Supporting Information for **"Facile *in situ* Copper(II) Mediated C–S Bond Activation Transforming Dithiocarbimate to Carbamate and Thiocarbamate Generating Cu(II) and Cu(I) Complexes"**

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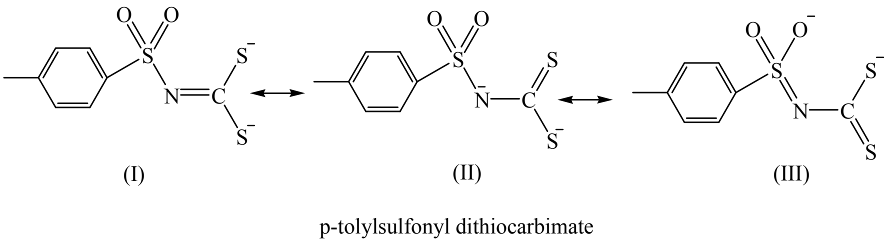


Scheme S1. Canonical forms of the ligand p-tolylsulfonyldithiocarbimate

Spectroscopy

In addition to the characteristic IR absorptions for the coordinated bpy, phen, PPh_3 and sulfonyl group of the ligands in complexes **1** and **2** display ν(C=O) at around 1690 cm^{-1} characteristic of carbamate moiety; complex **3** shows bands at 1400 and 1100 cm^{-1} due to the delocalized N⋯C⋯S unit of the thiocarbamate ligand because the C=N and C=S bonds appear not to be pure in nature in this complex.

As expected the paramagnetic complexes **1** and **2** show broad signals whereas the diamagnetic **3** displays ^{1}H and ^{13}C resonances characteristic of the ligating moieties and integrate well to the corresponding protons. In ^{31}P NMR a single resonance at δ -0.928 ppm in **3** is due to Cu(I) in tetrahedral environment in this complex.

X-Ray Crystallography

Diffraction intensities of **1**–**3** were collected on Oxford Diffraction X- Calibur CCD system with MoKα, λ = 0.71073, **1** and **2** at 150(2) K and 293(2) K. Data analyses were carried out with the CrysAlis program.[1] The structures were solved using direct methods with the

Shelxs97 program.[2] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon were refined in calculated positions. Those on bridging hydroxides in **2** were treated similarly but those on solvent water molecules could not be located and were not included. Absorption corrections for **1** and **2** were carried out using the ABSPACK program[3] and for **3** using SADABS.

Table S1 Crystallographic Data and Refinement Parameters

compound	**1**	**2**	**3**
empirical formula	$C_{33}H_{26}ClCuN_5O_8S$	$C_{58}H_{66}Cl_2Cu_4N_{10}O_{25}S_2$	$C_{45}H_{40}CuNO_3P_2S_2$
crystal color, morphology	blue, needle	blue, block	white, block
crystal system	triclinic	Monoclinic	triclinic
space group	P-1	$P2_1/n$	P-1
a, Å	8.2961(19)	12.1797(8)	13.1335(11)
b, Å	13.477(4)	18.8798(8)	13.5099(12)
c, Å	15.762(5)	29.5552(18)	14.0175(13)
α, deg	71.28(3)	(90)	91.287(7)
β, deg	77.77(2)	95.373(6)	107.473(8)
γ, deg	78.14(2)	(90)´	116.536(9)
volume, $Å^3$	1613.2(8)	6766.3(7)	2086.4(3)
Z	2	4	2
formula weight, g mol^{-1}	751.64	1692.39	832.38
density (calculated), g cm^{-3}	1.547	1.661	1.325
absorption coefficient, mm^{-1}	0.886	1.469	0.740
F(000)	770	3464	864
reflections collected	11479	42014	17347
independent reflections	9406	19385	8957
R(int)	0.0391	0.0986	0.0442
R_1[a], wR_2[b], [I>2σI]	0.0545, 0.0989	0.0733, 0.1494	0.0584, 0.1078
R_1[a], wR_2[b] (all data)	0.1540, 0.1127	0.1965, 0.1723	0.1101, 0.1274
GOF[c]	0.785	0.811	0.965
residuals, e/$Å^3$	0.418, -0.292	1.372, -1.034	0.408, -0.378

[a] $R1 = \sum(\|F_o| - |F\|/\sum |F|$. [b] $wR2 = [(w(\sum(|F_o|^2 - |F_c|^2)^2/\sum(w|F_o|^4)]^{1/2}$.
[c] $GOF = [(w(\sum(|F_o| - |F_c|^2)^2]/(n - p)^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

Table S2. Selected bond distances (Å) and bond angles (°) in complexes.

