Supporting Information

For

Ligand Structural Effects on Cu_2S_2 Bonding and Reactivity in Side-On Disulfido-Bridged Dicopper Complexes

Eric C. Brown, Itsik Bar-Nahum, John T. York, Nermeen W. Aboelella and William B. Tolman*

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455

Experimental Procedure for the Synthesis of (HL´^{Me2})Cu

The ligand HL'^{Me2} (**h**) was prepared by a procedure analogous to that used to prepare according to HL'^{iPr2} **(i)** (ref. 24 in main text). A 38% yield was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.53 (s, 1H), 8.38 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.06 – 7.22 (m, 6H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 8.40 Hz, 1H),2.25 (s, 6H), 2.19 (s, 6H) ppm. BuLi (0.366 mL of 2.5M solution in hexane, 0.91 mmol) was added dropwise to the solution of HL'^{Me2} (300 mg, 0.91 mmol) in a pentane (10 mL) / toluene (2 mL) mixture. The reaction was stirred for 30 min, during which time a yellow - orange precipitate formed. The precipitate was collected, washed with pentane (5 mL) and dried under reduced pressure (269 mg, 88%). The product was used without any further purification or characterization. A solution of (HL'^{Me2})Li (269 mg, 0.80 mmol) in THF (7 mL) was added to a solution of $Cu(CH_3CN)_4CF_3SO_3$ (303 mg, 0.80 mmol) in THF (7 mL). The reaction was stirred for 10 min before the solvent was removed under reduced pressure. The product was extracted with toluene (3 × 10 mL) and filtered through a plug of celite. The filtrate was then concentrated under reduced pressure and washed with a minimum amount of pentane (2 mL) to give a fine yellow - orange powder (285 mg, 82%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.71 (s, 1H), 6.80 – 7.25 (m, 8H), 6.49 (d, *J* = 9.00 Hz, 1H), 6.30 (t, *J* = 6.90 Hz, 1H), 2.06 (s, 6H), 1.90 (s, 6H). The product was used directly for the synthesis of $[(HL´^{Me2})Cu]_2(S_2)$ **(2h)**.

Table S1. Summary of X-ray Crystallographic Data.

	((**a**)Cu)$_2$(S$_2$) (**2a**)	[((**c**)Cu)$_2$(S$_2$)] (**2c**)	[((**d**)Cu)$_2$(S$_2$)] (**2d**)	[((**e**)Cu)$_2$(S$_2$)] (**2e**)	
formula	$C_{42}H_{50}Cu_2N_4S_2$	$C_{70}H_{106}Cu_2N_4S_2$	$C_{58}H_{66}Cu_2N_4S_2$	$C_{80}H_{98}Cu_2N_4S_2$	
Fw	802.06	1194.79	1010.35	1306.82	
space group	C2/c	C2/c	P2(1)/c	P-1	
a (Å)	23.6195(18)	21.2278(15)	12.857(5)	11.7632(9)	
b (Å)	10.7047(8)	21.6630(13)	8.352(3)	12.8233(9)	
c (Å)	15.6798(12)	15.8530(11)	24.115(9)	13.2525(10)	
α (deg)	90	90	90	111.4280(10)	
β (deg)	95.1130(10)	98.7570(10)	94.563(7)	90.9190(10)	
γ (deg)	90	90	90	104.9470(10)	
V (Å^3)	3948.7(5)	7205.1(8)	2581.4(17)	1784.3(2)	
Z	4	4	2	1	
T(K)	173	173	173	173	
ρ_{calcd} (Mg/m^3)	1.349	1.101	1.300	1.216	
θ range (deg)	1.73 to 27.55	1.35 to 25.04	1.59 to 25.06	1.66 to 25.06	
μ (mm^{-1})	1.217	0.687	0.946	0.700	
reflcns collcd	22982	18439	19381	17744	
Unique reflcns	4548	6360	4556	6304	
Params	232	376	298	422	
R1, wR2 (for $I > 2\sigma(I)$)	0.0321, 0.0788	0.0450, 0.0957	0.0386, 0.0784	0.0348, 0.0713	
GOF	1.059	1.021	1.051	1.040	
largest peak, hole (e. Å^{-3})	0.480, -0.358	0.397, -0.326	0.805, -0.403	0.304, -0.281	
	[((**f**)Cu)$_2$(S$_2$)] (**2f**)	[((**g**)Cu)$_2$(S$_2$)] (**2g**)	[((**h**)Cu)$_2$(S$_2$)] (**2h**)	[((**j**)Cu)$_2$(S$_2$)] (**2j**)	**5a**
formula	$C_{54}H_{46}Cu_2F_{12}N_4S_2$	$C_{70}H_{78}Cu_2F_{12}N_4S_2$	$C_{60}H_{62}Cu_2N_4S_2$	$C_{64}H_{82}Cu_2N_4S_2$	$C_{84}H_{100}Cu_4N_8S_4$
Fw	1170.15	1394.56	1030.34	1098.54	1604.12
space group	P-1	P-1	pbca	C2/c	I4
a (Å)	8.3136(9)	12.317(5)	16.0272(18)	19.927(3)	25.048(4)
b (Å)	12.5947(13)	13.019(5)	15.9956(18)	19.811(3)	25.048(4)
c (Å)	14.2544(15)	13.915(5)	20.072(2)	17.578(3)	8.611(3)
α (deg)	103.694(2)	81.263(5)	90	90	90
β (deg)	105.738(2)	81.293(5)	90	104.346(3)	90
γ (deg)	105.080(2)	78.555(5)	90	90	90
V (Å^3)	1309.1(2)	2144.6(14)	5145.6(10)	6722.9(18)	5403(2)
Z	1	1	4	4	2
T(K)	173	173	173	173	173
ρ_{calcd} (Mg/m^3)	1.484	1.080	1.330	1.085	0.986
θ range (deg)	1.57 to 25.08	1.49 to 25.04	2.03 to 25.06	1.47 to 25.14	1.63 to 25.06
μ (mm^{-1})	0.975	0.605	0.951	0.731	0.890
reflcns collcd	12758	21148	45716	31647	25405
Unique reflcns	4618	7590	4548	6012	4813
Params	348	416	312	335	232
R1, wR2 (for $I > 2\sigma(I)$)	0.0419, 0.0915	0.0380, 0.1007	0.0410, 0.0945	0.0446, 0.1104	0.0570, 0.1272
GOF	1.057	1.059	1.080	1.011	1.074
largest peak, hole (e. Å^{-3})	0.515, -0.376	0.964, -0.435	0.861, -0.486	0.662, -0.282	0.887, -0.594

