrogen as the donating atom. Moreover, the use of fivefold-symmetric building blocks distinguishes this research from other concepts developed by the groups of Fujita,<sup>[6]</sup> Stang,<sup>[7]</sup> Raymond,<sup>[8]</sup> and Nitschke,<sup>[1a,9]</sup> which are all based on the coordination of N- and O-donor polytopic linkers to transition metals.

In combination with various Lewis acidic metal cations, substituted pentaphosphaferrocenes [ $\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)$ ] have enabled the discovery and investigation of a large variety of one- and two-dimensional polymers (coordination via 2, 3, or 4 P atoms of the *cyclo*- $\text{P}_5$  ligand)<sup>[10]</sup> and discrete spherical compounds (mostly from the coordination of all 5 P atoms)<sup>[11]</sup> over the last decade. Selected examples are depicted in Figure 2. Among these, the most symmetric supramolecule to

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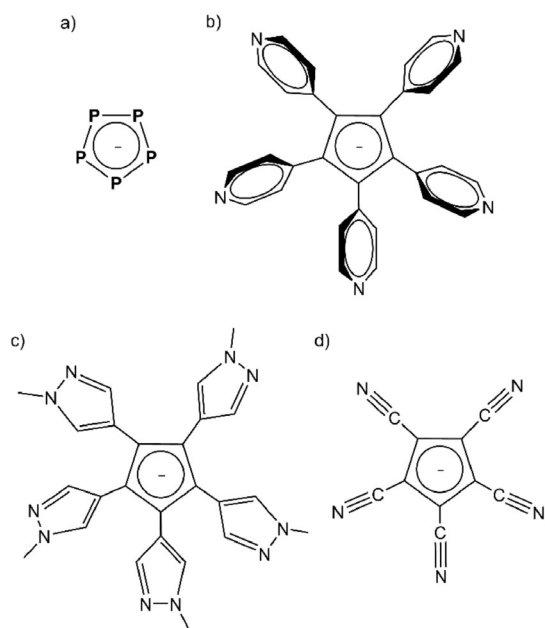


Figure 1. Fivefold-symmetric linking units.

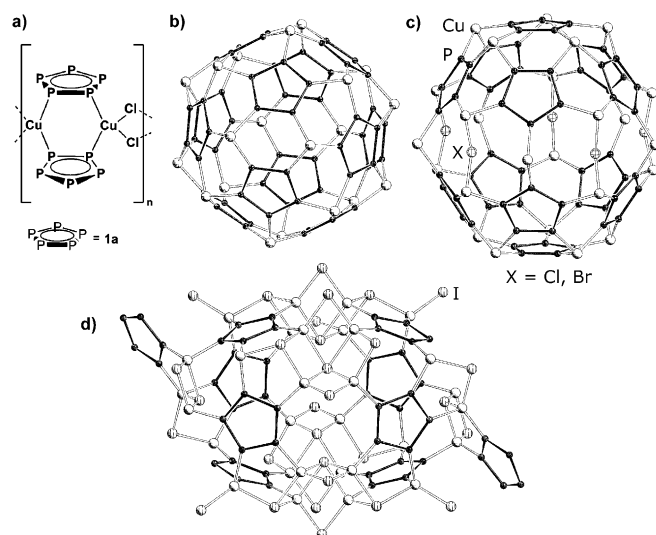


Figure 2. Selected coordination products based on **1a** as a building block: a) 1D polymer; supramolecules with b) fullerene, c) fullerene-like, and d) non-fullerene topology.

date consists of 12  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$  units and 20 Cu atoms and possesses a fullerene topology. Its 80-vertex inorganic core with  $I_h$  symmetry contains only five- and six-membered rings and is thus constructed according to the isolated pentagon rule (IPR; Figure 2b).<sup>[11a,b,e,f]</sup> In this core, all halogen atoms are terminal and therefore not scaffold-constructing.

