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

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List of numbered compounds:
For co-crystallized solvent molecules see X-ray part.

1a  [K(P₃C₂Mes₂)]
1b  [K(P₃C₂Bu₂)]
2  [(μ,η⁴:η³-P₃C₂Mes₂)₂{Cu(CH₂CN)}₂{Cu(CH₂CN)}]⁺[Cl⁻]ₙ
3  [(μ,η⁴:η³-P₃C₂Mes₂){Cu(CH₂CN)(μ₂-Cl)}₄{K(μ₂-dme)}{Cu(CH₂CN)₀.₅(μ₂-Cl)}]ₙ
4  [(μ,η⁴:η³-P₃C₂Mes₂){Cu(CH₂CN)(μ₂-Br)}₂{K(μ₂-thf)}{Cu(μ₂-Br)}]ₙ
5  [(μ,η⁴:η³-P₃C₂Mes₂){Cu(CH₂CN)(μ₂-I)}₂{Cu(CH₂CN)(μ₃-I)}₂Cu]ₙ
6  [(μ,η⁴:η³-P₃C₂Mes₂){Cu(CH₂CN)(μ₂-I)}₂{Cu(CH₂CN)(μ₃-I)}₂Cu₂{Cu(CH₂CN)}(μ₃-I)(μ₂-I)]ₙ
7  [(μ,η⁴:η³-P₃C₂Bu₂){CuCl₂(μ₂-Cl)}₂{Cu(CH₂CN)}₃{Cu(CH₂CN)₃}{Cu(CH₂CN)₃}]ₙ
8  [(P₃C₂Bu₂)₃Cu₉.₈₅Cl₆.₈₅(CH₂CN)₁.₅]ₙ
9  [(P₃C₂Bu₂)₃Cu₁₀.₁Br₇.₁(CH₂CN)₁.₂]ₙ
10 [K(thf)₆]ₙ[(μ,η⁴:η³-P₃C₂Bu₂)₂{Cu₅(μ₂-I)}₂{Cu(μ₂-I)}]ₙ

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1. Experimental Part

All reactions were performed under an inert atmosphere of dry nitrogen or argon with standard vacuum, Schlenk, and glove-box techniques. Solvents were purified, dried and degassed prior to use by standard procedures. [K(P₃C₃Mes₂)]⁺ and [K(P₃C₃Bu₃)]⁻ were synthesized following reported procedures. Commercially available chemicals were used without further purification. Solution NMR spectra were recorded on either Bruker Avance 300 or 400 spectrometer. The corresponding ESI-MS spectra were obtained on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer, while elemental analyses were performed on a Vario EL III apparatus.

1.1 Synthesis of 2

In a Schlenk tube a solution of [K(P₃C₃Mes₂)] (66 mg, 0.17 mmol) in dme (10 mL) is layered with a solution of CuCl (50 mg, 0.5 mmol) in CH₃CN (10 mL). At the phase boundary a color change to deep red can be observed. After complete diffusion and precipitation of a beige powder the red solution is decanted. While storing at 8°C the formation of red rods of 2 can be observed within a few days. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo. By concentrating the mother liquor and layering with Et₂O, a second crop of crystals can be obtained.

Analytical data of 2:

Yield: 40 mg (0.34 mmol, 20%)

³¹H NMR (CD₃CN): δ [ppm] = 2.02 (s, 3H, o-CH₃), 2.11 (s, 3H, o-CH₃), 2.25 (s, 3H, p-CH₃), 3.28 (s, (CH₂OCH₂)₂), 3.45 (s, (CH₂OCH₂)₂), 6.88 (s, 2H, aryl-H).

Positive ion ESI-MS (CH₃CN): m/z (%) = 2356.7 [[P₃C₃Mes₂]₄CuCl₂]⁺, 2257.6 [[P₃C₃Mes₂]₄CuCl]⁺, 2036.4 [[P₃C₃Mes₂]₄Cu₂Cl]⁺, 1936.6 [[P₃C₃Mes₂]₄Cu₂Cl]⁺, 1837.6 [[P₃C₃Mes₂]₄CuCl]⁺, 1739.6 [[P₃C₃Mes₂]₄Cu]⁺, 1517.3 [[P₃C₃Mes₂]₄CuCl]⁺, 1419.2 [[P₃C₃Mes₂]₄CuCl]⁺, 1319.3 [[P₃C₃Mes₂]₄CuCl]⁺, 998.9 [[P₃C₃Mes₂]₄CuCl]⁺, 901.2 [[P₃C₃Mes₂]₄Cu]⁺±

Negative ion ESI-MS (CH₃CN): m/z (%) = 232.6 [CuCl₂], 134.8 (100) [CuCl]⁻

1.2 Synthesis of 3

In a Schlenk tube a solution of [K(P₃C₃Mes₂)] (50 mg, 0.12 mmol) in dme (9 mL) is first layered with a solvent mixture of dme and CH₃CN (1:1; 3 mL), afterwards with a solution of CuCl (51 mg, 0.52 mmol) in CH₃CN (12 mL). After complete diffusion and precipitation of a beige powder the red solution is filtered and concentrated to 5 mL. While storing at -28°C the formation of yellow prisms of 3 can be observed within a few days. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo. By concentrating the mother liquor, a second crop of crystals can be obtained.

Analytical data of 3:

Yield: 66 mg (0.068 mmol, 57%)

³¹H NMR (CD₃CN): δ [ppm] = 1.95 (s, CH₃CN), 2.03 (s, 3H, o-CH₃), 2.19 (s, 3H, o-CH₃), 2.26 (s, 3H, p-CH₃), 6.90 (s, 2H, aryl-H).

³¹P[⁴H] NMR (mother liquor, dme/CH₃CN/C₆D₆): δ [ppm] = 31.3 (br), 117.7 (br), 218.3 (br).

Positive ion ESI-MS (CH₃CN): m/z (%) = 2333.9 [[P₃C₃Mes₂]₄Cu₃Cl₄]⁺, 2223.7 [[P₃C₃Mes₂]₄Cu₂Cl₄]⁺, 2134.4 [[P₃C₃Mes₂]₄CuCl₂]⁺, 2035.2 [[P₃C₃Mes₂]₄CuCl]⁺, 1978.5 [[P₃C₃Mes₂]₄CuCl₂(CH₃CN)]⁺, 1937.1 [[P₃C₃Mes₂]₄CuCl]⁺, 1837.2 [[P₃C₃Mes₂]₄CuCl]⁺, 1738.5 [[P₃C₃Mes₂]₄CuCl]⁺, 1617.1 [[P₃C₃Mes₂]₄CuCl]⁺, 1419.4 [[P₃C₃Mes₂]₄CuCl]⁺, 1319.0 [[P₃C₃Mes₂]₄CuCl]⁺, 1198.8 [[P₃C₃Mes₂]₄CuCl]⁺, 1139.8 [[P₃C₃Mes₂]₄CuCl₂(CH₃CN)]⁺, 1098.8 [[P₃C₃Mes₂]₄CuCl]⁺, 991.7 [[P₃C₃Mes₂]₄CuCl₂(CH₃CN)₂]⁺, 970.7 [[P₃C₃Mes₂]₄CuCl(CH₃CN)₂]⁺, 950.7 [[P₃C₃Mes₂]₄CuCl]⁺, 901.2 [[P₃C₃Mes₂]₄CuCl]⁺

Negative ion ESI-MS (CH₃CN): m/z (%) = 530.4 [Cu₃Cl₄]⁻, 232.8 [CuCl₂]⁻, 135.0 (100) [CuCl]⁻
Elemental analysis: Calculated (%) for \([\text{P(C}_2\text{Mes}_2)]_2\text{Cu}_5\text{K(CH}_3\text{CN)}\text{(dme)}_{0.5}\) (976 g/mol): C 29.55, H 3.10, N 1.44; found: C 29.12, H 3.29, N 1.83.

1.3 Synthesis of 4

In a Schlenk tube a solution of \([\text{K(P(C}_2\text{Mes}_2)]\) (50 mg, 0.12 mmol) in dme (9 mL) is first layered with a solvent mixture of dme and CH_3 CN (1:1; 3 mL), afterwards with a solution of CuBr (93 mg, 0.52 mmol) in CH_3 CN (12 mL). After complete diffusion and precipitation of a beige powder the red solution is stored at -28°C. Within one day the formation of yellow-orange blocks of 4 can be observed. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and thf (2 x 8 mL) and dried in vacuo. By concentrating the mother liquor and storing it at -28°C, a second crop of crystals can be obtained. 4 can also be synthesized by using thf instead of dme, however due to the lower solubility of \([\text{K(P(C}_2\text{Mes}_2)]\) in thf a larger volume is needed (20 mL).

Analytical data of 4:

Yield: 145 mg (0.106 mmol, 88%)

^1^H NMR (CD_3 CN): δ [ppm] = 1.79 (m, thf), 1.95 (s, CH_3 CN), 2.04 (s, 3H, o-CH_3), 2.11 (s, 3H, o-CH_3), 2.26 (s, 3H, p-CH_3), 3.63 (m, thf) 6.89 (s, 2H, ary-H).

^3^P[^1^H] NMR (CD_3 CN): δ [ppm] = 137.9 (br), 204.3 (br), 216.8 (br).

Positive ion ESI-MS (CH_3 CN): m/z (%) = 2457.8 [[P(C_2 Mes_2)]_2Cu_{10}Br_3]^+, 2313.5 [[P(C_2 Mes_2)]_2Cu_6Br_4]^+, 2169.1 [[P(C_2 Mes_2)]_2Cu_8Br_4]^+, 2025.2 [[P(C_2 Mes_2)]_2Cu_6Br_4]^+, 1881.4 [[P(C_2 Mes_2)]_2Cu_8Br_4]^+, 1749.0 [[P(C_2 Mes_2)]_2Cu_8Br_4]^+, 1738.6 [[P(C_2 Mes_2)]_2Cu_8Br_4]^+, 1474.5 [[P(C_2 Mes_2)]_2Cu_6Br_4]^+, 1423.6 [[P(C_2 Mes_2)]_2Cu_10Br_3(CH_3 CN)]^+, 1373.9 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1302.0 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1280 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1259 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1229.5 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1208 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1187.6 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1156.8 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1107.1 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1086.1 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1063.4 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 1013.7 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 993.4 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+, 973 [[P(C_2 Mes_2)]_2Cu_12Br_6(CH_3 CN)]^+.

Negative ion ESI-MS (CH_3 CN): m/z (%) = 796.2 [Cu_6Br_4]^-, 654.5 [Cu_6Br_4]^-, 508.5 [Cu_6Br_4]^-, 366.7 [Cu_6Br_4]^-, 222.8 [CuBr_2]^-

Elemental analysis: Calculated (%) for [[P(C_2 Mes_2)]_2Br_3Cu_5K(CH_3 CN)]_3(dme)] (1370 g/mol): C 28.05, H 3.38, Br 29.16, N 3.07; found: C 27.52, H 3.20, Br 29.20, N 3.24.

Elemental analysis (after drying in vacuo for several hours): Calculated (%) for [[P(C_2 Mes_2)]_2Br_3Cu_5K(CH_3 CN)] (1153 g/mol): C 22.92, H 2.19, N 1.22; found: C 22.57, H 2.53, N 1.34.