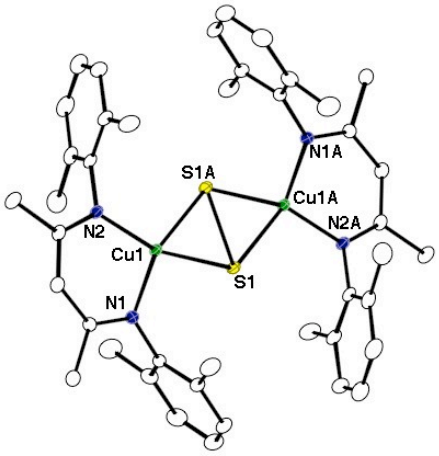

Figure S1. X-ray crystal structure of $[H(Me_2L^{Me2})Cu]_2(S_2)$ (**2a**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.8964(17); Cu1-N2, 1.8994(17); Cu1-S1, 2.1842(6); Cu1-S1A, 2.1868(6); Cu1•••Cu1A, 3.7687(5); S1-S1A, 2.2140(10); N1-Cu-N2, 99.43(7); N1-Cu-S1, 160.55(5); N2-Cu-S1, 99.98(5); N1-Cu1-S1A, 99.72(5); N2-Cu-S1A, 160.85(5); S1-Cu-S1A, 60.87(2); Cu1-S1-Cu1A, 119.13(2); Cu1A-S1-S1A, 59.51(2).

