Neutral two-dimensional organometallic-organic hybrid polymers from pentaphosphaferrocene, CuCl and bipyridyl linkers

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<u>General</u>

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. 4,4'-bipyridine and *trans*-1,2-di(pyridine-4-yl)ethene are commercially available (Sigma-Aldrich) and were used as received. CuCl was also purchased from Sigma-Aldrich and recrystallized from warm acetonitrile before usage. Pentaphosphaferrocene [Cp*Fe(η^5 -P₅)] (1, Cp*= η^5 -C₅Me₅) was synthesized as reported in the literature.¹ All solvents were degassed and distilled under nitrogen atmosphere from Na/K alloy (*n*-pentane), from Na (toluene) or from CaH₂ (CH₂Cl₂ and CH₃CN) prior to use. IR spectra were recorded on a Varian FTS-800 FT-IR spectrometer. ¹H, and ³¹P NMR spectra were performed at room temperature using the Bruker Avance 300 spectrometer. ¹H chemical shifts were reported in parts per million (ppm) relative to Me₄Si as external standard. ³¹P NMR chemical shifts were expressed in ppm relative to external 85% H₃PO₄ and were decoupled from the proton. For the ESI-MS a Finnignan Thermoquest TSQ 7000 mass spectrometer was used. Elemental analyses were performed by the microanalytical laboratory of the Universität Regensburg.

Synthesis of $[Cu_2Cl_2\{Cp^*Fe(\mu_3, \eta^{5:1:1}-P_5)\}(\mu, \eta^{1:1}-C_{10}H_8N_2)]_n$ (2):

In a Schlenk tube, two equivalents of CuCl (10 mg, 0.1 mmol) and one equivalent of 4,4'-bipyridine (8 mg, 0.05 mmol) were dissolved in a solvent mixture of CH_2Cl_2 (8 mL) and CH_3CN (5 mL) before pentaphosphaferrocene (1, 17 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was added dropwise and the resulting mixture was stirred for 3 h at ambient temperature. The brown solution was filtered to remove any suspended particles and crystallisation was performed by layering with the aid of *n*-pentane (20 mL) and storing at room temperature. In few days brown crystals of **2** x 0.5 C_5H_{12} are formed. The crystals were filtered, washed with *n*-pentane (4 x 2 mL) and dried under reduced pressure (**2**, 26 mg, 84%).

³¹P{¹H} NMR (121.49 MHz, CD₃CN): δ = 151.7 ppm. Positive ion ESI-MS (CH₃CN): m/z (%) = 854.8 (2) [Cu₂Cl(Cp*FeP₅)₂]⁺, 754.8 (20) [Cu(Cp*FeP₅)₂]⁺, 449.9 (100) [Cu(Cp*FeP₅)(CH₃CN)]⁺; Elemental analysis, calcd. (%) for C_{22.5}H₂₉Cl₂Cu₂FeN₂P₅ (736.20 g·mol⁻¹): C 36.70, H 3.97, N 3.80; found: C 36.23, H 3.60. N 3.88.

Synthesis of $[Cu_2Cl_2\{Cp^*Fe(\mu_3, \eta^{5:1:1}-P_5)\}(\mu, \eta^{1:1}-C_{10}H_8N_2)]_n$ (3):

In a Schlenk tube, two equivalents of CuCl (10 mg, 0.1 mmol) and one equivalent of 4,4'-bipyridine (8 mg, 0.05 mmol) were dissolved in a solvent mixture of CH_2Cl_2 (8 mL) and CH_3CN (5 mL) before pentaphosphaferrocene (1, 17 mg, 0.05 mmol) in toluene (3 mL) was added dropwise and the resulting mixture was stirred for 3 h at ambient temperature. The brown solution was filtered to remove any suspended particles and crystallisation was performed by layering with the aid of toluene (20 mL) and storing at room temperature. In few days brown crystals of **3** are formed. The crystals were filtered, washed with *n*-pentane (4 x 4 mL) and dried under reduced pressure (**3**, 24 mg, 75%).

