

Supplementary information

Second-order optical properties of inorganic metal clusters

[MoS₄Cu₄X₂Py₂] (M= Mo, W; X= Br, I)

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1. Table 1S. Cartesian coordinates (Å) of three model clusters, WS₄Cu₄Br₂Py₆ (**1**), WS₄Cu₄I₂Py₆ (**2**) and MoS₄Cu₄Br₂Py₆ (**3**).

WS ₄ Cu ₄ Br ₂ Py ₆ (1)				WS ₄ Cu ₄ I ₂ Py ₆ (2)			
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
W	0.0000	0.0000	0.0382	W	0.0000	0.0000	0.0599
Br	4.1627	-1.6029	1.6927	I	4.2407	-1.6659	1.9338
Br	-4.1627	1.6029	1.6927	I	-4.2407	1.6659	1.9338
Cu	1.6653	2.1881	0.0014	Cu	2.2284	-1.6596	0.1242
Cu	2.2106	-1.6600	0.0963	Cu	-1.6550	-2.2008	0.0158
Cu	-1.6653	-2.1881	0.0014	Cu	-2.2284	1.6596	0.1242
Cu	-2.2106	1.6600	0.0963	Cu	1.6550	2.2008	0.0158
S	1.8694	0.2225	-1.2324	S	0.2410	-1.8772	1.3128
S	-0.2373	1.8791	1.2961	S	-0.2410	1.8772	1.3128
S	-1.8694	-0.2225	-1.2324	S	-1.8737	-0.2277	-1.2035
S	0.2373	-1.8791	1.2961	S	1.8737	0.2277	-1.2035
N	1.6464	3.6967	-1.4459	N	2.8637	-3.0970	-1.2005
N	3.2515	2.7441	1.1566	N	3.2436	2.7669	1.1551
N	2.8448	-3.1249	-1.1974	N	1.5849	3.7166	-1.4141
N	-1.6464	-3.6967	-1.4459	N	-2.8637	3.0970	-1.2005
N	-3.2515	-2.7441	1.1566	N	-3.2436	-2.7669	1.1551
N	-2.8448	3.1249	-1.1974	N	-1.5849	-3.7166	-1.4141
C	2.2479	3.4887	-2.6389	C	2.0068	-3.5784	-2.1256
C	2.3908	4.4867	-3.6005	C	2.3823	-4.5054	-3.0957
C	1.8981	5.7653	-3.3264	C	3.7062	-4.9483	-3.1312
C	1.2742	5.9907	-2.0966	C	4.6024	-4.4424	-2.1864
C	1.1694	4.9360	-1.1921	C	4.1442	-3.5283	-1.2395
C	4.3357	1.9465	1.2814	C	4.3690	2.0207	1.2010
C	5.4577	2.3134	2.0241	C	5.4872	2.3894	1.9481
C	5.4740	3.5518	2.6669	C	5.4549	3.5776	2.6784
C	4.3518	4.3782	2.5505	C	4.2911	4.3531	2.6410
C	3.2698	3.9376	1.7935	C	3.2156	3.9126	1.8748
C	1.9937	-3.6537	-2.1015	C	2.1992	3.5490	-2.6070
C	2.3855	-4.5989	-3.0468	C	2.3068	4.5658	-3.5535
C	3.7210	-5.0074	-3.0794	C	1.7632	5.8200	-3.2632
C	4.6102	-4.4535	-2.1547	C	1.1288	6.0041	-2.0319
C	4.1349	-3.5256	-1.2294	C	1.0609	4.9330	-1.1430
C	-2.2479	-3.4887	-2.6389	C	-2.0068	3.5784	-2.1256
C	-2.3908	-4.4867	-3.6005	C	-2.3823	4.5054	-3.0957
C	-1.8981	-5.7653	-3.3264	C	-3.7062	4.9483	-3.1312
C	-1.2742	-5.9907	-2.0966	C	-4.6024	4.4424	-2.1864
C	-1.1694	-4.9360	-1.1921	C	-4.1442	3.5283	-1.2395

