

Electronic Supporting Information for:

**A lens-shaped supramolecule based on the bulky
pentaphosphaferrocene [Cp^{BiG}Fe(η⁵-P₅)] and CuBr₂**

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1. Experimental detail

Materials and methods

All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and Schlenk techniques. Solvents were purified, dried and degassed prior to use. CuBr_2 was used as obtained from commercial suppliers. $[\text{Cp}^{\text{BIG}}\text{Fe}(\eta^5\text{-P}_5)]$ was prepared according to the literature procedure.^[1] The NMR spectra in solution were measured on Bruker Avance 300, 400 or 600 spectrometers. The MAS NMR spectra were recorded on a Bruker Avance 300 spectrometer by using a double resonance 2.5 mm MAS probe (^{31}P : 121.495 MHz). All spectra were acquired at MAS rotation frequencies of up to 30 kHz with a 90° pulse length of about 2.3 μs and relaxation delays of 120 s (^{31}P). ESI-MS spectra were measured on a ThermoQuest Finnigan TSG 7000 mass spectrometer. The elemental analysis was determined on a Vario EL III apparatus or by external service (all elements) 'Lehrbereich Anorganische Chemie, TU Munich, Mikroanalytisches Labor, Tel.: +49-89-289-13128'.

General procedure for the synthesis of compound $[\{\text{Cp}^{\text{BIG}}\text{Fe}(\eta^5\text{-P}_5)\}_6(\text{CuBr})_{32}(\text{CH}_3\text{CN})_6]$ (2).

To a suspension of CuBr_2 (1.33 mmol) in 5 mL CH_3CN , a solution of $[\text{Cp}^{\text{BIG}}\text{Fe}(\eta^5\text{-P}_5)]$ (250 mg, 0.267 mmol) in CH_2Cl_2 is added and stirred for 30 min resulting in a red-brown solution. After the solvent is removed in vacuum, the residue is triturated with 10 mL CH_2Cl_2 and filtered through cannula into a thin Schlenk tube. The reaction mixture is layered with 20 mL of toluene. After complete diffusion, well-shaped dark brown crystals of the product are obtained.

Analytical data.

$[\{\text{Cp}^{\text{BIG}}\text{Fe}(\eta^5\text{-P}_5)\}_6(\text{CuBr})_{32}(\text{CH}_3\text{CN})_6]$: Yield: 285 mg (61%).

Elemental analysis (all elements):

Calculated (%) for $[\text{C}_{342}\text{H}_{408}\text{Br}_{32}\text{Cu}_{32}\text{Fe}_6\text{N}_6\text{P}_{30}]\cdot 6 \text{CH}_2\text{Cl}_2$ (10967.20 g/mol) C, 39.28; H, 3.93; Br, 24.45; Cu, 19.44; Fe, 3.20; N, 0.80; P, 8.89; found: C, 36.18; H, 3.58; Br, 28.34; Cu, 19.1; Fe, 4.13; N, 0.77; P, 8.19.

Positive ion ESI-MS ($\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$):

m/z (%) = 2079.7 (30%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)_2\text{Cu}_2\text{Br}]^+$), 1936.8 (100%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)_2\text{Cu}]^+$), 1431.0 (10%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)\text{Cu}_4\text{Br}_3]^+$), 1328.0 (12%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)\text{Cu}_3\text{Br}_2\text{CH}_3\text{CN}]^+$), 1287.3 (18%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)\text{Cu}_3\text{Br}_2]^+$), 1143.3 (40%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)\text{Cu}_2\text{Br}]^+$), 1040.5 (70%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)\text{CuCH}_3\text{CN}]^+$), 999.5 (10%, $[(\text{Cp}^{\text{BIG}}\text{FeP}_5)\text{Cu}]^+$), 726.4 (7%, $[\text{Cp}^{\text{BIG}}]^+$), 432.4 (20%, $[\text{Cu}_3\text{Br}_2(\text{CH}_3\text{CN})_2]^+$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ [ppm] = 1.1 (*pseudo-t*, $^1J_{\text{PP}} \approx 560$ Hz, 1P), 16.4 (*pseudo-t*, $^1J_{\text{PP}} \approx 520$ Hz, 1P), 25.1 (*pseudo-t*, $^1J_{\text{PP}} \approx 550$ Hz, 1P), 37.0 (*pseudo-t*, $^1J_{\text{PP}} \approx 550$ Hz, 1P), 59.0 (*pseudo-t*, $^1J_{\text{PP}} \approx 555$ Hz, 1P).

