Supporting Information

On the redox equilibrium of TPP/TPPO containingCu(I) and Cu(II) complexes

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1.Single Crystal X-Ray Diffraction

1.1. General Information

Single crystal X-ray diffraction studies were performed with suitable crystals of **1c**, **2**, **2a**, **2a·2b**, **2c**, **3**, and **CuCl·CH₃CN**. A single crys-

tal was mounted on a MiTeGen Dual Thickness MicroMount™ with Fomblin Y oil and transferred to a N_2 cold stream (100 K) by an OXFORD CRYOSYSTEMS 700 low temperature system. Data were collected at low temperatures (100 K) using φ- and ω-scans on a BRUKER D8 Venture system equipped with dual IμS microfocus sources and a PHOTON100 detector. Mo-K_α radiation with wavelength 0.71073 Å and a collimating Quazar multilayer mirror were used. Semi-empirical absorption corrections from equivalents were calculated with SADABS-2016/2 [1]. The space groups were determined using *XPREP* [2,3] through analysis of the Laue symmetry and systematic absences. The structures were solved with *SHELXT* [4] and refined by full-matrix least-squares based on F^2 using *SHELXL* [5] and *SHELXle* [6] as a graphical interface. All structures were checked for a higher symmetry using *PLATON* [7]. All non- hydrogen atoms were located and refined anisotropically. Hydrogen atoms were assigned to idealized positions and given thermal parameters equal to 1.2 times the thermal displacement parameters of the atoms to which they were attached.

The cif files have been deposited with the Cambridge Structural Database (CSD). All determined parameters such as bond distances, U_{ij} components, etc. can be retrieved free of charge from the CSD (CCDC and CSD numbers: 2255472- 2255478). General refinement and structure details for the structures are given below.

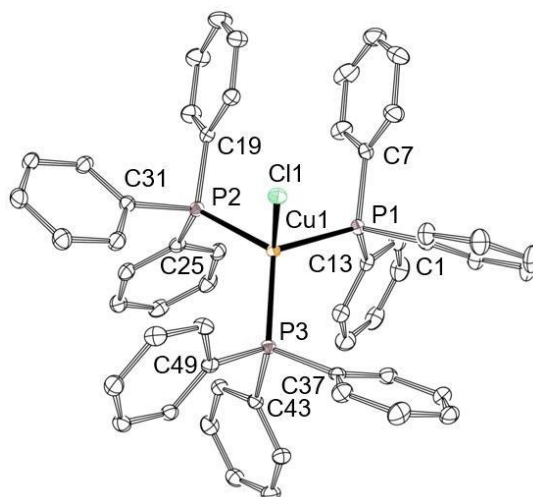### 1.2. Crystal and Refinement Data of **1c**

Figure S1. Molecular structure of **1c**. Solvent acetone and hydrogen atoms omitted for clarity, ellipsoids set at 50 % probability.

1c crystallized in the triclinic space group $P\bar{1}$ with one complex unit and two free acetone solvent molecules in the asymmetric unit.

Table S1. Crystal data and structure refinement for **1c**.

CCDC Number	2255472
Empirical formula	$C_{60}H_{57}ClCuO_2P_3$
Formula weight	1001.95
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.7077(6) Å α = 107.012(2)°
	b = 12.8639(7) Å β = 105.126(2)°
	c = 20.0151(12) Å γ = 91.042(2)°
Volume	2531.6(3) Å³
Z	2
Density (calculated)	1.314 Mg/m³
Absorption coefficient	0.622 mm⁻¹
$F(000)$	1048
Crystal size	0.330 x 0.288 x 0.193 mm³
Theta range for data collection	1.664 to 29.575°
Index ranges	-14<=h<=14, -17<=k<=17, -27<=l<=27
Reflections collected	116638
Independent reflections	14185 [R(int) = 0.0820]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14185 / 0 / 608
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0834
R indices (all data)	R1 = 0.0731, wR2 = 0.0946
Largest diff. peak and hole	0.490 and -0.460 e. Å⁻³

Table S2. Selected bond lengths [Å] and angles [°] of **1c**.

Cu(1)-P(3)	2.3028(5)	Cu(1)-P(2)	2.3092(5)	Cu(1)-P(1)	2.3108(5)
Cu(1)-Cl(1)	2.3426(5)				
P(3)-Cu(1)-P(2)	110.479(19)	P(3)-Cu(1)-P(1)	120.251(19)	P(2)-Cu(1)-P(1)	114.646(19)
P(3)-Cu(1)-Cl(1)	102.418(18)	P(2)-Cu(1)-Cl(1)	104.492(18)	P(1)-Cu(1)-Cl(1)	101.997(18)
C(13)-P(1)-Cu(1)	117.75(6)	C(7)-P(1)-Cu(1)	112.99(6)	C(1)-P(1)-Cu(1)	115.84(6)
C(31)-P(2)-Cu(1)	115.71(6)	C(19)-P(2)-Cu(1)	115.11(6)	C(25)-P(2)-Cu(1)	114.68(6)
C(43)-P(3)-Cu(1)	114.96(6)	C(37)-P(3)-Cu(1)	116.76(6)	C(49)-P(3)-Cu(1)	114.70(6)

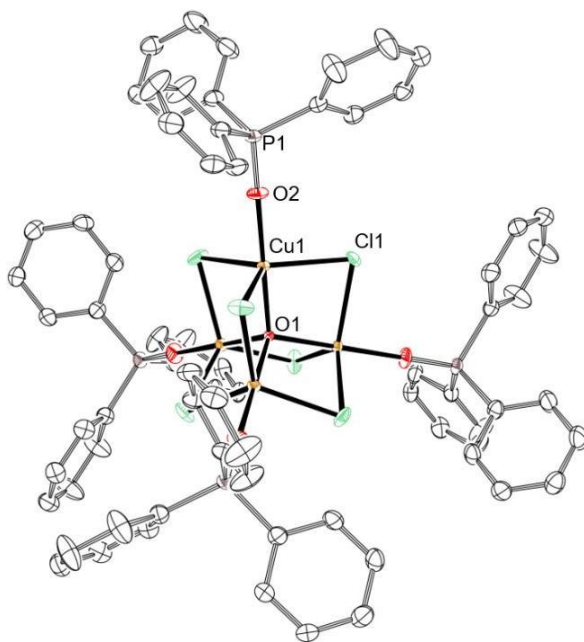**1.3.** Crystal and Refinement Data of **2**

Figure S2. Molecular structure of **2**. H atoms not shown for clarity. Thermal ellipsoids set at the 50 % level.