1.4 Synthesis of \(\{(\mu,\eta^1,\eta^2:\eta^2-P(C_2 Mes_2)_2)(Cu(CH_3 CN)(\mu_2-I))_4(Cu(CH_3 CN)_3)\}\)

In a Schlenk tube a solution of \([K(P(C_2 Mes_2)]\) (50 mg, 0.12 mmol) in dme (9 mL) is first layered with a solvent mixture of dme and CH_3 CN (1:1; 3 mL), afterwards with a solution of CuI (123 mg, 0.52 mmol) in CH_3 CN (12 mL). After complete diffusion and precipitation of a beige powder the red solution is filtered and concentrated to 10 mL. While storing at -28°C the formation of small orange polyhedrons of \(\{(\mu,\eta^1,\eta^2:\eta^2-P(C_2 Mes_2)_2)(Cu(CH_3 CN)(\mu_2-I))_4(Cu(CH_3 CN)_3)\}\) can be observed. The mother liquor is decanted, the crystals are washed with pentane (3 x 5 mL) and dried in vacuo. By concentrating the mother liquor to 2 mL and storing it at -28°C, a second crop of crystals can be obtained, which is isolated in the same way as before. \(\{(\mu,\eta^1,\eta^2:\eta^2-P(C_2 Mes_2)_2)(Cu(CH_3 CN)(\mu_2-I))_4(Cu(CH_3 CN)_3)\}\) can also be synthesized by using thf instead of dme, however due to the lower solubility of \([K(P(C_2 Mes_2)]\) in thf a larger volume is needed (20 mL). \(\{(\mu,\eta^1,\eta^2:\eta^2-P(C_2 Mes_2)_2)(Cu(CH_3 CN)(\mu_2-I))_4(Cu(CH_3 CN)_3)\}\) can also be synthesized by using [Cp*Fe(η^5-P(C_2 Mes_2))] as starting material.
Yield: 55 mg (0.042 mmol, crystalline, 40% referred to CuI)

^1^H NMR (CDCl₃): δ [ppm] = 1.95 (s, CH₃CN), 2.04 (s, 3H, p-CH₃), 2.13 (s, 3H, p-CH₃), 2.22 (s, 6H, o-CH₃), 2.27 (s, 6H, o-CH₃), 6.90 (s, 4H, aryl-H).

^1^C[^3]^H NMR (CDCl₃): δ [ppm] = 21.14, 23.50, 26.23, 128.66, 136.86, 138.37.

^3^P[^3]^H NMR (CDCl₃): δ [ppm] = 134 (br), 153.0 (br), 205 (br), 224 (br).

**Positive ion ESI-MS** (CH₃CN): m/z (%) = 2883.2 [[P₂C₆Mes₂]₂CuI₄]⁺, 2878.2 [[P₂C₆Mes₂]₅CuI₃]⁺, 2861.5 [[P₂C₆Mes₂]₆CuI₄]⁺, 2691.5 [[P₂C₆Mes₂]₅CuI₄]⁺, 2650.4 [[P₂C₆Mes₂]₅CuI₄]⁺, 2500.1 [[P₂C₆Mes₂]₅CuI₄]⁺, 2463.1 [[P₂C₆Mes₂]₅CuI₄]⁺, 2424.7 [[P₂C₆Mes₂]₅CuI₄]⁺, 2312.7 [[P₂C₆Mes₂]₅CuI₄]⁺, 2273.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 2234.7 [[P₂C₆Mes₂]₅CuI₄]⁺, 2191.7 [[P₂C₆Mes₂]₅CuI₄]⁺, 2081.2 [[P₂C₆Mes₂]₅CuI₄]⁺, 2042.9 [[P₂C₆Mes₂]₅CuI₄]⁺, 1929.1 [[P₂C₆Mes₂]₅CuI₄]⁺, 1890.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1742.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1700.9 [[P₂C₆Mes₂]₅CuI₄]⁺, 1661.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1511.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1472.4 [[P₂C₆Mes₂]₅CuI₄]⁺, 1321.6 [[P₂C₆Mes₂]₅CuI₄]⁺, 1285.2 [[P₂C₆Mes₂]₅CuI₄]⁺, 1242.2 [[P₂C₆Mes₂]₅CuI₄]⁺, 1172.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1131.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1090.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1052.4 [[P₂C₆Mes₂]₅CuI₄]⁺

**Negative ion ESI-MS** (CH₃CN): m/z (%) = 1270.1 [CuI]⁻, 1078.2 [Cu₂I]⁻, 888.3 [Cu₃I]⁻, 698.5 [Cu₄I]⁻, 506.6 [Cu₅I]⁻, 316.8 (100) [CuI]⁻

**Elemental analysis:** Calculated (%): for [P₂C₆Mes₂]₂CuI₄(CH₃CN)₂ (1304 g/mol): C 23.96, H 2.40, N 3.22; found: C 23.96, H 2.50, N 3.28.

1.5 **Synthesis of ([μ,η⁴:η³-P₂C₆Mes₂]₅Cu(CH₃CN)]₂{Cu(μ-Ι)}₄**

In a Schlenk tube [K(P₂C₆Mes₂)] (80 mg, 0.2 mmol) and CuI (190 mg, 1.0 mol) are dissolved in a solvent mixture of dme (15 mL) and CH₂CN (3 mL). An immediate colour change to deep red and turbidity can be observed. The solution is stirred for 10 hours. After filtration the solvent of the red solution is removed in vacuo. The red solid is dissolved in a solvent mixture of CH₂CN (ca. 8 mL) and CH₂Cl₂ (ca. 8 mL), again filtered and layerow with Et₂O. While storing at 8°C the formation of crystals of [μ,η⁴:η³-P₂C₆Mes₂]₂{Cu(CH₃CN)]₂{Cu(μ-Ι)}₄ can be observed. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

[μ,η⁴:η³-P₂C₆Mes₂]₂{Cu(CH₃CN)]₂{Cu(μ-Ι)}₄ can also be synthesized by using [Cp*Fe(η³-P₂C₆Mes₂)] as starting material.3

Analytical data of [μ,η⁴:η³-P₂C₆Mes₂]₂{Cu(CH₃CN)]₂{Cu(μ-Ι)}₄:

Yield: 45 mg (0.021 mmol, crystalline, 17% referred to CuI)

^1^H NMR (CDCl₃): δ [ppm] = 1.95 (s, CH₃CN), 2.04 (s, 3H, p-CH₃), 2.13 (s, 12H, o-CH₃), 2.22 (s, 6H, o-CH₃), 2.26 (s, 6H, p-CH₃), 6.90 (s, 4H, aryl-H).

^3^P[^3]^H NMR (CDCl₃): δ [ppm] = 135 (br), 206 (br), 223 (br).

**Positive ion ESI-MS** (CH₃CN): m/z (%) = 2693.1 [[P₂C₆Mes₂]₂CuI₄]⁺, 2501.1 [[P₂C₆Mes₂]₅CuI₃]⁺, 2462.7 [[P₂C₆Mes₂]₅CuI₄]⁺, 2311.2 [[P₂C₆Mes₂]₅CuI₄]⁺, 2274.7 [[P₂C₆Mes₂]₅CuI₄]⁺, 2191.2 [[P₂C₆Mes₂]₅CuI₄]⁺, 2082.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1929.4 [[P₂C₆Mes₂]₅CuI₄]⁺, 1891.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1740.1 [[P₂C₆Mes₂]₅CuI₄]⁺, 1701.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1662.6 [[P₂C₆Mes₂]₅CuI₄]⁺, 1550.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1511.1 [[P₂C₆Mes₂]₅CuI₄]⁺, 1472.8 [[P₂C₆Mes₂]₅CuI₄]⁺, 1322.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1283.6 [[P₂C₆Mes₂]₅CuI₄]⁺, 1173.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 1131.9 [[P₂C₆Mes₂]₅CuI₄]⁺, 1093.0 [[P₂C₆Mes₂]₅CuI₄]⁺, 996.2 [[P₂C₆Mes₂]₅CuI₄]⁺, 901.2 [[P₂C₆Mes₂]₅CuI₄]⁺

**Negative ion ESI-MS** (CH₃CN): m/z (%) = 2562.5 [[P₂C₆Mes₂]₅CuI₄]⁻, 2528.7 [[P₂C₆Mes₂]₅CuI₄]⁻, 2490.2 [[P₂C₆Mes₂]₅CuI₄]⁻, 2373.2 [[P₂C₆Mes₂]₅CuI₄]⁻, 2334.9 [[P₂C₆Mes₂]₅CuI₄]⁻, 2296.4 [[P₂C₆Mes₂]₅CuI₄]⁻, 2144.7 [[P₂C₆Mes₂]₅CuI₄]⁻, 2106.7 [[P₂C₆Mes₂]₅CuI₄]⁻, 2070.2 [[P₂C₆Mes₂]₅CuI₄]⁻, 1954.9 [[P₂C₆Mes₂]₅CuI₄]⁻, 1916.5
In a Schlenk tube a solution of $[\text{K(P(C_{2}Mes_{3})_{2})}]$ (16 mg, 0.042 mmol) in dme (5 mL) is layered with a solution of CuI (25 mg, 0.13 mmol) in CH$_{3}$CN (5 mL). After complete diffusion the red solution is concentrated to 5 mL and layered with hexane. The formation of small red-brown blocks of 5 at the phase boundary could be observed once. The mother liquor was decanted, the crystals were washed with hexane (3 x 5 mL) and dried in vacuo. Attempts to reproduce 5 failed every time.

Analytical data of 5:

**Yield:** a few crystals (< 5%)

**Positive ion ESI-MS** (CH$_{3}$CN): $m/z$ (%) = 2692.5 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{10}]^{+}$; 2500.6 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{2}]^{+}$; 2309.5 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{3}]^{+}$; 2119.5 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{4}]^{+}$; 2079.1 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{5}]^{+}$; 1929.4 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{6}]^{+}$; 1891.0 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{7}]^{+}$; 1739.6 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{8}]^{+}$; 1700.9 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{9}]^{+}$; 1552.1 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI(CH}_{3}\text{CN})]^{+}$; 1511.1 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}]^{+}$; 1472.6 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}_{2}]^{+}$; 1319.2 (100) $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}]^{+}$; 1172.8 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI(CH}_{3}\text{CN})_{2}]^{+}$; 1131.9 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI(CH}_{3}\text{CN})]^{+}$; 1090.9 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}]^{+}$; 901.0 $[\text{P(C_{2}Mes}_{3})_{2}\text{CuI}]^{+}$

**Negative ion ESI-MS** (CH$_{3}$CN): $m/z$ (%) = 888.4 [CuI$_{3}$]; 698.5 [CuI$_{4}$]; 506.6 [CuI$_{5}$]; 316.8 (100) [CuI$_{2}$]

1.7 **Synthesis of 6**

A solution of $[\text{K(P(C_{2}Mes}_{3})_{2})]$ (33 mg, 0.084 mmol) in dme (15 mL) is added to a solution of CuI (160 mg, 0.84 mmol) in CH$_{3}$CN (15 mL), whereas the solution turned deep red. It was stirred for three hours, filtered and layered with Et$_{2}$O. After several months at r.t. orange crystals of 6 at the upper level have formed. The mother liquor was decanted, the crystals were washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of 6:

**Yield:** 86 mg (0.05 mmol, crystalline, 60%)

**$^1$H NMR** (CD$_{3}$CN): $\delta$ [ppm] = 1.11 (t, Et$_2$O), 1.95 (s, CH$_3$CN), 2.26 (s, 6H, $\text{CH}_2$), 2.28 (s, 3H, $\text{CH}_3$), 2.28 (s, dme), 3.41 (q, 1H, Et$_2$O), 3.44 (s, dme), 6.93 (s, 2H, $\text{aryl-H}$).

**$^{31}$P($^1$H) NMR** (CD$_{3}$CN): $\delta$ [ppm] = 136 (br, 2P), 222 (br, 1P).

**Negative ion ESI-MS** (dme, CH$_{3}$CN, Et$_2$O): $m/z$ (%) = 888.3 [CuI$_{3}$]; 698.4 [CuI$_{4}$]; 506.6 [CuI$_{5}$]; 316.7 (100) [CuI$_{2}$]

**Elemental analysis:** Calculated (%) for $([\text{P(C_{2}Mes}_{3})_{2}\text{I}]_{2}\text{Cu(CH}_{3}\text{CN})_{4})$: C 19.84, H 2.05, N 3.08; found: C 20.92, H 2.20, N 3.16.

