Combined Theoretical and Time-Resolved Photoluminescence Investigations of $[Mo_6Br^i_8Br^a_6]^{2-}$ Metal Cluster Units: Evidences of dual emission

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Supporting Information

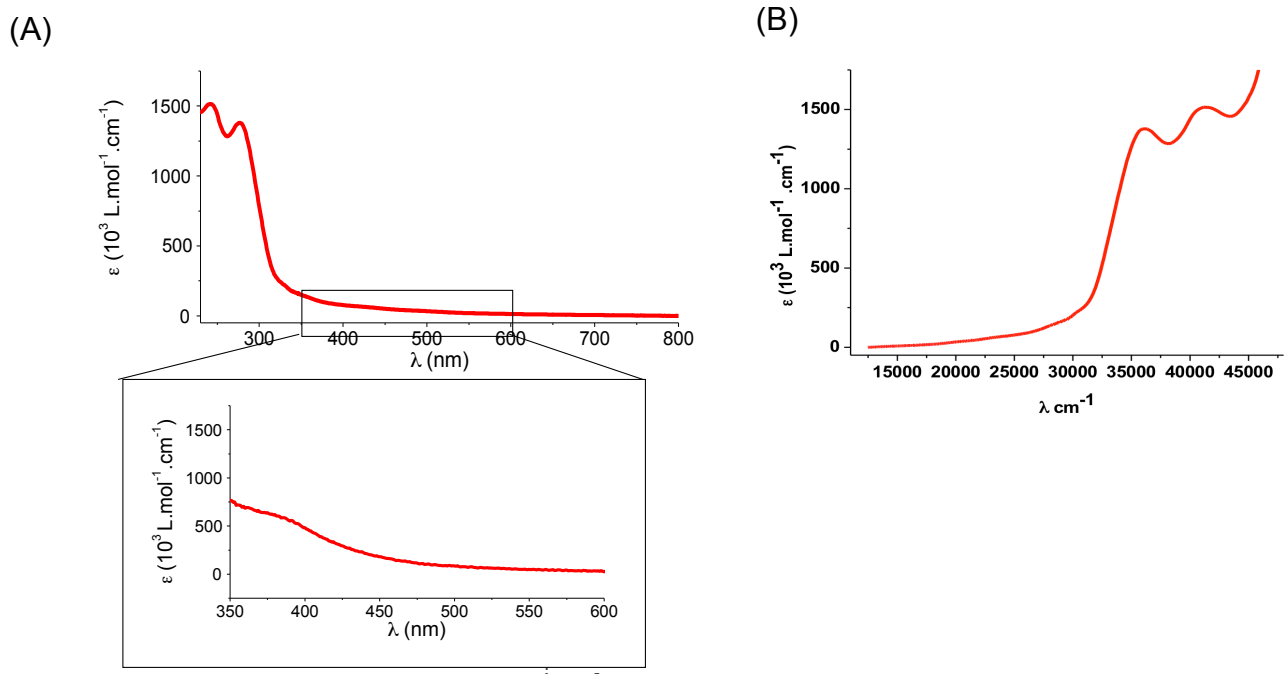


Fig. S1 Absorption spectra of $(Cs_2)[Mo_6Br^i_8Br^a_6]$ in acetonitrile recorded at room temperature (A) in nm, (B) in cm^{-1} (concentration: 2.10^{-6} $mol.L^{-1}$). *At the same concentration, $(TBA)_2[Mo_6Br^i_8Br^a_6]$ and $(Cs)_2[Mo_6Br^i_8Br^a_6]$ spectrum are identical in the UV-vis region. Changes in concentration only affect the absorbance.*