2 crystallizes in the cubic space group $\bar{F}43c$ with ¼ cluster fragment in the asymmetric unit.

Table S3. Crystal data and structure refinement for **2**.

CCDC number	2255477
Empirical formula	$C_{72}H_{60}Cl_6Cu_4O_5P_4$
Formula weight	1595.94
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	$\bar{F}43c$
Unit cell dimensions	a = 24.2694(9) Å $\alpha = 90°$
	b = 24.2694(9) Å $\beta = 90°$
	c = 24.2694(9) Å $\gamma = 90°$
Volume	14294.8(16) Å^3
Z	8
Density (calculated)	1.483 Mg/m³
Absorption coefficient	1.537 mm^{-1}
$F(000)$	6480
Crystal size	0.704 x 0.468 x 0.124 mm³
Theta range for data collection	1.678 to 29.515°
Index ranges	$-33 \leq h \leq 24$,
	$-33 \leq k \leq 29$
	$-32 \leq l \leq 33$

Reflections collected	34081
Independent reflections	1680 [R(int) = 0.0682]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7466 and 0.4935
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1680 / 0 / 70
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0628
R indices (all data)	R1 = 0.0424, wR2 = 0.0688
Absolute structure parameter	0.014(8)
Largest diff. peak and hole	0.411 and -0.383 e.Å^{-3}

Table S4. Selected bond lengths [Å] and angles [°] of **2**.

Cu(1)-O(1)	1.9042(5)	Cu(1)-O(2)	1.928(4)	Cu(1)-Cl(1)#1	2.3889(7)
Cu(1)-Cl(1)#2	2.3889(7)	Cu(1)-Cl(1)	2.3890(7)		
O(1)-Cu(1)-O(2)	180.00(7)	O(1)-Cu(1)-Cl(1)#1	84.66(2)	O(2)-Cu(1)-Cl(1)#1	95.34(2)
O(1)-Cu(1)-Cl(1)#2	84.66(2)	O(2)-Cu(1)-Cl(1)#2	95.34(2)	Cl(1)#1-Cu(1)-Cl(1)#2	119.144(6)
O(1)-Cu(1)-Cl(1)	84.66(2)	O(2)-Cu(1)-Cl(1)	95.34(2)	Cl(1)#1-Cu(1)-Cl(1)	119.145(6)
Cl(1)#2-Cu(1)-Cl(1)	119.145(6)	Cu(1)#3-Cl(1)-Cu(1)	81.20(4)	Cu(1)#3-O(1)-Cu(1)#4	109.5
Cu(1)#3-O(1)-Cu(1)#5	109.5	Cu(1)#4-O(1)-Cu(1)#5	109.5	Cu(1)#3-O(1)-Cu(1)	109.5
Cu(1)#4-O(1)-Cu(1)	109.5	Cu(1)#5-O(1)-Cu(1)	109.5	P(1)-O(2)-Cu(1)	180.0(4)

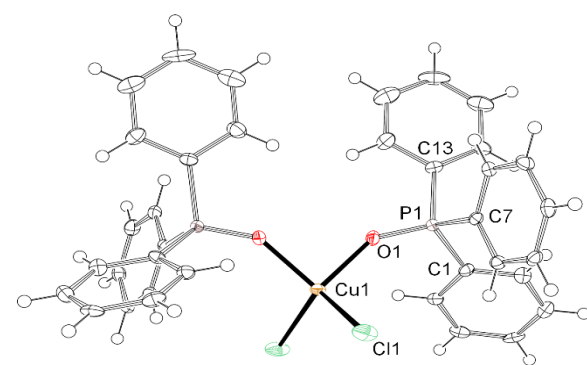## 1.4. Crystal and Refinement Data of **2a**

Figure S3. Molecular structure of **2a**. Thermal ellipsoids set at the 50 % level.

2a crystallized in the orthorhombic space group *Fdd*2 with half a complex molecule in the asymmetric unit.

Table S5. Crystal data and structure refinement for **2a**.

CCDC Number	2255473
Empirical formula	$C_{36}H_{30}Cl_2CuO_2P_2$
Formula weight	690.98
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Fdd*2
Unit cell dimensions	a = 20.904(2) Å α = 90°
	b = 31.157(4) Å β = 90°
	c = 9.8100(12) Å γ = 90°
Volume	6389.3(13) Å³
Z	8
Density (calculated)	1.437 Mg/m³
Absorption coefficient	0.983 mm⁻¹
F(000)	2840
Crystal size	0.916 x 0.125 x 0.120 mm³
Theta range for data collection	2.347 to 27.485°
Index ranges	-24 ≤ h ≤ 27
	-40 ≤ k ≤ 40
	-12 ≤ l ≤ 12
Reflections collected	19266
Independent reflections	3669 [R(int) = 0.0698]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on *F*²
Data / restraints / parameters	3669 / 1 / 196
Goodness-of-fit on *F*²	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0750
R indices (all data)	R1 = 0.0452, wR2 = 0.0790
Absolute structure parameter	0.022(18)
Largest diff. peak and hole	0.329 and -0.353 e. Å⁻³

Table S6. Selected bond lengths [Å] and angles [°] for **2a**.

Cu(1)-O(1)#1	1.971(3)	Cu(1)-O(1)	1.972(3)	Cu(1)-Cl(1)#1	2.1775(11)
Cu(1)-Cl(1)	2.1775(11)				
O(1)#1-Cu(1)-O(1)	89.21(15)	O(1)#1-Cu(1)-Cl(1)#1	135.45(8)	O(1)-Cu(1)-Cl(1)#1	101.02(8)
O(1)#1-Cu(1)-Cl(1)	101.02(8)	O(1)-Cu(1)-Cl(1)	135.45(8)	Cl(1)#1-Cu(1)-Cl(1)	101.20(6)
P(1)-O(1)-Cu(1)	147.14(18)				

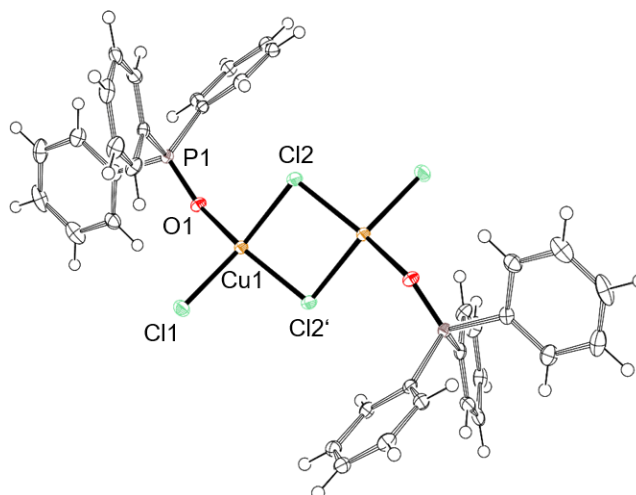**1.5.** Crystal and Refinement Data of **2a·2b**

Figure S4. Molecular structure of **2b**. **2a** not shown for clarity. Thermal ellipsoids set at the 50 % level.