To access even larger supramolecules, one can either expand the scaffold through the use of polynuclear Cu complexes coordinated to *cyclo*- $\text{P}_5$  rings of  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$  units or alter the electronic and steric influence of the substituents R of the cyclopentadienyl ligand. These two variations have been investigated,<sup>[11c,d]</sup> for example through

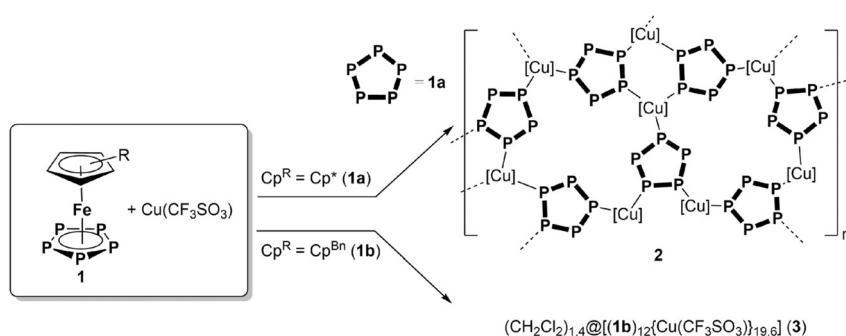
the implementation of five  $\text{Cu}(\text{MeCN})_2^+$  complexes and five halogen bridges to give 90-vertex spheres (Figure 2c),<sup>[11h]</sup> and culminated in such remarkable examples as the 312-vertex rugby-ball-shaped supramolecule  $[(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5))_{24}(\text{CuBr})_{96}]^{[11g]}$  and the giant molecule  $[(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5))_{12}\text{Cu}_{69,45}\text{Br}_{82,70}]$  with *I*- $\text{C}_{140}$  fullerene topology.<sup>[11a]</sup> In the largest representatives reported thus far, the  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$  units are connected via a  $\text{Cu}_n\text{X}_m$  network (Figure 2d). Control over the aggregation process can be partly achieved by using copper(II) halides in a redox process<sup>[11g]</sup> or with heavier copper(I) halides ( $\text{X} = \text{Br}, \text{I}$ ).<sup>[11b,f]</sup> The introduction of sterically demanding organic substituents at the cyclopentadienyl ligand as in **1b** and **1c** leads to a substantial increase in the solubility of the resulting spheres.<sup>[11a-c]</sup>

A different approach might be the use of multifunctional anions instead of a halide, which would avoid the limitations associated with uncontrollable oligomerization and at the same time allow for a scaffold expansion of the supramolecule. The anions could act as spacers between the Cu atoms that are additionally coordinated to the *cyclo*- $\text{P}_5$  units. After numerous preparative attempts with different anions, we now present trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_3^-$ , triflate) as a convenient spacer that possesses flexible coordination properties and renders the resulting spheres well soluble at the same time.<sup>[12]</sup>

Herein, we report on the first results of the self-assembly of pentaphosphaferrocene **1a** and the bulkier derivative **1b**, respectively, with  $\text{Cu}(\text{CF}_3\text{SO}_3)$ , which gave the novel 2D polymer  $[(\text{Cp}^*\text{Fe}(\mu_4, \eta^{5:1:1:1}\text{-P}_5))\{\text{Cu}(\text{CF}_3\text{SO}_3)\}]_n$  (**2**) as well as the spherical supramolecule  $(\text{CH}_2\text{Cl}_2)_{1,4} @ [(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5))_{12}(\text{Cu}(\text{CF}_3\text{SO}_3))_{19,6}]$  (**3**). The latter reveals an unprecedented connectivity and, because of the truly scaffold-constructing role of the triflates, opens a new chapter in supramolecular aggregation starting from fivefold-symmetric building blocks by alteration of the fullerene topology.

The reaction of **1b** with  $\text{Cu}(\text{CF}_3\text{SO}_3) \cdot 0.5 \text{C}_7\text{H}_8$  in  $\text{CH}_2\text{Cl}_2$  at room temperature gave a yellowish brown solution within 10 min. After filtration and layering with toluene, very small brown rhombohedra of the supramolecule  $[(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5))_{12}(\text{Cu}(\text{CF}_3\text{SO}_3))_{19,6}]$  (**3**) crystallized in a remarkable yield of 65% (Scheme 1). Interestingly, when the  $\text{Cp}^*$  derivative  $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$  was used, only the 2D polymer  $[(\text{Cp}^*\text{Fe}(\mu_4, \eta^{5:1:1:1}\text{-P}_5))\{\text{Cu}(\text{CF}_3\text{SO}_3)\}]_n$  (**2**) was obtained in 56% yield.