1.8 **Synthesis of 7**

A solution of $[\text{K(P(C_{2}Mes}_{3})(\text{Bu}_{3})_{2})]$ (50 mg, 0.18 mmol) in dme (10 mL) is added to a solution of CuCl (55 mg, 0.56 mmol) in CH$_{3}$CN (10 mL). Within one minute the colour changes from yellow to orange up to red and becomes turbid after 30 minutes of stirring. After two hours the reaction mixture is filtered, the solvent removed in vacuo and the red solid dissolved in as less as possible CH$_{3}$CN. By cooling the formation of neon
orange plates of 7 is observed. The mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of 7:
**Yield**: 65 mg (0.044 mmol, 73% referred to \([\text{K(P}_3\text{C}_2\text{Bu}_2])\))

**1H NMR** (CD$_2$CN): $\delta$ [ppm] = 1.77 (s, 3 Bu), 1.99 (s, CH$_3$CN).

**31P(1H) NMR** (CD$_2$CN): $\delta$ [ppm] = 136.7 (s, br, 2P), 264.8 (s, br, 1P).

Positive ion ESI-MS (CH$_3$CN): $m/z$ (%) = 2918.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_6$Cl$_8$]$^+$, 2821.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_3$Cl$_1$]$^+$, 2725.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_4$Cl$_1$]$^+$, 2621.2 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_5$Cl$_1$]$^+$, 2523.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_3$Cl$_1$]$^+$, 2425.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_6$Cl$_1$]$^+$, 2327.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_4$Cl$_1$]$^+$, 2227.1 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_3$Cl$_1$]$^+$, 2129.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_5$Cl$_1$]$^+$, 2030.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_6$Cl$_1$]$^+$, 1935.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_5$Cl$_1$]$^+$, 1835.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_6$Cl$_1$]$^+$, 1185.9 [[P$_3$C$_2$Bu$_2$]$_2$CuCl$_1$](CH$_3$CN)]$^+$, 1144.9 [[P$_3$C$_2$Bu$_2$]$_2$CuCl$_2$]$^+$, 1046.9 [[P$_3$C$_2$Bu$_2$]$_2$CuCl$_3$]$^+$, 947.1 (100) [[P$_3$C$_2$Bu$_2$]$_2$Cu$_4$]$^+$.

Negative ion ESI-MS (CH$_3$CN): $m/z$ (%) = 2988.3 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_6$Cl$_1$]$^-$, 2891.1 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_7$Cl$_1$]$^-$, 2792.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_8$Cl$_1$]$^-$, 2694.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_6$Cl$_1$]$^-$, 2595.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_7$Cl$_1$]$^-$, 2498.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_8$Cl$_1$]$^-$, 2398.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_9$Cl$_1$]$^-$, 2298.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_10$Cl$_1$]$^-$, 2201.0 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_11$Cl$_1$]$^-$, 2102.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_12$Cl$_1$]$^-$, 2004.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_13$Cl$_1$]$^-$, 1906.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_14$Cl$_1$]$^-$, 1806.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_15$Cl$_1$]$^-$, 1708.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_16$Cl$_1$]$^-$, 1610.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_17$Cl$_1$]$^-$, 1512.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_18$Cl$_1$]$^-$, 1412.7 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_19$Cl$_1$]$^-$, 1314.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_20$Cl$_1$]$^-$, 1216.6 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_21$Cl$_1$]$^-$, 1118.6 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_22$Cl$_1$]$^-$, 1020.7 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_23$Cl$_1$]$^-$, 920.7 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_24$Cl$_1$]$^-$, 822.6 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_25$Cl$_1$]$^-$, 724.6 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_26$Cl$_1$]$^-$, 624.8 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_27$Cl$_1$]$^-$, 528.7 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_28$Cl$_1$]$^-$, 428.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_29$Cl$_1$]$^-$, 328.9 [[P$_3$C$_2$Bu$_2$]$_2$Cu$_30$Cl$_1$]$^-$, 232.7 [[CuCl$_3$]$^-$.]

Elemental analysis: Calculated (%) for \([(P_3C_2Bu_2)Cl_6Cu_0(CH_3CN)_2]\) (1560 g/mol): C 26.17, H 3.88, N 1.80; found: C 26.02, H 3.74, N 1.73.

1.9 Synthesis of 8

In a Schlenk tube a solution of \([\text{K(P}_3\text{C}_2\text{Bu}_2])\) (30 mg, 0.11 mmol) in dme (15 mL) is layered with a solution of CuCl (55 mg, 0.55 mmol) in CH$_3$CN (10 mL). Already after several hours the formation of big dark red blocks of 8 at the red phase boundary is observed. After complete diffusion the mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of 8:
**Yield**: 56 mg (0.031 mmol, 85% referred to \([\text{K(P}_3\text{C}_2\text{Bu}_2])\))

Negative ion ESI-MS (mother liquor, dme/CH$_3$CN): $m/z$ (%) = 232.6 [CuCl$_3$]$^-$, 134.7 [CuCl$_2$]$^-$

Elemental analysis: Calculated (%) for \([(P_3C_2Bu_2)Cl_6Cu_0(CH_3CN)_2(C_2H_5O_2)]\) (1790 g/mol): C 26.83, H 4.11, Cl 13.86, N 2.35; found: C 26.61, H 4.00, Cl 13.84, N 2.51.

1.10 Synthesis of 9

In a Schlenk tube a solution of \([\text{K(P}_3\text{C}_2\text{Bu}_2])\) (30 mg, 0.11 mmol) in dme (15 mL) is layered with a solution of CuBr (80 mg, 0.55 mmol) in CH$_3$CN (10 mL). Already after several hours the formation of big dark red blocks of 9 at the red phase boundary is observed. After complete diffusion the mother liquor is decanted, the crystals are washed with hexane (3 x 5 mL) and dried in vacuo.

Analytical data of 9:
**Yield**: 50 mg (0.024 mmol, 65% referred to \([\text{K(P}_3\text{C}_2\text{Bu}_2])\))
Positive ion ESI-MS (thf/CH₃CN): m/z (%) = 3415.1 [(P₅C₅Bu₂)₃Cu₃Br₆]⁺, 3267.9 [(P₅C₅Bu₂)₂Cu₆Br₇]⁺, 3123.8 [(P₅C₅Bu₂)₃Cu₁₀Br₉]⁺, 2979.9 [(P₅C₅Bu₂)₃Cu₈Br₉]⁺, 2834.7 [(P₅C₅Bu₂)₆Cu₁₁Br₇]⁺, 2688.8 [(P₅C₅Bu₂)₆Cu₁₃Br₇]⁺, 2541.2 [(P₅C₅Bu₂)₅Cu₁₁Br₇]⁺, 2399.3 [(P₅C₅Bu₂)₂Cu₁₂Br₇]⁺, 2253.1 [(P₅C₅Bu₂)₃Cu₁₃Br₇]⁺, 1672.9 [(P₅C₅Bu₂)₄Cu₁₄Br₇]⁺, 1526.5 [(P₅C₅Bu₂)₄Cu₁₂Br₇]⁺, 1385.1 [(P₅C₅Bu₂)₆Cu₁₀Br₈]⁺, 1234.8 [(P₅C₅Bu₂)₆Cu₈Br₈]⁺, 1090.9 [(P₅C₅Bu₂)₂Cu₁₂Br₇]⁺, 947.0 [(P₅C₅Bu₂)₂Cu₁₃Br₇]⁺

Negative ion ESI-MS (thf/CH₃CN): m/z (%) = 3419.3 [(P₅C₅Bu₂)₆Cu₁₃Br₇⁻]⁻, 3281.9 [(P₅C₅Bu₂)₇Cu₁₀Br₉⁻]⁻, 3136.0 [(P₅C₅Bu₂)₈Cu₉Br₈⁻]⁻, 2993.8 [(P₅C₅Bu₂)₈Cu₂Br₈⁻]⁻, 2843.2 [(P₅C₅Bu₂)₉Cu₁₁Br₇⁻]⁻, 2701.4 [(P₅C₅Bu₂)₉Cu₁₃Br₇⁻]⁻, 2557.1 [(P₅C₅Bu₂)₈Cu₂₁Br₉⁻]⁻, 2409.0 [(P₅C₅Bu₂)₈Cu₁₂Br₇⁻]⁻, 2262.9 [(P₅C₅Bu₂)₂Cu₁₂Br₇⁻]⁻, 2114.8 [(P₅C₅Bu₂)₂Cu₁₁Br₇⁻]⁻, 1968.5 [(P₅C₅Bu₂)₂Cu₁₀Br₉⁻]⁻, 1826.3 [(P₅C₅Bu₂)₃Cu₉Br₈⁻]⁻, 1680.5 [(P₅C₅Bu₂)₃Cu₈Br₈⁻]⁻, 1538.6 [(P₅C₅Bu₂)₃Cu₁₂Br₇⁻]⁻, 1386.3 [(P₅C₅Bu₂)₃Cu₁₀Br₈⁻]⁻, 1242.4 [(P₅C₅Bu₂)₂Cu₈Br₈⁻]⁻, 1092.3 [(P₅C₅Bu₂)₂Cu₆Br₈⁻]⁻, 519.0 [(P₅C₅Bu₂)₂Cu₂Br₇⁻]⁻, 366.7 [Cu₄Br₉⁻]⁻, 222.9 [CuBr₃⁻]

Negative ion ESI-MS (mother liquor, dme/CH₃CN): m/z (%) = 366.4 [Cu₂Br₃⁻]⁻, 222.6 [CuBr₂⁻]

Elemental analysis: Calculated (%) for [(P₅C₅Bu₂)Br₃Cu₁₀(CH₃CN)] (2011 g/mol): C 21.50, H 3.16, Br 27.81, N 2.09; found: C 21.89, H 3.45, Br 26.73, N 1.65.

Elemental analysis (after two years in air): Calculated (%) for [(P₅C₅Bu₂)Br₃Cu₁₀(CH₃CN)] (1929 g/mol): C 19.92, H 2.98, N 0.73; found: C 19.83, H 3.48, N 0.92.

1.11 Synthesis of 10

In a Schlenk tube [K(P₅C₅Bu₂)] (50 mg, 0.18 mmol) and CuI (105 mg, 0.55 mmol) are dissolved in thf (12 mL). An immediate color change to deep red can be observed. The solution is stirred for 2 hours, before the solvent is removed in vacuo. The red solid is dissolved in CH₃CN and analyzed by mass spectrometry. After complete diffusion the mother liquor is almost colourless and dark red blocks of 10 have formed. The mother liquor is decanted, the crystals are washed with toluene (3 x 5 mL) and dried in vacuo. Attempts to reproduce 10 were successful only once.

