Electronic Supplementary Material (ESI) for

The Electronic Effects of Ligands on Metal-Coordination Geometry: A Key Role in the Visual Discrimination of Dimethylaminopyridine and its Application towards Chemo-switch

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1. General.

All commercial reagents and solvents were used directly without further purification. ^{1}H and ^{13}C NMR were recorded on Jeol ECA-400 and Bruker 500 DRX spectrometers. ESI-MS spectra were recorded on a Bruker micrOTOF II instrument. Scanning electron microscopy (SEM) experiments were carried out on a Philips XL30 microscope operated at 20 kV. Transmission electron microscopy (TEM) experiments were carried out on a JEOL JEM-2010 transmission electron microscope. UV-Vis absorption was recorded on a UV-Vis 2550 spectroscope (Shimadzu). All reactions were carried out under air unless otherwise noted. Cu(II)-terpyridine complexes **1**, **2** were synthesized according to our previous procedure.[S1]

2. Experimental techniques.

2.1. Gelation test.

For the preparation of the metallogel samples, the solvents were used as purchased. For 1 wt% gel: 5 mg Cu(II)-terpyridine complex was filled into a screw-cap tube and then solvent (0.5 mL) was added by syringe. The exact concentration was determined by differential weighting. The Cu(II)-terpyridine complex was dissolved by heating with a heat-gun or continuous shaking. Then, the samples were allowed to cool down slowly or rest at room temperature to form a gel.

2.2. Scanning electron microscopy (SEM).

SEM experiments were carried out on a Philips XL30 microscope operated at 20 kV. All pictures were taken digitally. For preparation of the samples, a silicon sheet was placed on the surface of the gel for a short time. The gel samples were partly destroyed by knocking the test tube on the table to provide a “print” of the inner volume of the gel.

2.3. Transmission electron microscopy (TEM).

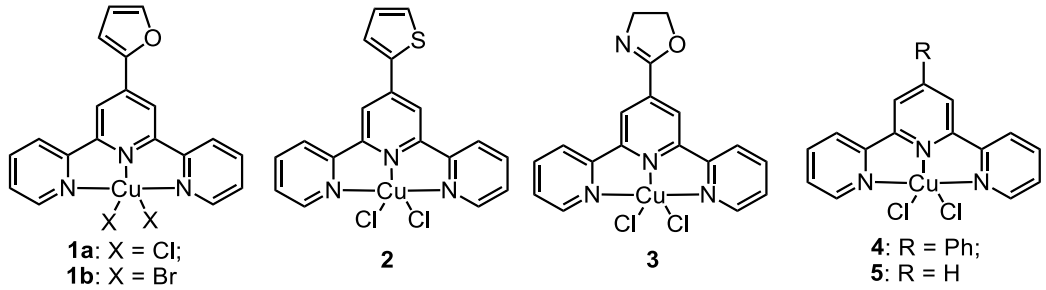
Transmission electron microscopy (TEM) experiments were carried out on a JEOL JEM-2010 transmission

electron microscope. All pictures were taken digitally. For preparation of the samples, carbon-coated copper grids (mesh 200 or 150) were placed on the surface of the gels for a short time. The gel samples were partly destroyed by knocking the test tube on the table to provide a "print" of the inner volume of the gel.

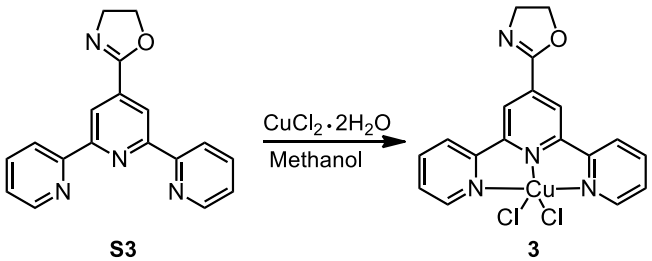
2.4. Single-crystal X-ray structure determination.

Crystal structure determination of complexes **6a**, **7-8**, **10** was performed on a Bruker Smart APEX diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, λ= 0.71073 Å) operating at 50 kV and 30 mA at 293 K. A hemisphere of intensity data was collected at room temperature with a scan width of 0.60° in ω. Empirical absorption corrections were based on SADABS program.[S2] The structures were solved by direct methods and refined by full-matrix least-squares refinement using the SHELXTL-97 program.[S3] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors.

3. Synthesis of Cu(II)-terpyridine complexes 1-5.



Scheme S1. Chemical structure of Cu(II)-terpyridine complexes **1**-**5**.

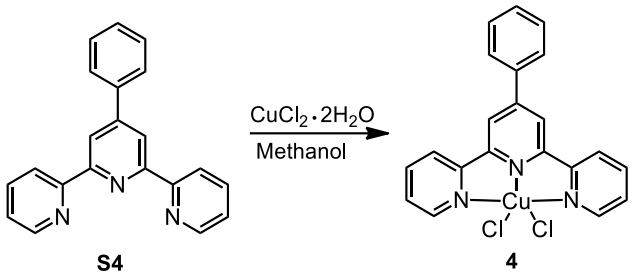


Scheme S2. Synthesis of Cu(II)-terpyridine complex **3**.

4'-(2-oxazolinyl)-2,2':6',2''-terpyridine (S3) was prepared according to literature procedure.[S4] ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.95 (s, 2H), 8.76-8.66 (m, 2H), 8.6 (d, *J* = 7.2 Hz, 2H), 7.85 (t, *J* = 6.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 4.51 (t, *J* = 9.2 Hz, 2H), 4.15 (t, *J* = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 163.36, 156.07; 155.47, 149.17, 137.11, 136.68, 124.03, 123.88, 121.15, 121.04, 119.37, 67.85, 55.15; HR-MS (ESI): *m/z*

303.1246 (Calcd. $[M+H]^+$), 303.1247 (Found. $[M+H]^+$).

Cu(II)-terpyridine complex 3: Ligand **S3** (151 mg, 0.5 mmol) and $CuCl_2 \bullet 2H_2O$ (102 mg, 0.6 mmol) were dissolved in CH_3OH (10 mL). The mixture was further stirred for 24h at r.t.. The green precipitate was collected after filtration, and washed with CH_3OH (3 × 30 mL). Complex **3** was obtained as a green solid after drying under vacuum (4.31 g, 99%). HR-MS (ESI): *m/z* 400.0152 (Calcd. $[M-Cl]^+$), 400.0157 (Found. $[M-Cl]^+$). Due to the poor solubility and paramagnetic property of complex **3**, it is hard to get satisfactory NMR spectra.

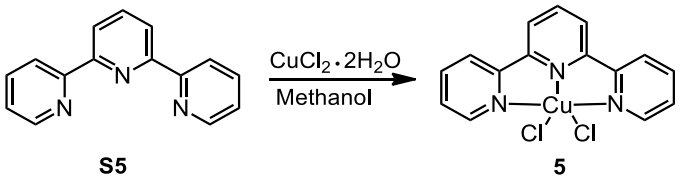


S4 **4**

Scheme S3. Synthesis of Cu(II)-terpyridine complex **4**.

4'-Phenyl-2,2':6',2''-terpyridine (S4) was prepared according to literature procedure.[S5] ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.75-8.73 (m, 4H), 8.68 (d, *J* = 8.0 Hz, 2H), 7.92-7.86 (m, 4H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.37-7.34 (m, 2H); HR-MS (ESI): *m/z* 310.1344 (Calcd. $[M+H]^+$), 310.1347 (Found. $[M+H]^+$).

Cu(II)-terpyridine complex 4: A similar synthetic procedure for complex **3** was applied, complex **4** was provided as a green solid (354 mg, 81%). HR-MS (ESI): *m/z* 407.0251 (Calcd. $[M-Cl]^+$), 407.0263 (Found. $[M-Cl]^+$). Due to the poor solubility and paramagnetic property of complex **4**, it is hard to get satisfactory NMR spectra.

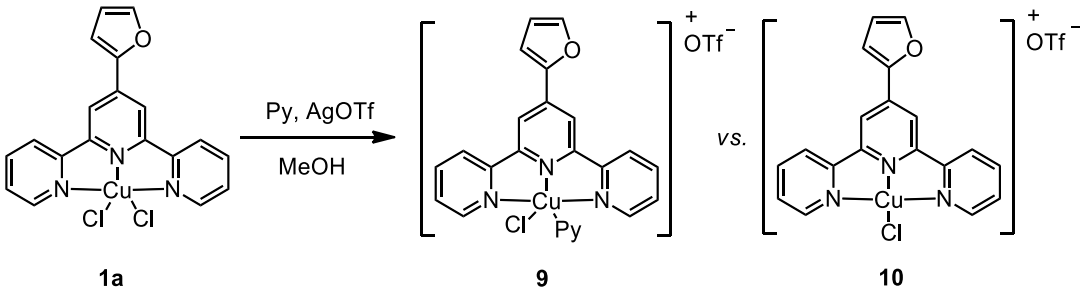


S5 **5**

Scheme S4. Synthesis of Cu(II)-terpyridine complex **5**.

Cu(II)-terpyridine complex 5: A similar synthetic protocol for complex **3** was applied, complex **5** was provided as a green solid (255 mg, 69%). HR-MS (ESI): *m/z* 330.9938 (Calcd. $[M-Cl]^+$), 330.9923 (Found. $[M-Cl]^+$). Due to the poor solubility and paramagnetic property of complex **5**, it is hard to get satisfactory NMR spectra.

4. Synthesis of Cu(II)-terpyridine complex 10



Scheme S5. Chemical structures of Cu(II)-terpyridine complexes **9** and **10.**

Cu(II)-terpyridine complex 10: complex **1a** (219 mg, 0.5 mmol), pyridine (79 mg, 1.0 mmol) and AgOTf (129 mg, 0.5 mmol) were added to MeOH (20 mL) and stirred at r.t. for 24 h under N_2 in darkness. The white AgCl was filtrated away through a short pad of Celite covered with a pad of $MgSO_4$, washed with CH_3OH (3 × 30 mL) and then the filtrate was dried under vacuum to give complex **10** as a blue-green solid (345 mg, 99%). HR-MS (ESI): *m/z* 181.0178 (Calcd. $[M\text{-}Cl\text{-}OTf]^{2+}$), 181.0195 (Found. $[M\text{-}Cl\text{-}OTf]^{2+}$).

5. Visual recognition of *p*-DMAP from various pyridine derivatives via selective metallogel 1a collapse.

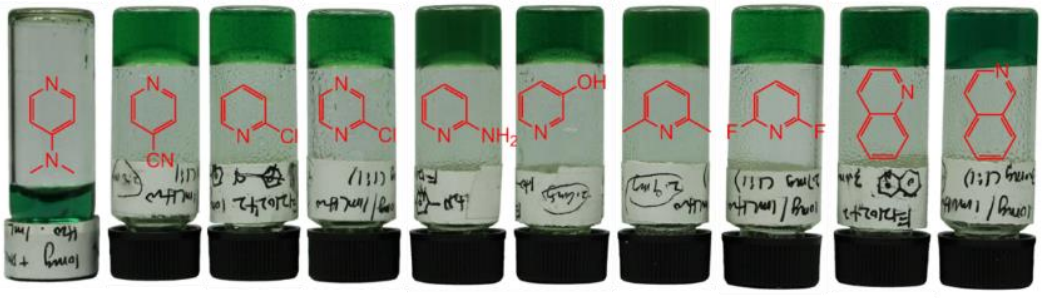


Figure S1. Collapsed sol and hydrogels formed by metallogel **1a**/H_2O (1.0 wt%) with various additional pyridine derivatives.

6. Crystal growth in situ from the collapsed sol formed by metallo-hydrogel with *p*-DMAP.

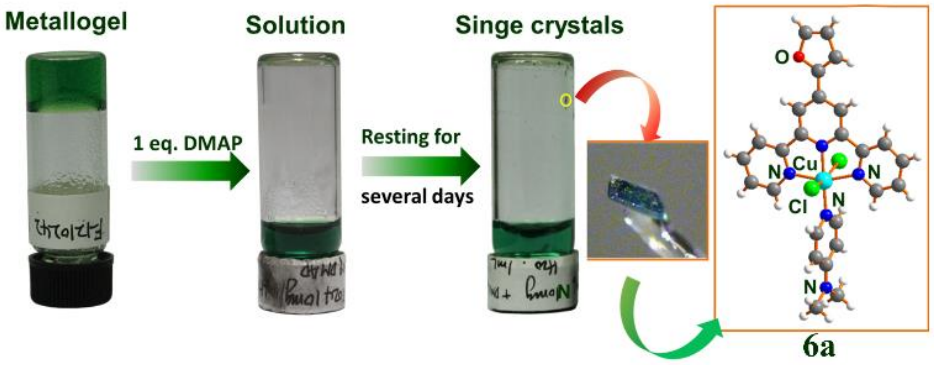


Figure S2. Crystal growth in situ from collapsed sol formed by metallo-hydrogel **1a** (1 wt%) with 1 equiv. *p*-DMAP.

7. The effect of mole ratio of *p*-DMAP to Cu(II)-terpyridine complex 1a to metallogel collapse.

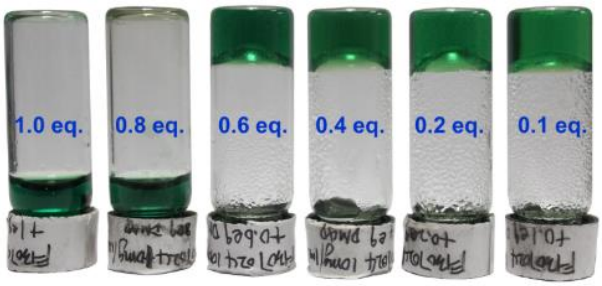


Figure S3. The correlation of mole ratio of *p*-DMAP to Cu(II)-terpyridine complex **1a** leading metallogel collapse.

8. Visual recognition of *p*-DMAP from its positional isomers via selective metallogel 1a collapse.

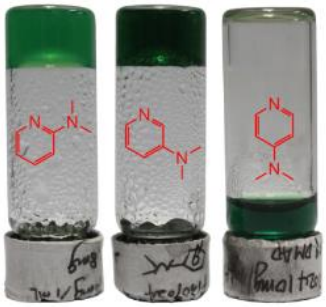


Figure S4. Collapsed sol and hydrogels formed by metallo-hydrogel **1a** (1 wt%) with *o*-, *m*- and *p*-DMAP.

9. The coordination of *p*-DMAP towards Cu(II)-terpyridine complexes.

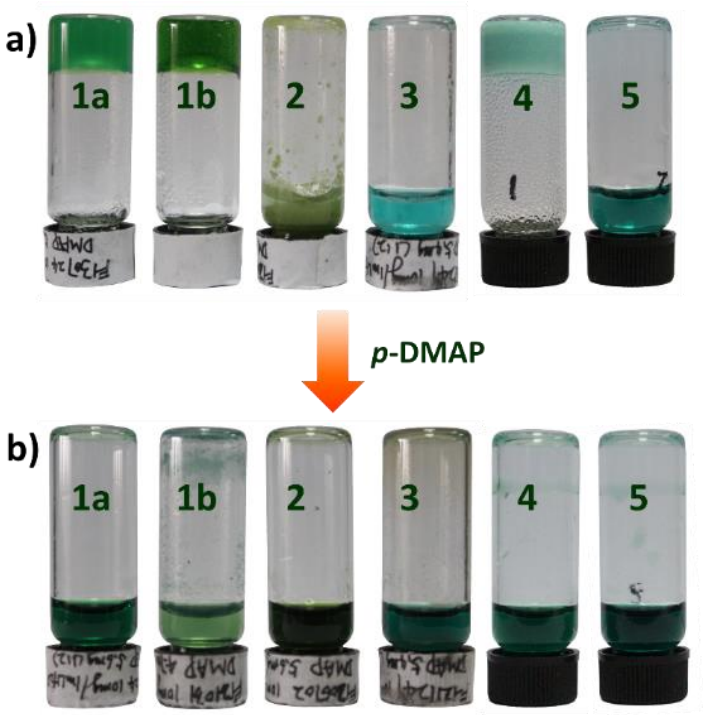


Figure S5. a) Gelation test of complexes **1**-**5** in water, and b) the resulted solutions formed by the samples after gelation test with additional 1 equiv. *p*-DMAP.

10. Hydrogels and collapsed sol formed by metallogel 1a with *p*-substituted pyridines.

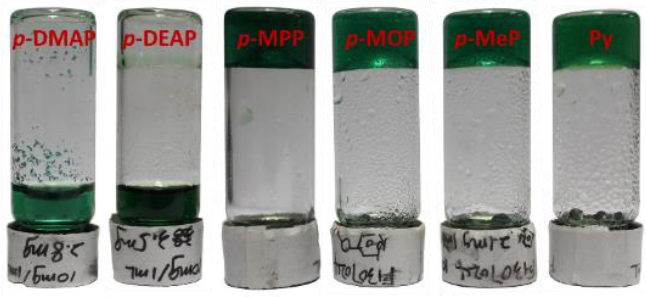


Figure S6. Metallo-hydrogels and solutions formed by metallogel **1a** after the addition of 1 equiv. 4-subsituted pyridines: *p*-DMAP, *p*-DEAP, *p*-MPP, *p*-MOP, *p*-MeP and Py.

11. Crystal structure of Cu(II)-terpyridine complex 6a

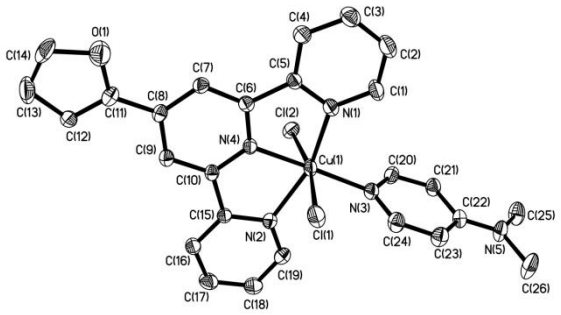


Figure S7. Molecular structure of complex **6a**.

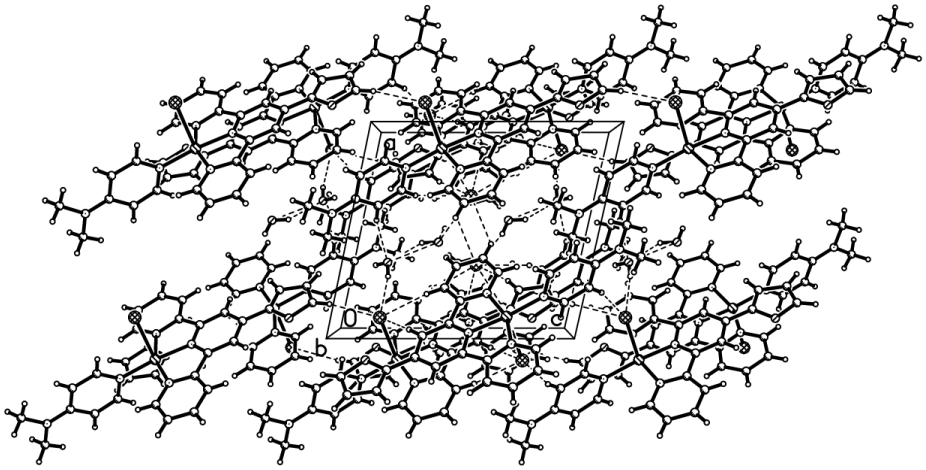


Figure S8. Cell unit formed by complex **6a**.

Table S1. Crystal data and structure refinement for complex **6a**.

Identification code	complex **6a**
Empirical formula	C26 H27 Cl2 Cu N5 O3
Formula weight	591.97
Temperature	293(2) K
Wavelength	0.71073 A

Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.671(8) A alpha = 89.450(9) deg. b = 11.025(8) A beta = 77.812(9) deg. c = 11.868(8) A gamma = 79.520(9) deg.
Volume	1341.3(16) A^3
Z, Calculated density	2, 1.466 Mg/m^3
Absorption coefficient	1.051 mm^-1
F(000)	610
Crystal size	0.15 x 0.13 x 0.10 mm
Theta range for data collection	1.99 to 25.02 deg.
Limiting indices	-11<=h<=12, -10<=k<=13, -13<=l<=14
Reflections collected / unique	5542 / 4609 [R(int) = 0.0982]
Completeness to theta = 25.02	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9022 and 0.8583
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4609 / 0 / 334
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1709
R indices (all data)	R1 = 0.0773, wR2 = 0.1815
Largest diff. peak and hole	1.330 and -0.571 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for complex **6a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	1129(1)	2152(1)	7022(1)	46(1)
Cl(1)	3328(1)	3440(1)	5418(1)	54(1)
Cl(2)	-940(1)	1187(1)	8059(1)	46(1)
N(1)	2139(4)	628(3)	6072(3)	42(1)
N(2)	-23(3)	3842(3)	7404(3)	36(1)
N(3)	2040(4)	1983(3)	8311(3)	41(1)
N(4)	402(3)	2376(3)	5664(3)	31(1)
N(5)	4182(4)	1401(4)	10888(3)	50(1)
O(1)	-872(4)	2075(4)	1830(3)	71(1)
C(1)	3104(5)	-236(4)	6337(4)	52(1)
C(2)	3720(5)	-1216(5)	5621(5)	62(2)
C(3)	3347(5)	-1379(5)	4604(4)	52(1)
C(4)	2356(4)	-524(4)	4324(4)	41(1)
C(5)	1787(4)	491(4)	5062(4)	34(1)
C(6)	764(4)	1506(4)	4828(4)	33(1)
C(7)	223(4)	1618(4)	3861(4)	34(1)

C(8)	-708(4)	2661(4)	3772(4)	34(1)
C(9)	-1068(4)	3566(4)	4667(3)	34(1)
C(10)	-487(4)	3392(4)	5597(3)	31(1)
C(11)	-1270(4)	2850(4)	2764(4)	41(1)
C(12)	-2163(4)	3782(4)	2583(4)	42(1)
C(13)	-2355(6)	3616(6)	1464(5)	71(2)
C(14)	-1596(6)	2612(6)	1023(5)	67(2)
C(15)	-730(4)	4235(4)	6606(3)	32(1)
C(16)	-1617(4)	5329(4)	6761(4)	40(1)
C(17)	-1803(5)	6018(4)	7759(4)	51(1)
C(18)	-1100(5)	5615(5)	8588(4)	54(1)
C(19)	-214(5)	4537(4)	8359(4)	49(1)
C(20)	1745(4)	1238(4)	9192(4)	44(1)
C(21)	2423(4)	1017(4)	10052(4)	43(1)
C(22)	3493(4)	1591(4)	10065(4)	39(1)
C(23)	3786(5)	2371(5)	9138(4)	47(1)
C(24)	3069(5)	2527(5)	8316(4)	46(1)
C(25)	3826(5)	622(5)	11859(4)	61(2)
C(26)	5270(5)	2023(6)	10917(5)	75(2)
O(2)	5531(4)	4527(4)	6372(4)	94(2)
O(3)	6498(4)	3430(6)	8289(5)	122(2)

Table S3. Bond lengths [A] and angles [deg] for complex **6a**.

