Supporting information

Unprecedented Iminobenzosemiquinone and Iminobenzoquinone Coordinated Mononuclear Cu(II) Complex Formation under Air

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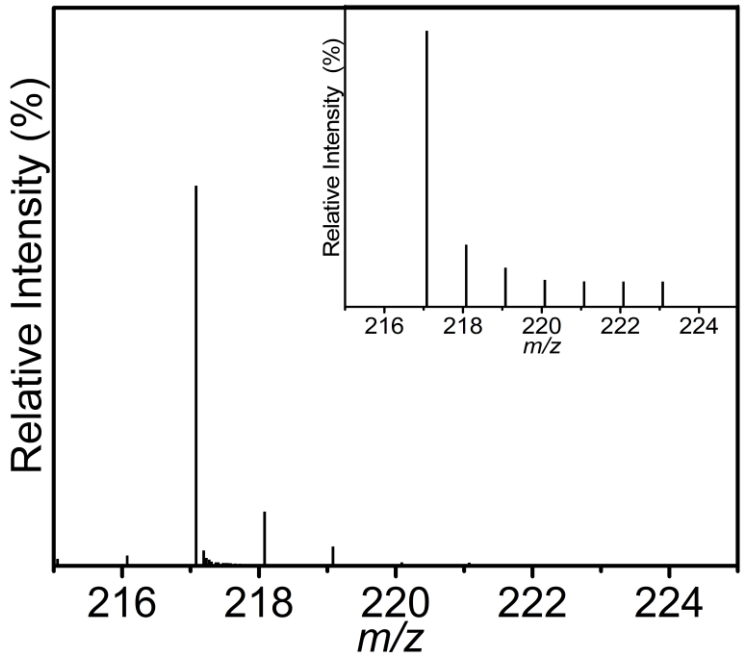

Figure 1. ESI-MS (positive mode) for **B** [$C_{12}H_{13}N_2S$]. Insert: Calculated isotope distribution pattern for $C_{12}H_{13}N_2S$.

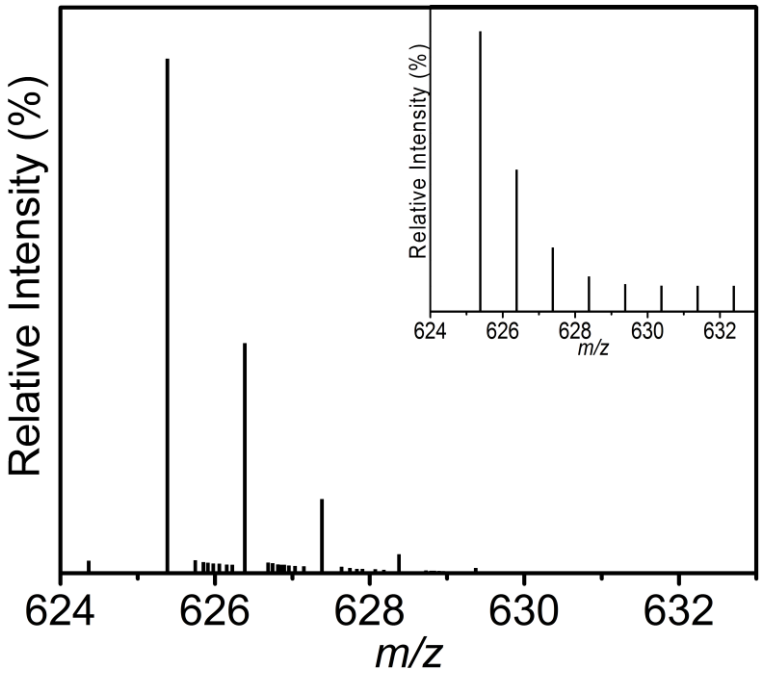

Figure 2. ESI-MS (positive mode) for $H_4L^{S(AP/AP)}$ [$C_{40}H_{53}N_2O_2S$]. Insert: Calculated isotope distribution pattern for [$C_{40}H_{53}N_2O_2S$].

