SUPPLEMENTARY INFORMATION

Copper Thiolate Center for Electron Transfer: Mononuclear versus Dinuclear Complexes

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General. H_2L was prepared according to a reported method.[1] All other reagents and solvents were used as received, except for THF, which was distilled over Na/benzophenone prior to use. The synthesis of **2** was performed under argon (glove box). DMF (Sigma Aldrich, anhydrous, 99.8%) and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), used for electrochemical analysis, were used as received and stored in a glove box.

Synthesis of [CuL] (2). H_2L (100 mg, 0.172 mmol) was added to a suspension of NaH 60% (14 mg, 0.350 mmol) in THF (20 ml). After 15 min, solid $Cu(OTf)_2$ (64 mg, 0.177 mmol) was added, with consequent formation of a dark green mixture. After 30 min the dark green solid was filtered, washed with THF (10 ml) and MeOH (15 ml), dried in vacuo and collected (**2**, 50 mg, 0.078 mmol, 45 %). X-ray suitable dark green single crystals were obtained by contact of a methanolic solution of $CuCl_2{\cdot}2H_2O$ with an equimolar solution of Na_2L in THF, corresponding to **2**. IR (KBr pellet, cm^{-1}): 3080w, 3055w, 3025w, 2957w, 1599s, 1573m, 1488m, 1441s, 1328w, 1311w, 1260m, 1180w, 1021w, 789m, 756m, 747m, 739m, 696vs, 646w, 596w. ESI-MS (DMF:H_2O:MeCN:HCOOH, *m/z*, I%): 642.1, 100 $[CuL]^+$+$[CuLH]^+$; 743.2, 76; 1123.0, 14; 1283.0, 10 $[2CuL+H]^+$. Anal. Calcd. for $C_{38}H_{30}N_2S_2Cu$ (642.34): C, 71.05; H, 4.71; N, 4.36; Found: C, 71.32; H, 4.97; N, 4.06.

Crystals of $[Cu_2K_2L_2(THF)_2]$ (3). H_2L (80 mg, 0.138 mmol) was added to a suspension of KH (0.275 mmol) in THF (15 ml). After 15 min, solid $[Cu(MeCN)_4]BF_4$ (44 mg, 0.140 mmol) was added, with consequent formation of a dark brown solution that was stirred for 15 min. X-ray suitable brown crystals were obtained by layering pentane over this solution.

Physical Measurements. The infrared spectrum of **2** was recorded on a Magna-IR TM 550 Nicolet spectrometer as KBr pellets. The electronic absorption spectrum of **2** and $\mathbf{2}^-$ were recorded on a Varian Cary 50 absorption spectrophotometer in quartz cells (optical path length: 1 mm). The X-band EPR spectrum of **2** was recorded with a Bruker EMX, equipped with the ER-4192 ST Bruker cavity and a ER-4131 VT. The elemental analysis of **2** was carried out with a C, H, N analyzer (SCA, CNRS). ESI-MS analysis of **2** was performed on a Bruker Esquire 3000 Plus ion trap spectrometer equipped with an electrospray ion source (ESI). The sample was analyzed in positive ionization mode by direct perfusion in the ESI-MS interface (ESI capillary voltage= 2 kV, sampling cone voltage= 40 V).

Crystal Structure Determination. A summary of data collection and structure refinement for compounds **2** and **3** is reported in Table S1. Selected bond distances and angles for **2** and **3** are provided in Table S2. Single-crystal diffraction data of **2** were taken using a Bruker AXS Enraf-Nonius Kappa CCD diffractometer (MoKα radiation, graphite monochromator, λ 0.71073 Å). The molecular structure was solved by direct methods and refined with the TEXSAN software package.[1] Single-crystal diffraction data of **3** were taken using an Oxford-Diffraction XCallibur S Kappa geometry diffractometer (MoKα radiation, graphite monochromator, λ 0.71073 Å). An absorption correction was applied for **3**, using the ABSPACK Oxford-diffraction program[2] with transmission factors in the range 0.770-0.877. The molecular structures of **3** was solved by direct methods and refined on F2 by full matrix least-squares techniques using SHELXTL package.[3] For **2** and **3**, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in ideal position and refined with a riding model.

