Electronic Supplementary Material (ESI) for Nanoscale.

The role of amine ligands in governing film morphology and electrical properties of copper films derived from copper formate-based molecular inks

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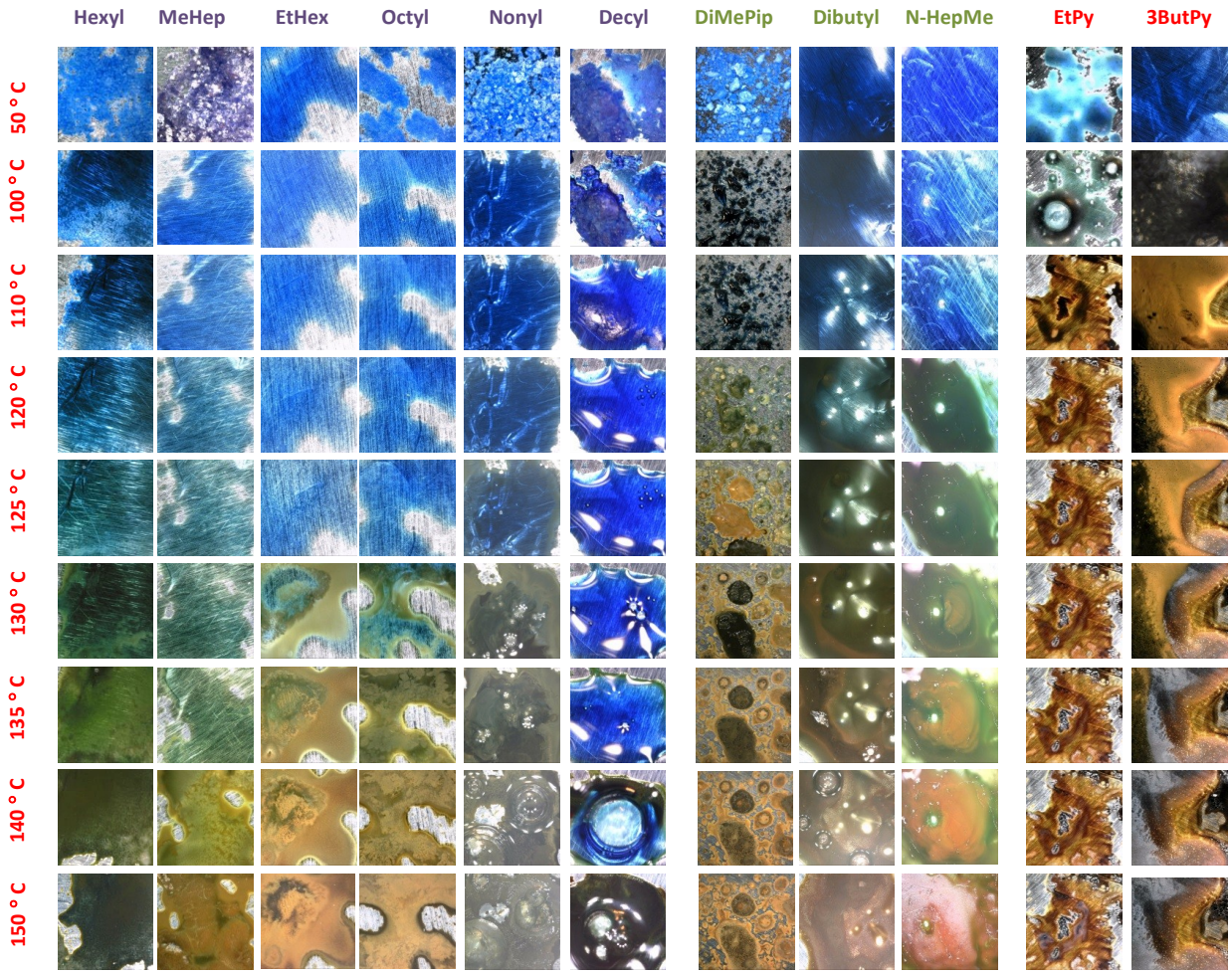

Figure S1. Optical images of copper formate complexes at incrementally increasing temperatures.

