

Supplementary Information

The Formation Reason of Intermolecular Charge Transfer bands: A series of Polyoxomolybdates as a Case Study

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Experimental section

Materials. Other chemicals were used as purchased without further purification. Water was deionized and distilled before use.

Measurements. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku DMAX 2500 diffractometer with CuK α radiation ($\lambda = 1.54056 \text{ \AA}$). Simulated PXRD pattern was derived from the Mercury Version 4.3.0 software using the X-ray single crystal diffraction data. UV-vis spectra were performed on a SHIMADZU UV-2600 UV-visible spectrophotometer by using the BaSO $_4$, and water as the blank, for solid and liquid sample, respectively.

Synthesis of (Hopda) $_4$ [β -Mo $_8$ O $_{26}$] \cdot 2H $_2$ O (1**, opda = o-phenylenediamine).**

(NH $_4$) $_6$ Mo $_7$ O $_{24}$ \cdot 4H $_2$ O (617.5 mg, 0.5 mmol) and opda (162 mg, 1.5 mmol) in 20 mL water were stirred at room temperature. The pH was adjusted to 2.3-2.5 with 20% HCl solution. and the orange-red powder will soon be obtained. The powder was washed with H $_2$ O, EtOH, and Et $_2$ O. The yield of **1** based on the tetraethylammonium was 81%.

Synthesis of (H $_2$ mpda) $_2$ [β -Mo $_8$ O $_{26}$] \cdot 4H $_2$ O (2**, mpda = m-phenylenediamine).**

(NH $_4$) $_6$ Mo $_7$ O $_{24}$ \cdot 4H $_2$ O (617.5 mg, 0.5 mmol) and mpda (162 mg, 1.5 mmol) in 80 mL water were stirred at room temperature. The pH was adjusted to 2.3-2.5 with 20% HCl solution. and the white powder will soon be obtained. The powder was washed with H $_2$ O, EtOH, and Et $_2$ O. The yield of **2** based on the tetraethylammonium was 75%.

Synthesis of (H $_2$ ppda) $_2$ [β -Mo $_8$ O $_{26}$] \cdot 6H $_2$ O (3**, ppda = p-phenylenediamine).**

(NH $_4$) $_6$ Mo $_7$ O $_{24}$ \cdot 4H $_2$ O (617.5 mg, 0.5 mmol) and ppda (162 mg, 1.5 mmol) in 20 mL water were stirred at room temperature. The pH was adjusted to 2.3-2.5 with 20% HCl solution. and the white powder will soon be obtained. The powder was washed with H $_2$ O, EtOH, and Et $_2$ O. The yield of **2** based on the tetraethylammonium was 82%.

Computational approaches

The structures of **1-3** were obtained from CCDC database. The crystal structure of POMo **1-3** were applied to build calculation models. Because the positions of H atoms are difficult to be accurately determined by the method of single crystal X-ray diffraction, the geometry optimizations of **1-3**, where the position of H atoms were optimized and other atoms were freezing, were performed with PBE/6-31g* level in the CP2K software.¹

The absorption spectra have been simulated by using the CP2K software at PBE function with basis set and pseudopotential being DZVP-MOLOPT-SR-GTH. Only Γ point has been considered for Brillouin zone sampling in the reciprocal space. The hole-electron analysis were derived using the Multiwfn software.² The hole-electron excitation properties of excited states are described by S_r :

$$S_r(r) = \sqrt{\rho^{hole}(r)\rho^{ele}(r)}$$

where ρ is the hole or electron density, and S_r (with value range of [0, 1]) is the overlap function between hole and electron distribution.

The Frontier molecular orbital for Hopda $^+$, Hopda $^{2+}$, H $_2$ mpda $^{2+}$ and H $_2$ ppda $^{2+}$ were done in Gaussian 09 D01 version³ at B3LYP/def2-TZVP level.

Supplementary Tables.

Table S1. List of main excited states for **2**.

Excited state	Wavelength (nm)	Oscillator strength	Electronic transition (%)	Assignment
S ₀ -S ₁₂	415.32	0.00782	HOMO→LUMO+3 (85.6%), HOMO-4→LUMO (12.1%)	H ₂ mpda→Mo ₈
S ₀ -S ₇₇	363.47	0.02069	HOMO-11→LUMO+1 (67.9%), HOMO-10→LUMO (24.5%)	Mo ₈

Table S2. List of main excited states for **3**.

Excited state	Wavelength (nm)	Oscillator strength	Electronic transition (%)	Assignment
S ₀ -S ₁	419.75	0.00256	HOMO→LUMO+1 (99.1%)	
S ₀ -S ₄₃	374.97	0.01161	HOMO-2→LUMO+4 (91.8%)	H ₂ ppda→Mo ₈
S ₀ -S ₁₆₄	344.14	0.02717	HOMO-3→LUMO+18 (99.2%)	

Supplementary Figures.