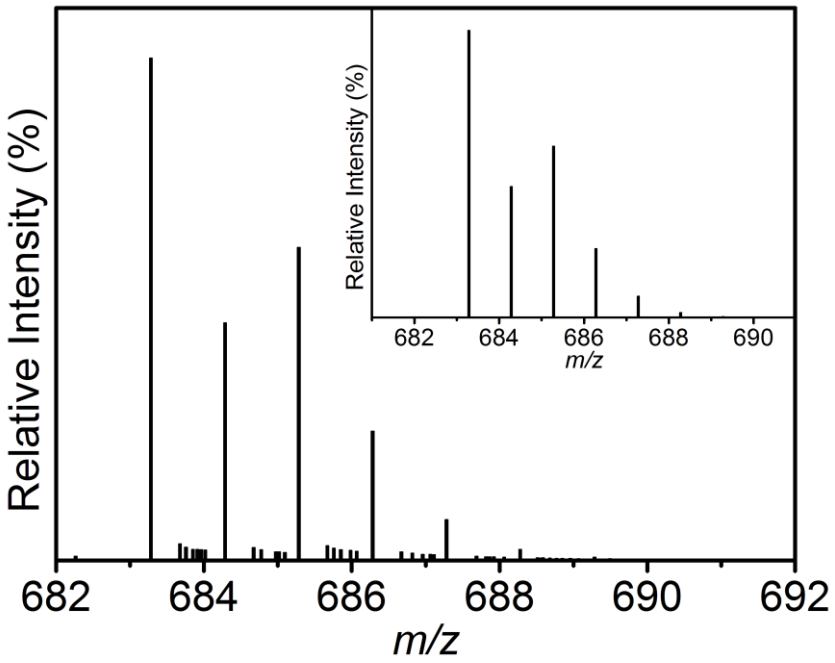

Figure 3. ESI-MS (positive mode) for **[1-Cl]** [$\{C_{40}H_{48}CuN_2O_2S\}^+$]. Insert: Calculated isotope distribution pattern for $C_{40}H_{48}CuN_2O_2S$.

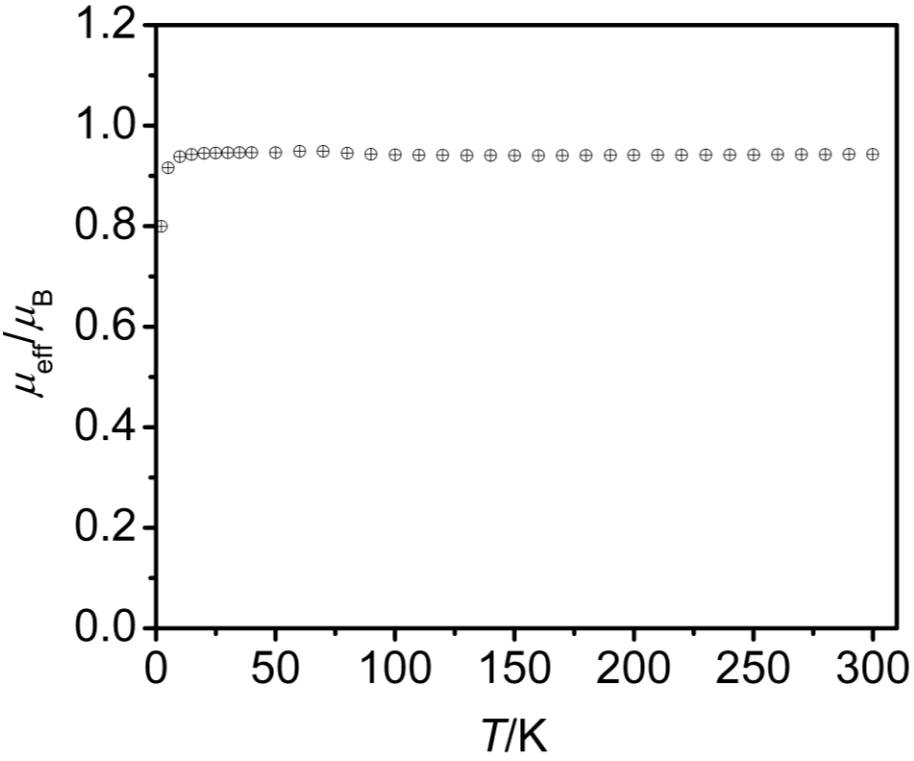

Figure 4. A μ_{eff} *vs T* plot for **1**•1CH_3CN.