Cu(1)-N(4)	1.926(3)
Cu(1)-N(3)	1.969(4)
Cu(1)-N(1)	2.030(4)
Cu(1)-N(2)	2.034(4)
Cu(1)-Cl(2)	2.6835(19)
Cu(1)-Cl(1)	3.228(2)
N(1)-C(5)	1.347(5)
N(1)-C(1)	1.356(6)
N(2)-C(19)	1.333(5)
N(2)-C(15)	1.351(5)
N(3)-C(20)	1.344(6)
N(3)-C(24)	1.344(6)
N(4)-C(6)	1.333(5)
N(4)-C(10)	1.344(5)
N(5)-C(22)	1.335(5)
N(5)-C(25)	1.458(6)
N(5)-C(26)	1.459(6)
O(1)-C(11)	1.352(6)
O(1)-C(14)	1.413(7)

C(1)-C(2)	1.359(7)
C(1)-H(1A)	0.9300
C(2)-C(3)	1.371(7)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.377(6)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.391(6)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.482(6)
C(6)-C(7)	1.385(6)
C(7)-C(8)	1.395(6)
C(7)-H(7A)	0.9300
C(8)-C(9)	1.408(6)
C(8)-C(11)	1.445(6)
C(9)-C(10)	1.371(5)
C(9)-H(9A)	0.9300
C(10)-C(15)	1.472(6)
C(11)-C(12)	1.318(6)
C(12)-C(13)	1.404(7)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.289(8)
C(13)-H(13A)	0.9300
C(14)-H(14A)	0.9300
C(15)-C(16)	1.379(6)
C(16)-C(17)	1.372(6)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.382(7)
C(17)-H(17A)	0.9300
C(18)-C(19)	1.367(7)
C(18)-H(18A)	0.9300
C(19)-H(19A)	0.9300
C(20)-C(21)	1.367(6)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.405(6)
C(21)-H(21A)	0.9300
C(22)-C(23)	1.408(6)
C(23)-C(24)	1.353(6)
C(23)-H(23A)	0.9300
C(24)-H(24A)	0.9300
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600

C(26)-H(26C)	0.9600
O(2)-H(1O2)	0.8500
O(2)-H(2O2)	0.8500
O(3)-H(1O3)	0.8499
O(3)-H(2O3)	0.8501

N(4)-Cu(1)-N(3)	173.77(15)
N(4)-Cu(1)-N(1)	79.80(14)
N(3)-Cu(1)-N(1)	98.69(15)
N(4)-Cu(1)-N(2)	79.97(14)
N(3)-Cu(1)-N(2)	100.87(14)
N(1)-Cu(1)-N(2)	159.12(15)
N(4)-Cu(1)-Cl(2)	89.03(11)
N(3)-Cu(1)-Cl(2)	97.17(13)
N(1)-Cu(1)-Cl(2)	97.57(12)
N(2)-Cu(1)-Cl(2)	87.18(11)
N(4)-Cu(1)-Cl(1)	80.84(11)
N(3)-Cu(1)-Cl(1)	92.98(13)
N(1)-Cu(1)-Cl(1)	82.34(12)
N(2)-Cu(1)-Cl(1)	89.41(11)
Cl(2)-Cu(1)-Cl(1)	169.73(4)
C(5)-N(1)-C(1)	118.1(4)
C(5)-N(1)-Cu(1)	114.2(3)
C(1)-N(1)-Cu(1)	127.7(3)
C(19)-N(2)-C(15)	118.1(4)
C(19)-N(2)-Cu(1)	127.8(3)
C(15)-N(2)-Cu(1)	113.9(3)
C(20)-N(3)-C(24)	115.6(4)
C(20)-N(3)-Cu(1)	122.2(3)
C(24)-N(3)-Cu(1)	121.9(3)
C(6)-N(4)-C(10)	121.5(3)
C(6)-N(4)-Cu(1)	119.4(3)
C(10)-N(4)-Cu(1)	119.1(3)
C(22)-N(5)-C(25)	121.5(4)
C(22)-N(5)-C(26)	122.4(4)
C(25)-N(5)-C(26)	116.0(4)
C(11)-O(1)-C(14)	104.9(4)
N(1)-C(1)-C(2)	122.3(5)
N(1)-C(1)-H(1A)	118.8
C(2)-C(1)-H(1A)	118.8
C(1)-C(2)-C(3)	120.0(5)
C(1)-C(2)-H(2A)	120.0
C(3)-C(2)-H(2A)	120.0
C(2)-C(3)-C(4)	118.7(5)

C(2)-C(3)-H(3A)	120.7
C(4)-C(3)-H(3A)	120.7
C(3)-C(4)-C(5)	119.3(4)
C(3)-C(4)-H(4A)	120.3
C(5)-C(4)-H(4A)	120.3
N(1)-C(5)-C(4)	121.5(4)
N(1)-C(5)-C(6)	114.0(4)
C(4)-C(5)-C(6)	124.5(4)
N(4)-C(6)-C(7)	120.8(4)
N(4)-C(6)-C(5)	112.4(4)
C(7)-C(6)-C(5)	126.8(4)
C(6)-C(7)-C(8)	118.9(4)
C(6)-C(7)-H(7A)	120.5
C(8)-C(7)-H(7A)	120.5
C(7)-C(8)-C(9)	119.1(4)
C(7)-C(8)-C(11)	121.4(4)
C(9)-C(8)-C(11)	119.5(4)
C(10)-C(9)-C(8)	118.7(4)
C(10)-C(9)-H(9A)	120.6
C(8)-C(9)-H(9A)	120.6
N(4)-C(10)-C(9)	121.0(4)
N(4)-C(10)-C(15)	112.4(3)
C(9)-C(10)-C(15)	126.5(4)
C(12)-C(11)-O(1)	110.4(4)
C(12)-C(11)-C(8)	127.2(4)
O(1)-C(11)-C(8)	122.3(4)
C(11)-C(12)-C(13)	107.3(4)
C(11)-C(12)-H(12A)	126.3
C(13)-C(12)-H(12A)	126.3
C(14)-C(13)-C(12)	107.8(5)
C(14)-C(13)-H(13A)	126.1
C(12)-C(13)-H(13A)	126.1
C(13)-C(14)-O(1)	109.5(5)
C(13)-C(14)-H(14A)	125.2
O(1)-C(14)-H(14A)	125.2
N(2)-C(15)-C(16)	121.5(4)
N(2)-C(15)-C(10)	114.5(3)
C(16)-C(15)-C(10)	124.0(4)
C(17)-C(16)-C(15)	119.0(4)
C(17)-C(16)-H(16A)	120.5
C(15)-C(16)-H(16A)	120.5
C(16)-C(17)-C(18)	120.0(4)
C(16)-C(17)-H(17A)	120.0
C(18)-C(17)-H(17A)	120.0

C(19)-C(18)-C(17)	117.6(4)
C(19)-C(18)-H(18A)	121.2
C(17)-C(18)-H(18A)	121.2
N(2)-C(19)-C(18)	123.8(4)
N(2)-C(19)-H(19A)	118.1
C(18)-C(19)-H(19A)	118.1
N(3)-C(20)-C(21)	124.0(4)
N(3)-C(20)-H(20A)	118.0
C(21)-C(20)-H(20A)	118.0
C(20)-C(21)-C(22)	120.4(4)
C(20)-C(21)-H(21A)	119.8
C(22)-C(21)-H(21A)	119.8
N(5)-C(22)-C(21)	122.4(4)
N(5)-C(22)-C(23)	122.8(4)
C(21)-C(22)-C(23)	114.8(4)
C(24)-C(23)-C(22)	120.7(4)
C(24)-C(23)-H(23A)	119.6
C(22)-C(23)-H(23A)	119.6
N(3)-C(24)-C(23)	124.3(4)
N(3)-C(24)-H(24A)	117.8
C(23)-C(24)-H(24A)	117.8
N(5)-C(25)-H(25A)	109.5
N(5)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
N(5)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(5)-C(26)-H(26A)	109.5
N(5)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
N(5)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
H(1O2)-O(2)-H(2O2)	107.7
H(1O3)-O(3)-H(2O3)	107.7

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for complex **6a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

	U11	U22	U33	U23	U13	U12

Cu(1)	57(1)	41(1)	42(1)	-4(1)	-29(1)	9(1)
Cl(1)	51(1)	51(1)	60(1)	10(1)	-20(1)	0(1)
Cl(2)	53(1)	49(1)	42(1)	5(1)	-16(1)	-20(1)
N(1)	42(2)	37(2)	44(2)	0(2)	-14(2)	3(2)
N(2)	39(2)	36(2)	34(2)	3(2)	-13(2)	-7(2)
N(3)	47(2)	40(2)	38(2)	0(2)	-17(2)	-2(2)
N(4)	31(2)	33(2)	31(2)	2(1)	-9(1)	-3(2)
N(5)	40(2)	68(3)	49(2)	17(2)	-22(2)	-15(2)
O(1)	73(3)	78(3)	60(2)	3(2)	-21(2)	-1(2)
C(1)	52(3)	49(3)	52(3)	2(2)	-22(2)	12(2)
C(2)	57(3)	52(3)	70(4)	4(3)	-22(3)	14(3)
C(3)	53(3)	46(3)	50(3)	-4(2)	-7(2)	5(2)
C(4)	43(3)	41(3)	36(2)	1(2)	-8(2)	-5(2)
C(5)	34(2)	31(2)	40(2)	6(2)	-10(2)	-6(2)
C(6)	30(2)	32(2)	37(2)	5(2)	-7(2)	-8(2)
C(7)	35(2)	35(2)	31(2)	-2(2)	-7(2)	-5(2)
C(8)	30(2)	41(2)	31(2)	5(2)	-8(2)	-11(2)
C(9)	31(2)	37(2)	35(2)	5(2)	-9(2)	-6(2)
C(10)	28(2)	34(2)	32(2)	5(2)	-7(2)	-6(2)
C(11)	41(3)	54(3)	33(2)	0(2)	-11(2)	-13(2)
C(12)	42(3)	35(2)	48(3)	-7(2)	-17(2)	2(2)
C(13)	64(4)	75(4)	84(4)	23(3)	-46(3)	-4(3)
C(14)	90(4)	91(5)	34(3)	4(3)	-31(3)	-31(4)
C(15)	31(2)	31(2)	37(2)	6(2)	-10(2)	-10(2)
C(16)	40(2)	38(2)	45(3)	7(2)	-13(2)	-8(2)
C(17)	56(3)	40(3)	52(3)	-8(2)	-8(2)	1(2)
C(18)	64(3)	46(3)	50(3)	-13(2)	-16(3)	-1(2)
C(19)	59(3)	47(3)	45(3)	-4(2)	-24(2)	-8(2)
C(20)	42(3)	47(3)	49(3)	6(2)	-19(2)	-11(2)
C(21)	40(2)	46(3)	47(3)	13(2)	-14(2)	-12(2)
C(22)	34(2)	46(3)	38(2)	6(2)	-11(2)	-1(2)
C(23)	43(3)	55(3)	47(3)	14(2)	-11(2)	-20(2)
C(24)	50(3)	54(3)	39(3)	15(2)	-14(2)	-13(2)
C(25)	63(3)	82(4)	44(3)	23(3)	-23(3)	-11(3)
C(26)	55(3)	109(5)	78(4)	24(4)	-38(3)	-34(3)
O(2)	81(3)	112(4)	105(4)	39(3)	-49(3)	-26(3)
O(3)	66(3)	150(5)	135(5)	59(4)	8(3)	-22(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for complex **6a**.

	x	y	z	U(eq)
H(1A)	3352	-154	7034	63
H(2A)	4396	-1777	5820	74

H(3A)	3754	-2054	4114	63
H(4A)	2071	-624	3649	49
H(7A)	477	1008	3279	41
H(9A)	-1688	4269	4629	41
H(12A)	-2588	4429	3100	50
H(13A)	-2928	4138	1104	85
H(14A)	-1534	2289	288	81
H(16A)	-2083	5597	6197	48
H(17A)	-2401	6756	7878	62
H(18A)	-1225	6061	9277	64
H(19A)	284	4274	8901	58
H(20A)	1036	850	9218	53
H(21A)	2175	482	10634	52
H(23A)	4481	2785	9090	56
H(24A)	3303	3044	7715	56
H(25A)	3110	249	11753	92
H(25B)	3572	1114	12560	92
H(25C)	4559	-12	11902	92
H(26A)	5428	2506	10242	112
H(26B)	6036	1419	10935	112
H(26C)	5061	2553	11593	112
H(1O2)	5567	4659	7068	113
H(2O2)	4871	5015	6233	113
H(1O3)	6639	3915	8782	146
H(2O3)	7156	2848	8132	146

12. Crystal structure of Cu(II)-terpyridine complex 7.

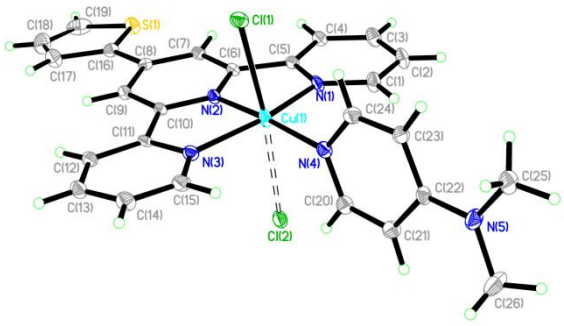


Figure S9. Molecular Structure of Complex **7**.

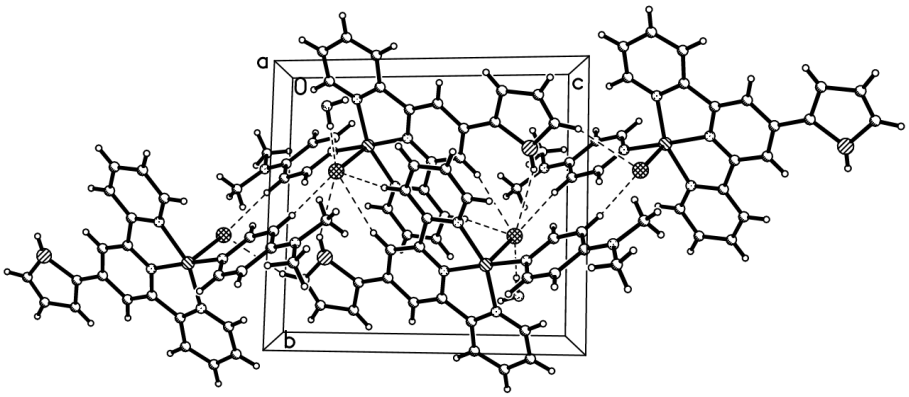


Figure S10. Cell unit formed by complex **7**.

Table S6. Crystal data and structure refinement for complex **7**.

Identification code	complex **7**	
Empirical formula	C26 H27 Cl2 Cu N5 O2 S	
Formula weight	608.02	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.634(3) Å	a= 89.311(4) °.
	b = 10.982(3) Å	b= 77.918(4) °.
	c = 11.926(3) Å	g = 79.929(4) °.
Volume	1340.6(6) $Å^3$	
Z	2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	1.126 mm^{-1}	
F(000)	626	
Crystal size	0.110 x 0.040 x 0.030 mm^3	
Theta range for data collection	1.747 to 25.997 °.	
Index ranges	-13<=h<=12, -12<=k<=13, -14<=l<=14	
Reflections collected	8686	
Independent reflections	5183 [R(int) = 0.0338]	
Completeness to theta = 25.242 °	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5183 / 8 / 352	

Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1666
R indices (all data)	R1 = 0.0831, wR2 = 0.2024
Extinction coefficient	n/a
Largest diff. peak and hole	1.465 and -0.907 e.$Å^{-3}$

Table S7. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for complex **7**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	3904(1)	2832(1)	2970(1)	25(1)
Cl(1)	5943(1)	3821(1)	1974(1)	27(1)
Cl(2)	8384(1)	8404(1)	5361(1)	31(1)
N(1)	2888(4)	4343(3)	3928(3)	23(1)
N(2)	4623(3)	2585(3)	4328(3)	19(1)
N(3)	5063(4)	1136(4)	2568(3)	23(1)
N(4)	2963(4)	3015(4)	1706(3)	23(1)
N(5)	782(4)	3640(4)	-853(4)	33(1)
C(1)	1909(5)	5189(5)	3670(4)	32(1)
C(2)	1287(5)	6195(5)	4384(4)	34(1)
C(3)	1681(5)	6325(5)	5405(4)	33(1)
C(4)	2675(4)	5474(4)	5676(4)	25(1)
C(5)	3241(4)	4478(4)	4936(4)	20(1)
C(6)	4266(4)	3452(4)	5167(4)	19(1)
C(7)	4825(4)	3323(4)	6126(4)	21(1)
C(8)	5755(4)	2281(4)	6213(4)	20(1)
C(9)	6101(4)	1381(4)	5316(4)	20(1)
C(10)	5511(4)	1566(4)	4377(4)	19(1)
C(11)	5768(4)	736(4)	3363(4)	18(1)
C(12)	6649(4)	-377(4)	3225(4)	25(1)
C(13)	6840(5)	-1039(4)	2203(4)	28(1)
C(14)	6146(5)	-592(5)	1376(4)	31(1)
C(15)	5263(5)	465(4)	1601(4)	28(1)
C(16)	6335(4)	2079(4)	7224(4)	23(1)
C(17)	7379(3)	1011(3)	7399(2)	35(1)
C(18)	7510(6)	1172(6)	8567(6)	50(2)
C(19)	6783(7)	2166(7)	9135(5)	48(2)
S(1)	5853(2)	3013(2)	8398(1)	29(1)
S(1')	7379(3)	1011(3)	7399(2)	35(1)
C(19')	7510(6)	1172(6)	8567(6)	50(2)

C(18')	6783(7)	2166(7)	9135(5)	48(2)
C(17')	5853(2)	3013(2)	8398(1)	29(1)
C(20)	1931(5)	2457(5)	1705(4)	27(1)
C(21)	1188(5)	2635(5)	893(4)	28(1)
C(22)	1484(4)	3448(4)	-27(4)	24(1)
C(23)	2565(5)	4022(5)	-11(4)	26(1)
C(24)	3252(5)	3791(5)	830(4)	28(1)
C(25)	1147(5)	4426(5)	-1821(4)	35(1)
C(26)	-298(5)	2993(6)	-878(5)	47(2)
O(1)	601(4)	9428(4)	6346(4)	47(1)
O(2)	8472(4)	1541(5)	1695(4)	62(1)

Table S8. Bond lengths [Å] and angles [°] for complex **7**.

Cu(1)-N(2)	1.927(4)
Cu(1)-N(4)	1.967(4)
Cu(1)-N(1)	2.032(4)
Cu(1)-N(3)	2.046(4)
Cu(1)-Cl(1)	2.6474(13)
Cu(1)-Cl(2)	3.2840(5)
N(1)-C(5)	1.350(6)
N(1)-C(1)	1.353(6)
N(2)-C(6)	1.338(5)
N(2)-C(10)	1.342(6)
N(3)-C(15)	1.334(6)
N(3)-C(11)	1.352(6)
N(4)-C(20)	1.348(6)
N(4)-C(24)	1.358(6)
N(5)-C(22)	1.349(6)
N(5)-C(26)	1.457(7)
N(5)-C(25)	1.461(6)
C(1)-C(2)	1.384(7)
C(1)-H(1)	0.9500
C(2)-C(3)	1.384(7)
C(2)-H(2)	0.9500
C(3)-C(4)	1.374(7)
C(3)-H(3)	0.9500
C(4)-C(5)	1.381(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.491(6)
C(6)-C(7)	1.390(6)
C(7)-C(8)	1.394(6)
C(7)-H(7)	0.9500

C(8)-C(9)	1.411(6)
C(8)-C(16)	1.463(6)
C(9)-C(10)	1.390(6)
C(9)-H(9)	0.9500
C(10)-C(11)	1.472(6)
C(11)-C(12)	1.393(6)
C(12)-C(13)	1.387(6)
C(12)-H(12)	0.9500
C(13)-C(14)	1.388(7)
C(13)-H(13)	0.9500
C(14)-C(15)	1.349(7)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-C(17)	1.512(6)
C(16)-S(1)	1.681(5)
C(17)-C(18)	1.445(7)
C(17)-H(17)	0.9500
C(18)-C(19)	1.323(10)
C(18)-H(18)	0.9500
C(19)-S(1)	1.625(7)
C(19)-H(19)	0.9500
C(20)-C(21)	1.364(7)
C(20)-H(20)	0.9500
C(21)-C(22)	1.425(6)
C(21)-H(21)	0.9500
C(22)-C(23)	1.408(6)
C(23)-C(24)	1.357(7)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
O(1)-H(1A)	0.85(2)
O(1)-H(1B)	0.840(19)
O(2)-H(2A)	0.845(18)
O(2)-H(2B)	0.830(19)

N(2)-Cu(1)-N(4)	172.42(15)
N(2)-Cu(1)-N(1)	79.82(15)
N(4)-Cu(1)-N(1)	98.06(15)
N(2)-Cu(1)-N(3)	80.25(15)

N(4)-Cu(1)-N(3)	101.03(15)
N(1)-Cu(1)-N(3)	159.43(15)
N(2)-Cu(1)-Cl(1)	89.43(11)
N(4)-Cu(1)-Cl(1)	98.08(12)
N(1)-Cu(1)-Cl(1)	97.43(11)
N(3)-Cu(1)-Cl(1)	87.44(11)
C(5)-N(1)-C(1)	118.2(4)
C(5)-N(1)-Cu(1)	114.5(3)
C(1)-N(1)-Cu(1)	127.3(3)
C(6)-N(2)-C(10)	122.1(4)
C(6)-N(2)-Cu(1)	119.4(3)
C(10)-N(2)-Cu(1)	118.5(3)
C(15)-N(3)-C(11)	118.6(4)
C(15)-N(3)-Cu(1)	127.7(3)
C(11)-N(3)-Cu(1)	113.4(3)
C(20)-N(4)-C(24)	116.2(4)
C(20)-N(4)-Cu(1)	122.0(3)
C(24)-N(4)-Cu(1)	121.7(3)
C(22)-N(5)-C(26)	121.8(4)
C(22)-N(5)-C(25)	121.1(4)
C(26)-N(5)-C(25)	116.8(4)
N(1)-C(1)-C(2)	122.5(5)
N(1)-C(1)-H(1)	118.7
C(2)-C(1)-H(1)	118.7
C(3)-C(2)-C(1)	118.2(5)
C(3)-C(2)-H(2)	120.9
C(1)-C(2)-H(2)	120.9
C(4)-C(3)-C(2)	119.9(5)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	119.1(4)
C(3)-C(4)-H(4)	120.5
C(5)-C(4)-H(4)	120.5
N(1)-C(5)-C(4)	122.1(4)
N(1)-C(5)-C(6)	113.7(4)
C(4)-C(5)-C(6)	124.3(4)
N(2)-C(6)-C(7)	120.3(4)
N(2)-C(6)-C(5)	112.3(4)
C(7)-C(6)-C(5)	127.3(4)
C(6)-C(7)-C(8)	119.7(4)
C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2
C(7)-C(8)-C(9)	118.5(4)
C(7)-C(8)-C(16)	121.8(4)

