Supporting Information

for

X-ray Absorption Spectroscopic and Theoretical Studies on $(L)[Cu_2(S_2)_n]^{2+}$ Complexes: Disulfide Versus Disulfide(•1-) Bonding

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Title Running Head: X-ray Absorption Spectroscopy of $[Cu_2S_n]^{2+}$ systems

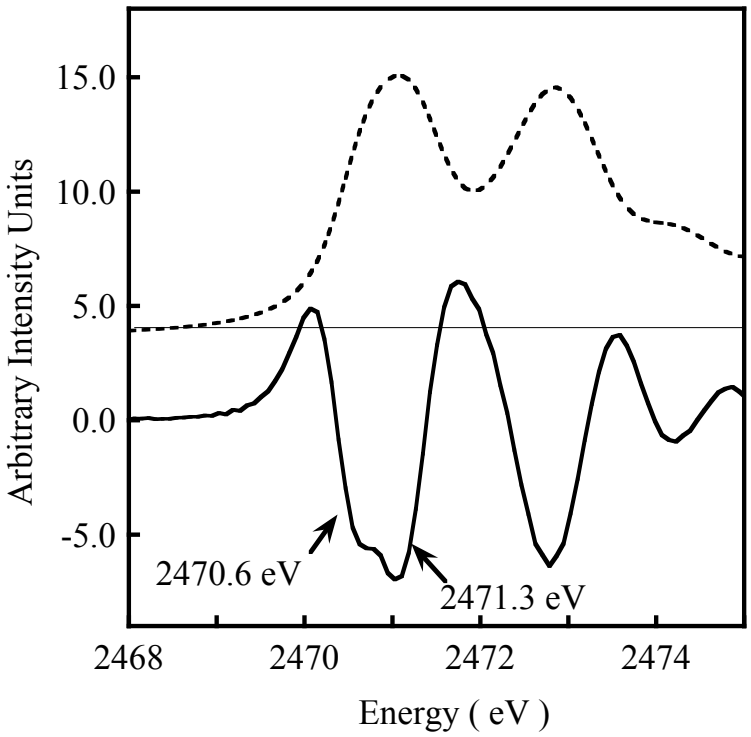

Figure S1. The S K-edge XAS data for **3** (-----) and the corresponding second derivative spectrum (—). The second derivative clearly shows the presence of two peaks in the pre-edge region.

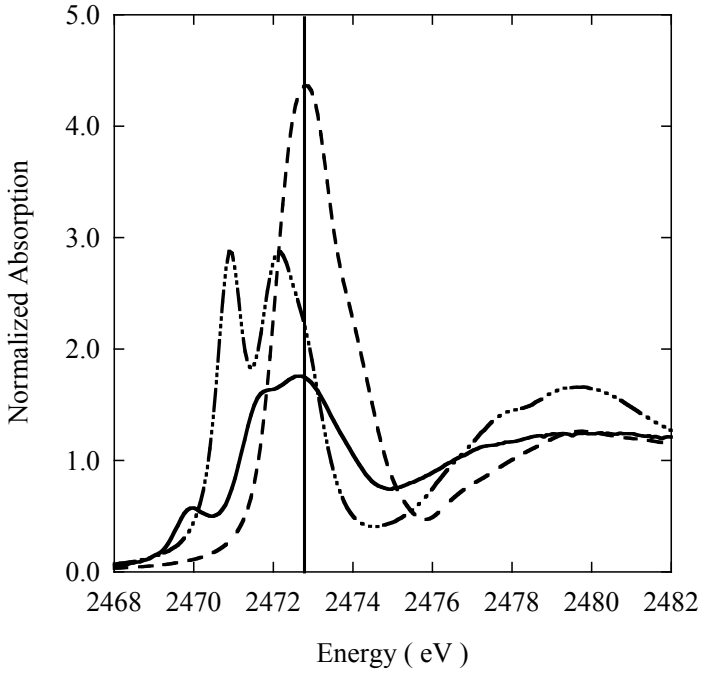

Figure S3. Comparison of the S K-edge XAS spectrum of **1** (——), **2** (—•••) and S_8 (– – –). Note that the intense low energy transition (2472.8 eV) in the S K-edge spectrum S_8 is separated by more than 1.5 eV relative to the pre-edge feature observed in both **1** and **2**. Thus, a fractional subtraction of the S_8 spectrum from the spectra of **1** and **2** was performed. DFT calculation indicate that there is no other low-lying orbital containing significant amount of S character which can contribute to the S K-edge spectrum of **1** and **2** in the 2472-2476 eV region. This allows for the quantitative subtraction of the S_8 spectrum from that of **1** and **2**.