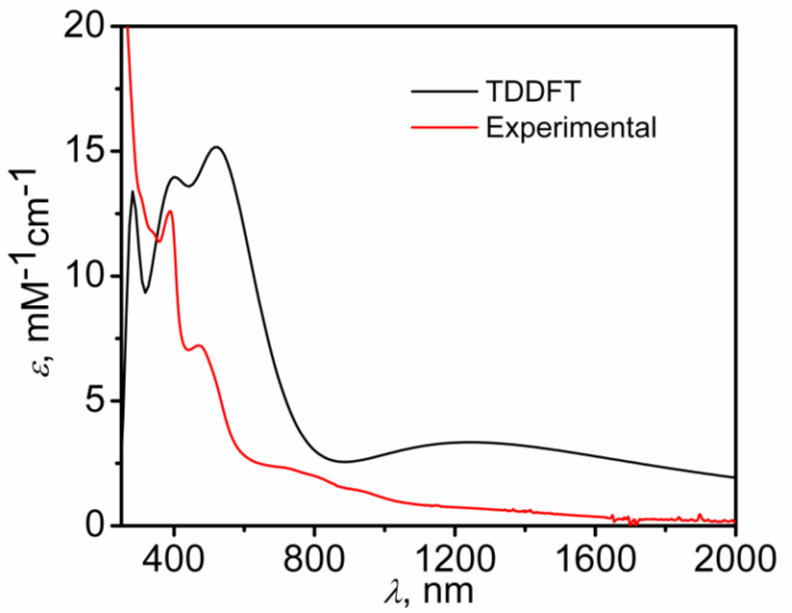

Figure 5. UV-Vis/NIR spectrum of **1**•1CH_3CN (experimental) in CH_2Cl_2, and theoretically (TDDFT) obtained spectrum of the same.

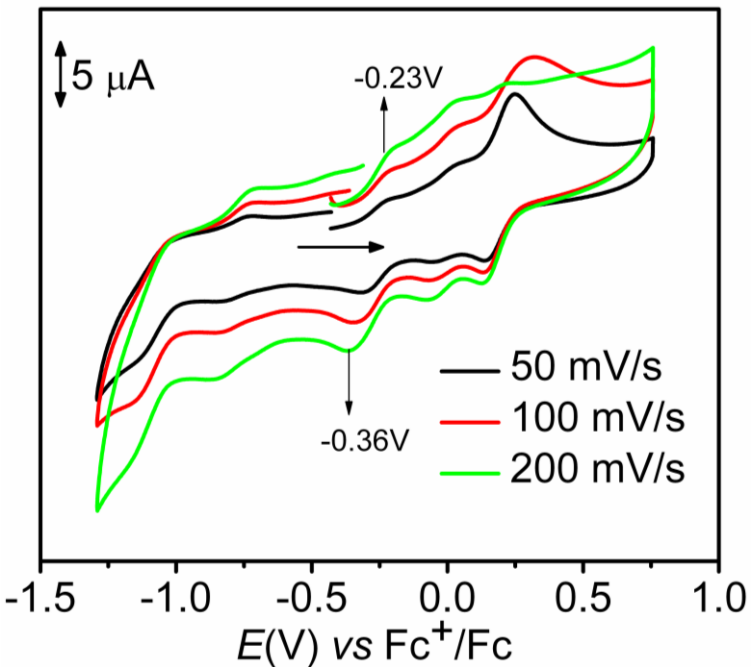

Figure 6. Cyclic voltammograms of the green compound in CH_2Cl_2 using glassy carbon working electrode and Pt counter electrode. Showing low value for the first oxidation peak.