C(9)-C(8)-C(16)	119.7(4)
C(10)-C(9)-C(8)	119.0(4)
C(10)-C(9)-H(9)	120.5
C(8)-C(9)-H(9)	120.5
N(2)-C(10)-C(9)	120.4(4)
N(2)-C(10)-C(11)	113.3(4)
C(9)-C(10)-C(11)	126.3(4)
N(3)-C(11)-C(12)	122.0(4)
N(3)-C(11)-C(10)	114.4(4)
C(12)-C(11)-C(10)	123.6(4)
C(13)-C(12)-C(11)	117.5(4)
C(13)-C(12)-H(12)	121.3
C(11)-C(12)-H(12)	121.3
C(12)-C(13)-C(14)	119.7(5)
C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1
C(15)-C(14)-C(13)	119.0(4)
C(15)-C(14)-H(14)	120.5
C(13)-C(14)-H(14)	120.5
N(3)-C(15)-C(14)	123.0(5)
N(3)-C(15)-H(15)	118.5
C(14)-C(15)-H(15)	118.5
C(8)-C(16)-C(17)	126.5(4)
C(8)-C(16)-S(1)	123.0(4)
C(17)-C(16)-S(1)	110.5(3)
C(18)-C(17)-C(16)	104.7(4)
C(18)-C(17)-H(17)	127.7
C(16)-C(17)-H(17)	127.7
C(19)-C(18)-C(17)	116.3(5)
C(19)-C(18)-H(18)	121.9
C(17)-C(18)-H(18)	121.9
C(18)-C(19)-S(1)	113.8(4)
C(18)-C(19)-H(19)	123.1
S(1)-C(19)-H(19)	123.1
C(19)-S(1)-C(16)	94.7(3)
N(4)-C(20)-C(21)	123.9(4)
N(4)-C(20)-H(20)	118.0
C(21)-C(20)-H(20)	118.0
C(20)-C(21)-C(22)	120.3(4)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9
N(5)-C(22)-C(23)	122.8(4)
N(5)-C(22)-C(21)	122.2(4)
C(23)-C(22)-C(21)	115.0(4)

C(24)-C(23)-C(22)	120.9(4)
C(24)-C(23)-H(23)	119.6
C(22)-C(23)-H(23)	119.6
C(23)-C(24)-N(4)	123.8(4)
C(23)-C(24)-H(24)	118.1
N(4)-C(24)-H(24)	118.1
N(5)-C(25)-H(25A)	109.5
N(5)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
N(5)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(5)-C(26)-H(26A)	109.5
N(5)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
N(5)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
H(1A)-O(1)-H(1B)	105(3)
H(2A)-O(2)-H(2B)	108(3)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **7**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	36(1)	18(1)	23(1)	-3(1)	-16(1)	3(1)
Cl(1)	34(1)	24(1)	27(1)	1(1)	-10(1)	-9(1)
Cl(2)	36(1)	23(1)	34(1)	2(1)	-14(1)	0(1)
N(1)	29(2)	14(2)	25(2)	5(2)	-10(2)	0(2)
N(2)	22(2)	15(2)	20(2)	-2(1)	-5(1)	0(1)
N(3)	27(2)	20(2)	22(2)	-1(2)	-7(2)	-5(2)
N(4)	32(2)	20(2)	20(2)	1(2)	-11(2)	-2(2)
N(5)	30(2)	40(3)	33(2)	14(2)	-16(2)	-10(2)
C(1)	34(3)	27(3)	32(3)	-6(2)	-12(2)	7(2)
C(2)	38(3)	23(3)	36(3)	0(2)	-8(2)	9(2)
C(3)	37(3)	24(3)	33(3)	-5(2)	-4(2)	5(2)
C(4)	31(3)	20(2)	25(2)	2(2)	-7(2)	-4(2)
C(5)	22(2)	19(2)	21(2)	1(2)	-5(2)	-5(2)

C(6)	23(2)	14(2)	19(2)	1(2)	-4(2)	-4(2)
C(7)	26(2)	17(2)	18(2)	-2(2)	-4(2)	-4(2)
C(8)	21(2)	21(2)	20(2)	0(2)	-5(2)	-7(2)
C(9)	23(2)	19(2)	17(2)	-1(2)	-5(2)	-2(2)
C(10)	21(2)	15(2)	21(2)	6(2)	-4(2)	-5(2)
C(11)	23(2)	12(2)	20(2)	3(2)	-4(2)	-6(2)
C(12)	28(2)	21(2)	27(2)	1(2)	-9(2)	-5(2)
C(13)	31(3)	21(2)	30(3)	-4(2)	-6(2)	0(2)
C(14)	40(3)	28(3)	26(2)	-5(2)	-10(2)	-5(2)
C(15)	39(3)	25(3)	25(2)	1(2)	-18(2)	-9(2)
C(16)	26(2)	28(3)	19(2)	1(2)	-7(2)	-8(2)
C(17)	48(2)	29(2)	31(2)	-3(1)	-19(1)	-2(1)
C(18)	50(4)	53(4)	55(4)	23(3)	-32(3)	-8(3)
C(19)	66(4)	64(4)	24(3)	-1(3)	-16(3)	-35(4)
S(1)	37(1)	26(1)	25(1)	-4(1)	-12(1)	-1(1)
S(1')	48(2)	29(2)	31(2)	-3(1)	-19(1)	-2(1)
C(19')	50(4)	53(4)	55(4)	23(3)	-32(3)	-8(3)
C(18')	66(4)	64(4)	24(3)	-1(3)	-16(3)	-35(4)
C(17')	37(1)	26(1)	25(1)	-4(1)	-12(1)	-1(1)
C(20)	31(3)	27(3)	22(2)	2(2)	-7(2)	-4(2)
C(21)	32(3)	29(3)	25(2)	10(2)	-7(2)	-11(2)
C(22)	26(2)	25(2)	21(2)	8(2)	-7(2)	-3(2)
C(23)	29(2)	27(3)	24(2)	8(2)	-10(2)	-7(2)
C(24)	30(2)	26(3)	29(2)	-1(2)	-9(2)	-7(2)
C(25)	42(3)	40(3)	25(2)	11(2)	-14(2)	-6(2)
C(26)	35(3)	70(5)	44(3)	12(3)	-21(3)	-20(3)
O(1)	49(2)	37(2)	63(3)	16(2)	-27(2)	-14(2)
O(2)	41(3)	74(4)	63(3)	23(3)	0(2)	-6(2)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **7**.

	x	y	z	U(eq)
H(1)	1638	5088	2972	38
H(2)	608	6782	4179	41
H(3)	1264	7000	5917	40
H(4)	2970	5569	6364	30
H(7)	4574	3942	6719	25
H(9)	6728	658	5353	24
H(12)	7101	-672	3809	30
H(13)	7444	-1796	2069	33

H(14)	6289	-1022	662	37
H(15)	4761	744	1046	33
H(17)	7845	375	6860	42
H(18)	8086	597	8908	60
H(19)	6804	2366	9903	57
H(19')	8086	597	8908	60
H(18')	6804	2366	9903	57
H(17')	5250	3768	8570	35
H(20)	1707	1908	2306	32
H(21)	471	2214	941	34
H(23)	2816	4580	-596	31
H(24)	3977	4194	806	33
H(25A)	1466	5133	-1556	53
H(25B)	383	4724	-2151	53
H(25C)	1837	3948	-2406	53
H(26A)	44	2175	-1245	70
H(26B)	-893	3471	-1314	70
H(26C)	-771	2900	-92	70
H(1A)	130(90)	9160(70)	5950(70)	140(40)
H(1B)	720(50)	10120(30)	6070(40)	23(13)
H(2A)	8750(40)	1350(40)	2300(30)	18(13)
H(2B)	8010(40)	2240(30)	1800(40)	27

Table S11. Hydrogen bonds for complex **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4)...Cl(1)#1	0.95	2.64	3.575(5)	167.9
C(7)-H(7)...Cl(1)#1	0.95	2.83	3.760(5)	165.3
C(9)-H(9)...Cl(2)#2	0.95	2.78	3.723(5)	173.7
C(12)-H(12)...Cl(2)#2	0.95	2.62	3.565(5)	177.0
C(21)-H(21)...O(2)#3	0.95	2.37	3.275(7)	159.7
C(23)-H(23)...Cl(1)#4	0.95	2.71	3.638(5)	164.8
O(1)-H(1A)...Cl(2)#3	0.85(2)	2.39(3)	3.213(5)	163(9)
O(1)-H(1B)...Cl(2)#5	0.840(19)	2.50(3)	3.293(4)	157(5)
O(2)-H(2A)...O(1)#1	0.845(18)	2.01(2)	2.846(7)	170(4)
O(2)-H(2B)...Cl(1)	0.830(19)	2.53(3)	3.303(5)	156(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 x,y-1,z #3 x-1,y,z #4 -x+1,-y+1,-z
#5 -x+1,-y+2,-z+1

13. Crystal structure of Cu(II)-pincer complex 8.

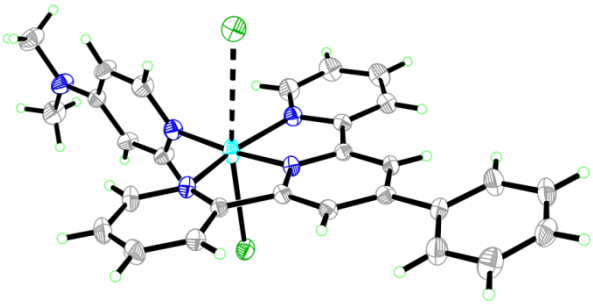


Figure S11. Molecular Structure of Complex **8**.

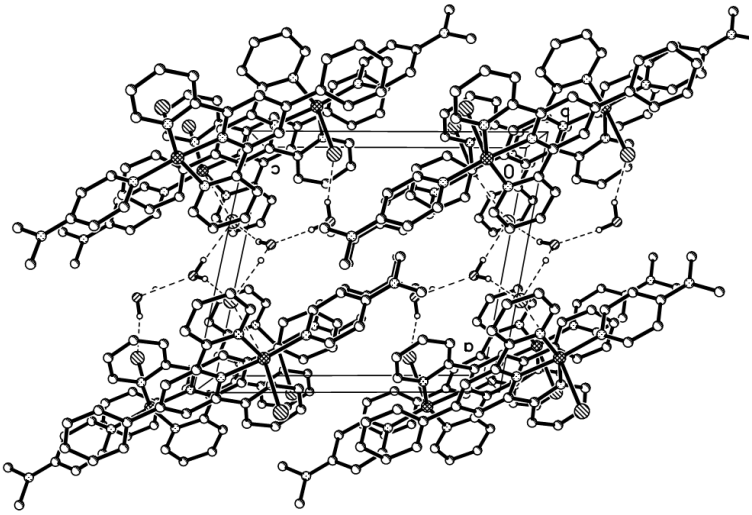


Figure S12. Cell unit formed by complex **8**.

Table S12. Crystal data and structure refinement for complex **8**.

Identification code	complex **8**	
Empirical formula	C28 H29 Cl2 Cu N5 O2	
Formula weight	602.00	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.758(4) Å	a= 87.424(5) °.
	b = 10.951(4) Å	b= 78.339(5) °.
	c = 12.045(5) Å	g = 79.489(5) °.
Volume	1366.4(9) $Å^3$	
Z	2	
Density (calculated)	1.463 Mg/m^3	

Absorption coefficient	1.030 mm^{-1}
F(000)	622
Crystal size	0.050 x 0.030 x 0.030 mm^3
Theta range for data collection	1.726 to 25.009 °.
Index ranges	-12<=h<=12, -12<=k<=13, -11<=l<=14
Reflections collected	5731
Independent reflections	4698 [R(int) = 0.0473]
Completeness to theta = 25.242 °	95.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.365
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4698 / 7 / 361
Goodness-of-fit on F^2	1.007
Final R indices [I>2sigma(I)]	R1 = 0.0705, wR2 = 0.1876
R indices (all data)	R1 = 0.0874, wR2 = 0.2032
Extinction coefficient	n/a
Largest diff. peak and hole	1.323 and -1.631 e.$Å^{-3}$

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	8840(1)	7882(1)	8020(1)	42(1)
Cl(1)	10828(1)	8927(1)	7050(1)	42(1)
Cl(2)	3376(1)	3408(1)	381(1)	52(1)
N(1)	9982(4)	6211(4)	7648(3)	35(1)
N(2)	9582(3)	7599(3)	9349(3)	28(1)
N(3)	7835(4)	9362(4)	8961(3)	38(1)
N(4)	7926(4)	8099(4)	6753(3)	39(1)
N(5)	5899(4)	8598(5)	4133(4)	53(1)
C(1)	10175(5)	5550(5)	6696(4)	46(1)
C(2)	11075(5)	4484(5)	6488(4)	50(1)
C(3)	11791(5)	4083(5)	7272(5)	46(1)
C(4)	11617(5)	4715(5)	8273(4)	39(1)
C(5)	10717(4)	5785(4)	8420(4)	30(1)
C(6)	10470(4)	6612(4)	9415(4)	30(1)

C(7)	11065(4)	6418(4)	10330(4)	33(1)
C(8)	10748(4)	7298(4)	11193(4)	32(1)
C(9)	9819(4)	8343(4)	11087(4)	32(1)
C(10)	9239(4)	8469(4)	10163(4)	30(1)
C(11)	8222(4)	9485(4)	9931(4)	32(1)
C(12)	7670(5)	10451(4)	10656(4)	40(1)
C(13)	6651(5)	11300(5)	10385(5)	50(1)
C(14)	6251(6)	11174(5)	9398(5)	55(2)
C(15)	6863(5)	10203(5)	8703(5)	49(1)
C(16)	11344(4)	7090(4)	12206(4)	34(1)
C(17)	10821(6)	7776(5)	13180(4)	51(1)
C(18)	11331(6)	7512(6)	14152(4)	57(2)
C(19)	12371(5)	6597(5)	14160(5)	50(1)
C(20)	12931(6)	5951(5)	13189(5)	59(2)
C(21)	12428(5)	6186(5)	12224(5)	51(1)
C(22)	8191(5)	8884(5)	5904(4)	43(1)
C(23)	7553(5)	9089(5)	5023(4)	41(1)
C(24)	6559(5)	8435(5)	4982(4)	40(1)
C(25)	6279(5)	7628(5)	5881(4)	50(1)
C(26)	6969(5)	7478(5)	6718(4)	48(1)
C(27)	4855(6)	7962(7)	4107(6)	69(2)
C(28)	6225(6)	9402(6)	3189(5)	62(2)
O(1)	5640(5)	4382(5)	1290(4)	71(1)
O(2)	3449(5)	6783(6)	6766(5)	91(2)

Table S14. Bond lengths [Å] and angles [°] for complex **8.**

Cu(1)-N(2)	1.917(4)
Cu(1)-N(4)	1.959(4)
Cu(1)-N(1)	2.022(4)
Cu(1)-N(3)	2.027(4)
Cu(1)-Cl(1)	2.6482(15)
Cu(1)-Cl(2)	3.2428(8)
N(1)-C(1)	1.343(6)
N(1)-C(5)	1.354(6)
N(2)-C(6)	1.316(6)
N(2)-C(10)	1.347(5)
N(3)-C(11)	1.338(6)
N(3)-C(15)	1.339(6)
N(4)-C(22)	1.326(6)
N(4)-C(26)	1.343(7)
N(5)-C(24)	1.347(6)
N(5)-C(27)	1.432(7)

N(5)-C(28)	1.432(7)
C(1)-C(2)	1.371(7)
C(1)-H(1)	0.9300
C(2)-C(3)	1.345(8)
C(2)-H(2)	0.9300
C(3)-C(4)	1.380(7)
C(3)-H(3)	0.9300
C(4)-C(5)	1.370(7)
C(4)-H(4)	0.9300
C(5)-C(6)	1.486(6)
C(6)-C(7)	1.373(6)
C(7)-C(8)	1.398(6)
C(7)-H(7)	0.9300
C(8)-C(9)	1.395(6)
C(8)-C(16)	1.480(6)
C(9)-C(10)	1.372(6)
C(9)-H(9)	0.9300
C(10)-C(11)	1.471(6)
C(11)-C(12)	1.371(6)
C(12)-C(13)	1.385(7)
C(12)-H(12)	0.9300
C(13)-C(14)	1.365(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.366(7)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.384(6)
C(16)-C(21)	1.389(7)
C(17)-C(18)	1.388(7)
C(17)-H(17)	0.9300
C(18)-C(19)	1.361(8)
C(18)-H(18)	0.9300
C(19)-C(20)	1.365(8)
C(19)-H(19)	0.9300
C(20)-C(21)	1.374(7)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-C(23)	1.366(7)
C(22)-H(22)	0.9300
C(23)-C(24)	1.402(7)
C(23)-H(23)	0.9300
C(24)-C(25)	1.386(7)
C(25)-C(26)	1.355(7)
C(25)-H(25)	0.9300

C(26)-H(26)	0.9300
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
O(1)-H(1A)	0.86(4)
O(1)-H(1B)	0.96(4)
O(2)-H(2A)	0.82(4)
O(2)-H(2B)	0.87(4)

N(2)-Cu(1)-N(4)	173.98(16)
N(2)-Cu(1)-N(1)	79.68(15)
N(4)-Cu(1)-N(1)	100.85(16)
N(2)-Cu(1)-N(3)	79.96(15)
N(4)-Cu(1)-N(3)	98.82(16)
N(1)-Cu(1)-N(3)	158.89(16)
N(2)-Cu(1)-Cl(1)	88.51(11)
N(4)-Cu(1)-Cl(1)	97.50(13)
N(1)-Cu(1)-Cl(1)	87.95(12)
N(3)-Cu(1)-Cl(1)	97.03(12)
C(1)-N(1)-C(5)	117.4(4)
C(1)-N(1)-Cu(1)	127.9(4)
C(5)-N(1)-Cu(1)	114.4(3)
C(6)-N(2)-C(10)	121.5(4)
C(6)-N(2)-Cu(1)	119.9(3)
C(10)-N(2)-Cu(1)	118.5(3)
C(11)-N(3)-C(15)	118.6(4)
C(11)-N(3)-Cu(1)	114.4(3)
C(15)-N(3)-Cu(1)	127.0(3)
C(22)-N(4)-C(26)	116.4(4)
C(22)-N(4)-Cu(1)	122.3(3)
C(26)-N(4)-Cu(1)	121.3(3)
C(24)-N(5)-C(27)	122.1(5)
C(24)-N(5)-C(28)	121.6(5)
C(27)-N(5)-C(28)	116.2(5)
N(1)-C(1)-C(2)	122.7(5)
N(1)-C(1)-H(1)	118.7
C(2)-C(1)-H(1)	118.7
C(3)-C(2)-C(1)	118.6(5)
C(3)-C(2)-H(2)	120.7
C(1)-C(2)-H(2)	120.7
C(2)-C(3)-C(4)	121.1(5)

C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	117.4(5)
C(5)-C(4)-H(4)	121.3
C(3)-C(4)-H(4)	121.3
N(1)-C(5)-C(4)	122.8(4)
N(1)-C(5)-C(6)	113.1(4)
C(4)-C(5)-C(6)	124.1(4)
N(2)-C(6)-C(7)	121.2(4)
N(2)-C(6)-C(5)	112.7(4)
C(7)-C(6)-C(5)	126.1(4)
C(6)-C(7)-C(8)	119.5(4)
C(6)-C(7)-H(7)	120.3
C(8)-C(7)-H(7)	120.3
C(9)-C(8)-C(7)	117.8(4)
C(9)-C(8)-C(16)	121.6(4)
C(7)-C(8)-C(16)	120.5(4)
C(10)-C(9)-C(8)	119.8(4)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
N(2)-C(10)-C(9)	120.2(4)
N(2)-C(10)-C(11)	112.8(4)
C(9)-C(10)-C(11)	127.1(4)
N(3)-C(11)-C(12)	122.2(4)
N(3)-C(11)-C(10)	114.0(4)
C(12)-C(11)-C(10)	123.8(4)
C(11)-C(12)-C(13)	118.4(5)
C(11)-C(12)-H(12)	120.8
C(13)-C(12)-H(12)	120.8
C(14)-C(13)-C(12)	119.6(5)
C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2
C(13)-C(14)-C(15)	118.9(5)
C(13)-C(14)-H(14)	120.5
C(15)-C(14)-H(14)	120.5
N(3)-C(15)-C(14)	122.4(5)
N(3)-C(15)-H(15)	118.8
C(14)-C(15)-H(15)	118.8
C(17)-C(16)-C(21)	117.6(4)
C(17)-C(16)-C(8)	121.0(4)
C(21)-C(16)-C(8)	121.4(4)
C(16)-C(17)-C(18)	120.5(5)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8

C(19)-C(18)-C(17)	120.8(5)
C(19)-C(18)-H(18)	119.6
C(17)-C(18)-H(18)	119.6
C(18)-C(19)-C(20)	119.2(5)
C(18)-C(19)-H(19)	120.4
C(20)-C(19)-H(19)	120.4
C(19)-C(20)-C(21)	120.8(5)
C(19)-C(20)-H(20)	119.6
C(21)-C(20)-H(20)	119.6
C(20)-C(21)-C(16)	121.0(5)
C(20)-C(21)-H(21)	119.5
C(16)-C(21)-H(21)	119.5
N(4)-C(22)-C(23)	124.1(5)
N(4)-C(22)-H(22)	117.9
C(23)-C(22)-H(22)	117.9
C(22)-C(23)-C(24)	119.5(5)
C(22)-C(23)-H(23)	120.3
C(24)-C(23)-H(23)	120.3
N(5)-C(24)-C(25)	122.1(5)
N(5)-C(24)-C(23)	122.0(5)
C(25)-C(24)-C(23)	115.9(4)
C(26)-C(25)-C(24)	120.6(5)
C(26)-C(25)-H(25)	119.7
C(24)-C(25)-H(25)	119.7
N(4)-C(26)-C(25)	123.5(5)
N(4)-C(26)-H(26)	118.3
C(25)-C(26)-H(26)	118.3
N(5)-C(27)-H(27A)	109.5
N(5)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
N(5)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
N(5)-C(28)-H(28A)	109.5
N(5)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
N(5)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
H(1A)-O(1)-H(1B)	99(4)
H(2A)-O(2)-H(2B)	104(6)