Table S1. Cu character in the ψ^{*}_{LUMO} obtained from *EDG_FIT* and the total orbital covalency (TOC) method.

	EDG_FIT[c,d]	TOC Method	
		Total Area	Covalency[e]
D_{4h} $[CuCl_4]^{2-}$	61.0%	10.1	61%
1	63.2%	10.3	62.2%
2	37.4%	6.4	38.7%
3	22.3%	7.9	23.9%

[c]Error in total intensity due to data processing and fitting is ± 5%. [d]Error in estimation of total intensity is 8% (see Experimental Section). [e]Error in estimation of total intensity is 8-10%.

Table S2. First shell bond distances and bond angles for **1**, **2** and **3**.

	Cu-S	Cu-N_{eq}	Cu-N_{ax}(O_{ax})	SCuS (°)	SCuN (°)	Cu-D (Å)
1	2.28	2.08[b]	2.09	-	-	-
2	2.26	2.02	2.22	54.5	104	0.3
3	2.27	2.04	2.30	74	98	0.17

[a]The distance between the SSNN plane (D) and the Cu atom. [b]The average Cu-N bond distance

The geometry-optimized xyz coordinates of **1**, **2**, **3** and $\mathbf{3}^{Red}$.

1 $[\{(TMPA)Cu\}_2S_2]^{2+}$

Cu	-2.661831	0.209200	-0.939916
Cu	2.661831	-0.209200	0.939916
S	-0.378097	0.162972	-0.943531
S	0.378097	-0.162972	0.943531
N	-4.775103	0.266294	-1.119652
N	-2.759196	0.737103	-2.885765
C	-1.786393	1.284023	-3.655926
C	-1.999586	1.671504	-4.983580
C	-3.273115	1.498865	-5.544246
C	-4.288181	0.940377	-4.752141
C	-3.997444	0.564579	-3.434844
H	-0.811732	1.412283	-3.170724
H	-1.178586	2.106830	-5.560399
H	-3.477292	1.798573	-6.576969
H	-5.297163	0.793329	-5.150683
C	-5.017678	-0.107152	-2.533215
H	-4.897429	-1.205479	-2.603975
H	-6.052067	0.127481	-2.856547
N	-3.116990	1.681466	0.509639
C	-2.342126	2.132519	1.522656
C	-2.787459	3.085513	2.448581
C	-4.089864	3.590090	2.327105
C	-4.901906	3.121703	1.282429
C	-4.379888	2.174858	0.390664
H	-1.335847	1.695444	1.585029
H	-2.123172	3.417206	3.251964
H	-4.473668	4.330025	3.036818
H	-5.926943	3.486865	1.159719
C	-5.167677	1.662185	-0.804918
H	-6.259078	1.755085	-0.634059
H	-4.926631	2.279702	-1.690921
N	-3.075035	-1.647260	-0.143960
C	-2.191552	-2.650077	0.076039
C	-2.590766	-3.945336	0.428137
C	-3.959931	-4.224163	0.543994
C	-4.881139	-3.189021	0.321605
C	-4.404044	-1.913745	-0.008956
H	-1.135995	-2.376212	-0.025026
H	-1.837495	-4.720004	0.598549
H	-4.308504	-5.229055	0.802923
H	-5.958222	-3.365922	0.408545
C	-5.327710	-0.716387	-0.156368
H	-6.353938	-1.030313	-0.433094
H	-5.400107	-0.208101	0.823373
N	4.775103	-0.266294	1.119652