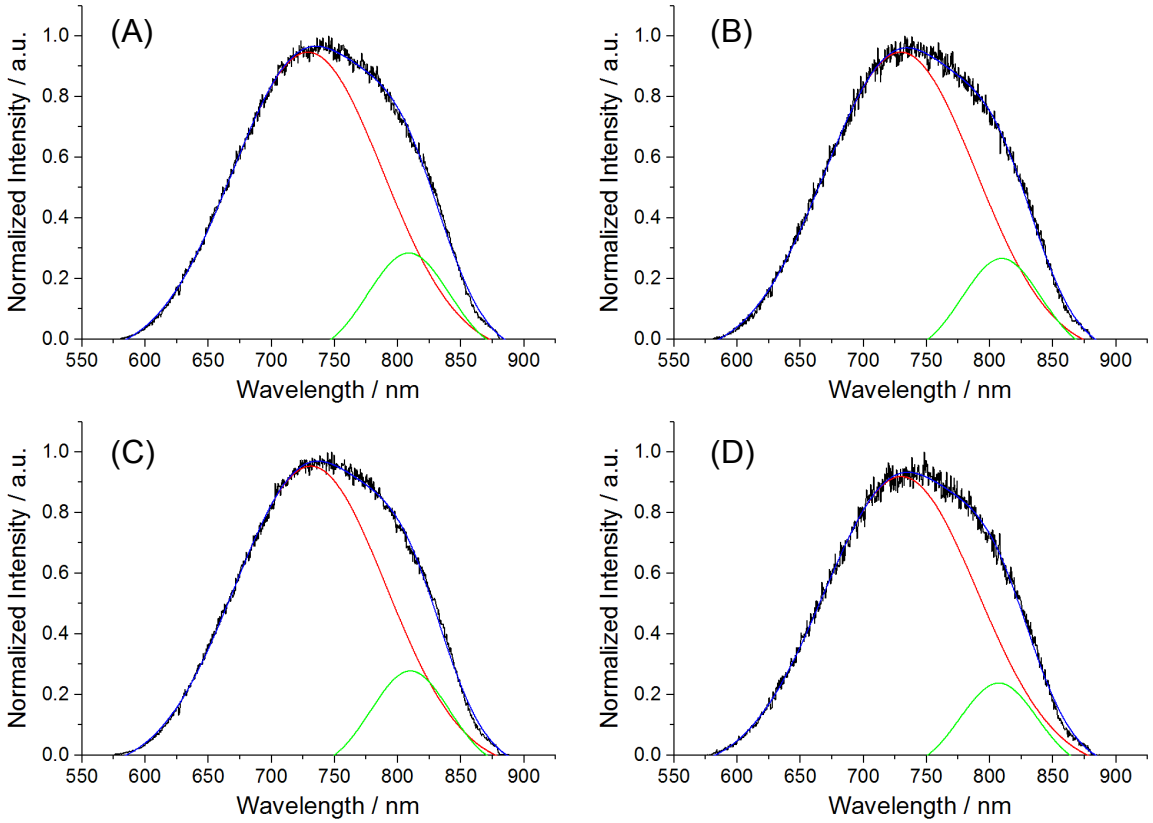


Fig. S2 Emission spectra collected at 298 K excited with λ_{exc} = 355 nm radiation of (A) $(Cs_2)[Mo_6Br^i_8Br^a_6]$ dissolved in acetone, (B) $(Cs_2)[Mo_6Br^i_8Br^a_6]$ dissolved in acetonitrile, (C) of $(TBA)_2[Mo_6Br^i_8Br^a_6]$ dissolved in acetone, (D) $(TBA)_2[Mo_6Br^i_8Br^a_6]$ dissolved in acetonitrile (concentration: 2.10^{-6} $mol.L^{-1}$). The spectra were fitted with Gaussian functions (red and green lines). The cumulative fit is plotted in blue. See Table S1 for details.

Tab. S1 Characteristic parameters of the spectra of Fig S2 fitted using functions of the general formula $y = y_0 + (A/(w \times \mathrm{sqrt}(\pi/2))) \times \exp(-2 \times ((x-x_c)/w)^2)$. Wavelengths in nm and FWMH in cm^{-1} of the two-component **1** and **2** are given for (A) $(Cs_2)[Mo_6Br^i_8Br^a_6]$ dissolved in acetone, (B) $(Cs_2)[Mo_6Br^i_8Br^a_6]$ dissolved in acetonitrile, (C) of $(TBA)_2[Mo_6Br^i_8Br^a_6]$ dissolved in acetone, (D) $(TBA)_2[Mo_6Br^i_8Br^a_6]$ dissolved in acetonitrile.

	λ_1	$FWMH_1$	λ_2	$FWMH_2$	R^2
(A)	728.9	3310	808.7	1442	0.99828
(B)	729.5	3318	809.5	1393	0.99766
(C)	731.1	3301	810.0	1392	0.99837
(D)	730.0	3384	807.0	1366	0.99681

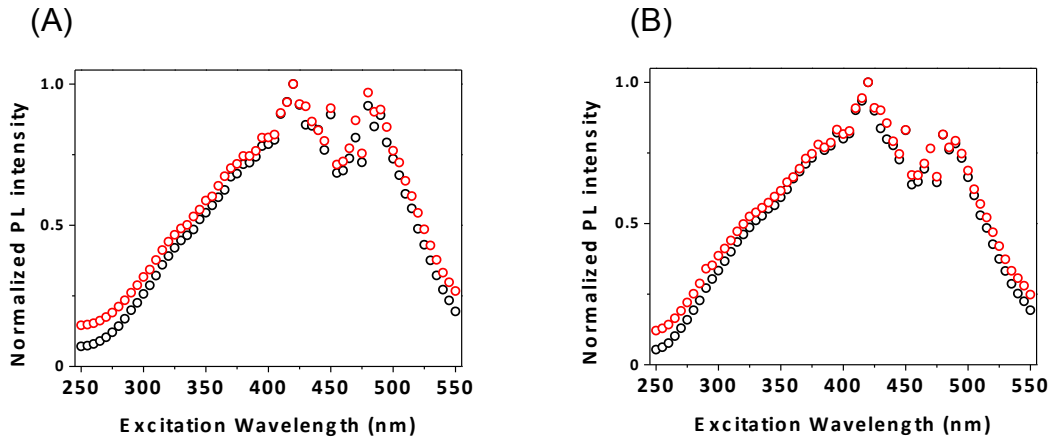


Fig. S3 Normalized excitation spectra extracted from measurements presented in Fig. 3 for (A) $(Cs_2)[Mo_6Br^i_8Br^a_6]$ for an emission wavelength at 722 nm (red circles) and 857 nm (black circles) (B) $(TBA)_2[Mo_6Br^i_8Br^a_6]$ for an emission wavelength at 720 nm (red circles) and 850 nm (black circles).

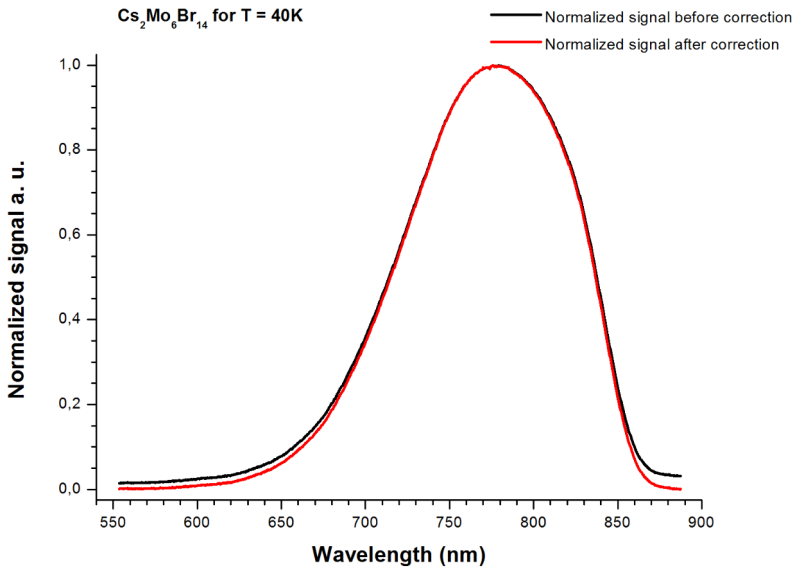


Fig S4. Detector response corrected and uncorrected TRPL measurements (streak camera).