Analytical data of 10:

Yield: 13 mg (0.006 mmol, 8% referred to CuI)

Negative ion ESI-MS (CH₃CN): m/z (%) = 1078.1 [Cu₃I₄]⁻, 888.3 [Cu₂I₃]⁻, 698.5 [CuI₃]⁻, 506.6 [Cu₂I₃]⁻, 316.7 (100) [CuI₂]⁻

2. X-ray Structure Analysis

The compounds including co-crystallized solvent molecules characterized with X-ray structure analysis are:

2  [(P₅C₅Mes₂)₂(Cu(CH₃CN))₂]Cu(CH₃CN)₂]Cl:0.6MeCN
3  K(dme)[Cu₂Cl₂(MeCN)₄(P₅C₅Mes₂)₃(CuCl)(MeCN)₉]·1.5MeCN·0.75dme
4  K(thf)[(P₅C₅Mes₂)(Cu(MeCN)Br)₄(CuBr)]·1.3MeCN
5  [Cu₄I₄(MeCN)₄(P₅C₅Mes₂)]
6  [Cu₄I₄(MeCN)₃(P₅C₅Mes₂)]·0.5MeCN·0.5C₆H₄·0.4Et₂O
7  [Cu₂Cl₂(MeCN)₄(P₅C₅Bu₂)₃(CuCl)(MeCN)₉]·8.1MeCN
8  [Cu₂Cl₂(P₅C₅Bu₂)₃(CuCl)(MeCN)₉]·0.25(Cu₉·867Cl₈·817(MeCN)ₙ·133)·0.367MeCN
9  [Cu₄Br₄(P₅C₅Bu₂)₃(CuBr)(MeCN)₉]·0.1(CuBr)(MeCN)₉·0.133ₙ·0.367MeCN
10 (K(thf))[Cu₄I₄(MeCN)₄(P₅C₅Bu₂)₃]·0.5thf
Crystals of 2-10 were taken from a Schlenk tube under a stream of argon and covered with mineral oil. The single crystal was taken to the pre-centered goniometer head with CryoMount® and directly attached to the diffractometer into a stream of cold nitrogen. The data for 6 were collected on an Agilent Technologies diffractometer equipped with Titan®2 CCD detector and a SuperNova CuKα microfocus source using 1° ω scans. The data for 2, 3, 4, 5, 9 were collected using 1° ω scans and for 7, 8 and 10 using 0.5° ω scans on an Agilent Technologies diffractometer equipped with Atlas CCD detector and a SuperNova CuKα microfocus source. All measurements were performed at 123 K. Crystallographic data and details of the diffraction experiments are given in Table S 1-Table S 3. The structures of 2-8, 10 were solved by direct methods with SIR97,4 SHELX97 or SHELX2013. The structures were refined by full-matrix least-squares method against |F|^2 in anisotropic approximation using either SHELXL97 or the multiprocessor and variable memory version SHELXL2013. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined riding on pivot atoms.

2: The structure was refined as an inversion twin with batch components 0.8(1)/0.2(1). We faced with unexplainably large displacement parameters for almost all atoms even at T=123K and quite bad quality factors in 2 despite the signs for a good experiment, clear symmetry (for detailed information: see Section 3) and a chemically reasonable structure of the complex. Despite this, only positions of two adjacent P atoms of the phospholyl ligands were split with the probability 0.7/0.3. The outer sphere counter anion Cl⁷⁻ is disordered over six close positions and therefore was refined in an isotropic approximation. The solvent molecules and one of the coordinated MeCN molecules are disordered over 2 and 3 positions, respectively. They were refined with geometric restraints.

3: The CuCl and Cu(MeCN)Cl fragments of the Cu₂Cl₂ bridges in 3 are disordered (1:1) over several close positions, probably because of a mixed trigonally and tetrahedrally coordinated Cu. The coordinated to K⁺ and solvated dme molecules as well as the solvated MeCN molecules are disordered.

4: In 4 the Cu₂Br₂ fragment is disordered around the direction of the chain so that there are three close positions of the Cu atom in the independent part. The corresponding Br atoms are disordered over total eight positions. The Cu and Br atoms have occupancies less than 0.2 and were therefore refined in an isotropic approximation. The residual electron density peaks of more than 2 e·Å⁻³ can only be avoided if the disorder of the Cu₂Br₂ fragment is described with such a high number of the split positions. The main factors that favor the disorder are presumably 1) a high steric demand of two Mes groups, which screen the disordered fragment and allow it to re-orientate freely in the resulted cavity, and 2) the choice between a trigonal and tetrahedral coordination environment of Cu that in some of disordered positions can additionally coordinate solvated MeCN molecule. The solvent MeCN molecules and thf molecules coordinated to K⁺ counter cation are disordered over 2 positions and were treated with some geometrical restraints.

5: The diffraction pattern of crystal 5 was featured by diffuse scattering (see Section 4) that is described below. The effect is strongly related to the disorder of the repeating units over 4-axis.

6: In 6 one of the MeCN molecules coordinated to copper is disordered over two close positions. Solvated MeCN and Et₂O were refined as 0.5 and 0.4 molecular occupancies, and their positions partly overlap. The hexane molecule is disordered over the inversion center.

7: In 7 the Cl atoms of the bridging Cu₆Cl₅(P₅C₅l₂(Bu)₂)₃ fragments are disordered over 3 close positions. One MeCN molecule coordinated to copper is disordered over two positions. Solvated MeCN is severely disordered in the inter-chain cavities.
8 and 9: Compound 8 and 9 are isotypical, and the model of 9 was used for the refinement of 8. The similar structures however differ in details. In the Cl analogue the copper atom and the Cl atom bonded to it are disordered over two positions (Fig. S ), while in the Br analogue it is ordered (Fig. S ). This difference leads to a variation of the polymeric chain structure. Another Cu atom belonging to the Cu(MeCN)₃ fragment occupies the position with different probability refined to 0.25 for the Cl and to 0.1 for the Br analogues, respectively. In both structures the Cu atoms in the Cu(2) position are bonded with X(2) (X=Cl, Br) that has less occupancy than Cu(2). We supposed that the environment of Cu(2) is most probably completed by a coordinated MeCN molecule (minor content of 0.183 or 0.133, respectively) that was not located in the mixed X/MeCN positions because of the proximity to the heavy X = Cl or Br atoms. The undetermined MeCN was nevertheless included into the final structural formula.

According to the Cambridge Structural Database, at least four crystal structures are known, where a MeCN ligand is coordinated in a monodentate-bridging mode to two Cu atoms. Three of them are complexes of Cu⁺ with N- and P-donor atom ligands and one is the complex of Cu²⁺. Two Cu-μ-N distances in [Cu(dpme)₂(μ-NMeCN)(NMeCN)₂]ClO₄·MeCN of 2.29 and 2.32 Å, are close to the Cu-X(2) distances in 8 and 9. The atomic coordinates of the {Cu₂(μ-NMeCN)} fragment were used to model a possible MeCN bridging ligand with coinciding positions of X(2) and N atoms. The analysis of the interatomic distances involving the atoms of the modelled MeCN proves that the corresponding cavity in both crystal structures is large enough to allow this ligand to occupy the mixed ligand X/MeCN position.

10: In 10 four of six thf molecules in the K(thf)₆⁺ cation are conformationally disordered over two positions. The solvated thf molecule is disordered in the space between polymeric layers.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for the products are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-1056476- CCDC-1056484, respectively. The topological features of the 3D polymers were performed using TOPOSPro³ (see Section 5).

Table S 1. Experimental details for compounds 2-4

|         | 2          | 3          | 4          |
|---------|------------|------------|------------|
| CCDC Codes | CCDC-1056476 | CCDC-1056477 | CCDC-1056478 |
| Chemical formula | C₃₉H₅₆ClCu₃N₆P₆·0.6(CH₃CN) | C₃₀H₅₇.5ClCu₅K₅N₅O₃·0.5P₃ | C₃₄.6H₅₉.9Br₅Cu₆K₅N₅₃₀·OP₃ |
| Mₑ     | 1125.49    | 1293.37    | 1401.32    |
| Crystal system, space group | Tetragonal, P42d | Monoclinic, P2₁/n | Monoclinic, C2/m |
| Temperature (K) | 123       | 150        | 123        |
| a, b, c (Å) | 25.9670 (2), 17.9760 (2) | 13.5753 (3), 26.0211 (6), 15.6295 (4) | 19.5159(3), 25.8364(4), 13.6766(2) |
| α, β, γ (°) | 12120.9 (2) | 97.061 (2) | 90, 127.405(1), 90 |
| V (Å³) | 8          | 5479.2 (2) | 5477.93(16) |
| Z      | 4634       | 4          | 4          |
| F(000) | 1.234      | 2622       | 2730       |
| Radiation type | Cu Kα      | Cu Kα      | Cu Kα      |
| μ (mm⁻¹) | 3.38       | 6.22       | 8.16       |
| Crystal colour and shape | red prism  | yellow prism | yellow-orange block |
| Crystal size (mm) | 0.18 × 0.13 × 0.03 | 0.11 × 0.05 × 0.04 | 0.09 × 0.06 × 0.04 |
|------------------|---------------------|---------------------|---------------------|
| Data collection  | Diffractometer      | Absorption correction | Analysis correction |
|                  | SuperNova, Single source at offset, Atlas diffractometer | Gaussian | Gaussian |
|                  | SuperNova, Single source at offset, Atlas diffractometer | Analytical | Analytical |
|                  | SuperNova, Single source at offset, Atlas diffractometer | Analytical | Analytical |
|                  |                     |                     |                     |
|                  | $T_{\text{min}}, T_{\text{max}}$ | 0.648, 0.893 | 0.601, 0.778 |
|                  |                     |                     | 0.569, 0.761 |
|                  | No. of measured, independent and observed $|I| > 2\sigma(I)$ reflections | 13152, 5757, 4063 | 20040, 10599, 6315 |
|                  |                     |                     | 34635, 5576, 4748 |
|                  | $R_{\text{int}}$ | 0.022 | 0.041 |
|                  |                     |                     | 0.030 |
|                  | $\sin \theta/\lambda_{\text{max}}$ (\AA$^{-1}$) | 0.622 | 0.622 |
|                  |                     |                     | 0.623 |
| Refinement       | $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.095, 0.260, 1.05 | 0.044, 0.108, 0.88 |
|                  | No. of reflections | 5757 | 10599 |
|                  |                     |                     | 5576 |
|                  | No. of parameters | 353 | 608 |
|                  |                     |                     | 312 |
|                  | No. of restraints | 12 | - |
|                  | H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
|                  |                     | H-atom parameters constrained | H-atom parameters constrained |
|                  | $\Delta_{\text{max}}, \Delta_{\text{min}}$ (e Å$^{-3}$) | 1.86, -0.54 | 0.57, -0.43 |
|                  |                     |                     | 1.80, -0.79 |

Computer programs: CrysAlis PRO, Agilent Technologies, SIR97 (Altomare, 1999), SHELXL97 (Sheldrick, 1997), PLATON (Spek, 1990), PLATON (Spek, 2003).
|                  | 5                          | 6                          | 7                          |
|------------------|----------------------------|----------------------------|----------------------------|
| CCDC Codes       | CCDC-1056479               | CCDC-1056480               | CCDC-1056481               |
| Chemical formula | C<sub>28</sub>H<sub>34</sub>Cu<sub>5</sub>I<sub>4</sub>N<sub>4</sub>P<sub>3</sub> | C<sub>35</sub>A<sub>49.5</sub>Cu<sub>7</sub>I<sub>6</sub>N<sub>5.5</sub>O<sub>6.4</sub>P<sub>3</sub> | C<sub>64.20</sub>H<sub>105.00</sub>Cl<sub>6</sub>Cu<sub>17.10</sub>P<sub>9</sub> |
| M<sub>r</sub>    | 1344.80                    | 1860.00                    | 2180.05                    |
| Crystal system, space group | Tetragonal, P4/n | Triclinic, P1 | Monoclinic, P2<sub>1</sub>/m |
| Temperature (K)  | 123                        | 123                        | 123                        |
| a, b, c (Å)      | 15.5501(2), 9.3497(2)      | 11.9259(10), 12.3005(7), 20.8887(11) | 13.1219 (2), 27.5544 (6), 13.9810 (4) |
| α, β, γ (°)      | 90, 90, 90                 | 79.096(5), 89.381(5), 64.029(7) | 95.626 (2) |
| V (Å³)           | 2260.81(8)                 | 2696.1(3)                  | 5030.7 (2)                 |
| Z                | 2                          | 2                          | 2                          |
| Radiation type   | Cu Kα                      | Cu Kα                      | Cu Kα                      |
| μ (mm<sup>−1</sup>) | 25.21                      | 31.04                      | 5.18                       |
| Crystal colour and shape | red-brown block           | orange lath                | orange plate               |
| Crystal size (mm) | 0.08 × 0.06 × 0.03         | 0.24 × 0.09 × 0.05         | 0.12 × 0.09 × 0.04         |
| Data collection  | SuperNova, Single source at offset, Atlas diffractometer | SuperNova, TitanS2 diffractometer | SuperNova, Single source at offset, Atlas diffractometer |
| Absorption correction | Gaussian                  | Gaussian                  | Analytical                 |
| T<sub>min</sub>, T<sub>max</sub> | 0.354, 0.540               | 0.093, 0.550               | 0.693, 0.857               |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 5373, 2050, 1615             | 16228, 10356, 8315          | 17849, 9906, 7571          |
| R<sub>int</sub>  | 0.035                      | 0.049                      | 0.032                      |
| (sin θ/λ)<sub>max</sub> (Å<sup>−1</sup>) | 0.605                   | 0.624                      | 0.623                      |
| Refinement       |                            |                            |                            |
| R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] | 0.076, 0.220, 1.06 | 0.051, 0.142, 1.01 | 0.047, 0.143, 1.03 |
| wR(F<sup>2</sup>)<sup>2</sup>, S | 0.076, 0.220, 1.06 | 0.051, 0.142, 1.01 | 0.047, 0.143, 1.03 |
| No. of reflections | 2050                      | 10356                      | 9906                       |
| No. of parameters | 193                       | 534                        | 569                        |
| No. of restraints | 0                         | 12                         | 0                          |
| H-atom treatment | H-atom parameters not refined | H-atom parameters constrained | H-atom parameters constrained |
| Δρ<sub>max</sub>, Δρ<sub>min</sub> (e Å<sup>−3</sup>) | 1.69, -1.24                | 2.46, -2.62                | 0.96, -0.62                |