2. NMR spectra

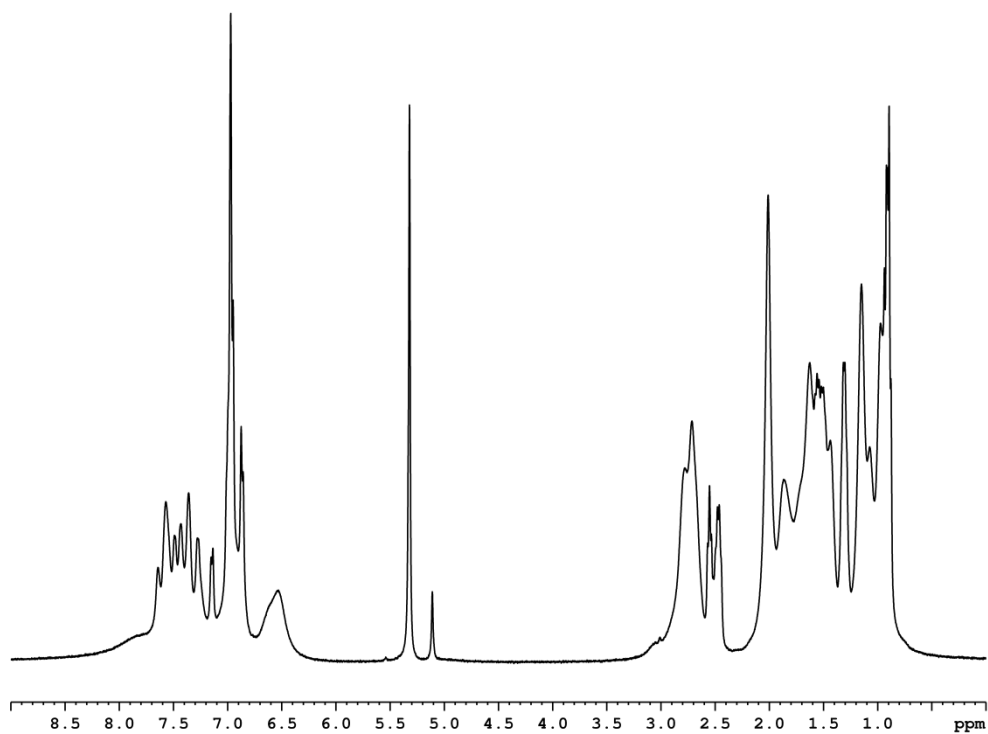


Figure S1. ^1H NMR spectrum of **2** in CD_2Cl_2 at 298 K.

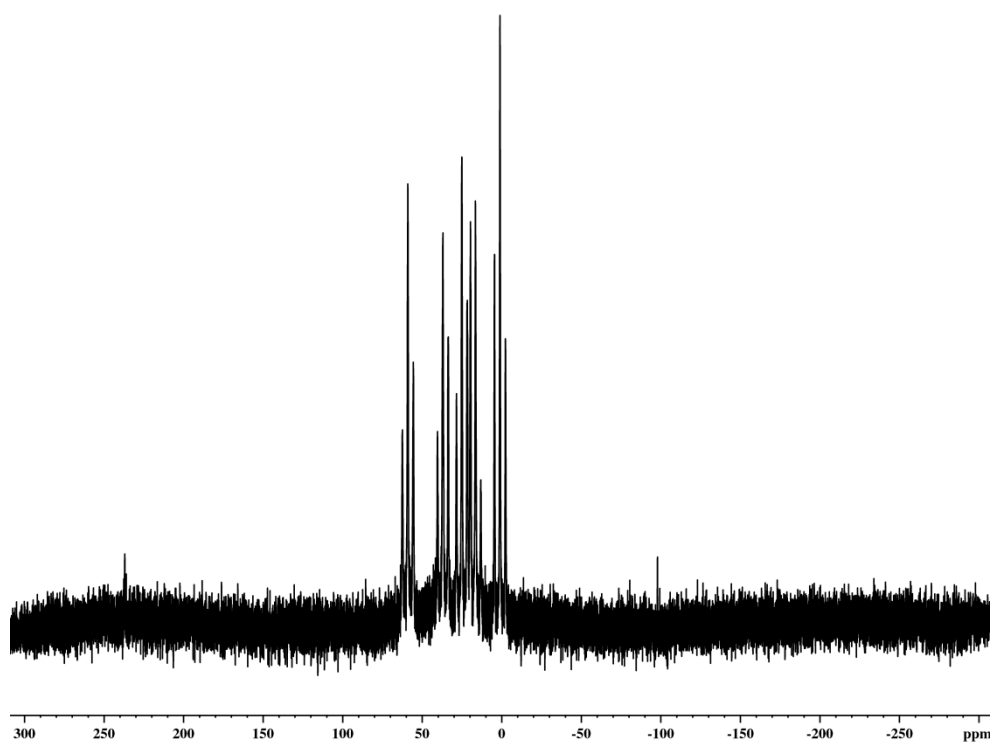


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CD_2Cl_2 at 298 K.