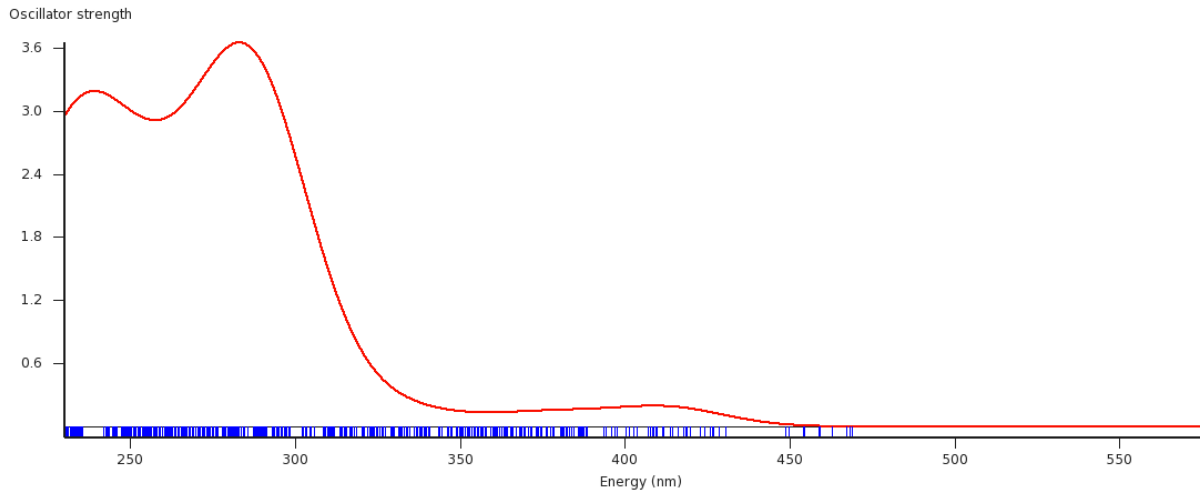


Fig. S5 TD-DFT simulated absorption spectra of $[Mo_6Br^i_8Br^a_6]^{2-}$ (oscillator strength versus wavelengths) in its experimental $(TBA)_2[Mo_6Br^i_8Br^a_6]$ arrangement obtained from data given in Table S1B.

Table S2 Mo-Mo, Mo-Br^i, and Mo-Br^a distances (Å, averaged and range) of experimental and DFT optimized $[Mo_6Br^i_8Br^a_6]^{2-}$units in O_h symmetry and without symmetry constraint starting from the X-Ray structure. Experimental values are taken from $(TBA)_2[Mo_6Br^i_8Br^a_6]$ and $(Cs)_2[Mo_6Br^i_8Br^a_6]$ from ref. 12.

	$(Cs)_2$ $[Mo_6Br_{14}]$ *Exp.*	$(TBA)_2$ $[Mo_6Br_{14}]$ *Exp.*	$(TBA)_2$ $[Mo_6Br_{14}]$ *Periodic DFT*	$[Mo_6Br_{14}]^{2-}$ *DFT (O_h)*
Mo-Mo	2.619 (x 3) 2.640 (x 6) 2.641 (x 3)	2.622 (× 2) 2.630 (× 2) 2.632 (× 2) 2.635 (× 2) 2.627 (× 2) 2.635 (× 2)	2.631 (× 2) 2.635 (× 2) 2.636 (× 2) 2.638 (× 2) 2.640 (× 2) 2.643 (× 2)	2.655
average	*2.635*	*2.630*	*2.638*	*2.655*
Mo-Br^i	2.584 (x 6) 2.594 (x 6) 2.607 (x 6) 2.620 (x 6)	2.582 (× 2) 2.592 (× 2) 2.602 (× 2) 2.606 (× 2) 2.593 (× 2) 2.596 (× 2) 2.597 (× 2) 2.600 (× 2) 2.593 (× 2) 2.593 (× 2) 2.593 (× 2) 2.601 (× 2)	2.605 (× 2) 2.615 (× 4) 2.616 (× 2) 2.618 (× 2) 2.619 (× 2) 2.620 (× 4) 2.623 (× 2) 2.628 (× 4) 2.635 (× 2)	2.642
average	*2.601*	*2.596*	*2.620*	*2.642*
Mo-Br^a	2.600 (x 6)	2.582 (× 2) 2.585 (× 2) 2.579 (× 2)	2.600 × 2 2.608 × 2 2.610 × 2	2.653
average	*2.600*	*2.582*	*2.606*	2.653

Table S3 TD-DFT singlet-singlet electronic excitations in eV calculated for $[Mo_6Br^i_8Br^a_6]^{2-}$ (A) in its O_h-DFT optimized geometry (symmetrically degenerated energies not reported) and (B) its experimental $(TBA)_2[Mo_6Br^i_8Br^a_6]$ arrangement (CH_2Cl_2 solvent effect taken into account by the COSMO formalism)

(A)

Excitation Energy	Oscillator Strength	Symmetry Nature
2.492	0	T_{1g}
2.498	0	T_{2g}
2.519	0	E_u
2.520	0	A_{1u}
2.565	0	A_{2u}
2.678	0	T_{2u}
2.689	0	A_{1u}
2.694	0	E_u
2.707	3.58E-03	T_{1u}
2.715	0	T_{2g}
2.722	0	T_{1g}
2.783	0	T_{1g}
2.789	0	T_{2g}
2.809	0	A_{2g}
2.819	9.39E-03	T_{1u}
2.838	0	T_{2g}
2.845	0	T_{1g}
2.851	0	E_g
2.875	0	T_{2u}
2.892	0	T_{1g}
2.916	0	E_u
2.924	4.36E-05	T_{1u}
2.935	0	T_{2u}
3.023	0	E_u
3.037	0	A_{2u}
3.047	0	T_{2u}
3.050	1.05E-03	T_{1u}
3.060	0	T_{1g}
3.063	0	T_{2g}
3.074	0	E_g
3.076	2.60E-03	T_{1u}
3.088	0	T_{2u}
3.097	0	E_u
3.109	0	A_{1g}
3.116	0	E_g
3.125	0	T_{1g}
3.125	0	T_{2g}
3.140	0	T_{1g}
3.140	0	A_{1g}
3.144	0	A_{2u}
3.150	0	T_{2g}
3.151	4.04E-03	T_{1u}
3.160	0	T_{2g}
3.164	0	T_{2u}
3.169	0	E_g
3.183	8.68E-05	T_{1u}
3.207	0	E_u
3.217	0	T_{1g}
3.223	0	A_{1g}
3.234	0	A_{2u}
3.236	0	T_{2u}
3.239	0	T_{2u}
3.243	6.83E-04	T_{1u}
3.252	0	T_{2u}
3.256	1.68E-03	T_{1u}
3.262	0	A_{1g}
3.267	0	E_g
3.277	0	T_{2g}
3.295	0	A_{2g}
3.344	4.93E-04	T_{1u}
3.354	0	E_u
3.366	0	E_g
3.376	7.44E-03	T_{1u}
3.408	0	T_{1g}
3.417	0	A_{2g}
3.422	0	T_{2g}
3.431	0	A_{2g}
3.432	0	T_{1g}
3.442	0	A_{1u}
3.447	0	T_{2g}
3.450	0	T_{2u}
3.453	0	E_g
3.461	0	E_u
3.471	0	T_{2u}
3.472	1.77E-04	T_{1u}
3.480	0	A_{1u}
3.492	0	E_g
3.528	0	A_{1u}
3.531	0	T_{1g}