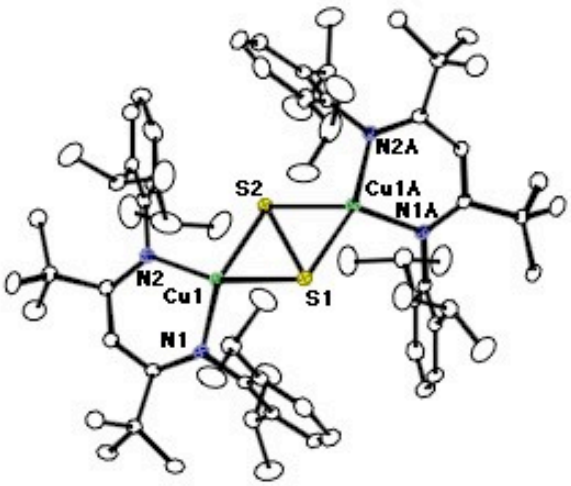

Figure S2. X-ray crystal structure of $[H(tBu_2L^{iPr2})Cu]_2(S_2)$ (**2c**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.942(2); Cu1-N2, 1.936(2); Cu1-S1, 2.2572(6); Cu1-S2, 2.2674(6); Cu1•••Cu1A, 3.9950(7); S1-S2, 2.1242(13); N1-Cu-N2, 99.50(10); N1-Cu-S1, 102.47(7); N2-Cu-S1, 103.63(7); N1-Cu1-S2, 155.81(7); N2-Cu-S2, 103.63(7); S1-Cu-S2, 56.00(3); Cu1-S1-Cu1A, 124.49(5); Cu1-S2-Cu1A, 123.51(5); Cu1-S1-S2, 62.24(2).

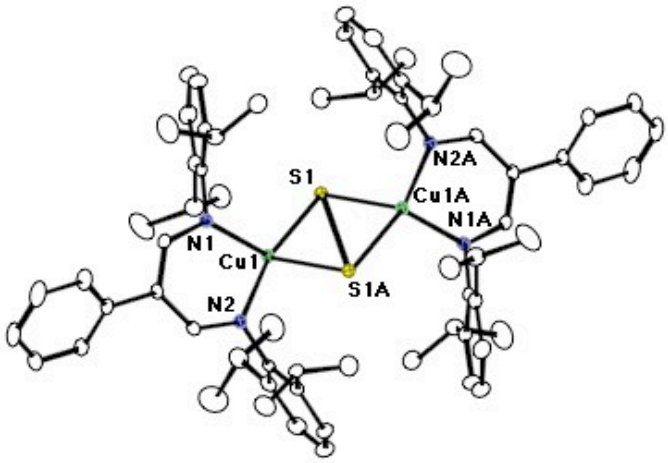

Figure S3. X-ray crystal structure of $[Ph(H_2L^{iPr2})Cu]_2(S_2)$ (**2e**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.9054(16); Cu1-N2, 1.9127(16); Cu1-S1, 2.1984(6); Cu1-S1A, 2.2051(6); Cu1•••Cu1A, 3.8143(5); S1-S1A, 2.2007(10); N1-Cu-N2, 96.95(7); N1-Cu-S1, 160.35(5); N2-Cu-S1, 102.53(5); N1-Cu1-S1A, 100.48(5); N2-Cu-S1A, 162.45(5); S1-Cu-S1A, 59.97(2); Cu1-S1-Cu1A, 120.03(2); Cu1A-S1-S1A, 59.87(2).

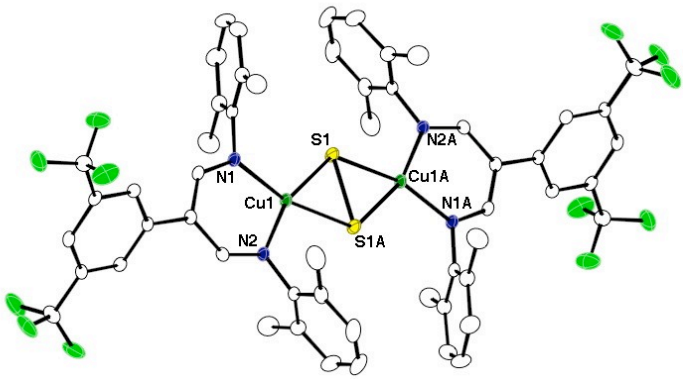

Figure S4. X-ray crystal structure of $[3,5\text{-}(CF_3)_2C_6H_3(H_2L^{Me2})Cu]_2(S_2)$ (**2f**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.912(2); Cu1-N2, 1.906(2); Cu1-S1, 2.1978(8); Cu1-S1A, 2.1976(8); Cu1•••Cu1A, 3.8045(7); S1-S1A, 2.2013(15); N1-Cu-N2, 98.07(10); N1-Cu-S1, 100.19(7); N2-Cu-S1, 161.67(7); N1-Cu1-S1A, 160.29(7); N2-Cu-S1A, 101.61(7); S1-Cu-S1A, 60.11(4); Cu1-S1-Cu1A, 119.89(4); Cu1-S1-S1A, 59.94(3).