2a·2b crystallized in the monoclinic space group $P2_1/c$ with each half a complex molecule of **2a** and **2b** in the asymmetric unit.

Table S7. Crystal data and structure refinement for **2a·2b**.

CCDC Number	2255474
Empirical formula	$C_{54}H_{45}Cl_4Cu_2O_3P_3$
Formula weight	1103.69
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.7008(8) Å $\alpha = 90°$
	b = 48.974(4) Å $\beta = 114.485(3)°$
	c = 11.4192(8) Å $\gamma = 90°$
Volume	4937.2(7) Å³
Z	4
Density (calculated)	1.485 Mg/m³
Absorption coefficient	1.219 mm⁻¹
$F(000)$	2256
Crystal size	0.154 x 0.098 x 0.029 mm³
Theta range for data collection	1.663 to 27.100°
Index ranges	-12<=h<=12, -62<=k<=62, -14<=l<=14
Reflections collected	75466
Independent reflections	10915 [R(int) = 0.0990]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10915 / 0 / 595
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0813
R indices (all data)	R1 = 0.0738, wR2 = 0.0945
Largest diff. peak and hole	0.454 and -0.656 e.Å⁻³

Table S8. Selected bond lengths [Å] and angles [°] for **2b**.

Cu(1)-O(1)	1.9133(19)	Cu(1)-Cl(1)	2.1977(8)	Cu(1)-Cl(2)	2.2684(8)
Cu(1)-Cl(2)#1	2.2877(8)				

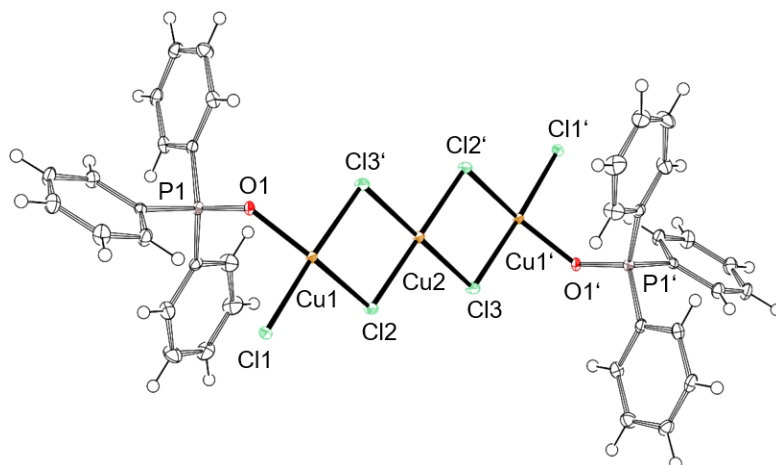|					
O(1)-Cu(1)-Cl(1)	94.27(6)	O(1)-Cu(1)-Cl(2)	155.22(6)	Cl(1)-Cu(1)-Cl(2)	94.94(3)
O(1)-Cu(1)-Cl(2)#1	94.75(6)	O(1)-Cu(1)-Cl(2)#1	94.75(6)	Cl(1)-Cu(1)-Cl(2)#1	154.14(3)
Cl(2)-Cu(1)-Cl(2)#1	86.81(3)	Cu(1)-Cl(2)-Cu(1)#1	93.19(3)	P(1)-O(1)-Cu(1)	148.09(13)

1.6. Crystal and Refinement Data of 2c

Figure S5. Molecular structure of **2c**. Thermal ellipsoids set at the 50 % level.

2c crystallized in the monoclinic space group $P2_1/n$ with half a complex molecule in the asymmetric unit.

Table S9. Crystal data and structure refinement for **2c**.

CCDC Number	2255475
Empirical formula	$C_{36}H_{30}Cl_6Cu_3O_2P_2$
Formula weight	959.86
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.2654(3) Å $\alpha = 90°$
	b = 21.0901(7) Å $\beta = 104.0830(10)°$
	c = 10.0078(4) Å $\gamma = 90°$
Volume	1896.83(12) Å³
Z	2
Density (calculated)	1.681 Mg/m³
Absorption coefficient	2.206 mm^{-1}
$F(000)$	962
Crystal size	0.182 x 0.092 x 0.085 mm³
Theta range for data collection	1.931 to 27.484°
Index ranges	-12<=h<=11, -27<=k<=27, -12<=l<=12
Reflections collected	31477
Independent reflections	4344 [R(int) = 0.0658]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4344 / 0 / 223
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0578

Table S10. Selected bond lengths [Å] and angles [°] for **2c**.

Cu(1)-O(1)	1.9485(17)	Cu(1)-Cl(1)	2.2618(6)	Cu(1)-Cl(2)	2.3269(6)
Cu(1)-Cl(3)#1	2.3288(7)	Cu(1)-Cl(1)#2	2.5490(7)	Cu(2)-Cl(3)#1	2.2501(6)
Cu(2)-Cl(3)	2.2501(6)	Cu(2)-Cl(2)#1	2.2535(6)	Cu(2)-Cl(2)	2.2535(6)
O(1)-Cu(1)-Cl(1)	94.46(5)	O(1)-Cu(1)-Cl(2)	149.17(6)	Cl(1)-Cu(1)-Cl(2)	93.83(2)
O(1)-Cu(1)-Cl(3)#1	88.51(5)	Cl(1)-Cu(1)-Cl(3)#1	177.00(3)	Cl(2)-Cu(1)-Cl(3)#1	83.41(2)
O(1)-Cu(1)-Cl(1)#2	102.78(5)	Cl(1)-Cu(1)-Cl(1)#2	87.75(2)	Cl(2)-Cu(1)-Cl(1)#2	107.18(2)
Cl(3)#1-Cu(1)-Cl(1)#2	91.96(2)	Cl(3)#1-Cu(2)-Cl(3)	180.00(2)	Cl(3)#1-Cu(2)-Cl(2)#1	93.10(2)
Cl(3)-Cu(2)-Cl(2)#1	86.90(2)	Cl(3)#1-Cu(2)-Cl(2)	86.90(2)	Cl(3)-Cu(2)-Cl(2)	93.10(2)
Cl(2)#1-Cu(2)-Cl(2)	180.00(3)	Cu(1)-Cl(1)-Cu(1)#2	92.25(2)	Cu(2)-Cl(2)-Cu(1)	94.76(2)
Cu(2)-Cl(3)-Cu(1)#1	94.80(2)	P(1)-O(1)-Cu(1)	132.48(11)		