3.532	0	E_u
3.532	0	E_u
3.537	0	T_{2u}
3.541	3.57E-04	T_{1u}
3.546	0	T_{1g}
3.546	0	T_{2u}
3.547	0	T_{2g}
3.552	0	E_u
3.565	1.97E-04	T_{1u}
3.568	0	T_{2u}
3.580	0	T_{2g}
3.619	0	A_{2g}
3.627	0	T_{2g}
3.642	0	T_{2u}
3.642	0	T_{1g}
3.656	9.72E-04	T_{1u}
3.659	0	T_{1g}
3.662	0	T_{2g}
3.755	0	A_{2u}
3.804	0	T_{2u}
3.805	0	E_u
3.819	1.14E-03	T_{1u}
3.834	0	T_{2g}
3.834	0	A_{2u}
3.842	0	T_{2u}
3.845	0	E_g
3.847	4.11E-03	T_{1u}
3.849	0	A_{1u}
3.852	0	T_{1g}
3.853	0	E_u
3.853	0	E_u
3.864	0	T_{2g}
3.897	0	T_{2u}
3.900	0	T_{2g}
3.901	0	E_g
3.905	1.43E-03	T_{1u}
3.910	0	T_{1g}
3.928	0	T_{2u}
3.937	0	T_{1g}
3.941	0	T_{2g}
3.945	0	A_{2g}
3.961	0	T_{1g}
3.965	0	A_{1g}
3.974	0	E_g
3.976	0	T_{2g}
3.982	0	T_{1g}
3.983	0	T_{2u}
3.989	0	A_{2g}
4.031	**0.162**	**T_{1u}**
4.046	0	T_{1g}
4.049	0	E_g
4.078	0	E_g
4.086	0	E_u
4.095	0	T_{1g}
4.095	0	A_{2u}
4.097	0	T_{2g}
4.118	0	T_{2u}
4.123	3.15E-02	T_{1u}
4.125	0	A_{1g}
4.135	0	E_g
4.149	0	E_u
4.168	0	T_{2u}
4.176	5.33E-03	T_{1u}
4.179	0	A_{2u}
4.204	0	T_{1g}
4.214	0	T_{2g}
4.225	0	T_{2g}
4.252	0	T_{1g}
4.268	0	E_u
4.276	0	A_{1g}
4.278	0	E_g
4.285	3.16E-04	T_{1u}
4.293	0	T_{2u}
4.303	1.34E-02	T_{1u}
4.321	0	A_{2u}
4.321	0	T_{2g}
4.333	0	A_{1g}
4.343	5.73E-02	T_{1u}
4.365	1.01E-03	T_{1u}
4.379	1.23E-02	T_{1u}
4.383	0	T_{2u}
4.386	0	E_g
4.413	0	A_{1u}
4.421	0	T_{2g}
4.445	0	E_u
4.455	0	T_{1g}
4.458	0	A_{2g}
4.463	0	T_{2u}
4.465	0	T_{1g}
4.467	0	T_{2g}
4.500	2.14E-02	T_{1u}

Mo-Mo to Mo-Mo*

4.507	0	A_{1u}	
4.508	0	E_g	
4.511	0	T_{1g}	
4.518	0	A_{1u}	
4.522	0	E_u	
4.529	0	T_{2u}	
4.535	0	A_{2u}	
4.556	0	T_{2g}	
4.570	0	T_{2g}	
4.577	0	T_{1g}	
4.579	0	T_{2u}	
4.588	0	E_u	
4.615	0	A_{2g}	
4.618	0	T_{2u}	
4.623	1.69E-02	T_{1u}	
4.641	0	T_{1g}	
4.672	0	T_{2g}	
4.714	0	T_{1g}	
4.726	0	T_{1g}	
4.742	0	T_{2g}	
4.818	0	T_{2u}	
4.831	4.52E-03	T_{1u}	
4.834	0	T_{2u}	
4.850	0	A_{1g}	
4.858	0	E_u	
4.884	0	A_{2u}	
4.918	0	E_g	
4.927	0	T_{2g}	
4.928	0	T_{1g}	
4.928	0	E_u	
4.988	**0.238**	**T_{1u}**	**Mo-Br to Mo-Br***
5.008	0	T_{1g}	
5.011	0	A_{2g}	
5.012	0	T_{2g}	
5.014	3.65E-02	T_{1u}	
5.033	0	T_{2u}	
5.046	5.96E-02	T_{1u}	
5.049	0	E_g	
5.049	0	T_{2g}	
5.082	0	A_{1g}	
5.099	0	T_{2u}	
5.110	0	E_g	
5.120	0	T_{2u}	
5.126	1.48E-02	T_{1u}	
5.142	0	T_{1g}	
5.147	0	E_g	
5.147	0	E_g	
5.159	0	T_{2u}	
5.168	0	T_{2g}	
5.193	0	E_g	
5.199	0	A_{2g}	
5.219	0	T_{2u}	
5.224	0	T_{1g}	
5.227	0	A_{2g}	
5.236	0	T_{2g}	
5.241	0	A_{1u}	
5.256	0	E_u	
5.259	0	T_{2u}	
5.267	5.75E-04	T_{1u}	
5.282	0	T_{2u}	
5.300	0	E_g	
5.336	0	T_{2u}	
5.348	0	T_{2g}	
5.359	0	T_{1g}	
5.363	0	T_{2g}	
5.377	0	A_{1g}	
5.382	**0.169**	**T_{1u}**	**Mo-Br to Mo-Br***
5.385	0	E_g	
5.386	2.63E-02	T_{1u}	
5.398	0	A_{2g}	
5.410	0	T_{1g}	
5.420	0	E_g	
5.423	0	T_{2g}	
5.446	0	A_{2u}	
5.448	0	T_{2u}	
5.450	0	E_u	
5.454	0	T_{1g}	
5.465	5.85E-03	T_{1u}	
5.482	8.92E-03	T_{1u}	
5.496	0	A_{1u}	
5.511	0	T_{2u}	
5.511	0	E_g	
5.515	0	E_u	
5.517	0	A_{2g}	
5.520	0	T_{2g}	
5.520	0	A_{1g}	
5.539	1.32E-02	T_{1u}	
5.569	0	T_{2g}	
5.618	0	T_{2u}	
5.629	4.01E-02	T_{1u}	