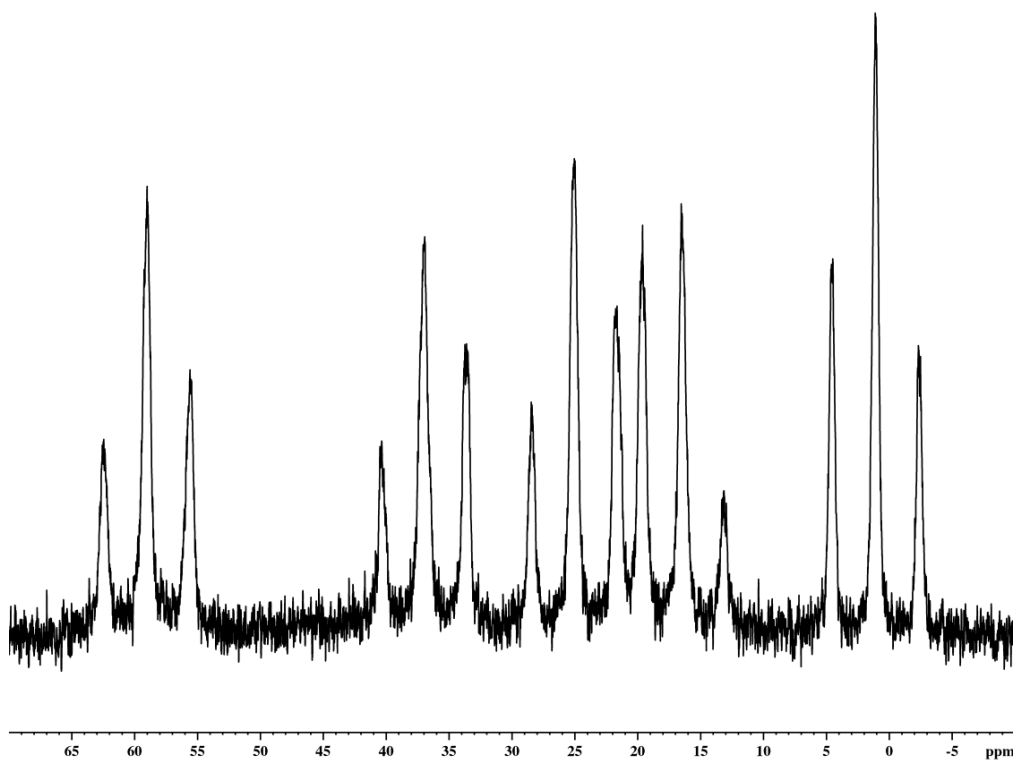


Figure S3. Zoomed section of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CD_2Cl_2 at 298 K.

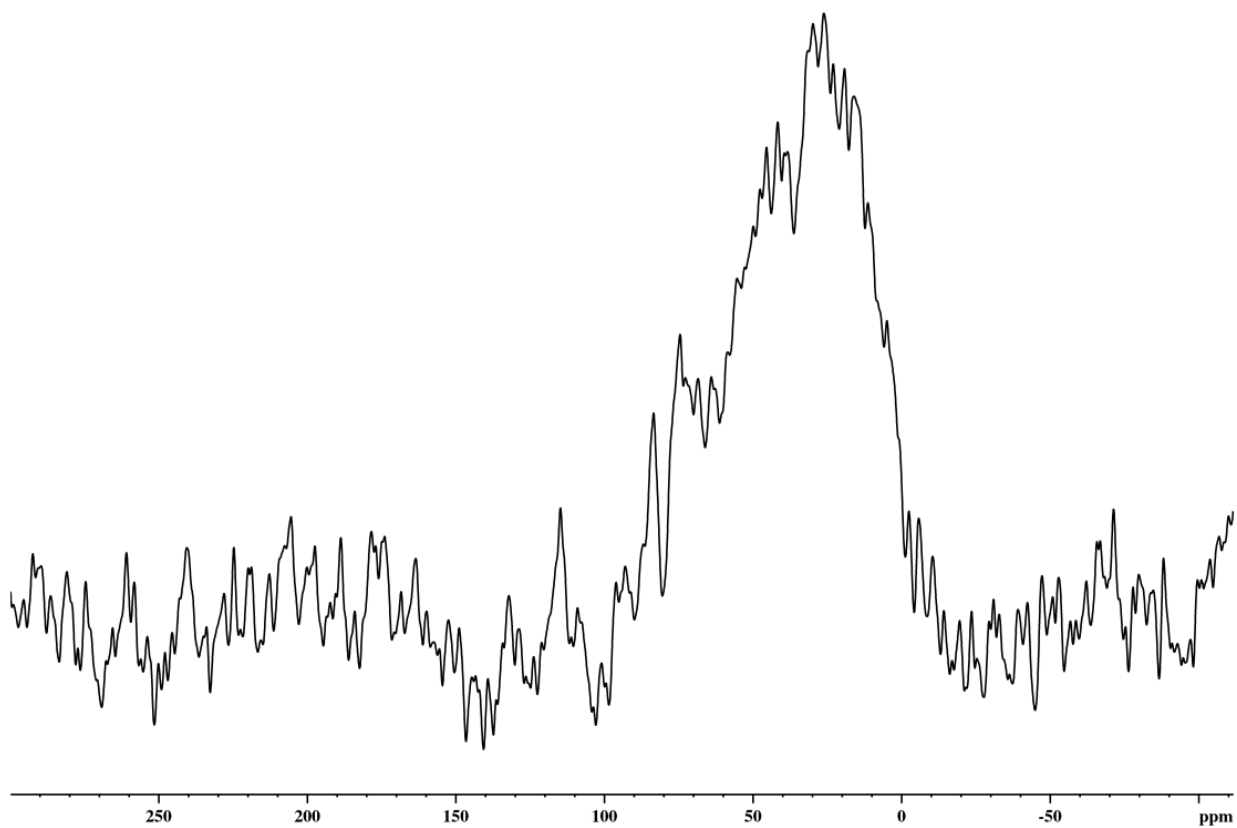


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ MAS NMR spectrum of **2** at 298 K.

2) Crystallographic Details:

The compound **2** crystallizes in the trigonal crystal system as dark brown prisms. Crystals of **2** were taken from a Schlenk flask under a stream of argon and immediately covered with perfluorinated Fomblin® mineral oil. Despite this precaution, the crystals lose solvent and are prone to quick amorphization out of mother solution. The quickly chosen single crystals covered by a droplet of the oil were taken to the pre-centered goniometer head with CryoMount® and directly placed on a diffractometer in a cold nitrogen flow (123 K).