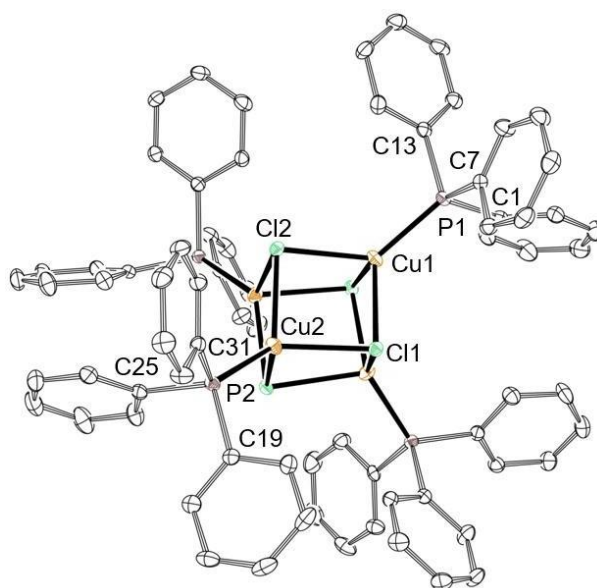## 1.7. Crystal and Refinement Data of **3**

Figure S6. Molecular structure of **3**. H atoms omitted for clarity. Thermal ellipsoids set at the 50 % level.

3 crystallized in the orthorhombic space group *Pbcn* with half a complex molecule in the asymmetric unit.
Table S11. Crystal data and structure refinement for **3**.

CCDC Number	2255476
Empirical formula	$C_{72}H_{60}Cl_4Cu_4P_4$
Formula weight	1445.04
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	a = 17.3025(12) Å α = 90°
	b = 20.2602(13) Å β = 90°
	c = 18.0032(11) Å γ = 90°
Volume	6311.1(7) Å³
Z	4
Density (calculated)	1.521 Mg/m³
Absorption coefficient	1.644 mm⁻¹
F(000)	2944
Crystal size	0.288 x 0.260 x 0.182 mm³
Theta range for data collection	1.917 to 28.700°
Index ranges	-23<=h<=23, -27<=k<=27, -24<=l<=24
Reflections collected	97544
Independent reflections	8165 [R(int) = 0.0829]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8165 / 0 / 379
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0717
R indices (all data)	R1 = 0.0553, wR2 = 0.0801
Largest diff. peak and hole	0.435 and -0.550 e.Å⁻³

Table S12. Selected bond lengths [Å] and angles [°] for **3**.

Cu(1)-P(1)	2.1924(6)	Cu(1)-Cl(2)	2.3515(6)	Cu(1)-Cl(1)	2.4319(6)
Cu(1)-Cl(2)#1	2.5041(6)	Cu(2)-P(2)	2.1896(6)	Cu(2)-Cl(1)	2.3992(6)
Cu(2)-Cl(1)#1	2.4098(6)	Cu(2)-Cl(2)	2.4747(6)		
P(1)-Cu(1)-Cl(2)	130.39(2)	P(1)-Cu(1)-Cl(1)	118.43(2)	Cl(2)-Cu(1)-Cl(1)	101.71(2)
P(1)-Cu(1)-Cl(2)#1	115.06(2)	Cl(2)-Cu(1)-Cl(2)#1	91.27(2)	Cl(1)-Cu(1)-Cl(2)#1	90.083(19)
P(2)-Cu(2)-Cl(1)	124.74(2)	P(2)-Cu(2)-Cl(1)#1	131.31(2)	Cl(1)-Cu(2)-Cl(1)#1	89.22(2)
P(2)-Cu(2)-Cl(2)	112.92(2)	Cl(1)-Cu(2)-Cl(2)	99.13(2)	Cl(1)#1-Cu(2)-Cl(2)	91.30(2)
Cu(2)-Cl(1)-Cu(2)#1	89.95(2)	Cu(2)-Cl(1)-Cu(1)	78.897(18)	Cu(2)#1-Cl(1)-Cu(1)	89.941(19)
Cu(1)-Cl(2)-Cu(2)	78.949(18)	Cu(1)-Cl(2)-Cu(1)#1	87.429(19)	Cu(2)-Cl(2)-Cu(1)#1	86.828(18)
C(13)-P(1)-Cu(1)	120.64(7)	C(7)-P(1)-Cu(1)	111.16(7)	C(1)-P(1)-Cu(1)	113.07(7)
C(25)-P(2)-Cu(2)	114.48(7)	C(31)-P(2)-Cu(2)	118.52(8)	C(19)-P(2)-Cu(2)	114.55(7)

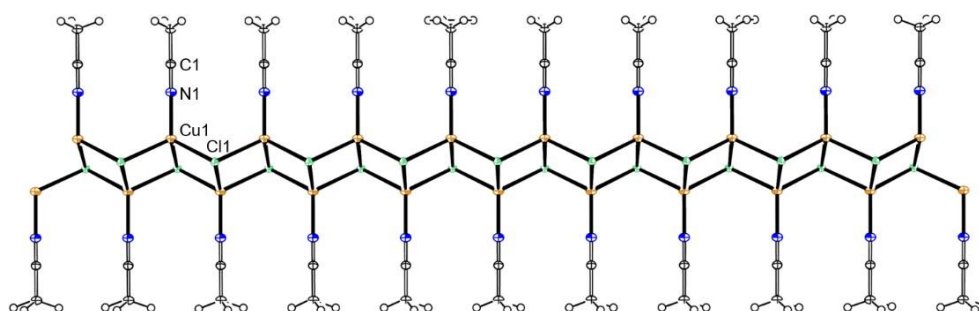1.8. Crystal and Refinement Data of **CuCl·CH₃CN**

Figure S7. Molecular structure of **CuCl·CH₃CN**. Thermal ellipsoids set at the 50 % level.

CuCl·CH₃CN crystallized in the orthorhombic space group *Pnma* with one formula unit CuCl·CH₃CN in the asymmetricunit.