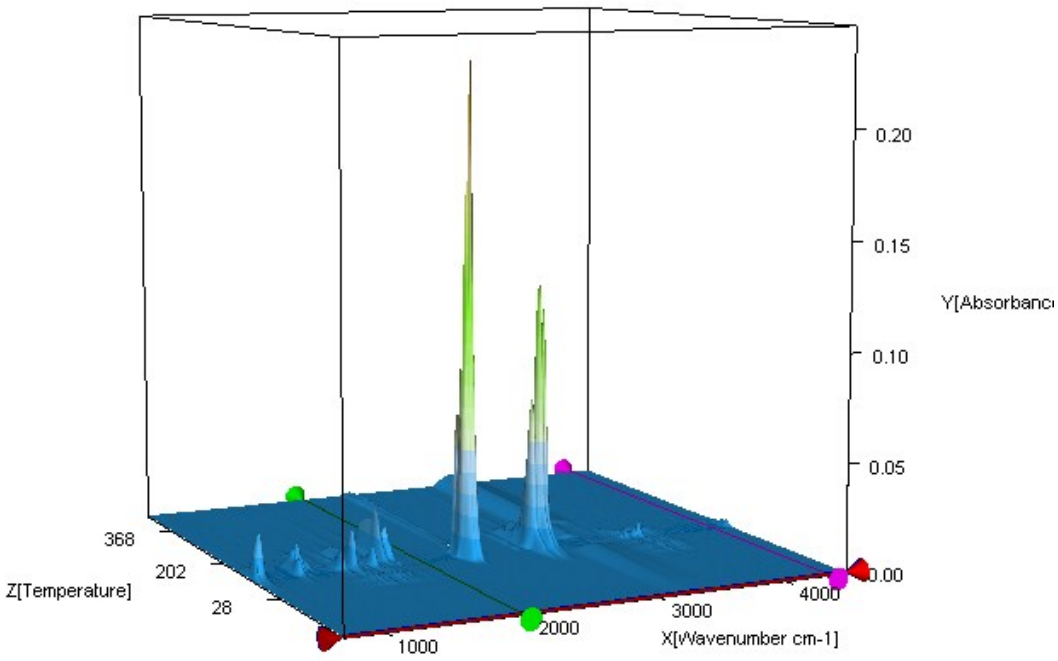

Figure S2. FT-IR absorbance of EtHex as a function of wavenumber and temperature measured during the TGA experiment (5°C/min) for EtHex. Trace amounts of water coordinated to EtHex are released near 50-60°C.