The data collection was performed on an Oxford Diffraction SuperNova diffractometer equipped with CuK α micro-focus source and Atlas detector. The data reduction was performed with CrysAlisPro software.^[2] An analytical absorption correction based on crystal faces was applied.^[3] The crystal structure was solved by direct methods using the program SIR-97^[4] and refined with the least square method on $|F^2|$ employing SHELXTL^[5] in anisotropic approximation for non-H atoms that occupy their positions with site occupancy factors of more than 0.5. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model.

Supplementary Information for more detail. Deposition Number CCDC-2245833 (**2**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe.

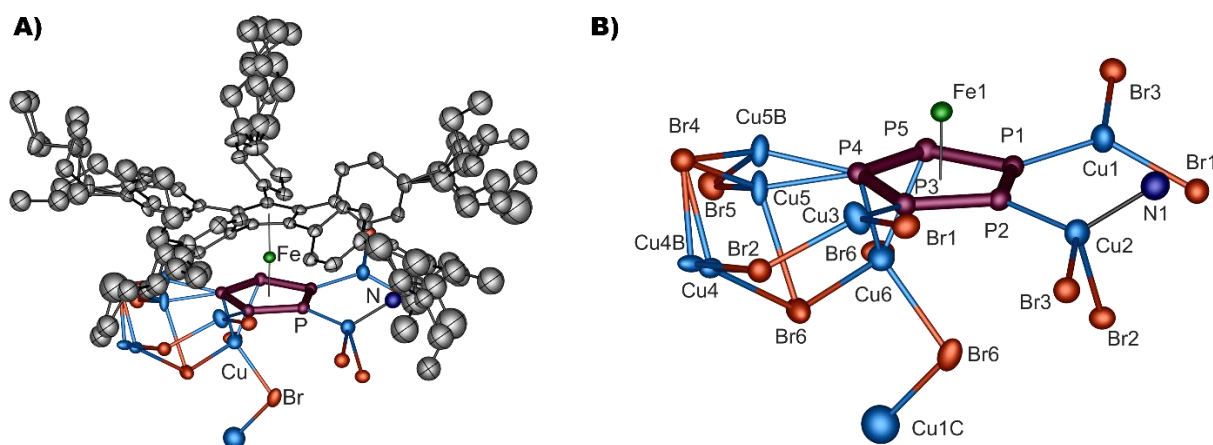


Figure S5. ORTEP plot of the molecular structure of the compound **2**: a) asymmetric part of the supramolecule. Solvent molecules and hydrogen atoms are omitted for clarity; b) asymmetric part of the inorganic core. Some copper positions are partly occupied and/or disordered over close positions.

Table 1. Crystallographic details for **2** (Å, °)

Crystal data	
Chemical formula	C ₃₄₂ H ₄₀₈ Br ₃₂ Cu ₃₂ Fe ₆ N ₆ P ₃₀ ·2.4(CH ₂ Cl ₂)
CCDC-Refcode	CCDC-2245833
<i>M_r</i>	10661.14
Crystal system, space group	Trigonal, <i>R3:H</i>
Temperature (K)	123
<i>a</i> , <i>c</i> (Å)	30.0348(4), 38.1116(9)
<i>V</i> (Å ³)	29774.0(11)
<i>Z</i>	3
<i>F</i> (000)	15770
<i>D_x</i> (Mg m ⁻³)	1.784
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	9.06
Crystal shape and colour	Dark brown prism
Crystal size (mm)	0.11 × 0.07 × 0.07
Data collection	
Diffractometer	SuperNova, Single source at offset, Atlas
Absorption correction	Analytical
<i>T_{min}</i> , <i>T_{max}</i>	0.521, 0.648
No. of measured, independent and observed [<i>I</i> > 2 <i>s</i> (<i>I</i>)] reflections	71417, 11894, 10124
<i>R_{int}</i>	0.036
(sin θ/λ) _{max} (Å ⁻¹)	0.599
Range of <i>h</i> , <i>k</i> , <i>l</i>	<i>h</i> = -35→29, <i>k</i> = -35→32, <i>l</i> = -45→45
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.158, 1.07
No. of reflections	11894
No. of parameters	900
No. of restraints	124
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.35, -0.85

Computer programs: *CrysAlis PRO*, Rigaku, Version 1.171.36.28 (release 01-02-2013 *CrysAlis171 .NET*), *SIR97* (Altomare, 1999), *SHELXL2018/3* (Sheldrick, 2018).