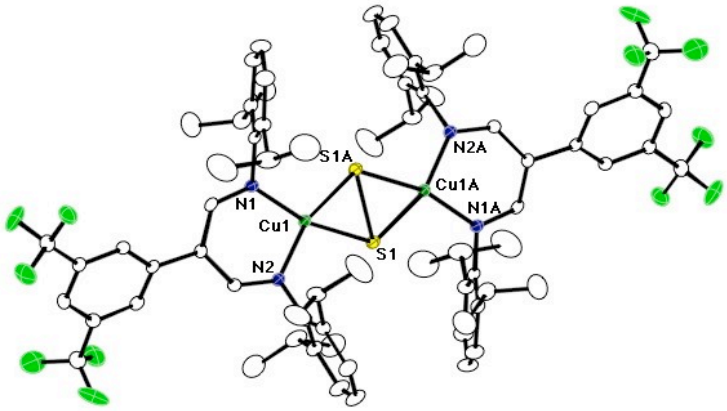

Figure S5. X-ray crystal structure of [3,5-$(CF_3)_2C_6H_3(H_2L^{iPr2})Cu]_2(S_2)$ (**2g**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.9213(18); Cu1-N2, 1.9047(17); Cu1-S1, 2.2060(9); Cu1-S1A, 2.1941(9); Cu1•••Cu1A, 3.8072(10); S1-S1A, 2.2060(12); N1-Cu-N2, 97.07(7); N1-Cu-S1, 163.41(5); N2-Cu-S1, 99.45(5); N1-Cu1-S1A, 103.32(5); N2-Cu-S1A, 159.60(5); S1-Cu-S1A, 60.18(2); Cu1-S1-Cu1A, 119.82(2); Cu1A-S1-S1A, 60.18(3).

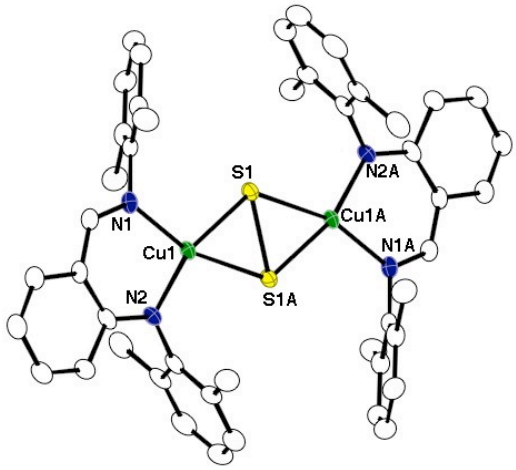

Figure S6. X-ray crystal structure of $[(HL'^{Me2})Cu]_2(S_2)$ (**2h**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.925(2); Cu1-N2, 1.893(2); Cu1-S1, 2.1936(8); Cu1-S1A, 2.1916(8); Cu1•••Cu1A, 3.7858(7); S1-S1A, 2.2130(15); N1-Cu-N2, 98.12(10); N1-Cu-S1, 160.10(8); N2-Cu-S1, 101.55(8); N1-Cu1-S1A, 99.60(8); N2-Cu-S1A, 162.05(8); S1-Cu-S1A, 60.62(3); Cu1-S1-Cu1A, 119.38(3); Cu1A-S1-S1A, 59.74(3).

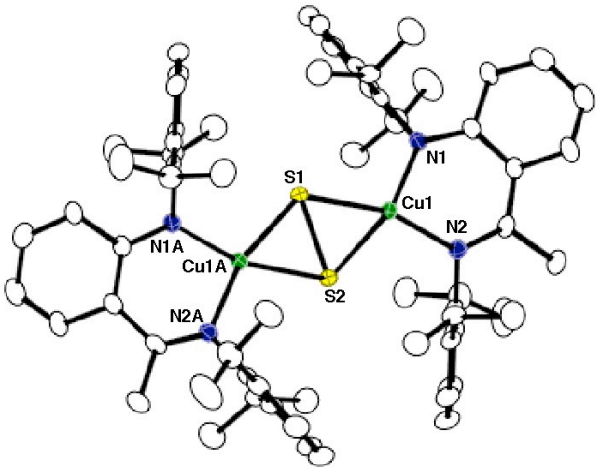

Figure S7. X-ray crystal structure of $[(MeL'^{iPr2})Cu]_2(S_2)$ (**2j**), with all nonhydrogen atoms shown as 50 % thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-N1, 1.889(2); Cu1-N2, 1.929(2); Cu1-S1, 2.2278(6); Cu1-S2, 2.2224(6); Cu1•••Cu1A, 3.8857(8); S1-S2, 2.1691(13); N1-Cu-N2, 96.10(10); N1-Cu-S1, 161.05(7); N2-Cu-S1, 102.73(7); N1-Cu1-S2, 102.83(7); N2-Cu-S2, 161.07(7); S1-Cu-S2, 58.34(3); Cu1-S1-Cu1A, 121.41(5); Cu1-S2-Cu1A, 121.91(5); Cu1-S1-S2, 60.71(2).