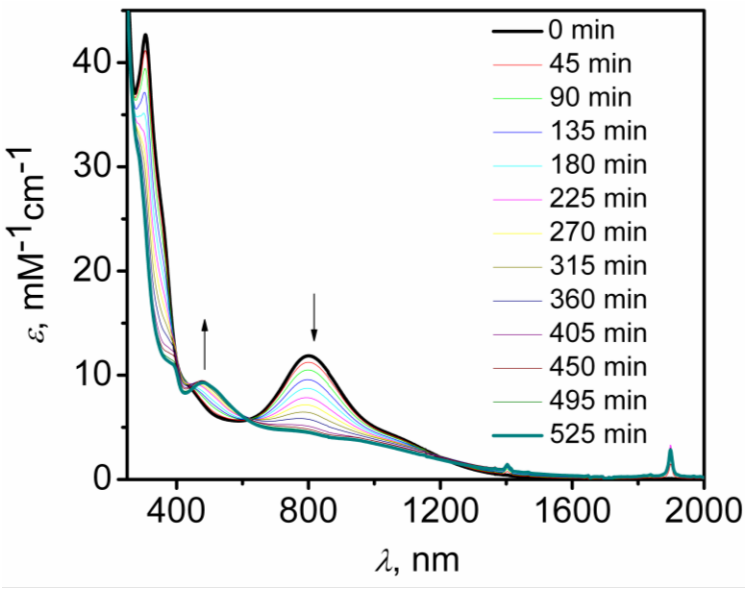

Figure 7. Time-dependent UV-Vis/NIR changes of the green solid [$Cu_2L_2^{S(ISQ/ISQ)}$] obtained initially by using $H_4L^{S(AP/AP)}$ as the ligand.

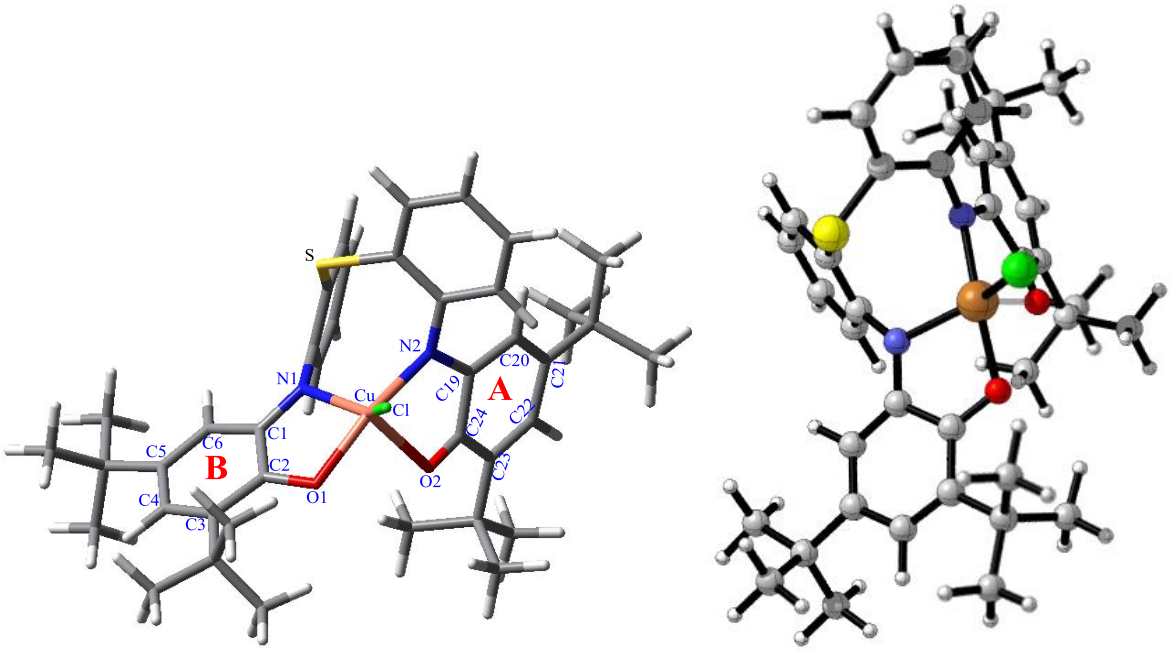

Figure 8. The optimized geometry of complex **1** at the B3LYP/6-31G (d, p) level of theory (white = hydrogen, gray = carbon, blue = nitrogen, red = oxygen, lime = chlorine and coral = copper).