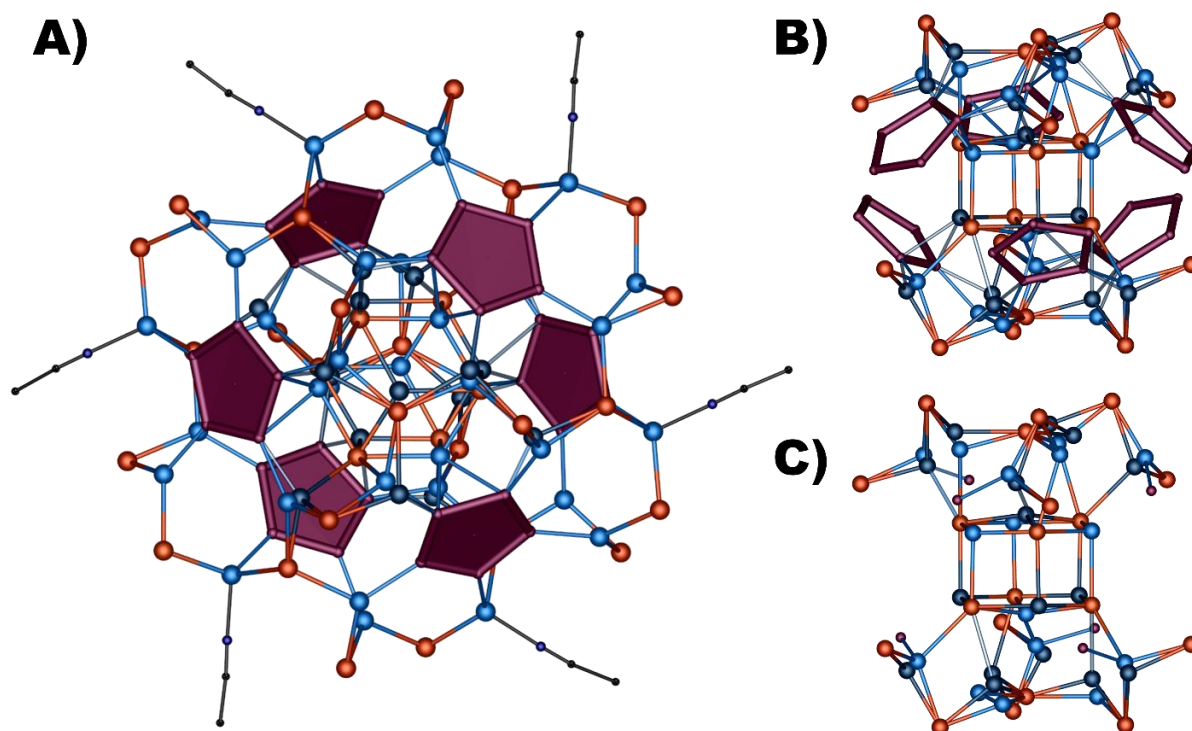
Table 2. Selected geometric parameters for **2** (Å, °)

Cu1C—Br6 ⁱ	2.4809 (12)	Cu5—Br5	2.386 (3)
Cu1C—Br6 ⁱⁱ	2.4809 (12)	Cu5—Br4	2.407 (3)
Cu1C—Br6	2.4809 (12)	Cu5—Br6 ^{iv}	2.818 (4)
Cu1C—Br5 ⁱⁱⁱ	2.905 (6)	Cu4B—P5 ⁱ	2.200 (8)
Cu1—P1	2.2105 (18)	Cu4B—Br4	2.315 (8)
Cu1—Br3	2.3675 (12)	Cu4B—Br2 ^{iv}	2.437 (8)
Cu1—Br1	2.3992 (11)	Cu5B—P4	2.227 (2)
Cu2—N1	1.991 (7)	Cu5B—Br4	2.334 (2)
Cu2—P2	2.1996 (17)	Cu5B—Br5	2.529 (2)
Cu2—Br3 ^{iv}	2.3923 (12)	Cu6—P4	2.280 (2)
Cu2—Br2	2.6011 (12)	Cu6—Br6 ^v	2.397 (2)
Cu3—P3	2.2137 (19)	Cu6—Br6 ^{iv}	2.490 (2)
Cu3—Br1 ^{iv}	2.3714 (12)	Cu6—P5	2.551 (3)
Cu3—Br2 ^{iv}	2.4166 (11)	Cu6—Br6	2.595 (2)
Cu4—P5 ⁱ	2.210 (6)	P1—P2	2.105 (2)
Cu4—Br2 ^{iv}	2.411 (6)	P1—P5	2.109 (2)
Cu4—Br4	2.440 (5)	P2—P3	2.102 (2)
Cu4—Br6 ^{iv}	2.679 (3)	P3—P4	2.107 (2)
Cu5—P4	2.208 (3)	P4—P5	2.124 (2)
Br6 ⁱ —Cu1C—Br6 ⁱⁱ	117.70 (7)	Cu3 ^v —Br2—Cu2	113.14 (4)
Br6 ⁱ —Cu1C—Br6	117.70 (7)	Cu4B ^v —Br2—Cu2	120.01 (18)
Br6 ⁱⁱ —Cu1C—Br6	117.70 (7)	Cu1—Br3—Cu2 ^v	100.91 (4)
Br6 ⁱ —Cu1C—Br5 ⁱⁱⁱ	98.81 (13)	Cu4B—Br4—Cu5B	100.72 (15)
Br6 ⁱⁱ —Cu1C—Br5 ⁱⁱⁱ	98.82 (13)	Cu6 ^{iv} —Br6—Cu6 ^v	118.89 (9)
Br6—Cu1C—Br5 ⁱⁱⁱ	98.81 (13)	Cu6 ^{iv} —Br6—Cu6	87.93 (7)
Br3—Cu1—Br1	111.90 (4)	Cu1C—Br6—Cu6	98.32 (14)
Br3 ^{iv} —Cu2—Br2	102.31 (4)	Cu6 ^v —Br6—Cu6	86.00 (6)
Br1 ^{iv} —Cu3—Br2 ^{iv}	107.85 (4)	Cu6 ^{iv} —Br6—Cu4 ^v	90.52 (13)
Br2 ^{iv} —Cu4—Br4	103.4 (2)	Cu1C—Br6—Cu4 ^v	119.31 (17)
Br2 ^{iv} —Cu4—Br6 ^{iv}	102.80 (15)	Cu6 ^v —Br6—Cu4 ^v	131.83 (13)
Br4—Cu4—Br6 ^{iv}	116.18 (19)	Cu6—Br6—Cu4 ^v	135.65 (13)
Br5—Cu5—Br4	107.35 (12)	Cu6 ^{iv} —Br6—Cu5 ^v	104.75 (8)
Br5—Cu5—Br6 ^{iv}	103.62 (14)	Cu6—Br6—Cu5 ^v	159.96 (8)
Br4—Cu5—Br6 ^{iv}	112.38 (14)	Cu5—Br5—Cu5 ⁱ	113.56 (8)
Br4—Cu4B—Br2 ^{iv}	106.4 (3)	Cu5—Br5—Cu5 ⁱⁱ	113.56 (8)
Br4—Cu5B—Br5	105.08 (8)	Cu5 ⁱ —Br5—Cu5 ⁱⁱ	113.56 (8)
Br6 ^v —Cu6—Br6 ^{iv}	120.64 (9)	Cu5—Br5—Cu5B ⁱ	109.46 (10)
Br6 ^v —Cu6—Br6	94.11 (7)	Cu5 ⁱⁱ —Br5—Cu5B ⁱ	128.77 (9)
Br6 ^{iv} —Cu6—Br6	91.96 (7)	Cu5B—Br5—Cu5B ⁱ	119.974 (4)
Cu4 ^v —Br2—Cu3 ^v	108.78 (11)	Cu5—Br5—Cu5B ⁱⁱ	128.77 (9)
Cu3 ^v —Br2—Cu4B ^v	117.31 (16)	Cu5 ⁱ —Br5—Cu5B ⁱⁱ	109.46 (10)
Cu4 ^v —Br2—Cu2	121.06 (13)		