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **8**. The anisotropic displacement factor

exponent takes the form: $-2p^2[\, h^2\, a^{*2}U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	55(1)	36(1)	36(1)	-6(1)	-20(1)	3(1)
Cl(1)	50(1)	43(1)	38(1)	1(1)	-11(1)	-17(1)
Cl(2)	55(1)	42(1)	58(1)	4(1)	-17(1)	-2(1)
N(1)	43(2)	30(2)	33(2)	-2(2)	-11(2)	-9(2)
N(2)	38(2)	18(2)	28(2)	1(2)	-8(2)	-2(2)
N(3)	40(2)	37(2)	36(2)	0(2)	-10(2)	-4(2)
N(4)	43(2)	40(2)	35(2)	2(2)	-12(2)	-5(2)
N(5)	53(3)	77(3)	40(2)	15(2)	-23(2)	-25(2)
C(1)	65(3)	41(3)	35(3)	-6(2)	-13(2)	-13(3)
C(2)	63(4)	45(3)	42(3)	-15(3)	-8(2)	-10(3)
C(3)	54(3)	28(3)	52(3)	-10(2)	-4(2)	0(2)
C(4)	40(3)	37(3)	41(3)	-5(2)	-7(2)	-8(2)
C(5)	36(2)	29(2)	28(2)	0(2)	-4(2)	-11(2)
C(6)	38(2)	24(2)	28(2)	1(2)	-2(2)	-8(2)
C(7)	33(2)	34(3)	30(2)	1(2)	-7(2)	-3(2)
C(8)	34(2)	33(3)	30(2)	5(2)	-6(2)	-8(2)
C(9)	38(2)	31(3)	27(2)	-3(2)	-4(2)	-7(2)
C(10)	34(2)	28(2)	30(2)	0(2)	-4(2)	-8(2)
C(11)	32(2)	28(2)	33(2)	3(2)	-4(2)	-4(2)
C(12)	46(3)	34(3)	37(3)	3(2)	-7(2)	-4(2)
C(13)	57(3)	31(3)	52(3)	-2(2)	-7(3)	10(2)
C(14)	54(3)	44(3)	61(4)	1(3)	-15(3)	12(3)
C(15)	47(3)	50(3)	47(3)	1(3)	-18(2)	5(2)
C(16)	41(3)	32(3)	31(2)	0(2)	-13(2)	-9(2)
C(17)	60(3)	50(3)	40(3)	-10(3)	-15(2)	5(3)
C(18)	66(4)	74(4)	33(3)	-11(3)	-15(3)	-11(3)
C(19)	62(4)	54(4)	43(3)	9(3)	-25(3)	-18(3)
C(20)	70(4)	47(3)	64(4)	3(3)	-34(3)	-2(3)
C(21)	57(3)	49(3)	47(3)	-9(3)	-20(3)	3(3)
C(22)	37(3)	49(3)	48(3)	4(3)	-15(2)	-12(2)
C(23)	39(3)	46(3)	39(3)	13(2)	-12(2)	-11(2)
C(24)	37(3)	46(3)	40(3)	-3(2)	-10(2)	-7(2)
C(25)	52(3)	65(4)	43(3)	13(3)	-16(2)	-31(3)
C(26)	57(3)	53(3)	37(3)	15(2)	-13(2)	-18(3)
C(27)	61(4)	92(5)	68(4)	12(4)	-35(3)	-31(3)
C(28)	73(4)	70(4)	48(3)	22(3)	-27(3)	-18(3)
O(1)	67(3)	75(3)	77(3)	18(3)	-26(2)	-17(2)
O(2)	60(3)	135(5)	71(4)	34(3)	-5(3)	-19(3)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **8**.

	x	y	z	U(eq)
H(1)	9677	5827	6156	55
H(2)	11188	4047	5820	60
H(3)	12413	3367	7137	55
H(4)	12093	4426	8825	47
H(7)	11675	5706	10375	39
H(9)	9593	8952	11641	39
H(12)	7973	10535	11315	48
H(13)	6243	11951	10872	59
H(14)	5573	11741	9201	66
H(15)	6594	10123	8027	58
H(17)	10123	8418	13184	61
H(18)	10957	7967	14806	68
H(19)	12697	6413	14819	60
H(20)	13661	5344	13181	70
H(21)	12820	5733	11572	61
H(22)	8853	9323	5909	52
H(23)	7777	9658	4455	49
H(25)	5613	7186	5910	60
H(26)	6769	6914	7298	57
H(27A)	5132	7086	4202	103
H(27B)	4587	8116	3392	103
H(27C)	4145	8257	4710	103
H(28A)	5758	10228	3357	92
H(28B)	6002	9106	2530	92
H(28C)	7135	9410	3047	92
H(1A)	4990(50)	4180(60)	1070(60)	90(30)
H(1B)	5760(60)	5080(50)	800(50)	80(20)
H(2A)	2660(40)	6970(70)	6990(60)	100(30)
H(2B)	3780(70)	6880(100)	7350(60)	140(40)

Table S17. Torsion angles [°] for complex **8**.

C(5)-N(1)-C(1)-C(2)	-0.2(7)
Cu(1)-N(1)-C(1)-C(2)	173.1(4)
N(1)-C(1)-C(2)-C(3)	0.2(8)

C(1)-C(2)-C(3)-C(4)	0.9(8)
C(2)-C(3)-C(4)-C(5)	-2.0(8)
C(1)-N(1)-C(5)-C(4)	-1.0(7)
Cu(1)-N(1)-C(5)-C(4)	-175.2(3)
C(1)-N(1)-C(5)-C(6)	177.4(4)
Cu(1)-N(1)-C(5)-C(6)	3.2(5)
C(3)-C(4)-C(5)-N(1)	2.0(7)
C(3)-C(4)-C(5)-C(6)	-176.2(4)
C(10)-N(2)-C(6)-C(7)	1.2(6)
Cu(1)-N(2)-C(6)-C(7)	176.7(3)
C(10)-N(2)-C(6)-C(5)	-179.0(4)
Cu(1)-N(2)-C(6)-C(5)	-3.5(5)
N(1)-C(5)-C(6)-N(2)	0.0(5)
C(4)-C(5)-C(6)-N(2)	178.3(4)
N(1)-C(5)-C(6)-C(7)	179.8(4)
C(4)-C(5)-C(6)-C(7)	-1.9(7)
N(2)-C(6)-C(7)-C(8)	-1.6(7)
C(5)-C(6)-C(7)-C(8)	178.6(4)
C(6)-C(7)-C(8)-C(9)	0.6(6)
C(6)-C(7)-C(8)-C(16)	177.9(4)
C(7)-C(8)-C(9)-C(10)	0.8(6)
C(16)-C(8)-C(9)-C(10)	-176.5(4)
C(6)-N(2)-C(10)-C(9)	0.2(6)
Cu(1)-N(2)-C(10)-C(9)	-175.3(3)
C(6)-N(2)-C(10)-C(11)	-179.3(4)
Cu(1)-N(2)-C(10)-C(11)	5.2(5)
C(8)-C(9)-C(10)-N(2)	-1.2(6)
C(8)-C(9)-C(10)-C(11)	178.2(4)
C(15)-N(3)-C(11)-C(12)	-1.1(7)
Cu(1)-N(3)-C(11)-C(12)	178.3(3)
C(15)-N(3)-C(11)-C(10)	176.4(4)
Cu(1)-N(3)-C(11)-C(10)	-4.2(5)
N(2)-C(10)-C(11)-N(3)	-0.4(5)
C(9)-C(10)-C(11)-N(3)	-179.8(4)
N(2)-C(10)-C(11)-C(12)	177.0(4)
C(9)-C(10)-C(11)-C(12)	-2.4(7)
N(3)-C(11)-C(12)-C(13)	2.2(7)
C(10)-C(11)-C(12)-C(13)	-175.0(4)
C(11)-C(12)-C(13)-C(14)	-1.9(8)
C(12)-C(13)-C(14)-C(15)	0.5(9)
C(11)-N(3)-C(15)-C(14)	-0.3(8)
Cu(1)-N(3)-C(15)-C(14)	-179.7(4)
C(13)-C(14)-C(15)-N(3)	0.6(9)
C(9)-C(8)-C(16)-C(17)	13.5(7)

C(7)-C(8)-C(16)-C(17)	-163.7(5)
C(9)-C(8)-C(16)-C(21)	-167.8(5)
C(7)-C(8)-C(16)-C(21)	15.0(7)
C(21)-C(16)-C(17)-C(18)	-3.4(8)
C(8)-C(16)-C(17)-C(18)	175.3(5)
C(16)-C(17)-C(18)-C(19)	1.6(9)
C(17)-C(18)-C(19)-C(20)	1.4(9)
C(18)-C(19)-C(20)-C(21)	-2.3(9)
C(19)-C(20)-C(21)-C(16)	0.4(9)
C(17)-C(16)-C(21)-C(20)	2.5(8)
C(8)-C(16)-C(21)-C(20)	-176.2(5)
C(26)-N(4)-C(22)-C(23)	0.3(8)
Cu(1)-N(4)-C(22)-C(23)	-178.0(4)
N(4)-C(22)-C(23)-C(24)	-0.7(8)
C(27)-N(5)-C(24)-C(25)	0.7(9)
C(28)-N(5)-C(24)-C(25)	-177.8(5)
C(27)-N(5)-C(24)-C(23)	-177.9(5)
C(28)-N(5)-C(24)-C(23)	3.5(8)
C(22)-C(23)-C(24)-N(5)	-179.9(5)
C(22)-C(23)-C(24)-C(25)	1.4(7)
N(5)-C(24)-C(25)-C(26)	179.5(5)
C(23)-C(24)-C(25)-C(26)	-1.8(8)
C(22)-N(4)-C(26)-C(25)	-0.7(8)
Cu(1)-N(4)-C(26)-C(25)	177.6(4)
C(24)-C(25)-C(26)-N(4)	1.5(9)

Symmetry transformations used to generate equivalent atoms:

Table S18. Hydrogen bonds for complex**8** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2B)...O(1)#1	0.87(4)	2.21(8)	2.877(7)	133(9)
O(2)-H(2A)...Cl(1)#2	0.82(4)	2.63(6)	3.293(6)	139(7)
O(1)-H(1B)...Cl(2)#3	0.96(4)	2.33(4)	3.265(5)	165(5)
O(1)-H(1A)...Cl(2)	0.86(4)	2.37(4)	3.225(5)	173(6)
C(25)-H(25)...O(2)	0.93	2.46	3.300(8)	150.7
C(23)-H(23)...Cl(1)#4	0.93	2.73	3.623(5)	162.0
C(12)-H(12)...Cl(1)#5	0.93	2.70	3.616(5)	168.0
C(9)-H(9)...Cl(1)#5	0.93	2.78	3.697(5)	168.1
C(7)-H(7)...Cl(2)#6	0.93	2.83	3.755(5)	173.8
C(4)-H(4)...Cl(2)#6	0.93	2.64	3.565(5)	174.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x-1,y,z #3 -x+1,-y+1,-z #4 -x+2,-y+2,-z+1 #5 -x+2,-y+2,-z+2 #6 x+1,y,z+1

14. Crystal structure of Cu(II)-pincer complex 10.

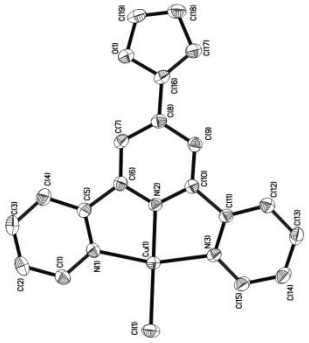


Figure S13. Molecular Structure of complex **10**.

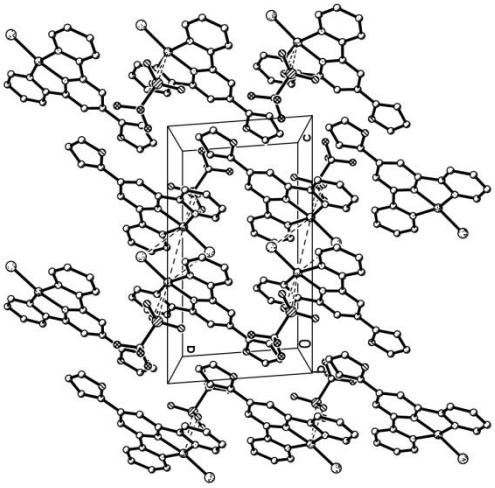


Figure S14. Cell unit formed by complex **10**.

Table S19. Crystal data and structure refinement for complex **10**.

Identification code	complex **10**
Empirical formula	C20 H13 Cl Cu F3 N3 O4 S
Formula weight	547.38
Temperature	293(2) K

Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 7.590(3) A alpha = 90 deg. b = 20.098(7) A beta = 94.218(4) deg. c = 13.487(5) A gamma = 90 deg.
Volume	2051.9(12) A^3
Z, Calculated density	4, 1.772 Mg/m^3
Absorption coefficient	1.359 mm^-1
F(000)	1100
Crystal size	0.250 x 0.200 x 0.200 mm
Theta range for data collection	1.822 to 25.996 deg.
Limiting indices	-9<=h<=8, -24<=k<=17, -16<=l<=15
Reflections collected / unique	9055 / 3971 [R(int) = 0.0430]
Completeness to theta = 25.242	99.1 %
Absorption correction	Multi=scan
Max. and min. transmission	1.000 and 0.199
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3971 / 0 / 298
Goodness-of-fit on F^2	0.914
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0891
R indices (all data)	R1 = 0.0548, wR2 = 0.0935
Extinction coefficient	n/a
Largest diff. peak and hole	0.503 and -0.586 e.A^-3

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for complex **10**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	10555(1)	5381(1)	3810(1)	39(1)
Cl(1)	12594(1)	5607(1)	5004(1)	54(1)
N(1)	11544(3)	4523(1)	3304(2)	38(1)
N(2)	8584(3)	5094(1)	2935(2)	34(1)
N(3)	8809(3)	6109(1)	4058(2)	37(1)
S(1)	8816(1)	1779(1)	2763(1)	46(1)
O(1)	4503(3)	3962(1)	413(2)	51(1)
O(2)	8348(3)	1088(1)	2632(2)	55(1)
O(3)	8116(4)	2205(1)	1969(2)	69(1)
O(4)	10614(3)	1900(1)	3116(2)	59(1)
F(1)	7722(3)	2684(1)	3951(2)	109(1)
F(2)	5839(3)	1924(1)	3600(2)	97(1)
F(3)	8101(4)	1707(2)	4615(2)	118(1)
C(1)	13132(4)	4261(2)	3560(2)	44(1)

C(2)	13657(5)	3656(2)	3208(2)	52(1)
C(3)	12495(5)	3301(2)	2578(2)	52(1)
C(4)	10855(4)	3564(2)	2305(2)	47(1)
C(5)	10408(4)	4180(1)	2665(2)	37(1)
C(6)	8711(4)	4524(1)	2424(2)	37(1)
C(7)	7312(4)	4312(1)	1786(2)	41(1)
C(8)	5776(4)	4694(1)	1680(2)	39(1)
C(9)	5661(4)	5269(1)	2263(2)	39(1)
C(10)	7094(4)	5456(1)	2882(2)	35(1)
C(11)	7217(4)	6040(1)	3550(2)	36(1)
C(12)	5857(4)	6479(2)	3669(2)	44(1)
C(13)	6153(5)	7020(2)	4298(2)	52(1)
C(14)	7805(5)	7096(2)	4785(2)	54(1)
C(15)	9094(5)	6633(2)	4657(2)	47(1)
C(16)	4295(4)	4514(1)	995(2)	41(1)
C(17)	2697(4)	4783(2)	772(2)	49(1)
C(18)	1848(5)	4384(2)	12(2)	54(1)
C(19)	2968(5)	3906(2)	-173(2)	53(1)
C(23)	7555(5)	2030(2)	3790(3)	69(1)

Table S21. Bond lengths [A] and angles [deg] for complex **10**.

Cu(1)-N(2)	1.925(2)
Cu(1)-N(3)	2.017(2)
Cu(1)-N(1)	2.020(2)
Cu(1)-Cl(1)	2.1979(10)
N(1)-C(1)	1.337(4)
N(1)-C(5)	1.360(4)
N(2)-C(6)	1.342(3)
N(2)-C(10)	1.343(4)
N(3)-C(15)	1.336(3)
N(3)-C(11)	1.351(4)
S(1)-O(4)	1.433(2)
S(1)-O(3)	1.441(2)
S(1)-O(2)	1.441(2)
S(1)-C(23)	1.812(4)
O(1)-C(19)	1.363(4)
O(1)-C(16)	1.374(3)
F(1)-C(23)	1.337(4)
F(2)-C(23)	1.326(4)
F(3)-C(23)	1.328(5)
C(1)-C(2)	1.376(4)
C(2)-C(3)	1.378(5)

C(3)-C(4)	1.376(4)
C(4)-C(5)	1.383(4)
C(5)-C(6)	1.477(4)
C(6)-C(7)	1.384(4)
C(7)-C(8)	1.393(4)
C(8)-C(9)	1.405(4)
C(8)-C(16)	1.448(4)
C(9)-C(10)	1.374(4)
C(10)-C(11)	1.478(4)
C(11)-C(12)	1.377(4)
C(12)-C(13)	1.387(4)
C(13)-C(14)	1.381(5)
C(14)-C(15)	1.371(4)
C(16)-C(17)	1.342(4)
C(17)-C(18)	1.418(4)
C(18)-C(19)	1.320(5)

N(2)-Cu(1)-N(3)	80.17(10)
N(2)-Cu(1)-N(1)	80.07(10)
N(3)-Cu(1)-N(1)	160.02(10)
N(2)-Cu(1)-Cl(1)	170.11(7)
N(3)-Cu(1)-Cl(1)	99.47(7)
N(1)-Cu(1)-Cl(1)	99.48(7)
C(1)-N(1)-C(5)	118.8(3)
C(1)-N(1)-Cu(1)	126.8(2)
C(5)-N(1)-Cu(1)	114.3(2)
C(6)-N(2)-C(10)	121.8(2)
C(6)-N(2)-Cu(1)	119.27(19)
C(10)-N(2)-Cu(1)	118.89(19)
C(15)-N(3)-C(11)	119.1(3)
C(15)-N(3)-Cu(1)	126.4(2)
C(11)-N(3)-Cu(1)	114.53(18)
O(4)-S(1)-O(3)	115.87(15)
O(4)-S(1)-O(2)	115.08(14)
O(3)-S(1)-O(2)	114.03(14)
O(4)-S(1)-C(23)	104.02(16)
O(3)-S(1)-C(23)	102.51(19)
O(2)-S(1)-C(23)	102.86(17)
C(19)-O(1)-C(16)	105.6(2)
N(1)-C(1)-C(2)	122.5(3)
C(3)-C(2)-C(1)	118.8(3)
C(4)-C(3)-C(2)	119.5(3)
C(3)-C(4)-C(5)	119.4(3)
N(1)-C(5)-C(4)	121.0(3)

N(1)-C(5)-C(6)	113.8(2)
C(4)-C(5)-C(6)	125.1(3)
N(2)-C(6)-C(7)	120.0(3)
N(2)-C(6)-C(5)	112.4(2)
C(7)-C(6)-C(5)	127.6(3)
C(6)-C(7)-C(8)	119.5(3)
C(7)-C(8)-C(9)	118.7(3)
C(7)-C(8)-C(16)	122.2(3)
C(9)-C(8)-C(16)	119.1(3)
C(10)-C(9)-C(8)	119.1(3)
N(2)-C(10)-C(9)	120.7(3)
N(2)-C(10)-C(11)	112.5(2)
C(9)-C(10)-C(11)	126.8(3)
N(3)-C(11)-C(12)	121.7(3)
N(3)-C(11)-C(10)	113.9(2)
C(12)-C(11)-C(10)	124.5(3)
C(11)-C(12)-C(13)	119.0(3)
C(14)-C(13)-C(12)	118.6(3)
C(15)-C(14)-C(13)	119.7(3)
N(3)-C(15)-C(14)	121.8(3)
C(17)-C(16)-O(1)	109.7(3)
C(17)-C(16)-C(8)	133.5(3)
O(1)-C(16)-C(8)	116.8(3)
C(16)-C(17)-C(18)	106.8(3)
C(19)-C(18)-C(17)	106.5(3)
C(18)-C(19)-O(1)	111.4(3)
F(2)-C(23)-F(3)	109.0(4)
F(2)-C(23)-F(1)	105.6(3)
F(3)-C(23)-F(1)	109.0(3)
F(2)-C(23)-S(1)	112.0(3)
F(3)-C(23)-S(1)	110.8(3)
F(1)-C(23)-S(1)	110.4(3)

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters (A^2 x 10^3) for complex **10**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu(1)	39(1)	38(1)	39(1)	-3(1)	-5(1)	1(1)
Cl(1)	54(1)	58(1)	47(1)	-1(1)	-16(1)	0(1)
N(1)	37(1)	36(1)	41(1)	3(1)	2(1)	2(1)

N(2)	36(1)	31(1)	36(1)	-2(1)	0(1)	-3(1)
N(3)	42(2)	34(1)	36(1)	-2(1)	1(1)	-4(1)
S(1)	45(1)	41(1)	52(1)	-4(1)	0(1)	-7(1)
O(1)	51(1)	45(1)	56(1)	-11(1)	-9(1)	-1(1)
O(2)	57(2)	38(1)	72(2)	-9(1)	12(1)	-9(1)
O(3)	76(2)	65(2)	63(2)	16(1)	-14(1)	-10(1)
O(4)	42(1)	66(2)	67(2)	-2(1)	-8(1)	-8(1)
F(1)	95(2)	86(2)	144(2)	-73(2)	2(2)	1(1)
F(2)	56(2)	127(2)	111(2)	-48(2)	23(1)	-14(1)
F(3)	124(3)	176(3)	56(2)	15(2)	12(2)	21(2)
C(1)	42(2)	44(2)	45(2)	6(1)	-1(1)	1(1)
C(2)	50(2)	47(2)	61(2)	15(2)	9(2)	13(2)
C(3)	60(2)	36(2)	61(2)	2(2)	14(2)	10(2)
C(4)	51(2)	36(2)	54(2)	-1(2)	9(2)	-3(2)
C(5)	40(2)	33(2)	38(2)	2(1)	5(1)	-3(1)
C(6)	39(2)	33(2)	40(2)	1(1)	5(1)	-2(1)
C(7)	49(2)	32(2)	41(2)	-4(1)	2(1)	-4(1)
C(8)	41(2)	37(2)	38(2)	3(1)	0(1)	-6(1)
C(9)	40(2)	36(2)	40(2)	2(1)	2(1)	1(1)
C(10)	39(2)	32(2)	35(1)	4(1)	3(1)	-1(1)
C(11)	40(2)	32(2)	34(2)	0(1)	1(1)	-3(1)
C(12)	44(2)	44(2)	43(2)	0(1)	0(1)	1(1)
C(13)	62(2)	44(2)	50(2)	-6(2)	10(2)	12(2)
C(14)	66(3)	43(2)	52(2)	-14(2)	0(2)	2(2)
C(15)	54(2)	41(2)	44(2)	-8(1)	-3(2)	-3(2)
C(16)	48(2)	36(2)	38(2)	-2(1)	-1(1)	-7(1)
C(17)	48(2)	45(2)	52(2)	-5(2)	-7(2)	-2(2)
C(18)	52(2)	54(2)	55(2)	1(2)	-16(2)	-6(2)
C(19)	62(2)	49(2)	48(2)	-4(2)	-10(2)	-17(2)
C(23)	56(3)	79(3)	72(3)	-22(2)	-2(2)	-7(2)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for complex **10**.

	x	y	z	U(eq)
H(1)	13912	4498	3993	52
H(2)	14777	3489	3391	63
H(3)	12814	2888	2340	62
H(4)	10056	3328	1883	56
H(7)	7396	3919	1431	49
H(9)	4629	5519	2231	46
H(12)	4756	6414	3334	53
H(13)	5258	7325	4389	62

H(14)	8043	7461	5199	65
H(15)	10196	6685	4997	56
H(17)	2235	5159	1061	59
H(18)	724	4448	-295	65
H(19)	2740	3572	-643	64

Table S24. Torsion angles [deg] for complex **10**.