5.639	0	E_u
5.655	0	T_{2u}
5.660	0	A_{2u}
5.707	0	E_g
5.713	0	A_{1g}
5.734	1.09E-03	T_{1u}
5.735	0	T_{1g}
5.739	0	T_{2u}
5.756	0	T_{2g}
5.771	0	A_{1u}
5.772	0	E_u
5.772	0	T_{2u}
5.774	0	T_{2u}
5.776	2.31E-03	T_{1u}
5.782	0	E_u
5.782	2.43E-03	T_{1u}
5.783	0	T_{2u}
5.792	0	A_{1g}
5.800	0	E_g
5.802	0	A_{2g}
5.807	0	T_{2g}
5.821	0	T_{1g}
5.823	0	T_{1g}
5.827	0	T_{2g}
5.827	0	E_g
5.843	**0.160**	**T_{1u}**
5.860	0	T_{2g}
5.862	0	A_{1g}
5.872	0	T_{1g}
5.888	3.11E-02	T_{1u}
5.899	0	T_{2g}
5.902	0	A_{2u}
5.910	0	T_{1g}
5.923	0	E_g
5.928	0	T_{2g}
5.961	0	T_{2u}
5.977	6.22E-02	T_{1u}
5.988	0	A_{1g}
5.997	0	E_g
6.000	0	A_{2g}

Mo-Br to Mo-Br*

(B)

Excitation Energy	Oscillator Strength	Nature
2.645	2.62E-05	
2.649	2.63E-05	
2.655	2.01E-05	
2.680	3.33E-05	
2.701	4.54E-09	
2.703	3.31E-09	
2.729	1.61E-09	**Mo-Mo / Mo-Br***
2.731	1.12E-09	
2.758	1.22E-09	
2.763	1.04E-08	**to**
2.880	3.80E-10	
2.895	1.61E-08	
2.904	1.82E-09	**Mo-Mo***
2.908	2.45E-09	
2.911	4.22E-10	
2.923	5.80E-09	
2.933	4.56E-04	
2.953	1.12E-03	
2.961	7.09E-03	
2.963	9.92E-04	
2.968	1.04E-02	
2.980	2.59E-02	
2.981	3.36E-03	
2.993	3.89E-02	
2.997	7.84E-03	
3.011	2.19E-02	
3.015	2.05E-02	
3.026	2.02E-09	
3.029	3.58E-02	
3.034	1.85E-09	
3.037	1.87E-03	
3.041	4.75E-09	
3.046	9.41E-04	
3.047	2.12E-03	
3.048	1.25E-08	
3.072	6.22E-09	
3.079	1.85E-08	
3.090	6.20E-09	
3.091	8.38E-09	
3.097	1.17E-08	
3.119	1.08E-08	
3.120	2.96E-09	
3.124	7.89E-10	
3.131	3.66E-08	
3.146	1.75E-09	
3.150	7.98E-09	
3.192	4.35E-08	
3.194	2.34E-03	
3.196	2.31E-08	
3.200	1.18E-08	
3.202	2.74E-08	
3.203	6.94E-03	
3.206	6.66E-08	
3.209	2.99E-03	
3.212	3.83E-08	
3.214	3.01E-03	
3.226	2.41E-03	
3.226	4.58E-03	
3.230	9.36E-05	
3.237	7.69E-04	
3.241	8.47E-07	
3.241	7.54E-03	
3.245	9.92E-04	
3.247	3.25E-03	
3.250	1.64E-03	
3.253	5.81E-08	
3.256	1.17E-03	
3.261	1.59E-03	
3.277	3.35E-04	
3.281	1.90E-02	

3.281	3.62E-07
3.286	9.32E-09
3.286	1.09E-03
3.295	1.67E-02
3.297	4.12E-08
3.310	1.17E-02
3.311	1.14E-02
3.318	1.91E-03
3.320	4.18E-03
3.325	1.93E-09
3.336	2.12E-08
3.338	1.63E-02
3.340	2.13E-08
3.346	2.73E-04
3.356	1.05E-04
3.358	8.20E-09
3.362	1.18E-07
3.368	8.67E-09
3.369	9.36E-04
3.380	4.35E-08
3.387	2.92E-03
3.392	2.79E-03
3.394	1.48E-08
3.404	3.57E-03
3.407	1.51E-08
3.409	1.28E-07
3.410	7.99E-04
3.414	5.94E-04
3.419	5.69E-05
3.426	8.05E-04
3.427	1.16E-09
3.433	6.25E-08
3.435	7.61E-04
3.438	4.87E-04
3.444	7.97E-08
3.445	5.40E-08
3.453	2.96E-08
3.464	1.29E-08
3.470	1.70E-08
3.474	5.55E-05
3.476	6.74E-09
3.479	5.36E-08
3.482	2.71E-09
3.488	1.70E-08
3.491	1.55E-04
3.499	2.10E-09

3.501	4.71E-05
3.509	1.76E-04
3.515	2.43E-09
3.517	7.88E-09
3.520	2.82E-05
3.520	3.64E-09
3.528	1.99E-04
3.529	5.03E-09
3.535	7.17E-09
3.538	2.24E-09
3.540	8.78E-05
3.546	5.77E-08
3.551	4.10E-08
3.552	3.64E-04
3.555	2.41E-08
3.569	1.97E-03
3.574	2.95E-04
3.579	8.25E-04
3.583	1.27E-03
3.600	1.18E-02
3.608	1.26E-02
3.611	1.04E-02
3.641	1.24E-04
3.642	1.15E-08
3.651	1.02E-04
3.653	2.53E-04
3.657	4.10E-04
3.664	9.31E-08
3.669	1.15E-03
3.674	1.15E-08
3.680	5.75E-08
3.682	2.45E-03
3.689	1.34E-03
3.692	8.37E-09
3.692	4.82E-04
3.704	1.75E-04
3.707	1.17E-08
3.707	1.18E-03
3.714	3.34E-03
3.717	4.68E-09
3.723	4.89E-04
3.733	4.29E-03
3.734	2.80E-03
3.738	5.05E-04
3.741	1.76E-04
3.743	8.28E-03