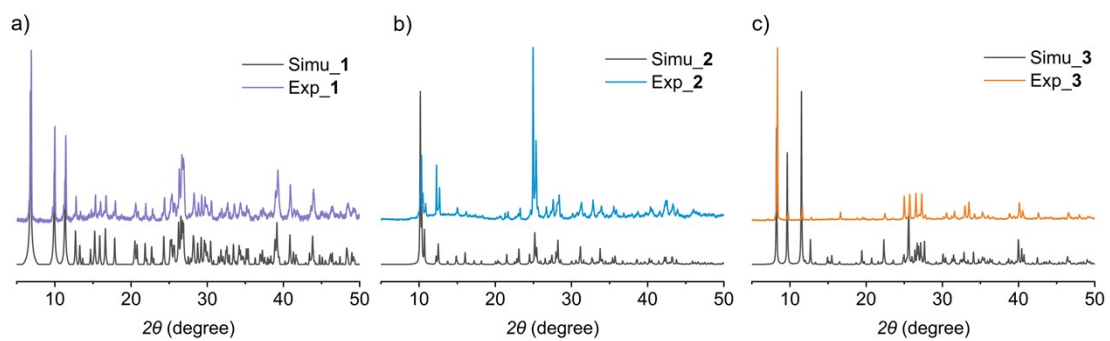


Fig. S1. PXR D patterns of **1**, **2**, and **3**. Experimental (Exp) and simulated (Simu) PXR D patterns of **1**, **2**, and **3**.

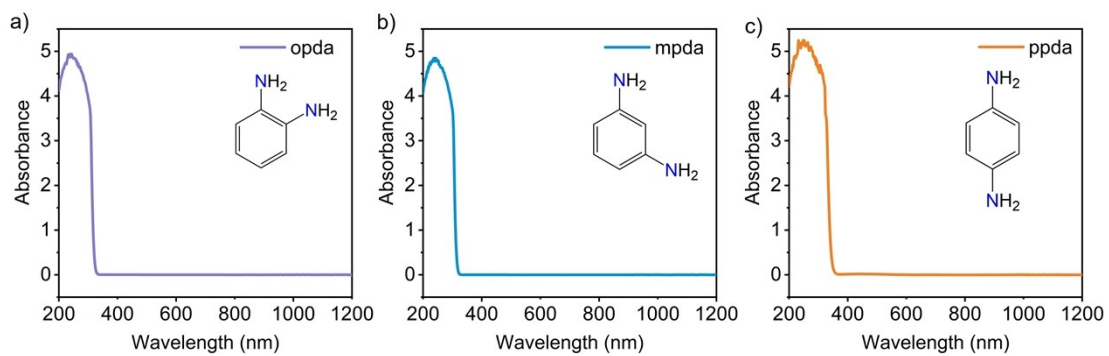


Fig. S2. UV-Vis absorption spectra of opda (a), mpda (b), and ppda (c) aq. (10^{-4} M). Aqueous solutions of opda, mpda and ppda were prepared separately and diluted to 10^{-4} mol/L. The tests were performed using water as a reference, subtract the solvent background. The test range was 200-1200 nm.

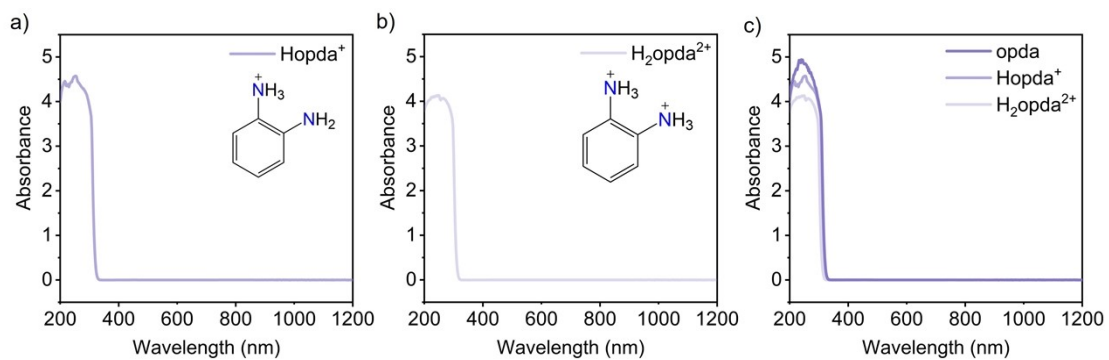


Fig. S3. UV-Vis absorption spectra of Hopda⁺ (a), H₂opda²⁺ (b), and compare opda, Hopda⁺ and H₂opda²⁺ (c) aq. (10⁻⁴ M). Hopda⁺ and H₂opda²⁺ are synthesized through the reaction of hydrochloric acid and opda in amount of substance ratios of 1:1 and 2:1, respectively.