Table 3. The selective bond distances (Å) and bond angles (º) of X-ray molecular structure and optimized geometry of complex **1**.

Bond Length	Experimental	Calculated
Cu1–O1	1.967(2)	1.971
Cu1–N1	1.973(3)	2.059
Cu1–N2	2.108(2)	2.035
Cu1–Cl1	2.2193(9)	2.296
Cu1–O2	2.418(2)	2.177
S1–C13	1.774(3)	1.787
S1–C12	1.776(3)	1.795
O1–C2	1.284(4)	1.272
N1–C1	1.354(3)	1.331
N1–C7	1.405(4)	1.405
O2–C24	1.229(3)	1.250
N2–C19	1.303(4)	1.323
N2–C18	1.432(4)	1.414
C1–C6	1.415(4)	1.429
C1–C2	1.443(4)	1.474
C21–C20	1.336(4)	1.366
C21–C22	1.470(4)	1.459
C21–C33	1.529(4)	1.534
C19–C20	1.435(4)	1.437
C19–C24	1.515(4)	1.499
C23–C22	1.344(4)	1.366
C23–C24	1.470(4)	1.459
C23–C37	1.532(4)	1.537
C13–C18	1.386(5)	1.414
C13–C14	1.395(4)	1.400
C7–C8	1.395(4)	1.407
C7–C12	1.405(4)	1.412
C2–C3	1.440(4)	1.445
C6–C5	1.358(4)	1.373
C25–C3	1.531(5)	1.537
C12–C11	1.387(4)	1.396
C3–C4	1.364(5)	1.375
C5–C4	1.426(5)	1.444
C5–C29	1.537(4)	1.537
C14–C15	1.380(5)	1.394
C18–C17	1.391(4)	1.409
C15–C16	1.365(5)	1.396
C16–C17	1.381(4)	1.390
C8–C9	1.376(5)	1.393
C9–C10	1.380(5)	1.397
C11–C10	1.375(5)	1.397

Bond Angle	Experimental	Calculated
O1 Cu1 N1	82.13(9)	79.57
O1 Cu1 N2	153.57(10)	162.91
N1 Cu1 N2	93.61(10)	96.15
O1 Cu1 Cl1	98.15(7)	95.23
N1 Cu1 Cl1	160.44(8)	137.54
N2 Cu1 Cl1	94.40(7)	98.91
O1 Cu1 O2	82.23(8)	87.33
N1 Cu1 O2	84.89(10)	103.30
N2 Cu1 O2	71.40(8)	77.50
Cl1 Cu1 O2	114.59(7)	118.63
C13 S1 C12	99.79(15)	109.30
C2 O1 Cu1	113.16(19)	114.86
C1 N1 C7	123.6(3)	121.46
C1 N1 Cu1	112.6(2)	112.79
C7 N1 Cu1	122.83(18)	121.53
C24 O2 Cu1	107.6(2)	110.86
C19 N2 C18	120.4(2)	119.61
C19 N2 Cu1	118.79(18)	115.95
C18 N2 Cu1	120.31(19)	122.16

Table 4. B3LYP/6-31G (d, p) optimized Cartesian coordinates of complex **1** and the corresponding electronic energies.

E = ⁻4311.96773 a.u

Cu	-0.22688400	-0.99707800	-1.10280100
S	0.27126700	-2.94592200	1.74453300
Cl	-0.22623500	-2.78918000	-2.53812400
O	-1.96257900	-0.28450400	-1.70596800
N	-1.07506900	-0.50029800	0.70686100
O	0.65921500	0.87570900	-1.77173000
N	1.68332700	-1.14327000	-0.41530900
C	-2.30240500	-0.00007100	0.58111500
C	4.36401200	1.33649600	-0.09597300
C	2.43420500	-0.06381400	-0.55843900
C	5.77174600	1.59149900	0.45784000
C	3.79166400	0.09679600	-0.11658100
C	2.32850800	2.43527600	-1.05782900
C	1.75759600	-3.27579300	0.80883200
C	-0.28696500	-0.23412500	1.83957200
C	-2.83165800	-0.14440900	-0.78727100
C	-3.14654400	0.51576300	1.61249700
C	1.56591800	3.67653200	-1.54691100