Complex **1**

Bond Distance (Å)		Bond Angle (°)	
Cu(1)–N(11)	2.011(3)	N(31)–Cu(1)–N(11)	174.27(12)
Cu(1)–N(22)	2.168(3)	N(31)–Cu(1)–N(51)	92.71(11)
Cu(1) –N(31)	1.999(3)	N(11)–Cu(1)–N(51)	92.86(11)
Cu(1)–N(42)	2.101(3)	N(31)–Cu(1)–N(42)	80.81(12)
Cu(1)–N(51)	2.078(3)	N(11)–Cu(1)–N(42)	95.82(11)
		N(51)–Cu(1)–N(42)	138.90(11)
		N(31)–Cu(1)–N(22)	97.00(12)
		N(11)–Cu(1)–N(22)	79.81(13)
		N(51)–Cu(1)–N(22)	110.00(11)
		N(42)–Cu(1)–N(22)	111.06(11)

Complex **2**

Cu(1)–O(4)	1.900(4)	O(4)–Cu(1)–O(3)	82.11(16)
Cu(1)–O(3)	1.977(4)	O(4)–Cu(1)–N(11)	167.94(18)
Cu(1)–N(11)	1.997(5)	O(3)–Cu(1)–N(11)	95.46(18)
Cu(1)–N(22)	2.014(5)	O(4)–Cu(1)–N(22)	95.40(19)
Cu(1)–N(111)	2.344(5)	O(3)–Cu(1)–N(22)	151.20(18)
Cu(1)–Cu(3)	2.898(1)	N(11)–Cu(1)–N(22)	81.0(2)
Cu(2)–O(1)	1.926(4)	O(4)–Cu(1)–N(111)	98.95(17)
Cu(2)–O(2)	1.973(4)	O(3)–Cu(1)–N(111)	96.54(17)
Cu(2)–N(31)	1.993(5)	N(11)–Cu(1)–N(111)	93.06(19)
Cu(2)–N(42)	2.003(5)	N(22)–Cu(1)–N(111)	112.15(18)
Cu(2)–N(91)	2.393(5)	O(1)–Cu(2)–O(2)	81.83(16)
Cu(2)–Cu(4)	2.912(1)	O(1)–Cu(2)–N(31)	94.82(19)
Cu(3)–O(4)	1.929(4)	O(2)–Cu(2)–N(31)	153.65(18)
Cu(3)–O(3)	1.962(4)	O(1)–Cu(2)–N(42)	168.87(19)
Cu(3)–N(51)	1.972(5)	O(2)–Cu(2)–N(42)	97.06(18)
Cu(3)–N(62)	2.021(5)	N(31)–Cu(2)–N(42)	81.2(2)
Cu(3)–O(2)	2.290(4)	O(1)–Cu(2)–N(91)	98.80(17)
Cu(4)–O(1)	1.918(4)	O(2)–Cu(2)–N(91)	95.27(17)
Cu(4)–O(2)	1.969(4)	N(31)–Cu(2)–N(91)	111.05(18)
Cu(4)–N(71)	2.000(5)	N(42)–Cu(2)–N(91)	92.33(19)
Cu(4)–N(82)	2.011(5)	O(4)–Cu(3)–O(3)	81.79(17)
Cu(4)–O(3)	2.279(4)	O(4)–Cu(3)–N(51)	98.78(19)
		O(3)–Cu(3)–N(51)	176.38(18)
		O(4)–Cu(3)–N(62)	163.28(18)
		O(3)–Cu(3)–N(62)	97.28(18)
		N(51)–Cu(3)–N(62)	81.1(2)
		O(4)–Cu(3)–O(2)	97.48(16)

		O(3)–Cu(3)–O(2)	81.71(14)
		N(51)–Cu(3)–O(2)	101.72(16)
		N(62)–Cu(3)–O(2)	98.90(17)
		O(1)–Cu(4)–O(2)	82.14(16)
		O(1)–Cu(4)–N(71)	163.14(18)
		O(2)–Cu(4)–N(71)	98.85(19)
		O(1)–Cu(4)–N(82)	96.72(19)
		O(2)–Cu(4)–N(82)	177.53(17)
		N(71)–Cu(4)–N(82)	81.6(2)
		O(1)–Cu(4)–O(3)	98.11(16)
		O(2)–Cu(4)–O(3)	81.85(14)
		N(71)–Cu(4)–O(3)	98.69(17)
		N(82)–Cu(4)–O(3)	100.49(17)

Complex **3**

Cu(1)–P(1)	2.2310(9)	N(73)–Cu(1)–P(1)	113.32(8)
Cu(1)–P(2)	2.2464(9)	N(73)–Cu(1)–P(2)	112.22(8)
Cu(1)–S(71)	2.5053(10)	P(1)–Cu(1)–P(2)	129.97(4)
Cu(1)–N(73)	2.111(3)	N(73)–Cu(1)–S(71)	67.10(7)
		P(1)–Cu(1)–S(71)	115.38(4)
		P(2)–Cu(1)–S(71)	100.49(3)