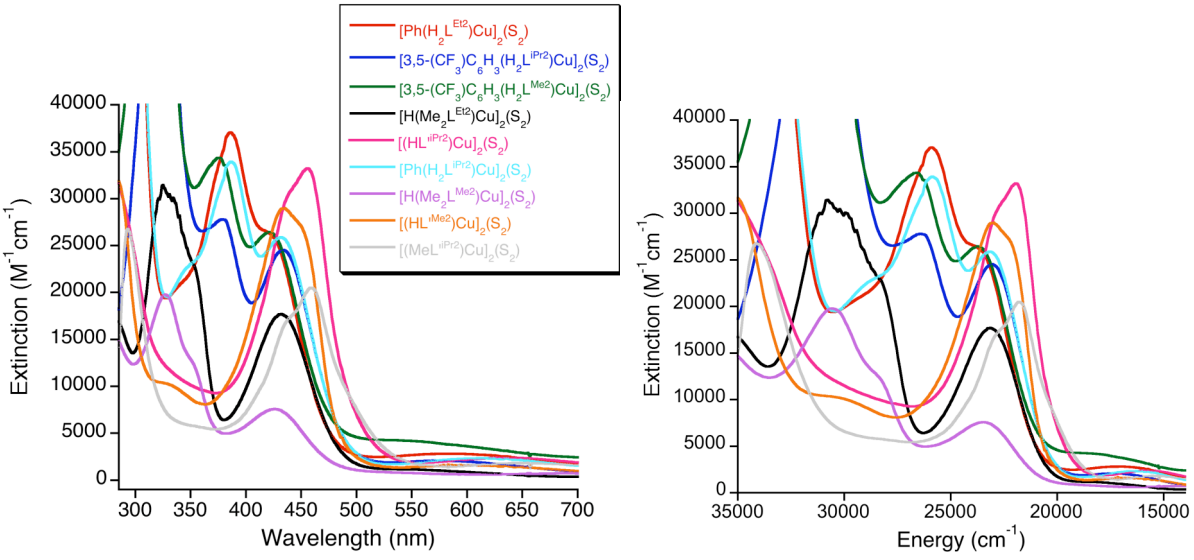

Figure S8. Electronic absorption spectra for the indicated disulfido dicopper complexes, shown as extinction vs. (a) wavelength and (b) energy. All data collected in THF at ambient temperature.

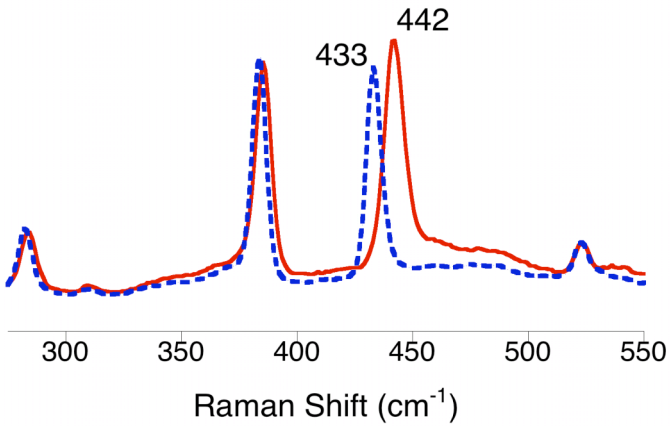

Figure S9. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[H(Me_2L^{Me2})Cu]_2(S_2)$ (**2a**) (solid line for ^{32}S, dashed line for ^{34}S).