Table S13. Crystal data and structure refinement for **CuCl·CH₃CN**.

CCDC Number	2255478
Empirical formula	C_2H_3ClCuN
Formula weight	140.04
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	a = 8.5426(5) Å α = 90°
	b = 3.8471(2) Å β = 90°
	c = 12.5341(7) Å γ = 90°
Volume	411.92(4) Å³
Z	4
Density (calculated)	2.258 Mg/m³
Absorption coefficient	5.732 mm⁻¹
F(000)	272
Crystal size	0.871 x 0.543 x 0.054 mm³
Theta range for data collection	2.886 to 40.210°
Index ranges	-15<=h<=15, -6<=k<=6, -22<=l<=22
Reflections collected	12539
Independent reflections	1421 [R(int) = 0.0648]
Completeness to theta = 25.242°	99.3 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1421 / 0 / 33
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0678
R indices (all data)	R1 = 0.0340, wR2 = 0.0715
Extinction coefficient	0.056(4)
Largest diff. peak and hole	0.951 and -1.448 e.Å⁻³

Table S14. Selected bond lengths [Å] and angles [°] for **CuCl·CH₃CN**.

Cu(1)-N(1)	1.9267(13)	Cu(1)-Cl(1)	2.3896(2)	Cu(1)-Cl(1)#1	2.3896(2)
Cu(1)-Cl(1)#2	2.4004(4)				
N(1)-Cu(1)-Cl(1)	113.57(2)	N(1)-Cu(1)-Cl(1)#1	113.57(2)	Cl(1)-Cu(1)-Cl(1)#1	107.212(15)
N(1)-Cu(1)-Cl(1)#2	119.83(4)	Cl(1)-Cu(1)-Cl(1)#2	100.448(10)	Cl(1)#1-Cu(1)-Cl(1)#2	100.447(10)
Cu(1)#3-Cl(1)-Cu(1)	107.213(15)	Cu(1)#3-Cl(1)-Cu(1)#2	79.552(10)	Cu(1)-Cl(1)-Cu(1)#2	79.552(10)
C(1)-N(1)-Cu(1)	175.37(13)				

2. IR spectroscopy

2.1. General Information

All samples were measured on a device of the type Jasco FT/IR-6000. If not mentioned otherwise all samples weremeasured as KBr pellets at room temperature.
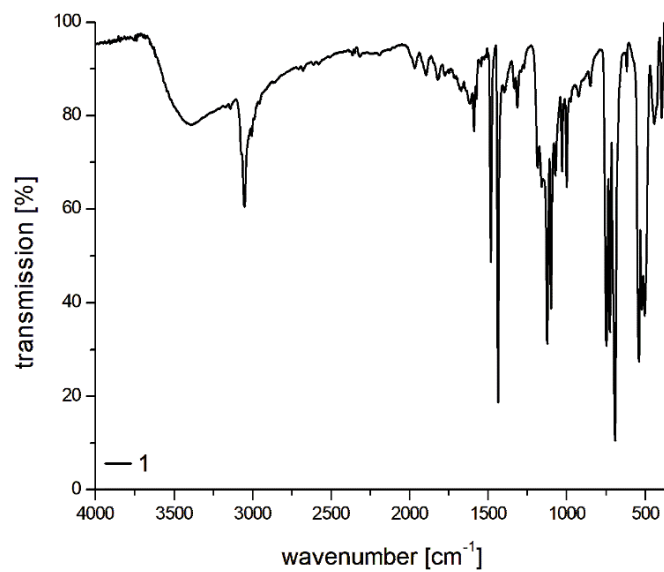
2.2. IR spectrum of **1**

Figure S8. IR spectrum of **1** (c = 2.92 · 10⁻⁵ mol/g(KBr)). ṽ = 3050 [νC-H$_{arom.}$], 1480-1433 [νC-C$_{arom.}$], 1121-1095 [νC-H$_{arom.}$],1027-996 [phenyl breathing mode], 747-725, 693 [δC-H$_{arom.}$ *(out of plane)*], 540 [νCu$_4$O], 522 [νP-C].

2.3. IR spectrum of **1a**
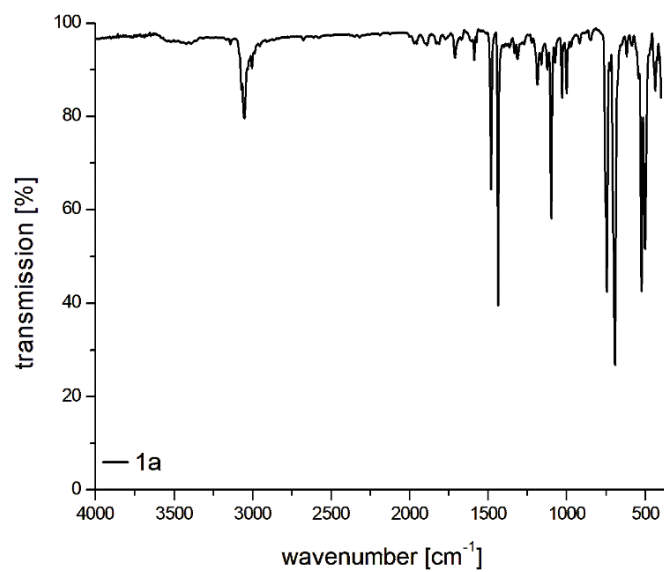
Figure S9. IR spectrum of **1a** (c = 1.54 · 10⁻⁵ mol/g(KBr)). ṽ = 3050 [νC-H$_{arom.}$], 1479-1434 [νC-C$_{arom.}$], 1121, 1093 [νC-H$_{arom.}$], 1027-996 [phenyl breathing mode], 744-694 [δC-H$_{arom.}$ *(out of plane)*], 542-501 [νP-C].