Magnetic, electronic absorption and emission spectra

The room temperature μ_{eff} value 1.95 μ_B in **1** corresponds to one unpaired electron. The temperature dependent magnetic susceptibility of **2** was investigated in the 2–300 K temperature range (figure S1 and S2). The $\chi_M T$ value at 300 K (ca. 1.01 cm^3 K mol^{-1}) is considerably lower than the value expected for four non interacting copper(II) centers ($\chi_M T$ = 1.82 cm^3 K mol^{-1}, S = ½). When the temperature is decreased, the $\chi_M T$ product slightly decreases to reach a value of 0.90 cm^3 K mol^{-1} at 2 K indicating weak intramolecular antiferromagnetic coupling. This is corroborated by a sharp decrease in χ_M^{-1} value from 294.82 mol cm^{-3} at 300 K to 2.63 mol cm^{-3} at 2 K. Further the saturated magnetization value 2.23 μ_B at 7 T confirms the presence of antiferromagnetism in this complex which is consistent with the weak Cu···Cu interactions in the crystal structure.

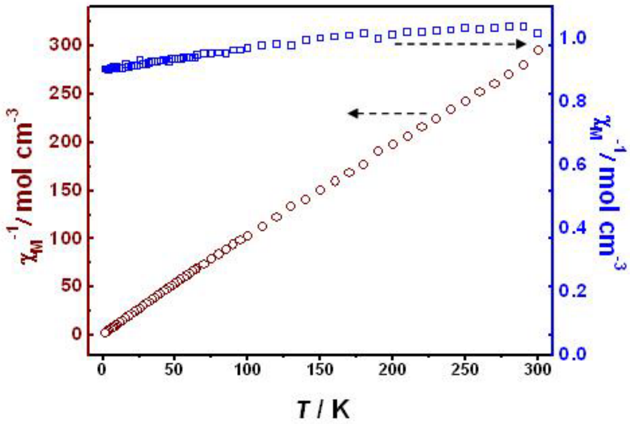


Figure S1. Plot of χ_M^{-1} vs T and χ_MT vs T for Complex **2** in the temperature range of 2 – 300 K.

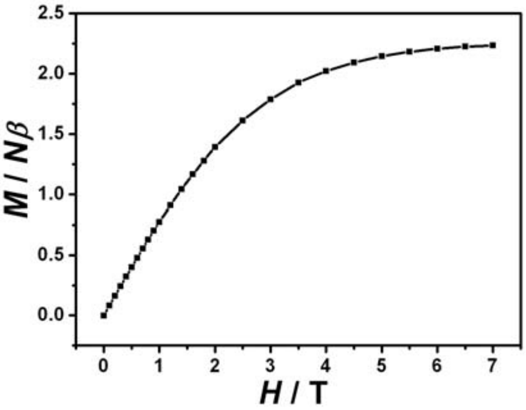


Figure S2. Magnetization vs applied field at 2 K.

The electronic absorption spectra of **1** and **2** in solid as nujol mull (figure S3) and in CH_2Cl_2 solution (figure S4 and S5 respectively) show virtually similar features and encompass an envelope of unsymmetrical absorption bands in the vis-NIR region i.e. 500–1100 nm due to several overlapping transitions. A shoulder observed at around 450 nm is assigned to d-d transitions consistent with the distorted square pyramidal geometry around the copper(II) center. In all the complexes the bands observed below 350 nm are attributed to intraligand charge transfer (ILCT) transitions and metal to ligand charge transfer (MLCT) transition in **3** (figure S6).

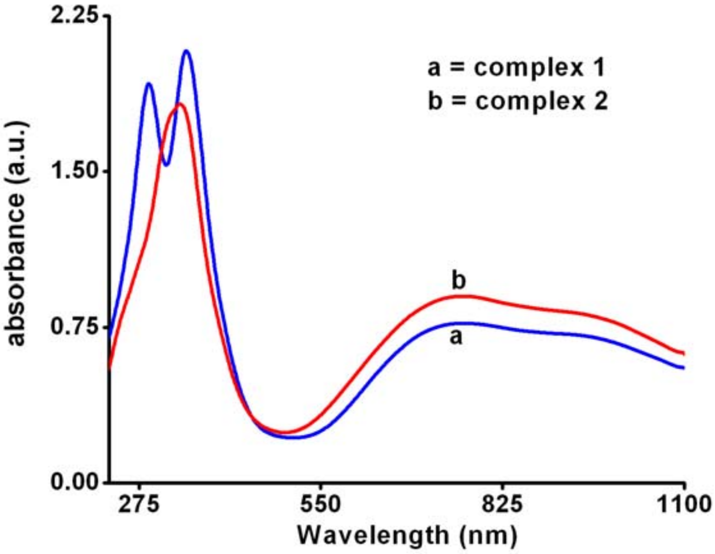
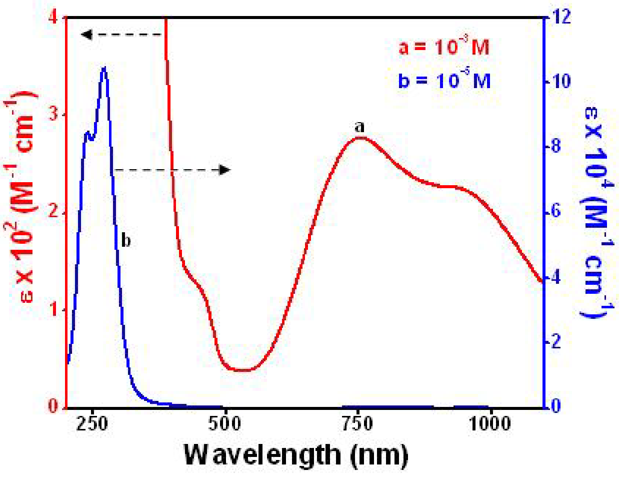