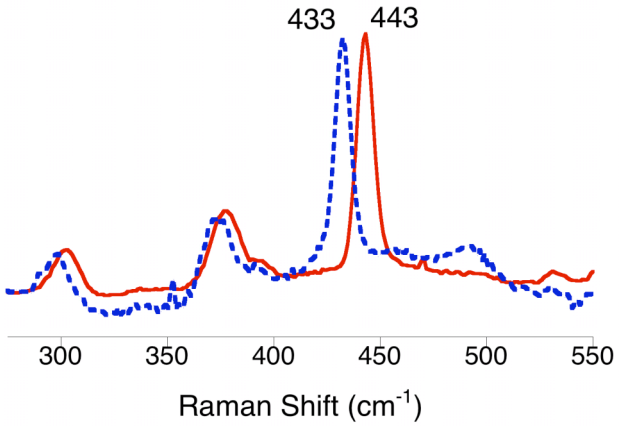

Figure S10. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[H(Me_2L^{Et2})Cu]_2(S_2)$ (**2b**) (solid line for ^{32}S, dashed line for ^{34}S).

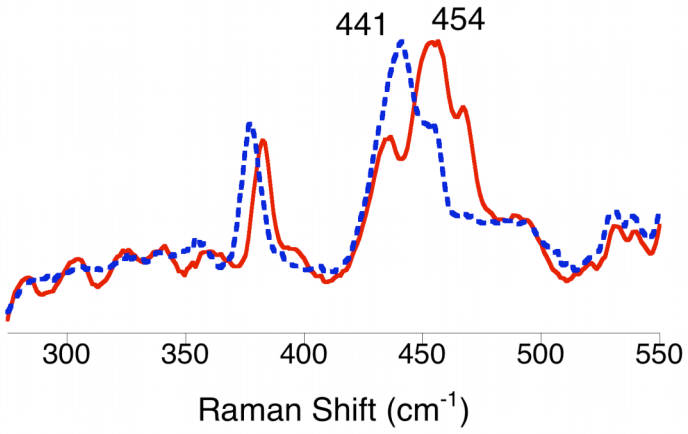

Figure S11. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[H(tBu_2L^{iPr2})Cu]_2(S_2)$ (**2c**) (solid line for ^{32}S, dashed line for ^{34}S).

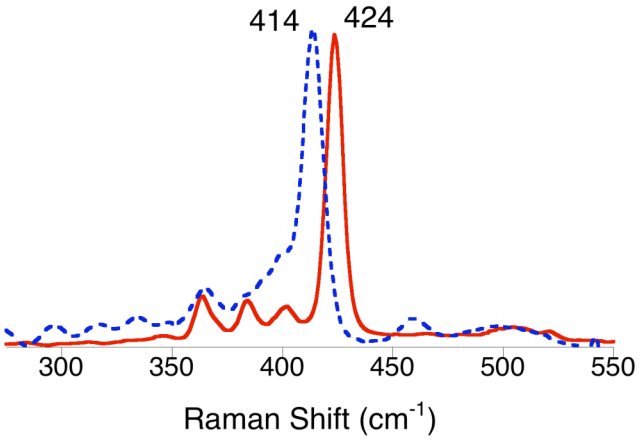

Figure S12. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[Ph(H_2L^{Et2})Cu]_2(S_2)$ (**2d**) (solid line for ^{32}S, dashed line for ^{34}S).

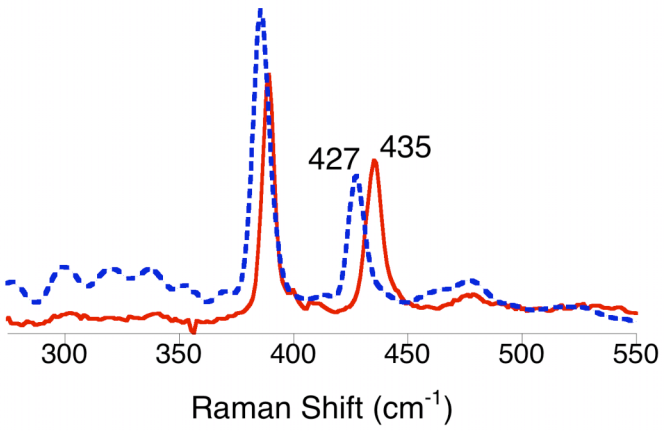

Figure S13. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[Ph(H_2L^{iPr2})Cu]_2(S_2)$ (**2e**) (solid line for ^{32}S, dashed line for ^{34}S).