2.4. IR spectrum of **1b**
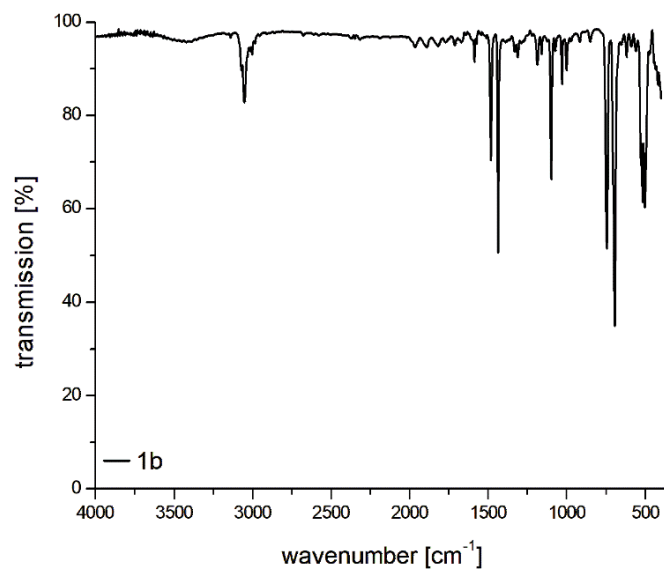
Figure S10. IR spectrum of **1b** (c = 0.99 · 10^{-5} mol/g(KBr)). $\tilde{\upsilon}$ = 3050 [νC-H$_{arom.}$], 1480-1434 [νC-C$_{arom.}$], 1095 [νC-H$_{arom.}$], 1027-996 [phenyl breathing mode], 744-694 [δC-H$_{arom.}$ *(out of plane)*], 527 [νP-C].

2.5. IR spectrum of **1c**

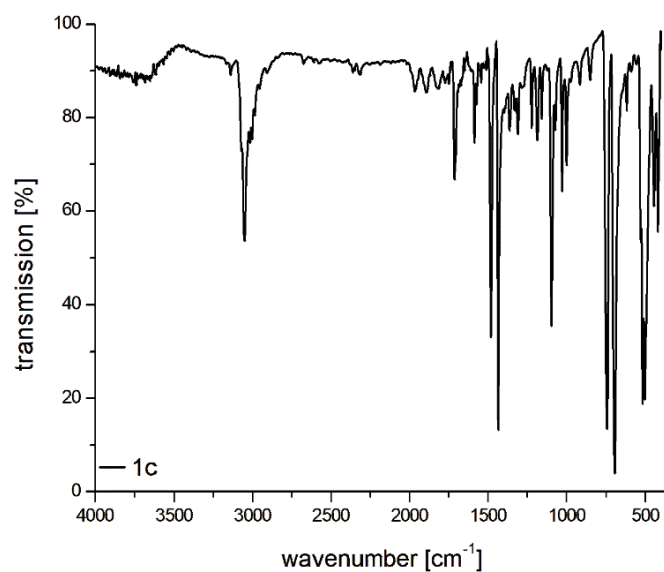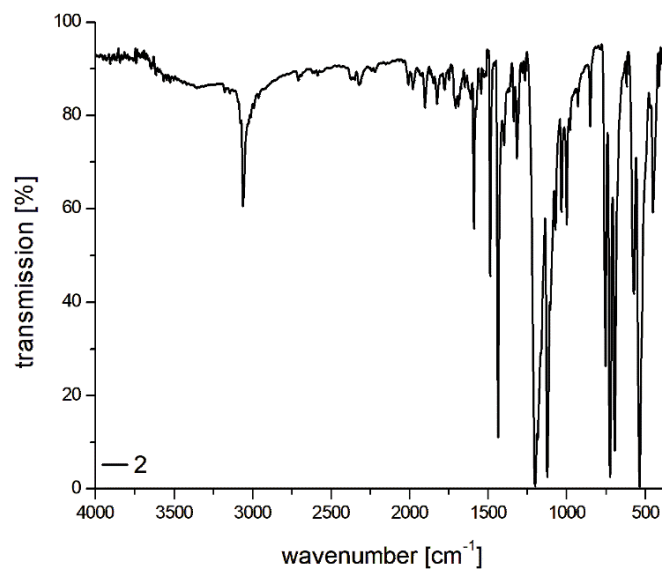**Figure S11**. IR spectrum of **1c** (c = 1.28 · 10^{-5} mol/g(KBr)). $\tilde{\upsilon}$ = 3050 [νC-H$_{arom.}$], 1479-1433 [νC-C$_{arom.}$], 1121, 1184, 1156,1095 [νC-H$_{arom.}$], 1027-997 [phenyl breathing mode], 742-694 [δC-H$_{arom.}$ *(out of plane)*], 527 [νP-C].

2.6. IR spectrum of **2**

Figure S12. IR spectrum of **2** (c = 8.35 · 10^{-5} mol/g(KBr)). ῦ = 3050 [νC-H$_{arom.}$], 1480-1433 [νC-C$_{arom.}$], 1198 [νP-O], 1121-1095 [νC-H$_{arom.}$], 1025-993 [phenyl breathing mode], 752, 723-694 [δC-H$_{arom.}$ *(out of plane)*], 572 [νCu$_4$O], 536 [νP-C].

2.7. IR spectrum of **2a**
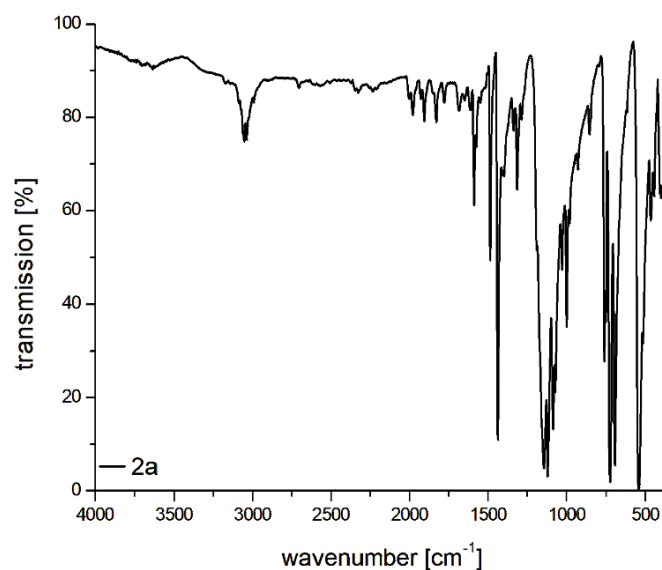
Figure S13. IR spectrum of **2a** (c = 2.54 · 10^{-5} mol/g(KBr)). ῦ = 3051-3036 [νC-H$_{arom.}$], 1483-1436 [νC-C$_{arom.}$], 1336-1283, 1143[νP-O], 1117, 1083, 1068, [δC-H$_{arom.}$ *(in plane)*] 1026-996 [phenyl breathing mode], 759-750, 722-692 [δC-H$_{arom.}$ *(out of plane)*], 544 [νP-C].