Figure S3. Solid state absorption spectra for complex **1** and **2.**



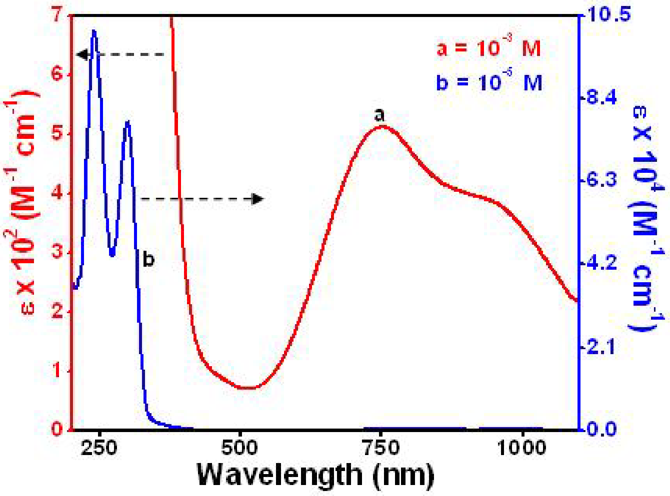
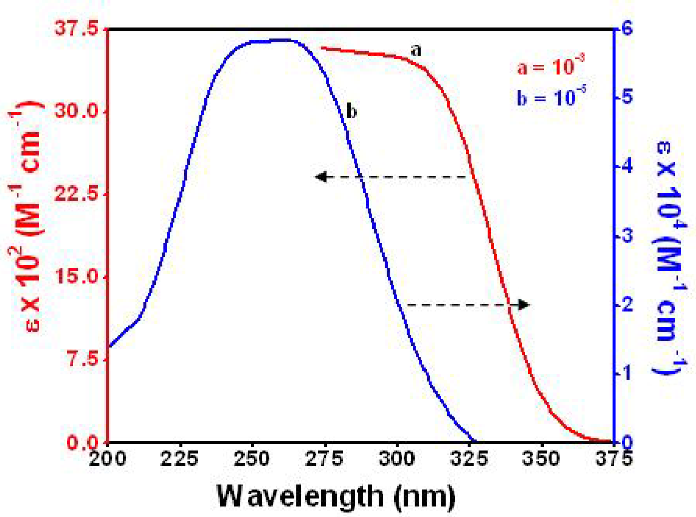


Figure S4. Absorption spectra of complex **1** in CH_2Cl_2 solution.

Figure S5. Absorption spectra of **2** in CH_2Cl_2 solution.

When irradiated at 263 nm complex **3** exhibits one strong and a medium photoluminescence emission bands at about 325 and 475 nm respectively (figure S7) originating from the intraligand π–π^* transitions together with some admixture of copper d-orbitals.[4]



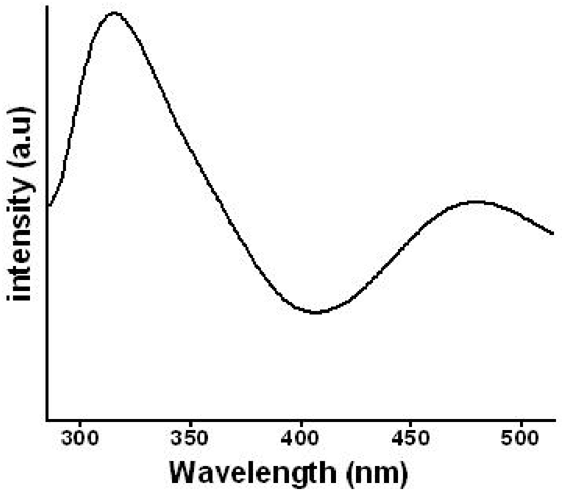


Figure S6. Absorption spectra of complex **3** CH_2Cl_2 solution.

Figure S7. Emission spectra of complex **3** in 10^{-5} CH_2Cl_2 solution.

