

# PSEUDOHALIDE IONS AS LIGANDS TO TUNE ARCHITECTURE AND LUMINESCENCE OF POLYMETALLIC CU(I) ASSEMBLIES

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## I. Experimental section

All the preliminary chemicals were purchased from commercial sources (Sigma-Aldrich, Across and Fisher Scientific) and used without further purification unless otherwise stated. Deuterated solvents were purchased from Sigma-Aldrich and Cambridge Isotope Laboratories.

Synthesis of L1 and L2 : Solvents were dried and distilled by refluxing for one day under N<sub>2</sub>-atmosphere using appropriate drying agents (calcium hydride for hexane; magnesium and iodine for methanol; sodium for ethanol, and molecular sieves for DMF), and then degassed prior to use. Solvents were stored in glass ampoules under argon. Alternatively, they could be obtained from a solvent purification device (MBRAUN). All the reactions were performed under argon or nitrogen atmosphere by using a dual manifold vacuum/argon line and standard Schlenk techniques. All the glassware and cannula were stored in an oven (>373 K). Thin layer chromatography (TLC) analysis was performed on pre-coated silica gel aluminium-backed plates purchased from Merck (silica gel 60F<sub>254</sub>). The organic compounds were purified using flash column chromatography on silica gel (230-400 mesh) purchased from Fisher Scientific.

Synthesis of compounds A-I : Procedures were performed under air, in a simple flask and solvents were used as received without further purification. The precursors A and A' were synthesized according to synthetic procedure previously reported.<sup>1,2</sup>

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded in CDCl<sub>3</sub>, acetone-d<sub>6</sub> or CD<sub>2</sub>Cl<sub>2</sub> deuterated solvents on Bruker AV400 or Bruker AMX-400 spectrometers. <sup>1</sup>H NMR chemical shifts were reported in parts per million (ppm) relative to Me<sub>4</sub>Si as external standard. <sup>31</sup>P{<sup>1</sup>H} NMR downfield chemical shifts were expressed with in ppm, relative to 85% H<sub>3</sub>PO<sub>4</sub> respectively.

FT-IR measurements have been performed on Perkin Elmer Frontier or Bruker ATR Vertex70 spectrometers using UATR (Universal Attenuated Total Reflectance) accessory. Spectra have been recorded between 4000-650 cm<sup>-1</sup> and 4000-400 cm<sup>-1</sup>, respectively, on pure solid samples.

UV-vis solid-state diffuse reflectance measurements were recorded on a Perkin-Elmer Lambda 650 spectrometer using a 60 mm integrating sphere. Reflectance spectra were recorded in relation to an external white reference (Spectralon®), between 800 nm and 200 nm with a spectral resolution of 1 nm on pure polycrystalline samples. The UV-vis spectra were transformed to apparent absorbance through log(reflectance<sup>-1</sup>).

Steady-state excitation and emission spectra measurements were recorded on a *Horiba Jobin-Yvon (HJY) Fluorolog-3 (FL3-2iHR550)* fluorescence spectrofluorometer equipped with an IR R928P PMT /

HJY FL-1073 detector. Low temperature measurements were allowed by using an OptistatCF (*Oxford Inst.*) in the range of 77 K to 300 K. Excited-state lifetimes in the range of 80 K to 300 K were measured with a delta diode system allowing to measure excited-state lifetimes longer than 10  $\mu$ s. Solid samples were placed in a quartz sample holder inside the cryostat and maintained at the desired temperature until equilibrium was reached before recording the spectrum.

The experimental data were then fitted according to the following equation<sup>3</sup>

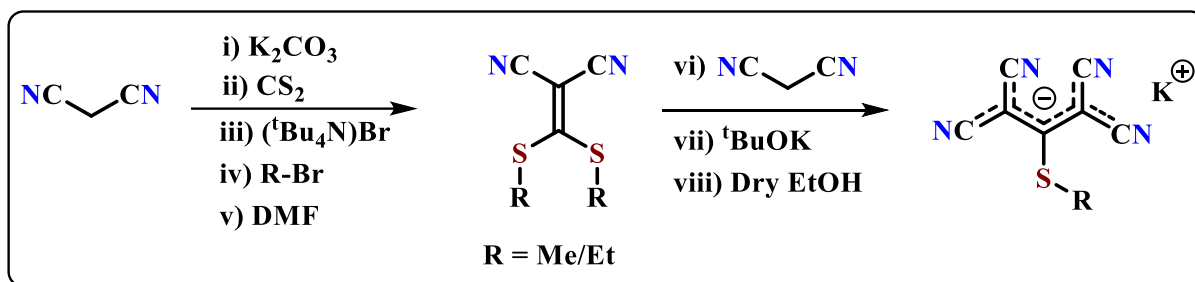
$$\tau(obs) = \frac{1 + \frac{1}{3} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right)}{\frac{1}{\tau(T_1)} + \frac{1}{3\tau(S_1)} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right)} \quad \text{Equation (S1)}$$

where  $\tau(obs)$ ,  $\tau(S_1)$ ,  $\tau(T_1)$ ,  $k_B$ ,  $T$  and  $\Delta E_{ST}$  represent the observed lifetime, singlet state decay lifetime, triplet state decay lifetime, Boltzmann constant, temperature and singlet-triplet energy difference, respectively.

## I.1. Synthesis

### Synthesis of **L1** and **L2**:

The potassium salts of 1,1,3,3-tetracyano-2-thiomethylpropenide cyanocarbanion (**L1**) and 1,1,3,3-tetracyano-2-thioethylpropenide cyanocarbanion (**L2**) were prepared following two-steps synthesis (see Scheme S1).<sup>4,5</sup>



**Scheme S1.** Synthesis of potassium salt of **L1** and **L2** anions.

(i) **2-[bis(methyl/ethyl-thio)methylene]malononitrile.** A suspension of  $K_2CO_3$  (8.37 g, 60.55 mmol) in DMF (25 mL) was treated with the addition of malononitrile (4.0 g, 60.55 mmol). The mixture was cooled down to 0 °C, and  $CS_2$  (3.6 mL, 66.6 mmol) was added dropwise. The resulting yellow suspension was stirred at 20 °C for 10 minutes, after which methyl/ethyl bromide (121.1 mmol) and tetrabutylammonium bromide (4 g, 10 mmol) were added over 30 minutes. The reaction mixture was stirred for 2 hours at 50 °C, and subsequently for an additional 24 to 48 hours at room temperature while monitoring the reaction status with TLC (2:98, ethylacetate:hexane). The final mixture was diluted with water (200 mL) and extracted with  $Et_2O$  (4×200 mL); the combined organic layers were washed with

Brine solution (100 mL) and dried over MgSO<sub>4</sub>, then filtered and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (hexane: EtOAc, 9.5:0.5 (v/v)) to provide 2-[(bismethyl/ethyl-thio)methylene]malononitrile with reasonable yields (75 %).

2-[bis(methylthio)methylene]malononitrile:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, δ (ppm)): 2.76 (s, -SCH<sub>3</sub>, 6H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K, δ (ppm)): 184.0 (-C(S-Me)<sub>2</sub>), 112.8 (-CN), 76.3 (-C(CN)<sub>2</sub>), 19.3 (-SCH<sub>3</sub>)

IR data (ν, cm<sup>-1</sup>): 3003w, 2926w, 2827w, 2417w, 2351w, 2308w, 2209s, 1489w, 1442s, 1417s, 1316m, 1211w, 983w, 960w, 922m, 869s, 708w, 610w, 475w, 457w

2-[bis(ethylthio)methylene]malononitrile:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, δ (ppm)): 3.27 (q, -SCH<sub>2</sub>-, 4H), 1.39 (t, -CH<sub>3</sub>, 6H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K, δ (ppm)): 181.4 (-C(S-Et)<sub>2</sub>), 112.8 (-CN), 78.1 (-C(CN)<sub>2</sub>), 31.1 (-SCH<sub>2</sub>-), 14.3 (-CH<sub>3</sub>)

IR data (ν, cm<sup>-1</sup>): 2970w, 2930w, 2874w, 2407w, 2349w, 2322w, 2219s, 1486s, 1463m, 1411w, 1377w, 1265w, 1240w, 1206w, 1057m, 1043m, 964s, 939w, 852w, 801w, 751w, 646m, 505m, 454m, 436w.

(ii) **Potassium 1,1,3,3-tetracyano-2-thioalkylpropenide salts (L1/L2)**. A warm solution of the previously synthesized thioacetal, 2- [bis(methyl/ethyl-thio)methylene]malononitrile (10 mmol) in dry EtOH (40 mL), was added dropwise to an ethanol solution (15 mL) of malononitrile (0.66 g, 10 mmol) and <sup>t</sup>BuOK (1.12 g, 10 mmol). The resulting solution was refluxed for 1h, and then the reaction mixture was cooled down to room temperature, and finally kept at 4 °C for two days. The resulting compound was filtered on a sintered-glass funnel and washed with distilled diethyl ether, and ultimately dried under vacuum to obtain light yellow crystalline powders of **L1/L2** salt in good yields (70 %).

**L1:**

<sup>1</sup>H NMR (400 MHz, Acetone-D<sub>6</sub>, 298 K, δ (ppm)): 2.54 (s, -SCH<sub>3</sub>, 3H)

<sup>13</sup>C NMR (100 MHz, Acetone-D<sub>6</sub>, 298 K, δ (ppm)): 170.2 (-C(S-Me)(C(CN)<sub>2</sub>)<sub>2</sub>), 119.0 (-CN), 117.0 (-CN), 53.6 (-C(CN)<sub>2</sub>), 18.4 (-SCH<sub>3</sub>)

IR data (ν, cm<sup>-1</sup>): 2186s, 1447s, 1426m, 1332m, 1310m, 1247w, 956w, 929w, 856w, 642w, 576w, 527m, 473w

**L2:**

<sup>1</sup>H NMR (400 MHz, Acetone-D<sub>6</sub>, 298 K, δ (ppm)): 3.06 (q, -CH<sub>2</sub>-, 2H), 1.27 (t, -CH<sub>3</sub>, 3H)

<sup>13</sup>C NMR (100 MHz, Acetone-D<sub>6</sub>, 298 K, δ (ppm)): 167.1 (-C(S-Et)(C(CN)<sub>2</sub>)<sub>2</sub>) 119.1 (-CN), 116.9 (-CN), 54.7 (-C(CN)<sub>2</sub>), 29.8 (-SCH<sub>2</sub>-), 14.6 (-SCH<sub>3</sub>)

IR data (ν, cm<sup>-1</sup>): 2189s, 1644w, 1445s, 1373w, 1325w, 934w, 777w, 640w, 531w, 477w, 458w

Synthesis of derivative C:

A tetrahydrofuran suspension (30 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.112 g, 0.3 mmol) and dppm (0.115 g, 0.3 mmol) was stirred for 30 min at room temperature. A methanol solution (3 ml) of  $\text{NaN}_3$  (0.010 g, 0.15 mmol) was then added to the mixture affording an uncolored solution which was stirred for 2 hours. The stirring was stopped and the solution was filtered over cotton and was left upon diethyl ether vapor diffusion to obtain the product **C** after crystallization. The final product after filtration was a pure colorless crystalline powder obtained with a yield of 64% (0.104 g, 0.048 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): 7.19 (*m*,  $\text{Ar}_{\text{dppm}}$ , 32H), 7.02 (*m*,  $\text{Ar}_{\text{dppm}}$ , 48H), 3.68 (*m*, thf, 8H), 1.82 (*m*, thf, 8H), 3.26 (*s*,  $\text{CH}_2$ , 8H)

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): - 9.51 (*s*,  $\text{P}_{\text{dppm}}$ ), - 144.29 (*sept*,  $\text{PF}_6^-$ ,  $^1J_{\text{P,F}} = 713$  Hz)

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3057, 2361, 2325, 2097 ( $\nu(\text{N}_3)$ ), 1976, 1894, 1816, 1669, 1588, 1574, 1484, 1435, 1368, 1334, 1311, 1282, 1189, 1160, 1099, 1064, 1026, 1000, 923, 831 (*s*,  $\nu(\text{PF}_6^-)$ ), 779, 736, 690.

#### Synthesis of derivative **D**:

A dichloromethane solution (30 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.112 g, 0.3 mmol) and dppm (0.115 g, 0.3 mmol) was stirred for 30 min at room temperature. A methanol solution (6 ml) of  $\text{NaN}(\text{CN})_2$  (0.014 g, 0.15 mmol) was then added to the mixture affording an uncolored solution which was stirred for 1 hour. The stirring was stopped and the solution was filtered over cotton and was left upon n-pentane vapor diffusion to obtain the product **D** after crystallization. The final product after filtration was a pure colorless crystalline powder obtained with a yield of 83% (0.139 g, 0.062 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): 7.40 (*m*,  $\text{Ar}_{\text{dppm}}$ , 32H), 7.18 (*m*,  $\text{Ar}_{\text{dppm}}$ , 48H), 3.36 (*broad s*,  $\text{CH}_2$ , 4H), 3.08 (*broad s*,  $\text{CH}_2$ , 4H)

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): - 10.56 (*s*,  $\text{P}_{\text{dppm}}$ ), - 144.41 (*sept*,  $\text{PF}_6^-$ ,  $^1J_{\text{P,F}} = 713$  Hz)

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3057, 2320 ( $\nu(\text{C}\equiv\text{N})$ ), 2238 ( $\nu(\text{C}\equiv\text{N})$ ), 2179 ( $\nu(\text{C}\equiv\text{N})$ ), 1981, 1892, 1816, 1758, 1663, 1617, 1588, 1574, 1484, 1435, 1379, 1336, 1307, 1282, 1190, 1160, 1139, 1098, 1026, 1000, 920, 827 (*s*,  $\nu(\text{PF}_6^-)$ ), 776, 734, 689.

#### Synthesis of derivative **E**:

A tetrahydrofuran suspension (10 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.037 g, 0.1 mmol) and dppm (0.038 g, 0.1 mmol) was stirred for 30 min at room temperature. A methanol solution (2 ml) of  $\text{NaC}(\text{CN})_3$  (0.011 g, 0.1 mmol) was then added to the mixture affording an uncolored solution inside which a white precipitate forms almost instantaneously ( $\text{NaPF}_6$ ) under stirring for 2 hours. The stirring was stopped and the solution was filtered over cotton and was left upon diethyl ether vapor diffusion to obtain the product **E** after crystallization. The final product after filtration was a pure colorless crystalline powder obtained with a yield of 52% (0.028 g, 0.013 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): 7.23 (*m*,  $\text{Ar}_{\text{dppm}}$ , 48H), 7.14 (*m*,  $\text{Ar}_{\text{dppm}}$ , 32H), 3.04 (*s*,  $\text{CH}_2$ , 8H)

$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): - 14.28 (*s*,  $\text{P}_{\text{dppm}}$ )

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3058, 2946, 2893, 2187 ( $\nu(\text{C}\equiv\text{N})$ ), 2175 ( $\nu(\text{C}\equiv\text{N})$ ), 2161 ( $\nu(\text{C}\equiv\text{N})$ ), 2148 ( $\nu(\text{C}\equiv\text{N})$ ), 1972, 1895, 1815, 1753, 1667, 1588, 1576, 1484, 1435, 1380, 1332, 1307, 1246, 1188, 1160, 1139, 1098, 1026, 1000, 972, 916, 835, 790, 736, 689.

#### Synthesis of derivative F:

A dichloromethane solution (15 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.65 g, 0.175 mmol) and dppm (0.67 g, 0.175 mmol) was stirred for 30 min at room temperature. A methanol solution (2 ml) of potassium salt of **L1** ligand (0.020 g, 0.088 mmol) was then added to the mixture affording a yellowish solution that was stirred overnight. The stirring was stopped and the solution was filtered over cotton and was left upon diethyl ether vapor diffusion to obtain the product **F** after crystallization. The final product after filtration was a pure yellow crystalline powder obtained with a yield of 92% (0.099 g, 0.08 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K  $\delta$  (ppm)): 7.37-7.19 (*m*,  $\text{Ar}_{\text{dppm}}$ , 40H), 2.82 (*s*,  $\text{CH}_2(\text{dppm})$ , 4H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): -9.13 (*s*,  $\text{P}_{\text{dppm}}$ ), -144.40 (*sept*,  $\text{PF}_6^-$ ,  $^1J_{\text{P-F}} = 713$  Hz)

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3060, 2201 ( $\nu(\text{C}\equiv\text{N})$ ), 1980, 1892, 1817, 1761, 1666, 1588, 1484, 1435, 1376, 1334, 1311, 1249, 1190, 1160, 1139, 1096, 1027, 1000, 920, 835 (*s*,  $\nu(\text{PF}_6^-)$ ), 779, 736, 721, 690.

#### Synthesis of derivative G:

A dichloromethane solution (15 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.65 g, 0.175 mmol) and dppm (0.67 g, 0.175 mmol) was stirred for 30 min at room temperature. A methanol solution (2 ml) of potassium salt of **L2** ligand (0.021 g, 0.088 mmol) was then added to the mixture affording a yellowish solution that was stirred overnight. The stirring was stopped and the solution was filtered over cotton and was left upon diethyl ether vapor diffusion to obtain the product **G** after crystallization. The final product after filtration was a pure yellow crystalline powder obtained with a yield of 82% (0.090 g, 0.07 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): 7.35-7.18 (*m*,  $\text{Ar}_{\text{dppm}}$ , 40H), 3.18-3.13 (*m*,  $\text{CH}_2(\text{dppm}/\text{CNSE})$ , 6H), 1.3 (*t*,  $\text{CH}_3(\text{CNSE})$ , 3H,  $J = 7.40$  Hz)

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): - 9.89 (*s*,  $\text{P}_{\text{dppm}}$ ), - 144.38 (*sept*,  $\text{PF}_6^-$ ,  $^1J_{\text{P-F}} = 713$  Hz)

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3055, 2929, 2199 ( $\nu(\text{C}\equiv\text{N})$ ), 1981, 1895, 1816, 1624, 1587, 1573, 1484, 1436, 1411, 1379, 1326, 1262, 1248, 1188, 1160, 1138, 1097, 1027, 1000, 966, 924, 833 ( $\nu(\text{PF}_6^-)$ ), 786, 737, 716, 690.

#### Synthesis of derivative H:

A dichloromethane solution (15 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.65 g, 0.175 mmol) and dppa (0.67 g, 0.175 mmol) was stirred for 30 min at room temperature. A methanol solution (2 ml) of potassium salt of **L2** ligand (0.021 g, 0.088 mmol) was then added to the mixture affording a yellowish solution that was stirred overnight. The stirring was stopped and the solution was filtered over cotton and was left upon diethyl ether vapor diffusion to obtain the product **H** after crystallization. The final product after filtration was a pure yellow crystalline powder obtained with a yield of 85% (0.093 g, 0.7 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  (ppm)): 7.58-7.11 (*m*,  $\text{Ar}_{\text{dppa}}$ , 40H), 3.71 (*s*,  $\text{NH}_{(\text{dppa})}$ , 2H), 3.00 (*m*,  $\text{CH}_{2(\text{CNSEt})}$ , 2H), 1.25 (*m*,  $\text{CH}_{3(\text{CNSEt})}$ , 3H)

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ , 300K,  $\delta$  (ppm)): 45.84 (*s*,  $\text{P}_{\text{dppa}}$ ), -144.56 (*sept*,  $\text{PF}_6^-$ ,  $^1J_{\text{P-F}} = 713$  Hz)

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3309, 3059, 2205 ( $\nu(\text{C}\equiv\text{N})$ ), 1984, 1900, 1820, 1773, 1587, 1573, 1483, 1435, 1339, 1310, 1276, 1255, 1248, 1186, 1160, 1099, 1073, 1058, 1029, 998, 967, 914, 894, 835 (*s*,  $\nu(\text{PF}_6^-)$ ), 784, 738, 695.

#### Synthesis of derivative I:

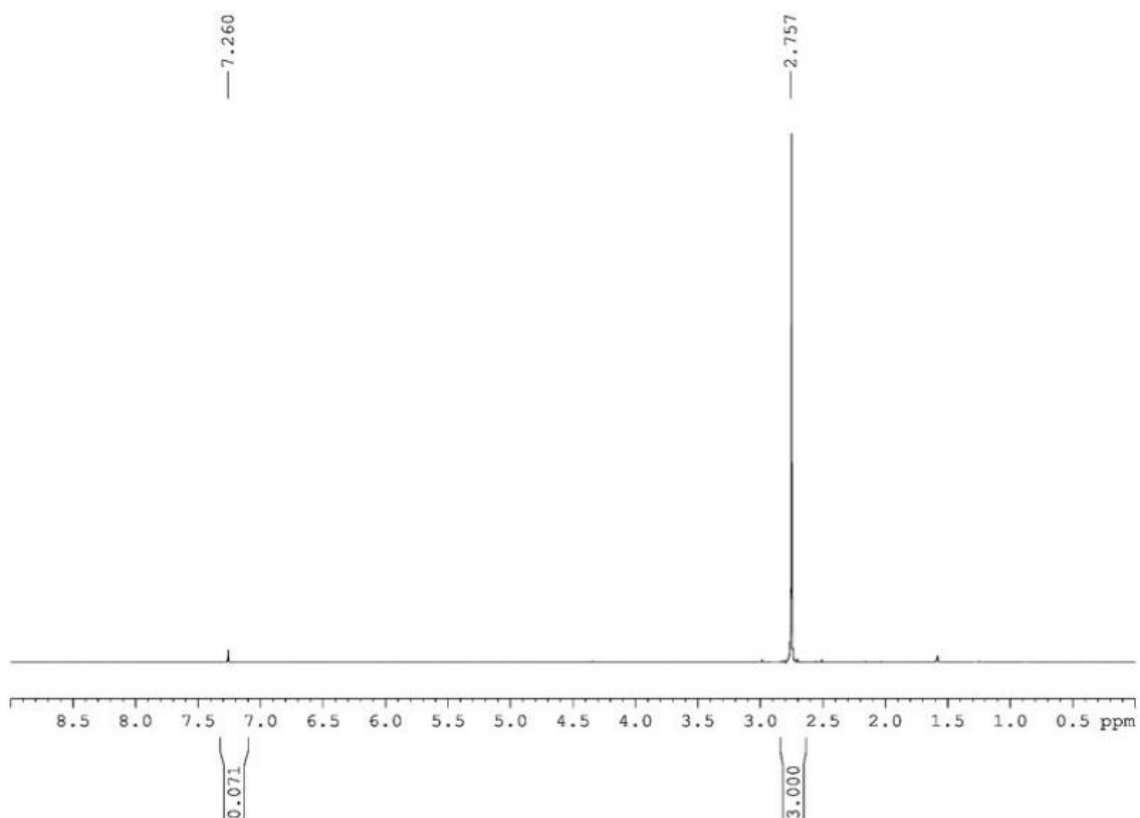
A dichloromethane solution (15 ml) of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.65 g, 0.175 mmol) and dppa (0.67 g, 0.175 mmol) was stirred for 30 min at room temperature. A methanol solution (2 ml) of potassium salt of **L1** ligand (0.021 g, 0.088 mmol) was then added to the mixture affording a yellowish solution that was stirred overnight. The stirring was stopped and the solution was filtered over cotton and was left upon diethyl ether vapor diffusion to obtain the product **I** after crystallization. The final product after filtration was a pure yellow crystalline powder obtained with a yield of 92% (0.087 g, 0.08 mmol).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):

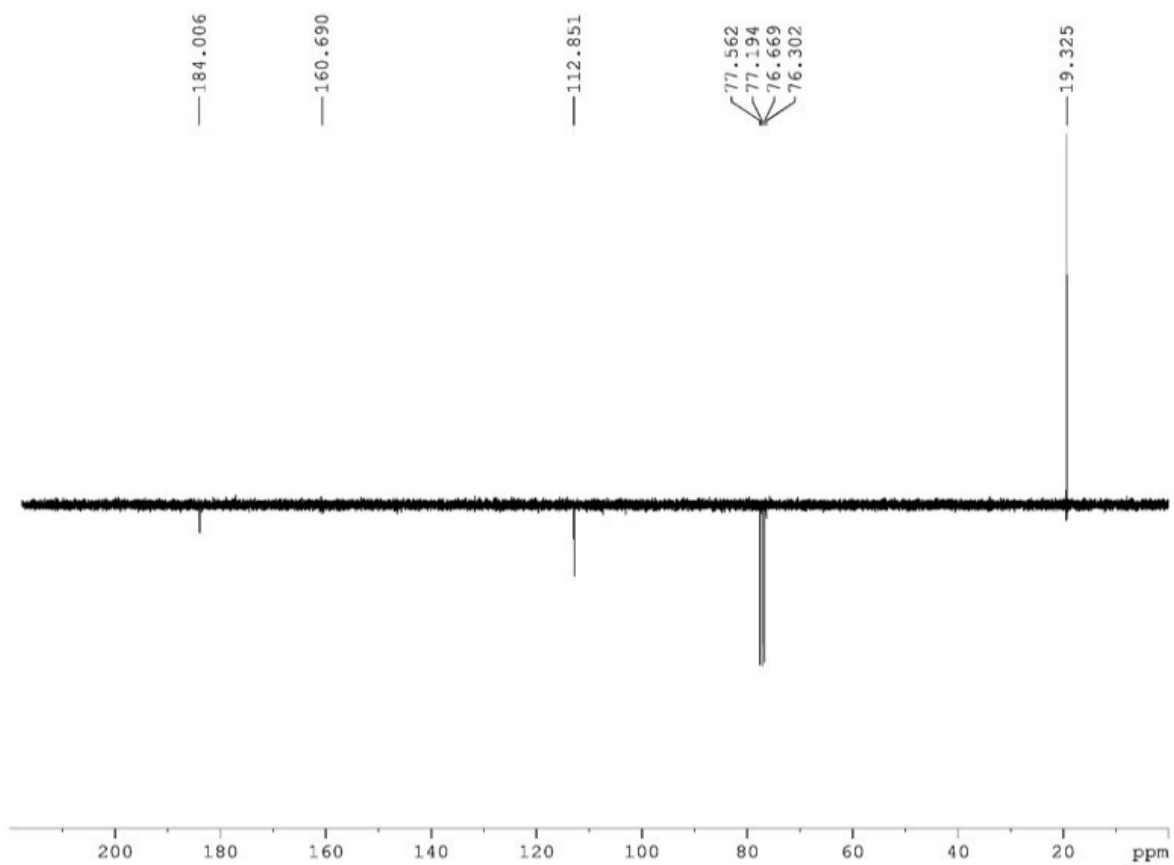
$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ , ppm):

IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3299, 3166, 3057, 2206 ( $\nu(\text{C}\equiv\text{N})$ ), 1972, 1897, 1812, 1588, 1574, 1483, 1428, 1329, 1309, 1288, 1271, 1220, 1186, 1158, 1100, 1071, 1028, 1001, 934, 924, 910, 835 (*s*,  $\nu(\text{PF}_6^-)$ ), 799, 752, 739, 694

#### I.2. NMR spectroscopy

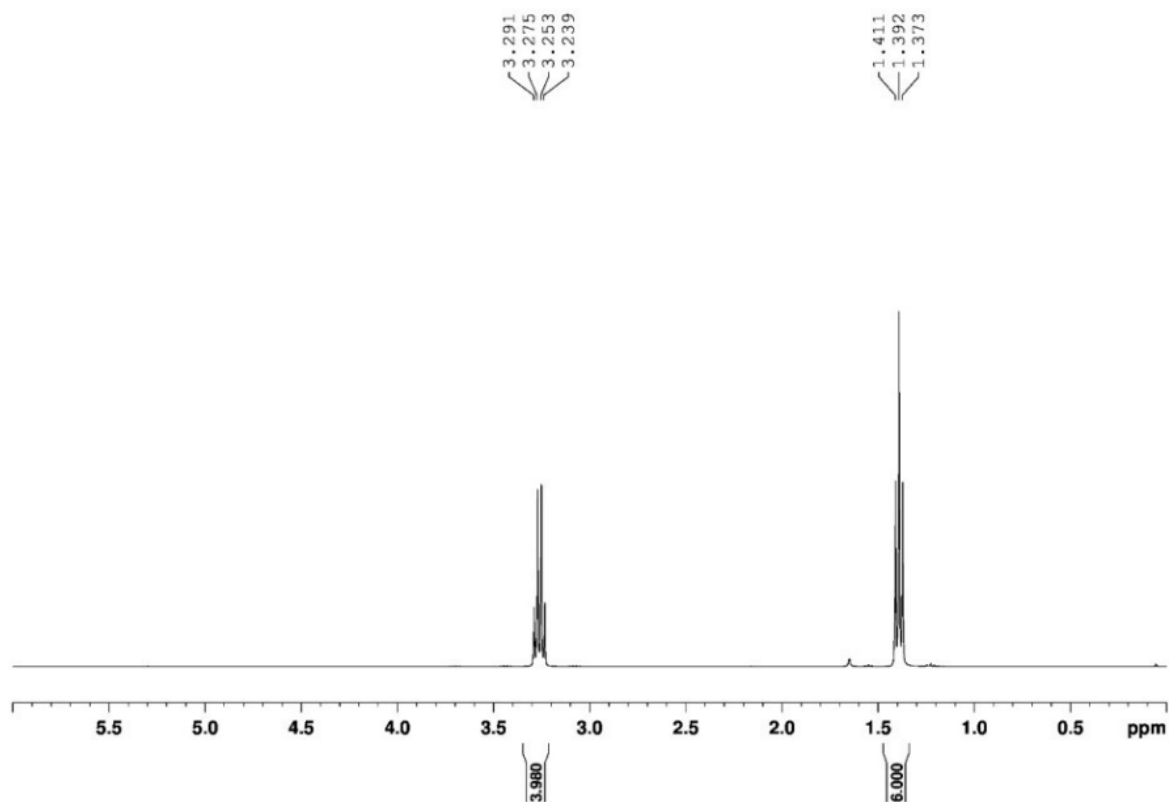


**Figure S1.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of 2-[bis(methylthio)methylene]malononitrile.

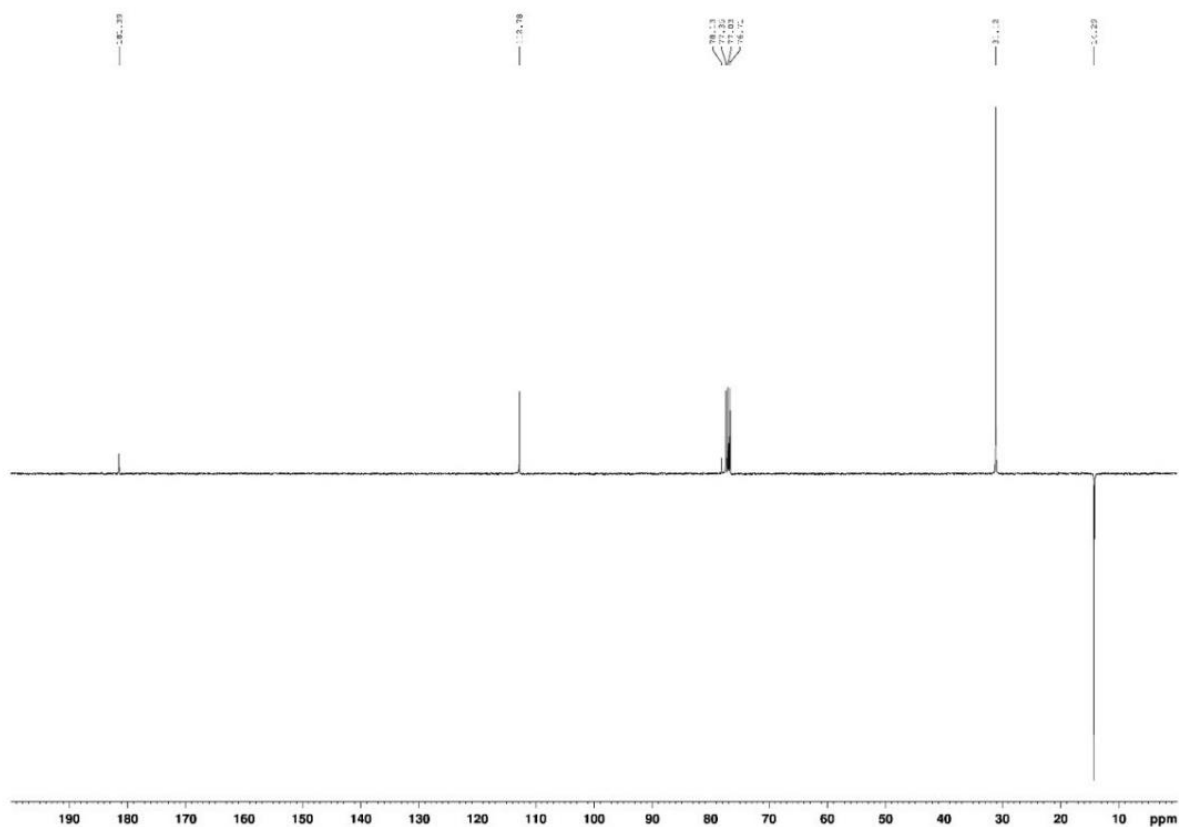




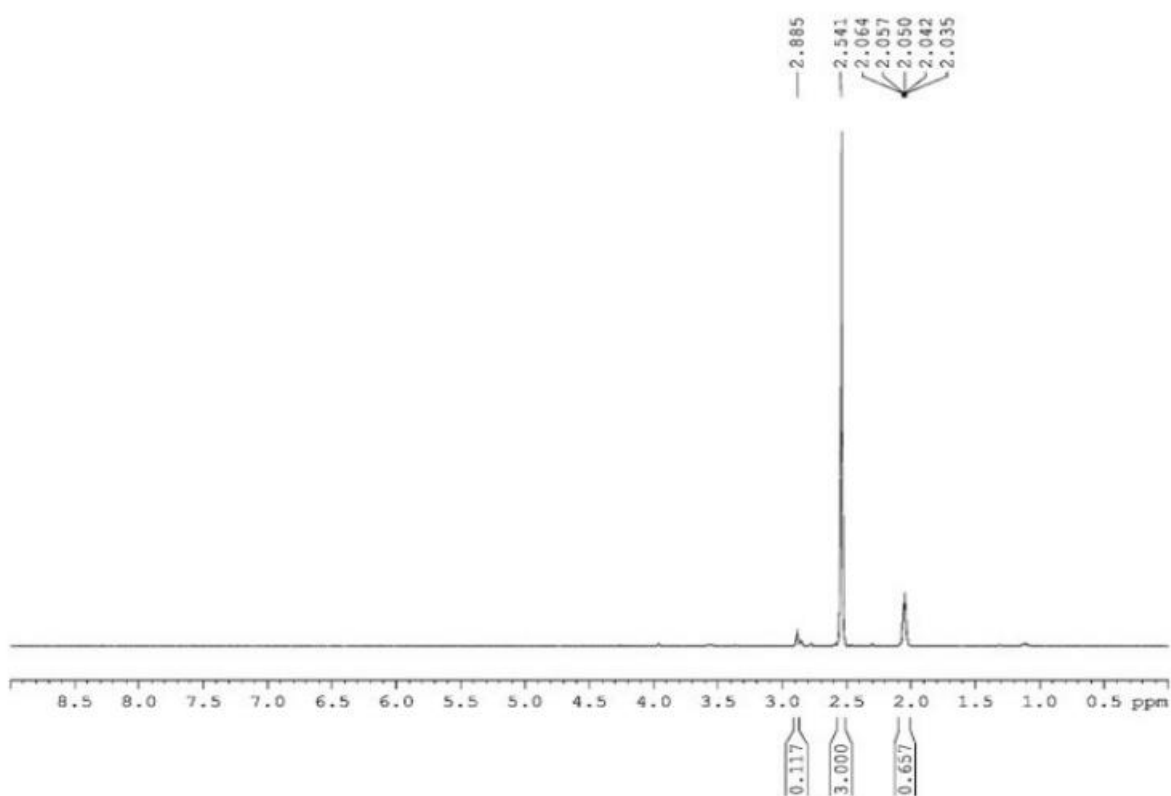
**Figure S2.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K) of 2-[bis(methylthio)methylene]malononitrile.



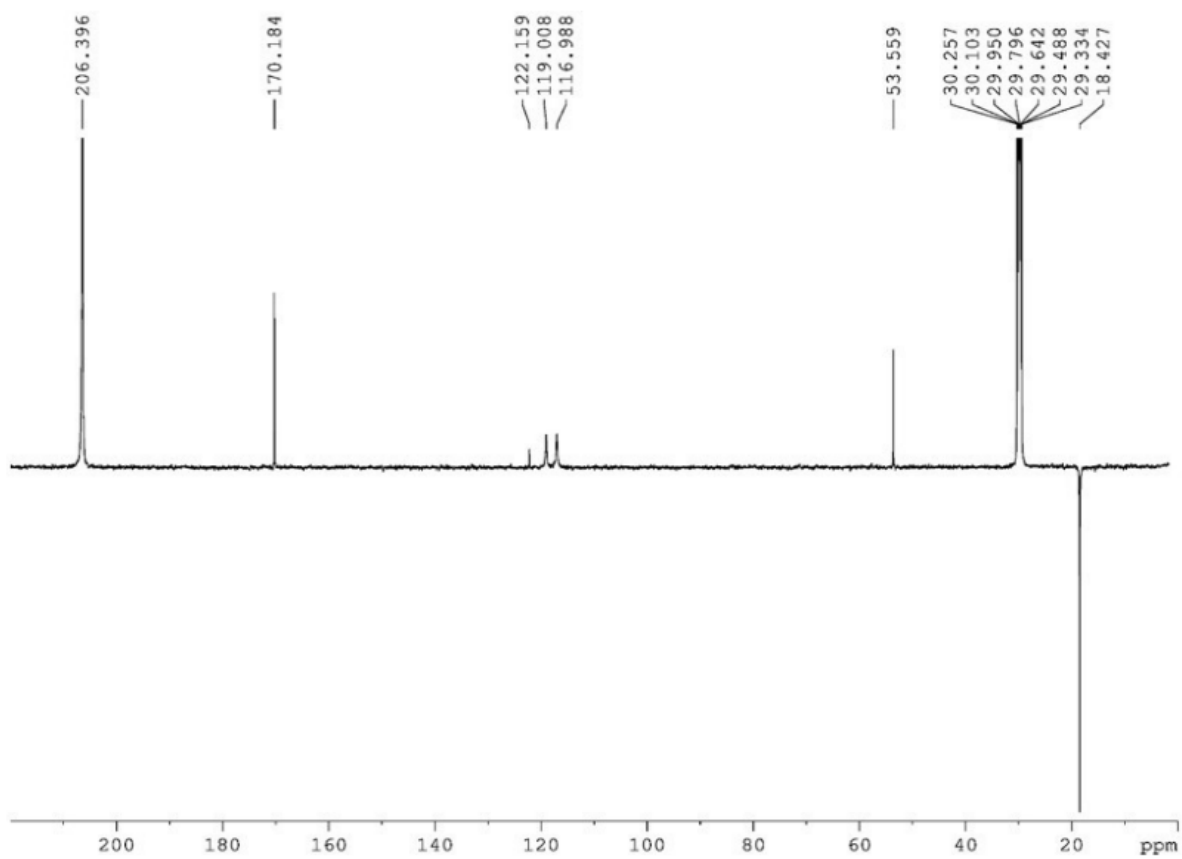
**Figure S3.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K) of 2-[bis(ethylthio)methylene]malononitrile.



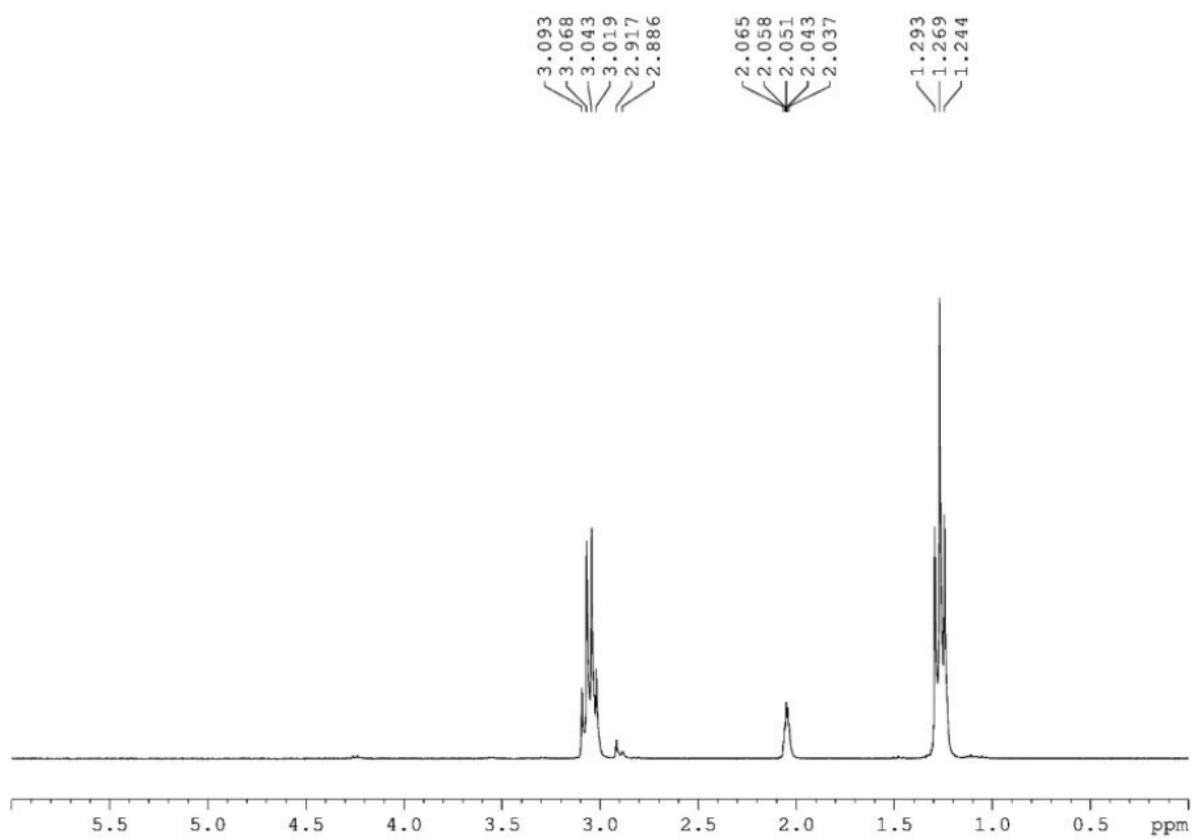
**Figure S4.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K) of 2-[bis(ethylthio)methylene]malononitrile.



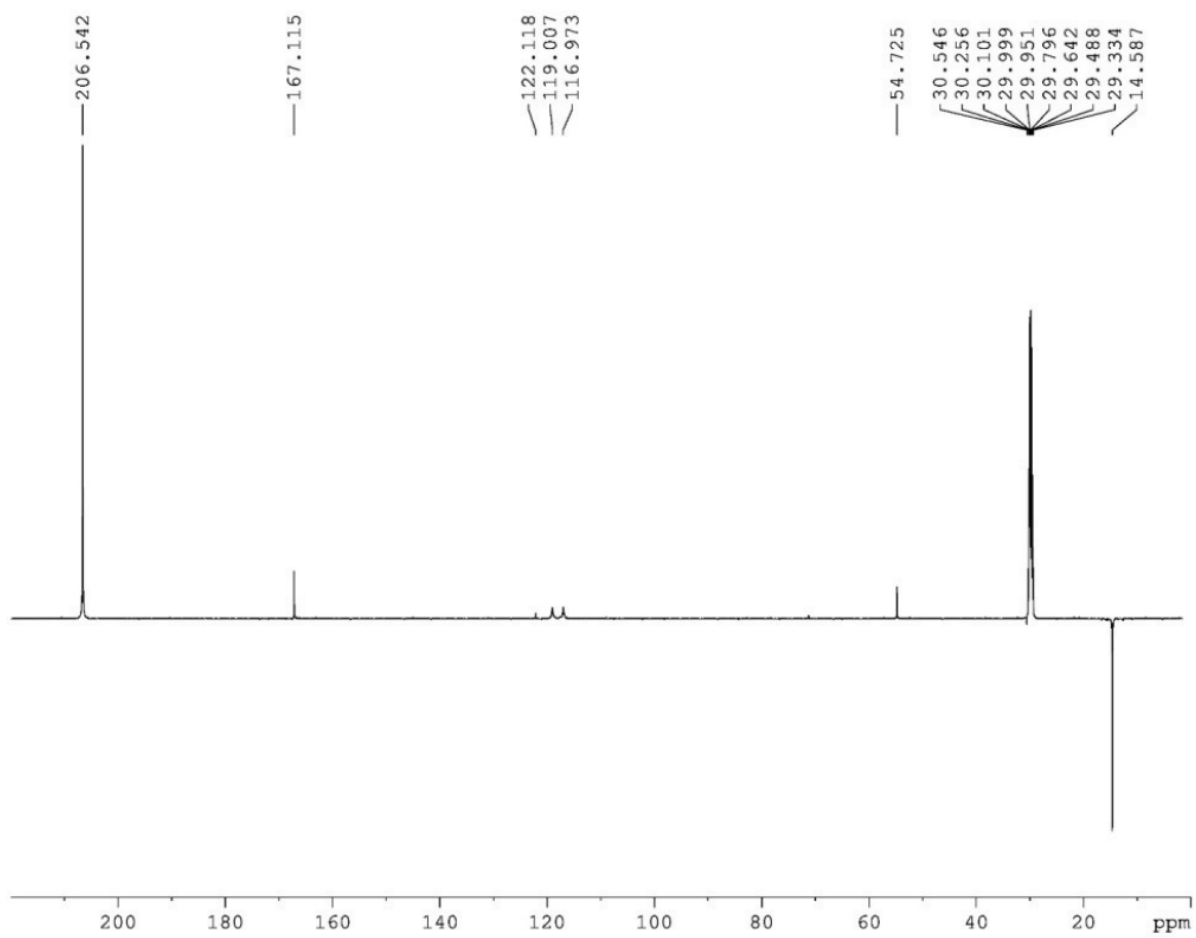
**Figure S5.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K) of potassium salt of **L1** anion.



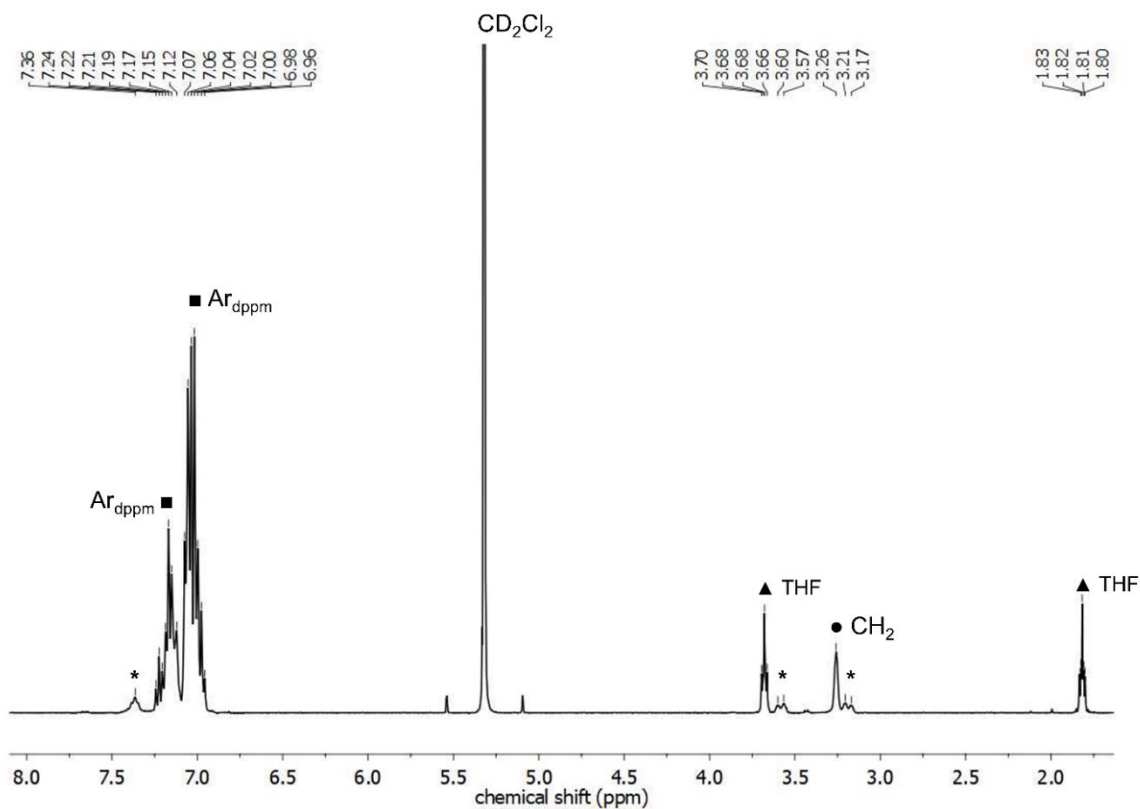
**Figure S6.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K) of potassium salt of **L1** anion.



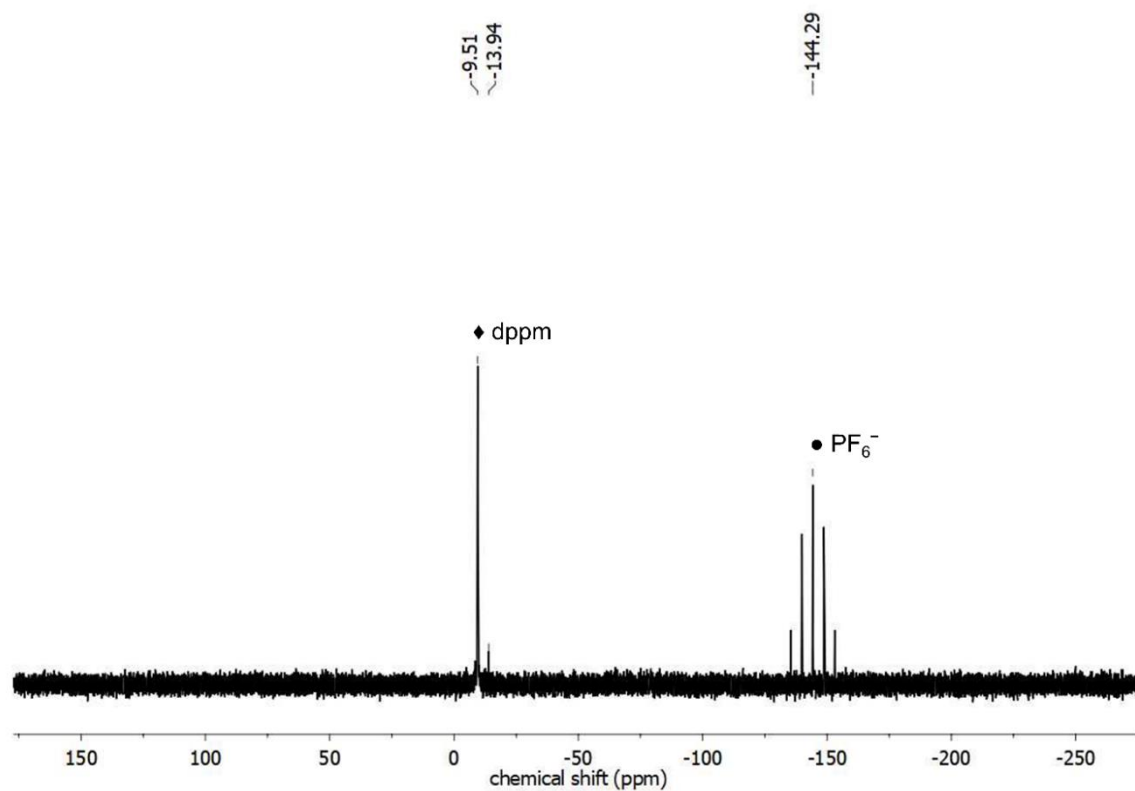
**Figure S7.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K) of potassium salt of **L2** anion.