C(5)-N(1)-C(1)-C(2)	-0.5(4)
Cu(1)-N(1)-C(1)-C(2)	176.9(2)
N(1)-C(1)-C(2)-C(3)	-0.9(5)
C(1)-C(2)-C(3)-C(4)	1.0(5)
C(2)-C(3)-C(4)-C(5)	0.3(5)
C(1)-N(1)-C(5)-C(4)	1.9(4)
Cu(1)-N(1)-C(5)-C(4)	-175.9(2)
C(1)-N(1)-C(5)-C(6)	-179.0(2)
Cu(1)-N(1)-C(5)-C(6)	3.3(3)
C(3)-C(4)-C(5)-N(1)	-1.8(4)
C(3)-C(4)-C(5)-C(6)	179.2(3)
C(10)-N(2)-C(6)-C(7)	3.1(4)
Cu(1)-N(2)-C(6)-C(7)	-179.5(2)
C(10)-N(2)-C(6)-C(5)	-174.8(2)
Cu(1)-N(2)-C(6)-C(5)	2.6(3)
N(1)-C(5)-C(6)-N(2)	-3.7(4)
C(4)-C(5)-C(6)-N(2)	175.4(3)
N(1)-C(5)-C(6)-C(7)	178.5(3)
C(4)-C(5)-C(6)-C(7)	-2.4(5)
N(2)-C(6)-C(7)-C(8)	-0.1(4)
C(5)-C(6)-C(7)-C(8)	177.5(3)
C(6)-C(7)-C(8)-C(9)	-3.1(4)
C(6)-C(7)-C(8)-C(16)	177.4(3)
C(7)-C(8)-C(9)-C(10)	3.3(4)
C(16)-C(8)-C(9)-C(10)	-177.2(3)
C(6)-N(2)-C(10)-C(9)	-2.8(4)
Cu(1)-N(2)-C(10)-C(9)	179.73(19)
C(6)-N(2)-C(10)-C(11)	176.5(2)
Cu(1)-N(2)-C(10)-C(11)	-0.9(3)
C(8)-C(9)-C(10)-N(2)	-0.4(4)
C(8)-C(9)-C(10)-C(11)	-179.7(3)
C(15)-N(3)-C(11)-C(12)	-3.0(4)
Cu(1)-N(3)-C(11)-C(12)	177.2(2)
C(15)-N(3)-C(11)-C(10)	177.6(2)
Cu(1)-N(3)-C(11)-C(10)	-2.2(3)

N(2)-C(10)-C(11)-N(3)	2.0(3)
C(9)-C(10)-C(11)-N(3)	-178.6(3)
N(2)-C(10)-C(11)-C(12)	-177.4(3)
C(9)-C(10)-C(11)-C(12)	1.9(5)
N(3)-C(11)-C(12)-C(13)	2.5(4)
C(10)-C(11)-C(12)-C(13)	-178.1(3)
C(11)-C(12)-C(13)-C(14)	-0.3(5)
C(12)-C(13)-C(14)-C(15)	-1.4(5)
C(11)-N(3)-C(15)-C(14)	1.2(4)
Cu(1)-N(3)-C(15)-C(14)	-179.1(2)
C(13)-C(14)-C(15)-N(3)	1.0(5)
C(19)-O(1)-C(16)-C(17)	0.0(3)
C(19)-O(1)-C(16)-C(8)	-178.8(3)
C(7)-C(8)-C(16)-C(17)	178.6(3)
C(9)-C(8)-C(16)-C(17)	-0.9(5)
C(7)-C(8)-C(16)-O(1)	-3.0(4)
C(9)-C(8)-C(16)-O(1)	177.5(2)
O(1)-C(16)-C(17)-C(18)	-0.1(4)
C(8)-C(16)-C(17)-C(18)	178.4(3)
C(16)-C(17)-C(18)-C(19)	0.1(4)
C(17)-C(18)-C(19)-O(1)	-0.1(4)
C(16)-O(1)-C(19)-C(18)	0.1(4)
O(4)-S(1)-C(23)-F(2)	-177.5(3)
O(3)-S(1)-C(23)-F(2)	61.4(3)
O(2)-S(1)-C(23)-F(2)	-57.2(3)
O(4)-S(1)-C(23)-F(3)	-55.6(3)
O(3)-S(1)-C(23)-F(3)	-176.7(3)
O(2)-S(1)-C(23)-F(3)	64.7(3)
O(4)-S(1)-C(23)-F(1)	65.2(3)
O(3)-S(1)-C(23)-F(1)	-55.9(3)
O(2)-S(1)-C(23)-F(1)	-174.5(3)

Symmetry transformations used to generate equivalent atoms:

15. Density functional theory (DFT) calculations

Table S25. The global properties[a] and of the nuleophilic reagents

Entry	*p*-R-Py	HOMO	LUMO	*N*	Charge at N atom (e)
1	*p*-CNP	-0.2797	-0.0763	1.51	-0.432
2	Py	-0.2526	-0.0225	2.25	-0.452
3	*p*-MeP	-0.2496	-0.0183	2.33	-0.458
4	*p*-MOP	-0.2450	-0.0076	2.46	-0.476
5	*p*-MPP	-0.2156	-0.0044	3.26	-0.481

6	*p*-DMAP	-0.2055	0.0059	3.54	-0.490
7	*o*-DMAP	-0.1939	-0.0070	3.85	-0.519
8	*m*-DMAP	-0.1934	-0.0075	3.87	-0.438
9	*p*-DEAP	-0.2025	0.0049	3.62	-0.493
10	Piperidine	-0.2090	0.0825	3.44	-0.691
11	*p*-DMAP·TFA	-0.253	-0.0287	2.23	-0.460

[a] HOMO, LUMO in au; global nuleophilicity (*N*), values in eV.

Table S26. Cartesian coordinates and free energies (298 ℃) for DFT optimized structures formed by complex **1a** with DMAP positional isomers.

1a + *o*-DMAP -2470.075968 a.u

Cu	-0.74059500	0.32462100	-0.39700500
Cl	-0.98367000	0.62478500	-2.58707400
Cl	-1.42048200	0.23436700	1.72606900
N	0.09980800	2.29735000	-0.12823700
N	-0.42206700	-1.79767300	-0.57211900
N	-4.22775000	-0.90058600	-0.51338200
N	1.40239000	0.03889600	-0.19220200
O	6.28060700	0.55457500	0.57232100
C	-0.64775100	3.39500200	-0.12841300
C	-0.10248300	4.66516200	0.03280600
C	1.27333200	4.77356700	0.19757800
C	2.05286600	3.62248800	0.19735100
C	1.43120900	2.38638000	0.03170800
C	2.17230200	1.09680600	0.01721800
C	3.54499300	0.95046300	0.20553100
C	4.08815500	-0.34138800	0.17253700
C	3.23902300	-1.43540600	-0.04886900
C	1.87972900	-1.19766900	-0.22877800
C	5.50999300	-0.55137800	0.36664100
C	6.30148900	-1.66733700	0.39189000
C	7.63207000	-1.21904100	0.62621200
C	7.55746300	0.13606600	0.72678300
C	0.84476500	-2.23886500	-0.46994400
C	1.14672100	-3.59329800	-0.59045300
C	0.11501000	-4.49721300	-0.81993400
C	-1.18699900	-4.02678400	-0.92517200

C	-1.41298400	-2.65796200	-0.79697600
C	-4.61398800	-0.34224300	0.64723600
C	-4.99437500	1.01745200	0.71722300
C	-4.96188900	1.77624000	-0.43823400
C	-4.55417500	1.20119900	-1.64197700
C	-4.20045800	-0.13961500	-1.60979500
H	-1.71957600	3.23901600	-0.26304300
H	-0.74464300	5.54257300	0.02759500
H	1.74020700	5.74882300	0.32508800
H	3.13157200	3.69091300	0.32142000
H	4.19879600	1.80069700	0.38158600
H	3.64717600	-2.44373900	-0.07346700
H	5.97619300	-2.69258800	0.25930000
H	8.52609300	-1.82469600	0.70665000
H	8.29075600	0.91315300	0.89694000
H	2.17426400	-3.94231400	-0.51078200
H	0.33142500	-5.55987900	-0.91674000
H	-2.02266800	-4.69967200	-1.10408900
H	-2.41849400	-2.22817100	-0.85402700
H	-4.48203800	1.77187100	-2.56463100
H	-3.84961500	-0.63282200	-2.51908500
H	-5.24680300	2.82802200	-0.39662800
H	-5.28949400	1.47172200	1.65900600
N	-4.63935400	-1.15123400	1.76043000
C	-4.73485300	-0.53893000	3.06821000
H	-5.69482100	-0.01890600	3.19617700
H	-4.68519700	-1.32495100	3.82854400
H	-3.91167900	0.17192800	3.25312500
C	-4.00947700	-2.45376400	1.69679700
H	-2.90928300	-2.37736500	1.74673400
H	-4.36223200	-3.05771800	2.54129400
H	-4.28628000	-2.95895100	0.76619700

1a + *m*-DMAP -2470.068733 a.u

Cu	-0.76317700	0.09272600	0.34304600
Cl	-0.33401600	0.24525600	2.60020000
Cl	-0.95979500	-0.06612200	-1.96648000
N	-0.13029500	-2.10337300	0.39853400
N	-0.09034200	2.25511500	0.08746500
N	-2.90683600	0.13687200	0.64031400
N	1.38987500	0.04838700	0.04449600
O	6.19407500	-1.23347500	-0.36510600

C	-0.95988200	-3.12520100	0.56227300
C	-0.53702500	-4.45109700	0.53011500
C	0.81344000	-4.69826900	0.31432900
C	1.68319800	-3.62734000	0.14825600
C	1.17288500	-2.32850100	0.20004800
C	2.02733600	-1.12049000	0.04241500
C	3.41279900	-1.18531400	-0.09239200
C	4.13733700	0.00069500	-0.23057200
C	3.43803000	1.21153700	-0.22984400
C	2.05372200	1.19673000	-0.08794300
C	5.58082800	-0.01564300	-0.37063200
C	6.52281400	0.96605300	-0.51455700
C	7.78450900	0.31205300	-0.60212000
C	7.52273900	-1.01957100	-0.50566100
C	1.22465600	2.43326900	-0.07566600
C	1.76515800	3.71171200	-0.22908600
C	0.91345400	4.80972000	-0.21147700
C	-0.45153900	4.60983700	-0.04396900
C	-0.90473400	3.30189100	0.10163900
C	-3.71087700	-0.21593500	-0.36543400
C	-5.11660200	-0.17389600	-0.29235100
C	-5.66780800	0.29342700	0.91261100
C	-4.82124700	0.65309600	1.95197100
C	-3.44478400	0.56046600	1.79436300
H	-2.00757000	-2.86602300	0.72885400
H	-1.24934500	-5.26129800	0.66915200
H	1.19155800	-5.71860300	0.27559100
H	2.74112700	-3.81105600	-0.02411300
H	3.94186400	-2.13382300	-0.08489700
H	3.98036000	2.14815700	-0.33653900
H	6.34115000	2.03378400	-0.55271300
H	8.75776500	0.77195700	-0.72121900
H	8.14329700	-1.90574400	-0.51741000
H	2.83410700	3.86132700	-0.36256300
H	1.31760500	5.81388700	-0.32973100
H	-1.15042300	5.44304500	-0.02625800
H	-1.96547000	3.07831000	0.23419300
H	-3.19369500	-0.52010300	-1.27168800
H	-5.23094800	1.01402500	2.89352900
H	-2.74040500	0.81612100	2.58371300
H	-6.74479900	0.37766800	1.04203900
N	-5.88907500	-0.57283800	-1.36497800
C	-7.30602900	-0.29827900	-1.33795300
H	-7.52951700	0.78090700	-1.25811900

H	-7.76228800	-0.67459300	-2.25835700
H	-7.79425100	-0.81099900	-0.49658800
C	-5.24584100	-0.80447100	-2.64399600
H	-6.00458200	-1.10629600	-3.37203300
H	-4.72552200	0.09003700	-3.02622600
H	-4.50821300	-1.61524200	-2.57637300

1a + *p*-DMAP -2470.075047 a.u

Cu	-0.65036800	0.02691200	-0.00006800
Cl	-0.52127200	0.03132800	2.30776000
Cl	-0.52079000	0.03475400	-2.30778400
N	0.03439800	-2.15116500	-0.00114800
N	0.00512300	2.21302300	0.00140300
N	-2.80509500	0.00054100	-0.00008300
N	1.53305700	0.04175700	0.00020000
N	-7.00744100	-0.07952100	-0.00067400
O	6.38556300	-1.12640700	-0.00057400
C	-0.78634900	-3.19270600	-0.00100600
C	-0.33264400	-4.50839700	0.00027900
C	1.04046300	-4.72328100	0.00156700
C	1.90019000	-3.63131900	0.00144100
C	1.35742800	-2.34430200	0.00000400
C	2.19497600	-1.11362800	-0.00010800
C	3.58821500	-1.14600200	-0.00047500
C	4.29493100	0.05866100	-0.00026000
C	3.57079400	1.25460100	0.00027700
C	2.18005800	1.20737900	0.00040500
C	5.74529300	0.07749900	-0.00058200
C	6.67163900	1.08411500	-0.00092800
C	7.95202600	0.46133500	-0.00112700
C	7.71609800	-0.87846800	-0.00092900
C	1.32481700	2.42610600	0.00084700
C	1.84678200	3.72163300	0.00068400
C	0.97015900	4.80001000	0.00113900
C	-0.39954900	4.56385300	0.00174000
C	-0.83233400	3.24120400	0.00182100
C	-3.51259300	-0.01347800	-1.14438000
C	-4.89331300	-0.04065200	-1.19596700
C	-5.64072900	-0.05431500	-0.00046900
C	-4.89363300	-0.04055500	1.19523600
C	-3.51290400	-0.01343000	1.14401700
C	-7.72733000	-0.10163900	-1.25549600

C	-7.72776500	-0.10168500	1.25389100
H	-1.85303000	-2.95847800	-0.00186500
H	-1.03760600	-5.33674800	0.00035400
H	1.44383100	-5.73464900	0.00276000
H	2.97602700	-3.79008400	0.00263600
H	4.13565700	-2.08404900	-0.00102600
H	4.09933100	2.20507400	0.00064000
H	6.46804500	2.14856700	-0.00107700
H	8.92009900	0.94681300	-0.00142400
H	8.35682400	-1.75021600	-0.00096400
H	2.91998900	3.89815900	0.00014800
H	1.35744500	5.81765300	0.00099800
H	-1.11732800	5.38110200	0.00209800
H	-1.89489000	2.98869500	0.00220500
H	-2.91709000	-0.00289000	-2.05779800
H	-5.37649200	-0.05202800	-2.16936900
H	-5.37707200	-0.05187900	2.16850900
H	-2.91761200	-0.00298000	2.05757800
H	-7.48535800	-0.99687600	-1.84884800
H	-7.50360100	0.78592300	-1.86660800
H	-8.80197200	-0.11009200	-1.05435800
H	-7.48591000	-0.99688200	1.84734300
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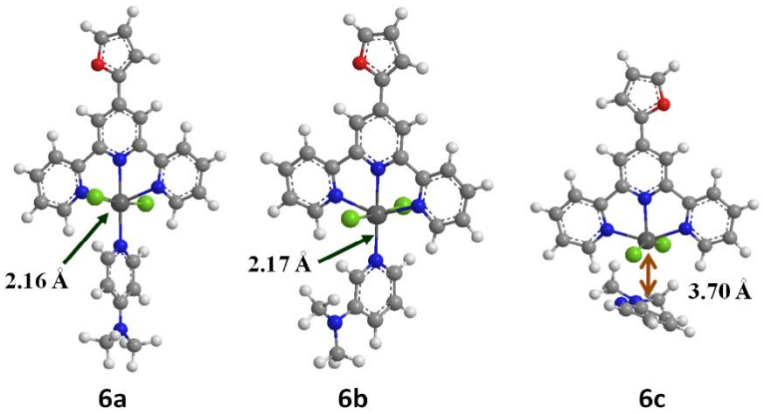

Figure S15. Calculated chemical structures of complexes **6a-c**.

16. pK_a value of pyridine derivatives

Table S27. pK_a value of pyridine derivatives

Entry	Pyridine derivatives	pK_a (exp.)	pK_a (predicted)[a]
1	Py	5.25[S6]	5.23 ± 0.10
2	*p*-MeP	6.02[S6]	5.94 ± 0.10
3	*p*-MOP	6.59[S7]	6.59 ± 0.10
4	*p*-MPP	/	7.97 ± 0.26
5	*p*-DMAP	9.70[S8]	9.52 ± 0.10
6	*m*-DMAP	6.37[S8]	6.33 ± 0.10
7	*o*-DMAP	6.94[S8]	7.04 ± 0.10
8	*p*-DEMP	/	10.19 ± 0.10
9	*p*-CNP	2.25[S7]	1.92 ± 0.10
10	3-Hydroxypyridine	4.75[S9]	9.15 ± 0.10
11	2-Aminopyridine	6.86[S6]	6.67 ± 0.11
12	2-Chloropyridine	0.72[S6]	0.14 ± 0.10
13	2,6-Dimethylpyridine	6.79[S10]	6.67 ± 0.10
14	2,6-Difluoropyridine	/	-6.09 ± 0.10
15	2-Chloropyrazine	/	-1.10 ± 0.10
16	Quinoline	4.94[S11]	4.97 ± 0.17
17	Isoquinoline	5.40[S12]	5.37 ± 0.23
18	Piperidine	11.21 ± 0.04[S13]	10.45 ± 0.10

[a] Most Basic Temp: 25 ℃, Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02

17. UV/Vis spectra

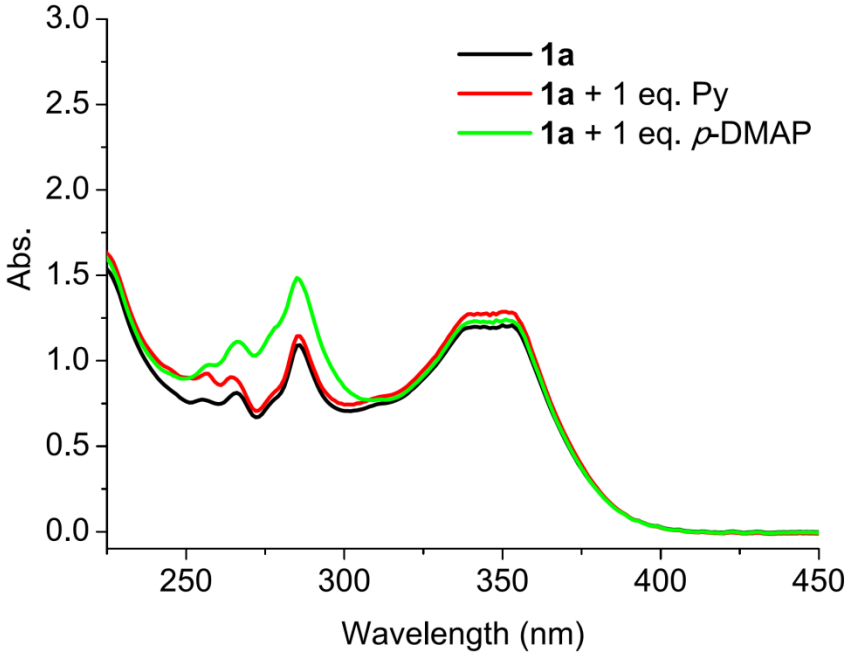

Figure S16. The UV-Vis spectrum of: a) Cu(II)-terpyridine complex **1a**, b) Cu(II)-terpyridine complex **1a** with 1 equiv. Py and c) Cu(II)-terpyridine complex **1a** with 1 equiv. *p*-DMAP in H_2O (1.0×10^{-5} M).

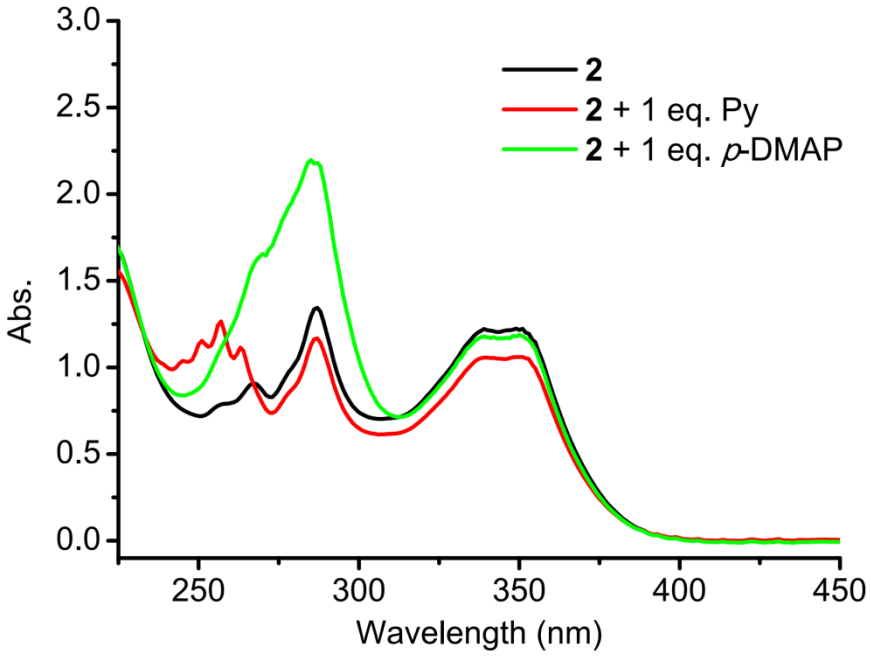

Figure S17. The UV-Vis spectrum of: a) Cu(II)-terpyridine complex **2**, b) Cu(II)-terpyridine complex **2** with 1 equiv. Py and c) Cu(II)-terpyridine complex **2** with 1 equiv. *p*-DMAP in H_2O (1.0×10^{-5} M).

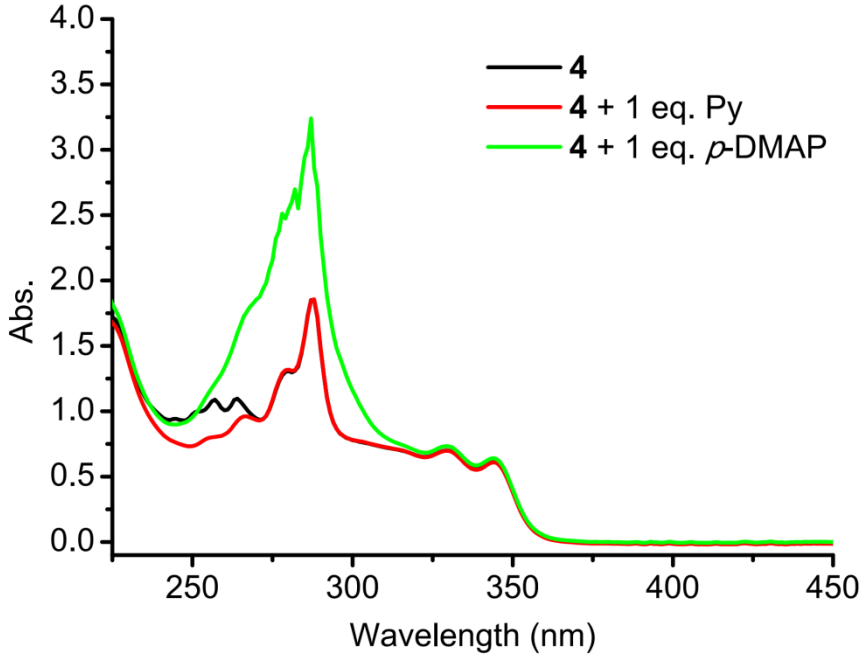

Figure 18. The UV-Vis spectrum of: a) Cu(II)-terpyridine complex **4**, b) Cu(II)-terpyridine complex **4** with 1 equiv. Py and c) Cu(II)-terpyridine complex **4** with 1 equiv. *p*-DMAP in H_2O (1.0×10^{-5} M).