³¹P{¹H} NMR (121.49 MHz, CD₃CN): δ = 151.7 ppm. Positive ion ESI-MS (CH₃CN): m/z (%) = 854.1 (14) [Cu₂Cl(Cp*FeP₅)₂]⁺, 754.4 (28) [Cu(Cp*FeP₅)₂]⁺, 450.92 (100) [Cu(Cp*FeP₅)(CH₃CN)]⁺; Elemental analysis, calcd. (%) for C₂₁H₂₅Cl₂Cu₂FeN₂P₅ (714.15 g·mol⁻¹): C 35.32, H 3.53, N 3.92; found: C 35.42, H 3.52, N 4.02.

Synthesis of $[(CuCl)_2 \{Cp^*Fe(\mu_3, \eta^{5:1:1}-P_5)\}_2(\mu, \eta^{1:1}-C_{12}H_{10}N_2)]_n$ (4):

In a Schlenk tube, two equivalents of CuCl (10 mg, 0.1 mmol) and one equivalent of 1,2-di(4pyridyl)ethylene (9 mg, 0.05 mmol) were dissolved in a solvent mixture of CH_2Cl_2 (8 mL) and CH_3CN (5 mL) before pentaphosphaferrocene (**1**, 17 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was added dropwise and the resulting mixture was stirred for 3 h at ambient temperature. The brown solution was filtered to remove any suspended particles and crystallisation was performed by layering with the aid of *n*-pentane (20 mL) and storing at room temperature. In few days brown crystals of **4** are formed. The crystals were filtered, washed with *n*-pentane (6 x 2 mL) and dried under reduced pressure (**4**, 14 mg, 40%).

³¹P{¹H} NMR (121.49 MHz, CD₃CN): δ = 151.7 ppm. Positive ion ESI-MS (CH₃CN): m/z (%) = 853.9 (8) [Cu₂Cl(Cp*FeP₅)₂]⁺, 754.8 (30) [Cu(Cp*FeP₅)₂]⁺, 449.98 (92) [Cu(Cp*FeP₅)(CH₃CN)]⁺.

Crystallographic Details

Single crystals suitable for single crystal X-ray structural analysis were obtained for derivatives **2**, **3** and **4** as reported above. All data were collected either with an Rigaku (former Agilent Technologies) Gemini diffractometer (former Agilent Technologies) equipped with an Atlas (**2**) detector or with an Rigaku SuperNova diffractometer equipped with an Atlas (**3**) or Titan (**4**) detector with Cu*K* α radiation ($\lambda = 1.54178$ Å) using 1° ω scans. The data processing was performed with the CrysAlis software package.² Absorption corrections were applied analytically based on crystal faces. Structure of all compounds was solved by direct methods using the programs SHELXS³ or SIR-97⁴. The *SHELXL-2014/7* program was used to refine the structures by full-matrix least-squares based on *F*². All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and included into refinement with isotropic displacement parameters riding on pivot atoms.

In **3** one of the Cp* ligands is disordered by rotation over two positions; the carbon atoms of the major (0.8) and minor (0.2) positions were refined anisotropically and isotropically, respectively.

An overview of all crystallographic data is given in Table S1; Figures S1-S4 contain colour drawings and the corresponding Tables S2-S4 include detailed information about relevant bond lengths and angles. The analysis of intermolecular interactions and topological features of the crystal structures **2**, **3** and **4** was performed using TOPOSPro.⁵

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for **2**, **3** and **4** are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-1583104 (**2**), CCDC-1583105 (**3**), and CCDC-1583106 (**4**).