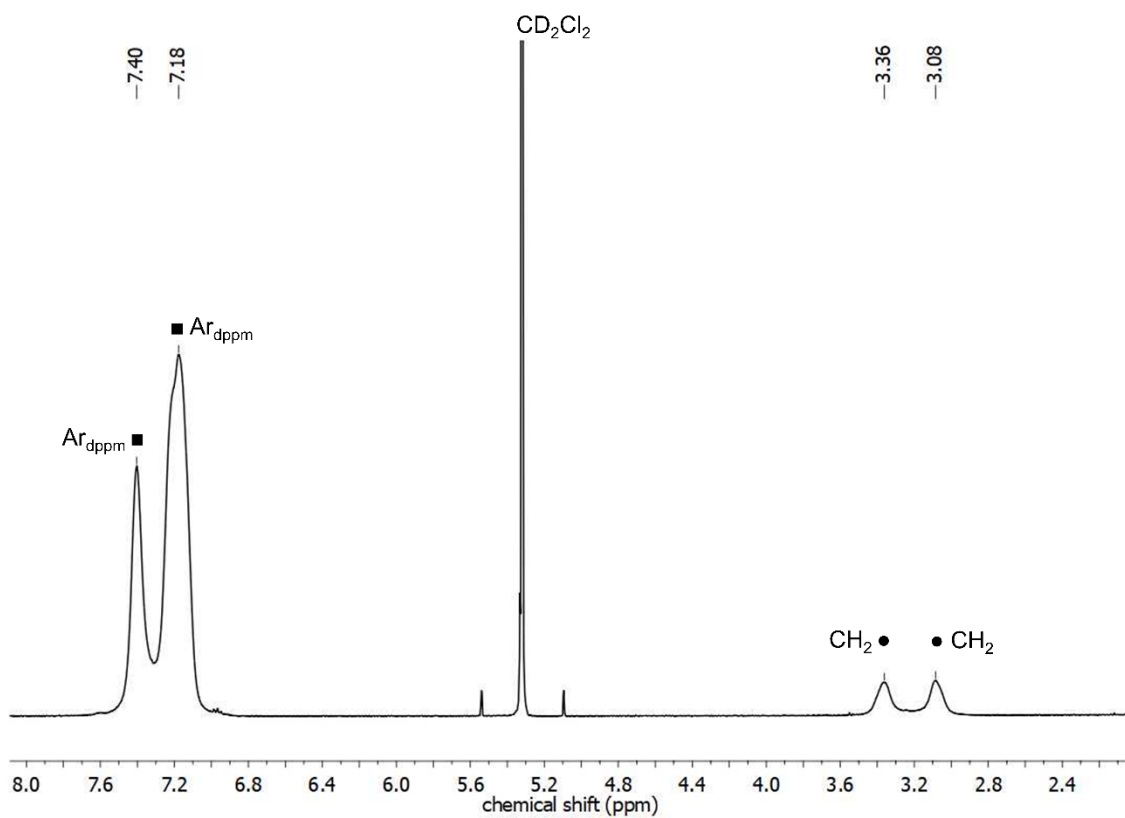
**Figure S8.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K) of potassium salt of **L2** anion.



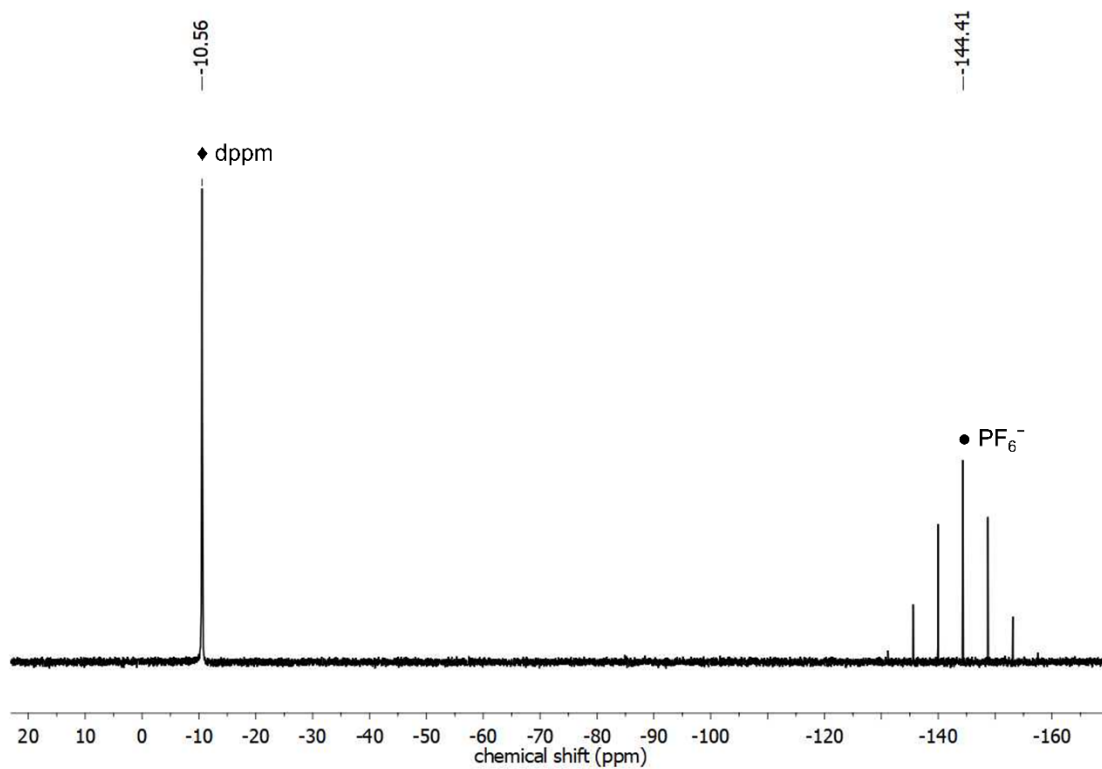
**Figure S9.**  $^1\text{H}$  NMR spectrum at RT (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **C**. Asterisk (\*) denotes an unidentified minor side product in solution.



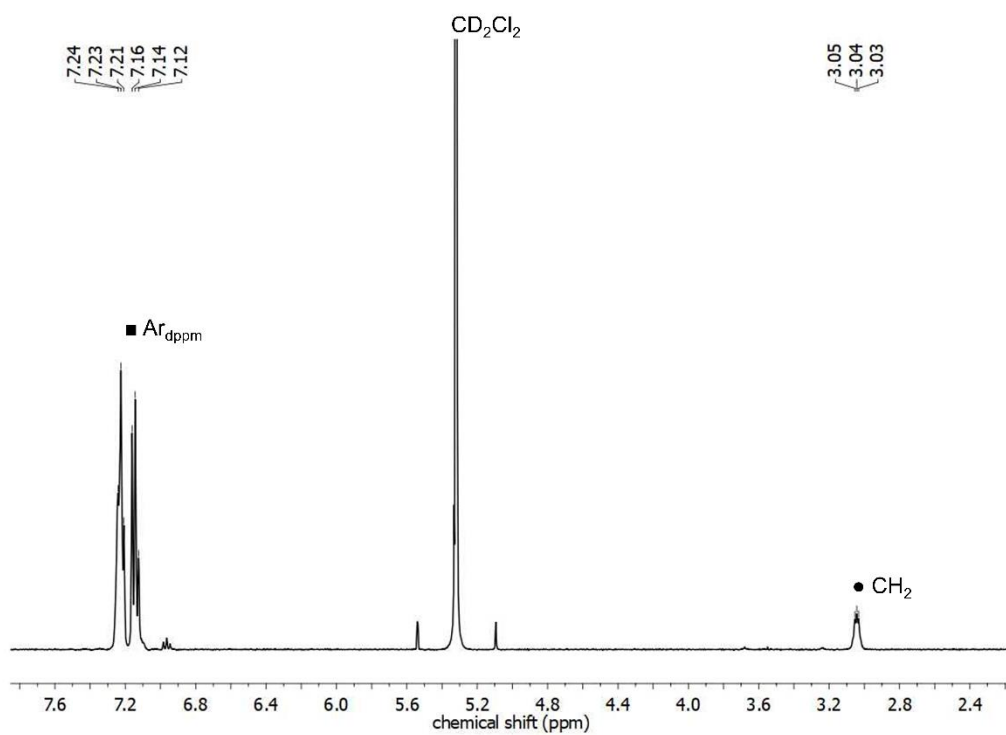
**Figure S10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at RT (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **C**.



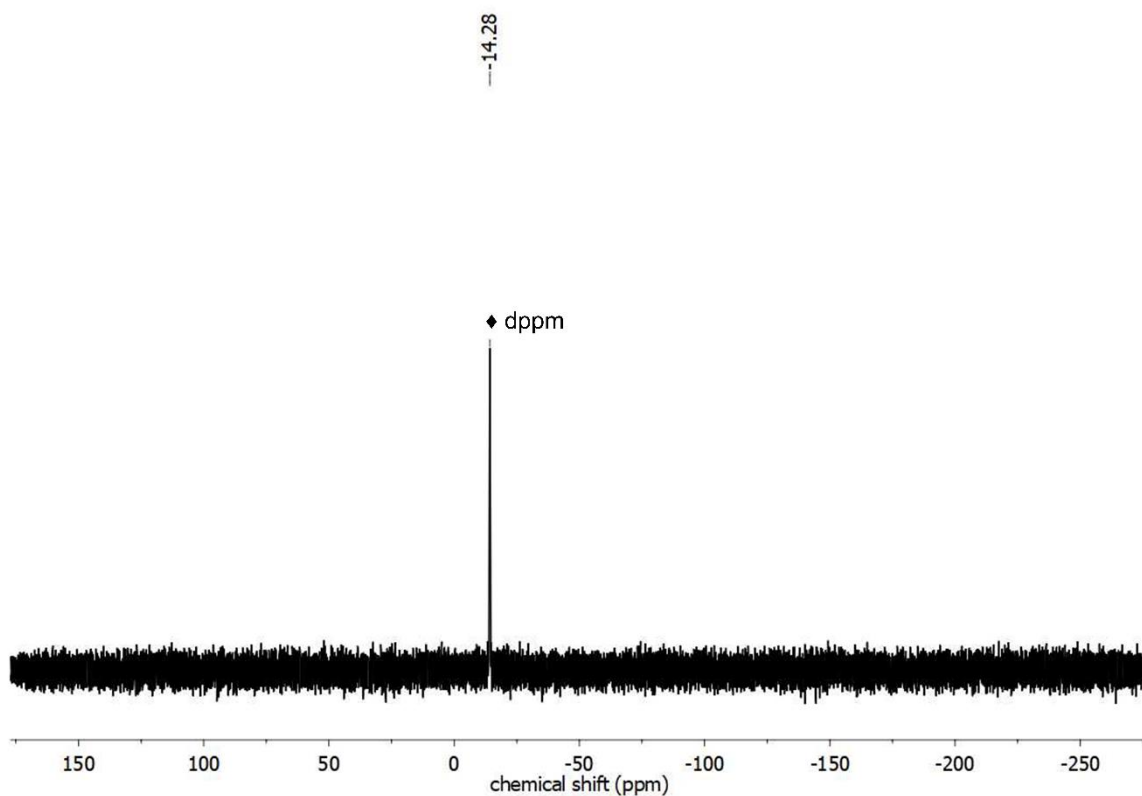
**Figure S11.**  $^1\text{H}$  NMR spectrum at RT (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **D**.



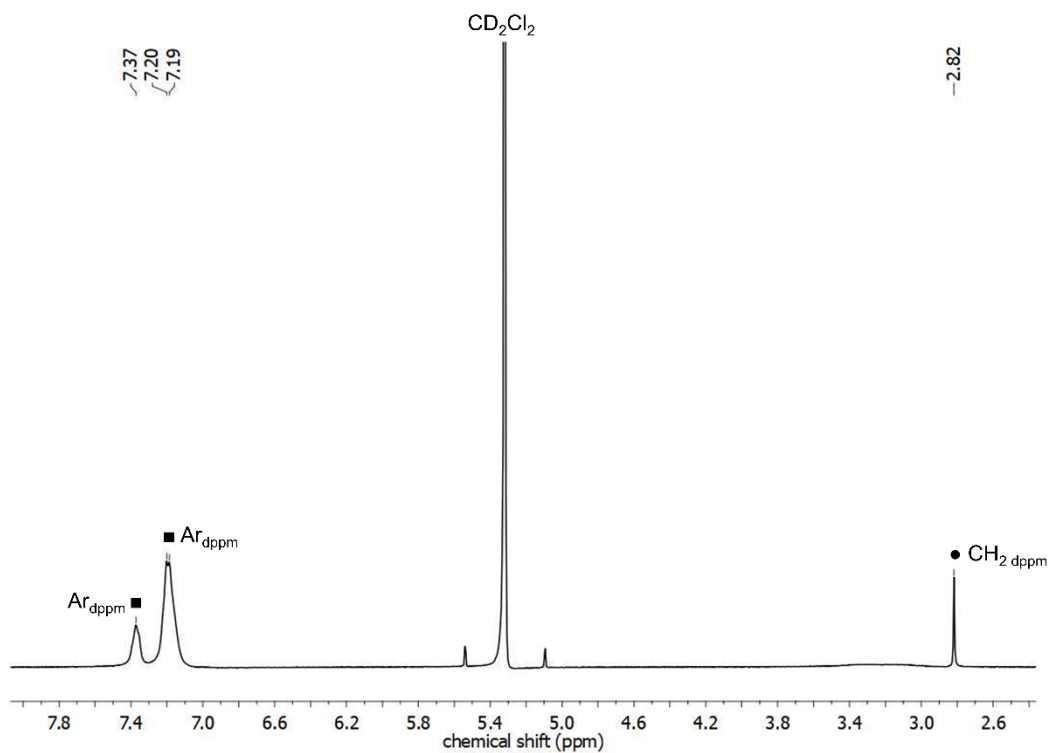
**Figure S12.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at RT (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **D**.



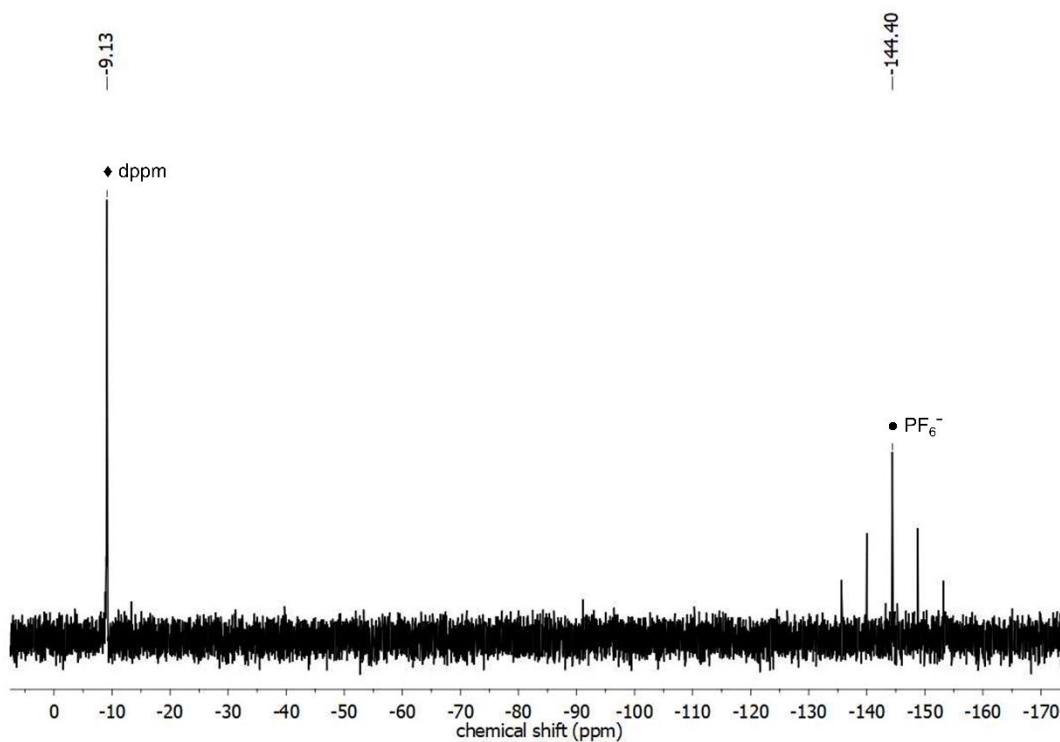
**Figure S13.**  $^1\text{H}$  NMR spectrum at RT (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative E.



**Figure S14.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at RT (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative E.

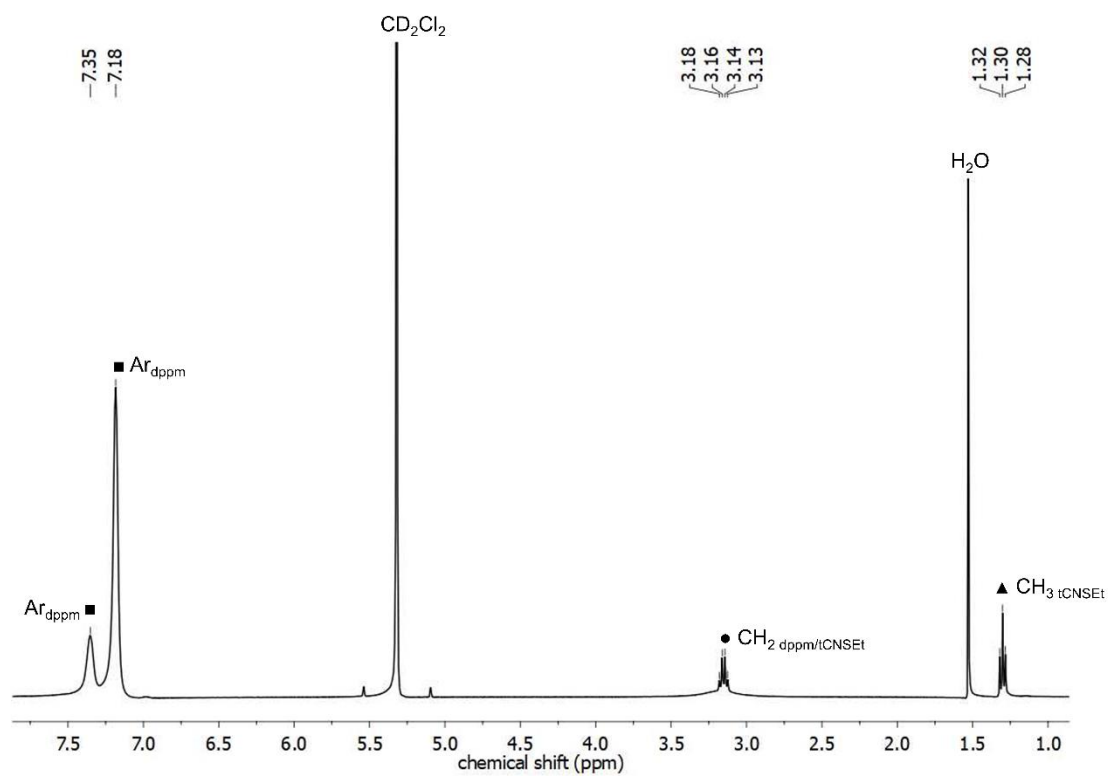


**Figure S15.**  $^1\text{H}$  NMR spectrum at RT (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **F**.

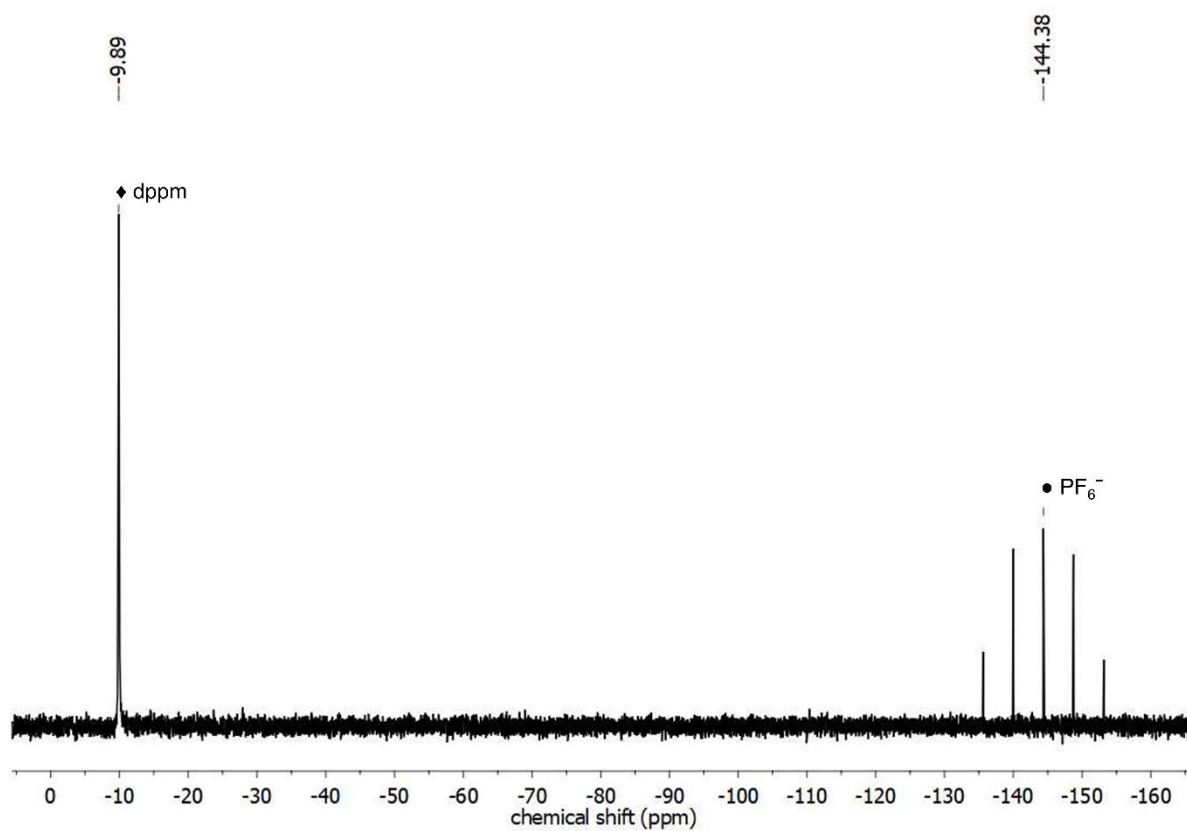


**Figure S16.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at RT (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **F**.