Crystal Structure

Complex 1

The five coordinate geometry about the Cu(II) center is intermediate between a trigonal bipyramid and a square pyramid with a tau factor[5] of 0.60 indicating that the geometry is slightly closer to the former (ideal tau = 1) than the latter (ideal tau = 0). The metal is bonded to four nitrogen atoms of the two coordinated phen groups and the nitrogen of ligand L″ (Cu(1)–N(51) = 2.063(4) Å). The differences in bond lengths from the copper atom to the four similar nitrogen atoms of the bidentate ligands are indicative of the distortions in geometry. When considered as a trigonal bipyramid the two shorter bonds are those to the two nitrogen atoms N(11) at 2.001(4) Å and N(31) at 1.988(4) Å in axial positions and the longer bonds to N(22) at 2.161(4) Å and N(42) 2.079(3) Å in equatorial positions. The complex packs in extended columns because of hydrogen bonding between the perchlorate ion and the phen ligand and the aromatic ring of the ligand L″ respectively. The π–π stacking interaction between aromatic rings of the π acceptor phen moieties of adjacent chains (average centroid–centroid distance of 3.443 and 3.812 Å, figure S8) very likely contribute to the 3D arrangement of the monomeric cations. Intramolecular π-π stacking interactions (figure S8) between the aromatic rings of the phen and ligand L″ are found with a seperation of 3.941 Å, thus stabilizing the structure of the complex via the relative positioning of the phen and the ligand L″. The dihedral angle between the ligands phen and L″ is – 14.2(2)°.

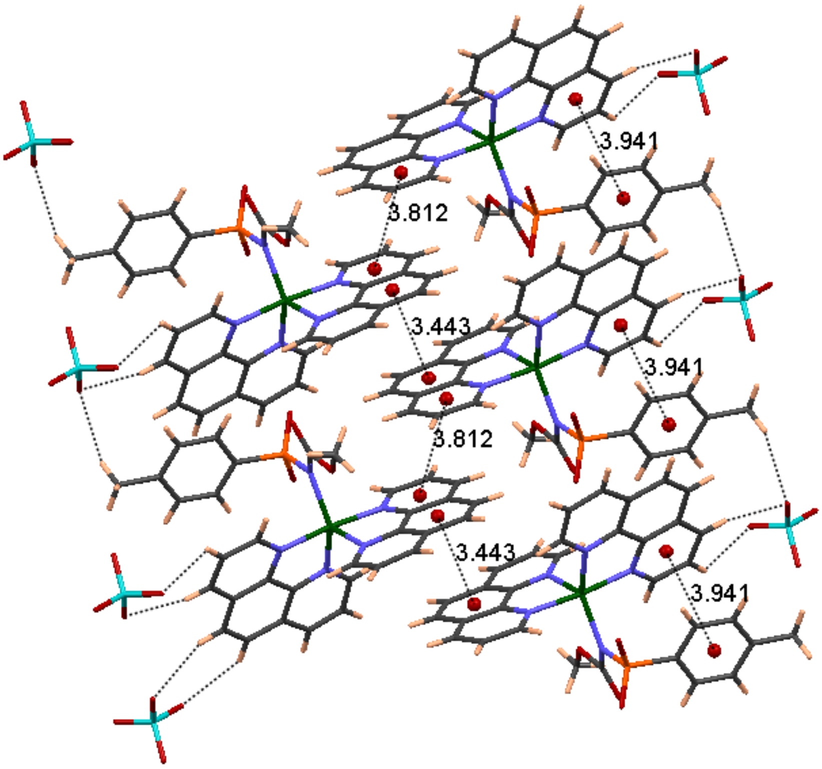


Figure S8. Intermolecular (3.812 and 3.443 Ǻ) and intramolecular (3.941 Ǻ) π-π interactions together with perchlorate to C–H hydrogen bonds in complex **1** (copper-green, oxygen-red, nitrogen-blue, sulfur- orange, carbon-grey, chlorine-light blue, hydrogen-pink, centroid of phenyl ring-red).

Complex 2

The crystal packing (Figure S9) shows alternate channels formed by the cations and anions. The square pyramid environments around copper atoms consists of two nitrogen atoms from a bipyridyl ligand, and two hydroxides in the equatorial plane together with either ligand $CH_3C_6H_4SO_2NCOOCH_3$ for Cu(1) and Cu(2) or μ_3-OH for Cu(3) and Cu(4) in the axial position. It is interesting to note that the donor atoms in each equatorial plane show similar r.m.s deviations from planarity, namely 0.146, 0.131, 0.114, 0.123 Ǻ respectively but the deviations of the copper atoms above the planes differ considerably with distances of 0.350(2), 0.320(2), 0.173(2) and 0.163(2) Ǻ for Cu(1), Cu(2), Cu(3) and Cu(4). The difference clearly arises from the nature of the axial ligand being L″ for the first two and (μ_3-OH) for the second two. The dication depicts a central $[Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(bpy)_4(L'')_2]^{2+}$ core whose topology can be described as "opened" cubane derived by three condensed Cu_2O_2 squares. The Cu–Cu distances are indicative of weak intermetallic interaction. The positioning of the ligands bpy and L″ facilitate the intramolecular π-π stacking interactions (Figure S10) between the aromatic rings of the bpy ligands with a seperation of 3.615, 3.650, 3.673 and 3.703 Ǻ and between the aromatic ring of bpy and L″ with separations of 3.774 and 3.816 Ǻ thus stabilizing the structure of the complex. The dihedral angle between adjacent rings of the bpy in the tetramer are 2.18(9)º for the bpy ligands bonded to Cu(1) and Cu(2) and 5.07(9)º for the bpy bonded to Cu(3) and Cu(4) and that between the rings of bpy and L″ is 7.63(2)º for those bonded to Cu(4) and Cu(2) and 8.17(2)º for those bonded to Cu(3) and Cu(1).