Symmetry codes: (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$; (iii) $-x+2/3, -y+4/3, -z+4/3$; (iv) $x-y+2/3, x+1/3, -z+4/3$; (v) $y-1/3, -x+y+1/3, -z+4/3$.

Table 3. Site occupancy factors for non-carbon atoms in the core of **2**

Atom	x	y	z	U _{iso}	s.o.f. of crystallogr. position	s.o.f.
Cu1C	0.333333	0.666667	0.71224(15)	0.0753(13)	1/3	1/2
Cu1	0.57320(4)	0.93346(4)	0.65195(3)	0.0391(2)	1	1
Cu2	0.44634(4)	0.96218(4)	0.68642(3)	0.0373(2)	1	1
Cu3	0.30009(4)	0.86324(4)	0.60626(3)	0.0424(2)	1	1
Cu4	0.22562(17)	0.7167(2)	0.58169(12)	0.0268(8)	1	1/2
Cu4B	0.2115(3)	0.7122(3)	0.57308(17)	0.0287(12)	1	1/3
Cu5	0.32359(13)	0.73808(12)	0.56106(10)	0.0339(7)	1	1/3
Cu5B	0.33975(9)	0.75388(9)	0.54379(7)	0.0325(5)	1	1/2
Cu6	0.38454(8)	0.75994(7)	0.63420(5)	0.0393(4)	1	1/2
Br1	0.59870(3)	0.97641(2)	0.70758(2)	0.03487(16)	1	1
Br2	0.45541(2)	0.90628(2)	0.73491(2)	0.03164(16)	1	1
Br3	0.64133(3)	0.92888(3)	0.62422(2)	0.03532(16)	1	1
Br4	0.26052(2)	0.73862(2)	0.52238(2)	0.03344(16)	1	1
Br6	0.38327(3)	0.76086(3)	0.70227(2)	0.04093(18)	1	1
Br5	0.333333	0.666667	0.54487(3)	0.0365(3)	1/3	1

**Figure S6.** Disordering of the inorganic core in the molecule of the compound **2**. Dark blue balls show the second position of the disordered copper atoms.

Partly occupied Cu(I) positions and symmetry-imposed restrictions lead to the following interpretation of the crystallographic disorder: the molecular structure can be presented as two isomers (**A** and **B**) overlapping in the same crystallographic position. It is disordered over total six positions each arising from inversion and 120°-rotation.