N	2.759196	-0.737103	2.885765
C	1.786393	-1.284023	3.655926
C	1.999586	-1.671504	4.983580
C	3.273115	-1.498865	5.544246
C	4.288181	-0.940377	4.752141
C	3.997444	-0.564579	3.434844
H	0.811732	-1.412283	3.170724
H	1.178586	-2.106830	5.560399
H	3.477292	-1.798573	6.576969
H	5.297163	-0.793329	5.150683
C	5.017678	0.107152	2.533215
H	4.897429	1.205479	2.603975
H	6.052067	-0.127481	2.856547
N	3.075035	1.647260	0.143960
C	2.191552	2.650077	-0.076039
C	2.590766	3.945336	-0.428137
C	3.959931	4.224163	-0.543994
C	4.881139	3.189021	-0.321605
C	4.404044	1.913745	0.008956
H	1.135995	2.376212	0.025026
H	1.837495	4.720004	-0.598549
H	4.308504	5.229055	-0.802923
H	5.958222	3.365922	-0.408545
C	5.327710	0.716387	0.156368
H	6.353938	1.030313	0.433094
H	5.400107	0.208101	-0.823373
N	3.116990	-1.681466	-0.509639
C	2.342126	-2.132519	-1.522656
C	2.787459	-3.085513	-2.448581
C	4.089864	-3.590090	-2.327105
C	4.901906	-3.121703	-1.282429
C	4.379888	-2.174858	-0.390664
H	1.335847	-1.695444	-1.585029
H	2.123172	-3.417206	-3.251964
H	4.473668	-4.330025	-3.036818
H	5.926943	-3.486865	-1.159719
C	5.167677	-1.662185	0.804918
H	6.259078	-1.755085	0.634059
H	4.926631	-2.279702	1.690921

2 $[\{(TPB)Cu\}_2S_2]^{2+}$

Cu	1.859864	0.000646	0.326781
Cu	-1.859852	-0.000706	-0.326978
S	-0.000510	1.150918	0.000443
S	0.000554	-1.150959	-0.001012
H	-4.351740	-4.179498	-2.210584
H	-4.206552	0.008763	4.797792
H	-4.351577	4.171379	-2.226111
H	4.206994	-0.009799	-4.797827

H	4.351432	4.179166	2.211497
H	4.351782	-4.171113	2.226443
N	2.985865	-0.001482	-1.701533
N	4.341381	-0.001989	-1.511534
N	3.040477	1.432622	0.907422
N	4.378252	1.261081	0.683498
N	3.040528	-1.430271	0.910711
N	4.378358	-1.259094	0.686925
H	-6.111460	0.000168	0.081095
H	6.111353	0.000063	-0.080985
H	1.782442	-0.004662	-3.430467
C	2.798641	-0.004639	-3.033357
C	4.034090	-0.006930	-3.722535
C	4.993835	-0.005082	-2.710847
H	6.082922	-0.005724	-2.750674
H	1.887594	2.949181	1.823887
C	2.885797	2.614454	1.541009
C	4.139968	3.225622	1.731311
C	5.057507	2.332177	1.172350
H	6.142214	2.376980	1.085395
H	1.887730	-2.943340	1.832998
C	2.885985	-2.609387	1.549386
C	4.140294	-3.219266	1.742914
C	5.057788	-2.327809	1.180688
H	6.142590	-2.372430	1.094829
B	4.900046	-0.000029	-0.075592
N	-2.985698	0.001946	1.701368
N	-3.040683	-1.432680	-0.907135
N	-3.040717	1.430136	-0.910800
N	-4.341203	0.002193	1.511522
C	-2.798348	0.004609	3.033214
N	-4.378466	-1.261055	-0.683312
C	-2.886035	-2.614642	-1.540583
N	-4.378586	1.259185	-0.686951
C	-2.885971	2.609337	-1.549274
C	-4.993562	0.004902	2.710859
B	-4.900150	0.000247	0.075587
H	-1.782097	0.004821	3.430189
C	-4.033709	0.006547	3.722488
C	-5.057734	-2.332145	-1.172040
H	-1.887794	-2.949348	-1.823359
C	-4.140185	-3.225804	-1.730736
C	-5.057802	2.328146	-1.180450
H	-1.887637	2.943139	-1.832796
C	-4.140163	3.219521	-1.742570
H	-6.082642	0.005586	2.750832
H	-6.142445	-2.377012	-1.085174
H	-6.142570	2.373143	-1.094343