Computer programs: CrysAlis PRO, Agilent Technologies, SIR97 (Altomare, 1999), SHELXL97 (Sheldrick, 1997), PLATON (Spek, 1990), PLATON (Spek, 2003).
Table S 3. Experimental details for compounds 8-10

|          | 8                  | 9                  | 10                |
|----------|--------------------|--------------------|-------------------|
| CCDC Codes | CCDC-1056482       | CCDC-1056483       | CCDC-1056484      |
| Chemical formula | C_{33.8}H_{59.67}Cl_{6.85}Cu_{9.85}N_{1.9}P_{9} | C_{33.13}H_{58.7}Br_{1.1}Cu_{10.1}P_{9}N_{1.97} | C_{46}H_{88}Cu_{1}I_{6}KO_{6.84}P_{6} |
| 8          | 9                  | 10                |
| Mr         | 1640.10            | 1966.89           | 2176.26           |
| Crystal system, space group | Cubic, F43c | Cubic, F43c | Orthorhombic, Pbcn |
| Temperature (K) | 123               | 123              | 123               |
| a, b, c (Å) | 35.5021(1)         | 35.7790(1)        | 13.3881(3)        |
| V (Å³)     | 44746.8(4)         | 45802.0(4)        | 7226.6(2)         |
| Z          | 32                 | 32                | 4                 |
| F(000)     | 26011              | 30236             | 4184              |
| Radiation type | Cu Kα             | Cu Kα            | Cu Kα             |
| μ (mm⁻¹)   | 9.651              | 12.383            | 24.429            |
| Crystal colour and shape | dark red block | dark red block | dark brown block |
| Crystal size (mm) | 0.19 × 0.14 × 0.13 | 0.18 × 0.16 × 0.10 | 0.24 × 0.20 × 0.12 |
| Data collection | SuperNova, Single source at offset, Atlas diffractometer | SuperNova, Single source at offset, Atlas diffractometer | SuperNova, Single source at offset, Atlas diffractometer |
| Absorption correction | Gaussian | Analytical       | Gaussian          |
| T_{min}, T_{max} | 0.325, 0.508      | 0.211, 0.427      | 0.033, 0.211      |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 48284, 3910, 3826 | 91270, 3957, 3934 | 34111, 7067, 6829 |
| R_{int}    | 0.031              | 0.024             | 0.095             |
| (sin θ/λ)_{max} (Å⁻¹) | 0.630            | 0.627             | 0.622             |
| Refinement |                    |                    |                   |
| R[F² >2σ(F²)], wR(F²), S | 0.046, 0.132, 1.07 | 0.030, 0.0875, 1.069 | 0.080, 0.2173, 1.097 |
| No. of reflections | 3910            | 3957              | 7067              |
| No. of parameters | 207             | 197               | 338               |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δ(Å), Δ(Å)_{max} (e Å⁻³) | 2.14, -0.95      | 1.50, -1.25       | 2.14, -1.13       |
| Absolute structure parameter | 0.020 (13)       | -0.027(5)         | -                 |

Computer programs: CrysAlis PRO, Agilent Technologies, SIR97 (Altomare, 1999), SHELXL97 (Sheldrick, 1997), SHELXL2014 (Sheldrick, 2014), PLATON (Spek, 2003).
Fig. S 1: Section of the polymeric structure of 2. The counter anion Cl\(^-\) (disordered over 6 positions) and solvated MeCN molecules (disordered over 2 positions) are not shown for clarity.

Table S 4: Selected geometric parameters for 2 (Å)

| Bond/Distance | Value (Å) |
|---------------|-----------|
| Cu1—N1B\(^i\) | 1.83 (3)  |
| Cu1—N1B      | 1.83 (3)  |
| Cu1—N1A      | 2.07 (2)  |
| Cu1—N1A\(^i\)| 2.07 (2)  |
| Cu1—P1\(^i\) | 2.243 (3) |
| Cu1—P1       | 2.243 (3) |
| Cu1—N1       | 2.36 (4)  |
| Cu1—N1\(^i\) | 2.36 (4)  |
| Cu2—P2       | 2.195 (6) |
| Cu2—P2\(^ii\)| 2.027 (10) |
| Cu2—P3\(^iii\)| 2.277 (4) |
| Cu2—P3\(^ii\)| 2.277 (4) |
| Cu2—P3A\(^iii\)| 2.317 (6) |

Symmetry code(s): (i) \(x, -y+1/2, -z+1/4\); (ii) \(-x, -y, z\); (iii) \(-y, x, -z\); (iv) \(y, -x, -z\).
Fig. S 2: Section of the polymeric structure of 3

Table S 5: Selected geometric parameters for 3 (Å)

| Bond                        | Distance (Å) | Bond                        | Distance (Å) |
|-----------------------------|--------------|-----------------------------|--------------|
| Cu1—N1                      | 1.972 (4)    | Cu5A—Cl5A                  | 2.338 (12)   |
| Cu1—P2                      | 2.2795 (13)  | Cu5A—Cl5A'                 | 2.455 (12)   |
| Cu1—Cl1                     | 2.3692 (13)  | Cl5A—Cu5B                  | 2.407 (5)    |
| Cu1—Cl2                     | 2.4056 (13)  | Cl5A—Cu5B'                 | 2.425 (6)    |
| Cu2—N2                      | 1.960 (4)    | Cl5A—Cu5A'                 | 2.455 (12)   |
| Cu2—P2                      | 2.2900 (13)  | Cu5B—N6A                   | 2.084 (13)   |
| Cu2—Cl2                     | 2.3686 (12)  | Cu5B—Cl5B                  | 2.107 (6)    |
| Cu2—Cl3                     | 2.3733 (12)  | Cu5B—P1                    | 2.174 (4)    |
| Cu3—N3                      | 1.962 (4)    | Cu5B—Cl5B'                 | 2.296 (6)    |
| Cu3—P3                      | 2.2964 (13)  | Cu5B—Cl5A'                 | 2.425 (6)    |
| Cu3—Cl4                     | 2.3707 (12)  | Cl5B—Cu5A'                 | 2.132 (13)   |
| Cu3—Cl1                     | 2.3823 (12)  | Cl5B—Cu5B'                 | 2.296 (6)    |
| Cu4—N4                      | 1.964 (4)    | N6A—C35A                   | 1.196 (18)   |
| Cu4—P3                      | 2.2742 (12)  | P1—C1                      | 1.721 (5)    |
| Cu4—Cl3                     | 2.3541 (13)  | P1—Cl1                     | 1.721 (5)    |
| Cu4—Cl4                     | 2.4251 (13)  | P2—C1                      | 1.737 (5)    |
| Cu5A—P1                     | 2.125 (10)   | P2—P3                      | 2.0862 (14)  |
| Cu5A—Cl5B'                 | 2.132 (13)   | P3—Cl11                    | 1.742 (5)    |
| Cu5A—Cl5B                  | 2.231 (11)   |                            |              |

Symmetry code(s): (i) -x+2, -y+1, -z.
**Fig. S 3:** Section of the polymeric structure of 4

**Table S 6:** Selected geometric parameters for 4 (Å)

| Bond                              | Distance   | Bond                              | Distance   |
|-----------------------------------|------------|-----------------------------------|------------|
| Cu1A—Br1B                         | 2.423 (11) | C4—C5                             | 1.379 (8)  |
| Cu1A—Br1E                         | 2.468 (7)  | C5—C6                             | 1.368 (9)  |
| Cu1A—Br1C                         | 2.688 (7)  | C5—C9                             | 1.535 (8)  |
| Br1C—Cu1A                         | 2.688 (7)  | C6—C7                             | 1.391 (7)  |
| Br1C—Cu1A                         | 2.688 (7)  | C7—C10                            | 1.506 (7)  |
| Br1E—Cu1A                         | 2.370 (7)  | C11—N2                            | 1.125 (6)  |
| Br1E—Cu1A                         | 2.468 (7)  | C11—C12                           | 1.445 (7)  |
| Br1E—Cu1A                         | 2.468 (7)  | C13—N1                            | 1.131 (6)  |
| Br1B—Cu1A                         | 2.423 (11) | C13—C14                           | 1.454 (6)  |
| Cu1B—P1                           | 2.159 (4)  | P1—C1<sup>a</sup>                 | 1.725 (5)  |
| Cu1B—Br1A<sup>i</sup>             | 2.429 (10) | P1—Cu1B<sup>a</sup>               | 2.159 (4)  |
| Cu1B—Br1K                         | 2.495 (9)  | P1—Cu1A<sup>b</sup>               | 2.198 (4)  |
| Cu1B—Br1K<sup>i</sup>             | 2.632 (9)  | P1—Cu1C<sup>a</sup>               | 2.328 (9)  |
| Br1A—Cu1B<sup>i</sup>             | 2.429 (10) | P2—P2<sup>a</sup>                 | 2.092 (2)  |
| Br1A—Cu1B<sup>ii</sup>            | 2.429 (10) | K1—O1                             | 2.600 (10) |
| Br1F—Cu1B<sup>a</sup>             | 2.307 (8)  | K1—O2                             | 2.82 (6)   |
| Br1F—Cu1B<sup>b</sup>             | 2.307 (8)  | K1—N4<sup>v</sup>                 | 3.110 (17) |
| Br1K—Cu1B<sup>ii</sup>            | 2.495 (9)  | K1—N4                             | 3.110 (17) |
| Br1K—Cu1B<sup>ii</sup>            | 2.632 (9)  | K1—Br3<sup>vi</sup>               | 3.2102 (12) |
| Br1K—Cu1B<sup>vi</sup>            | 2.632 (9)  | K1—Br2<sup>ii</sup>               | 3.3438 (8) |
| Cu1C—P1                           | 2.328 (9)  | N3—C19<sup>v</sup>                | 1.297 (17) |
| Cu1C—Br1D                         | 2.679 (14) | N3—C19                            | 1.298 (16) |
| Br1D—Cu1C<sup>iii</sup>           | 2.679 (14) | C19—C20                           | 1.57 (3)   |
| Cu2—N2                            | 1.975 (4)  | C19—C19<sup>v</sup>               | 1.84 (3)   |
| Cu2—P2                            | 2.2802 (12) | O1—C18                          | 1.405 (19) |
| Cu2—Br3                           | 2.4801 (8) | O1—C15                           | 1.45 (2)   |
| Cu2—Br2                           | 2.5287 (8) | O1—K1<sup>vi</sup>                | 2.600 (10) |
Cu2—Cu3 & 2.5477 (9) & C15—C16 & 1.58 (2) \\
Cu2—K1 & 3.9192 (15) & C15—K1\(^{iv}\) & 3.442 (18) \\
Cu3—N1 & 1.968 (4) & C16—C17 & 1.57 (2) \\
Cu3—P2 & 2.2938 (13) & C17—C18 & 1.59 (2) \\
Cu3—Br2 & 2.4907 (8) & C18—K1\(^{iv}\) & 3.380 (14) \\
Cu3—Br3\(^{iv}\) & 2.5047 (8) & O2—C26 & 1.49 (3) \\
Cu3—K1 & 3.9334 (15) & O2—C23 & 1.51 (3) \\
Br3—Cu3\(^{iv}\) & 2.5046 (8) & O2—K1\(^{iv}\) & 2.74 (5) \\
Br3—K1 & 3.2102 (12) & C23—C24 & 1.57 (2) \\
Br2—K1 & 3.3438 (8) & C24—C25 & 1.58 (2) \\
C1—C2 & 1.491 (6) & C25—C26 & 1.58 (2) \\
C1—P1 & 1.725 (5) & N4—C21 & 1.21 (4) \\
C1—P2 & 1.735 (5) & N4—K1\(^{iv}\) & 3.110 (17) \\
C2—C3 & 1.403 (7) & C21—C22 & 1.49 (5) \\
C2—C7 & 1.411 (7) & N4A—C21A & 1.19 (7) \\
C3—C4 & 1.395 (7) & C21A—C22A & 1.55 (8) \\
C3—C8 & 1.512 (7) & \\