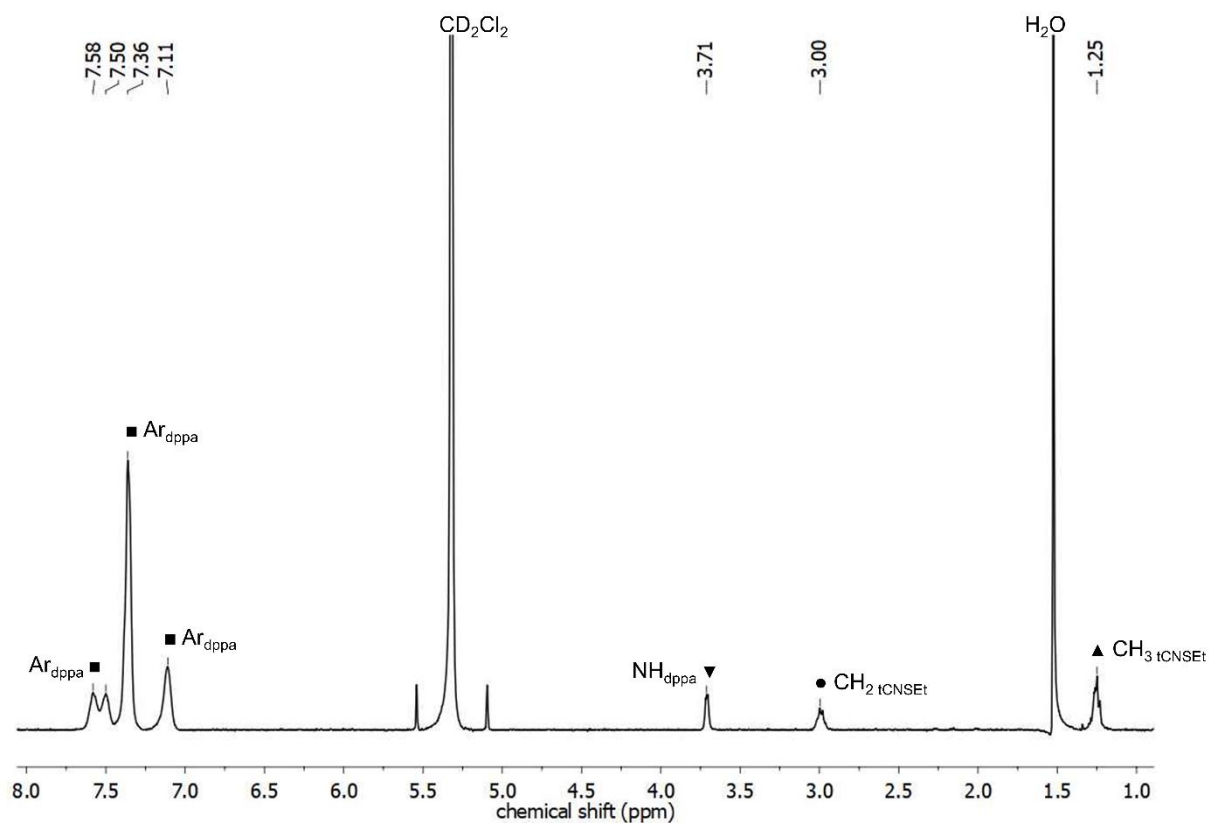




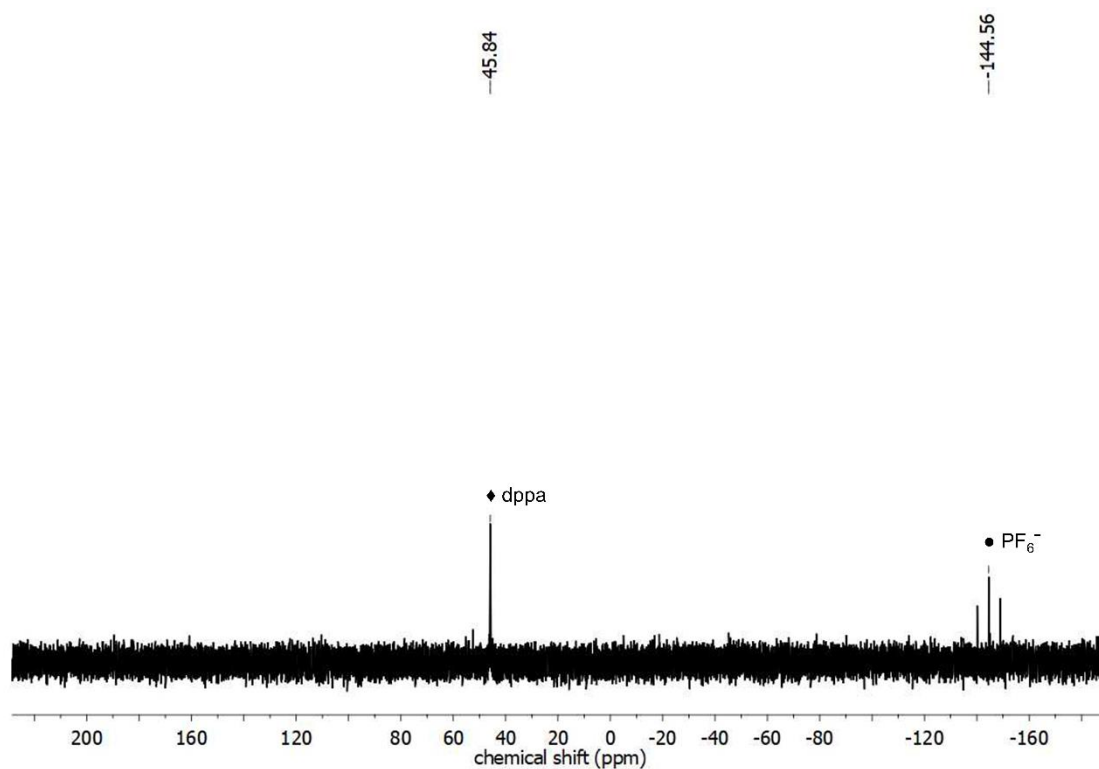
**Figure S17.**  $^1\text{H}$  NMR spectrum at RT (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **G**.



**Figure S18.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at RT (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **G**.

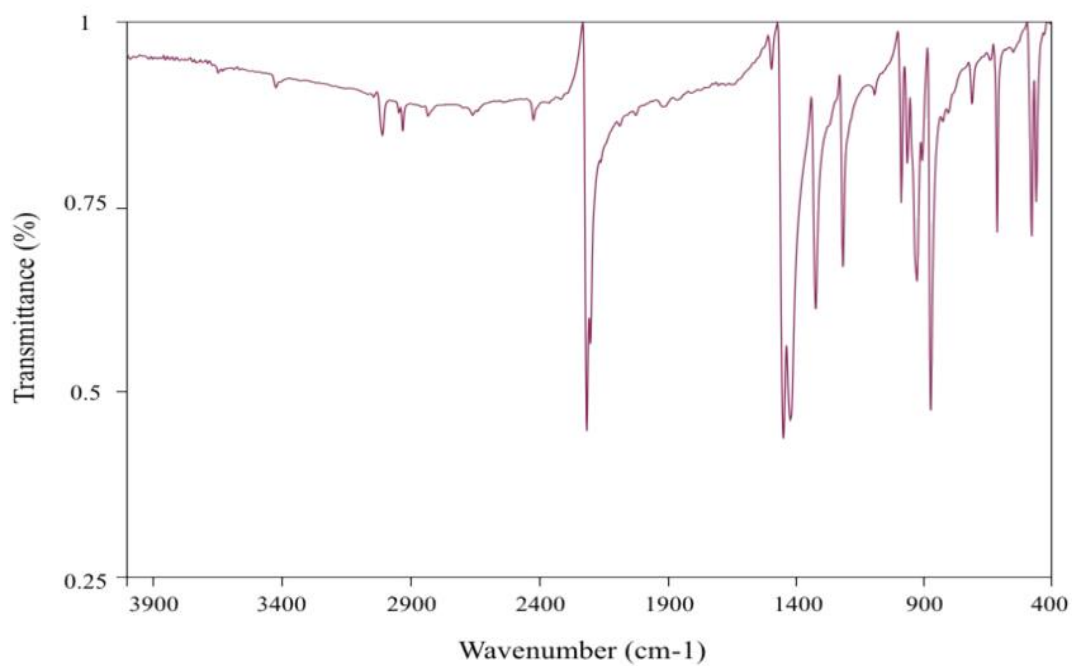


**Figure S19.**  $^1\text{H}$  NMR spectrum at RT (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **H**.

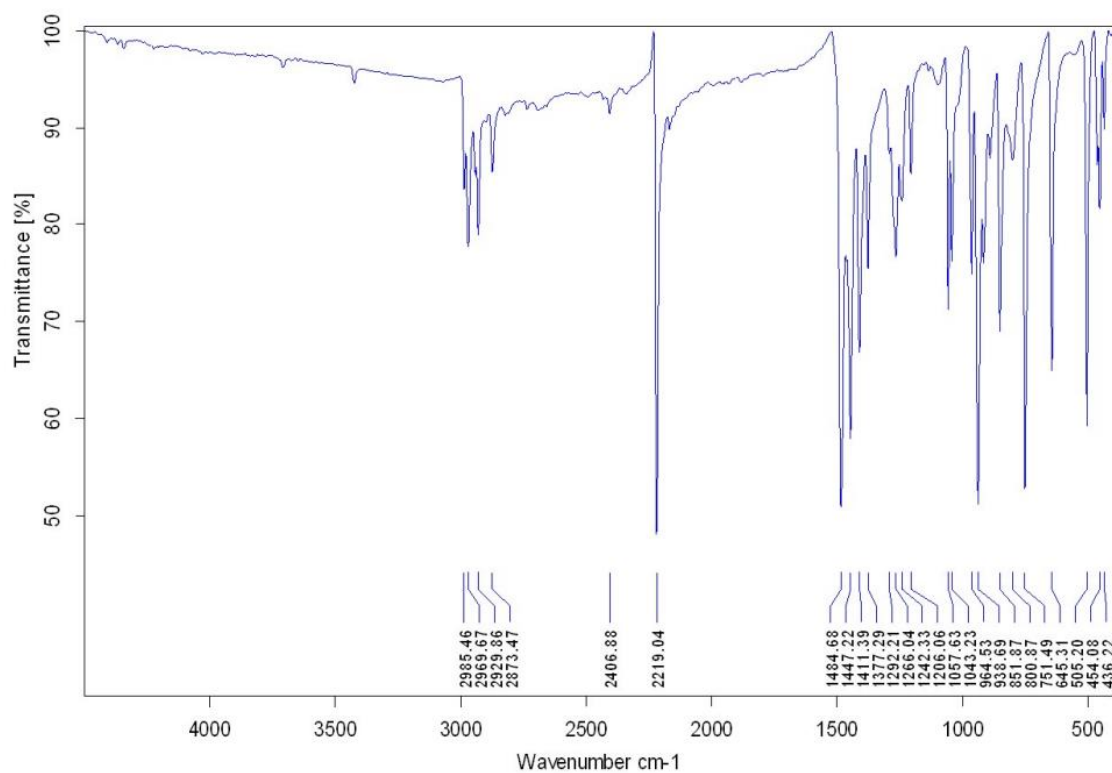


**Figure S20.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at RT (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of derivative **G**.

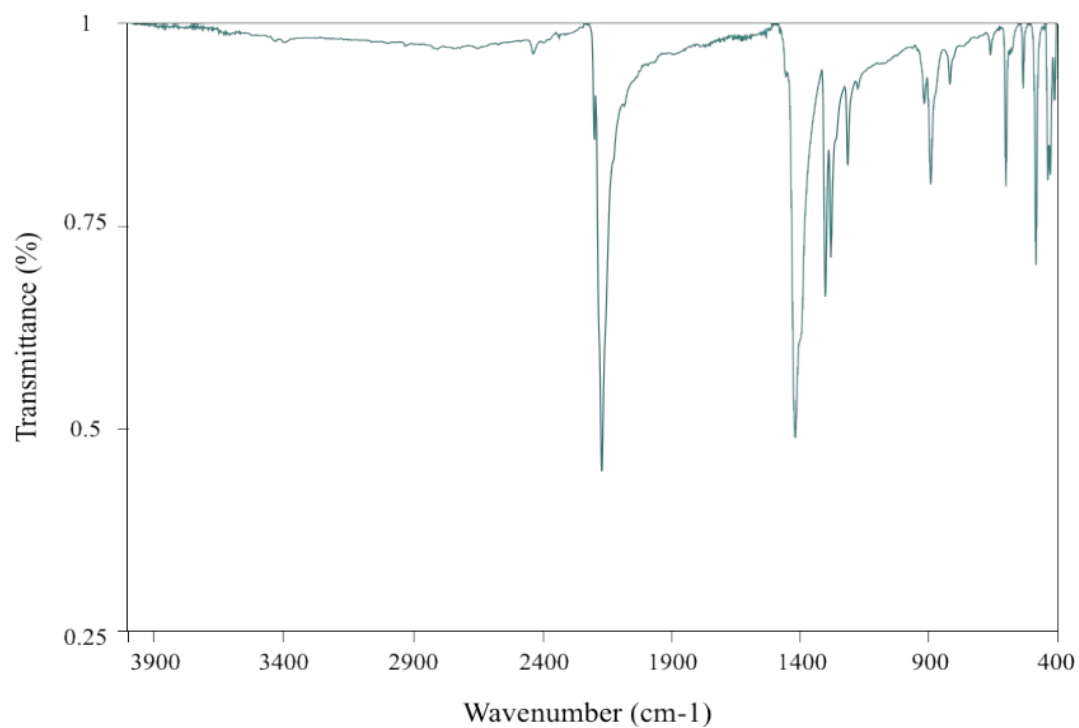
### I.3. Infrared spectroscopy



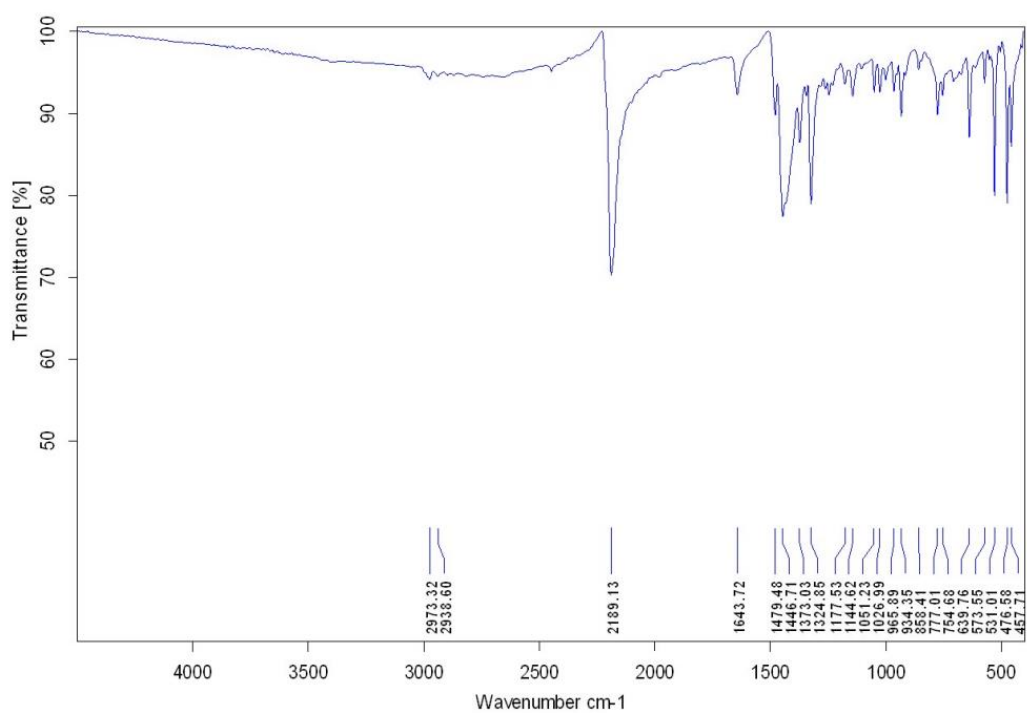
**Figure S21.** Infrared spectrum of 2-[bis(methylthio)methylene]malononitrile.



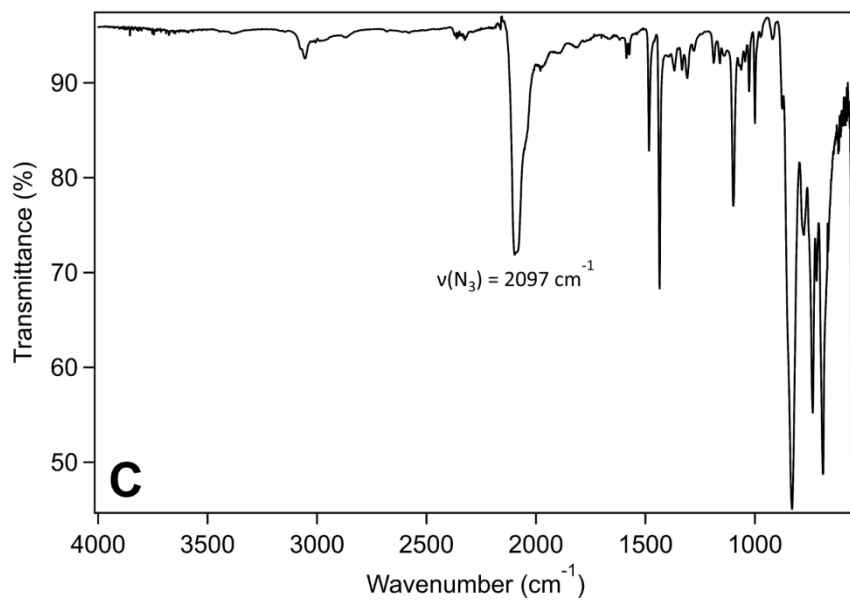
**Figure S22.** Infrared spectrum of 2-[bis(ethylthio)methylene]malononitrile.



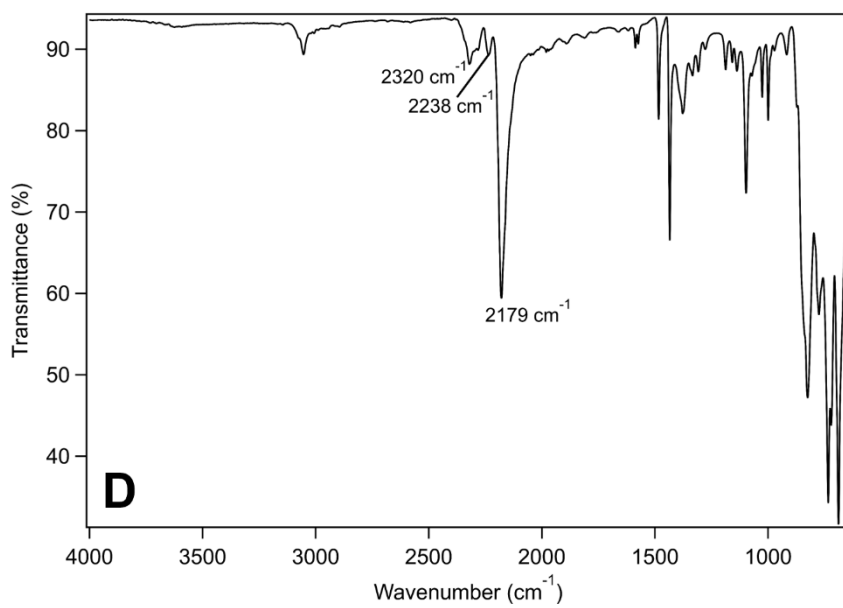
**Figure S23.** Infrared spectrum of potassium salt of L1 anion.



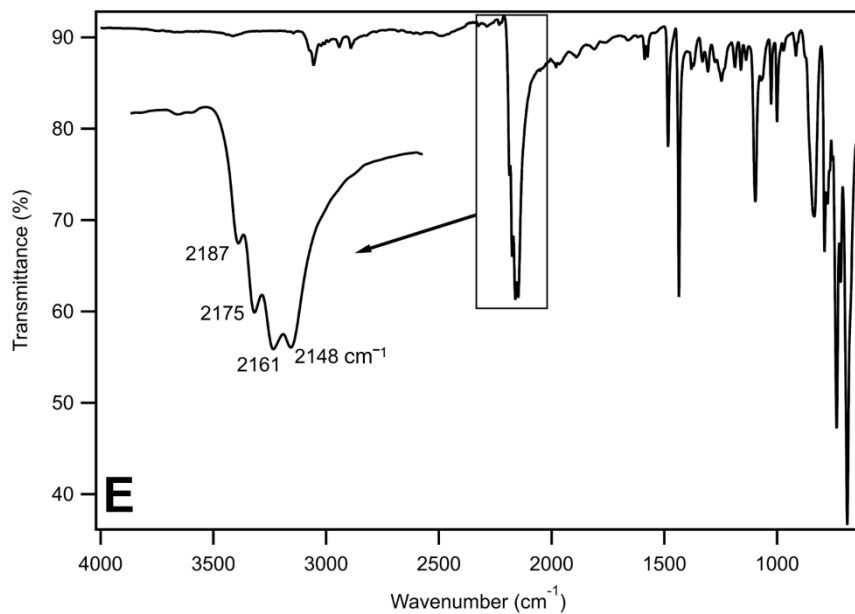
**Figure S24.** Infrared spectrum of potassium salt of L2 anion.



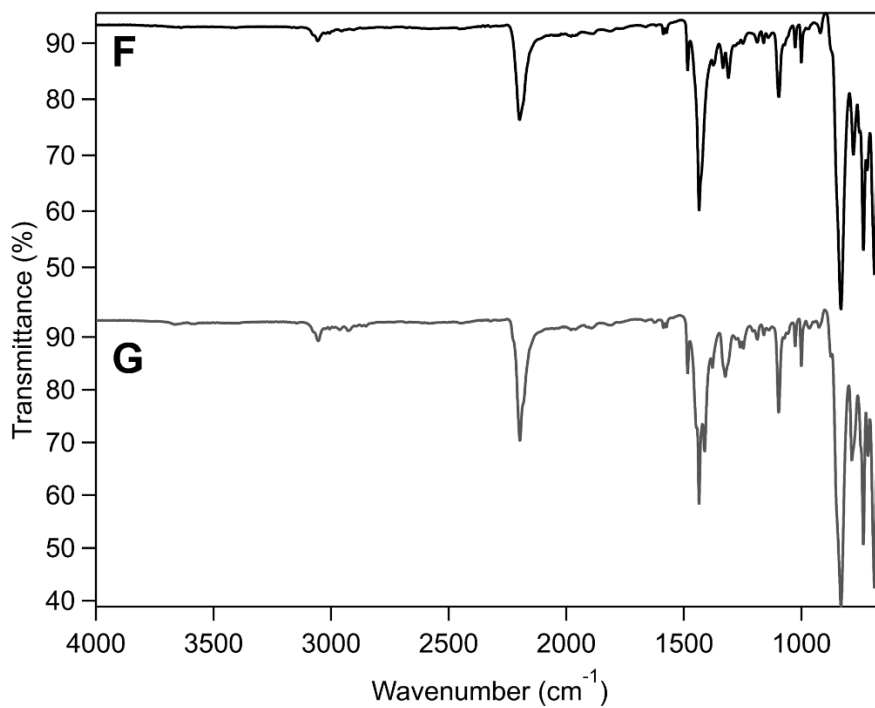
**Figure S25.** Infrared spectrum of derivative **C**



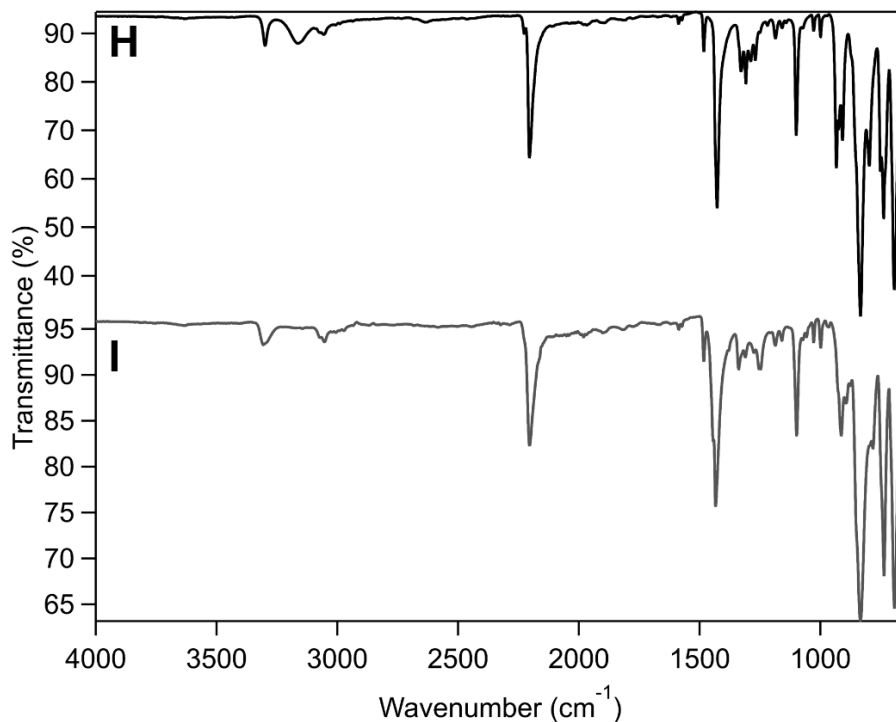
**Figure S26.** Infrared spectrum of derivative **D**



**Figure S27.** Infrared spectrum of derivative **E**. The frame corresponds to the vibrational  $\nu(\text{C}\equiv\text{N})$  region of the TCM ligand



**Figure S28.** Infrared spectra of derivatives **F** (black) and **G** (grey)



**Figure S29.** Infrared spectra of derivatives **H** (black) and **I** (grey)

## II. X-Ray Crystallographic study

Single crystal data collection for derivatives **C**, **D**, **E**, **F**, **G**, **H** and **I** were performed at 150 K with a D8 Venture Bruker AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.<sup>6</sup> Structure determinations were performed by direct methods with the solving program SIR97,<sup>7</sup> that revealed all the non-hydrogen atoms. SHELXL program<sup>8</sup> 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.

Single crystals of were always coated in paratone oil, mounted at low temperature on the diffractometer goniometer as quickly as possible in the case of these solvated crystals. X-ray data collection were performed at low temperature. In the crystal lattices of the coordination complexes studied, included solvent molecules (Dichloromethane or TH) were found in addition to the cationic coordination

complexes and their counter-anions. The included dichloromethane solvent molecules were found to be highly disordered and a correct modelling of the disorder of these solvent molecules was not always possible leading to rather high anisotropic displacement parameters for some of their atoms. We have therefore proceeded to a ‘squeeze’ treatment<sup>9,10</sup> in order to remove the scattering contribution of these molecules which cannot be satisfactorily modelled (per unit cell, 2 THF molecules in the case of derivative **C**, 3 dichloromethane molecules in the case of derivative **D**, 2 dichloromethane molecules in the case of derivative **E**, 3 dichloromethane molecules in the case of derivative **F**, 4 dichloromethane molecules in the case of derivative **G**, 2.5 dichloromethane molecules in the case of derivative **H** and 2 dichloromethane molecules in the case of derivative **I**). As a result, since these disordered molecules occupy a significant volume of the unit cell, an ALERT level A appears in the checkcif reports since "VERY LARGE Solvent Accessible VOIDS" are present in the structure resolution. In the case of the crystal of the derivative **I**, the hexafluorophosphate counter anion was found highly disordered and a correct modelling of its disorder was not possible leading to rather high anisotropic displacement parameters for some of their atoms. We have therefore proceeded to a ‘squeeze’ treatment<sup>9,10</sup> in order to remove the scattering contribution of this counter-anion which cannot be satisfactorily modelled. As a result, since this disordered counter-anion occupies a significant volume of the unit cell, an ALERT level A appears in the checkcif reports since "VERY LARGE Solvent Accessible VOIDS" are present in the structure resolution.