Electrochemistry. Electrochemical measurements were carried out under an argon atmosphere in glove box at room temperature. Cyclic voltammetry and controlled potential electrolysis experiments were performed by using an EG&G model 173 potentiostat/galvanostat equipped with a PAR model universal programmer and a PAR model 179 digital coulometer. A standard three-electrode electrochemical cell was used. Potentials were referred to an Ag/0.01 M $AgNO_3$ reference electrode in CH_3CN + 0.1 M Bu_4NClO_4. Measured potentials were calibrated through the use of an internal Fc/Fc^+ standard. The working electrode was a vitreous carbon disk (3 mm in diameter) polished with 2 µm diamond paste (Mecaprex Presi) for cyclic voltammetry ($E\mathrm{p}_a$, anodic peak potential; $E\mathrm{p}_c$, cathodic peak potential; $E_{1/2} = (E\mathrm{p}_a + E\mathrm{p}_c)/2$; $\Delta E\mathrm{p} = E\mathrm{p}_a - E\mathrm{p}_c$). Exhaustive electrolysis was carried out on reticulated vitreous carbon electrode 45 PPI (the electrosynthesis Co. Inc.) (1 cm^3). The auxiliary electrode was a Pt wire in DMF + 0.1 M Bu_4NPF_6 solution.

Theoretical Calculations. Theoretical calculations were based on Density Functional Theory (DFT) and have been performed with the ORCA program package.[4] Full geometry optimizations were carried out for complexes **2** and **2**$^-$ using the hybrid functional B3LYP[5, 6] in combination with the TZV/P [7] basis set for all atoms and by taking advantage of the resolution of the identity (RI) approximation in the Split-RI-J variant[8] with the appropriate Coulomb fitting sets.[9] The structure optimizations of the mononuclear Cu^I and Cu^{II} complexes were both initiated from the X-ray structure of **2**$^-$ and **2**, respectively. Tight SCF convergence criteria were used. Relative energies were obtained by single point calculations on the two optimized structures of **2** and **2**$^-$ and directly on the X-ray structures of **1** and **1**$^+$ also with the B3LYP method. Indeed geometry optimizations of **1** and **1**$^+$ lead to a notable increase of the Cu…Cu distance in both structures and therefore to structural modifications around the metal ions. Thus we have provilegiated results calculated from their X-ray structures. On the other hand, the absence of X-ray structure for the mononuclear **2**$^-$ complex precludes direct calculations on the **2** and **2**$^-$ complexes. The resulting optimized geometry of **2** compare well with the crystallographic data (Table S1), thus validating the calculated structure obtained for **2**$^-$. The inner-sphere reorganization enery (λ_i) has been calculated by summing the reorganization energy of the the two redox states. The reorganization energy corresponding to the oxidized state can be calculated as the difference between the energy of the oxidized complex at the geometry of the reduced complex and of the oxidized complex, while the reorganization energy corresponding to the reduced state is the energy difference of the reduced complex at the geometry of the oxidized complex and of the reduced complex. [10]

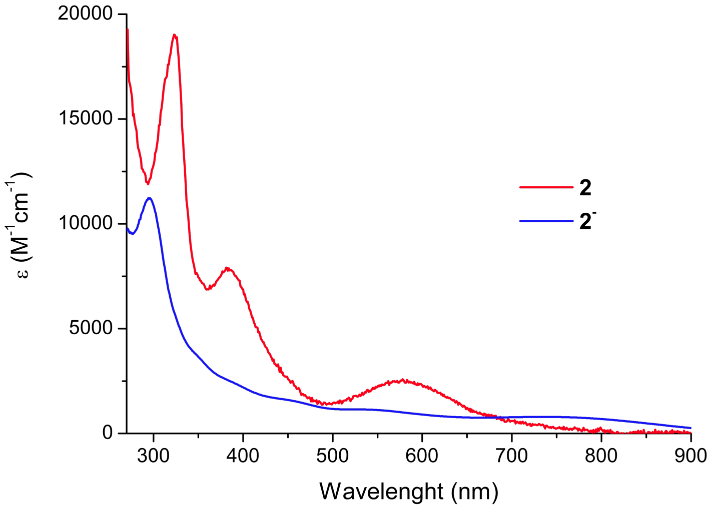

Figure S1: UV-visible spectra of **2** (red line) and **2**$^{-}$ (blue line) in DMF.

Table S1. Summary of X-ray crystallographic data for **2** and **3**.

	2	**3**
Empirical formula	$C_{38}H_{30}N_2S_2Cu$	$C_{86}H_{80}N_4O_{2.5}S_4Cu_2K_2$
Formula weight	642.34	1543.06
Colour, shape	Dark green, needle	Black, bloc
Crystal size, mm	0.40 x 0.10 x 0.10	0.33x 0.30 x 0.16
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
a, Å	9.109(2)	15.7411(4)
b, Å	12.802(3)	14.8294(4)
c, Å	13.188(2)	32.7134(13)
α, deg.	88.37(1)	90
β, deg.	76.90(2)	91.330(3)
γ, deg.	84.81(2)	90
V, Å^3	1491.7(6)	7634.2(4)
Z	2	4
T, K	200	150
ρ (calc), Mg/m^3	1.430	1.343
μ, mm^{-1}	0.903	0.827
θ range, deg.	1.59 to 25.00	3.40 to 26.37
No.of rflcn/obsv	19203 / 5202	29519 / 15396
GooF	1.930	0.891
*R*1	0.0653	0.0635
*wR*2	0.0672	0.1499

Table S2. Selected bond lengths (Å) and angles (°) for **2** and **3**.