Compound	2	3	4
Formula	$C_{22.5}H_{29}Cl_2Cu_2FeN_2P_5$	$C_{21}H_{25}Cl_2Cu_2FeN_2P_5$	$C_{32}H_{40}CI_2Cu_2Fe_2N_2P_{10}\\$
CCDC number	1583104	1583105	1583106
Mr	736.16	785.01	1072.04
T [K]	123(1)	123(2)	123(2)
crystal system	orthorhombic	monoclinic	monoclinic
space group	Pnma (62)	P2 ₁ /n (14)	P2 ₁ /c (14)
a [Å]	12.3031(2)	14.4625(2)	10.6499(2)
b [Å]	19.7158(3)	12.2860(2)	12.1659(2)
c [Å]	24.8166(4)	17.1230(3)	17.0371
β [°]	90	100.6290(19)	105.903
V[ų]	6019.65(17)	2990.32(8)	2122.94(6)
Z	8	4	2
colour	brown	brown	brown
crystal size [mm]	0.20 × 0.18 × 0.08	0.17 × 0.06 × 0.05	0.19 × 0.15 × 0.08
δ _{calc} [Mg m ⁻³]	1.625	1.744	1.677
F(000)	2968	1568	1080
µ [mm ⁻¹]	9.729	11.444	11.443
λ [Å]	1.54178	1.54178	1.54178
diffractometer	Rigaku SuperNova	Rigaku Gemini R Ultra	Rigaku SuperNova
Index ranges hkl	$-15 \le h \le 9$ $-20 \le k \le 24$ $-24 \le l \le 29$	$-17 \le h \le 17$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-14 \le k \le 9$ $-21 \le l \le 16$
θ limit [°]	$3.56 \le \theta \le 74.27$	$3.68 \le \theta \ \le 67.03$	$4.32 \le \theta \le 73.77$
Reflections collected	13320	23535	6696
Independent reflections	6092	5284	4047
Reflections [I>2σ (I)]	5396	4592	3488
Data/restraints/parameters	6092/0/360	5284/0/321	4047/0/231
Goodness-of-fit on F ²	1.025	1.062	0.967
R(int)	0.0240	0.0251	0.0277
Final R indices [I>2σ(I)]	R1 = 0.0286 wR2 = 0.0693	R1 = 0.0297 wR2 = 0.0814	R1 = 0.0310 wR2 = 0.0738
R indices (all data)	R1 = 0.0343 wR2 = 0.0727	R1 = 0.0349 wR2 = 0.0834	R1 = 0.0310 wR2 = 0.0747
Largest diff peak and hole [e Å ⁻³]	0.334 and -0.492	1.075 and -0.714	0.695 and -0.627

Table S1. Crystallographic data of the polymers 2, 3 and 4.



Figure S1. a) View of the repeating unit in polymer **2** in the solid-state. Cu: aqua, Cl: green, N: blue, P: pink, C: grey, Fe: olive. Cp* residues as well as parts of the *bipy* ligands are depicted in stick style; hydrogen atoms as well as solvent molecules are omitted for clarity. b) View of the independent part in crystal structure of polymer **2** (a.d.p. parameters of 50% probability). Hydrogen atoms are omitted for clarity.

Table S2	Selected	geometric	parameters	for com	pound 2
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bond lengths [Å]		bond angles [°]				
Cu1—Cl1	2.3351(6)	Cu1—Cl1—Cu2	72.809(19)	P5—Cu2—Cu1	135.99 (2)	
Cu1—Cl2	2.3681(6)	Cu2—Cl2—Cu1	72.080(19)	P5—Cu2—Cl1	120.14(3)	
Cu2—Cl1	2.3524(6)	P2—Cu1—Cu2	131.31(2)	P5—Cu2—Cl2	110.70(3)	
Cu2—Cl2	2.3603(7)	P2—Cu1—Cl1	122.90(2)	N2 ⁱ —Cu2—P5	112.54(6)	
Cu1—N1	2.0247(18)	P2—Cu1—Cl2	103.33(2)	N2 ⁱ —Cu2—Cu1	111.27(6)	
Cu1—P2	2.1736(7)	N1—Cu1—P2	113.49(6)	N2 ⁱ —Cu2—Cl1	101.20(6)	
Cu1—Cu2	2.7820(5)	N1—Cu1—Cu2	114.17(6)	N2 ⁱ —Cu2—Cl2	103.25(6)	
Cu2—N2 ⁱ	2.0405(19)	N1—Cu1—Cl1	102.35(6)	Cl1—Cu2—Cu1	53.308(16)	
Cu2—P5	2.1820(7)	N1—Cu1—Cl2	105.99(5)	Cl1—Cu2—Cl2	107.40(2)	
Cu1—Cl1	2.3351(6)	Cl2—Cu1—Cu2	53.831(17)	Cl2—Cu2—Cu1	54.089(16)	
Cu1—Cl2	2.3681(6)	Cl2-Cu1-Cl1	107.71(2)	Cl1–Cu1–Cu2	53.883(17)	