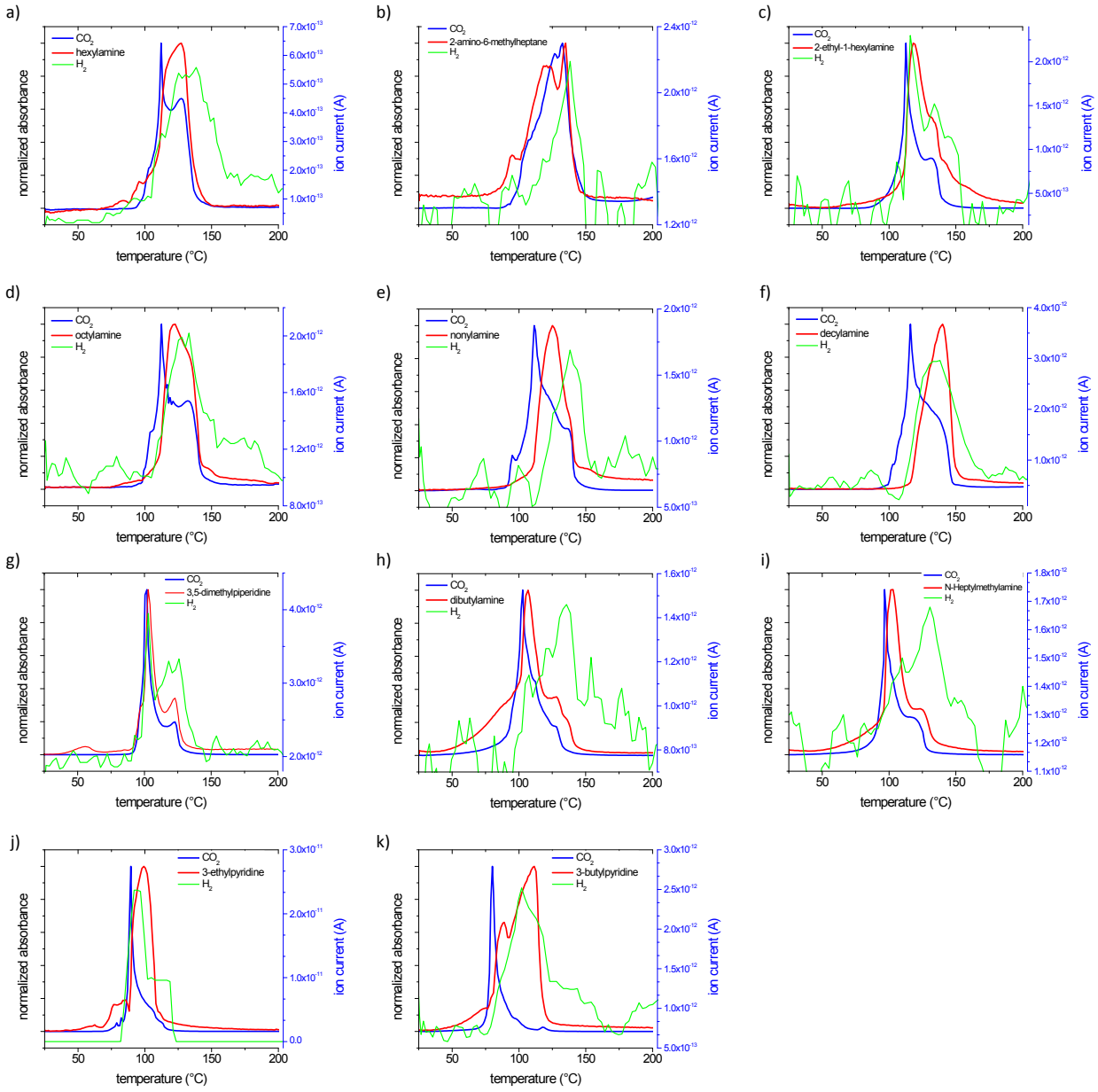

Figure S3. The release of CO_2, the amine ligand and H_2 during thermogravimetric analysis of a) *Hexyl*, b) *MeHep*, c) *EtHex*, d) *Octyl*, e) *Nonyl*, f) *Decyl*, g) *DiMePip*, h) *Dibutyl*, i) *N-HepMe*, j) *3EtPy* and k) *3ButPy* . The gases were detected by TGA-FTIR-MS experiments performed at 5°C/min under Argon.

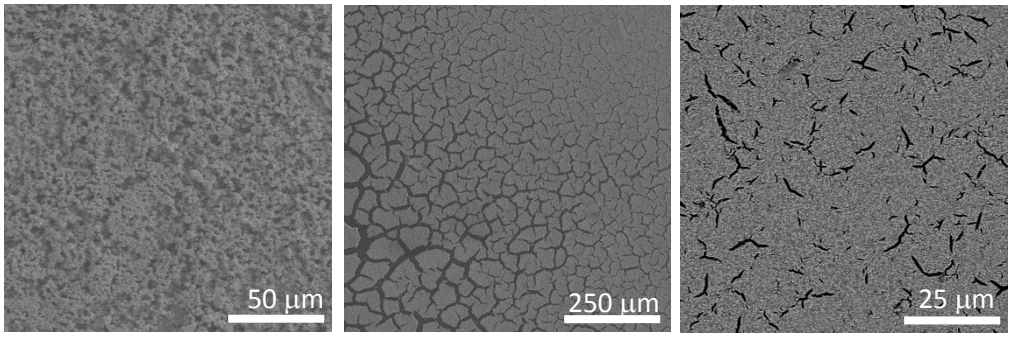

Figure S4. Low magnification SEM images of films made from a) *N-HepMe*, b) *3EtPy* and c) *3BuPy*. The cracks in the *3EtPy* and *3BuPy* prevent these complexes from forming conductive films.