Compound **3** crystallizes in the monoclinic space group  $C2/c$  with giant unit cell constants of  $a = 45.771(1) \text{ \AA}$ ,  $b = 31.615(1) \text{ \AA}$ ,  $c = 91.429(1) \text{ \AA}$ ,  $\beta = 98.008(1)^\circ$ , and  $V = 131014(4) \text{ \AA}^3$ . X-ray structure analysis was performed in our laboratory as well as at the DESY PETRA III synchrotron (beamline P11),<sup>[13]</sup> revealing the atomic-resolution structure of an unprecedented spherical supramolecule with unique crystallographic symmetry and disorder. The inorganic scaffold of supramolecule **3** is formed by 12 units of **1b** with a similar icosahedral mutual arrangement as in the 80-vertex ball  $[(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5))_{12}(\text{CuX})_{20}]$  (Figure 2b). However, the scaffold in **3** is expanded through the insertion of the bridging triflate ligands in between the copper atoms (Figure 3c). Every Cu atom is located in a tetrahedral coordination environment comprising two oxygen atoms of  $\text{CF}_3\text{SO}_3^-$

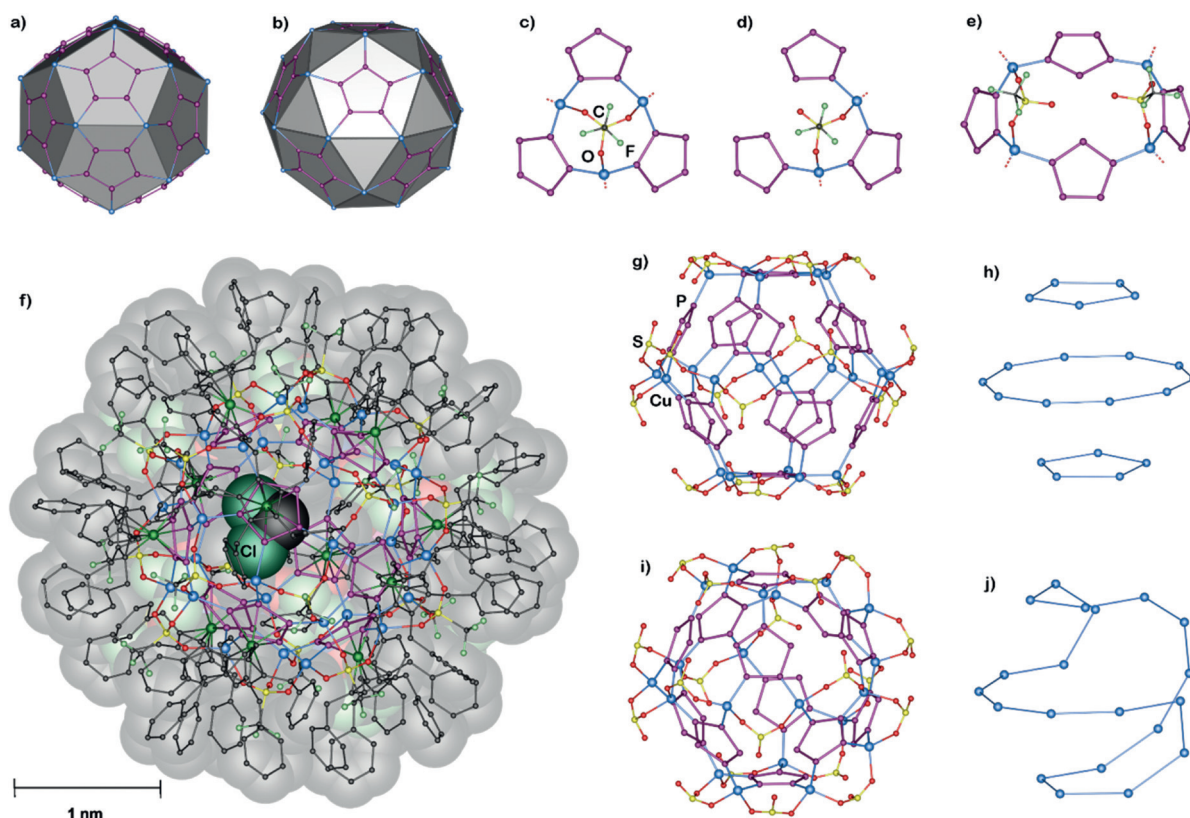


**Scheme 1.** Reaction of **1a** and **1b** with  $\text{Cu}(\text{CF}_3\text{SO}_3)$ .

ligands and two phosphorus atoms of **1b** units (Figure 3d). The sulfur atoms of the 20 triflate ligands in **3** form a dodecahedron in a similar manner as the copper halide units in the 80-vertex balls (Figure 3a). Oxygen atoms of the 20 triflate ligands truncate each of the 20 vertices of this dodecahedron with triangles to give an icosidodecahedron with 12 pentagonal and 20 triangular faces (Figure 3b). If each of the 20 triangular faces was negatively “charged” and each of the 30 vertices was positively charged while leaving the pentagonal faces neutral, the resulting fully occupied icosidodecahedral supramolecule would be  $[(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5))_{12}\text{Cu}_{30}(\text{CF}_3\text{SO}_3)_{20}]^{10+}$  and would therefore be tenfold