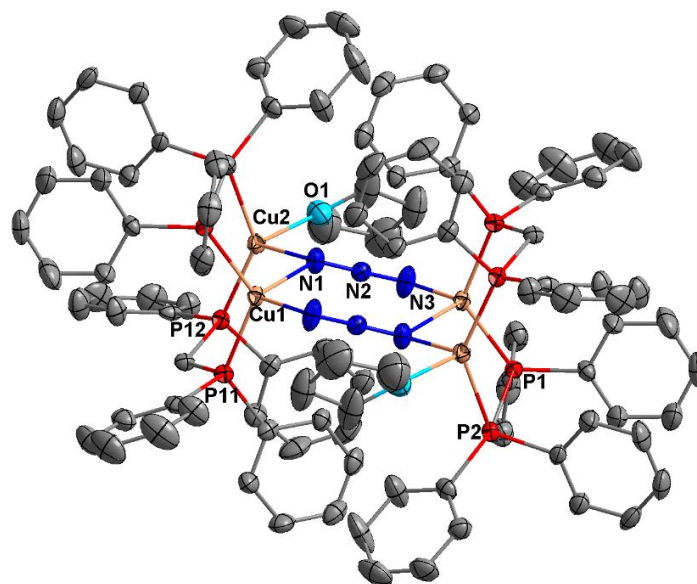
Regarding derivative **D**, in the asymmetric unit, three phenyl ring of the dppm ligands were found disordered over two neighboring positions and the relative occupancies were ponderated. Similarly, the dca ligands within the metallacycle were also found disordered over two positions and the relative occupancies were ponderated. However, these modelling afforded several atomic positions associated with anisotropy factors bearing ‘ADP max/min Ratio’ that led to ALERT level A appears in the checkcif report.

Finally, regarding the derivatives **D** and **F**, very tiny needles were always obtained that exhibited a very weak diffraction intensity, yet affording well defined diffraction peaks. For this reason, it was possible to perform a full data collection of good quality in spite of the very weak intensity of these peaks.

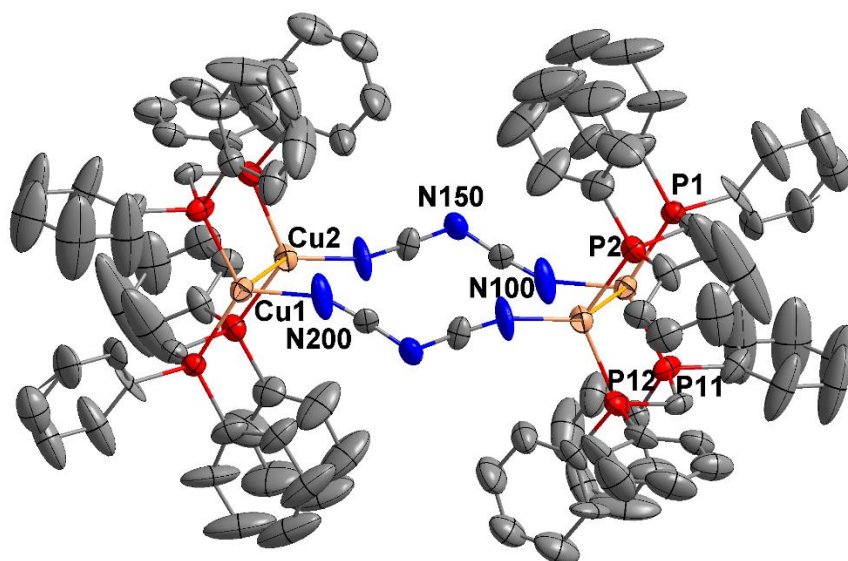


Consequently, ALERT level A appear in the checkcif report since several atomic positions associated with anisotropy factors bearing ‘ADP max/min Ratio.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.<sup>11</sup> CCDC reference numbers 2305990, 2305989, 2305991, 2305985, 2305984, 2305986 and 2305987 contain the supplementary crystallographic data for the reference measurements of the X-ray crystal structures of the derivatives **C**, **D**, **E**, **F**, **G**, **H** and **I** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

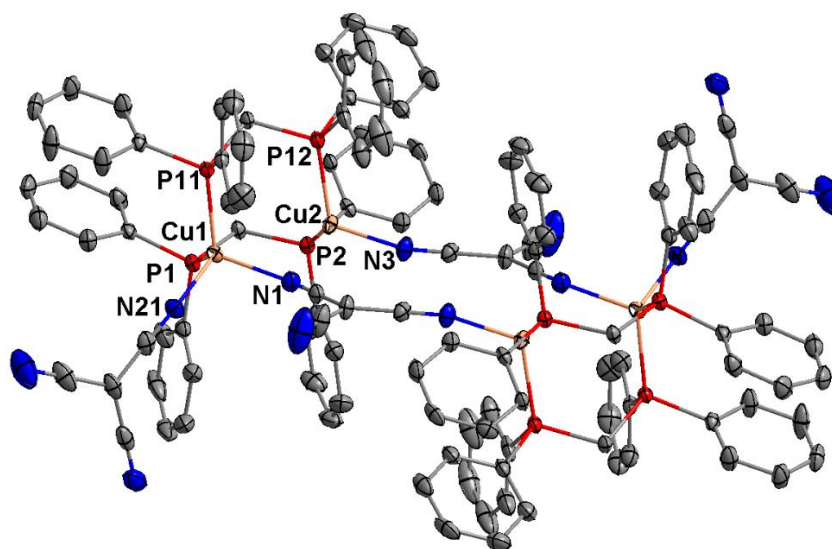


**Figure S30.** ORTEP<sup>11</sup> representation on the 50 % probability level of the crystal structure of the dicationic metallacycle **C**. H atoms, counter-anions and non-coordinated solvent molecules have been omitted for clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue) and Carbon (grey).

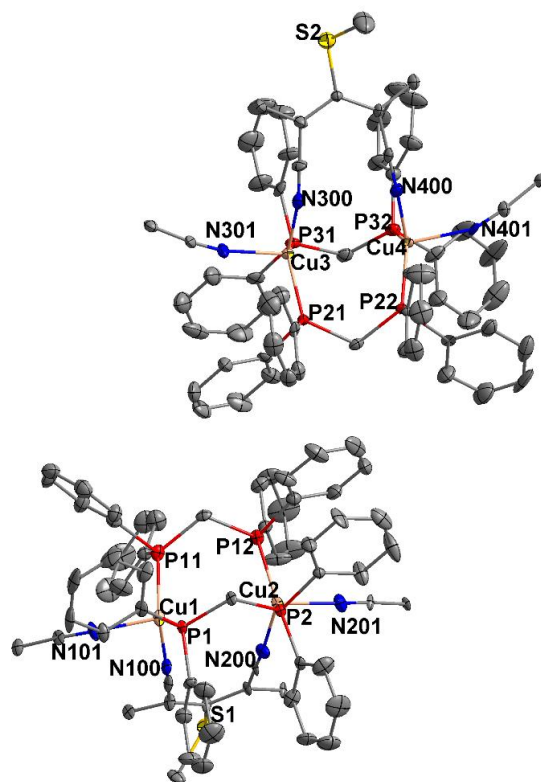


**Figure S31.** ORTEP<sup>12</sup> representation on the 50 % probability level of the crystal structure of the dicationic metallacycle **D**. H atoms, counter-anions and solvent molecules have been omitted for clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue) and Carbon (grey).

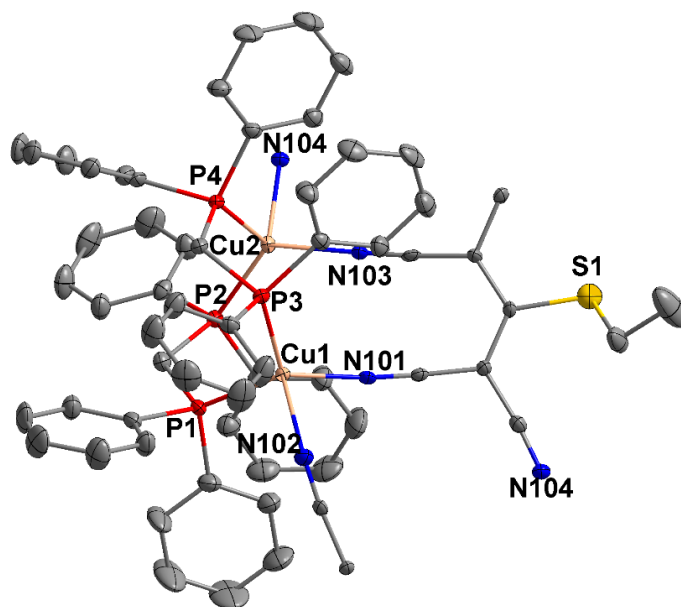
The N≡C–N<sup>–</sup>–C≡N linkers are disordered and their relative occupancies were refined in anti-parallel position, outside of the Cu<sub>4</sub> metallacycle plan, to minimize their dipolar moment interactions (N–N–N = 123.14°, **Erreur ! Source du renvoi introuvable**.b).



**Figure S32.** ORTEP<sup>12</sup> representation on the 50 % probability level of the crystal structure of the metallacycle **E**. H atoms, counter-anions and solvent molecules have been omitted for clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue) and Carbon (grey).

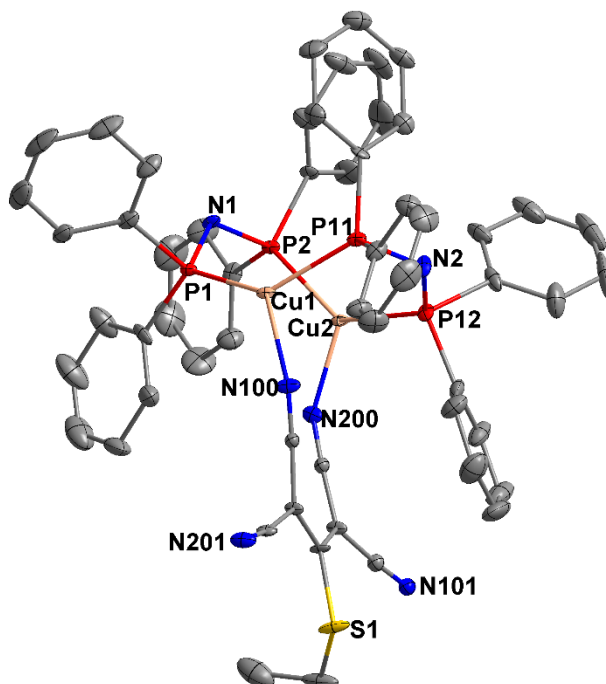


**Figure S33.** ORTEP<sup>12</sup> representation on the 50 % probability level of the crystal structure of the monocationic metallacycle **F**. H atoms, counter-anions and solvent molecules have been omitted for clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue), Sulfur (yellow) and Carbon (grey).

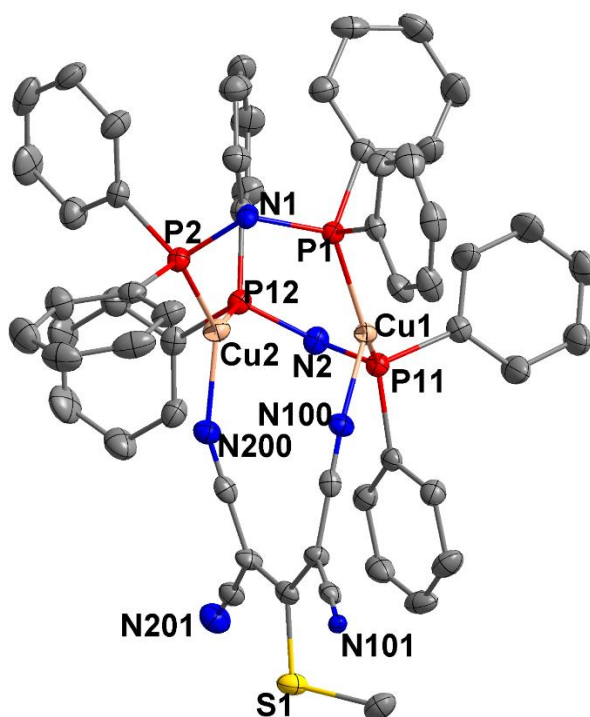


**Figure S34.** ORTEP<sup>12</sup> representation on the 50 % probability level of the crystal structure of the monocationic metallacycle **G**. H atoms, counter-anions and solvent molecules have been omitted for

clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue), Sulfur (yellow) and Carbon (grey).



**Figure S35.** ORTEP<sup>12</sup> representation on the 50 % probability level of the crystal structure of the monocationic metallacycle **H**. H atoms, counter-anions and solvent molecules have been omitted for clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue), Sulfur (yellow) and Carbon (grey).



**Figure S36.** ORTEP<sup>12</sup> representation on the 50 % probability level of the crystal structure of the tetracationic metallacycle **I**. H atoms, counter-anions and solvent molecules have been omitted for clarity. Atoms are depicted as follow: Copper (light pink), Phosphorus (red), Nitrogen (blue), Oxygen (light blue), Sulfur (yellow) and Carbon (grey).

**Table S1.** Bond Lengths for derivative **C**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N3	2.114(3)	C15	C16	1.402(6)	N1	N2	1.177(4)	C110	C111	1.389(7)
Cu1	N1	2.146(3)	C16	C17	1.358(7)	N2	N3 <sup>1</sup>	1.162(4)	C111	C112	1.376(6)
Cu1	P11	2.2438(13)	C17	C18	1.400(7)	O1	C203	1.339(7)	C114	C119	1.376(6)
Cu1	P1	2.2585(12)	C18	C19	1.371(6)	O1	C200	1.520(8)	C114	C115	1.403(6)
Cu1	Cu2	3.0128(10)	C20	C25	1.376(6)	C200	C201	1.521(9)	C115	C116	1.385(6)
Cu2	N1	2.096(3)	C20	C21	1.391(6)	C201	C202	1.617(9)	C116	C117	1.387(7)
Cu2	P12	2.2491(13)	C21	C22	1.380(6)	C202	C203	1.422(8)	C117	C118	1.360(7)
Cu2	P2	2.2588(12)	C22	C23	1.364(7)	C1	C2	1.399(6)	C118	C119	1.401(6)
Cu2	O1	2.302(3)	C23	C24	1.370(8)	C1	C6	1.401(6)	C120	C125	1.376(6)
P1	C1	1.823(4)	C24	C25	1.398(7)	C2	C3	1.387(6)	C120	C121	1.382(6)
P1	C7	1.827(4)	N3	N2 <sup>1</sup>	1.162(4)	C3	C4	1.374(7)	C121	C122	1.383(6)
P1	C13	1.837(4)	C101	C102	1.389(6)	C4	C5	1.384(7)	C122	C123	1.370(7)
P2	C14	1.821(4)	C101	C106	1.394(6)	C5	C6	1.375(6)	C123	C124	1.359(7)
P2	C20	1.837(4)	C102	C103	1.371(7)	C7	C12	1.378(6)	C124	C125	1.397(6)
P2	C13	1.838(4)	C103	C104	1.379(8)	C7	C8	1.382(6)	F100	P100	1.543(4)
P11	C101	1.818(4)	C104	C105	1.377(8)	C8	C9	1.381(6)	F101	P100	1.568(3)
P11	C107	1.829(4)	C105	C106	1.382(6)	C9	C10	1.363(7)	F102	P100	1.571(3)
P11	C113	1.837(4)	C107	C108	1.391(6)	C10	C11	1.366(8)	F103	P100	1.591(4)
P12	C114	1.823(4)	C107	C112	1.397(6)	C11	C12	1.375(7)	F104	P100	1.583(3)
P12	C120	1.828(4)	C108	C109	1.384(6)	C14	C15	1.391(6)	F105	P100	1.580(3)
P12	C113	1.846(4)	C109	C110	1.360(6)	C14	C19	1.397(6)			

<sup>1</sup>2-x,1-y,-z

**Table S2.** Bond Angles for derivative **C**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	Cu1	N1	94.11(13)	C10	C11	C12	120.7(5)
N3	Cu1	P11	107.79(12)	C11	C12	C7	120.8(5)
N1	Cu1	P11	112.38(10)	P1	C13	P2	112.7(2)
N3	Cu1	P1	108.16(11)	C15	C14	C19	119.7(4)
N1	Cu1	P1	105.97(11)	C15	C14	P2	117.6(3)
P11	Cu1	P1	124.22(4)	C19	C14	P2	122.7(3)
N3	Cu1	Cu2	138.19(10)	C14	C15	C16	119.8(4)
N1	Cu1	Cu2	44.08(9)	C17	C16	C15	120.0(4)
P11	Cu1	Cu2	92.49(3)	C16	C17	C18	120.3(4)
P1	Cu1	Cu2	87.96(4)	C19	C18	C17	120.4(5)
N1	Cu2	P12	111.57(11)	C18	C19	C14	119.8(4)
N1	Cu2	P2	97.81(11)	C25	C20	C21	119.0(4)
P12	Cu2	P2	138.16(4)	C25	C20	P2	119.0(4)
N1	Cu2	O1	91.98(13)	C21	C20	P2	121.9(3)
P12	Cu2	O1	107.42(9)	C22	C21	C20	120.1(4)
P2	Cu2	O1	100.36(9)	C23	C22	C21	121.0(5)
N1	Cu2	Cu1	45.43(9)	C22	C23	C24	119.5(5)
P12	Cu2	Cu1	88.88(3)	C23	C24	C25	120.4(5)

P2	Cu2	Cu1	91.52(4)	C20	C25	C24	120.0(5)
O1	Cu2	Cu1	137.17(9)	N2 <sup>1</sup>	N3	Cu1	122.6(3)
C1	P1	C7	101.66(17)	C102	C101	C106	118.7(4)
C1	P1	C13	105.31(19)	C102	C101	P11	116.3(3)
C7	P1	C13	103.73(19)	C106	C101	P11	124.9(3)
C1	P1	Cu1	112.70(14)	C103	C102	C101	120.8(5)
C7	P1	Cu1	121.99(14)	C102	C103	C104	119.8(5)
C13	P1	Cu1	109.90(13)	C105	C104	C103	120.5(5)
C14	P2	C20	105.2(2)	C104	C105	C106	119.8(5)
C14	P2	C13	104.29(19)	C105	C106	C101	120.3(5)
C20	P2	C13	100.03(18)	C108	C107	C112	119.1(4)
C14	P2	Cu2	117.95(15)	C108	C107	P11	119.5(3)
C20	P2	Cu2	114.01(14)	C112	C107	P11	121.3(3)
C13	P2	Cu2	113.35(14)	C109	C108	C107	119.8(4)
C101	P11	C107	102.9(2)	C110	C109	C108	121.2(4)
C101	P11	C113	104.44(19)	C109	C110	C111	119.2(4)
C107	P11	C113	103.67(18)	C112	C111	C110	120.9(4)
C101	P11	Cu1	111.46(13)	C111	C112	C107	119.6(4)
C107	P11	Cu1	121.97(14)	P11	C113	P12	112.8(2)
C113	P11	Cu1	110.73(14)	C119	C114	C115	118.2(4)
C114	P12	C120	102.73(18)	C119	C114	P12	122.9(3)
C114	P12	C113	101.80(18)	C115	C114	P12	118.9(3)
C120	P12	C113	104.12(19)	C116	C115	C114	121.3(5)
C114	P12	Cu2	117.50(14)	C115	C116	C117	119.3(5)
C120	P12	Cu2	114.32(14)	C118	C117	C116	120.1(4)
C113	P12	Cu2	114.56(13)	C117	C118	C119	120.8(5)
N2	N1	Cu2	127.4(3)	C114	C119	C118	120.3(4)
N2	N1	Cu1	131.5(3)	C125	C120	C121	119.1(4)
Cu2	N1	Cu1	90.49(13)	C125	C120	P12	122.1(3)
N3 <sup>1</sup>	N2	N1	178.2(4)	C121	C120	P12	118.7(3)
C203	O1	C200	96.2(4)	C120	C121	C122	121.2(5)
C203	O1	Cu2	133.9(3)	C123	C122	C121	118.9(5)
C200	O1	Cu2	129.0(3)	C124	C123	C122	120.8(5)
O1	C200	C201	105.6(6)	C123	C124	C125	120.5(5)
C200	C201	C202	104.4(5)	C120	C125	C124	119.4(4)
C203	C202	C201	95.5(5)	F100	P100	F101	90.6(3)
O1	C203	C202	122.4(7)	F100	P100	F102	90.3(3)
C2	C1	C6	118.5(4)	F101	P100	F102	89.8(2)
C2	C1	P1	124.6(3)	F100	P100	F105	91.8(3)
C6	C1	P1	116.8(3)	F101	P100	F105	90.1(2)
C3	C2	C1	120.2(4)	F102	P100	F105	177.8(3)
C4	C3	C2	120.2(4)	F100	P100	F104	91.9(3)
C3	C4	C5	120.2(4)	F101	P100	F104	176.7(2)
C6	C5	C4	120.2(5)	F102	P100	F104	92.5(2)
C5	C6	C1	120.6(4)	F105	P100	F104	87.5(2)
C12	C7	C8	117.7(4)	F100	P100	F103	179.8(3)
C12	C7	P1	119.4(3)	F101	P100	F103	89.2(2)
C8	C7	P1	122.9(3)	F102	P100	F103	89.8(2)
C9	C8	C7	121.2(5)	F105	P100	F103	88.1(2)
C10	C9	C8	120.0(5)	F104	P100	F103	88.3(2)
C9	C10	C11	119.5(5)				

<sup>1</sup>2-x,1-y,-z

**Table S3.** Bond Lengths for derivative **D**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N100	1.9457(6)	C24	C25	1.3900	C3	C4	1.3900	C545	C546	1.3900
Cu1	N700	1.9616(6)	C31	C32	1.3900	C4	C5	1.3900	C546	C547	1.3900
Cu1	P11	2.2359(13)	C31	C36	1.3900	C5	C6	1.3900	C547	C548	1.3900
Cu1	P1	2.2505(13)	C32	C33	1.3900	C501	C502	1.3900	C548	C549	1.3900
Cu1	Cu2	2.9256(9)	C33	C34	1.3900	C501	C506	1.3900	C50	C51	1.3900
Cu2	N200	1.9190(6)	C34	C35	1.3900	C502	C503	1.3900	C50	C55	1.3900
Cu2	N800	2.0373(6)	C35	C36	1.3900	C503	C504	1.3900	C51	C52	1.3900
Cu2	P12	2.2438(14)	C37	C38	1.3900	C504	C505	1.3900	C52	C53	1.3900
Cu2	P2	2.2557(14)	C37	C42	1.3900	C505	C506	1.3900	C53	C54	1.3900
P1	C1	1.813(5)	C38	C39	1.3900	C7	C8	1.3900	C54	C55	1.3900
P1	C7	1.817(3)	C39	C40	1.3900	C7	C12	1.3900	F100	P100	1.562(4)
P1	C13	1.835(4)	C40	C41	1.3900	C8	C9	1.3900	F101	P100	1.535(5)
P1	C501	1.846(5)	C41	C42	1.3900	C9	C10	1.3900	F102	P100	1.479(5)
P2	C14	1.820(3)	C537	C538	1.3900	C10	C11	1.3900	F103	P100	1.510(6)
P2	C20	1.832(3)	C537	C542	1.3900	C11	C12	1.3900	F104	P100	1.536(5)
P2	C13	1.833(4)	C538	C539	1.3900	C14	C15	1.3900	F105	P100	1.551(6)
P11	C37	1.803(4)	C539	C540	1.3900	C14	C19	1.3900	N700	C700	1.1347(3)
P11	C31	1.810(3)	C540	C541	1.3900	C15	C16	1.3900	C700	N750	1.3382(3)
P11	C43	1.834(4)	C541	C542	1.3900	C16	C17	1.3900	N750	C200	1.2954(3)
P11	C537	1.918(7)	C44	C45	1.3900	C17	C18	1.3900	C200	N800 <sup>1</sup>	1.2414(3)
P12	C43	1.817(4)	C44	C49	1.3900	C18	C19	1.3900	N800	C200 <sup>1</sup>	1.2415(3)
P12	C44	1.834(3)	C45	C46	1.3900	C20	C21	1.3900	N100	C100	1.2230(3)
P12	C50	1.837(3)	C46	C47	1.3900	C20	C25	1.3900	C100	N150	1.3151(4)
P12	C544	1.897(10)	C47	C48	1.3900	C21	C22	1.3900	N150	C800	1.2753(3)
C1	C2	1.3900	C48	C49	1.3900	C22	C23	1.3900	C800	N200 <sup>1</sup>	1.1988(2)
C1	C6	1.3900	C544	C545	1.3900	C23	C24	1.3900	N200	C800 <sup>1</sup>	1.1988(3)
C2	C3	1.3900	C544	C549	1.3900						

<sup>1</sup>-x,-1-y,-z**Table S4.** Bond Angles for derivative **D**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N100	Cu1	N700	0.6	C16	C17	C18	120.0
N100	Cu1	P11	121.95(4)	C19	C18	C17	120.0
N700	Cu1	P11	121.61(4)	C18	C19	C14	120.0
N100	Cu1	P1	115.03(4)	C21	C20	C25	120.0
N700	Cu1	P1	115.29(4)	C21	C20	P2	122.88(17)
P11	Cu1	P1	122.38(4)	C25	C20	P2	117.06(17)
N100	Cu1	Cu2	66.838(18)	C22	C21	C20	120.0
N700	Cu1	Cu2	66.304(17)	C21	C22	C23	120.0
P11	Cu1	Cu2	97.57(3)	C24	C23	C22	120.0
P1	Cu1	Cu2	96.79(3)	C23	C24	C25	120.0
N200	Cu2	N800	1.674(1)	C24	C25	C20	120.0
N200	Cu2	P12	115.93(4)	C32	C31	C36	120.0
N800	Cu2	P12	117.06(4)	C32	C31	P11	116.84(19)
N200	Cu2	P2	114.86(4)	C36	C31	P11	123.15(19)
N800	Cu2	P2	113.27(4)	C31	C32	C33	120.0
P12	Cu2	P2	122.36(4)	C34	C33	C32	120.0
N200	Cu2	Cu1	126.42(2)	C35	C34	C33	120.0
N800	Cu2	Cu1	127.33(2)	C34	C35	C36	120.0