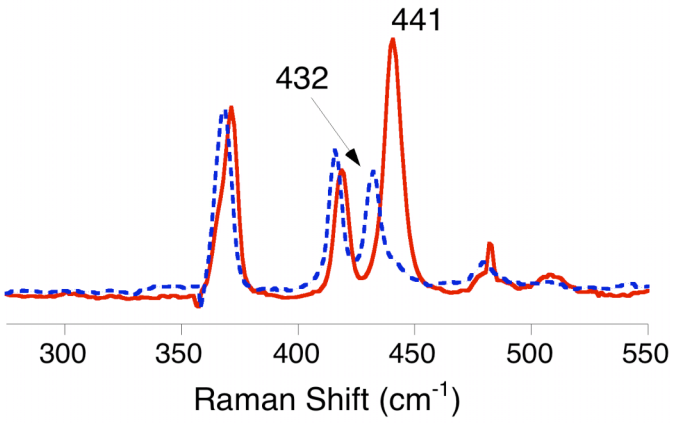

Figure S14. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[3,5\text{-}(CF_3)_2C_6H_3(H_2L^{Me2})Cu]_2(S_2)$ (**2f**) (solid line for ^{32}S, dashed line for ^{34}S).

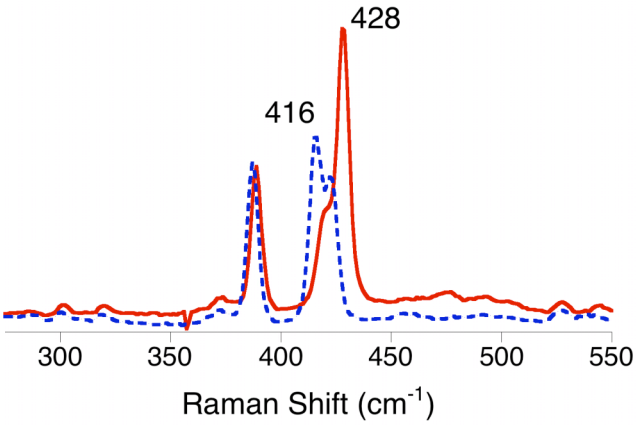

Figure S15. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of [3,5-$(CF_3)_2C_6H_3(H_2L^{iPr2})Cu]_2(S_2)$ (**2g**) (solid line for ^{32}S, dashed line for ^{34}S).

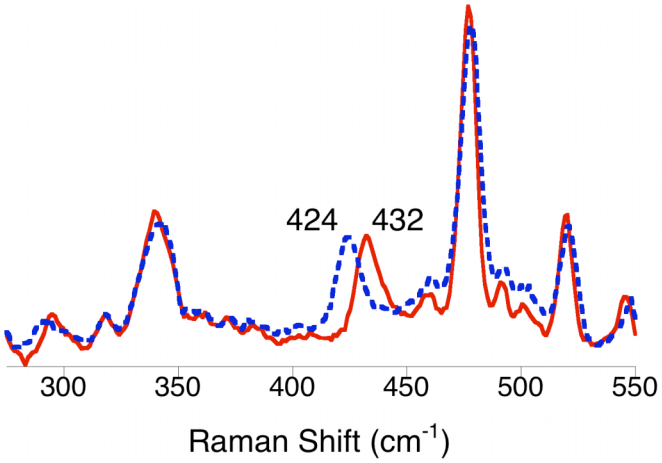

Figure S16. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[(HL'^{Me2})Cu]_2(S_2)$ (**2h**) (solid line for ^{32}S, dashed line for ^{34}S).

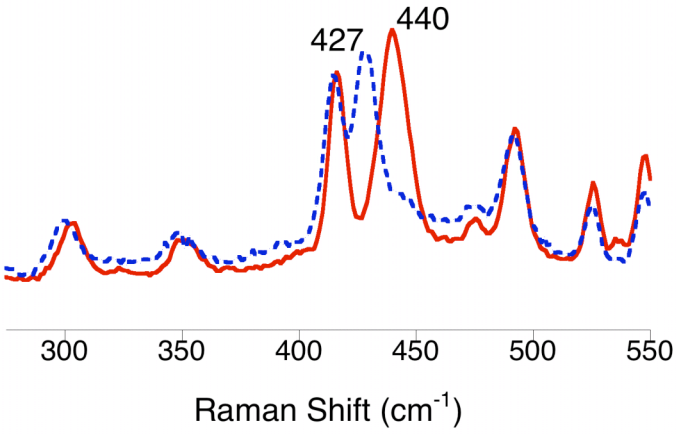

Figure S17. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[(HL'^{iPr2})Cu]_2(S_2)$ (**2i**) (solid line for ^{32}S, dashed line for ^{34}S).