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

**Fig. S 4:** Section of the polymeric structure of 5
### Table S 7: Selected geometric parameters for 5 (Å)

| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| Cu1—Cu2               | 2.541 (4)    | Cu3—I2               | 2.978 (12)   |
| Cu1—N1B               | 1.94 (2)     | Cu3—P1<sup>iv</sup>  | 2.249 (6)    |
| Cu1—I1<sup>ii</sup>   | 2.673 (4)    | I1—Cu1<sup>ii</sup>  | 2.673 (4)    |
| Cu1—I2                | 2.677 (3)    | I1—Cu3<sup>ii</sup>  | 2.59 (3)     |
| Cu1—P2                | 2.277 (5)    | P1—Cu3<sup>v</sup>   | 2.249 (6)    |
| N1A—Cu1<sup>iii</sup>| 2.28 (3)     | P1—Cu3<sup>vi</sup>  | 2.249 (6)    |
| N1A—Cu2               | 2.02 (4)     | P1—Cu3<sup>vii</sup>| 2.249 (6)    |
| Cu2—N1B<sup>iii</sup>| 2.03 (2)     | P1—Cu3<sup>viii</sup>| 2.249 (6)    |
| Cu2—I1                | 2.676 (4)    | P1—C1<sup>iii</sup>  | 1.706 (16)   |
| Cu2—I2                | 2.678 (3)    | P1—C1                | 1.706 (16)   |
| Cu2—P2                | 2.319 (6)    | P1—C1<sup>iii</sup>  | 1.706 (16)   |
| Cu2—P2<sup>iii</sup>  | 2.529 (6)    | P2—C1                | 1.738 (15)   |
| Cu3—I1<sup>ii</sup>   | 2.59 (3)     | P2—P2<sup>ii</sup>   | 2.099 (9)    |
| Cu3—I1                | 2.67 (3)     | P2—Cu1<sup>iii</sup>| 2.697 (6)    |

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

---

**Fig. S 5:** Section of the polymeric structure of 6
Table S 8: Selected geometric parameters for 6 (Å)

|      |      |     |      |
|------|------|-----|------|
| P1—P2 | 2.101 (3) | Cu3—I4 | 2.6997 (13) |
| P1—C1  | 1.731 (7) | Cu3—Cu4 | 2.5229 (19) |
| P2—C2  | 1.740 (8) | Cu3—Cu6 | 2.9783 (19) |
| P3—Cu7<sup>i</sup> | 2.214 (2) | Cu4—P2 | 2.319 (2) |
| P3—C1  | 1.726 (9) | Cu4—N4 | 1.961 (8) |
| P3—C2  | 1.740 (8) | Cu4—I3 | 2.6770 (15) |
| N1—C61 | 1.163 (12) | Cu4—I4 | 2.7529 (13) |
| N2—C71 | 1.138 (12) | Cu4—Cu6 | 2.9091 (19) |
| N3—C31 | 1.136 (13) | Cu5—I1 | 2.7423 (15) |
| N4—C41 | 1.150 (12) | Cu5—I2 | 2.7004 (14) |
| N5—C51 | 1.110 (14) | Cu5—I5 | 2.6437 (15) |
| Cu1—P1 | 2.289 (2) | Cu5—I6 | 2.6174 (15) |
| Cu1—N1 | 1.964 (7) | Cu5—Cu6 | 2.759 (2) |
| Cu1—I2 | 2.7070 (14) | Cu5—Cu7 | 2.7347 (18) |
| Cu1—I3 | 2.6363 (13) | Cu6—I1 | 2.7022 (16) |
| Cu1—Cu2 | 2.5225 (19) | Cu6—I3 | 2.6484 (15) |
| Cu2—P1 | 2.289 (2) | Cu6—I4 | 2.6978 (15) |
| Cu2—N2 | 1.952 (8) | Cu6—I5 | 2.6417 (14) |
| Cu2—I1 | 2.7278 (13) | Cu7—P3<sup>i</sup> | 2.214 (2) |
| Cu2—I2 | 2.6736 (14) | Cu7—N5 | 2.046 (8) |
| Cu3—P2 | 2.285 (2) | Cu7—I5 | 2.6977 (15) |
| Cu3—N3 | 1.971 (9) | Cu7—I6 | 2.6490 (16) |
| Cu3—I1 | 2.6760 (15) |

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

Fig. S 6: Section of the polymeric structure of 7
Table S 9: Selected geometric parameters for 7 (Å)

|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| C1—P1 | 1.731 (4) | Cl4—Cu5 | 2.300 (2) |
| C1—P2 | 1.737 (4) | Cl5A—Cu5 | 2.142 (9) |
| C1—C2 | 1.545 (5) | Cl5B—Cu5 | 2.281 (9) |
| C2—C3 | 1.519 (6) | Cu1—N5 | 1.858 (13) |
| C2—C5 | 1.520 (5) | Cu1—N3S | 2.190 (18) |
| C2—C4 | 1.529 (6) | Cu1—P2' | 2.3250 (11) |
| C6—C7 | 1.542 (5) | Cu1—P2 | 2.3250 (11) |
| C6—P3 | 1.736 (4) | Cu1—Cu2 | 2.4961 (14) |
| C6—P1 | 1.742 (4) | Cu2—P2 | 2.3612 (11) |
| C7—C8 | 1.520 (6) | Cu2—P2' | 2.3612 (11) |
| C7—C9 | 1.527 (6) | Cu3—P3 | 2.3493 (10) |
| C7—Cl0 | 1.533 (6) | Cu3—P4 | 2.3566 (11) |
| C11—C12 | 1.542 (6) | Cu3—Cu4 | 2.4823 (9) |
| C11—P5 | 1.733 (4) | Cu4—N4 | 1.972 (4) |
| C11—P4 | 1.737 (4) | Cu4—P4 | 2.3207 (10) |
| C12—C14 | 1.511 (7) | Cu4—P3 | 2.3449 (12) |
| C12—C13 | 1.524 (6) | Cu5—P5' | 2.1908 (15) |
| C12—C15 | 1.531 (7) | Cu5—Cl5B' | 2.281 (9) |
| C11—Cu2 | 2.4085 (16) | Cu6—N1 | 2.020 (4) |
| C11—Cu4 | 2.4159 (9) | Cu6—N3 | 2.053 (5) |
| C11—Cu4' | 2.4160 (9) | Cu6—N2 | 2.061 (4) |
| C12—Cu1 | 2.3897 (14) | Cu6—P1 | 2.2317 (10) |
| C12—Cu3 | 2.4409 (9) | P2—P3 | 2.0966 (13) |
| C12—Cu3' | 2.4410 (9) | P4—P4' | 2.0964 (19) |
| C13—Cu3 | 2.2305 (11) | P5—C11' | 1.733 (4) |
| Cl4—Cu2 | 2.2791 (16) | P5—Cu5' | 2.1908 (15) |

Symmetry code(s): (i) x, -y+1/2, z; (ii) x+1, y, z; (iii) x-1, y, z.
Fig. S 7: Section of the polymeric structure of 8: (a) Major (0.867) and (c) minor (0.133) part in the disordered structure of 8 and occupation factors of the disordered atoms in major (b) and minor (d) parts, respectively. The structure 8 cannot be represented as an overlap of only two alternative cores according to occupancy factors (compare with 9). The coordinated MeCN molecules have larger occupancies as the corresponding Cu1s ion. Therefore, they are coordinated in the major part and solvated in the minor one.

| Table S 10: Selected geometric parameters for 8 (Å) |
|-----------------------------------------------|
| Cu1S—N1S                                      | 2.22 (5)  | Cu3A—P3                      | 2.314 (2) |
| Cu1S—N1S                                      | 2.22 (5)  | Cu3A—Cl4                     | 2.354 (2) |
| Cu1S—N1S                                      | 2.22 (5)  | Cu3A—Cl3A                    | 2.466 (3) |
| Cu1S—Cu1Si                                    | 2.395 (17) | Cu3A—Cu3A                   | 2.808 (3) |
| Cu1S—Cu1Si                                    | 2.395 (17) | Cu3A—Cu3A                   | 2.808 (3) |
| Cu1S—Cl3A                                    | 2.522 (11) | Cl3A—Cu3A                  | 2.466 (3) |
| N1S—Cl1                                      | 1.14 (7)   | Cu3B—Cl4                    | 2.026 (9) |
| Bond 1 | Bond 2 | Distance |
|--------|--------|----------|
| N1S—Cu1S | 2.22 (5) | Cu3B—P3 | 2.325 (9) |
| N1S—Cu1S | 2.22 (5) | Cu3B—P3<sup>iv</sup> | 2.335 (9) |
| C1S—C2S | 1.46 (5) | Cu3B—Cl3B | 2.367 (18) |
| Cl1—Cu1 | 2.216 (6) | Cl3B—Cu3B<sup>v</sup> | 2.367 (18) |
| Cl1—Cu1 | 1.42 (8) | Cl3B—Cu3B<sup>iv</sup> | 2.367 (18) |
| C1N—C1N<sup>iv</sup> | 1.00 (9) | P1—C1 | 1.733 (8) |
| C2N—C2N<sup>iv</sup> | 1.98 (14) | P1—Cu4<sup>iv</sup> | 2.200 (2) |
| Cu1—P2 | 2.3529 (19) | P2—P3 | 2.108 (3) |
| Cu1—P2<sup>iv</sup> | 2.3529 (19) | P3—C6 | 1.746 (7) |
| Cu1—Cu2<sup>iv</sup> | 2.6826 (17) | P3—Cu3A<sup>v</sup> | 2.314 (2) |
| Cu1—Cu2<sup>v</sup> | 2.6826 (17) | P3—Cu3B<sup>v</sup> | 2.335 (9) |
| Cu1—Cu2 | 2.6827 (17) | C1—C2 | 1.544 (10) |
| Cu2—Cl2 | 2.200 (3) | C2—C3 | 1.493 (13) |
| Cu2—P2 | 2.275 (3) | C2—C4 | 1.515 (13) |
| Cu2—P2<sup>iv</sup> | 2.304 (3) | C2—C5 | 1.542 (15) |
| Cu2—P3 | 2.655 (2) | C6—C7 | 1.539 (10) |
| Cu2—Cu3A | 2.778 (2) | C7—C10 | 1.533 (11) |
| Cl2—Cu4 | 2.299 (3) | C7—C9 | 1.545 (11) |
| Cu3A—P3 | 2.302 (2) | C7—C8 | 1.545 (11) |

Symmetry code(s): (i) -x+3/2, y, -z+3/2; (ii) -x+3/2, -y+3/2, z; (iii) x, -y+3/2, -z+3/2; (iv) z, x, y; (v) y, z, x; (vi) y, -z+2, -x+2; (vii) -z+2, x, -y+2; (viii) -z+2, -y+3/2, x; (ix) z, -y+3/2, -x+2.
Fig. S 8: Section of the polymeric structure of 9: (a) Numerating scheme, (b) major (0.867) and (c) minor (0.133) part in the disordered structure of 9. All positions of Cu are fully occupied, the environment of Cu anions in case of the disorder is completed by Br or MeCN molecules. The latter is localized in the position Br1 and not localized in position Br2 due to its smaller contribution. The coordinated MeCN molecules have larger occupancies as the corresponding Cu1s ion. Therefore, they are coordinated in minor part and solvated in major one.