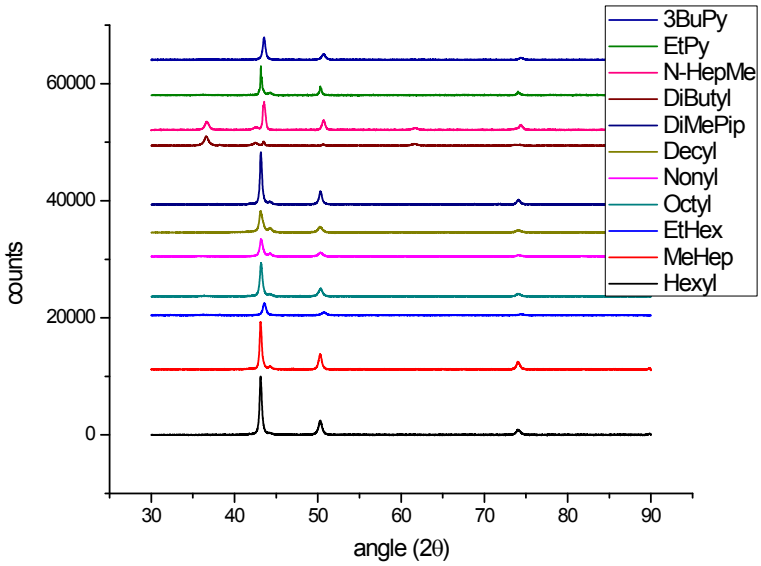

Figure S5. Powder XRD of copper films made from the various complexes. Complexes Dibutyl and N-HepMe formed films with a high concentration of oxides as revealed by the strong Cu_2O peak at 36.6°.

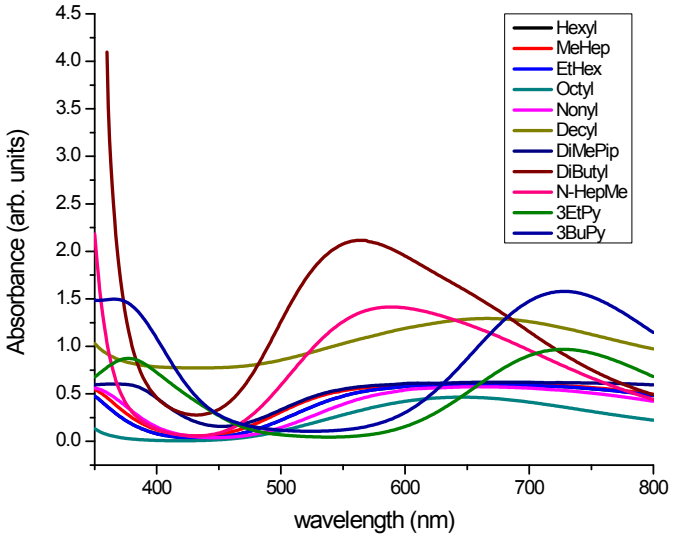

Figure S6. UV-VIS spectra of the complexes in toluene (~10mg/mL)