2		**3**	
Cu(1)-N(1)	2.014(4)	Cu(1)-N(1)	2.034(4)
Cu(1)-N(2)	2.016(4)	Cu(1)-N(2)	2.035(4)
Cu(1)-S(1)	2.227(1)	Cu(1)-S(1)	2.252(2)
Cu(1)-S(2)	2.227(1)	Cu(1)-S(2)	2.287(2)
		Cu(2)-N(3)	2.054(4)
N(1)-Cu(1)-N(2)	81.5(2)	Cu(2)-N(4)	2.029(4)
N(1)-Cu(1)-S(1)	98.5(1)	Cu(2)-S(3)	2.250(2)
N(1)-Cu(1)-S(2)	156.4(1)	Cu(2)-S(4)	2.304(1)
N(2)-Cu(1)-S(1)	153.3(1)		
N(2)-Cu(1)-S(2)	99.0(1)	N(1)-Cu(1)-N(2)	79.6(2)
S(1)-Cu(1)-S(2)	91.49(5)	N(1)-Cu(1)-S(1)	100.5(1)
		N(1)-Cu(1)-S(2)	129.0(1)
		N(2)-Cu(1)-S(1)	138.4(1)
		N(2)-Cu(1)-S(2)	92.8(1)
		S(1)-Cu(1)-S(2)	116.48(6)
		N(3)-Cu(2)-N(4)	79.3(2)
		N(3)-Cu(2)-S(3)	100.3(1)
		N(3)-Cu(2)-S(4)	133.5(1)
		N(4)-Cu(2)-S(3)	140.5(1)
		N(4)-Cu(2)-S(4)	93.5(1)
		S(3)-Cu(2)-S(4)	112.73(6)

Table S3. Selected bond distances (Å) for the DFT geometry-optimized [Cu^{II}L] and [Cu^{I}L]$^-$models and comparison with the experimental data.

	[Cu^{II}L]		[Cu^{I}L]$^-$	
	Calc	Exp	Calc	Exp
Cu-N	2.071	2.016	2.118	2.035
Cu-N	2.070	2.014	2.130	2.034
Cu-S	2.268	2.227	2.348	2.287
Cu-S	2.269	2.227	2.334	2.252

Table S4. Optimized cartesian coordinates (Å) of [Cu^{I}L]$^-$.

Cu	5.113125	3.763891	14.534112
S	5.916361	3.671822	16.738134

S	6.918597	4.312815	13.160170
N	3.527899	2.385793	14.803758
N	3.574506	4.621655	13.336763
C	7.527418	6.579592	11.831892
C	7.444135	0.464291	17.505237
C	3.792056	5.562812	12.395319
C	4.014376	1.064384	19.397409
C	2.523642	3.378325	19.682270
C	6.007014	5.046628	10.536883
C	8.628416	0.013572	18.087938
C	6.675091	1.467629	18.102437
C	2.249071	2.286161	20.498421
C	2.335310	0.876864	16.219106
C	6.345268	5.607654	11.933700
C	3.537735	3.313258	18.727951
C	3.522499	1.454674	15.780249
C	5.742601	3.693854	10.327035
C	2.349275	2.802798	14.278086
C	5.378353	3.220414	9.067980
C	3.003602	1.123631	20.350743
C	5.069272	6.350719	12.473037
C	5.390903	2.034267	17.482268
C	1.126929	2.275855	14.700142
C	4.299110	2.157057	18.566018
C	4.849563	1.068458	16.366450
C	2.460884	3.850763	13.255466
C	7.548727	7.840030	12.435243
C	8.664311	8.672148	12.338665
C	9.075051	0.551124	19.288199
C	1.121871	1.289270	15.672067
C	7.143261	1.999746	19.314833
C	8.320269	1.553177	19.897686
C	1.509808	4.031565	12.248659
C	9.788134	8.266271	11.631272
C	1.707720	5.030566	11.310426
C	5.897202	5.912589	9.440346
C	5.275465	4.090023	7.987512
C	2.867004	5.798847	11.381810
C	5.540214	5.443789	8.180159
C	9.785064	7.008959	11.027344
C	8.674704	6.184123	11.126358
H	7.141674	0.034673	16.560700
H	4.602629	0.158095	19.307301
H	1.948371	4.292008	19.788023
H	9.203370	-0.759911	17.590271
H	1.462907	2.338608	21.244030
H	2.364926	0.121585	16.993533
H	3.771809	4.161699	18.097042
H	5.843301	3.023203	11.171484
H	5.176566	2.162974	8.932995