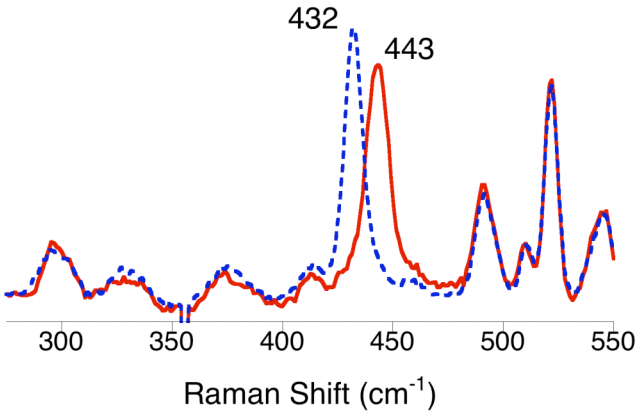

Figure S18. Resonance Raman spectra (λ_{ex} = 457.9 nm) of frozen benzene solutions (77K) of $[(MeL'^{iPr2})Cu]_2(S_2)$ (**2j**) (solid line for ^{32}S, dashed line for ^{34}S).

Table S2. S-S Bond Lengths (Å) and Vibrational Frequencies (cm^{-1}).

compound	S-S distance (Å)	^{32}S
$[H(Me_2L^{Me2})Cu]_2(S_2)$	2.214	442[a]
$[H(Me_2L^{Et2})Cu]_2(S_2)$	2.2007	443[a]
$[H(tBu_2L^{iPr2})Cu]_2(S_2)$	2.1265	454[a]
$[Ph(H_2L^{Et2})Cu]_2(S_2)$	2.2138	424[a]
$[Ph(H_2L^{iPr2})Cu]_2(S_2)$	2.2007	435[a]
$[3,5\text{-}(CF_3)_2C_6H_3(H_2L^{Me2})Cu]_2(S_2)$	2.2013	441[a]
$[3,5\text{-}(CF_3)_2C_6H_3(H_2L^{iPr2})Cu]_2(S_2)$	2.2060	428[a]
$[(HL'^{Me2})Cu]_2(S_2)$	2.2130	432[a]
$[(HL'^{iPr2})Cu]_2(S_2)$	2.165	440[a]
$[(MeL'^{iPr2})Cu]_2(S_2)$	2.1691	443[a]
$[\{Cu[HB(3,5\text{-}Pr^i{}_2pz)_3]\}_2(S_2)]$,	2.073[b]	500[c]
$[((TMPA)Cu)_2(S_2)]^{2+}$,	2.044	499[d]
$[Cu_2(tmeda)_2(\mu\text{-}1,2\text{-}S_2)_2]^{2+}$	1.9500	613[e]
$[Ir(dppe)_2(S_2)]^+$	2.07	528[f]
$[MoO(S_2)(mtox)_2]^{2-}$	2.01	530[f]
$MoO(S_2)(dtc)_2$	2.02	558[f]
$Cp_2Nb(S_2)Me$	2.01	540[f]
$[Mo_2O_2S_2(S_2)_2]^{2-}$	2.08	510[f]
$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$	2.04	536[f]
$[Mo_4(NO)_4(S_2)_5S_3]^{4-}$	2.05	550[f]
$[(NH_3)_5Ru(S_2)Ru(NH_3)_5]^{4+}$	2.01	514[f]
$Cp_2Fe_2(S_2)(Set)_2$	2.02	507[f]
$[Mo_4(NO)_4(S_2)_6O]^{2-}$	2.08	480[f]
$Cp_4Fe_4(S_2)_2S_2$	2.04	503[f]
$[(Cp_4Fe_4(S_2)_2S_2)_2Ag]^+$	2.05	478[f]
$[Mo_2(S_2)_6]^{2-}$	2.04	550[f]
$\{Mo_2(S_2)_2Cl_4Cl_{4/2}\}_n$	1.98	561[f]
$Nb_2(S_2)_2Cl_4$	2.03	588[f]
$[Mo_3S(S_2)_6]^{2-}$	2.02	545[f]
$Mo_3S(S_2)_3Cl_4$	2.03	562[f]
$Fe_2(S_2)(CO)_6$	2.01	555[f]
$Mo_2(S_2)(S_2C_2Ph_2)_4$	2.04	518[f]
$[Mo_2(S_2)(SO_2)(CN)_8]^{4-}$	2.00	520[f]
S_2	1.892[g]	718[h]

[a] This work. [b] Reference 1. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] Reference 5. [g] Reference 6. [h] Reference 7.

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