P12	Cu2	Cu1	85.05(4)	C35	C36	C31	120.0
P2	Cu2	Cu1	86.08(3)	C38	C37	C42	120.0
C1	P1	C7	100.8(2)	C38	C37	P11	122.6(2)
C1	P1	C13	106.3(2)	C42	C37	P11	117.4(2)
C7	P1	C13	105.24(16)	C39	C38	C37	120.0
C1	P1	C501	5.4(3)	C40	C39	C38	120.0
C7	P1	C501	105.0(2)	C41	C40	C39	120.0
C13	P1	C501	101.7(2)	C40	C41	C42	120.0
C1	P1	Cu1	118.74(19)	C41	C42	C37	120.0
C7	P1	Cu1	117.70(11)	C538	C537	C542	120.0
C13	P1	Cu1	106.84(14)	C538	C537	P11	116.8(4)
C501	P1	Cu1	118.48(19)	C542	C537	P11	123.1(4)
C14	P2	C20	103.83(14)	C537	C538	C539	120.0
C14	P2	C13	103.84(17)	C540	C539	C538	120.0
C20	P2	C13	102.52(15)	C539	C540	C541	120.0
C14	P2	Cu2	117.78(11)	C540	C541	C542	120.0
C20	P2	Cu2	109.23(11)	C541	C542	C537	120.0
C13	P2	Cu2	117.77(13)	P12	C43	P11	112.2(2)
C37	P11	C31	97.32(18)	C45	C44	C49	120.0
C37	P11	C43	110.1(2)	C45	C44	P12	118.97(19)
C31	P11	C43	103.15(16)	C49	C44	P12	121.02(19)
C37	P11	C537	16.0(2)	C46	C45	C44	120.0
C31	P11	C537	113.0(3)	C45	C46	C47	120.0
C43	P11	C537	101.8(3)	C48	C47	C46	120.0
C37	P11	Cu1	120.53(14)	C49	C48	C47	120.0
C31	P11	Cu1	118.05(14)	C48	C49	C44	120.0
C43	P11	Cu1	106.34(13)	C545	C544	C549	120.0
C537	P11	Cu1	112.4(2)	C545	C544	P12	124.4(6)
C43	P12	C44	100.75(18)	C549	C544	P12	115.5(6)
C43	P12	C50	103.13(15)	C544	C545	C546	120.0
C44	P12	C50	106.46(15)	C547	C546	C545	120.0
C43	P12	C544	117.2(4)	C548	C547	C546	120.0
C44	P12	C544	18.8(3)	C549	C548	C547	120.0
C50	P12	C544	92.9(3)	C548	C549	C544	120.0
C43	P12	Cu2	115.79(15)	C51	C50	C55	120.0
C44	P12	Cu2	119.06(12)	C51	C50	P12	116.52(14)
C50	P12	Cu2	110.04(10)	C55	C50	P12	123.44(14)
C544	P12	Cu2	114.2(4)	C50	C51	C52	120.0
C2	C1	C6	120.0	C51	C52	C53	120.0
C2	C1	P1	118.5(3)	C54	C53	C52	120.0
C6	C1	P1	121.5(3)	C53	C54	C55	120.0
C3	C2	C1	120.0	C54	C55	C50	120.0
C2	C3	C4	120.0	F102	P100	F103	91.6(4)
C5	C4	C3	120.0	F102	P100	F101	174.5(3)
C4	C5	C6	120.0	F103	P100	F101	93.8(4)
C5	C6	C1	120.0	F102	P100	F104	93.5(4)
C502	C501	C506	120.0	F103	P100	F104	90.6(4)
C502	C501	P1	116.4(3)	F101	P100	F104	86.6(3)
C506	C501	P1	123.5(3)	F102	P100	F105	91.3(4)
C503	C502	C501	120.0	F103	P100	F105	90.1(4)
C504	C503	C502	120.0	F101	P100	F105	88.6(4)
C503	C504	C505	120.0	F104	P100	F105	175.2(4)



C506	C505	C504	120.0	F102	P100	F100	86.8(3)
C505	C506	C501	120.0	F103	P100	F100	177.3(4)
C8	C7	C12	120.0	F101	P100	F100	87.7(3)
C8	C7	P1	118.08(17)	F104	P100	F100	91.7(3)
C12	C7	P1	121.90(16)	F105	P100	F100	87.8(3)
C7	C8	C9	120.0	C700	N700	Cu1	153.425(16)
C10	C9	C8	120.0	N700	C700	N750	175.178(1)
C9	C10	C11	120.0	C200	N750	C700	125.473(7)
C12	C11	C10	120.0	N800 <sup>1</sup>	C200	N750	177.808(1)
C11	C12	C7	120.0	C200 <sup>1</sup>	N800	Cu2	148.719(17)
P2	C13	P1	112.1(2)	C100	N100	Cu1	155.357(16)
C15	C14	C19	120.0	N100	C100	N150	174.969(2)
C15	C14	P2	118.74(18)	C800	N150	C100	125.780(5)
C19	C14	P2	121.10(18)	N200 <sup>1</sup>	C800	N150	177.102(1)
C14	C15	C16	120.0	C800 <sup>1</sup>	N200	Cu2	162.083(17)
C15	C16	C17	120.0				

<sup>1</sup>-x,1-y,-z

**Table S5.** Bond Lengths for derivative **E**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N21	2.012(2)	C8	C9	1.395(4)	N2	C102	1.142(5)	C35	C36	1.391(4)
Cu1	N1	2.162(3)	C9	C10	1.364(6)	N3	C103	1.141(4)	C37	C42	1.385(4)
Cu1	P1	2.2562(9)	C10	C11	1.386(6)	N21	C201	1.157(4)	C37	C38	1.394(4)
Cu1	P11	2.2634(9)	C11	C12	1.388(5)	N22	C202	1.157(5)	C38	C39	1.382(4)
Cu2	N3	2.007(2)	C14	C19	1.388(4)	N23	C203	1.148(4)	C39	C40	1.374(5)
Cu2	P12	2.2362(9)	C14	C15	1.389(4)	C100	C101	1.389(4)	C40	C41	1.372(4)
Cu2	P2	2.2408(9)	C15	C16	1.387(4)	C100	C103 <sup>1</sup>	1.410(4)	C41	C42	1.375(4)
Cu2	N1	2.288(2)	C16	C17	1.378(5)	C100	C102	1.424(5)	C44	C49	1.380(5)
P1	C7	1.819(3)	C17	C18	1.381(5)	C103	C100 <sup>1</sup>	1.410(4)	C44	C45	1.385(5)
P1	C1	1.828(3)	C18	C19	1.392(4)	C200	C202	1.391(5)	C45	C46	1.391(5)
P1	C13	1.839(3)	C20	C21	1.390(4)	C200	C201	1.405(4)	C46	C47	1.364(7)
P2	C20	1.821(3)	C20	C25	1.400(4)	C200	C203	1.414(5)	C47	C48	1.365(7)
P2	C14	1.819(3)	C21	C22	1.390(4)	C1	C6	1.385(4)	C48	C49	1.401(5)
P2	C13	1.838(3)	C22	C23	1.382(4)	C1	C2	1.404(4)	C50	C51	1.381(4)
P11	C31	1.822(3)	C23	C24	1.389(5)	C2	C3	1.381(4)	C50	C55	1.394(4)
P11	C37	1.825(3)	C24	C25	1.384(4)	C3	C4	1.377(5)	C51	C52	1.386(4)
P11	C43	1.838(3)	C31	C32	1.391(4)	C4	C5	1.389(5)	C52	C53	1.383(5)
P12	C50	1.823(3)	C31	C36	1.389(4)	C5	C6	1.384(4)	C53	C54	1.374(5)
P12	C44	1.835(3)	C32	C33	1.386(4)	C7	C8	1.380(4)	C54	C55	1.387(4)
P12	C43	1.838(3)	C33	C34	1.384(5)	C7	C12	1.401(4)			
N1	C101	1.158(4)	C34	C35	1.382(5)						

<sup>1</sup>2-x,1-y,1-z

**Table S6.** Bond Angles for derivative **E**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N21	Cu1	N1	92.90(10)	C5	C6	C1	120.2(3)
N21	Cu1	P1	108.28(8)	C8	C7	C12	119.1(3)
N1	Cu1	P1	120.76(7)	C8	C7	P1	119.8(2)
N21	Cu1	P11	115.01(7)	C12	C7	P1	121.1(3)
N1	Cu1	P11	105.97(7)	C7	C8	C9	120.2(3)
P1	Cu1	P11	112.72(4)	C10	C9	C8	120.5(4)
N3	Cu2	P12	112.50(8)	C9	C10	C11	120.2(3)
N3	Cu2	P2	109.54(7)	C12	C11	C10	119.8(4)
P12	Cu2	P2	115.95(4)	C11	C12	C7	120.1(4)
N3	Cu2	N1	95.70(10)	P2	C13	P1	109.54(15)
P12	Cu2	N1	111.26(7)	C19	C14	C15	119.4(3)
P2	Cu2	N1	110.06(7)	C19	C14	P2	121.6(2)
C7	P1	C1	102.39(13)	C15	C14	P2	119.1(2)
C7	P1	C13	104.46(13)	C16	C15	C14	120.5(3)
C1	P1	C13	103.77(13)	C17	C16	C15	119.9(3)
C7	P1	Cu1	120.07(11)	C16	C17	C18	120.1(3)
C1	P1	Cu1	110.69(9)	C17	C18	C19	120.2(3)
C13	P1	Cu1	113.71(9)	C14	C19	C18	119.9(3)
C20	P2	C14	103.05(12)	C21	C20	C25	119.3(2)
C20	P2	C13	104.86(13)	C21	C20	P2	123.3(2)
C14	P2	C13	104.09(13)	C25	C20	P2	117.0(2)
C20	P2	Cu2	109.27(9)	C20	C21	C22	120.0(3)
C14	P2	Cu2	118.08(10)	C23	C22	C21	120.4(3)
C13	P2	Cu2	115.99(9)	C22	C23	C24	120.1(3)
C31	P11	C37	101.28(12)	C25	C24	C23	119.8(3)
C31	P11	C43	104.41(13)	C24	C25	C20	120.4(3)
C37	P11	C43	103.48(13)	C32	C31	C36	119.4(3)
C31	P11	Cu1	115.70(10)	C32	C31	P11	121.6(2)
C37	P11	Cu1	114.74(9)	C36	C31	P11	119.0(2)
C43	P11	Cu1	115.45(9)	C33	C32	C31	120.0(3)
C50	P12	C44	102.73(13)	C34	C33	C32	120.2(3)
C50	P12	C43	105.13(13)	C35	C34	C33	120.3(3)
C44	P12	C43	104.54(13)	C34	C35	C36	119.6(3)
C50	P12	Cu2	109.36(9)	C35	C36	C31	120.6(3)
C44	P12	Cu2	119.89(12)	C42	C37	C38	118.2(3)
C43	P12	Cu2	113.74(9)	C42	C37	P11	124.7(2)
C101	N1	Cu1	146.9(2)	C38	C37	P11	117.1(2)
C101	N1	Cu2	115.8(2)	C39	C38	C37	120.5(3)
Cu1	N1	Cu2	88.07(10)	C40	C39	C38	120.4(3)
C103	N3	Cu2	162.6(3)	C41	C40	C39	119.5(3)
C201	N21	Cu1	159.9(2)	C40	C41	C42	120.5(3)
C101	C100	C103 <sup>1</sup>	121.0(3)	C41	C42	C37	120.9(3)
C101	C100	C102	120.6(3)	P12	C43	P11	110.59(15)
C103 <sup>1</sup>	C100	C102	118.3(3)	C49	C44	C45	120.0(3)
N1	C101	C100	179.1(3)	C49	C44	P12	121.7(3)
N2	C102	C100	179.2(5)	C45	C44	P12	118.3(2)
N3	C103	C100 <sup>1</sup>	177.7(3)	C46	C45	C44	119.8(4)
C202	C200	C201	118.8(3)	C47	C46	C45	120.2(5)
C202	C200	C203	120.1(3)	C46	C47	C48	120.3(4)

C201	C200	C203	120.8(3)	C47	C48	C49	120.6(4)
N21	C201	C200	178.4(3)	C44	C49	C48	119.0(4)
N22	C202	C200	178.6(4)	C51	C50	C55	119.3(3)
N23	C203	C200	179.1(4)	C51	C50	P12	124.9(2)
C6	C1	C2	118.9(3)	C55	C50	P12	115.8(2)
C6	C1	P1	124.3(2)	C50	C51	C52	119.8(3)
C2	C1	P1	116.7(2)	C51	C52	C53	120.6(3)
C3	C2	C1	120.4(3)	C54	C53	C52	120.0(3)
C2	C3	C4	120.3(3)	C53	C54	C55	119.7(3)
C3	C4	C5	119.7(3)	C54	C55	C50	120.5(3)
C6	C5	C4	120.5(3)				

<sup>1</sup>2-x,1-y,1-z

**Table S7.** Bond Lengths for derivative **F**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N100	2.038(6)	C44	C49	1.363(12)	N100	C500	1.149(10)	C138	C139	1.402(14)
Cu1	N101	2.080(6)	C44	C45	1.409(12)	N101	C502	1.158(10)	C139	C140	1.396(18)
Cu1	P1	2.246(2)	C45	C46	1.399(13)	N200	C550	1.134(9)	C140	C141	1.378(17)
Cu1	P11	2.283(2)	C46	C47	1.392(16)	N201	C552	1.128(9)	C141	C142	1.384(13)
Cu2	N200	2.019(6)	C47	C48	1.362(16)	N300	C600	1.160(10)	C144	C149	1.360(13)
Cu2	N201	2.088(7)	C48	C49	1.403(13)	N301	C602	1.136(11)	C144	C145	1.407(12)
Cu2	P2	2.243(2)	C50	C55	1.389(12)	N400	C650	1.143(10)	C145	C146	1.368(13)
Cu2	P12	2.265(2)	C50	C51	1.403(12)	N401	C652	1.130(10)	C146	C147	1.408(17)
Cu3	N300	2.007(8)	C51	C52	1.381(13)	C1	C6	1.369(12)	C147	C148	1.353(16)
Cu3	N301	2.072(7)	C52	C53	1.390(16)	C1	C2	1.403(11)	C148	C149	1.400(14)
Cu3	P21	2.248(2)	C53	C54	1.362(15)	C2	C3	1.391(12)	C150	C155	1.371(13)
Cu3	P31	2.253(2)	C54	C55	1.382(13)	C3	C4	1.410(15)	C150	C151	1.381(14)
Cu4	N400	2.038(7)	C101	C102	1.363(13)	C4	C5	1.355(15)	C151	C152	1.401(16)
Cu4	N401	2.122(7)	C101	C106	1.403(12)	C5	C6	1.415(12)	C152	C153	1.360(18)
Cu4	P22	2.254(2)	C102	C103	1.410(13)	C7	C8	1.368(12)	C153	C154	1.314(19)
Cu4	P32	2.272(2)	C103	C104	1.344(16)	C7	C12	1.377(13)	C154	C155	1.403(16)
S1	C560	1.741(7)	C104	C105	1.373(16)	C8	C9	1.394(13)	C500	C501	1.429(10)
S1	C561	1.807(8)	C105	C106	1.419(13)	C9	C10	1.373(16)	C501	C560	1.388(10)
S2	C661	1.733(12)	C107	C112	1.397(12)	C10	C11	1.381(17)	C501	C502 <sup>1</sup>	1.400(10)
S2	C660	1.759(8)	C107	C108	1.400(12)	C11	C12	1.394(15)	C502	C501 <sup>1</sup>	1.400(11)
P1	C1	1.833(7)	C108	C109	1.367(13)	C14	C15	1.354(11)	C550	C551	1.420(10)
P1	C13	1.844(7)	C109	C110	1.375(15)	C14	C19	1.411(11)	C551	C560	1.423(9)
P1	C7	1.845(8)	C110	C111	1.376(16)	C15	C16	1.409(12)	C551	C552 <sup>2</sup>	1.426(9)
P2	C20	1.831(8)	C111	C112	1.391(14)	C16	C17	1.351(15)	C552	C551 <sup>2</sup>	1.426(9)
P2	C13	1.844(7)	C114	C115	1.370(12)	C17	C18	1.410(15)	C600	C601	1.410(11)
P2	C14	1.858(8)	C114	C119	1.388(12)	C18	C19	1.372(14)	C601	C660	1.391(10)
P11	C31	1.830(9)	C115	C116	1.398(13)	C20	C21	1.383(11)	C601	C602 <sup>3</sup>	1.412(12)
P11	C37	1.831(8)	C116	C117	1.367(15)	C20	C25	1.389(11)	C602	C601 <sup>3</sup>	1.412(12)
P11	C43	1.847(8)	C117	C118	1.371(16)	C21	C22	1.377(12)	C650	C651	1.421(11)
P12	C44	1.816(8)	C118	C119	1.368(14)	C22	C23	1.402(14)	C651	C660	1.393(10)
P12	C50	1.819(9)	C120	C121	1.366(13)	C23	C24	1.391(14)	C651	C652 <sup>4</sup>	1.439(11)
P12	C43	1.842(8)	C120	C125	1.422(13)	C24	C25	1.386(12)	C652	C651 <sup>4</sup>	1.439(11)
P21	C107	1.824(8)	C121	C122	1.390(14)	C31	C32	1.364(12)	F100	P100	1.595(6)
P21	C101	1.833(8)	C122	C123	1.372(18)	C31	C36	1.391(12)	F101	P100	1.529(8)
P21	C113	1.850(8)	C123	C124	1.358(19)	C32	C33	1.428(13)	F102	P100	1.602(6)
P22	C114	1.826(7)	C124	C125	1.387(14)	C33	C34	1.370(15)	F103	P100	1.525(10)
P22	C113	1.841(8)	C131	C136	1.367(14)	C34	C35	1.380(14)	F104	P100	1.533(10)

P22	C120	1.841(8)	C131	C132	1.407(13)	C35	C36	1.383(13)	F200	P200	1.445(10)
P31	C143	1.824(8)	C132	C133	1.367(14)	C37	C38	1.363(12)	F201	P200	1.457(12)
P31	C131	1.833(9)	C133	C134	1.426(18)	C37	C42	1.413(13)	F202	P200	1.428(10)
P31	C137	1.860(8)	C134	C135	1.355(17)	C38	C39	1.381(13)	F203	P200	1.486(10)
P32	C144	1.833(9)	C135	C136	1.394(14)	C39	C40	1.390(17)	F204	P200	1.583(6)
P32	C150	1.836(9)	C137	C138	1.343(13)	C40	C41	1.405(17)	F205	P200	1.633(6)
P32	C143	1.846(9)	C137	C142	1.378(12)	C41	C42	1.380(13)	F350	P100	1.516(8)

<sup>1</sup>2-x,-y,1-z; <sup>2</sup>1-x,-y,1-z; <sup>3</sup>1-x,1-y,2-z; <sup>4</sup>-x,1-y,2-z

**Table S8.** Bond Angles for derivative **F**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N100	Cu1	N101	88.2(3)	C46	C45	C44	119.5(8)
N100	Cu1	P1	119.1(2)	C47	C46	C45	120.6(9)
N101	Cu1	P1	106.2(2)	C48	C47	C46	119.2(10)
N100	Cu1	P11	111.0(2)	C47	C48	C49	120.6(11)
N101	Cu1	P11	99.5(2)	C44	C49	C48	121.1(9)
P1	Cu1	P11	123.44(9)	C55	C50	C51	117.9(8)
N200	Cu2	N201	89.2(3)	C55	C50	P12	123.1(7)
N200	Cu2	P2	124.5(2)	C51	C50	P12	118.7(7)
N201	Cu2	P2	108.08(19)	C52	C51	C50	121.4(9)
N200	Cu2	P12	113.0(2)	C51	C52	C53	118.9(9)
N201	Cu2	P12	98.3(2)	C54	C53	C52	120.5(9)
P2	Cu2	P12	115.69(8)	C53	C54	C55	120.6(10)
N300	Cu3	N301	89.0(3)	C54	C55	C50	120.7(9)
N300	Cu3	P21	120.6(2)	C102	C101	C106	118.5(8)
N301	Cu3	P21	99.5(2)	C102	C101	P21	122.0(7)
N300	Cu3	P31	114.4(2)	C106	C101	P21	119.2(7)
N301	Cu3	P31	107.7(2)	C101	C102	C103	121.2(10)
P21	Cu3	P31	118.26(9)	C104	C103	C102	120.3(11)
N400	Cu4	N401	89.4(3)	C103	C104	C105	120.4(9)
N400	Cu4	P22	118.5(2)	C104	C105	C106	120.0(10)
N401	Cu4	P22	104.9(2)	C101	C106	C105	119.5(10)
N400	Cu4	P32	112.4(2)	C112	C107	C108	119.9(8)
N401	Cu4	P32	98.7(2)	C112	C107	P21	118.9(6)
P22	Cu4	P32	123.35(9)	C108	C107	P21	121.0(7)
C560	S1	C561	104.3(4)	C109	C108	C107	119.9(9)
C661	S2	C660	105.5(5)	C108	C109	C110	119.8(9)
C1	P1	C13	102.9(3)	C109	C110	C111	121.6(10)
C1	P1	C7	100.5(3)	C110	C111	C112	119.3(10)
C13	P1	C7	104.6(4)	C111	C112	C107	119.4(10)
C1	P1	Cu1	110.3(3)	P22	C113	P21	112.9(4)
C13	P1	Cu1	118.7(2)	C115	C114	C119	118.6(8)
C7	P1	Cu1	117.4(3)	C115	C114	P22	122.5(6)
C20	P2	C13	101.4(3)	C119	C114	P22	118.8(6)
C20	P2	C14	102.3(3)	C114	C115	C116	119.9(9)
C13	P2	C14	106.1(3)	C117	C116	C115	120.6(10)
C20	P2	Cu2	111.7(2)	C116	C117	C118	119.3(9)
C13	P2	Cu2	117.5(2)	C119	C118	C117	120.4(10)
C14	P2	Cu2	115.8(2)	C118	C119	C114	121.1(9)
C31	P11	C37	102.3(4)	C121	C120	C125	119.3(8)
C31	P11	C43	100.6(4)	C121	C120	P22	124.3(7)
C37	P11	C43	107.3(4)	C125	C120	P22	116.3(7)

C31	P11	Cu1	109.0(3)	C120	C121	C122	120.3(10)
C37	P11	Cu1	115.8(3)	C123	C122	C121	120.4(12)
C43	P11	Cu1	119.3(3)	C124	C123	C122	119.9(10)
C44	P12	C50	100.9(4)	C123	C124	C125	121.5(11)
C44	P12	C43	107.1(4)	C124	C125	C120	118.4(11)
C50	P12	C43	102.4(4)	C136	C131	C132	119.0(9)
C44	P12	Cu2	116.8(3)	C136	C131	P31	118.2(8)
C50	P12	Cu2	106.6(3)	C132	C131	P31	122.9(7)
C43	P12	Cu2	120.2(3)	C133	C132	C131	120.4(11)
C107	P21	C101	101.0(4)	C132	C133	C134	119.8(11)
C107	P21	C113	104.9(4)	C135	C134	C133	119.1(10)
C101	P21	C113	103.9(4)	C134	C135	C136	120.7(11)
C107	P21	Cu3	117.8(3)	C131	C136	C135	120.9(11)
C101	P21	Cu3	107.3(3)	C138	C137	C142	120.5(9)
C113	P21	Cu3	119.5(3)	C138	C137	P31	122.2(7)
C114	P22	C113	106.4(4)	C142	C137	P31	117.2(6)
C114	P22	C120	101.6(4)	C137	C138	C139	120.8(11)
C113	P22	C120	102.1(4)	C140	C139	C138	117.9(11)
C114	P22	Cu4	116.6(2)	C141	C140	C139	121.5(10)
C113	P22	Cu4	119.8(3)	C140	C141	C142	118.1(10)
C120	P22	Cu4	107.9(2)	C137	C142	C141	121.0(9)
C143	P31	C131	103.2(4)	P31	C143	P32	117.2(5)
C143	P31	C137	103.1(4)	C149	C144	C145	119.1(9)
C131	P31	C137	103.0(4)	C149	C144	P32	119.2(7)
C143	P31	Cu3	116.7(3)	C145	C144	P32	121.6(7)
C131	P31	Cu3	110.9(3)	C146	C145	C144	121.4(10)
C137	P31	Cu3	118.1(3)	C145	C146	C147	118.2(10)
C144	P32	C150	101.8(4)	C148	C147	C146	120.7(10)
C144	P32	C143	106.3(4)	C147	C148	C149	120.5(11)
C150	P32	C143	99.8(4)	C144	C149	C148	120.0(10)
C144	P32	Cu4	118.6(3)	C155	C150	C151	118.2(9)
C150	P32	Cu4	109.6(3)	C155	C150	P32	123.8(8)
C143	P32	Cu4	118.0(3)	C151	C150	P32	118.0(8)
C500	N100	Cu1	158.1(7)	C150	C151	C152	122.0(11)
C502	N101	Cu1	161.2(6)	C153	C152	C151	117.4(12)
C550	N200	Cu2	159.0(6)	C154	C153	C152	121.6(12)
C552	N201	Cu2	166.2(6)	C153	C154	C155	122.0(11)
C600	N300	Cu3	161.9(7)	C150	C155	C154	118.6(11)
C602	N301	Cu3	165.7(7)	N100	C500	C501	177.1(9)
C650	N400	Cu4	153.9(7)	C560	C501	C502 <sup>1</sup>	122.3(7)
C652	N401	Cu4	157.0(7)	C560	C501	C500	124.1(7)
C6	C1	C2	119.1(7)	C502 <sup>1</sup>	C501	C500	112.9(6)
C6	C1	P1	124.3(6)	N101	C502	C501 <sup>1</sup>	175.9(8)
C2	C1	P1	116.4(6)	N200	C550	C551	178.4(7)
C3	C2	C1	120.0(9)	C550	C551	C560	125.1(6)
C2	C3	C4	119.8(9)	C550	C551	C552 <sup>2</sup>	114.8(6)
C5	C4	C3	120.3(8)	C560	C551	C552 <sup>2</sup>	120.0(6)
C4	C5	C6	119.6(10)	N201	C552	C551 <sup>2</sup>	174.8(8)
C1	C6	C5	121.2(9)	C501	C560	C551	123.1(7)
C8	C7	C12	121.4(8)	C501	C560	S1	122.1(5)
C8	C7	P1	118.4(6)	C551	C560	S1	114.8(5)
C12	C7	P1	120.1(7)	N300	C600	C601	178.8(9)