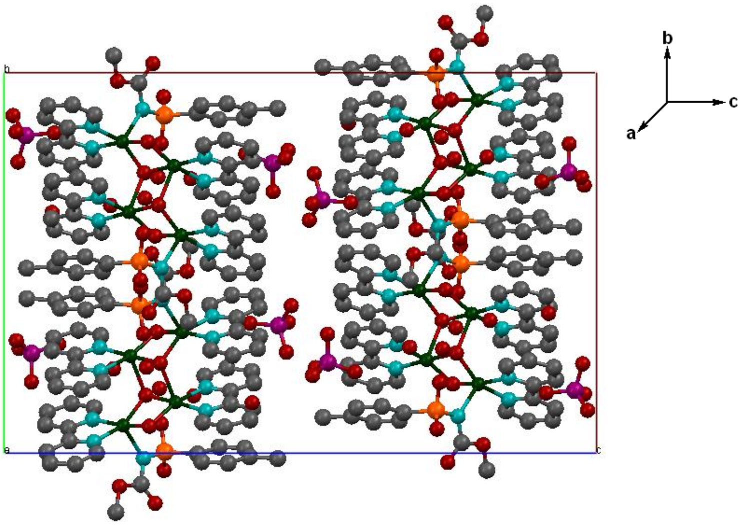


Figure S9. Crystal packing in complex **2**, viewed down the a axis (copper- dark green, oxygen-red, sulfur-orange, nitrogen-blue, chlorine-violet, carbon-grey; the hydrogen atoms bonded to carbon and the solvent water molecules have been omitted for clarity).

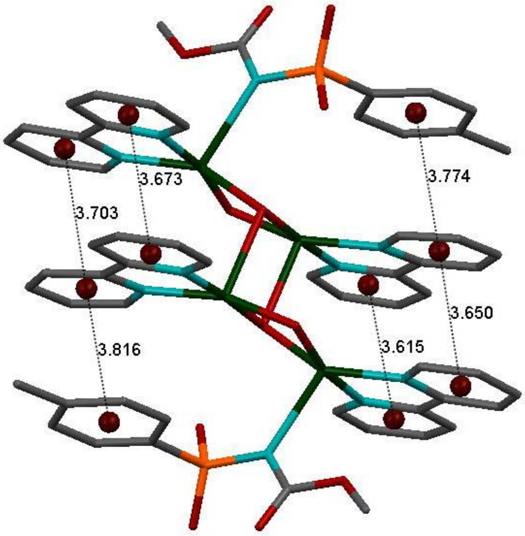


Figure S10. Intramolecular π-π stacking interactions in **2** (copper-green, nitrogen-blue, oxygen-red, sulfur-orange, carbon-black, centroid of phenyl ring-maroon: anion molecules and the hydrogen atoms are omitted for clarity).

One (μ_2-OH) and one (μ_3-OH) groups occupy the basal coordination sites of the copper atoms[6] alongwith the two nitrogen atoms from the bidentate ligand. Bond lengths to the μ_2-hydroxide are shorter than those to the μ_3-hydroxide, thus Cu(1)–O(4), Cu(2)–O(1), Cu(3)–O(4) and Cu(4)–O(1) are 1.900(4), 1.926(4), 1.929(4) and 1.918(4) Ǻ while Cu(1)–O(3), Cu(3)–O(3), Cu(2)–O(2), Cu(4)–O(2) are 1.977(4), 1.962(4), 1.973(4) and 1.969(4) Ǻ respectively. The Cu–N distances are all very similar in the range 1.972(5)-2.014(5) Ǻ. The μ_3-hydroxides are in axial positions of the Cu(3) and Cu(4) coordination spheres at distances of 2.290(4), 2.279(4) Ǻ, while L″ occupies apical positions of Cu(1) and Cu(2) at distances of 2.344(5) and 2.393(5) Ǻ. All four bridging hydroxides show weak hydrogen bonds to perchlorate oxygen atoms. Further hydrogen bonding contributed by the perchlorate ions, water molecules and the hydrogen of bpy and between L″ and water molecules alongwith CH–π interactions between the bpy and L″ lead to the 3D structure of the molecule.