3.757	5.67E-08
3.760	1.34E-02
3.761	9.73E-07
3.762	1.14E-02
3.763	3.98E-07
3.765	1.18E-07
3.767	1.10E-02
3.769	1.17E-07
3.771	1.14E-03
3.771	1.74E-08
3.789	1.15E-07
3.795	4.09E-03
3.801	4.24E-03
3.811	4.87E-08
3.816	1.59E-09
3.820	1.92E-03
3.827	2.51E-07
3.827	2.93E-03
3.829	2.68E-08
3.831	2.09E-08
3.835	3.44E-08
3.840	2.47E-08
3.843	6.14E-04
3.844	1.94E-03
3.851	1.69E-03
3.854	1.82E-03
3.863	3.89E-04
3.869	2.67E-04
3.873	1.07E-03
3.891	1.17E-08
3.895	1.91E-09
3.899	4.29E-02
3.912	4.71E-09
3.912	4.07E-02
3.917	4.08E-02
3.919	3.23E-08
3.929	3.16E-08
3.933	4.65E-09
3.940	7.77E-09
3.949	1.43E-08
3.953	2.91E-08
3.956	9.50E-09
3.979	1.06E-08
3.982	2.08E-08
3.982	1.17E-03
3.987	1.70E-08

3.992	2.99E-03	
3.992	1.06E-08	
3.995	1.07E-08	
3.999	6.24E-03	
4.003	7.18E-09	
4.011	3.15E-08	
4.015	2.12E-08	
4.022	4.57E-09	
4.055	3.12E-05	
4.068	9.72E-05	
4.072	7.53E-05	
4.075	2.39E-04	
4.087	9.71E-05	
4.092	2.44E-04	
4.094	3.01E-04	
4.101	8.82E-04	
4.106	2.26E-04	
4.158	3.59E-09	
4.160	5.36E-09	
4.173	5.89E-09	
4.174	5.83E-09	**Mo-Mo / Mo-Br**
4.179	1.88E-08	
4.187	1.41E-09	
4.190	9.30E-09	**to**
4.192	9.19E-09	
4.204	7.89E-03	
4.207	2.77E-09	**Mo-Mo***
4.213	1.02E-08	
4.215	9.85E-03	
4.223	4.25E-09	
4.229	4.05E-08	
4.235	1.34E-02	
4.258	**0.327**	
4.261	**0.308**	
4.266	**0.413**	
4.270	2.20E-08	
4.274	4.55E-09	
4.277	2.23E-08	
4.280	1.23E-02	
4.282	1.41E-08	
4.284	2.12E-08	
4.284	1.15E-02	
4.287	2.36E-06	
4.287	1.37E-02	
4.288	1.54E-02	
4.290	4.95E-09	
4.294	5.05E-08	
4.294	1.09E-03	
4.296	1.39E-02	
4.297	1.69E-08	
4.299	4.51E-02	
4.300	5.43E-02	
4.303	1.27E-08	
4.306	5.59E-03	
4.308	7.54E-02	
4.310	7.96E-03	
4.311	2.92E-08	
4.319	7.88E-04	
4.342	1.34E-02	
4.360	**0.698**	
4.364	**0.540**	
4.372	**0.576**	
4.373	1.87E-06	
4.376	5.00E-03	
4.382	2.96E-03	
4.388	1.84E-04	
4.389	1.62E-09	
4.392	1.04E-08	
4.401	1.23E-07	
4.402	4.83E-10	
4.404	1.74E-02	
4.405	3.59E-10	
4.410	2.89E-08	
4.414	1.02E-02	
4.416	5.09E-03	
4.421	6.85E-10	
4.422	6.04E-03	
4.425	4.79E-03	
4.425	5.85E-09	
4.427	2.78E-03	
4.433	4.46E-09	
4.436	1.19E-08	
4.439	2.47E-08	
4.447	4.25E-02	
4.449	1.90E-09	
4.451	2.30E-07	**Mo-Br**
4.453	3.77E-02	
4.455	4.23E-09	
4.457	2.71E-03	**to**
4.461	3.17E-02	
4.462	2.14E-08	
4.465	2.96E-08	**Br**
4.485	1.12E-03	
4.494	7.86E-08	
4.498	9.32E-09	**and**
4.506	8.74E-09	
4.513	1.62E-09	
4.515	7.84E-04	**Mo-Br**
4.521	6.73E-09	
4.526	1.89E-08	
4.528	7.45E-09	**to**
4.533	5.24E-09	
4.537	1.04E-08	
4.540	2.27E-08	**Mo-Mo***
4.552	4.52E-08	
4.560	2.91E-09	
4.561	4.51E-09	
4.562	2.01E-08	
4.565	4.10E-08	
4.576	2.86E-08	
4.582	2.48E-09	
4.585	1.98E-03	
4.600	2.87E-08	
4.600	3.33E-03	
4.606	2.81E-03	
4.613	4.01E-03	
4.617	1.64E-03	
4.626	3.32E-03	
4.629	2.97E-03	
4.631	1.06E-02	
4.641	5.11E-03	
4.644	6.40E-03	
4.652	1.51E-02	
4.655	4.48E-03	
4.661	9.20E-03	
4.664	4.06E-03	
4.669	2.01E-02	
4.671	5.02E-03	
4.684	8.38E-03	
4.688	2.78E-03	
4.705	1.23E-03	
4.708	1.16E-03	
4.709	2.41E-08	
4.722	1.67E-08	
4.725	6.68E-09	
4.727	2.00E-02	
4.728	2.96E-08	
4.733	4.07E-02	

4.733	1.68E-06
4.736	4.89E-09
4.738	4.99E-02
4.741	4.63E-08
4.741	4.39E-02
4.742	2.94E-07
4.744	6.87E-08
4.745	4.76E-02
4.748	9.44E-09
4.754	4.46E-08
4.754	3.32E-08
4.755	4.15E-02
4.763	3.49E-02
4.763	1.34E-08
4.766	5.61E-09
4.779	1.32E-08
4.786	8.92E-03
4.787	1.08E-02
4.788	1.70E-08
4.791	2.01E-08
4.792	1.06E-02
4.793	1.75E-08
4.804	2.65E-08
4.808	7.56E-09
4.809	8.77E-05
4.813	5.76E-09
4.815	8.24E-09
4.818	4.49E-08
4.826	1.10E-08
4.839	4.86E-03
4.840	**0.129**
4.840	1.59E-04
4.846	2.64E-04
4.847	2.74E-08
4.852	1.11E-08
4.856	2.05E-03
4.859	4.32E-08
4.863	2.68E-08
4.864	8.24E-04
4.866	0.1074
4.870	3.17E-09
4.871	3.51E-03
4.878	4.44E-03
4.881	8.38E-09
4.881	1.54E-03
4.885	9.41E-03