Table S 5: Selected geometric parameters for 9 (Å)

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| Cu1S—N1S              | 2.23 (4)     |
| Cu1S—N1S              | 2.23 (4)     |
| Cu1S—N1S              | 2.23 (4)     |
| Cu1S—Br3              | 2.80 (4)     |
| N1S—C1S               | 1.19 (5)     |
| N1S—Cu1S              | 2.23 (4)     |
| N1S—Cu1S              | 2.23 (4)     |
| C1S—C2S               | 1.35 (4)     |
| Br1—Cu1               | 2.402 (5)    |
| N1N—C1N               | 1.16 (6)     |
| N1N—C1N               | 1.16 (6)     |
| N1N—Cu1               | 2.100 (14)   |
| C1N—C1N               | 1.52 (11)    |
| C1N—Cu1               | 1.52 (11)    |
| C1N—C2N               | 1.54 (3)     |
| C2N—C2N               | 1.35 (10)    |
| Cu1—P2                | 2.3587 (15)  |
| Cu1—P2                | 2.3588 (15)  |
| Cu1—P2                | 2.3588 (15)  |
Cu1—Cu2  2.6939 (14)  C2—C3  1.509 (10)
Cu1—Cu2iii  2.6939 (14)  C2—C4  1.527 (11)
Cu1—Cu2iv  2.6939 (14)  C2—C5  1.536 (11)
Cu2—P2iv  2.2878 (19)  C6—C7  1.535 (8)
Cu2—P2  2.3324 (19)  C7—C8  1.521 (9)
Cu2—Br2  2.3384 (14)  C7—C10  1.533 (9)
Cu2—P3  2.6195 (19)  C7—C9  1.561 (10)

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

Fig. S 9: Section of the polymeric structure of 10.

Table S 6: Selected geometric parameters for 10 (Å)

| Bond                  | Distance (Å) | Error (Å) |
|-----------------------|--------------|-----------|
| I1—Cu2¹               | 2.4869 (18)  | 1.52 (2)  |
| I1—Cu1                | 2.5485 (18)  | 1.540 (18)|
| I2—Cu3                | 2.5399 (18)  | 3.45 (6)  |
| I2—Cu1                | 2.545 (2)    | 3.49 (4)  |
| I3—Cu4                | 2.5692 (13)  | 1.31 (4)  |
| I3—Cu3                | 2.6503 (19)  | 1.60 (5)  |
| Cu1—P1¹               | 2.215 (3)    | 1.33 (5)  |
| Cu2—P3¹               | 2.254 (3)    | 1.48 (4)  |
| Cu2—P2                | 2.471 (3)    | 1.70 (6)  |
| Cu2—P3                | 2.484 (3)    | 1.33 (5)  |
| Cu2—I1¹               | 2.4869 (18)  | 1.51 (5)  |
| Cu2—Cu3               | 2.663 (2)    | 1.20 (6)  |
| Cu2—Cu2³              | 2.793 (3)    | 1.57 (5)  |
| Cu3—P2²               | 2.398 (3)    | 1.32 (6)  |
| Cu3—Cu4               | 2.540 (2)    | 1.43 (4)  |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| Cu₃—P₃       | 2.559 (3)    | O₂—C₂₁       | 1.50 (4)     |
| Cu₃—Cu₂ образования | 2.663 (2)    | C₂₁—C₂₂      | 1.49 (5)     |
| Cu₄—P₂       | 2.463 (3)    | C₂₂—C₂₃      | 1.528 (19)   |
| Cu₄—Cu₃ образование | 2.463 (3)    | C₂₃—C₂₄      | 1.535 (19)   |
| Cu₄—Cu₃ образования | 2.540 (2)    | O₂A—C₂₄A     | 1.45 (9)     |
| Cu₄—I₃ образование | 2.569 (3)    | O₂A—C₂₁A     | 1.66 (7)     |
| P₁—C₆        | 1.710 (11)   | C₂₁A—C₂₂A    | 1.55 (2)     |
| P₁—C₁        | 1.739 (12)   | C₂₂A—C₂₃A    | 1.76 (7)     |
| P₁—Cu₁образования | 2.215 (3)    | C₂₃A—C₂₄A    | 1.54 (2)     |
| P₂—C₁        | 1.751 (11)   | O₃—C₃₄      | 1.42 (2)     |
| P₂—P₂        | 2.120 (4)    | O₃—C₃₁      | 1.45 (2)     |
| P₂—Cu₃ образование | 2.398 (3)    | C₃₁—C₃₂      | 1.49 (2)     |
| P₃—C₆        | 1.743 (11)   | C₃₂—C₃₃      | 1.54 (2)     |
| P₃—Cu₂ образование | 2.254 (3)    | C₃₃—C₃₄      | 1.46 (3)     |
| C₁—C₂        | 1.525 (16)   | O₁S—C₁S      | 1.37 (2)     |
| C₂—C₃        | 1.497 (17)   | O₁S—C₄S      | 1.38 (2)     |
| C₂—C₅        | 1.515 (17)   | C₁S—C₂S      | 1.52 (8)     |
| C₂—C₄        | 1.522 (19)   | C₂S—C₃S      | 1.50 (9)     |
| C₆—C₇        | 1.545 (15)   | C₄S—C₃S      | 1.53 (2)     |
| C₇—C₁₀       | 1.514 (18)   |              |              |
| P₁—Cu₁—I₂    | 116.92 (11)  | P₂—Cu₃—I₃    | 110.87 (10)  |
| P₁—Cu₁—I₁    | 127.43 (11)  | I₂—Cu₃—I₃    | 109.25 (7)   |
| I₂—Cu₁—I₁    | 115.64 (7)   | P₃—Cu₃—I₃    | 115.69 (9)   |
| P₃—Cu₂—P₂    | 97.82 (11)   | P₂—Cu₄—P₂ образование | 95.99 (15)   |
| P₃—Cu₂—P₃    | 98.29 (11)   | P₂—Cu₄—I₃    | 103.55 (7)   |
| P₂—Cu₂—P₃    | 50.67 (10)   | P₂—Cu₄—I₃ образование | 111.51 (7)   |
| P₃—Cu₂—I₁ образование | 142.20 (10)  | P₂—Cu₄—I₃ образование | 111.51 (7)   |
| P₂—Cu₂—I₁ образование | 116.35 (9)   | P₂—Cu₄—I₃ образование | 103.55 (7)   |
| P₃—Cu₂—I₁ образование | 115.42 (9)   | I₃—Cu₄—I₃ образование | 126.65 (11)  |
| P₂—Cu₃—I₂    | 121.49 (10)  | P₁—C₁—P₂     | 115.3 (7)    |
| P₂—Cu₃—I₃ образование | 91.89 (11)   | P₁—C₆—P₃     | 116.1 (6)    |
| I₂—Cu₃—I₃    | 106.91 (9)   |              |              |

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

3. **Crystallographic problem in 2**: Quality of the diffraction experiment

3.1 **Indexation of the diffraction pattern**

It is obvious that

1) Primitive and Bravais unit cell are correct (no superstructural reflections, no multiplied axes, see Fig. S 10);
2) Most of the reflections belong to the reciprocal lattice (have integer $hkl$) (Fig. S 11);  
3) There is no visible signs for twinning (Fig. S 10 – S 11).

**Fig. S 10:** An example of a frame at low (a) and at high (b) resolution and (c) indexation in the chosen unit cell (*Crysalis Pro* software).
Fig. S11: View along (a) $a^*$, (b) $b^*$ and (c) $c^*$ directions (CrysAlis Pro software)
3.2 Intensity statistics visualization by means of Wilson plot

![Wilson Plot](image)

Fig. S12: Wilson plot (SIR Software).

3.3 Data analysis in XPREP

Original cell in Angstroms and degrees:
25.853 25.853 17.996 90.00 90.00 90.00
25827 Reflections read from file tp.hkl; mean (I/sigma) = 5.56

| Lattice exceptions: | P | A | B | C | I | F | Obv | Rev | All |
|---------------------|---|---|---|---|---|---|-----|-----|-----|
| N (total) =         | 0 | 12903 | 12876 | 12941 | 12986 | 19360 | 17163 | 17173 | 25827 |
| N (int>3sigma) =    | 0 | 3762 | 3796 | 3914 | 4 | 5736 | 5061 | 5059 | 7609 |
| Mean intensity =    | 0.0 | 4.2 | 4.3 | 4.4 | 0.1 | 4.3 | 4.4 | 4.4 | 4.3 |
| Mean int/sigma =    | 0.0 | 5.7 | 5.8 | 6.0 | 0.3 | 5.8 | 5.8 | 5.8 | 5.7 |

Search for higher metric symmetry
Identical indices and Friedel opposites combined before calculating R(sym)

Option A: FOM = 0.000 deg. TETRAGONAL I-lattice R(sym) = 0.027 [4785]
Cell: 25.853 25.853 17.996 90.00 90.00 90.00 Volume: 12027.65
Matrix: 1.0000 0.0000 0.0000 0.0000 1.0000 0.0000 0.0000 0.0000 1.0000

SPACE GROUP DETERMINATION
Lattice exceptions: P A B C I F Obv Rev All

| N (total) =         | 0 | 12903 | 12876 | 12941 | 12986 | 19360 | 17163 | 17173 | 25827 |
| N (int>3sigma) =    | 0 | 3762 | 3796 | 3914 | 4 | 5736 | 5061 | 5059 | 7609 |
| Mean intensity =    | 0.0 | 4.2 | 4.3 | 4.4 | 0.1 | 4.3 | 4.4 | 4.4 | 4.3 |
| Mean int/sigma =    | 0.0 | 5.7 | 5.8 | 6.0 | 0.3 | 5.8 | 5.8 | 5.8 | 5.7 |

Crystal system T and lattice type I selected
Mean |E*E| = 0.885 [expected .968 centrosym and .736 non-centrosym]

Chiral flag NOT set

Systematic absence exceptions:
41/43 a-- -c-- --d
N I>3s 5 226 352 232
N I>3s 0 97 229 0
<I> 0.1 22.0 23.8 0.1
<I/s> 0.2 12.6 19.1 0.3
Identical indices and Friedel opposites combined before calculating R(sym)

| Option | Space Group | No. | Type   | Axes | CSD  | R(sym) | N(eq)  | Syst. Abs. | CFOM |
|--------|-------------|-----|--------|------|------|--------|--------|------------|-------|
| [A]    | I-42d       | #122| non-cen| 1    | 36  | 0.030  | 7526   | 0.3 / 5.7  | 6.75  |
| [B]    | I4(1)md     | #109| non-cen| 1    | 6   | 0.030  | 7526   | 0.3 / 5.7  | 18.34 |