Complex 3

The immediate coordination geometry about Cu(I) in this complex is defined by the coordination of two *cis*-PPh_3 and N, S chelated $CH_3C_6H_4SO_2NCSOCH_3^-$ moiety. The metal environment is an approximate tetrahedron, severely distorted by the small bite of the bidentate ligand. The intraligand S···S separations of 3.571 Ǻ, Figure S11, in **3** are shorter than the sum of van der Waals radii of two sulphur atoms 3.60 Ǻ, suggesting significant non bonding S···S interaction.

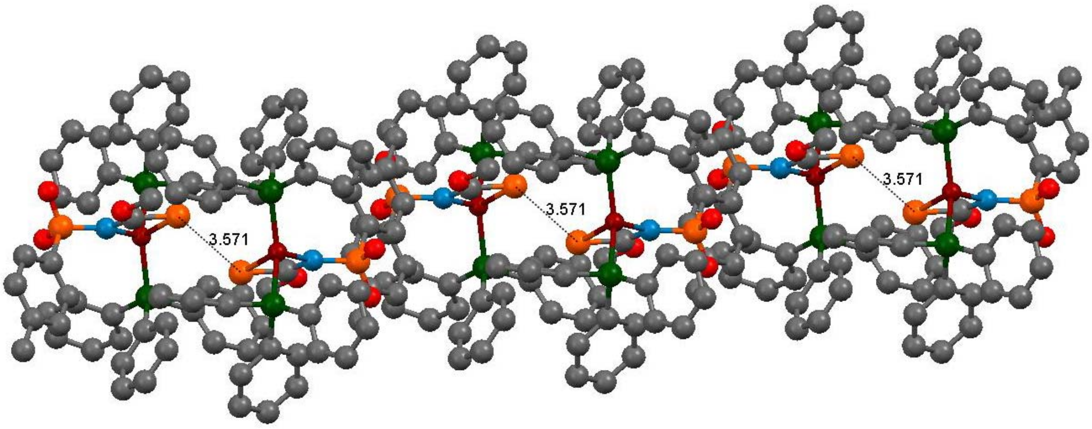


Figure S11. S···S interaction in complex **3** (copper-maroon, phosphorus-green, nitrogen-blue, oxygen-red, sulfur-orange).

Experimental

All reactions were carried out at room temperature under aerobic conditions. The chemicals $Cu(ClO_4)_2{\cdot}6H_2O$, p-methylphenylsulfonamide, 2,2-bipyridine (bpy), 1,10-phenanthroline monohydrate (phen), triphenylphosphine (PPh_3), CS_2 and KOH and solvents dichloromethane, methanol, diethyl ether, and dimethylformamide) were procured from commercial sources. The solvents were purified prior to use by standard methods when required. The dipotassium salt of the ligand p-tolylsulfonyldithiocarbimate, $4\text{-}CH_3C_6H_4SO_2N{=}CS_2K_2{\cdot}2H_2O$ was prepared by reaction of p- tolylsulfonamide, KOH and carbon disulfide in DMF by literature method[7] and was characterized by IR, ^1H and ^{13}C NMR spectroscopy.

Melting points of the complexes were determined in open capillaries with a Gallenkamp apparatus. C, H, N and S elemental analyses were performed on a Model CE-440 CHN analyzer. The IR (4000 – 400 cm^{-1}) spectra were recorded as KBr discs on a Varian 3100 FTIR Spectrophotometer. ^{1}H and ^{13}C NMR of **1** and **2** (DMSO-d6) together with ^{31}P NMR for **3** (CH_2Cl_2) were obtained on a JEOL AL 300 FTNMR spectrometer. TMS as internal standard for ^{1}H and ^{13}C and PCl_3 as external standard (δ 220 ppm) for ^{31}P NMR were used and the chemical shifts were quoted in parts per million. Magnetic susceptibility of the complex **1** was measured at room temperature on a Cahn Faraday electrobalance using $CoHg(SCN)_4$ as calibrant. The variable-temperature magnetic susceptibility of complex **2** was measured in the range of 2-300 K on a Quantum Design MPMS XL-7 SQUID magnetometer under a magnetic field of 1000 Oe. Magnetic data was calibrated for the sample holder, blank and diamagnetism estimated from Pascal's constants. The electronic absorption spectra of all the complexes in solid as nujol mull and in CH_2Cl_2 solution and the emission spectra of **3** in CH_2Cl_2 were collected at room temperature with Shimadzu UV-1700 Pharma Spec and Varian Cary Eclipse fluorescence spectrophotometers respectively.