4.891	3.53E-02
4.901	3.26E-02
4.904	5.32E-04
4.906	2.61E-02
4.910	**0.207**
4.913	**0.144**
4.918	**0.117**
4.929	1.02E-02
4.939	3.17E-04
4.939	3.23E-08
4.942	3.78E-03
4.943	1.40E-08
4.955	1.57E-07
4.955	6.52E-04
4.958	3.97E-08
4.962	9.78E-09
4.964	9.69E-03
4.966	3.48E-07
4.967	3.02E-04
4.970	1.18E-07
4.971	1.59E-07
4.978	2.96E-08
4.979	4.53E-04
4.981	7.24E-04
4.982	5.99E-08
4.984	1.16E-04
4.985	3.94E-08
4.988	1.58E-07
4.989	1.09E-03
4.991	7.29E-09
4.992	1.37E-08
4.995	4.40E-03
4.996	1.12E-07
4.999	2.03E-05
5.007	6.00E-09
5.008	2.02E-08
5.015	3.46E-09
5.044	1.94E-07
5.047	2.70E-05
5.052	2.55E-08
5.054	1.30E-07
5.055	1.49E-04
5.056	1.61E-08
5.058	1.75E-04
5.065	1.26E-04
5.065	1.41E-09

5.073	2.26E-08
5.091	7.96E-03
5.096	5.06E-08
5.097	1.03E-02
5.102	4.61E-08
5.108	1.12E-02
5.110	1.38E-08
5.112	1.14E-02
5.129	2.78E-02
5.130	1.80E-02
5.269	7.89E-08
5.270	**0.292**
5.275	4.41E-07
5.276	**0.244**
5.282	**0.290**
5.290	1.51E-07
5.294	2.00E-08
5.298	1.50E-02
5.302	2.82E-09
5.307	4.22E-03
5.316	7.80E-08
5.318	2.92E-02
5.323	5.12E-08
5.325	4.22E-08
5.328	**0.140**
5.334	**0.101**
5.339	**0.275**
5.347	**0.234**
5.349	**0.214**
5.369	5.64E-02
5.373	4.07E-08
5.376	1.00E-03
5.380	3.26E-07
5.382	4.20E-04
5.386	4.10E-07
5.391	1.85E-04
5.392	4.14E-07
5.397	1.94E-08
5.401	8.71E-09
5.420	2.07E-07
5.434	1.35E-02
5.440	8.71E-03
5.444	1.46E-02
5.449	2.04E-02
5.454	1.39E-02
5.464	1.02E-02

5.484	1.62E-08
5.488	**0.184**
5.490	1.73E-08
5.494	3.81E-08
5.497	6.09E-08
5.498	4.68E-08

5.505	**0.192**
5.510	2.95E-05
5.510	**0.185**
5.520	7.98E-07
5.526	2.43E-06
5.529	4.29E-04

5.532	3.26E-04
5.538	5.11E-06
5.541	7.65E-05
5.543	1.90E-04

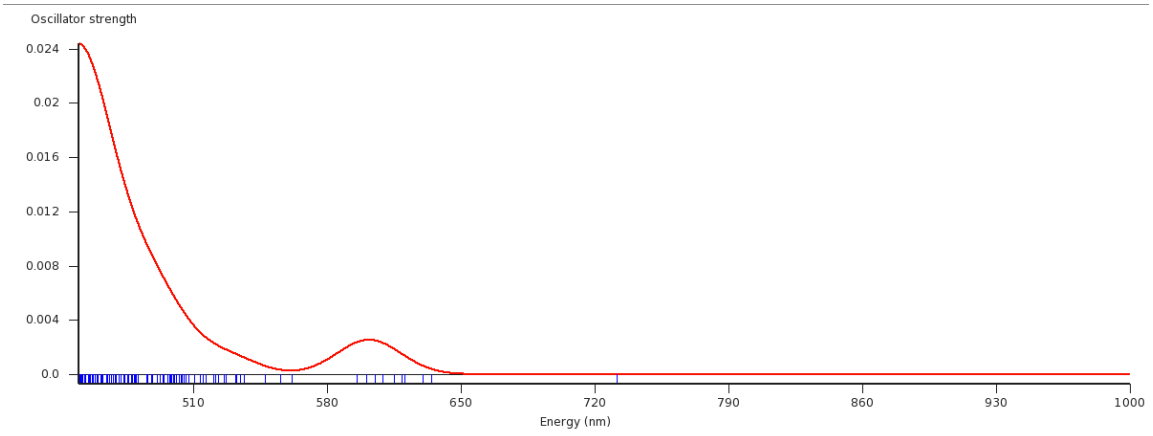
Table S4 TD-DFT singlet-triplet electronic excitations in eV calculated for $[Mo_6Br^i_8Br^a_6]^{2-}$ (A) in its O_h-DFT optimized geometry (symmetrically degenerated energies not reported) and (B) in its experimental $(TBA)_2[Mo_6Br^i_8Br^a_6]$ arrangement.

(A)

Excitation Energy	Symmetry	Nature
2.390	A_{1u}	**Mo-Mo**
2.401	T_{1g}	
2.424	E_u	**to**
2.445	T_{2g}	
2.475	A_{2u}	**Mo-Mo***
2.613	E_u	

(B)

Excitation Energy	Nature
2.508	
2.510	
2.518	
2.537	**Mo-Mo**
2.542	
2.544	**to**
2.561	
2.580	**Mo-Mo***
2.587	
2.589	
2.750	
2.761	
2.766	