H	2.809930	0.263818	20.983675
H	4.927986	7.270488	11.896766
H	5.256555	6.619906	13.512563
H	0.199623	2.649350	14.285993
H	4.759345	0.061569	16.785828
H	5.583980	1.044429	15.562579
H	6.698824	8.184884	13.007831
H	8.646914	9.642013	12.823801
H	9.998153	0.203776	19.737654
H	0.188926	0.863060	16.020821
H	6.579708	2.791114	19.791970
H	8.654618	1.992153	20.831203
H	0.644389	3.384173	12.194018
H	10.656140	8.912002	11.556332
H	0.987805	5.191549	10.516369
H	6.112542	6.966951	9.571291
H	4.998825	3.719389	7.006436
H	3.065297	6.569921	10.649045
H	5.473953	6.135804	7.347028
H	10.657044	6.669112	10.478745
H	8.694077	5.203742	10.669121

Table S5. Optimized cartesian coordinates (Å) of [Cu^{II}L].

Cu	5.135205	3.614910	14.462741
S	6.298706	3.399747	16.397325
S	6.926533	4.295456	13.247443
N	3.595959	2.281195	14.839785
N	3.624312	4.473518	13.337972
C	7.496990	6.569571	11.903250
C	7.478761	0.260186	17.676021
C	3.774294	5.552891	12.555761
C	3.943397	1.349191	19.190720
C	2.722133	3.832980	19.140950
C	5.929834	5.041871	10.646599
C	8.581571	-0.194040	18.396169
C	6.742667	1.365762	18.106672
C	2.260155	2.862900	20.021081
C	2.532648	0.490594	15.980890
C	6.314234	5.598958	12.032829
C	3.788359	3.561118	18.285230
C	3.671328	1.243971	15.688261
C	5.731821	3.684656	10.400850
C	2.424218	2.613031	14.258082
C	5.324160	3.235717	9.145133
C	2.879992	1.615502	20.043789
C	5.064874	6.324031	12.623672
C	5.554977	1.941416	17.324374
C	1.258600	1.902031	14.527540
C	4.412754	2.315583	18.290793
C	5.001841	0.899642	16.301493

C	2.473375	3.770515	13.331442
C	7.545580	7.811038	12.540480
C	8.659529	8.639994	12.417536
C	8.977306	0.452766	19.559717
C	1.319958	0.825339	15.400477
C	7.156507	2.009074	19.280733
C	8.258249	1.562289	19.996022
C	1.412997	4.131771	12.505059
C	9.751595	8.242460	11.657613
C	1.552615	5.245073	11.688867
C	5.714058	5.939594	9.591814
C	5.106145	4.136667	8.110371
C	2.737334	5.963009	11.715632
C	5.306829	5.495804	8.339526
C	9.720723	7.002510	11.023818
C	8.608894	6.181215	11.144074
H	7.214987	-0.255022	16.762180
H	4.429512	0.381670	19.239333
H	2.258452	4.812652	19.121245
H	9.133558	-1.054613	18.036730
H	1.433704	3.075297	20.689134
H	2.607068	-0.339821	16.669371
H	4.160072	4.322906	17.613195
H	5.920104	2.980776	11.200474
H	5.184595	2.173691	8.977255
H	2.541384	0.851605	20.734499
H	4.914082	7.258627	12.078884
H	5.270127	6.575673	13.665603
H	0.318870	2.183924	14.075739
H	4.888984	-0.061828	16.807097
H	5.735905	0.771850	15.504606
H	6.721842	8.148659	13.154633
H	8.667308	9.598697	12.922601
H	9.838112	0.101908	20.116008
H	0.426473	0.258755	15.631114
H	6.613227	2.877321	19.631246
H	8.557712	2.082669	20.898176
H	0.498999	3.555850	12.489710
H	10.618024	8.886242	11.562731
H	0.743544	5.545270	11.034621
H	5.889438	6.998026	9.746294
H	4.794767	3.786441	7.133329
H	2.873088	6.832214	11.087524
H	5.155448	6.210867	7.538927
H	10.567837	6.673928	10.432942
H	8.602761	5.218263	10.650195

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