Synthesis of the complexes

[Cu(phen)$_2$(L″)](ClO$_4$) (**1**)

To a stirred solution of phen (0.099 g, 0.49 mmol) in methanol (10 ml) was added gradually an aqueous solution (10 ml) of the ligand $K_2L\cdot 2H_2O$ (0.180 g, 0.501 mmol) followed by an aqueous solution (10 ml) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.185 g, 0.499 mmol). The reaction mixture was additionally stirred for about 24 h producing greenish blue solution containing black precipitate of copper sulfide. This was filtered and the black precipitate thus obtained was discarded. The greenish blue solution was taken in a 100 ml round bottom flask and its mouth was covered with parafilm and kept for crystallization at room temperature (27-30° C). Greenish blue crystals thus obtained within three weeks were filtered off and washed with methanol/water mixture.

Color, Greenish Blue; Yield (101mg, 0.134 mmol, 81% of maximum achievable 33% based on copper consumption), m.p. 198-200ºC; Anal. Calc. for $CuC_{33}H_{26}N_5O_8ClS$: Calcd. C, 52.73; H, 3.49; N, 9.32; S, 4.27 % Found C, 52.72; H, 3.50, N, 9.28; S, 4.31 %. IR(KBr, cm^{-1}): 1684 ν(C=O); 1257 $\nu_{asym}(SO_2)$; 1146 $\nu_{sym}(SO_2)$. UV-vis [CH_2Cl_2, λ_{max} (nm), ε (M^{-1}cm^{-1})]: 945 (2.25 × 10^{2}), 750 (2.78 × 10^{2}), 450 (1.20 × 10^{2}), 270 (10.5 × 10^{4}), 235 (8.52 × 10^{4}).

$[Cu_4(OH)_4(bpy)_4(L'')_2](ClO_4)_2$ (2)

This blue colored complex was prepared and isolated in good yield adopting exactly the similar procedure for **1** using bpy (0.078 g, 0.49 mmol) in place of phen.

Color, Blue; Yield (98 mg, 0.058 mmol, 93% of maximum achievable 50% based on copper consumption), m.p 190-191ºC; Anal. Calc. for $Cu_4C_{58}H_{66}N_{10}O_{25}Cl_2S_2$: Calcd. C, 41.26; H, 3.70; N, 8.30; S, 3.80 %. Found. C, 41.21, H, 3.72; N, 8.26; S, 3.74 %. IR(KBr, cm^{-1}): 1692 ν(C=O); 1255 $\nu_{asym}(SO_2)$; 1149 $\nu_{sym}(SO_2)$. UV-vis [CH_2Cl_2, λ_{max} (nm), ε ($M^{-1}cm^{-1}$)]: 955 (3.87×10^2), 750 (5.15×10^2), 475 (0.89×10^2), 295 (7.84×10^4), 240 (10.12×10^4).

$[Cu(PPh_3)_2(CH_3C_6H_4SO_2NCSOCH_3)]$ (3)

To a stirring solution containing PPh_3 (0.262 g, 0.998 mmol) in 15 ml methanol and the ligand $K_2L{\cdot}2H_2O$ (0.180 g, 0.501 mmol) in 10 ml water was added slowly an aqueous solution (10 ml) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.185 g, 0.499 mmol). This was, additionally stirred for 10 h and the precipitate thus formed was filtered off and dissolved in CH_2Cl_2. The insoluble black precipitate of copper sulfide was discarded and the yellow solution thus obtained was taken in a 100 ml round bottom flask, its mouth was covered with parafilm and kept for crystallization in a refrigerator. Block shaped crystals of **3** were obtained after complete evaporation of solvent after two weeks.

Color, White; Yield (189 mg, 0.227 mmol, 91% of maximum achievable 50% based on copper consumption), m.p 183-185ºC; Anal. Calc. for $CuC_{45}H_{40}NO_3P_2S_2$: Calcd. C, 64.93; H, 4.84; N, 1.68; S, 7.70. Found. C, 64.89, H, 4.82, N, 1.66, S, 7.72. IR(KBr, cm^{-1}): 1437, 1090, 1046 ν(N—C—S), 1225 $\nu_{asym}(SO_2)$; 1142 $\nu_{sym}(SO_2)$; 873 ν(CS). ^1H NMR (300.40 MHz, $CDCl_3$, ppm): δ 7.18 (d, J = 7.51 Hz, 2H, H2 and H6), 6.89(d, J = 7.81 Hz, 2H, H3 and H5), 2.29 (s, 3H, CH_3), 3.63 (3H, OCH_3), 7.32-7.22 (m, 30H, PPh_3). ^{13}C NMR (75.45 MHz, $CDCl_3$, ppm): δ 197.14 (NCS) 141.43 (C4), 139.43 (C1), 129.31 (C3 and C5), 127.17 (C2 and C6), 21.40 (CH_3), 58.16 (OCH_3); 133.78, 129.58, 128.56, 128.43 (PPh_3). ^{31}P NMR (121.50 MHz, $CDCl_3$): δ –0.928 ppm. UV-vis [CH_2Cl_2, λ_{max} (nm), ε ($M^{-1}cm^{-1}$)]: 310 (3.32×10^3), 265 (5.93×10^4), 240 (5.87×10^4), 230 (4.66×10^4).

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