2.8. IR spectrum of **3**

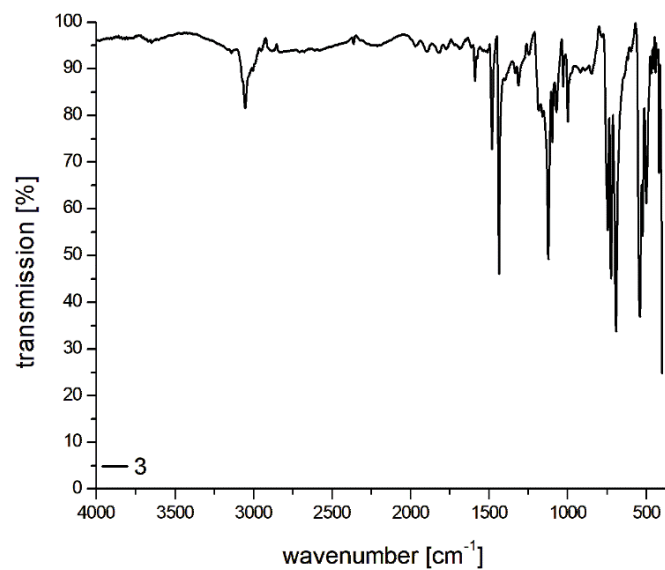**Figure S14**. IR spectrum of **3** (c = 4.30 · 10^{-3} mol/g(KBr)). $\tilde{\upsilon}$ = 3052 [νC-H$_{arom.}$], 1475-1433 [νC-C$_{arom.}$], 1120-1094 [νC-H$_{arom.}$], 1026-997 [phenyl breathing mode], 745, 722-690 [δC-H$_{arom.}$ *(out of plane)*], 542 [νCu$_4$Cl$_4$], 523 [νP-C].
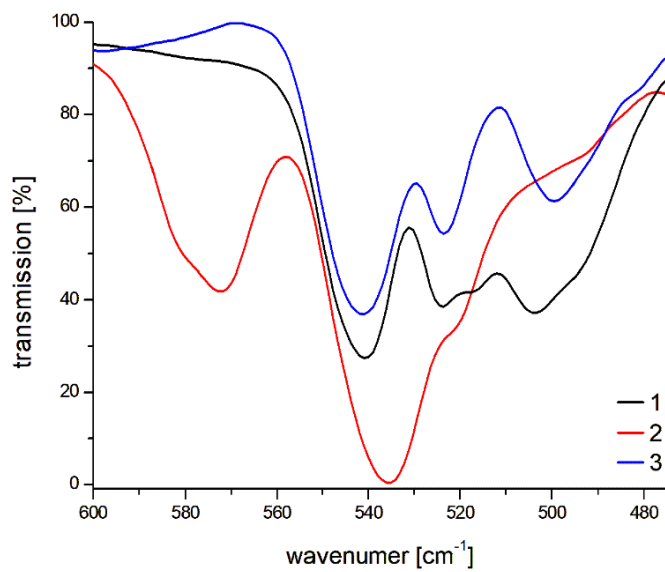
2.9. Comparison of IR spectra

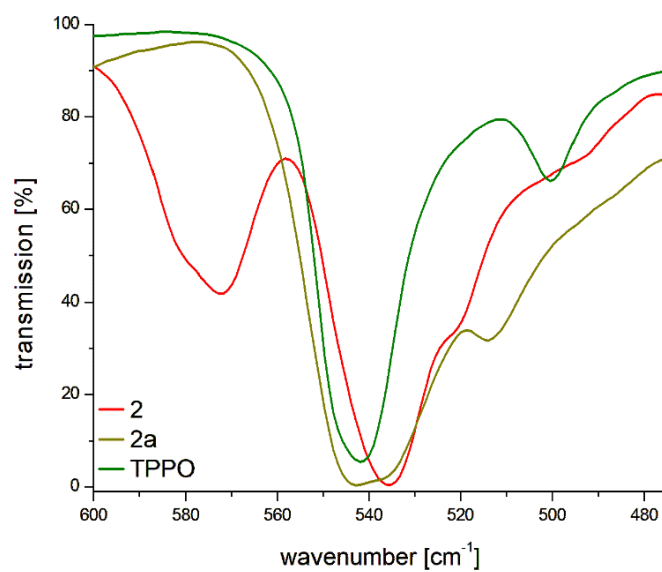**Figure S15.** IR spectra of **1**, **2** and **3** (range 600-475 cm^{-1}).