positively charged. However, supramolecule **3** is neutral and must therefore have exactly ten vacancies, with the 20 copper atoms being somehow distributed over the 30 vertices of the icosidodecahedron. In other words, the scaffold of **3** with the ideal composition  $[(\text{Cp}^{\text{Bn}}\text{FeP}_5)_{12}\{\text{Cu}(\text{CF}_3\text{SO}_3)\}_{20}]$  intrinsically contains copper vacancies.

Different possibilities to occupy two thirds of the copper sites in the icosidodecahedral scaffold give rise to a number of permutational isomers. One would intuitively think that the number of these isomers must be huge. A systematic search for all possible isomers was performed by coding a computer program for this purpose<sup>[14]</sup> starting from a hypothetical fully occupied icosidodecahedral scaffold. The algorithm works as follows: After removal of one copper atom, the subsequent nine Cu atoms are systematically removed from nine other positions. That way, the upper estimate of possible isomers resulted in  $C(29,9) = 10015005$  combinations (permutations). In fact, the number of isomers can be decreased dramatically by additionally implying reasonable structural requirements. First of all, it was assumed that the idealized structure of the inorganic shell must not be disconnected into fragments. This implies



**Figure 3.** Molecular structure of **3** in the crystal. H atoms, solvent molecules, and minor parts of disorder are omitted for clarity. a) Dodecahedron of copper halide derived from 80-vertex balls. b) Icosidodecahedron of **3**. Connectivity in the c) idealized and d) partially vacant scaffold of **3**. e) The 14-membered cycle formed as a result of the vacancies. f) The whole supramolecule **3** from X-ray data. Only one position of a  $\text{CH}_2\text{Cl}_2$  molecule is shown in the space-filling model. g)  $D_5$  isomer of **3** and h) the corresponding arrangement of Cu atoms. i)  $D_2$  isomer of **3** and j) arrangement of the Cu atoms.

that each triflate must be at least bidentate towards copper atoms (Figure 3d). Moreover, although monodentate coordination is possible in principle, it is unlikely to lead to the same coordination geometry as the bond angle Cu-O-S for the monodentate coordination would then change so that the O<sub>3</sub> plane would not be parallel to the “Cu<sub>3</sub>” plane anymore. As this feature was not observed in the crystal structure of **3**, the monodentate coordination mode can be excluded from further consideration (Figure 3d). Therefore, all isomers with terminal triflates were excluded from the total number of isomers generated, and only 12 arrangements remained. These were further checked for topological equivalence to separate only truly unique isomers from their rotations and reflections. As a result, only four individual isomers of the neutral scaffold **3** were derived, which correspond to two enantiomeric pairs with *D*<sub>2</sub> and *D*<sub>5</sub> point symmetry, respectively.<sup>[15]</sup>

In the *D*<sub>5</sub> isomer, the Cu atoms form three distinct rings around the fivefold axis (Figure 3g,h). The Cu<sub>20</sub>P<sub>60</sub> portion of the scaffold even obeys the higher *D*<sub>5d</sub> point symmetry, which is violated by the presence of coordinating triflate anions, giving rise to two enantiomers via the slight (ca. 0.1 Å) mutual rotation of the SO<sub>3</sub> groups.<sup>[15]</sup> In this inorganic scaffold, two and ten pentaphosphaferrocene ligands show 1,2,3,4,5- and 1,2,4-coordination to copper, respectively.

In the *D*<sub>2</sub> isomer, the Cu atoms form a loop on the surface of the icosidodecahedron (Figure 3i,j). This arrangement is more uniform than that in the *D*<sub>5</sub> configuration and resembles an “endless staircase” sculpture by Olafur Eliasson.<sup>[15]</sup> The *cyclo*-P<sub>5</sub> ligands adopt the 1,2,3,4- and 1,2,4-coordination modes for four and eight **1b** units, respectively. This sphere is the first example of a supramolecular assembly systematically involving less than five P atoms of **1** in the coordination to Cu. Its scaffold is truly chiral as the transformation of one *D*<sub>2</sub> enantiomer into the other one requires a rearrangement of the copper atoms.