18. SEM images of collapsed sols and hydrogels formed by metallogel 1a with *p*-substituted pyridines.

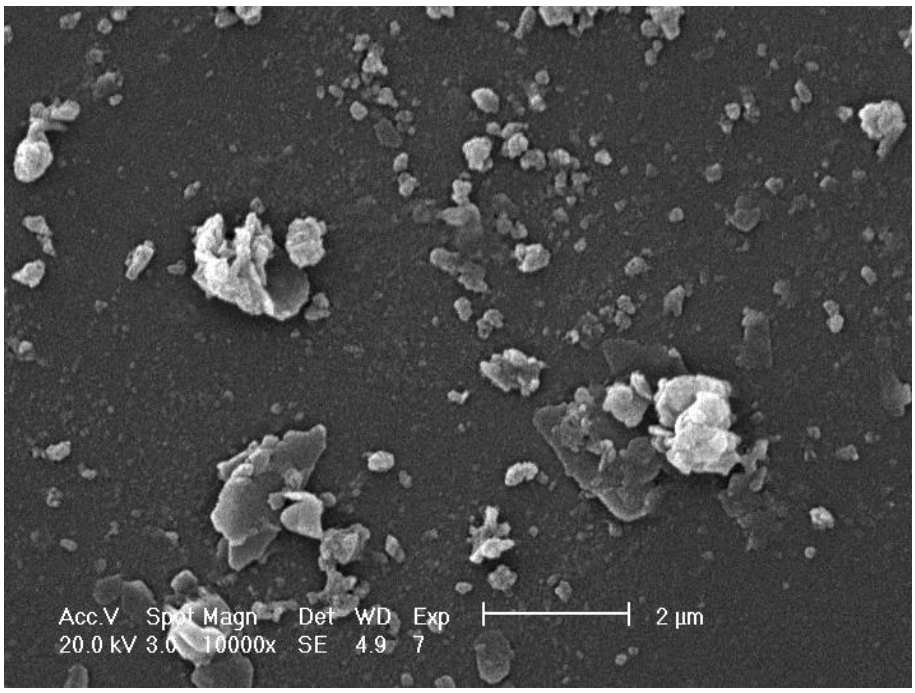

Figure S19. SEM image of metallogel formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. Py, scale of bar 2 µm.

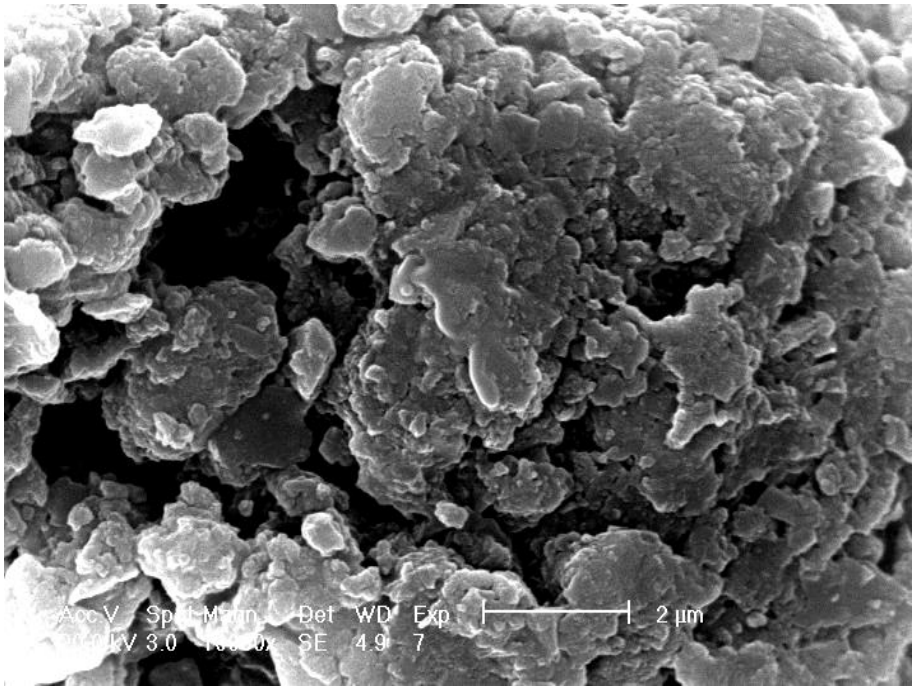

Figure S20. SEM image of metallogel formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *p*-MeP, scale of bar 2 µm.

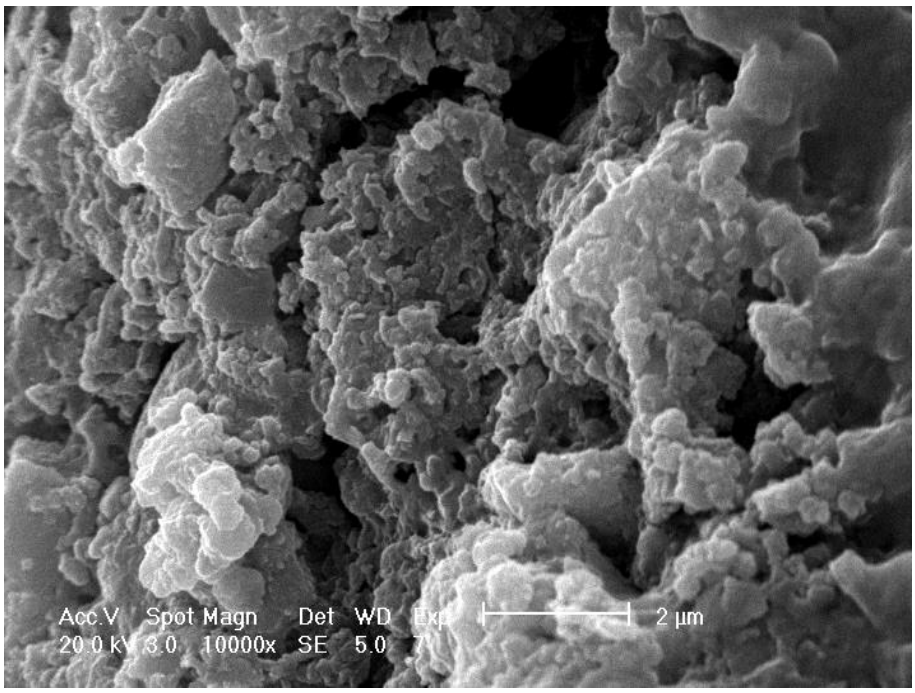

Figure S21. SEM image of metallogel formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *p*-MOP, scale of bar 2 μm.

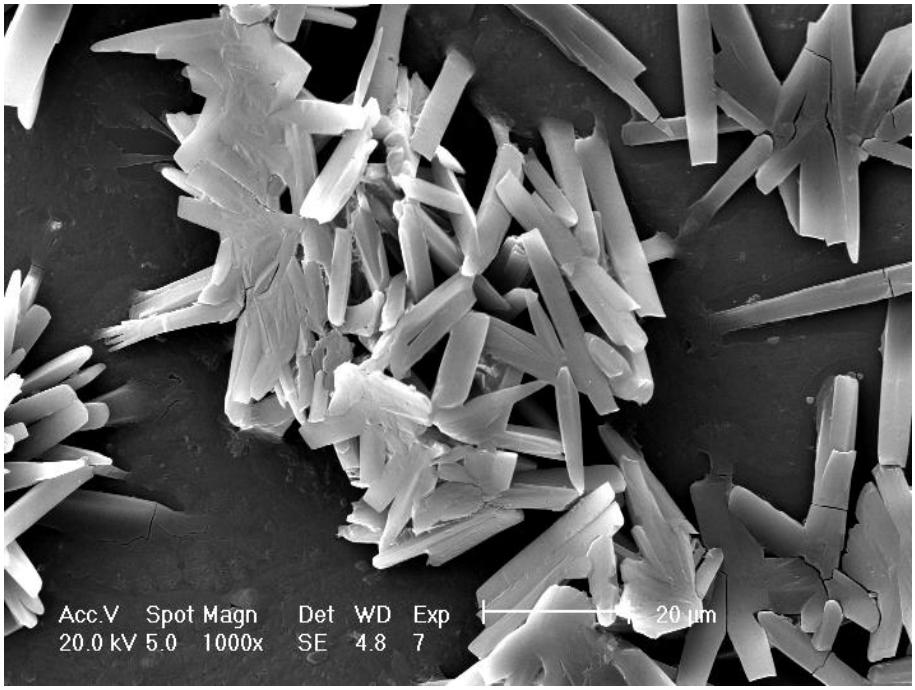

Figure S22. SEM image of weak metallogel formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *p*-MPP, scale of bar 20 μm.

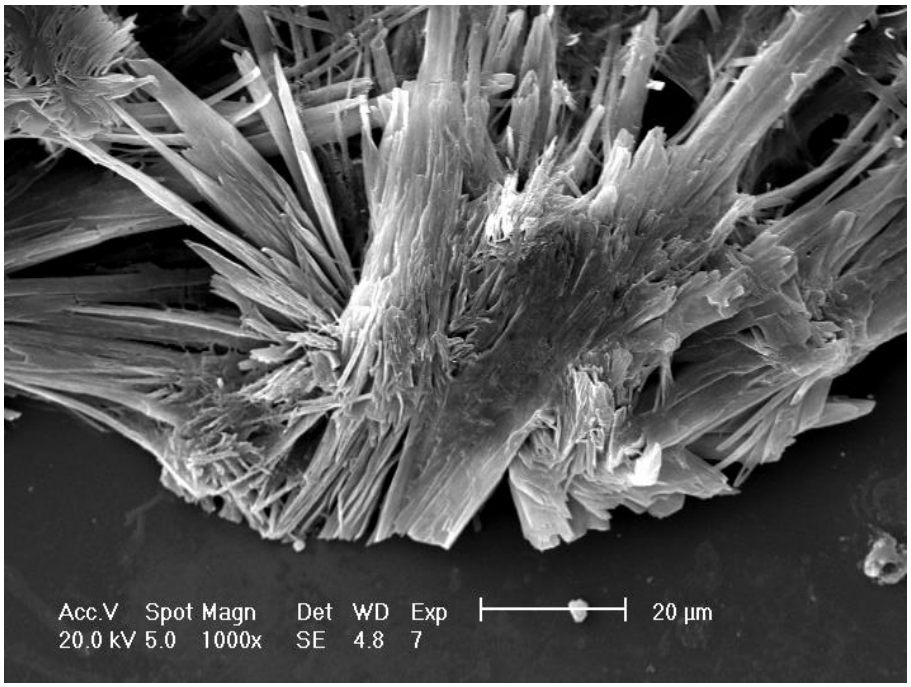

Figure S23. SEM image of collapsed sol formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *p*-DEAP, scale of bar 20 µm.

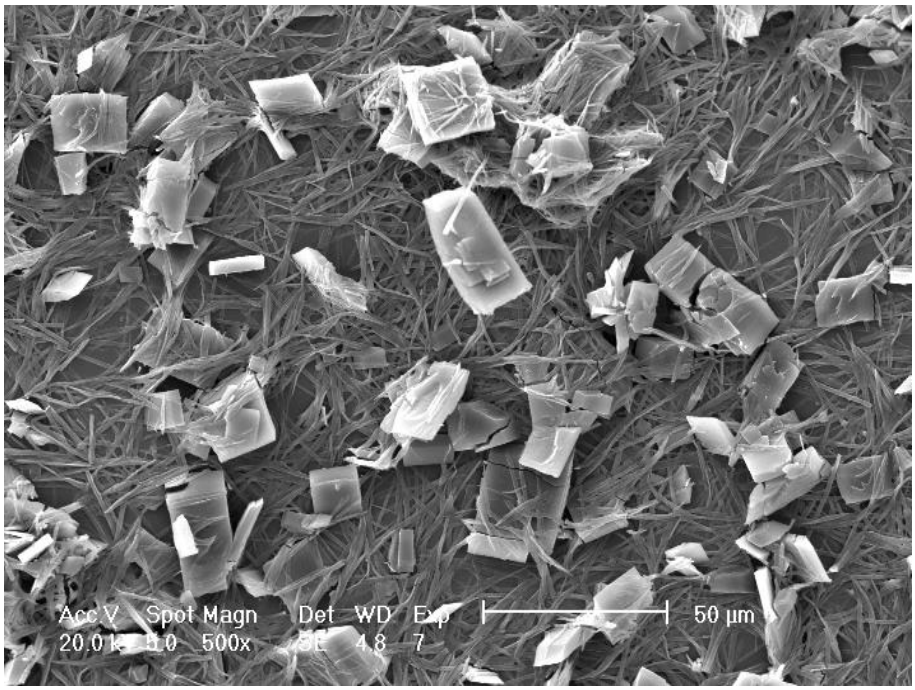

Figure S24. SEM image of sol formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *p*-DMAP, scale of bar 50 µm.

19. SEM images of collapsed sol and hydrogels formed by metallogel 1a with *p*-DMAP positional isomers.

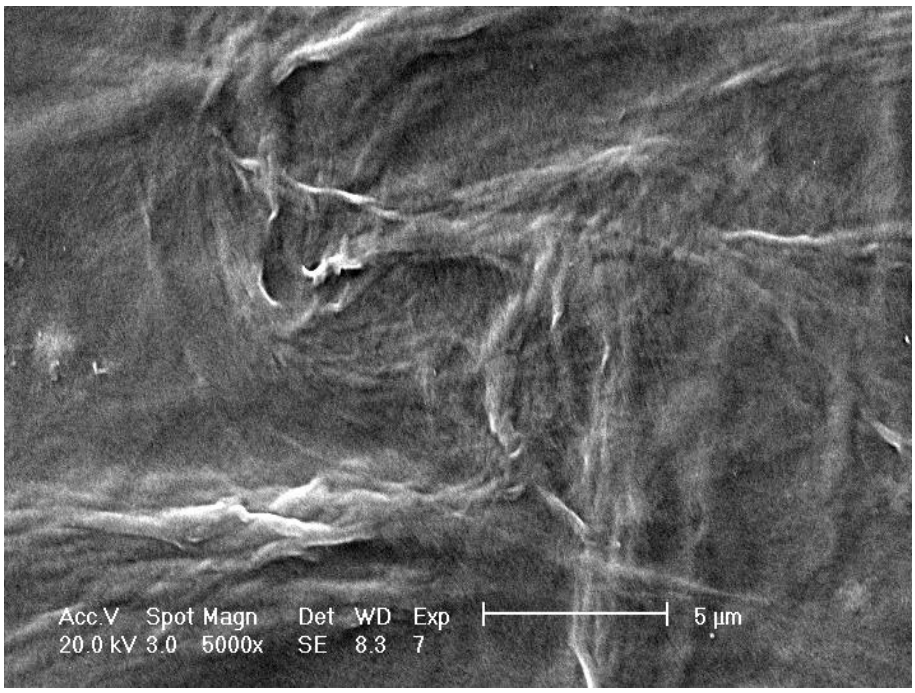

Figure S25. SEM image of metallogel formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *o*-DMAP, scale of bar 5 µm.

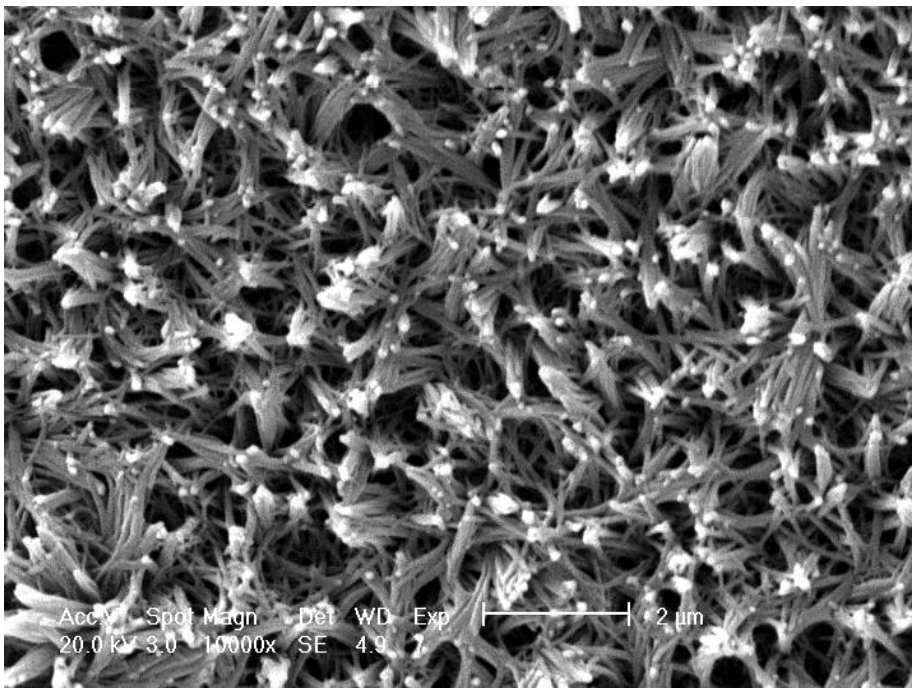

Figure S26. SEM image of metallogel formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *m*-DMAP, scale of bar 2 µm.

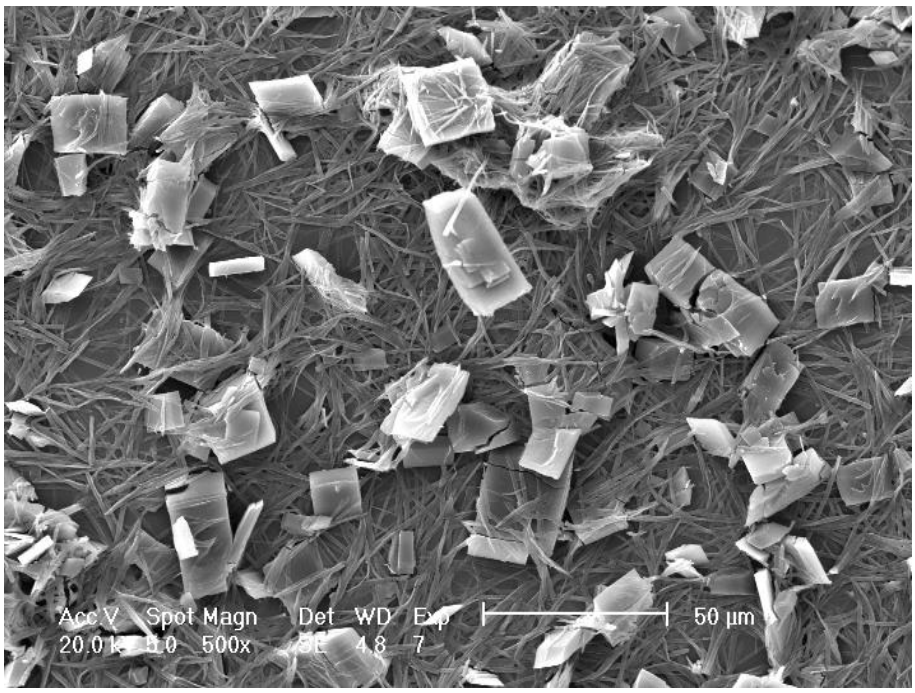

Figure S27. SEM image of sol formed by gel **1a**/H_2O (1.0 wt%) with 1 equiv. *p*-DMAP, scale of bar 50 μm.

20. Reversible gel-to-sol phase transition of metallogel 1a controlled by adding *p*-DMAP and TFA.

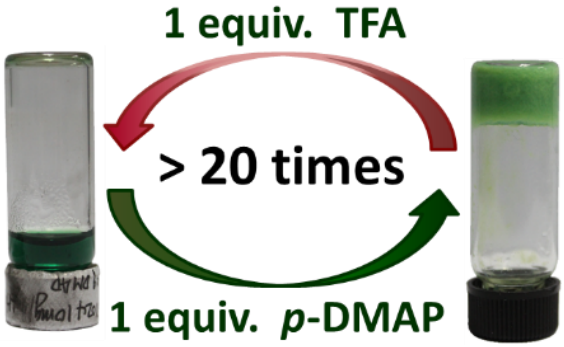

Figure S28. Reversible gel-to-sol phase transition of metallogel **1a** controlled by adding *p*-DMAP and TFA.

21. ^{1}H NMR studies of *p*-DMAP without and with TFA.

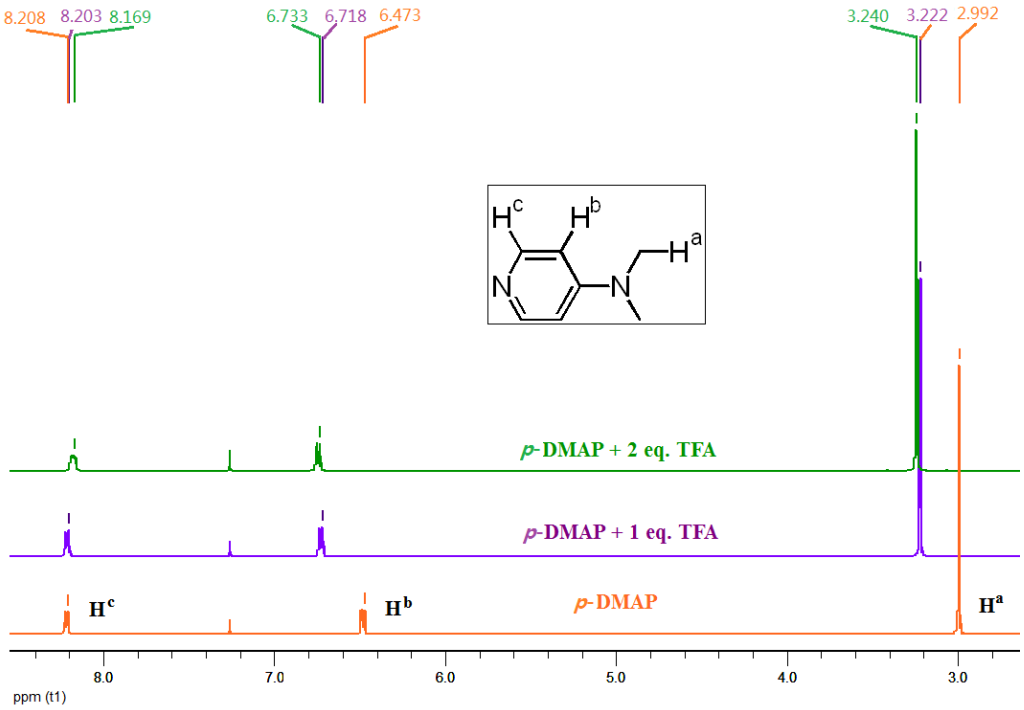

Figure S29 ^{1}H NMR studies of *p*-DMAP without and with TFA.