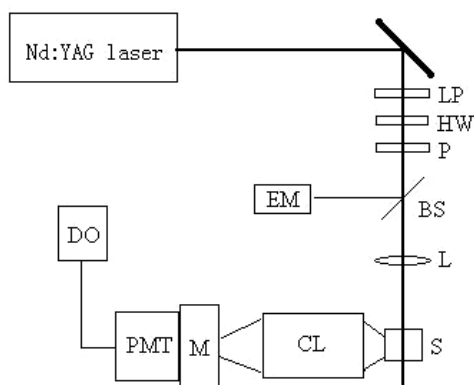
C	-4.3357	-1.9465	1.2814	C	-4.3690	-2.0207	1.2010
C	-5.4577	-2.3134	2.0241	C	-5.4872	-2.3894	1.9481
C	-5.4740	-3.5518	2.6669	C	-5.4549	-3.5776	2.6784
C	-4.3519	-4.3782	2.5505	C	-4.2911	-4.3531	2.6410
C	-3.2699	-3.9376	1.7935	C	-3.2156	-3.9126	1.8748
C	-1.9937	3.6537	-2.1015	C	-2.1992	-3.5490	-2.6070
C	-2.3855	4.5989	-3.0468	C	-2.3068	-4.5658	-3.5535
C	-3.7210	5.0074	-3.0794	C	-1.7632	-5.8200	-3.2632
C	-4.6102	4.4535	-2.1547	C	-1.1288	-6.0041	-2.0319
C	-4.1349	3.5255	-1.2294	C	-1.0609	-4.9330	-1.1430

MoS₄Cu₄Br₂Py₆ (**3**)

	<i>x</i>	<i>y</i>	<i>z</i>
Mo	0.0000	0.0000	0.0417
Br	4.4390	0.2829	1.6930
Br	-4.4390	-0.2829	1.6930
Cu	2.6890	-0.5838	0.0753
Cu	0.5850	2.6712	0.0099
Cu	-2.6890	0.5838	0.0753
Cu	-0.5850	-2.6712	0.0099
S	1.6073	0.9985	-1.2190
S	-1.6073	-0.9985	-1.2190
S	-1.0241	1.6186	1.2825
S	1.0241	-1.6186	1.2825
N	3.8943	-1.6421	-1.2062
N	-1.7955	-3.8359	1.1719
N	0.0689	-4.0443	-1.4277
N	-3.8943	1.6421	-1.2062
N	1.7955	3.8359	1.1719
N	-0.0689	4.0443	-1.4277
C	3.3560	-2.4892	-2.1082
C	4.1209	-3.1893	-3.0385
C	5.5040	-2.9949	-3.0583
C	6.0653	-2.1065	-2.1376
C	5.2329	-1.4581	-1.2267
C	-3.1182	-3.5761	1.2757
C	-3.9865	-4.3792	2.0145
C	-3.4818	-5.4993	2.6757
C	-2.1127	-5.7680	2.5821
C	-1.3112	-4.9158	1.8277
C	-0.5631	-4.1193	-2.6207
C	-0.2550	-5.0788	-3.5829
C	0.7474	-6.0131	-3.3090
C	1.4061	-5.9445	-2.0786
C	1.0391	-4.9508	-1.1734

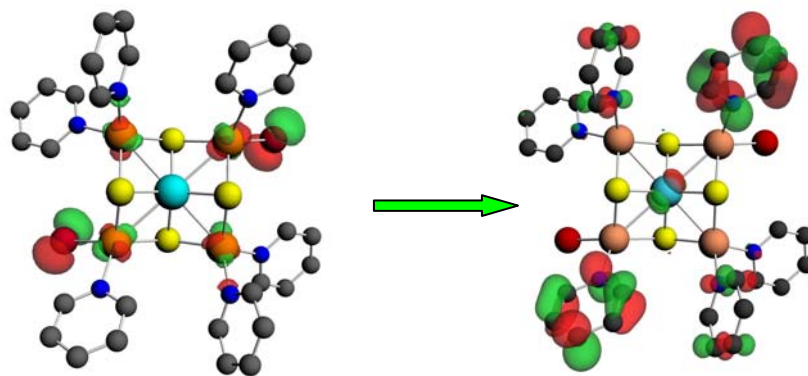
C	-3.3560	2.4892	-2.1082
C	-4.1209	3.1893	-3.0385
C	-5.5040	2.9949	-3.0583
C	-6.0653	2.1065	-2.1376
C	-5.2329	1.4581	-1.2267
C	3.1182	3.5761	1.2757
C	3.9865	4.3792	2.0145
C	3.4818	5.4993	2.6757
C	2.1127	5.7680	2.5821
C	1.3112	4.9158	1.8277
C	0.5631	4.1193	-2.6207
C	0.2550	5.0788	-3.5829
C	-0.7474	6.0131	-3.3090
C	-1.4061	5.9445	-2.0786
C	-1.0391	4.9508	-1.1734

2. **Fig. 1S** HRS experimental setup.



LP, long pass filter; HW, half-wave plate; P, polarizer; BS, beam splitter; EM, energy meter; L, lens; S, sample cell; CL, collection lens; M, monochromator; PMT, photo-multiplied tube; DO, digital oscilloscope.

3. **Fig. 2S** Illustrations of the orbital-pair transitions and corresponding CT routes involved in the intense lowest-energy electronic excitation.



H-7 → L+7, LLCT