C	-4.85312800	-0.31932300	-2.40359500
C	0.49330600	-1.28129100	2.37729800
C	3.60664300	2.48082600	-0.57868300
C	2.35460800	4.97151000	-1.27355400
C	1.71937900	1.11196200	-1.15399700
C	-4.25251100	-0.02510300	-1.01926000
C	-4.48221700	0.70903900	1.36251000
C	2.34450100	-4.53369600	0.99164600
C	2.29548500	-2.39027800	-0.15369000
C	3.42890700	-4.93957400	0.21531100
C	-4.99873200	0.42846700	0.04304100
C	3.95258500	-4.07733700	-0.74996800
C	-0.13730900	1.06138900	2.36764400
C	-5.46921400	1.17741600	2.44317700
C	1.32302500	3.57791600	-3.07402100
C	3.39532100	-2.81565400	-0.92425900
C	-4.47041100	-1.75613200	-2.83390400
C	0.20993200	3.77847500	-0.80624700
C	-6.39039700	-0.21930400	-2.39179600
C	0.74697800	1.30226700	3.41672800
C	6.64809500	2.21198300	-0.65941800
C	1.36389600	-1.03398800	3.44031900
C	1.49844900	0.25649100	3.95704100
C	-4.77886300	1.42566400	3.79672200
C	-6.12888200	2.50266700	1.98719700
C	-6.56308800	0.10090800	2.64752800
C	5.68440600	2.57357800	1.65239800
C	-4.31603200	0.69703700	-3.44169900
C	6.45225600	0.29863000	0.94203700
H	4.30521700	-0.76069400	0.29196400
H	-2.73535000	0.65209700	2.60240000
H	4.10671600	3.43961700	-0.54146900
H	2.56963800	5.10359600	-0.20785400
H	3.30070900	5.00238100	-1.82381800
H	1.75900700	5.82916800	-1.60041500
H	1.94084300	-5.19673200	1.74980700
H	3.86055300	-5.92371800	0.36615600
H	-6.05743500	0.59252300	-0.10997100
H	4.78526800	-4.38794000	-1.37235800
H	-0.69786900	1.87878100	1.92717100
H	2.27352200	3.51637600	-3.61456000
H	0.79535000	4.47299700	-3.42117600
H	0.72291900	2.70331100	-3.32757500

H	3.77488300	-2.15717400	-1.69793300
H	-3.38779400	-1.88573800	-2.87933000
H	-4.88488900	-1.96869100	-3.82549500
H	-4.87940500	-2.49309300	-2.13409000
H	0.36334300	3.88358000	0.27322100
H	-0.41156100	2.89977000	-0.98547200
H	-0.33596400	4.66125000	-1.15558800
H	-6.77489800	-0.48520400	-3.38129000
H	-6.73698800	0.79510200	-2.16853600
H	-6.83957800	-0.90487800	-1.66552100
H	0.85139000	2.30889600	3.80899000
H	7.65340300	2.40698100	-0.27184900
H	6.73787500	1.52966900	-1.51058400
H	6.24653000	3.16078300	-1.02643400
H	1.93616600	-1.85385700	3.86158400
H	2.18410100	0.44063000	4.77775100
H	-4.00256100	2.19413900	3.72354800
H	-5.51882100	1.77086500	4.52518400
H	-4.32411700	0.51343400	4.19608400
H	-6.67622300	2.39067600	1.04699000
H	-5.37771300	3.28713800	1.84960100
H	-6.84128500	2.84317300	2.74618300
H	-7.12845800	-0.09353900	1.73177400
H	-6.12236300	-0.84443800	2.98016100
H	-7.27403500	0.43240900	3.41187100
H	6.68733200	2.76145000	2.04970900
H	5.07150900	2.15590000	2.45747200
H	5.25628900	3.53878800	1.36715900
H	-3.23093400	0.63508900	-3.53430800
H	-4.75961300	0.49400100	-4.42287800
H	-4.58234100	1.72070900	-3.15701000
H	7.45561400	0.53245300	1.30997100
H	6.55726200	-0.43299700	0.13467500
H	5.90082600	-0.16977600	1.76348500