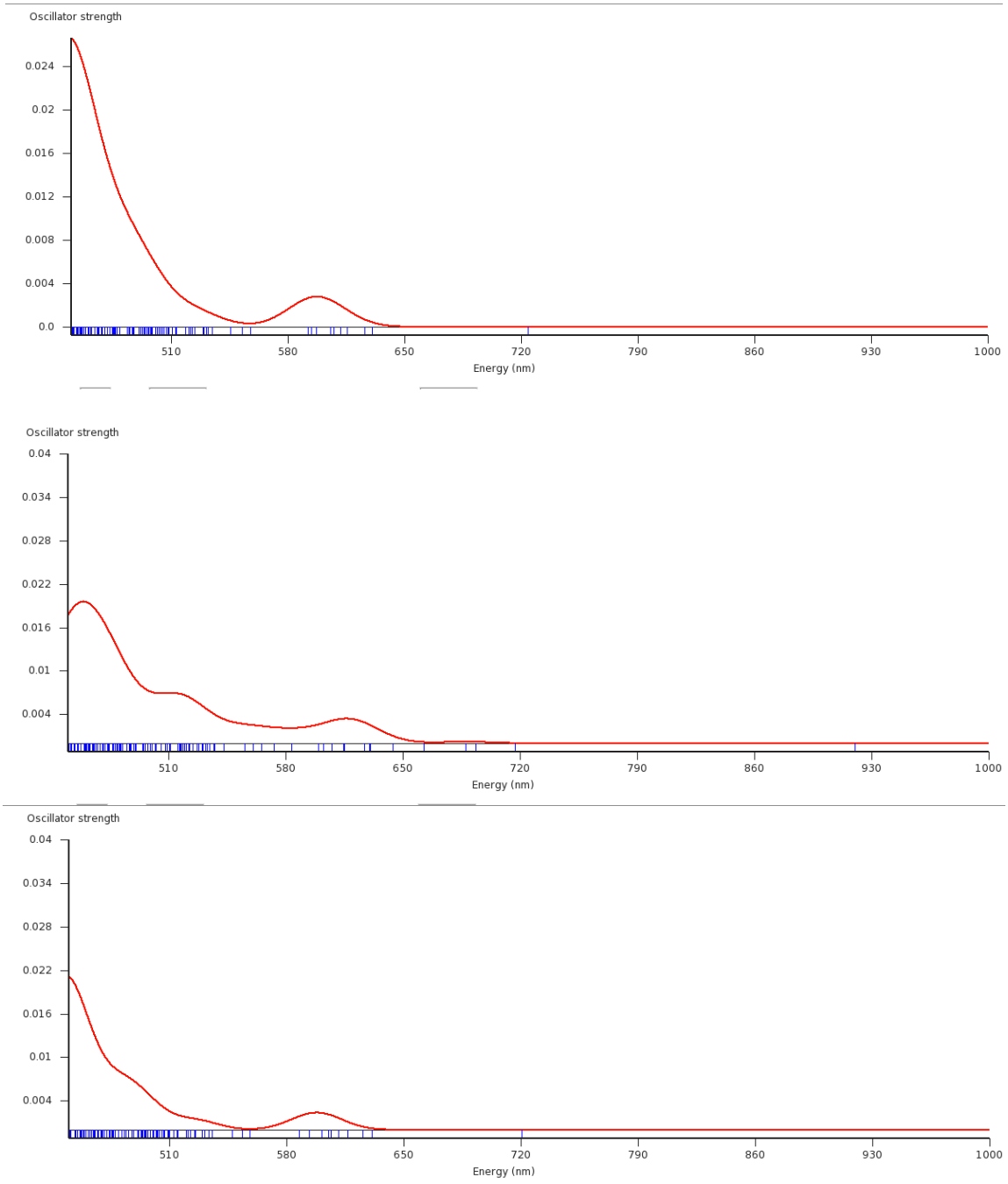


Fig. S6 TD-DFT simulated absorption spectra of $[Mo_6Br^i_8Br^a_6]^{2-}$ (oscillator strength versus wavelength) for the excited states T_1, T_2, T_3, T_4 (from top to bottom).

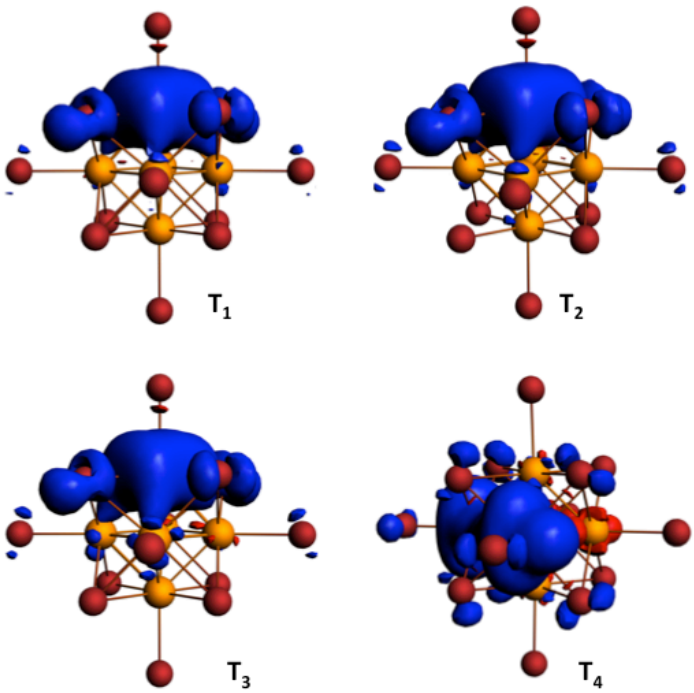


Fig. S7 Spatial distributions of the computed spin density for T_1, T_2, T_3, T_4. Isocontour value: ± 0.001 [e/bohr^3].

Table S5 Mo Mulliken atomic spin-densities of T_1, T_2, T_3, T_4. See Scheme 1 for labeling.

	T_1	T_2	T_3	T_4
Mo1	0.009	0.001	0.022	0.999
Mo2	0.005	0.002	0.022	0.999
Mo3	-0.004	0.002	-0.017	-0.050
Mo4	-0.006	0.001	-0.017	-0.050
Mo5	1.729	1.718	1.713	-0.022
Mo6	0.005	0.005	0.004	-0.022

Table S6 Cartesian coordinates of the optimized transition state connecting T_1, T_2, T_3 to T_4

	x	y	y
Mo	-1.341314	-0.01164	-0.01438
Mo	1.316621	0.024622	0.02297
Mo	1.466358	-0.049287	2.6958
Mo	-1.326629	0.086917	2.64272
Mo	0.002779	-1.848939	1.35876
Mo	-0.073159	1.871597	1.37002
Br	0.035448	-1.879467	1.280482
Br	-2.645503	-1.874931	1.339559
Br	-2.802673	1.84359	1.143477
Br	-0.020926	1.869001	1.327537
Br	-3.150165	-0.127972	-1.953303
Br	3.201803	0.089693	1.834221
Br	-3.142861	0.214242	4.539624
Br	-0.011987	-4.494917	1.434209
Br	-0.135542	4.498067	1.489389
Br	2.658095	-1.913381	1.251668
Br	2.660244	1.892106	1.373294
Br	3.422191	-0.172866	4.448336
Br	0.053370	-1.830221	4.026085
Br	0.230087	1.796158	4.067145