C7	C8	C9	119.8(9)	C660	C601	C600	123.6(7)
C10	C9	C8	118.5(10)	C660	C601	C602 <sup>3</sup>	121.9(7)
C9	C10	C11	122.2(10)	C600	C601	C602 <sup>3</sup>	114.5(7)
C10	C11	C12	118.5(11)	N301	C602	C601 <sup>3</sup>	173.3(9)
C7	C12	C11	119.4(10)	N400	C650	C651	177.4(9)
P2	C13	P1	115.5(4)	C660	C651	C650	123.1(7)
C15	C14	C19	121.8(8)	C660	C651	C652 <sup>4</sup>	122.6(7)
C15	C14	P2	117.3(6)	C650	C651	C652 <sup>4</sup>	114.0(7)
C19	C14	P2	120.9(6)	N401	C652	C651 <sup>4</sup>	173.8(9)
C14	C15	C16	119.0(8)	C601	C660	C651	125.0(7)
C17	C16	C15	120.5(9)	C601	C660	S2	115.0(6)
C16	C17	C18	120.1(9)	C651	C660	S2	120.1(6)
C19	C18	C17	120.4(9)	F350	P100	F103	94.1(10)
C18	C19	C14	118.2(9)	F350	P100	F101	179.0(5)
C21	C20	C25	118.7(7)	F103	P100	F101	86.0(9)
C21	C20	P2	117.3(6)	F350	P100	F104	86.9(10)
C25	C20	P2	124.0(6)	F103	P100	F104	178.9(9)
C22	C21	C20	121.2(8)	F101	P100	F104	93.0(9)
C21	C22	C23	119.5(9)	F350	P100	F100	90.8(4)
C24	C23	C22	120.2(8)	F103	P100	F100	89.3(5)
C25	C24	C23	118.8(9)	F101	P100	F100	90.2(4)
C24	C25	C20	121.6(8)	F104	P100	F100	91.1(5)
C32	C31	C36	120.0(8)	F350	P100	F102	88.5(4)
C32	C31	P11	123.2(7)	F103	P100	F102	91.0(4)
C36	C31	P11	116.8(6)	F101	P100	F102	90.6(4)
C31	C32	C33	118.7(9)	F104	P100	F102	88.5(5)
C34	C33	C32	120.6(9)	F100	P100	F102	179.2(4)
C33	C34	C35	120.1(9)	F202	P200	F200	166.7(16)
C34	C35	C36	119.4(10)	F202	P200	F201	89.0(15)
C35	C36	C31	121.2(9)	F200	P200	F201	78.0(13)
C38	C37	C42	118.3(8)	F202	P200	F203	96.9(13)
C38	C37	P11	119.0(7)	F200	P200	F203	96.2(13)
C42	C37	P11	122.6(7)	F201	P200	F203	174.2(15)
C37	C38	C39	122.6(9)	F202	P200	F204	91.2(5)
C38	C39	C40	118.5(10)	F200	P200	F204	91.2(5)
C39	C40	C41	120.8(9)	F201	P200	F204	88.9(5)
C42	C41	C40	118.8(10)	F203	P200	F204	91.4(4)
C41	C42	C37	120.9(10)	F202	P200	F205	88.7(5)
P12	C43	P11	115.6(4)	F200	P200	F205	89.2(5)
C49	C44	C45	118.7(8)	F201	P200	F205	92.2(5)
C49	C44	P12	120.1(7)	F203	P200	F205	87.6(4)
C45	C44	P12	121.2(6)	F204	P200	F205	179.0(4)

<sup>1</sup>2-x,-y,1-z; <sup>2</sup>1-x,-y,1-z; <sup>3</sup>1-x,1-y,2-z; <sup>4</sup>-x,1-y,2-z

**Table S9.** Bond Lengths for derivative **G**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N101	1.996(2)	C20	C25	1.381(4)	N102	C205	1.149(3)	C48	C49	1.391(4)
Cu1	N102	2.125(2)	C20	C21	1.396(4)	N103	C206	1.146(3)	C50	C51	1.390(4)
Cu1	P3	2.2581(9)	C21	C22	1.386(4)	N104	C207	1.152(3)	C50	C55	1.392(4)
Cu1	P1	2.2701(8)	C22	C23	1.378(5)	N104	Cu2 <sup>2</sup>	2.192(2)	C51	C52	1.382(4)
Cu2	N103	1.991(2)	C23	C24	1.365(5)	C1	C6	1.386(4)	C52	C53	1.377(5)
Cu2	N104 <sup>1</sup>	2.192(2)	C24	C25	1.387(5)	C1	C2	1.390(4)	C53	C54	1.374(5)
Cu2	P2	2.2592(9)	C31	C32	1.382(4)	C2	C3	1.383(5)	C54	C55	1.386(4)
Cu2	P4	2.2829(9)	C31	C36	1.390(4)	C3	C4	1.381(7)	C201	C202	1.417(4)
P1	C1	1.827(3)	C32	C33	1.380(5)	C4	C5	1.373(6)	C202	C203	1.400(4)
P1	C7	1.837(3)	C33	C34	1.366(5)	C5	C6	1.383(5)	C202	C207	1.421(4)
P1	C13	1.842(3)	C34	C35	1.368(5)	C7	C8	1.389(4)	C203	C204	1.412(3)
P2	C20	1.824(3)	C35	C36	1.385(5)	C7	C12	1.395(4)	C204	C205 <sup>1</sup>	1.417(4)
P2	C14	1.824(3)	C37	C42	1.388(4)	C8	C9	1.390(4)	C204	C206	1.420(4)
P2	C13	1.837(3)	C37	C38	1.396(4)	C9	C10	1.372(5)	C205	C204 <sup>2</sup>	1.416(4)
P3	C37	1.824(3)	C38	C39	1.380(4)	C10	C11	1.384(5)	C208	C209	1.495(5)
P3	C31	1.826(3)	C39	C40	1.392(5)	C11	C12	1.391(4)	F100	P100	1.592(2)
P3	C43	1.826(3)	C40	C41	1.376(5)	C14	C15	1.391(4)	F101	P100	1.557(3)
P4	C44	1.830(3)	C41	C42	1.395(4)	C14	C19	1.396(4)	F102	P100	1.554(3)
P4	C50	1.833(3)	C44	C49	1.391(4)	C15	C16	1.386(5)	F103	P100	1.548(3)
P4	C43	1.849(3)	C44	C45	1.400(4)	C16	C17	1.373(5)	F104	P100	1.553(3)
S1	C203	1.751(3)	C45	C46	1.400(4)	C17	C18	1.375(5)	F105	P100	1.594(2)
S1	C208	1.809(3)	C46	C47	1.371(5)	C18	C19	1.383(5)			
N101	C201	1.148(3)	C47	C48	1.382(5)						

<sup>1</sup>+x,1/2-y,1/2+z; <sup>2</sup>+x,1/2-y,-1/2+z**Table S10.** Bond Angles for derivative **G**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N101	Cu1	N102	88.12(9)	C21	C20	P2	122.2(2)
N101	Cu1	P3	117.74(7)	C22	C21	C20	120.4(3)
N102	Cu1	P3	111.35(7)	C23	C22	C21	119.9(3)
N101	Cu1	P1	121.31(8)	C24	C23	C22	120.0(3)
N102	Cu1	P1	99.04(7)	C23	C24	C25	120.5(3)
P3	Cu1	P1	113.24(3)	C20	C25	C24	120.6(3)
N103	Cu2	N104 <sup>1</sup>	90.08(9)	C32	C31	C36	118.1(3)
N103	Cu2	P2	118.85(7)	C32	C31	P3	124.2(2)
N104 <sup>1</sup>	Cu2	P2	113.16(7)	C36	C31	P3	117.6(2)
N103	Cu2	P4	117.04(7)	C33	C32	C31	120.8(3)
N104 <sup>1</sup>	Cu2	P4	97.82(7)	C34	C33	C32	120.6(3)
P2	Cu2	P4	114.54(3)	C33	C34	C35	119.6(3)
C1	P1	C7	103.77(13)	C34	C35	C36	120.4(3)
C1	P1	C13	102.43(14)	C35	C36	C31	120.5(3)
C7	P1	C13	101.35(13)	C42	C37	C38	119.5(3)
C1	P1	Cu1	113.56(11)	C42	C37	P3	119.0(2)
C7	P1	Cu1	110.83(10)	C38	C37	P3	121.6(2)
C13	P1	Cu1	122.72(9)	C39	C38	C37	120.2(3)
C20	P2	C14	102.71(13)	C38	C39	C40	120.1(3)
C20	P2	C13	104.61(13)	C41	C40	C39	120.1(3)
C14	P2	C13	101.95(13)	C40	C41	C42	120.0(3)
C20	P2	Cu2	118.75(10)	C37	C42	C41	120.1(3)

C14	P2	Cu2	114.45(10)	P3	C43	P4	115.99(14)
C13	P2	Cu2	112.48(10)	C49	C44	C45	118.7(3)
C37	P3	C31	103.54(13)	C49	C44	P4	119.0(2)
C37	P3	C43	103.09(12)	C45	C44	P4	122.3(2)
C31	P3	C43	102.75(12)	C46	C45	C44	120.0(3)
C37	P3	Cu1	121.75(9)	C47	C46	C45	120.1(3)
C31	P3	Cu1	111.43(9)	C46	C47	C48	120.7(3)
C43	P3	Cu1	112.26(9)	C47	C48	C49	119.5(3)
C44	P4	C50	105.04(12)	C48	C49	C44	121.0(3)
C44	P4	C43	103.38(13)	C51	C50	C55	118.8(3)
C50	P4	C43	100.05(12)	C51	C50	P4	123.6(2)
C44	P4	Cu2	113.66(9)	C55	C50	P4	117.6(2)
C50	P4	Cu2	110.50(9)	C52	C51	C50	120.4(3)
C43	P4	Cu2	122.22(9)	C53	C52	C51	120.3(3)
C203	S1	C208	105.14(14)	C54	C53	C52	120.0(3)
C201	N101	Cu1	166.0(2)	C53	C54	C55	120.2(3)
C205	N102	Cu1	149.1(2)	C54	C55	C50	120.3(3)
C206	N103	Cu2	171.5(2)	N101	C201	C202	176.9(3)
C207	N104	Cu2 <sup>2</sup>	149.2(2)	C203	C202	C201	120.4(2)
C6	C1	C2	119.2(3)	C203	C202	C207	124.9(2)
C6	C1	P1	119.4(2)	C201	C202	C207	114.6(2)
C2	C1	P1	121.4(3)	C202	C203	C204	124.1(2)
C3	C2	C1	119.6(4)	C202	C203	S1	122.49(19)
C2	C3	C4	121.0(4)	C204	C203	S1	113.39(19)
C5	C4	C3	119.3(4)	C203	C204	C205 <sup>1</sup>	122.0(2)
C4	C5	C6	120.5(4)	C203	C204	C206	124.6(2)
C5	C6	C1	120.4(3)	C205 <sup>1</sup>	C204	C206	113.4(2)
C8	C7	C12	118.8(3)	N102	C205	C204 <sup>2</sup>	174.4(3)
C8	C7	P1	123.9(2)	N103	C206	C204	176.5(3)
C12	C7	P1	117.3(2)	N104	C207	C202	173.8(3)
C7	C8	C9	120.4(3)	C209	C208	S1	111.1(3)
C10	C9	C8	120.3(3)	F103	P100	F104	90.7(3)
C9	C10	C11	120.3(3)	F103	P100	F102	90.0(2)
C10	C11	C12	119.6(3)	F104	P100	F102	179.1(2)
C11	C12	C7	120.6(3)	F103	P100	F101	179.4(2)
P2	C13	P1	116.06(14)	F104	P100	F101	89.9(3)
C15	C14	C19	118.5(3)	F102	P100	F101	89.5(2)
C15	C14	P2	124.6(2)	F103	P100	F100	90.08(17)
C19	C14	P2	116.9(2)	F104	P100	F100	90.97(14)
C16	C15	C14	120.3(3)	F102	P100	F100	88.45(14)
C17	C16	C15	120.4(3)	F101	P100	F100	89.65(17)
C16	C17	C18	120.2(3)	F103	P100	F105	89.57(17)
C17	C18	C19	119.9(3)	F104	P100	F105	88.03(14)
C18	C19	C14	120.7(3)	F102	P100	F105	92.56(15)
C25	C20	C21	118.5(3)	F101	P100	F105	90.72(17)
C25	C20	P2	119.3(2)	F100	P100	F105	178.93(14)

<sup>1</sup>+x,1/2-y,1/2+z; <sup>2</sup>+x,1/2-y,-1/2+z



**Table S11.** Bond Lengths for derivative **H**

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N100	2.004(3)	C19	C24	1.388(7)	N101	C202	1.143(5)	C47	C48	1.400(8)
Cu1	N101	2.097(4)	C19	C20	1.391(7)	N200	C200 <sup>1</sup>	1.153(5)	C49	C50	1.379(7)
Cu1	P1	2.2498(12)	C20	C21	1.388(7)	N201	C102	1.144(5)	C49	C54	1.398(6)
Cu1	P11	2.2664(12)	C21	C22	1.386(9)	N201	Cu2 <sup>2</sup>	2.106(4)	C50	C51	1.403(7)
Cu2	N200	2.047(3)	C22	C23	1.377(9)	C1	C6	1.393(6)	C51	C52	1.367(8)
Cu2	N201 <sup>1</sup>	2.106(4)	C23	C24	1.391(7)	C1	C2	1.396(6)	C52	C53	1.388(9)
Cu2	P2	2.2485(13)	C31	C32	1.385(6)	C2	C3	1.388(7)	C53	C54	1.378(7)
Cu2	P12	2.2687(13)	C31	C36	1.394(6)	C3	C4	1.375(9)	C100	C101	1.423(5)
P1	N1	1.685(3)	C32	C33	1.387(6)	C4	C5	1.356(9)	C101	C300	1.402(5)
P1	C1	1.815(4)	C33	C34	1.373(7)	C5	C6	1.383(7)	C101	C102	1.416(5)
P1	C7	1.825(4)	C34	C35	1.390(7)	C7	C12	1.371(7)	C200	N200 <sup>2</sup>	1.154(5)
P2	N1	1.689(3)	C35	C36	1.378(7)	C7	C8	1.411(7)	C200	C201	1.425(5)
P2	C13	1.813(4)	C37	C38	1.381(6)	C8	C9	1.379(7)	C201	C300 <sup>2</sup>	1.392(5)
P2	C19	1.824(4)	C37	C42	1.394(6)	C9	C10	1.357(10)	C201	C202	1.422(6)
P11	N2	1.692(4)	C38	C39	1.395(7)	C10	C11	1.377(10)	C300	C201 <sup>1</sup>	1.392(5)
P11	C31	1.822(4)	C39	C40	1.373(8)	C11	C12	1.422(8)	C301	C302	1.500(9)
P11	C37	1.840(4)	C40	C41	1.392(7)	C13	C18	1.375(6)	F100	P100	1.568(5)
P12	N2	1.689(3)	C41	C42	1.385(7)	C13	C14	1.396(6)	F101	P100	1.579(4)
P12	C49	1.825(5)	C43	C48	1.385(7)	C14	C15	1.382(8)	F102	P100	1.605(4)
P12	C43	1.826(4)	C43	C44	1.395(7)	C15	C16	1.370(10)	F103	P100	1.569(5)
S1	C300	1.758(4)	C44	C45	1.383(7)	C16	C17	1.380(9)	F104	P100	1.581(4)
S1	C301	1.812(5)	C45	C46	1.377(10)	C17	C18	1.399(7)	F105	P100	1.554(4)
N100	C100	1.143(5)	C46	C47	1.357(11)						

<sup>1</sup>1/2-x,-1/2+y,3/2-z; <sup>2</sup>1/2-x,1/2+y,3/2-z**Table S12.** Bond Angles for derivative **H**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N100	Cu1	N101	94.30(14)	C24	C19	P2	119.1(4)
N100	Cu1	P1	115.94(11)	C20	C19	P2	121.8(4)
N101	Cu1	P1	100.83(12)	C21	C20	C19	120.5(5)
N100	Cu1	P11	105.28(11)	C22	C21	C20	119.8(6)
N101	Cu1	P11	101.20(11)	C23	C22	C21	120.3(5)
P1	Cu1	P11	131.07(4)	C22	C23	C24	119.8(5)
N200	Cu2	N201 <sup>1</sup>	91.94(13)	C19	C24	C23	120.6(5)
N200	Cu2	P2	120.14(11)	C32	C31	C36	118.5(4)
N201 <sup>1</sup>	Cu2	P2	96.70(11)	C32	C31	P11	122.1(3)
N200	Cu2	P12	104.36(11)	C36	C31	P11	119.2(3)
N201 <sup>1</sup>	Cu2	P12	98.85(12)	C31	C32	C33	120.6(4)
P2	Cu2	P12	132.05(4)	C34	C33	C32	120.4(4)
N1	P1	C1	100.91(18)	C33	C34	C35	119.7(5)
N1	P1	C7	105.10(19)	C36	C35	C34	119.9(4)
C1	P1	C7	104.6(2)	C35	C36	C31	120.9(4)
N1	P1	Cu1	115.19(13)	C38	C37	C42	119.0(4)
C1	P1	Cu1	109.15(14)	C38	C37	P11	123.2(4)
C7	P1	Cu1	119.83(17)	C42	C37	P11	117.8(3)
N1	P2	C13	102.99(18)	C37	C38	C39	120.3(5)
N1	P2	C19	106.29(18)	C40	C39	C38	120.3(5)
C13	P2	C19	103.0(2)	C39	C40	C41	120.1(5)
N1	P2	Cu2	117.78(12)	C42	C41	C40	119.4(5)

C13	P2	Cu2	113.47(14)	C41	C42	C37	120.9(4)
C19	P2	Cu2	111.86(15)	C48	C43	C44	119.8(5)
N2	P11	C31	104.08(19)	C48	C43	P12	122.6(4)
N2	P11	C37	102.48(19)	C44	C43	P12	117.6(4)
C31	P11	C37	103.55(19)	C45	C44	C43	119.8(5)
N2	P11	Cu1	114.00(13)	C46	C45	C44	120.2(6)
C31	P11	Cu1	119.71(14)	C47	C46	C45	120.3(5)
C37	P11	Cu1	111.17(15)	C46	C47	C48	120.9(6)
N2	P12	C49	104.1(2)	C43	C48	C47	119.0(6)
N2	P12	C43	103.29(19)	C50	C49	C54	118.5(4)
C49	P12	C43	102.8(2)	C50	C49	P12	121.9(3)
N2	P12	Cu2	121.27(13)	C54	C49	P12	119.3(4)
C49	P12	Cu2	114.37(14)	C49	C50	C51	120.1(5)
C43	P12	Cu2	108.96(16)	C52	C51	C50	120.6(6)
C300	S1	C301	107.2(2)	C51	C52	C53	119.8(5)
P1	N1	P2	118.72(19)	C54	C53	C52	119.7(5)
P12	N2	P11	126.3(2)	C53	C54	C49	121.3(5)
C100	N100	Cu1	170.0(4)	N100	C100	C101	176.0(4)
C202	N101	Cu1	160.0(4)	C300	C101	C102	124.5(3)
C200 <sup>1</sup>	N200	Cu2	149.2(3)	C300	C101	C100	123.6(3)
C102	N201	Cu2 <sup>2</sup>	166.6(3)	C102	C101	C100	111.9(3)
C6	C1	C2	118.0(4)	N201	C102	C101	170.9(4)
C6	C1	P1	123.8(3)	N200 <sup>2</sup>	C200	C201	177.2(4)
C2	C1	P1	118.0(3)	C300 <sup>2</sup>	C201	C202	124.9(4)
C3	C2	C1	120.9(5)	C300 <sup>2</sup>	C201	C200	122.7(4)
C4	C3	C2	119.6(5)	C202	C201	C200	112.0(3)
C5	C4	C3	120.2(5)	N101	C202	C201	174.5(4)
C4	C5	C6	121.2(5)	C201 <sup>1</sup>	C300	C101	124.1(3)
C5	C6	C1	120.0(5)	C201 <sup>1</sup>	C300	S1	122.9(3)
C12	C7	C8	119.0(5)	C101	C300	S1	112.9(3)
C12	C7	P1	120.4(4)	C302	C301	S1	114.6(4)
C8	C7	P1	120.6(4)	F105	P100	F100	91.7(4)
C9	C8	C7	120.7(6)	F105	P100	F103	91.6(4)
C10	C9	C8	120.2(6)	F100	P100	F103	176.5(4)
C9	C10	C11	120.8(6)	F105	P100	F101	91.1(3)
C10	C11	C12	119.8(6)	F100	P100	F101	90.6(3)
C7	C12	C11	119.6(6)	F103	P100	F101	90.6(3)
C18	C13	C14	119.1(4)	F105	P100	F104	90.1(2)
C18	C13	P2	121.7(3)	F100	P100	F104	91.0(3)
C14	C13	P2	118.9(3)	F103	P100	F104	87.8(3)
C15	C14	C13	119.9(5)	F101	P100	F104	178.0(3)
C16	C15	C14	120.7(6)	F105	P100	F102	178.1(3)
C15	C16	C17	120.2(5)	F100	P100	F102	88.8(4)
C16	C17	C18	119.4(5)	F103	P100	F102	87.9(3)
C13	C18	C17	120.6(5)	F101	P100	F102	90.7(2)
C24	C19	C20	119.0(4)	F104	P100	F102	88.0(2)