22. TEM images of metallo-hydrogel reformed by collapsed sol containing *p*-DMAP after adding TFA.

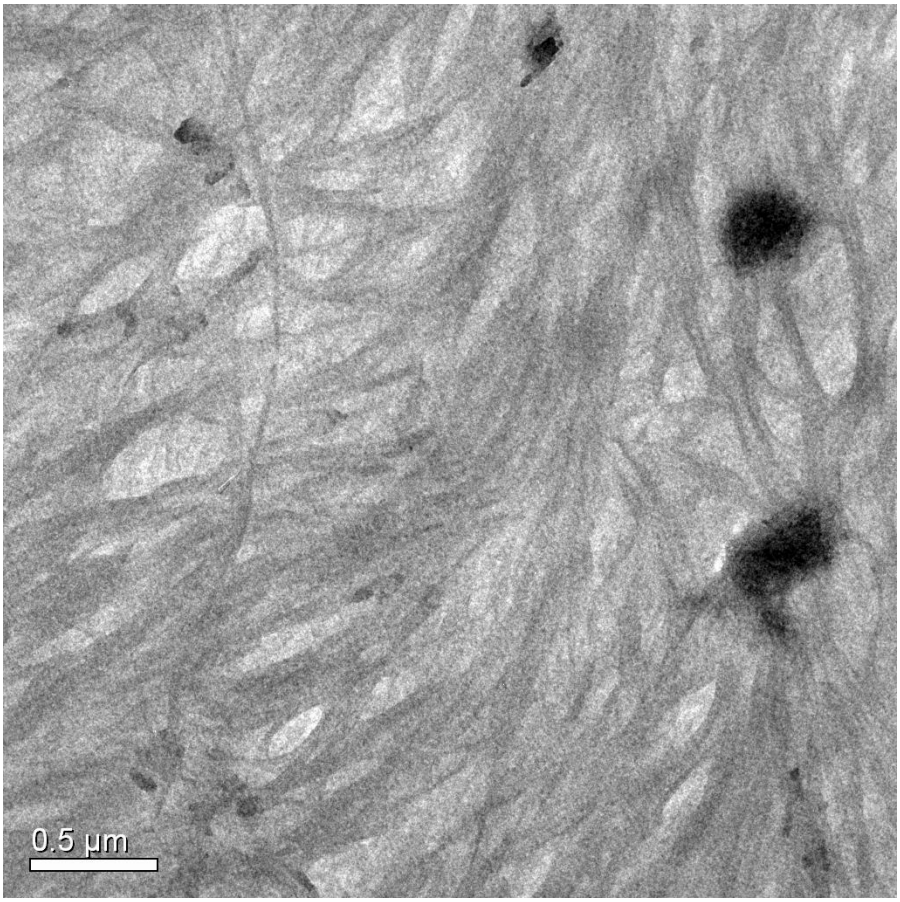

Figure S30. TEM image of metallo-hydrogel (1.0 wt%) reformed by collapsed sol **1a** in H_2O containing 1 equiv. *p*-DMAP after the addition of 1 equiv. TFA, scale of bar 0.5 µm.

23. SEM images of gel-to-sol phase transition of metallogel 1a controlled by adding *p*-DMAP and TFA.

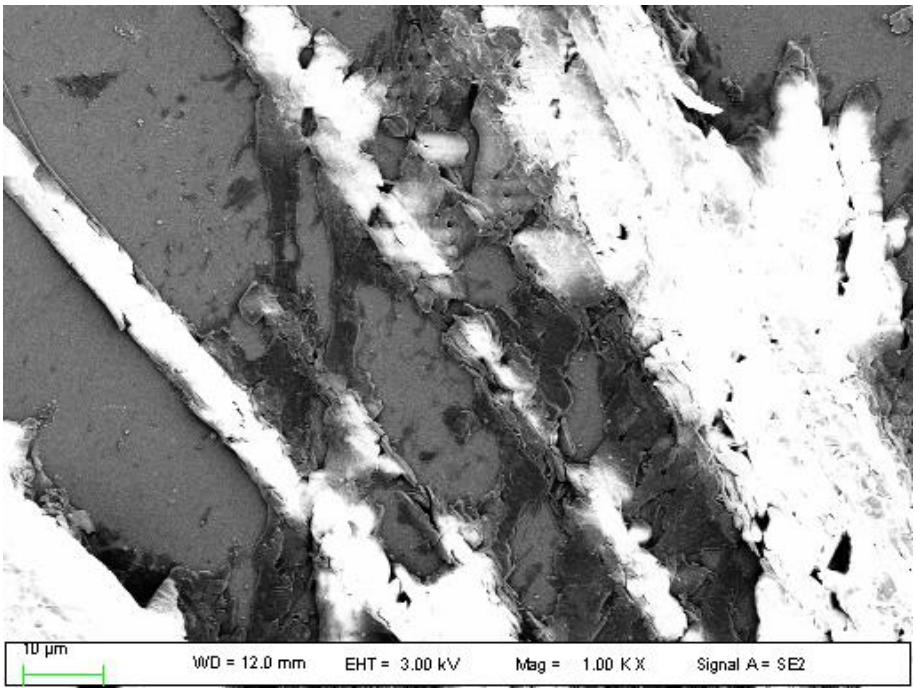

Figure S31. SEM image of sol (1.0 wt%) collapsed by metallo-hydrogel containing 1 equiv. *p*-DMAP and 1 equiv. TFA after the addition of 1 equiv. *p*-DMAP, scale of bar 10 µm.

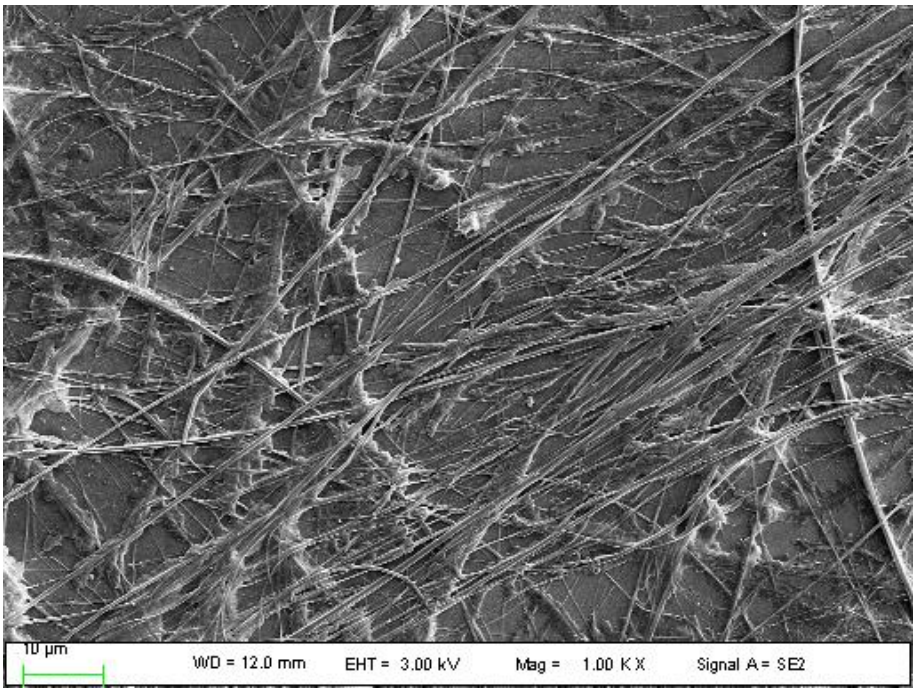

Figure S32. SEM image of metallo-hydrogel (1.0 wt%) reformed by collapsed sol **1a** in H_2O containing 2 equiv. *p*-DMAP and 1 equiv. TFA after the addition of 1 equiv. TFA, scale of bar 10 µm.

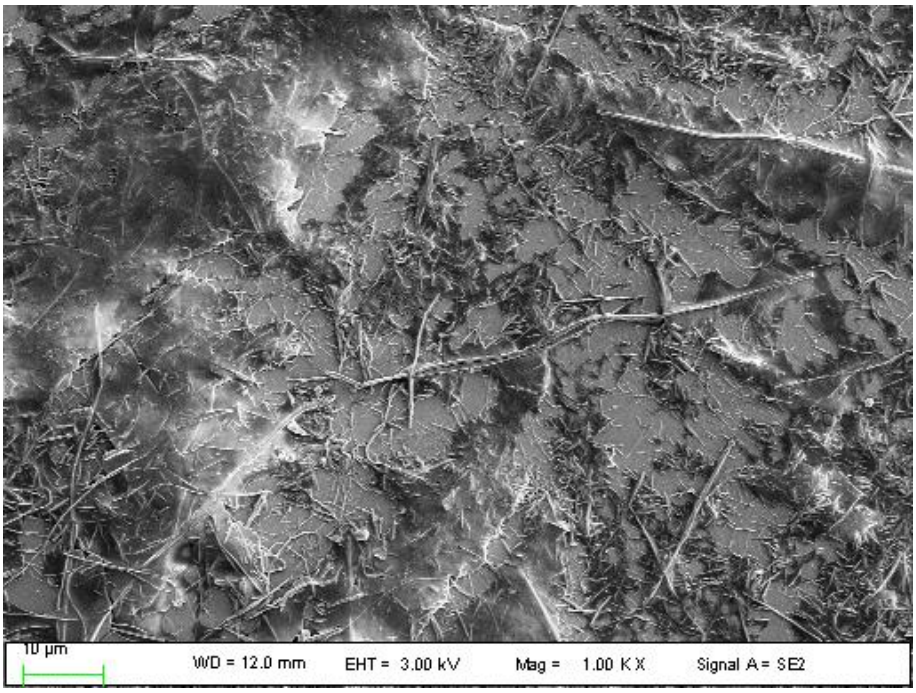

Figure S33. SEM image of metallo-hydrogel (1.0 wt%) reformed by collapsed sol **1a** in H_2O containing 5 equiv. *p*-DMAP and 4 equiv. TFA after the addition of 1 equiv. TFA, scale of bar 10 µm.

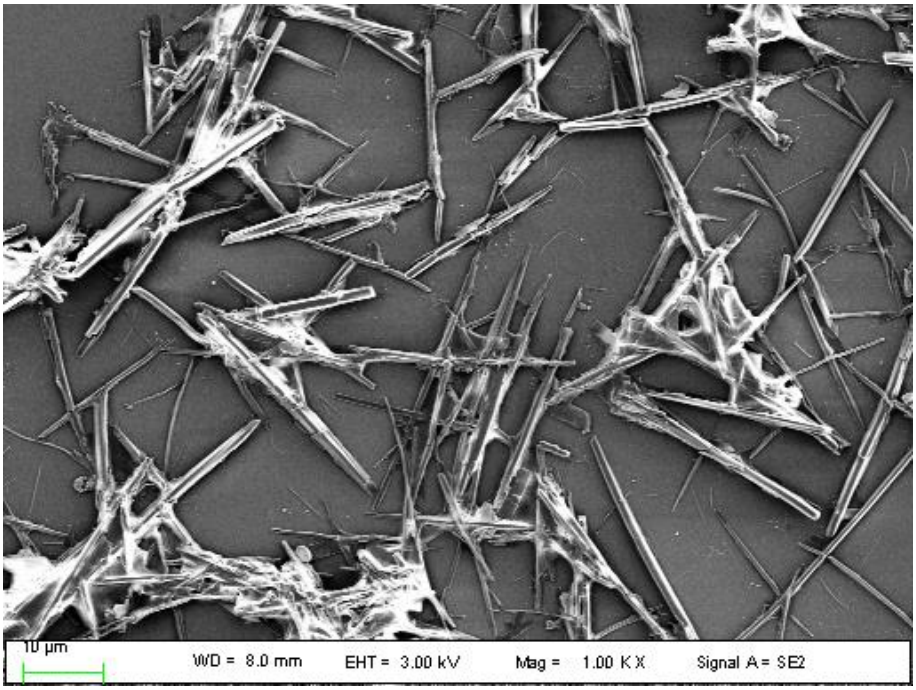

Figure S34. SEM image of sol (1.0 wt%) collapsed by metallo-hydrogel containing 5 equiv. *p*-DMAP and 5 equiv. TFA after the addition of 1 equiv. *p*-DMAP, scale of bar 10 µm.

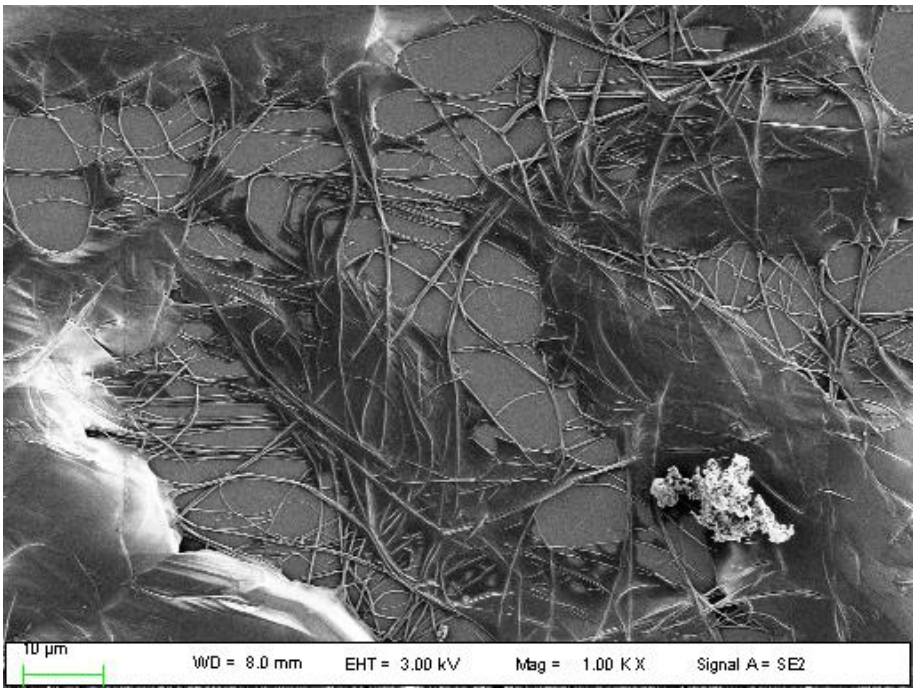

Figure S35. SEM image of metallo-hydrogel (1.0 wt%) reformed by collapsed sol **1a** in H_2O containing 17 equiv. *p*-DMAP and 16 equiv. TFA after the addition of 1 equiv. TFA, scale of bar 10 µm.

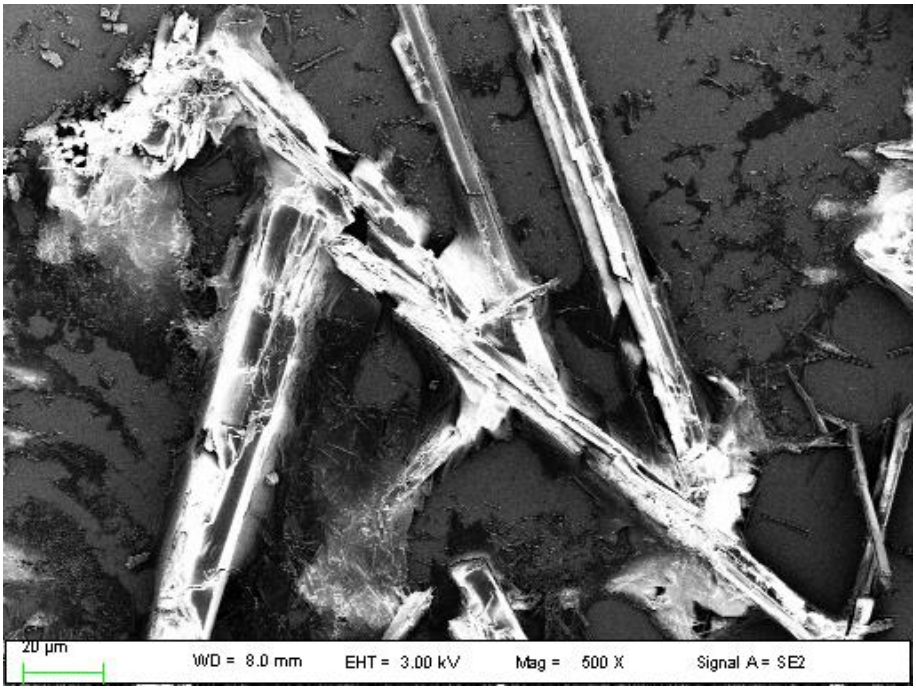

Figure S36. SEM image of sol (1.0 wt%) collapsed by metallo-hydrogel containing 17 equiv. *p*-DMAP and 17 equiv. TFA after the addition of 1 equiv. *p*-DMAP, scale of bar 20 µm.

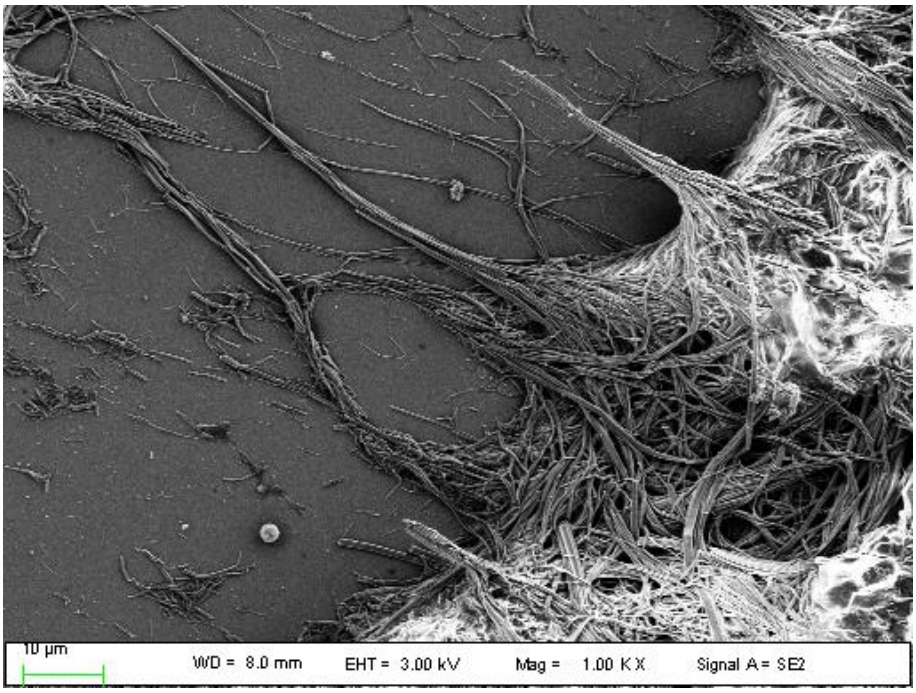

Figure S37. SEM image of metallo-hydrogel (1.0 wt%) reformed by collapsed sol **1a** in H_2O containing 20 equiv. *p*-DMAP and 19 equiv. TFA after the addition of 1 equiv. TFA, scale of bar 10 µm.

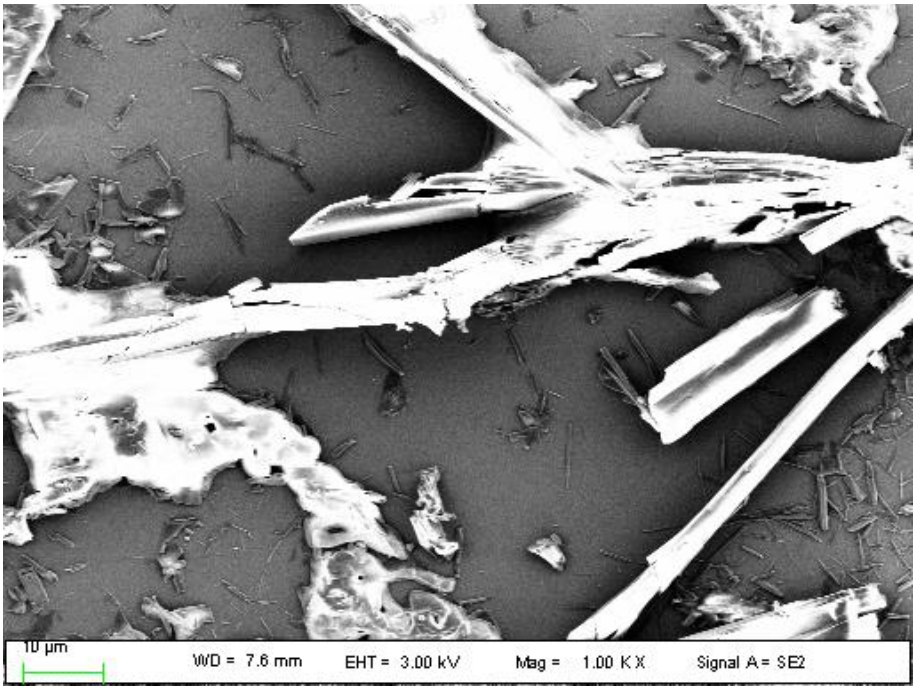

Figure S38. SEM image of sol (1.0 wt%) collapsed by metallo-hydrogel containing 20 equiv. *p*-DMAP and 20 equiv. TFA after the addition of 1 equiv. *p*-DMAP, scale of bar 10 µm.

24. ^{1}H NMR, ^{13}C NMR and ESI-MS spectra for important compounds.

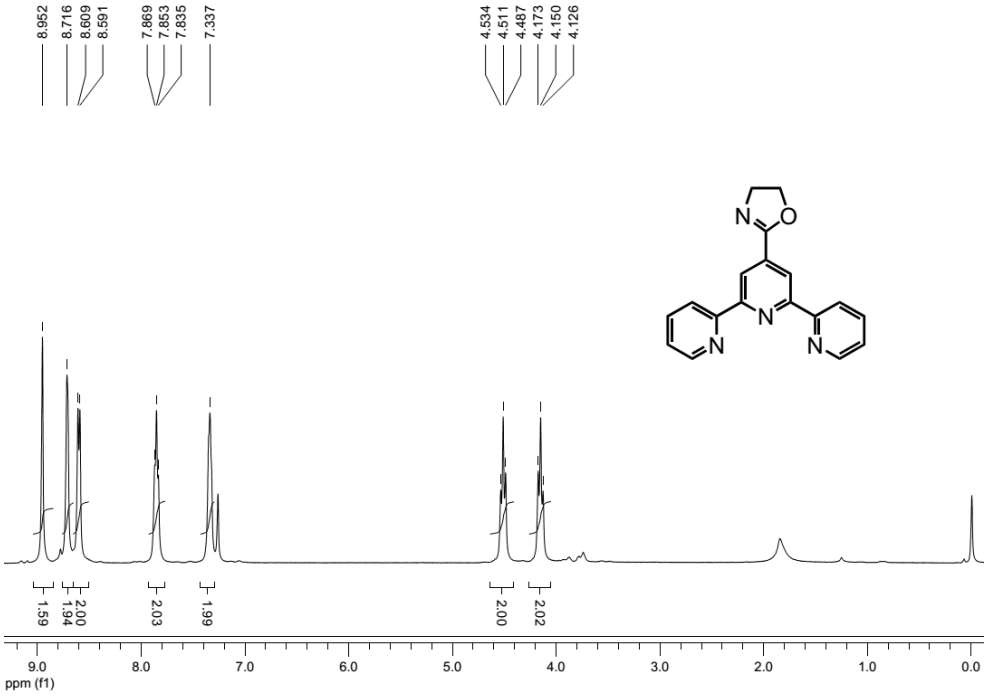

Figure S39. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of ligand **S3**.