Both inorganic cores can easily be described as ten equal 14-membered cycles {Cu<sub>4</sub>P<sub>10</sub>} with two adjacent P<sub>5</sub> cycles. However, the way these cycles are joined is different.<sup>[15]</sup> As there are no six-membered rings in the isomeric scaffolds of **3**, it shows no fullerene topology despite the presence of 12 *cyclo*-P<sub>5</sub> rings.

The question arises as to which of these isomers is more stable, the more symmetric *D*<sub>5</sub> or the more uniform *D*<sub>2</sub> isomer? To answer this question, DFT geometry optimizations at the EDF1<sup>[16]</sup>/SBKJC<sup>[17]</sup> level of theory were performed. The EDF1 method was chosen as it produces one of the most accurate electron densities among the GGA functionals.<sup>[18]</sup> The starting structures for one *D*<sub>5</sub> and one *D*<sub>2</sub> isomer were obtained from the idealized “parent” icosidodecahedral structure. These were simplified by replacing the Cp\* with Cp groups and the CF<sub>3</sub> with CH<sub>3</sub> groups. At the beginning of the optimization, the energies of the isomers differed by approximately 40 kcal mol<sup>-1</sup> in favor of the *D*<sub>2</sub> isomer; however, after relaxation, the difference decreased to 2.5 kcal mol<sup>-1</sup>, which is well beyond the accuracy of the calculations for a system of this size. Therefore, the *D*<sub>5</sub> and *D*<sub>2</sub> isomers should be equally stable and co-exist in the solid state.

It is important to note that the optimized geometries are distorted compared to the input structure.<sup>[15]</sup>

X-ray structural analysis for **3** revealed 30 crystallographically unique Cu sites, which all show occupancy factors between 0.2 and 0.9. This means that in the solid state, isomers in multiple orientations overlap in different ratios. Unfortunately, we cannot unambiguously derive the type and relative content of the isomers from the diffraction data. Moreover, two of 20 triflate positions also show reduced occupancies of 0.85 and 0.75, respectively. The total contents of copper and triflate are equal and correspond to the average sum formula of [(**1b**)<sub>12</sub>{Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>19.6</sub>}. Therefore, the intrinsically vacant supramolecules can also have vacancies in the triflate positions; their disorder is thus accompanied by additional vacancies in copper sites. Hence, the crystal of **3** is best described as a mixture of [(**1b**)<sub>12</sub>{Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>20</sub>} (**3a**, as an overlay of four isomeric forms) and [(**1b**)<sub>12</sub>{Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>19</sub>} (**3b**) in a 60:40 ratio (20 × 0.6 + 19 × 0.4 = 19.6). However, the more porous spheres [(**1b**)<sub>12</sub>{Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>18</sub>} (**3c**) might also be present. Therefore, **3** might also represent a 80:20 solid solution of **3a/3c** or a 70:20:10 mixture of **3a/3b/3c** to give the same average value of 19.6.<sup>[19]</sup>

On the other hand, isomerism as a result of disorder in molecules and ions is an ordinary phenomenon. For small clusters, it is usually discussed in detail and can often be supported by NMR data.<sup>[11b,20]</sup> Cases are known where the thermodynamically favored co-crystallization of isomers was fortunately governed kinetically to discriminate different isomers as different crystalline phases.<sup>[20b]</sup> However, for larger clusters, isomerism as well as disorder are to be expected even more.<sup>[21]</sup> One of the reasons for this is the complexity of an average disordered structure.<sup>[22c,d]</sup> To the best of our knowledge, in numerous contributions from different research groups,<sup>[22]</sup> the disorder of cluster cores has only been formally described in terms of site occupancy factors. The next step has hardly been achieved, namely, the chemically essential interpretation of these occupancy factors as the result of an overlap of different orientations of the same cores, their isomerism, or the co-crystallization of similar clusters. Such an interpretation can sometimes be ambiguous but cannot always be precluded. For instance, in the giant cluster [Ga<sub>84</sub>(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>20</sub>]<sup>3-</sup>, the partial occupancy of three Ga positions points to the co-existence of three species, {Ga<sub>83</sub>} and two isomers of {Ga<sub>84</sub>}, which was not discussed.<sup>[21a]</sup> The partial disorder of the copper atoms in [Cu<sub>28</sub>Se<sub>6</sub>(SPh)<sub>16</sub>(PPh<sub>3</sub>)<sub>8</sub>] and [Cu<sub>54</sub>Se<sub>8</sub>(SPh)<sub>30</sub>(OAc)<sub>8</sub>(PPh<sub>3</sub>)<sub>6</sub>] leads to the co-crystallization of different isomers overlaying in the same crystallographic position, which was beyond the scope of that study.<sup>[21b]</sup> On the other hand, Fujita and co-workers have extensively used a geometrically restricted topological approach to predict giant molecules or even intermediates, but its application to a disordered structure has never been reported.<sup>[6]</sup> With **3** as an example, we went further by not only reporting the average structure, but also by first presenting a mathematical reconstruction of the isomers based on X-ray diffraction data.