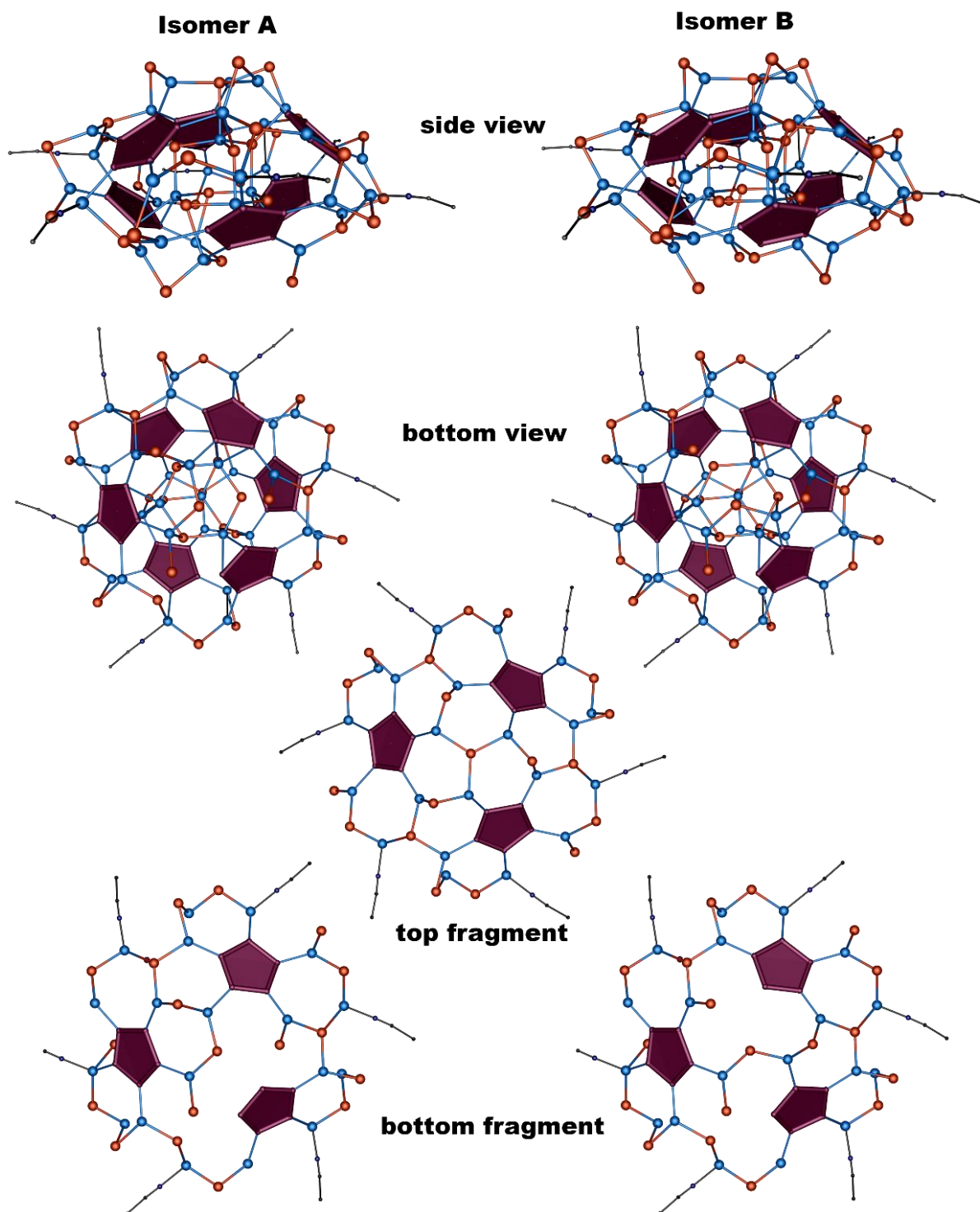


Figure S7. Side-by-side comparison of the isomeric forms **A** and **B** co-crystallizing in **2** in a ratio 1:1.

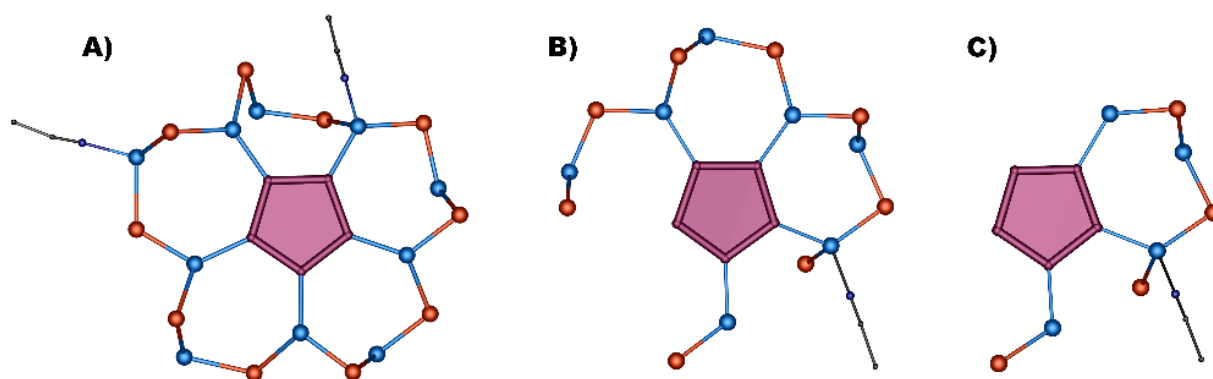


Figure S8. Coordination modes of pentaphosphaferrocene **1d** in **2**: a) penta-, b) tetra-, c) 1,2,3-tri-coordination.