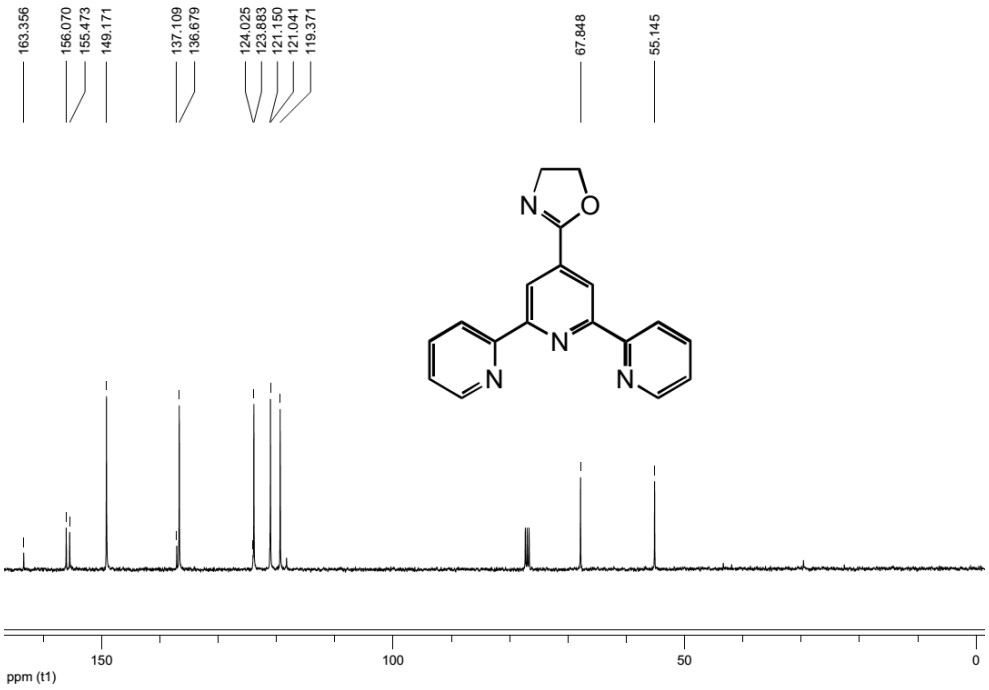

Figure S40. ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) spectrum of ligand **S3**.

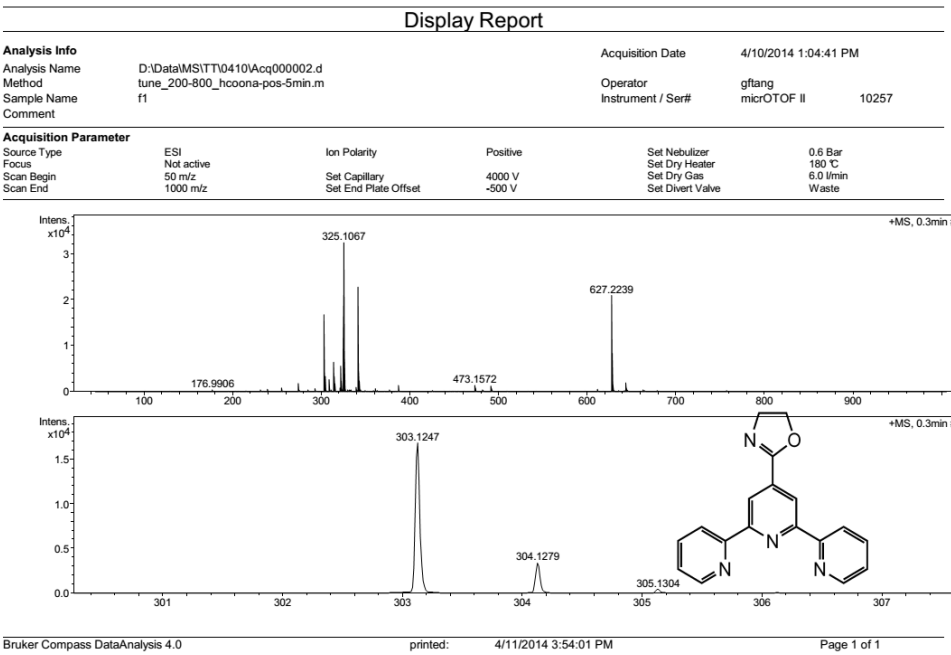

Figure S41. ESI-MS spectrum of ligand **S3**.

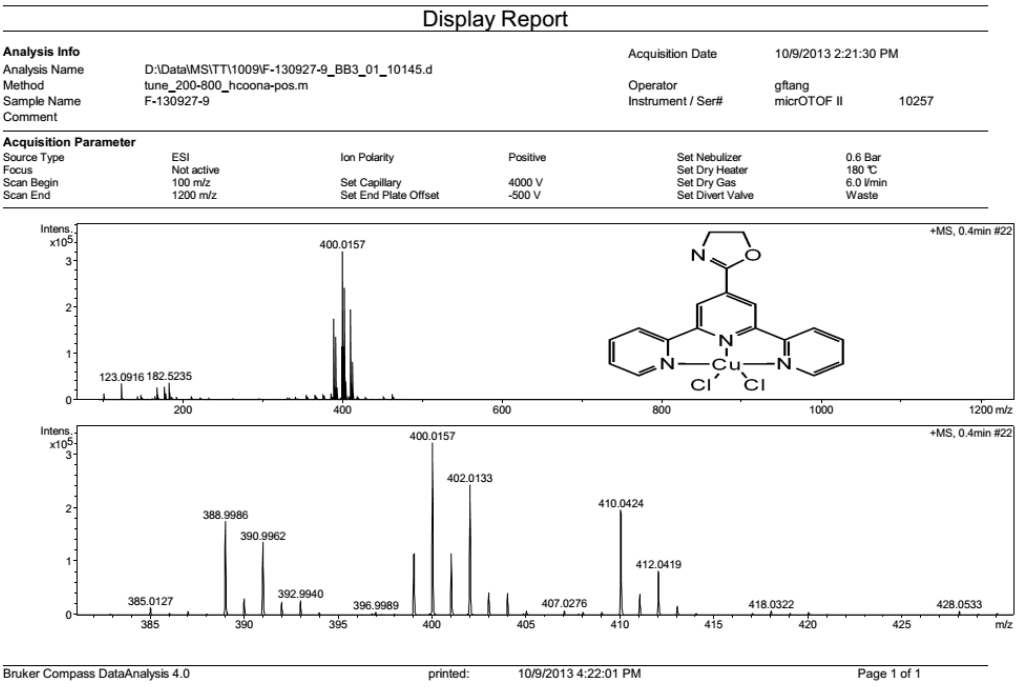

Figure S42. ESI-MS spectrum of ligand **3**.

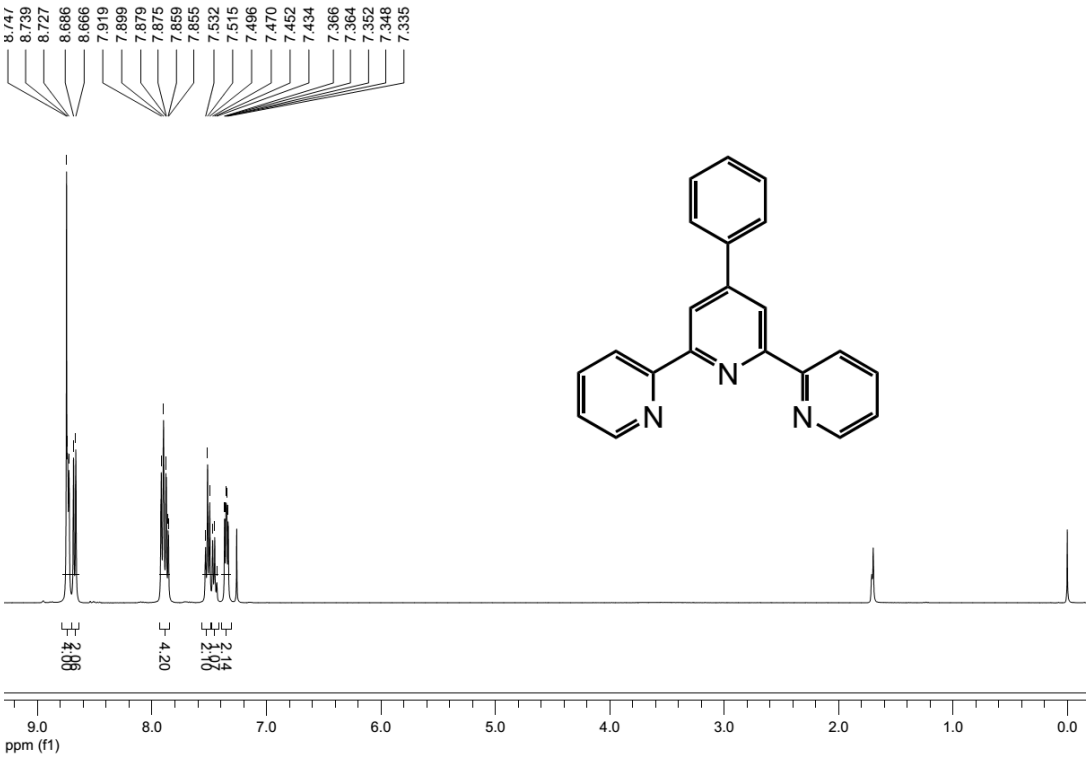

Figure S43. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of ligand **S4**.

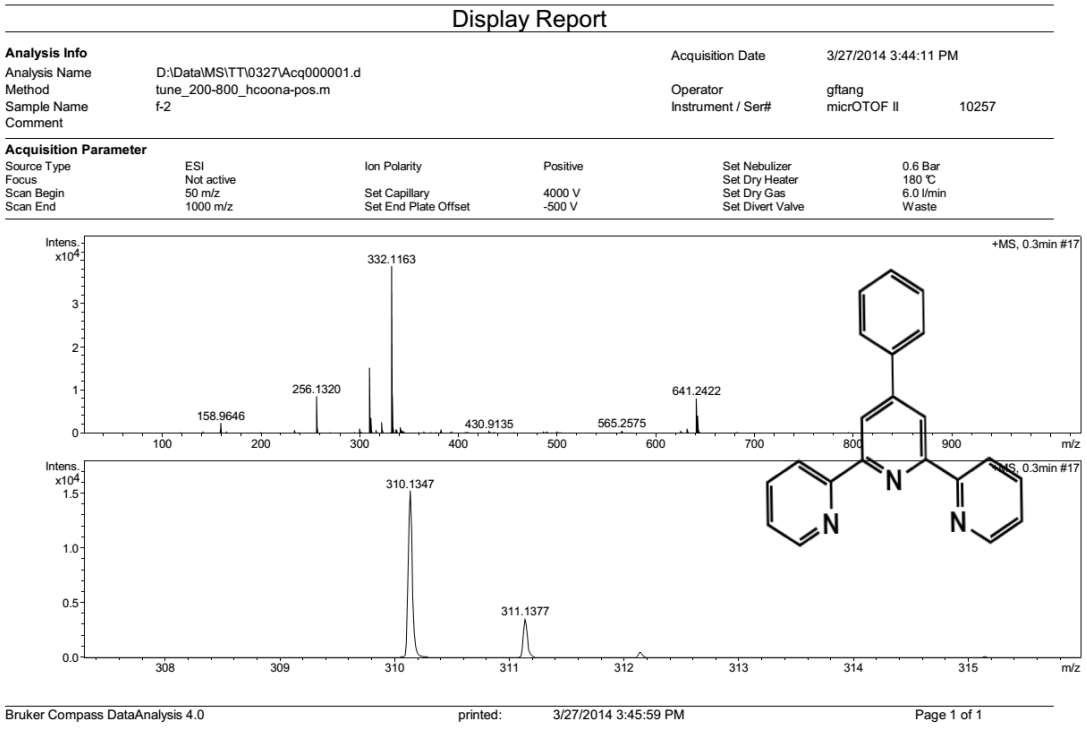

Figure S44. ESI-MS spectrum of ligand **S4**.

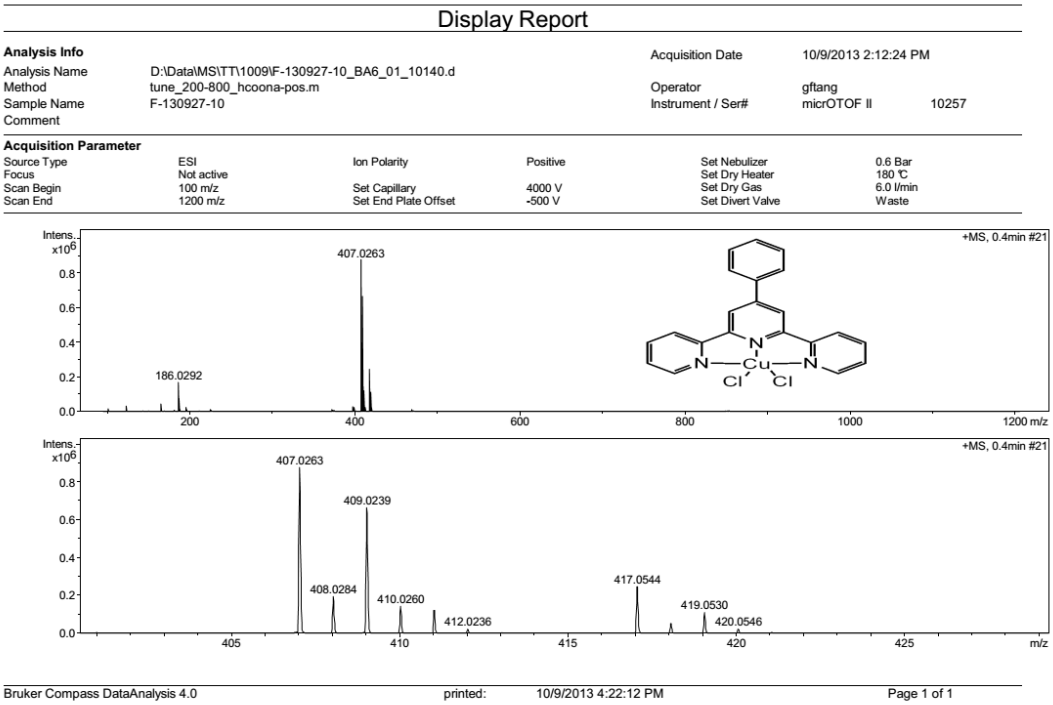

Figure S45. ESI-MS spectrum of complex **4**.

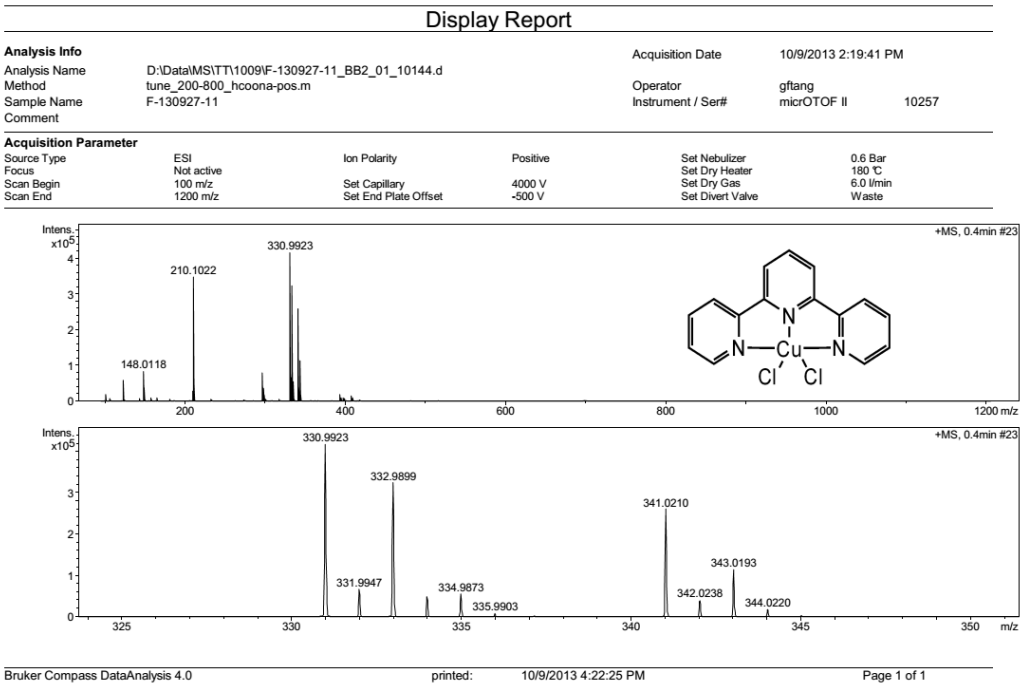

Figure S46. ESI-MS spectrum of complex **5**.

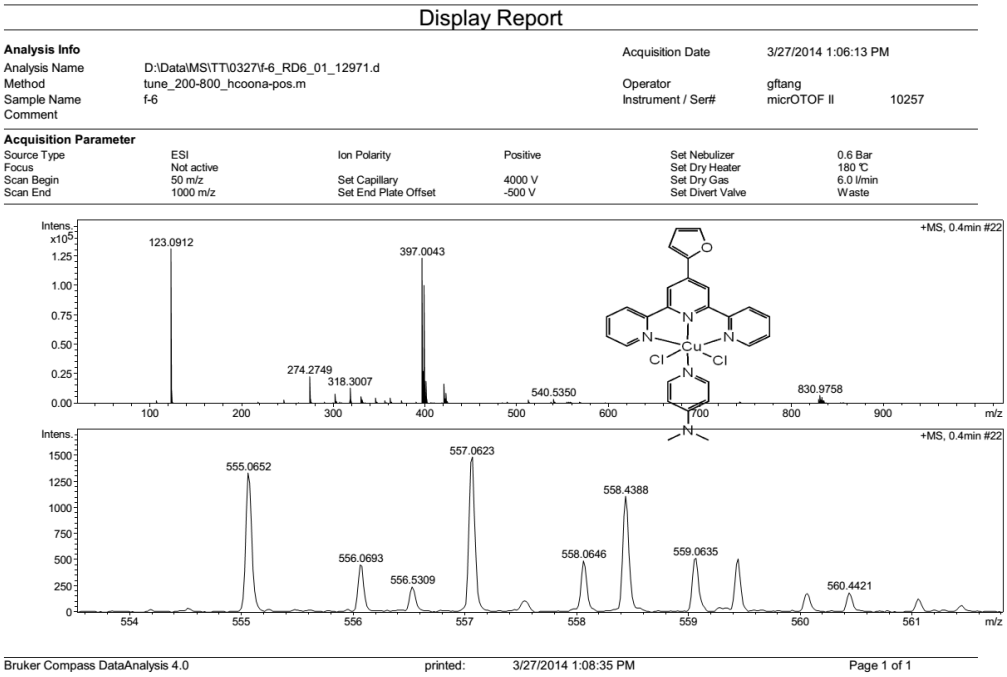

Figure S47. ESI-MS spectrum of complex **6a**.

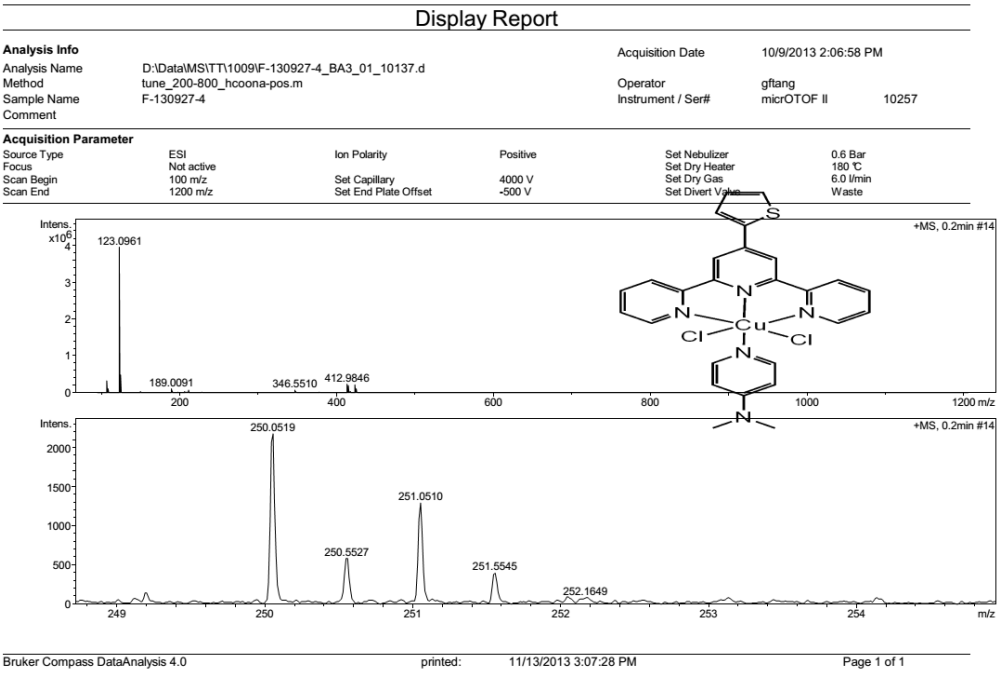

Figure S48. ESI-MS spectrum of complex **7**.

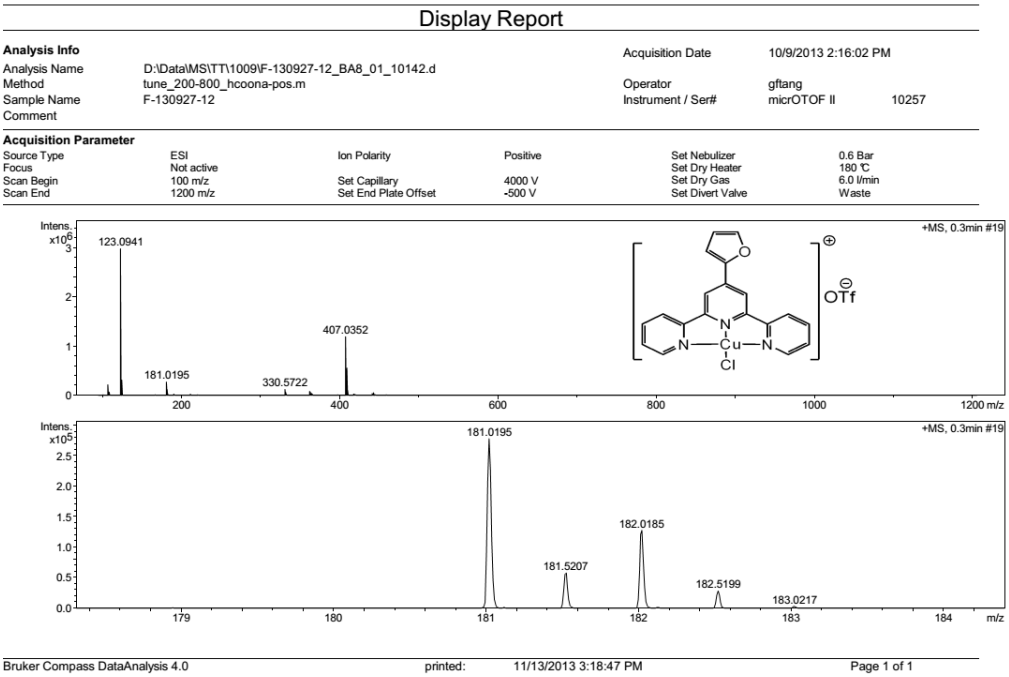

Figure S49. ESI-MS spectrum of complex **10**.

25. References

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