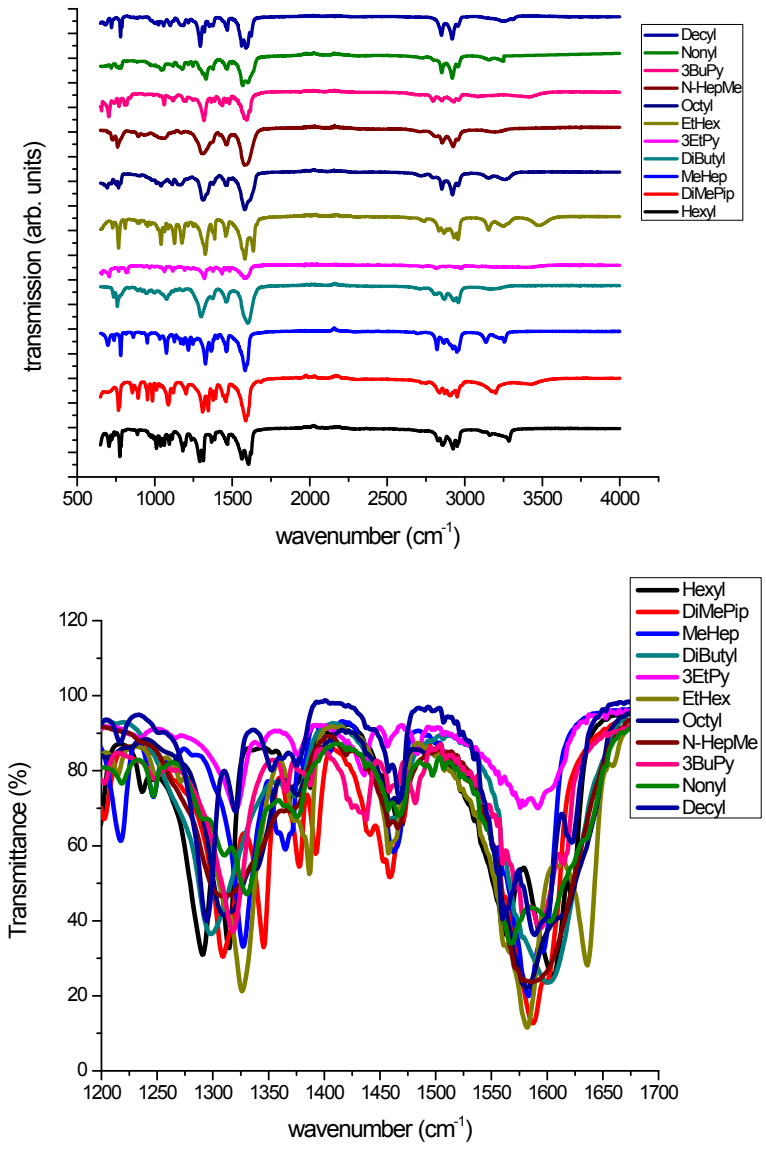

Figure S7. FTIR spectra of the copper formate complexes.

Table S1. The % ligands found at the ½ reaction and the boiling points of ligands for the compounds. The particle size, the lowest resistivity and the sintering temperatures used to achieve the lowest resistivity for films formed from various compounds.

Complex	% ligand at 1/2 reaction	boiling point of ligand (°C)	particle size (nm)	stdev on particle size (nm)	lowest resistivity (μΩ·cm)	optimized sintering temperature (°C)
Hexyl	39	131	330	120	12.7 +/- 2.3	140
MeHep	48	156	480	170	16.7 +/- 1.6	166
EtHex	22	169	100	30	6.2 +/- 0.8	140
Octyl	24	176	192	54	7.1 +/- 0.8	140
Nonyl	15	201	135	47	10.9 +/- 0.7	182
Decyl	10	216	77	25	7.1 +/- 0.6	166
Dibutyl	66	159	830	249	NA	NA
N-MeHep	34	196	247	295	~1500	125
DiMePip	36	144	304	82	14.0 +/- 1.9	155
3BuPy	12	198	24	4	NA	NA
3EtPy	25	165	52	21	NA	NA

Figure SX: Crystal structure of Hexyl.

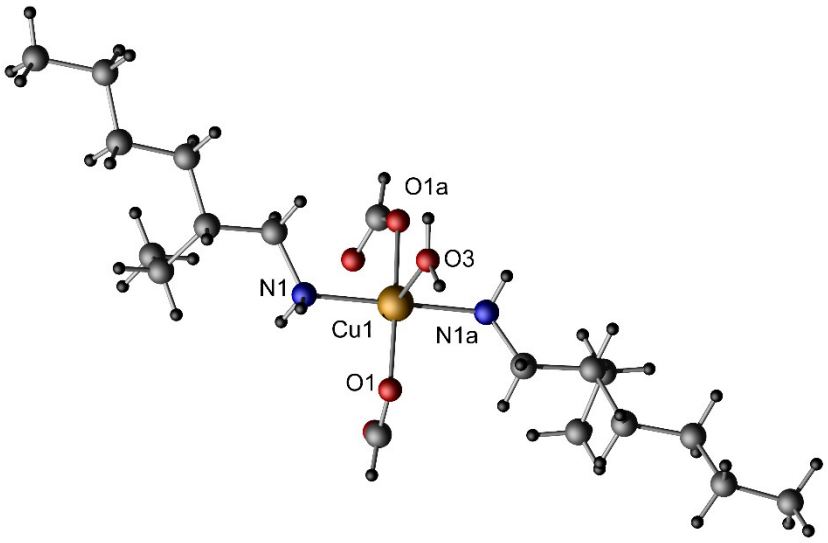

Figure S8: Crystal structure of *EtHex*.