The outer shell of the molecule slightly resembles two fused fullerene-like fragments in which the pentagonal rings are represented by three *cyclo*-P₅ ligands and tentative six-membered rings are represented by folded {P₂Cu₃Br}(Br) rings (Figure S9a). A similar fragment was observed in the other **1d**-based supramolecule **3** possessing a C₁₄₀-fullerene topology (Figure S9 b,c). However, the shorter Cu...Cu distances in the cycles {P₂Cu₃Br}(Br) of a fullerene-like supramolecule indicated the existence of Cu₂ dimers and allowed to consider the {P₂Cu₃Br}(Br) rings as six-membered ones (P–Cu–Br–Cu...Cu–P) with a Br bridge. As the corresponding Cu...Cu distances are longer in **2**, the fullerene topology is, strictly speaking, not fulfilled for **2**.

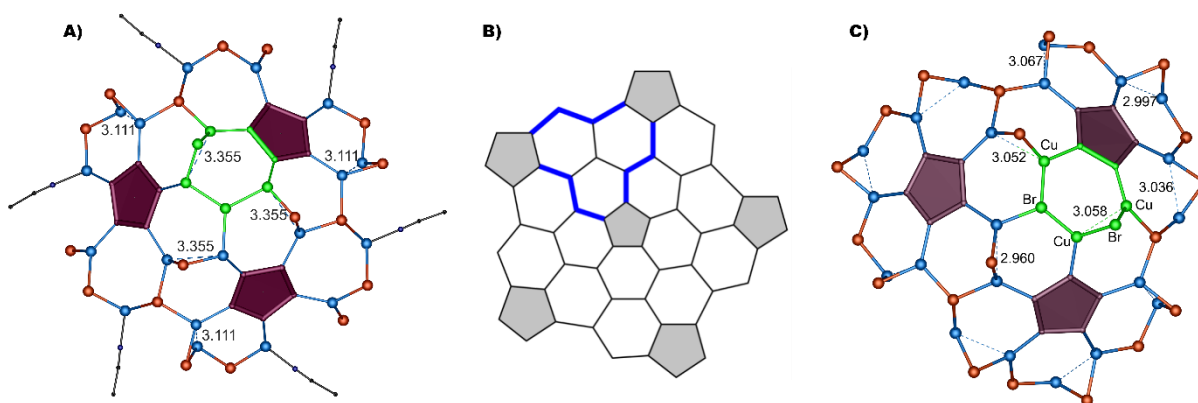


Figure S9. Side-by-side comparison of the b) fullerene-like fragments a) in **2** and b) in *I*-C₁₄₀ inorganic fullerene **3** based on **1d**.^[6]

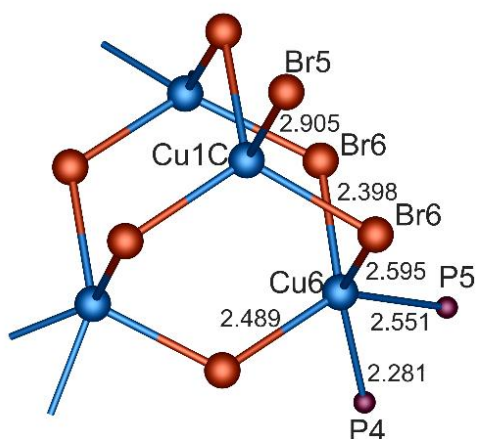


Figure S10. Bond lengths in the central adamantane-like fragment of the inorganic core. In forms A and B co-crystallizing in **2** it is similar.

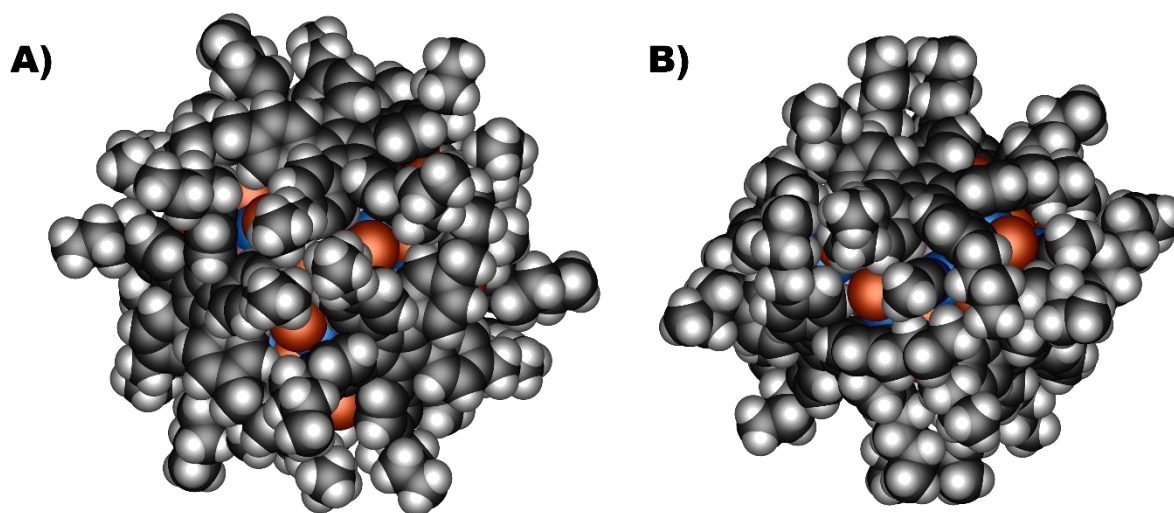


Figure S11. Supramolecule **2**, a) top and b) side view in van der Waals spheres. Isomeric forms are indistinguishable from the outer shape and can therefore co-crystallize in the solid state.

References

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