3 [{(TMEDA)Cu}$_2$(S_2)$_2$](OTf)$_2$ (This structure includes the triflate counterions)

C	3.196785	-3.631542	-0.647446
C	-6.077260	-1.004476	0.276795
C	6.077197	1.003688	-0.276654
C	-3.196555	3.631647	0.646829
C	2.574745	-3.971901	0.638407
C	-2.574640	3.971829	-0.638475
H	2.916594	-2.334633	-2.158483
H	-2.916962	2.334166	2.158753
H	1.530626	-3.078099	-1.796107
H	-1.531752	3.077317	1.796051
H	1.430755	-2.948695	1.995915
H	-1.430927	2.948678	-1.994708
H	2.974797	-2.465950	2.028504
H	-2.975651	2.465735	-2.028894
Cu	-1.873738	1.298739	-0.007721
Cu	1.873672	-1.299383	0.007864
F	6.095853	0.751552	-1.590562
F	-6.095708	-0.751347	1.590496
F	6.914334	0.136189	0.303851
F	-6.914467	-0.137094	-0.303726
F	6.572349	2.230764	-0.078621
F	-6.572543	-2.231689	0.079693
N	2.359804	-2.680182	-1.403033
N	-2.360857	2.679977	1.402906
N	2.227866	-2.748445	1.426547
N	-2.229065	2.747954	-1.426446
O	3.691448	1.881035	-0.245503
O	-3.691649	-1.881548	0.246579
O	4.603428	1.018636	1.808057
O	-4.603006	-1.018383	-1.807227
O	4.032509	-0.492384	0.002688
O	-4.032251	0.492399	-0.002972
S	0.946646	0.246398	-1.370661
S	-0.946381	-0.246460	1.370393
S	-0.937023	-0.262429	-1.366546
S	0.936878	0.262006	1.367668
S	4.414444	0.843865	0.405891
S	-4.415155	-0.846004	-0.406381
H	-3.113170	4.527218	1.083899
H	-4.159927	3.363772	0.634608
H	-3.251720	4.573324	-1.062431
H	-1.773017	4.567155	-0.585033
H	3.121180	-4.568748	-0.988041
H	1.731489	-4.489066	0.492327
H	4.156468	-3.352276	-0.615413
H	3.314548	-4.533269	1.009389

3^{Red} [{(TMEDA)Cu}$_2$(S$_2$)$_2$]^0

Cu	-1.666007	0.034614	0.763735
Cu	1.665927	-0.034570	-0.763713
C	4.395257	-0.553692	0.323466
C	-4.395067	0.553653	-0.324112
C	3.931890	0.756671	0.947012
C	-3.931686	-0.756969	-0.947103
H	3.446650	-2.042794	-0.755380
H	-3.446535	2.043007	0.754463
H	2.761207	-1.752313	0.684563
H	-2.760821	1.751999	-0.685259
H	2.414326	2.077019	0.502814
H	-2.414380	-2.077335	-0.502137
H	3.535105	1.955808	-0.683464
H	-3.535385	-1.955585	0.683875
N	3.218455	-1.301202	-0.104556
N	-3.218288	1.301192	0.103912
N	3.032024	1.429857	0.021714
N	-3.032087	-1.429932	-0.021373
S	0.215827	-1.809637	-0.787349
S	-0.215923	1.809625	0.787618
S	-0.102603	-1.523546	1.220491
S	0.102577	1.523709	-1.220247
H	-5.026257	1.104261	-1.030822
H	-5.001763	0.344141	0.561808
H	-4.797888	-1.362623	-1.237604
H	-3.363133	-0.540733	-1.855681
H	5.026659	-1.104487	1.029841
H	3.363567	0.540069	1.855648
H	5.001730	-0.343813	-0.562520
H	4.798103	1.362303	1.237527

Complete Reference 21:

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