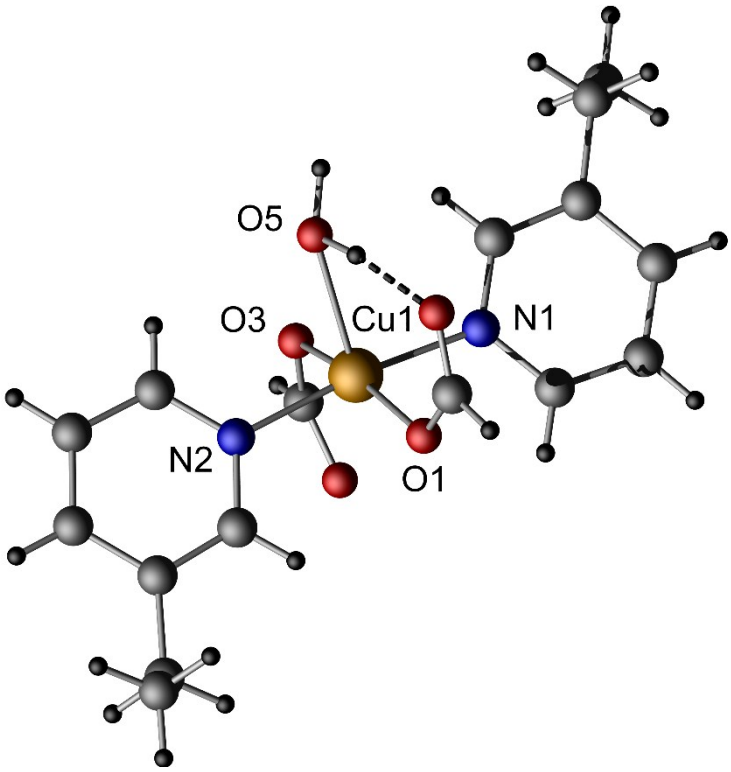

Figure S9: Crystal structure of *3EtPy*.

Table S1: Cu-L bond distances.

Compound	Bond	Distance (Å)
MeHep	Cu1-N1	2.0054(54)
	Cu1-O1	1.9609(48)
EtHex	Cu1-N1	2.0195(48)
	Cu1-O1	1.9683(39)
	Cu1-O3	2.3597(41)
DiMePip	Cu1-N1	2.0287(19)
	Cu1-N2	2.0230(19)
	Cu1-O1	2.0061(15)
	Cu1-O3	1.9909(15)
	Cu1-O5	2.2626(19)
3EtPy	Cu1-N1	2.0086(20)
	Cu1-N2	2.0134(20)
	Cu1-O1	1.9630(19)
	Cu1-O3	1.9486(19)
	Cu1-O5	2.3254(20)

Table S2: Hydrogen bonding motifs observed from crystallographic data.

Compound	H-bond	Distance (Å)	Inter or Intra?
MeHep	H1B-O2	2.07	Inter
EtHex	H1B-O2	2.37	Inter
	H1C-O1	2.13	Inter
	H3B-O2	2.01	Inter
DiMePip	H1-O1	2.40	Inter
	H2-O4	2.20	Intra
	H5d-O4	1.91	Inter
	H5c-O2	2.09	Inter
3EtPy	H5b-O4	1.84	Inter
	H5c-O2	1.73	Intra