Option [A] chosen

INTENSITY STATISTICS FOR DATASET # 1 tp.hkl

| Resolution | #Data | #Theory | %Complete Redundancy | Mean I | Mean I/s | R(int) | Rsigma |
|------------|-------|---------|----------------------|--------|----------|--------|--------|
| Inf - 2.32 | 168   | 171     | 98.2                 | 3.48   | 76.4     | 75.94  | 0.0181 |
| 2.32 - 1.81| 173   | 173     | 100.0                | 3.46   | 39.6     | 37.12  | 0.0286 |
| 1.81 - 1.56| 173   | 177     | 100.0                | 3.12   | 21.7     | 22.17  | 0.0381 |
| 1.56 - 1.41| 178   | 178     | 100.0                | 2.94   | 9.3      | 13.02  | 0.0494 |
| 1.41 - 1.30| 173   | 173     | 100.0                | 6.27   | 5.4      | 44.30  | 0.0529 |
| 1.30 - 1.22| 174   | 174     | 100.0                | 6.33   | 4.8      | 41.20  | 0.0219 |
| 1.22 - 1.16| 170   | 170     | 100.0                | 5.44   | 4.3      | 33.83  | 0.0612 |
| 1.16 - 1.10| 197   | 197     | 100.0                | 4.27   | 3.3      | 27.09  | 0.0362 |
| 1.10 - 1.05| 205   | 205     | 100.0                | 4.25   | 1.9      | 16.56  | 0.0465 |
| 1.05 - 1.01| 186   | 186     | 100.0                | 4.07   | 1.6      | 14.30  | 0.0521 |
| 1.01 - 0.98| 170   | 170     | 100.0                | 4.03   | 1.9      | 16.75  | 0.0467 |
| 0.98 - 0.95| 189   | 189     | 100.0                | 3.77   | 1.2      | 11.07  | 0.0593 |
| 0.95 - 0.92| 205   | 205     | 100.0                | 3.77   | 1.0      | 9.64   | 0.0621 |
| 0.92 - 0.89| 242   | 242     | 100.0                | 3.51   | 0.7      | 7.81   | 0.0744 |
| 0.89 - 0.87| 177   | 177     | 100.0                | 3.26   | 0.6      | 6.79   | 0.0783 |
| 0.87 - 0.85| 197   | 200     | 98.5                 | 3.05   | 0.4      | 5.63   | 0.0953 |
| 0.85 - 0.83| 195   | 203     | 96.1                 | 2.57   | 0.3      | 3.89   | 0.1018 |
| 0.83 - 0.80| 135   | 199     | 67.8                 | 1.33   | 0.2      | 3.28   | 0.1006 |
| 0.90 - 0.80| 874   | 949     | 92.1                 | 2.70   | 0.5      | 5.48   | 0.0848 |
| Inf - 0.80 | 3311  | 3389    | 97.7                 | 3.79   | 1.1      | 21.05  | 0.0327 |

Merged [A], lowest resolution = 9.73 Angstroms, 281 outliers downweighted

3.4 Space Group Determination and Refinement

In the tetragonal I\(\bar{4}\)\(2d\) space group (best R(sym)=0.03, current model) the quality factors are R\(_{1}\)=0.095, wR\(_{2}\)=0.248 (for observed reflections), GooF=1.043 providing that racemic twinning batch refined to 0.20(10). In this space group no other twinning by merohedry is possible. All atoms have high displacement parameters, and the splitting of their positions does not improve the geometry of the complex.

The attempts to find another better solution failed with both SHEXL and SIR2014. The attempts to solve the structure in I\(41md\) did not return a more reasonable model. It is also in contradiction with the refined twinning batch. The attempts to solve the structure in the t-subgroup I\(4\) and I\(_2\)2\(_1\)2\(_1\) with corresponding twinning models did not yield better quality factors.

We assumed also the possibility of an orthorhombic-to-tetragonal twinning from Fdd2 (with UC a=36.7180, b=36.6889, c=17.9812) to I\(\bar{4}\)2\(_d\) with \{0 1 0, -1 0 0, 0 0 -1\} twinning element. The disorder does not disappear.

In addition, a second X-ray diffraction experiment of crystals of 2, crystallized from a different sample, shows the same phenomenon as described above.
4. Diffuse scattering in 5

The diffraction pattern of 5 shows quite strong diffuse scattering (Fig. S 13) that is visible even during the routine diffraction experiment. The diffraction pattern in the reciprocal space reconstructed with CrysAlisPro (Agilent Technologies) software shows that in addition to the Braggs peaks, two types of diffuse spots appear.

![Typical frame in the diffraction experiment of 5](image)

**Fig. S 13**: Typical frame in the diffraction experiment of 5 (correlated 1° ω-scan with total exposure of 20 sec). The black round dots correspond to the Bragg peaks.

The diffuse spots of the first type lie on the planes perpendicular to the $c^*$ with the $l = \text{integer}$, near to the points where $h$ and $k$ values are both half-integer. If $h$ or $k$ is integer, the diffuse scattering in the planes is not observed. It is also true for the area near to the systematically absent Bragg reflections with $h0l$, $h+k=2n+l$ (due to the presence of the glide plane $n\perp c$). The spots of this type have quite a complex shape with two close maximums (Fig. S 10). The distribution of the diffuse scattering intensity is quite narrow but noticeably wider than those for the Bragg peaks (Fig. S 14c-e). The spots of the first types are observed up to high $l$ values (Fig. S 15).
Fig. S 14: The reconstruction of \(hk1\) section showing diffuse spots of the first type: general view (a), close view (b) and intensity profile (c, d, e) along the highlighted rows at (b).

Fig. S 15: The reconstruction of the \(hk-7\) section: general view (a), close view (b) and intensity profiles (c, d) along the highlighted rows at (b).
The spots of the second type are cross-shaped and lie on the planes perpendicular to $c^*$, but on the contrary, with the half-integer $l$ and near to the points with integer $h$ and $k$ values (Fig. S 16). These spots are observed for the whole range $-10.5 \leq l \leq 7.5$. The ‘arms’ of the ‘crosses’ are directed along $a^* \pm b^*$ diagonals. The reconstruction of the detailed profile for these spots appeared to be impossible due to the artefacts resulting from the wide $\omega$-scans taken during a routine diffraction experiment.

![Image](image_url)

**Fig. S 16**: The reconstruction of the $hk0.5$ diffraction section: general (a) and close view (b).

The symmetry of the diffuse scattering spots of both types is in a good agreement with the symmetry of the Bragg diffraction (point group $4/m$).

The diffuse scattering obviously originates from the disorder of the polymeric chains and/or $\{\text{Cu}_5\text{I}_4(\text{MeCN})_4\text{(P}_3\text{C}_2\text{Mes}_2)\}$ repeating units by $90^\circ$ rotation around the 4-fold axis parallel to $c$. At that, each orientation of the $\{\text{Cu}_5\text{I}_4(\text{MeCN})_4\text{(P}_3\text{C}_2\text{Mes}_2)\}$ repeating unit may require a preferable orientation either of the units of the neighboring chains or within the single chain due to the sterical hindering between the bulky Mes groups. Therefore, there is a correlation between the neighboring orientations despite their equal probability in the averaged crystal structure imposed by the 4-fold axis.

The correct reduction of diffuse intensities for the modelling of the real crystal would require special diffraction techniques (using a strong monochromatic radiation source, noise-free detector etc.). The data from a routine structural determination we possess are obviously not enough to make final conclusions. Nevertheless, preliminary consideration shows that we can propose two possible disorder models. One model assumes coexistence of differently oriented chains, but the orientation of all repeating units in every chain is identical. Another more complicated model assumes that the repeating units of the same chain can be rotated around the Cu-P bond in respect to each other. The results of preliminary calculations prove that only the latter model, sophisticated with local relaxation of atomic groups, explains the presence of both types of the diffuse scattering spots. Qualitatively the best result corresponds to the models where the orientation of the closest repeating units alternate both within the polymeric chain and, less strictly, between them.
5. **Topological analysis of the 3D polymers**

The topological features of the 3D polymers 2, 8, 9 were studied with TOPOS 4.0 Professional program. The search in TTO collection implemented in TOPOS gave 8 compounds of the same hsg topology deposited in Cambridge Structural Database (corresponding Refcodes are DEGPEL, FUTPUG, KAGCAY, KELJAN, QALHAO, QALHES, VIRPOC and YEMGED). In these complexes of similar structure the {M₃[μ₃-O]} or {M₃[μ₃-OH]} units (M²⁺ = Cu²⁺, Ni²⁺) join each other by N-heterocyclic bridging ligands, 1,2,4-triazolate, 5-(4-pyrindyl)tetrazolate, or pyrazole-4-carboxylate.

![Fig. S17: Similarity of the structures of (a) polybenzene (calculated) (b) 3D polymer 8 and (c) [Cu₃(μ₃-OH)(μ₃-L)(H₂O)₄(OH)₂], L=1,2,4-triazolate.](image)

6. **Pictures of the crystal packing of the polymers 2 - 10**

![Fig. S18: Section of the polymeric structure of 2. Short Cl···H distances are illustrated with green dashed lines.](image)
**Fig. S19:** Section of the polymeric structure of 3. Short Cl···H distances are illustrated with green dashed lines.

**Fig. S20:** Section of the polymeric structure of 4. Short Br···H distances are illustrated with green dashed lines.
**Fig. S21:** Section of the polymeric structure of 5. Short I···H distances are illustrated with green dashed lines.

**Fig. S22:** Section of the polymeric structure of 6. Short I···H distances are illustrated with green dashed lines.
Fig. S23: Section of the polymeric structure of 7. Short Cl···H distances are illustrated with green dashed lines.

Fig. S24: Section of the polymeric structure of 8. Short Cl···H distances are illustrated with green dashed lines.
Fig. S25: Section of the polymeric structure of 10 illustrating the alternating cationic and anionic ‘layers’.

Fig. S26: Section of the polymeric structure of 10 illustrating the mesh-like network.

7. UV-vis Spectroscopy
Furthermore, solutions of the polymeric compounds 2, 4, 7-9 and the monomeric compound [(P₃C₂Mes₂)₄(Cu(CH₃CN)₄(Cu(CH₃CN)₃)] (marked as 1aCu5I₄) in CH₃CN were analysed by UV-vis spectroscopy. The solubility of the 3D polymer 9 is too poor, even for UV-vis spectroscopy analysis, therefore no absorption could be detected. All other compounds show several partially overlapping absorption bands. The spectra of [(P₃C₂Mes₂)₄(Cu(CH₃CN)(μ₂-I)]₄{Cu(CH₃CN)₃}], the bromine-containing 1D polymer 4 and the chlorine-containing 3D polymer 2 all show an absorption band at λ = 532 nm, responsible for the red colour of the respective solution. In contrast, the solutions of the 1D chain 7 and the 3D network 8 are yellow. Therefore no relation between absorption and dimensionality or the present halide of the polymeric scaffolds can be drawn, respectively. However, a relationship between absorption and the R group of the phospholyl group is indicated, since [(P₃C₂Mes₂)₄(Cu(CH₃CN)(μ₂-I)]₄{Cu(CH₃CN)₃}], 4 and 2 all contain the mesityl substituted building block 1a, whereas 7 and 8 are built up by the 'Bu derivative 1b.

Fig. S27: UV-vis spectra of 2, 4, 7-9 and [(P₃C₂Mes₂)₄(Cu(CH₃CN)(μ₂-I)]₄{Cu(CH₃CN)₃}] in CH₃CN.