Owing to the bulky Cp<sup>Bn</sup> ligands, the whole assembly of **3** reaches an outer diameter of 3.3 nm. The supramolecule **3** is therefore 0.2 nm larger than the (80-*n*) vertex fullerene

analogue  $[(\mathbf{1b})_{12}(\text{CuX})_{20-n}]$  ( $\text{X} = \text{Cl}, \text{Br}; n < 6$ ).<sup>[11]</sup> To illustrate this point, **3** is 36 times larger than the Buckminster fullerene  $\text{C}_{60}$  ( $V = 0.52 \text{ nm}^3$ ) given the  $18.8 \text{ nm}^3$  volume of the spherical supramolecule. Furthermore, **3** has a spherical cavity with an inner diameter of  $1.0 \text{ nm}$ , which is  $0.2 \text{ nm}$  larger than that of the  $\text{CuX}$ -derived 80-vertex balls ( $\text{X} = \text{Cl}, \text{Br}$ ). This void is occupied with either one or two severely disordered dichloromethane molecules ( $1.4 \text{ CH}_2\text{Cl}_2$  on average).

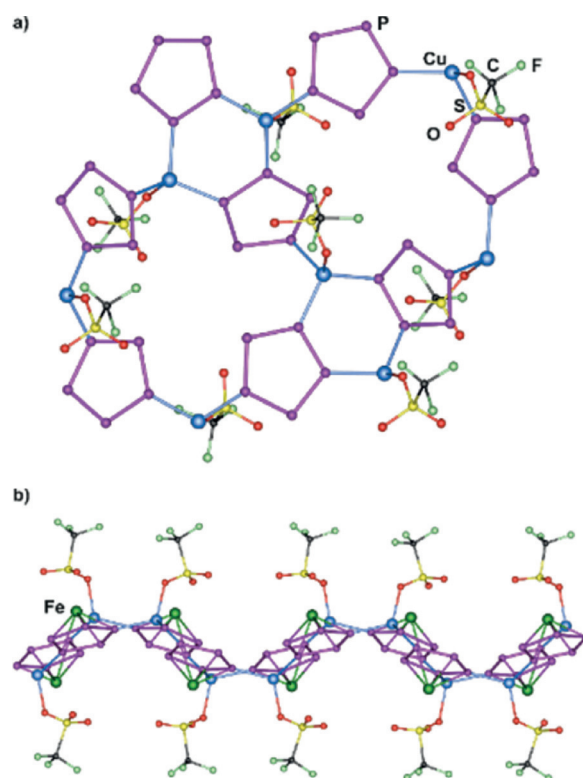
Compound **3** is poorly soluble in toluene whereas fragmentation was observed when it was dissolved in  $\text{CH}_3\text{CN}$ . However, its moderate solubility in  $\text{CH}_2\text{Cl}_2$  allowed its characterization in solution. In the  $^1\text{H}$  NMR spectra of **3** in  $\text{CD}_2\text{Cl}_2$ , a set of four broad signals was observed corresponding to the methylene as well as the aromatic protons (*o*-CH, *m*-CH, and *p*-CH) of the  $\text{Cp}^{\text{Bn}}$  ligand ( $\delta = 4.48, 6.23, 6.67, 6.93 \text{ ppm}$ ). In addition, the triflate ligand of **3** can be detected in the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum as a broad singlet at  $\delta = -76.7 \text{ ppm}$ . Unfortunately, no signal was observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** at ambient temperature, and low-temperature studies could not be performed because of the limited solubility of **3** in  $\text{CD}_2\text{Cl}_2$  already at room temperature.