Symmetry code(s): (i) -x+1/2, -y+1, z-1/2; (ii) x, -y+3/2, z, (iii) x, -y+1/2, z, (iv) -x+1/2, -y+1, z+1/2.



Figure S2. a) View of the repeating unit in polymer **3** in the solid-state. Cu: aqua, Cl: green, N: blue, P: pink, C: grey, Fe: olive. Cp* residues as well as parts of the *bipy* ligands are depicted in stick style; hydrogen atoms are omitted for clarity. b) View of the independent part in crystal structure of polymer **3** (a.d.p. parameters of 50% probability). Hydrogen atoms are omitted for clarity

bond lengths [Å]		bond angles [°]				
Cu1–N1	2.061 (2)	P1–Cu1–P4 ⁱ	109.70 (3)	N1–Cu1–P4	92.77 (6)	
Cu1–P1	2.2109 (7)	P1–Cu1–Cl1	121.42 (3)	N1–Cu1–Cl1	107.50 (6)	
Cu1–Cl1	2.2474 (7)	N1-Cu1-P1	115.03 (6)	CI1–Cu1–P4 ⁱ	106.35 (3)	
Cu1–P4 ⁱ	2.3154 (7)					

Table S3. Selected geometric parameters for compound 3.

Symmetry code(s): (i) -x+1, y-1/2, -z+1/2, -z+1/2; (ii) -x+1, y+1/2.



Figure S3. Constitutional isomerism of plane layers in 2 (left) and 3 (right) representing two or one type of meshes, respectively and showing partially entrapped pentane (2) or dichloromethane (3) molecules. No significant π - π stacking interactions between the layers are found. Cu: aqua, Cl: green, N: blue, P: pink, C: grey, Fe: olive. H atoms (unless for the solvent molecules) are omitted for clarity. See also Table S7 for topology.



Figure S4. a) View of the repeating unit in polymer **4** in the solid-state. Cu: aqua, Cl: green, N: blue, P: pink, C: grey, Fe: olive. Cp* residues as well as parts of the *dpe* ligands are depicted in stick style; hydrogen atoms are omitted for clarity. b) View of the independent part in crystal structure of polymer **4** (a.d.p. parameters of 50% probability).

Table S4. Selected geometric parameters for compound 4.

bond lengths [Å]		bond angles [°]			
Cu1–N1	2.061(2)	P1–Cu1–P4 ⁱ	109.70(3)	N1–Cu1–P4 ⁱ	92.77(6)
Cu1–P1	2.2109(7)	P1–Cu1–Cl1	121.42(3)	N1–Cu1–Cl1	107.50(6)
Cu1–Cl1	2.2474(7)	N1-Cu1-P1	115.03(6)	Cl1–Cu1–P4 ⁱ	106.35(3)
Cu1–P4 ⁱ	2.3154(7)				
P4–Cu1 ⁱⁱ	2.3154(7)				

Symmetry code(s): (i) -x+1, y+1/2, -z+1/2; (ii) -x+1, y-1/2, -z+1/2.



Figure S5. Intralayer stacking interactions between Cp* and *dpe* in 4. Cu: aqua, Cl: green, N: blue, P: pink, C: grey, Fe: olive. H atoms are omitted for clarity.

	node	spacer	coordination figure	network	topology
2D		•			
2 3		<i>bipy</i> , Cp*FeP₅			sql ⁶
4	Cu ₂ Cl ₂	dpe,			hcb⁵
	CuCl	Cp*⊦eP₅	Ψ-tetrahedron		

Table S5. Topological features of the 2D polymers 2, 3 and 4.

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