Figure S16. IR spectrum of **2**, **2a**, and **TPPO** (range 600-475 cm^{-1}).
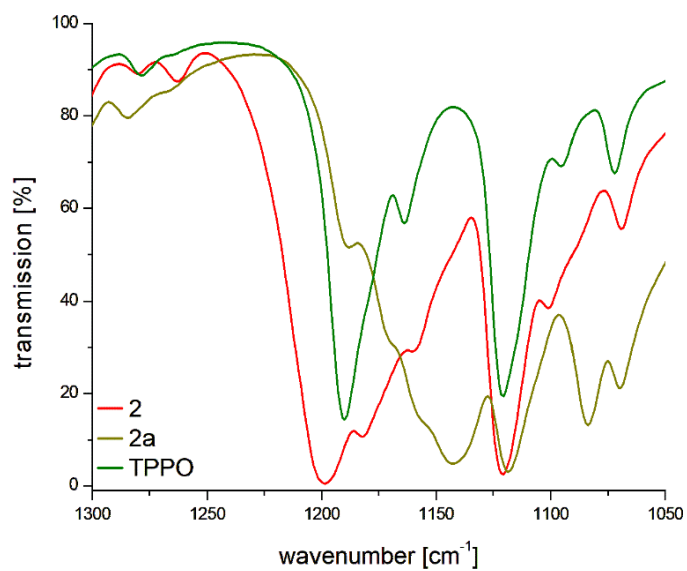
Figure S17. IR spectrum of **2**, **2a**, and **TPPO** (range 1300-1050 cm^{-1}).
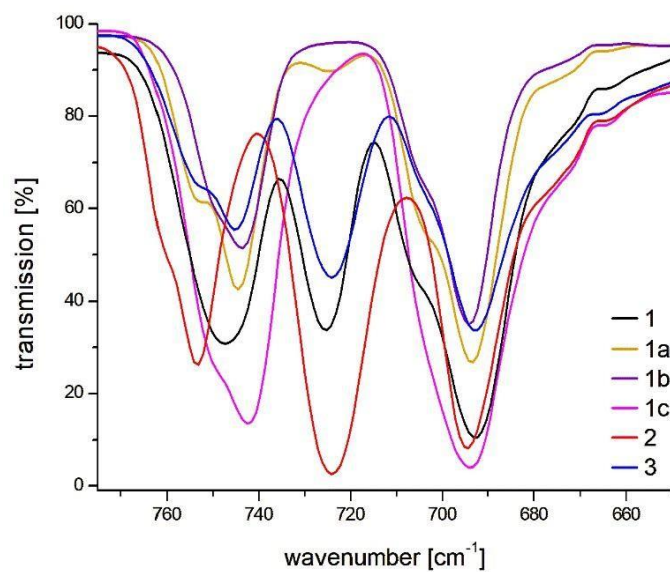
Figure S18. IR spectrum of **1**, **1a**, **1b**, **1c**, **2**, and **3** (range 775-650 cm⁻¹).
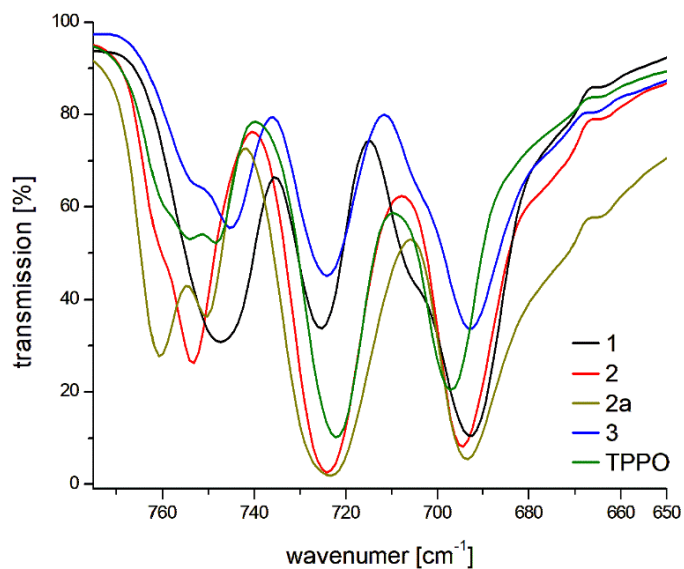
Figure S19. IR spectrum of **1**, **2**, **2a**, **3**, and **TPPO** (range 775-650 cm⁻¹).
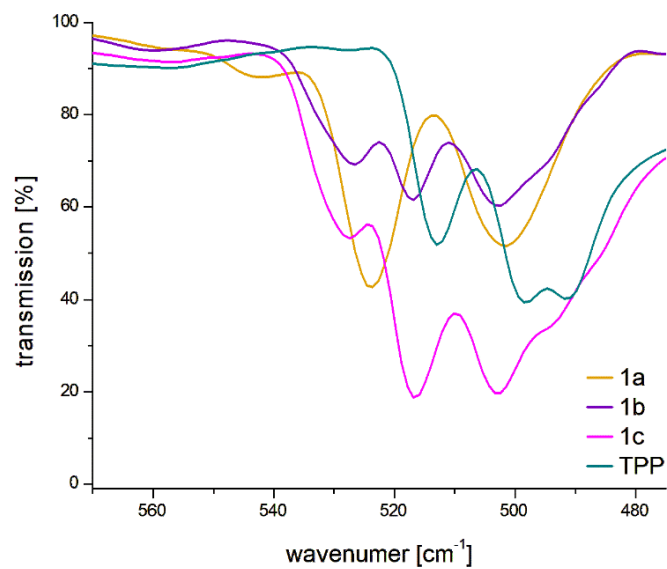
Figure S20. IR spectrum of **1a**, **1b**, **1c**, and **TPP** (range 570-475 cm^{-1}).
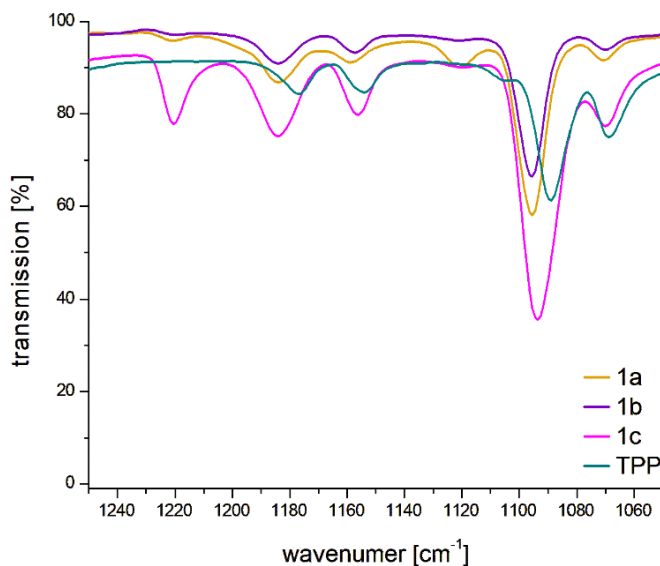
Figure S21. IR spectrum of **1a**, **1b**, **1c**, and **TPP** (range 570-475 cm^{-1}).

3. Elemental analyses and melting points

3.1. General Information

The measurements were performed in the analytical division of the organic chemistry department of the TUKaiserslautern. The measurements were performed on an Elementar Analysensysteme vario MICRO cube device.

The melting points were measured with a DigiMelt MPA161 SRS SI Scientific Instruments GmbH instrument.

3.2. Elemental analyses

Table S15. Elemental analysis of **1**, **1a**, **1b**, **1c**, **2**, **2a** and **3**.

		Carbon / %	Hydrogen / %	Nitrogen / %
1	Calculated	**56.45**	**3.95**	–
	Measurement	**56.08**	**4.05**	–
1a	Calculated	**59.84**	**4.18**	–
	Measurement	**58.67**	**4.03**	–
1b	Calculated	**69.34**	**4.85**	–
	Calculated **1b**·2H$_2$0	**65.55**	**5.20**	–
	Measurement	**65.61**	**4.56**	–
1c	Calculated	**73.22**	**5.12**	–
	Calculated **1c**·1.5 acetone	**72.21**	**5.59**	–
	Measurement	**72.03**	**5.38**	–
2	Calculated	**54.18**	**3.79**	–
	Measurement	**54.00**	**3.89**	–

2a	Calculated	**62.57**	**4.38**	–
	Measurement	**62.61**	**4.22**	–
3	Calculated	**59.84**	**4.18**	–
	Measurement	**59.95**	**4.35**	–

3.3. Melting points

Table S16. Melting points of **1a**, **1b**, **1c**, **2**, and **2a**.

	1a	1b	1c	2	2a
Melting point / °C	160-168	236-240.5	168-175	255-258.8	164.9-174.1

4. References

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