In the ESI-MS spectrum of **3** recorded in the positive-ion mode, numerous peaks can be attributed to fragments containing pentaphosphaferrocene, copper, and triflate. The largest peak at  $m/z = 2879.4$  was assigned to  $[(\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)_3)_3\text{Cu}_4(\text{CF}_3\text{SO}_3)_3]^+$ .

X-ray structure analysis of **2** revealed a two-dimensional network with the *cyclo*- $\text{P}_5$  ligands of **1a** in a 1,2,4-coordination mode to copper, with a similar structural motif to pentaphosphaferrocene-containing polymers, now reproduced with triflate.<sup>[10c,e]</sup> Thus six-membered  $\{\text{Cu}_2\text{P}_4\}$  rings as well as distorted 16-membered  $\{\text{Cu}_4\text{P}_{12}\}$  rings are formed, resembling a porphyrin-like structural motif (Figure 4a). Here, the triflate anion acts as a terminal ligand with one oxygen atom coordinated to copper. It therefore completes the preferred tetrahedral environment of the metal center ( $3 \times \text{P}, 1 \times \text{O}$ ). This geometry is also responsible for the distortion of the  $\text{Cu}$ -containing rings. Hence, the 2D network consists of corrugated layers with the triflate and pentaphosphaferrocene (**1a**) units alternatingly pointing upwards and downwards (Figure 4b).

Compound **2** is insoluble in common solvents such as *n*-hexane, toluene,  $\text{CH}_2\text{Cl}_2$ , THF, and  $\text{Et}_2\text{O}$ . Only in  $\text{CH}_3\text{CN}$ , **2** is poorly soluble although the dissolution is accompanied by the partial fragmentation of the coordination network. Therefore, only the signals of free complex **1a** are present in both the  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of **2** in  $\text{CD}_3\text{CN}$ . However, mass-spectrometric investigations revealed the presence of at least some oligomeric moieties. For example, in the respective positive-ion ESI-MS spectra of **2** in  $\text{CH}_3\text{CN}$ , numerous peaks corresponding to fragments containing pentaphosphaferrocene units were observed. The most intense peak was found for  $[(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))_4\text{Cu}_9(\text{CF}_3\text{SO}_3)_8]^+$  at  $m/z = 3148.2$ .

In summary, we have shown that the formation of pentaphosphaferrocene-derived supramolecules is not restricted to copper halides anymore, but is also feasible for the combination of copper triflate with **1b**. The use of this anion and its different spatial requirements allowed us to expand and at the same time to maintain the inorganic



**Figure 4.** Section of the 2D polymeric structure of **2** based on **1a**: a) top view and b) side view of a layer.

scaffold  $\text{Cu}_{20}\text{P}_{60}(\text{anion})_{20}$  (anion = X, triflate) and its composition as in the 80-vertex sphere based on copper(I) halides. This became possible because of the truly scaffold-constructing role of the triflate anion. The resulting unique supramolecule  $(\text{CH}_2\text{Cl}_2)_{1.4} @ [(\mathbf{1b})_{12}\{\text{Cu}(\text{CF}_3\text{SO}_3)\}_{19.6}]$  with a size of  $3.3 \text{ nm}$  has an intrinsically vacant inorganic core with an inner cavity that is about 22 % larger than those in the 80-vertex supramolecules. As the average structure obtainable from X-ray diffraction cannot provide explicit information on the structure of the individual, ordered moieties of **3** owing to disorder, all possible isomers were systematically modeled. To the best of our knowledge, such modeling had previously never been attempted for giant clusters. Two enantiomeric pairs with  $D_2$  and  $D_5$  point symmetry and different coordination modes of **1b** were shown to be the most representative isomers of **3** in agreement with the experimental diffraction data. Their relative stabilities are similar according to DFT calculations, which supports their possible co-existence in the solid state. In contrast, starting from the  $\text{Cp}^*$  derivative **1a** and  $\text{Cu}(\text{CF}_3\text{SO}_3)$ , the only product formed is the novel 2D coordination polymer  $[(\text{Cp}^*\text{Fe}(\mu_4, \eta^{5:1:1:1}\text{-P}_5))\{\text{Cu}(\text{CF}_3\text{SO}_3)\}]_n$ , where, on the contrary, triflate acts as a terminal ligand.

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### Conflict of interest

The authors declare no conflict of interest.

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