Table S3: Crystallographic data for select complexes

Compound	*MeHep*	*EtHex*	*DiMePip*	*3EtPy*
Empirical Formula	$C_{18}H_{40}CuN_2O_4$	$C_{18}H_{42}CuN_2O_5$	$C_{16}H_{34}CuN_2O_5$	$C_{16}H_{22}CuN_2O_5$
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	C2/c	P21/c	Cc
a (Å)	15.9235(15)	34.494(4)	12.5495(11)	10.8381(3)
b (Å)	6.9220(6)	6.7114(7)	11.6952(8)	15.1085(4)
c (Å)	10.4447(8)	9.7554(11)	13.8103(13)	11.1446(3)
α (°)	90	90	90	90
β (°)	97.090(5)	90.350(5)	96.169(3)	98.5042(16)
γ (°)	90	90	90	90
Volume (Å^3)	1142.44(17)	2258.4(4)	2015.2(3)	1804.83(8)
Z	2	4	4	4
ρ (g cm^{-3})	1.198	1.265	1.3117	1.420
λ (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	200(2)	200(2)	100(2)	200(2)
μ (mm^{-1})	0.977	0.995	1.109	1.237
F (000)	446	932	854	804
Reflections Collected	8559	6407	33541	7786
Independent Reflections	1939	2748	4024	2955
Relfections with I > 2σ(I)	1247	2234	3360	2755
Goodness of fit on F^2	1.008	1.051	0.878	1.014
R1, wR2 (I > 2σ(I))	0.0978, 0.2381	0.0532, 0.1541	0.0304, 0.0960	0.0216, 0.0522
R1, wR2 (all data)	0.1363, 0.2758	0.0738, 0.1639	0.0418, 0.1118	0.0246, 0.0538

Comparison of the Octyl complex made from anhydrous copper formate and hydrated copper formate.

We observed that water is a labile ligand to copper formate. For instance during preparation (weighing…), changes in copper formate anhydrous can change in color to its hydrated color over time if left out. Conversely, copper formate hydrate is easily dried by putting the powder under vacuum. We also observed that starting with the anhydrous or hydrated copper salt did not affect the results significantly. For most of the complex, we believe that water desorbs during the isolation of the complex (the complexes are filtered and put under vacuum to remove the solvent used to crystallize). In the cases where the water remained after isolation, the water desorbs prior to its decomposition into copper. For instance, the EtHex complex appears to accommodate the presence of water more than other complexes, as shown in the crystal structure (XRD is performed at low temperatures). Figure S2 is the TGA-FTIR 3D plot showing that trace amounts of water desorbs at ~60°C.

Unfortunately, we were unable to prepare the EtHex complex using anhydrous conditions (the branched nature of the ligand made this complex difficult to crystallize) and this specific complex could only be isolated when starting with hydrated copper formate. However, we prepared the Octyl complex starting from the hydrated and anhydrous form of copper formate. The isolated complexes were analyzed by TGA and showed the same residual mass (~15% which corresponds to a 1:2 ratio of copper formate to octylamine) suggesting that the water desorbed during the isolation. The resistivity and the particle size of the two films prepared by sintering at 145°C had values within error as shown in the table below.

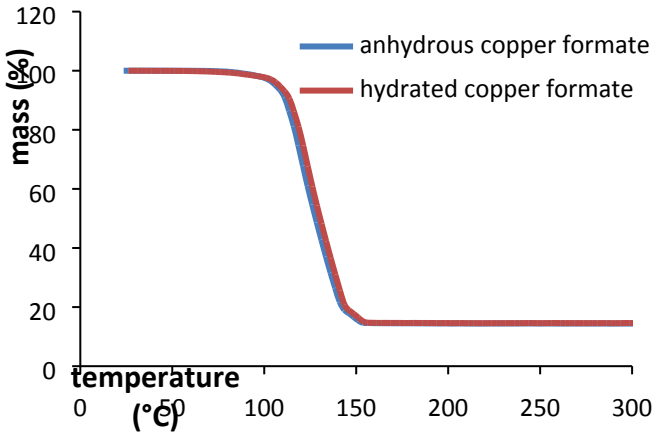

Figure S11. A comparison of the TGA analysis of Octyl complexes that were prepared starting from hydrated copper formate and anhydrous copper formate.

Table S4. A comparison of the resistivity and particle diameters of films made from the Octyl complexes that were prepared starting from hydrated copper formate and anhydrous copper formate.

	hydrated copper formate	anhydrous copper formate
Resistivity	9.31+/- 1.04	11.29+/- 2.74
Particle Diameter (nm)	158 +/- 103	106 +/- 44