<sup>1</sup>1/2-x,-1/2+y,3/2-z; <sup>2</sup>1/2-x,1/2+y,3/2-z

**Table S13.** Bond Lengths for derivative I

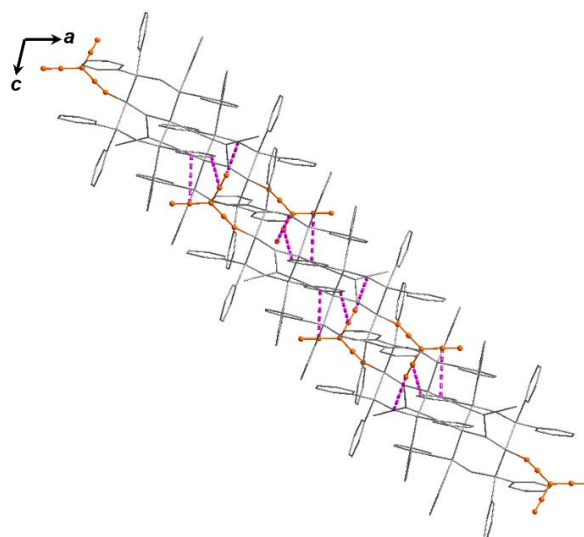
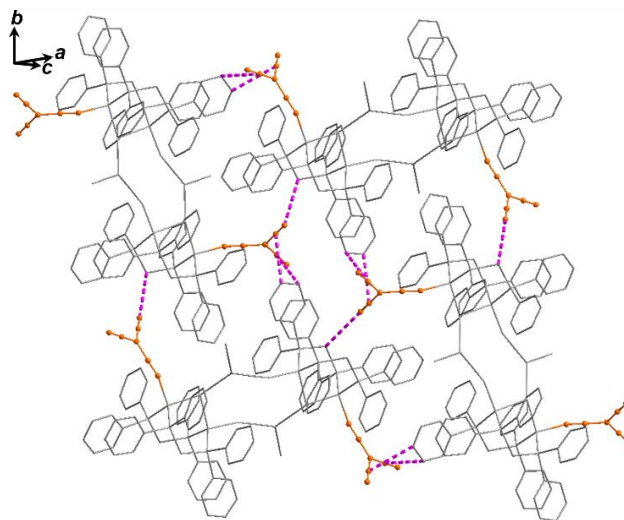
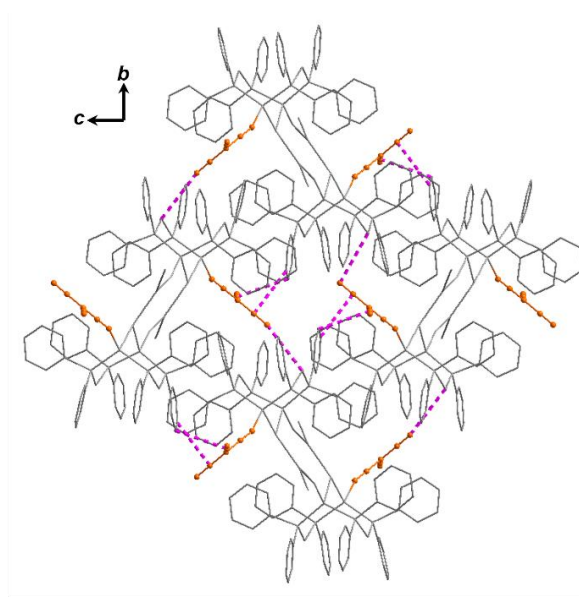
Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N100	2.061(3)	C8	C9	1.377(6)	S1	C301	1.810(4)	C35	C36	1.388(6)
Cu1	N101	2.112(3)	C9	C10	1.387(6)	N100	C100	1.146(4)	C37	C42	1.388(5)
Cu1	P1	2.2718(10)	C10	C11	1.382(6)	N101	C102	1.143(4)	C37	C38	1.398(5)
Cu1	P11	2.2960(10)	C11	C12	1.404(6)	N200	C200	1.150(5)	C38	C39	1.386(5)
Cu1	Cu2	2.9297(9)	C13	C14	1.381(5)	N201	C202	1.144(5)	C39	C40	1.374(6)
Cu2	N200	1.945(3)	C13	C18	1.397(5)	C100	C101	1.420(5)	C40	C41	1.385(6)
Cu2	P2	2.2063(10)	C14	C15	1.379(6)	C101	C300	1.411(5)	C41	C42	1.395(5)
Cu2	P12	2.2327(11)	C15	C16	1.387(7)	C101	C102 <sup>1</sup>	1.432(5)	C43	C48	1.382(5)
P1	N1	1.708(3)	C16	C17	1.378(6)	C102	C101 <sup>2</sup>	1.432(5)	C43	C44	1.393(5)
P1	C1	1.824(4)	C17	C18	1.381(6)	C200	C201	1.405(5)	C44	C45	1.377(6)
P1	C7	1.830(4)	C19	C24	1.395(5)	C201	C300	1.413(5)	C45	C46	1.389(6)
P2	N1	1.665(3)	C19	C20	1.399(5)	C201	C202	1.421(5)	C46	C47	1.367(6)
P2	C13	1.819(4)	C20	C21	1.394(5)	C1	C6	1.381(5)	C47	C48	1.393(5)
P2	C19	1.824(4)	C21	C22	1.359(7)	C1	C2	1.400(5)	C49	C50	1.394(5)
P11	N2	1.685(3)	C22	C23	1.388(7)	C2	C3	1.384(5)	C49	C54	1.399(5)
P11	C31	1.828(4)	C23	C24	1.389(6)	C3	C4	1.377(6)	C50	C51	1.390(6)
P11	C37	1.830(4)	C31	C36	1.374(5)	C4	C5	1.371(6)	C51	C52	1.369(7)
P12	N2	1.693(3)	C31	C32	1.382(5)	C5	C6	1.398(5)	C52	C53	1.368(6)
P12	C49	1.812(4)	C32	C33	1.369(6)	C7	C12	1.385(5)	C53	C54	1.384(6)
P12	C43	1.818(4)	C33	C34	1.358(6)	C7	C8	1.390(5)			
S1	C300	1.747(4)	C34	C35	1.363(6)						

<sup>1</sup>5/4-y,1/4+x,1/4-z; <sup>2</sup>-1/4+y,5/4-x,1/4-z**Table S14.** Bond Angles for derivative I

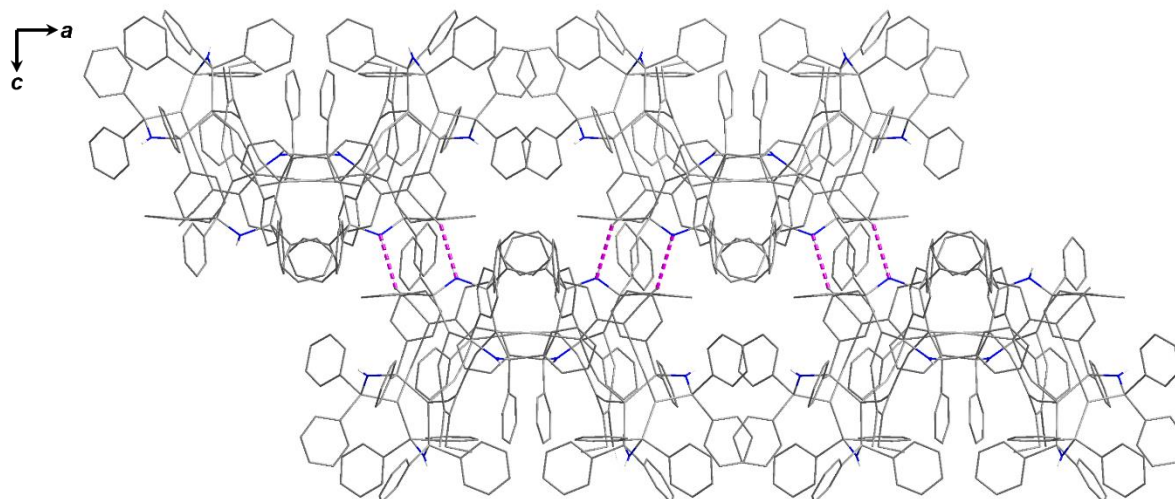
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N100	Cu1	N101	96.87(11)	C3	C2	C1	120.3(4)
N100	Cu1	P1	115.29(9)	C4	C3	C2	119.9(4)
N101	Cu1	P1	102.28(8)	C5	C4	C3	120.3(4)
N100	Cu1	P11	105.91(9)	C4	C5	C6	120.5(4)
N101	Cu1	P11	93.11(9)	C1	C6	C5	119.6(4)
P1	Cu1	P11	133.41(4)	C12	C7	C8	118.7(4)
N100	Cu1	Cu2	85.83(8)	C12	C7	P1	123.2(3)
N101	Cu1	Cu2	174.61(9)	C8	C7	P1	118.1(3)
P1	Cu1	Cu2	80.65(3)	C9	C8	C7	121.0(4)
P11	Cu1	Cu2	81.64(3)	C8	C9	C10	120.3(4)
N200	Cu2	P2	123.82(10)	C11	C10	C9	119.9(4)
N200	Cu2	P12	106.59(9)	C10	C11	C12	119.4(4)
P2	Cu2	P12	127.08(4)	C7	C12	C11	120.7(4)
N200	Cu2	Cu1	93.45(9)	C14	C13	C18	118.1(4)
P2	Cu2	Cu1	98.18(3)	C14	C13	P2	121.0(3)
P12	Cu2	Cu1	93.48(3)	C18	C13	P2	120.5(3)
N1	P1	C1	100.92(15)	C15	C14	C13	121.1(4)
N1	P1	C7	104.37(16)	C14	C15	C16	120.0(4)
C1	P1	C7	101.44(17)	C17	C16	C15	119.7(4)
N1	P1	Cu1	121.67(11)	C16	C17	C18	119.9(4)
C1	P1	Cu1	109.55(13)	C17	C18	C13	121.0(4)
C7	P1	Cu1	116.10(12)	C24	C19	C20	118.4(4)
N1	P2	C13	104.26(17)	C24	C19	P2	118.6(3)
N1	P2	C19	107.42(17)	C20	C19	P2	122.9(3)

C13	P2	C19	102.82(17)	C21	C20	C19	120.2(4)
N1	P2	Cu2	108.51(11)	C22	C21	C20	120.4(4)
C13	P2	Cu2	121.89(12)	C21	C22	C23	120.6(4)
C19	P2	Cu2	111.00(12)	C22	C23	C24	119.5(4)
N2	P11	C31	103.12(16)	C23	C24	C19	120.8(4)
N2	P11	C37	106.77(16)	C36	C31	C32	117.6(4)
C31	P11	C37	101.31(16)	C36	C31	P11	124.0(3)
N2	P11	Cu1	120.13(11)	C32	C31	P11	118.2(3)
C31	P11	Cu1	111.02(12)	C33	C32	C31	120.4(4)
C37	P11	Cu1	112.51(12)	C34	C33	C32	121.8(5)
N2	P12	C49	105.08(16)	C33	C34	C35	118.7(4)
N2	P12	C43	107.94(16)	C34	C35	C36	120.2(4)
C49	P12	C43	103.22(17)	C31	C36	C35	121.2(4)
N2	P12	Cu2	108.61(11)	C42	C37	C38	119.9(3)
C49	P12	Cu2	109.11(12)	C42	C37	P11	123.6(3)
C43	P12	Cu2	121.64(13)	C38	C37	P11	116.5(3)
C300	S1	C301	104.78(18)	C39	C38	C37	119.5(4)
P2	N1	P1	124.35(18)	C40	C39	C38	121.2(4)
P11	N2	P12	122.32(18)	C39	C40	C41	119.3(4)
C100	N100	Cu1	159.8(3)	C40	C41	C42	120.7(4)
C102	N101	Cu1	162.9(3)	C37	C42	C41	119.4(4)
C200	N200	Cu2	156.4(3)	C48	C43	C44	118.6(4)
N100	C100	C101	173.4(4)	C48	C43	P12	118.1(3)
C300	C101	C100	120.8(3)	C44	C43	P12	123.3(3)
C300	C101	C102 <sup>1</sup>	120.2(3)	C45	C44	C43	119.9(4)
C100	C101	C102 <sup>1</sup>	119.0(3)	C44	C45	C46	121.2(4)
N101	C102	C101 <sup>2</sup>	176.7(4)	C47	C46	C45	119.1(4)
N200	C200	C201	178.7(4)	C46	C47	C48	120.1(4)
C200	C201	C300	122.1(3)	C43	C48	C47	121.1(4)
C200	C201	C202	115.4(3)	C50	C49	C54	118.2(4)
C300	C201	C202	122.5(3)	C50	C49	P12	120.4(3)
N201	C202	C201	175.7(4)	C54	C49	P12	121.0(3)
C101	C300	C201	123.7(3)	C51	C50	C49	120.2(4)
C101	C300	S1	122.1(3)	C52	C51	C50	120.9(4)
C201	C300	S1	114.2(3)	C51	C52	C53	119.4(4)
C6	C1	C2	119.3(3)	C52	C53	C54	121.1(4)
C6	C1	P1	120.0(3)	C53	C54	C49	120.2(4)
C2	C1	P1	120.7(3)				

<sup>1</sup>5/4-y,1/4+x,1/4-z; <sup>2</sup>-1/4+y,5/4-x,1/4-z



**Figure S37.** Non-covalent interaction networks in the crystal packing of derivative **E**. The external TCM ligands are depicted in orange and the C...H interactions are represented in pink dotted lines.



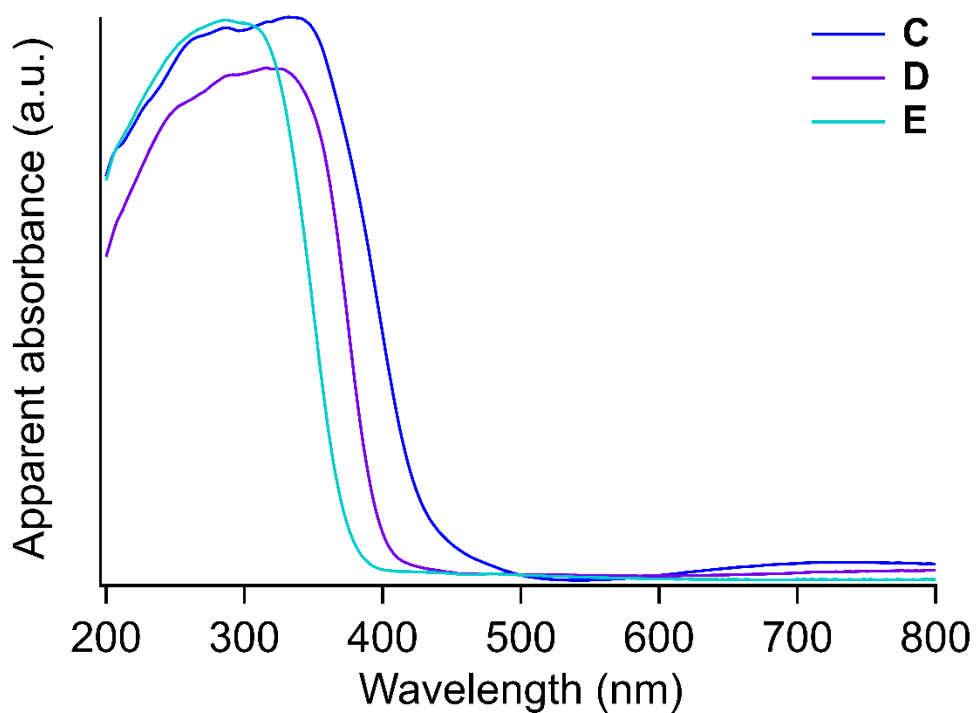
**Figure S38.** Non-covalent interaction networks in the crystal packing of derivatives **I**. The  $\pi$ -NH interactions are represented in pink dotted lines. Nitrogen atoms from amido groups are depicted in blue.

**Table S15.** Percentage of voids volumes per unit cell volume in the X-ray crystal structures of the derivatives **C-I** as calculated by Platon along application of a squeeze procedure<sup>9</sup> in the crystal structure resolution procedure.

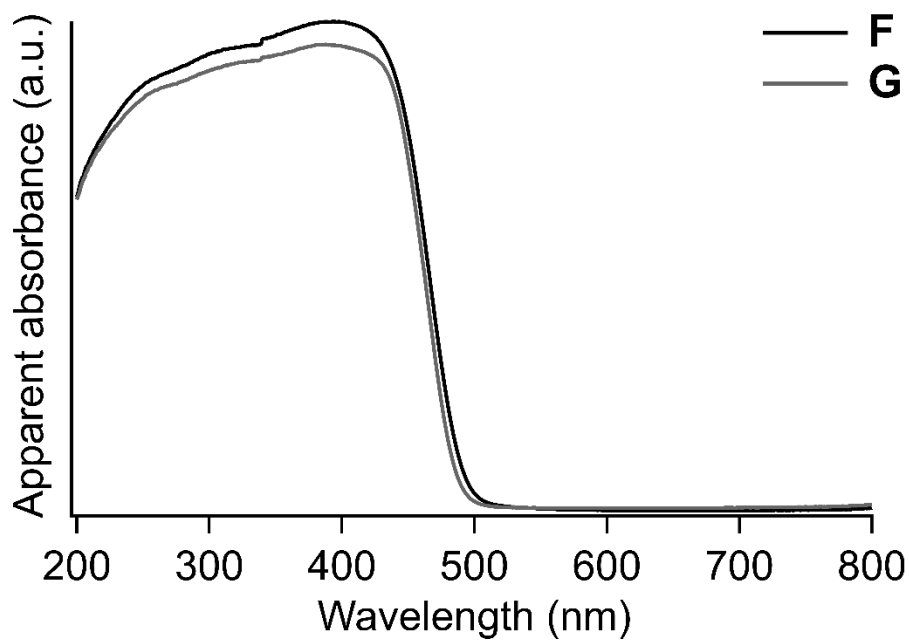
<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>	<b>G</b>	<b>H</b>	<b>I</b>
19 %	13 %	18 %	21 %	23 %	19 %	19 %

### III. Photophysical study

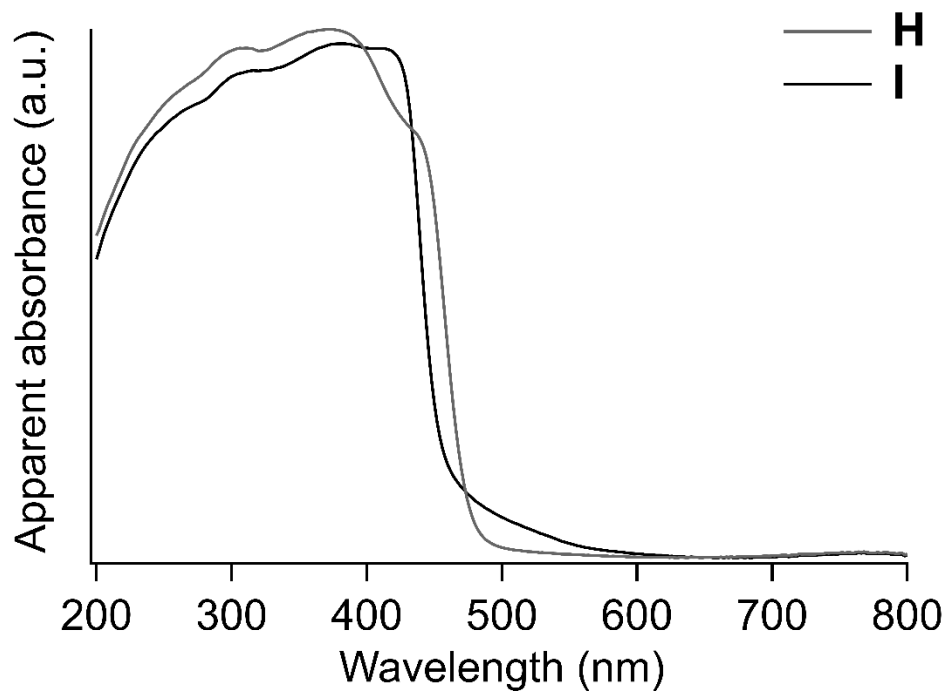
#### III.1. Absorbance



**Figure S39.** Solid-state absorbance spectra at room temperature of derivatives **C** (dark blue), **D** (purple) and **E** (light blue).



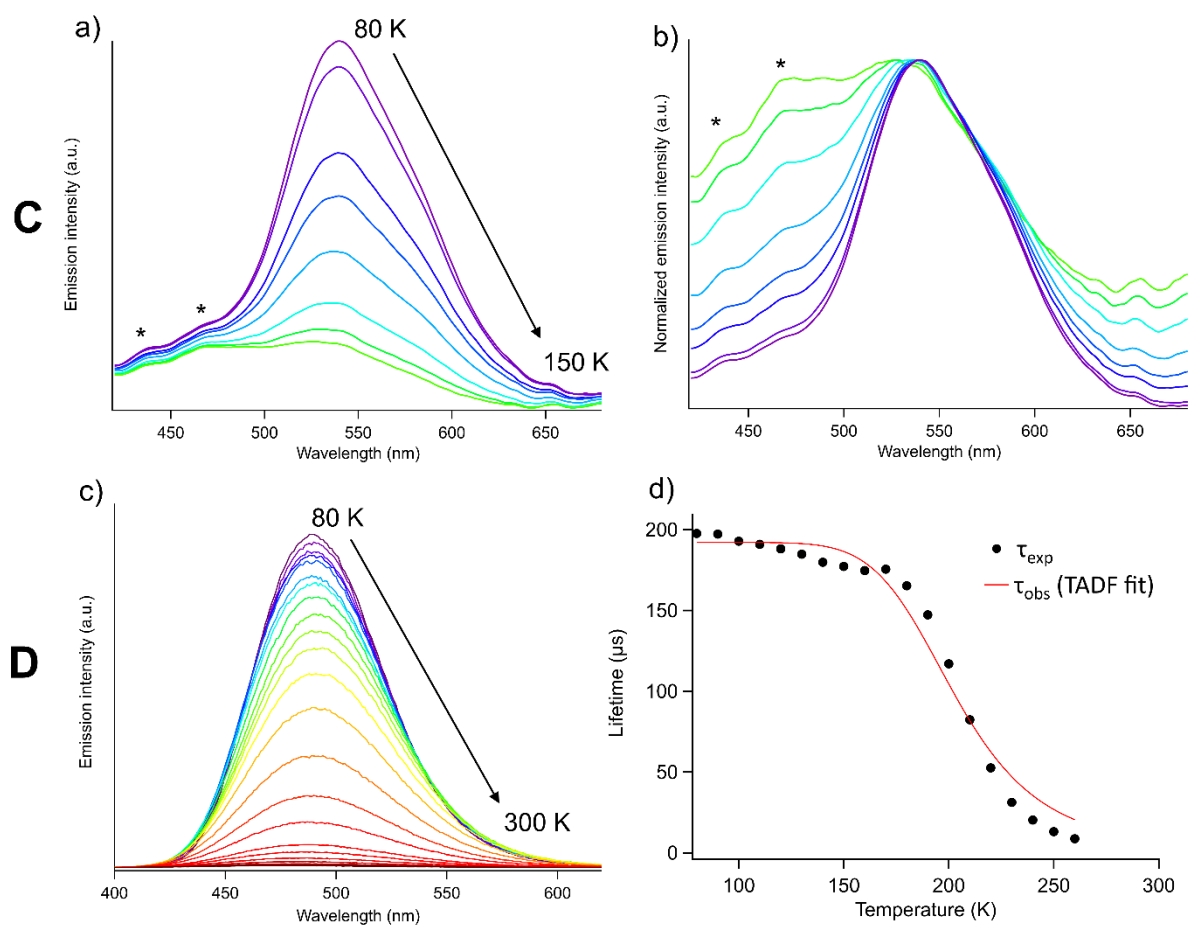
**Figure S40.** Solid-state absorbance spectra at room temperature of derivatives **F** (black) and **G** (grey)



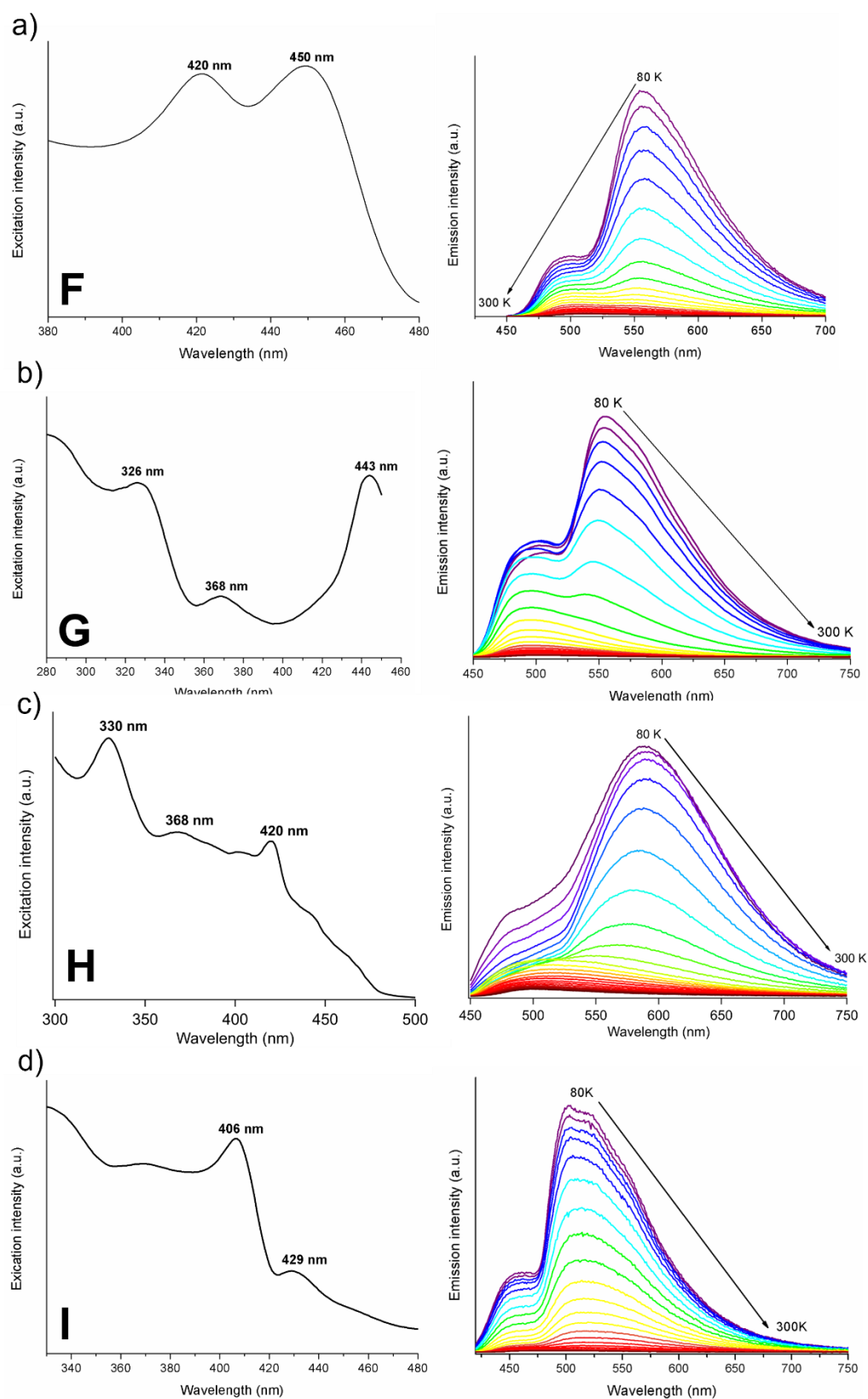
**Figure S41.** Solid-state absorbance spectra at room temperature of derivatives **H** (black) and **I** (grey)



### III.2. Temperature-dependent photophysical studies



**Figure S42.** a) Temperature-dependent emission spectra and b) normalized emission spectra of derivative **C** upon excitation at 398 nm in solid state. Asterisk (\*) indicates the emission of the spectroscopic cell. c) Temperature-dependent emission spectra of derivative **D** upon excitation at 324 nm in solid-state. d) Decay-time temperature variation of derivative **D** upon excitation at 330 nm; red curve represents the TADF fit according to eqn (S1).



**Figure S43.** Excitation spectra at 80 K (left) and temperature-dependent emission spectra (right) of derivatives **F** ( $\lambda_{\text{ex}} = 420$  nm (a)), **G** ( $\lambda_{\text{ex}} = 440$  nm (b)), **H** ( $\lambda_{\text{ex}} = 440$  nm (c)), and **I** ( $\lambda_{\text{ex}} = 408$  nm (d)) in solid-state.

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