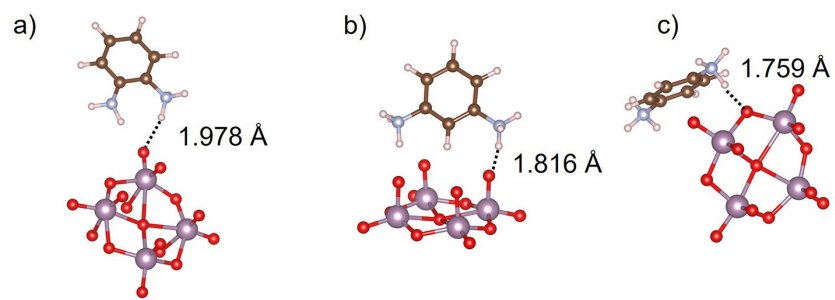


Fig. S4. Shortest distance between aniline and Mo₈, **1** (a), **2** (b), and **3** (c).

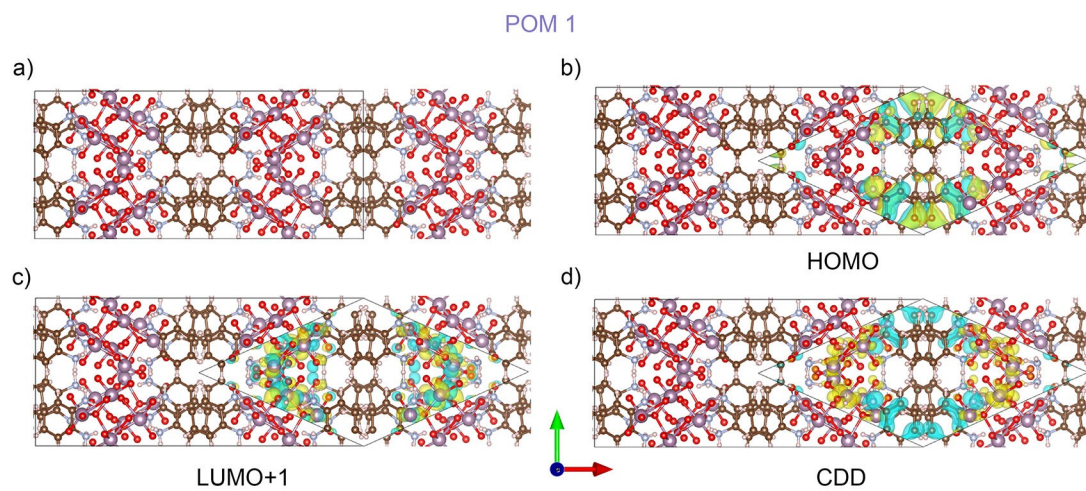


Fig. S5. For **1**. Structure (a), HOMO(b), LUMO +1 (c) and CDD (d) map for excited state S_0 - S_2 .
Crystal axis: a, red; b, green; c, blue.

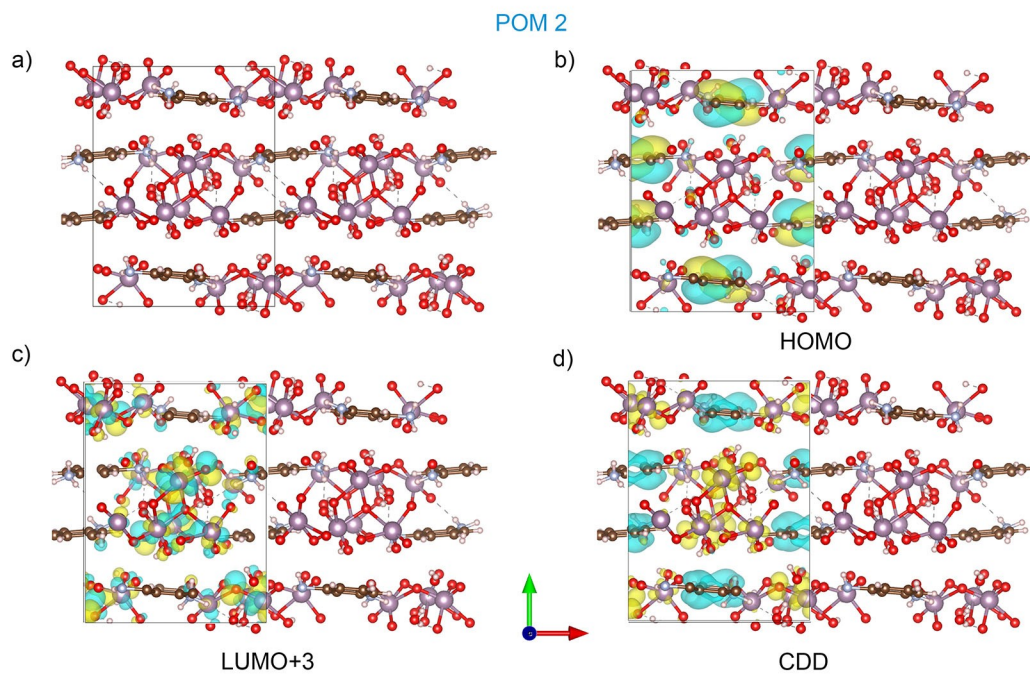


Fig. S6. For **2**. Structure (a), HOMO(b), LUMO +3 (c) and CDD (d) map for excited state S_0 - S_{12} .
Crystal axis: a, red; b, green; c, blue.

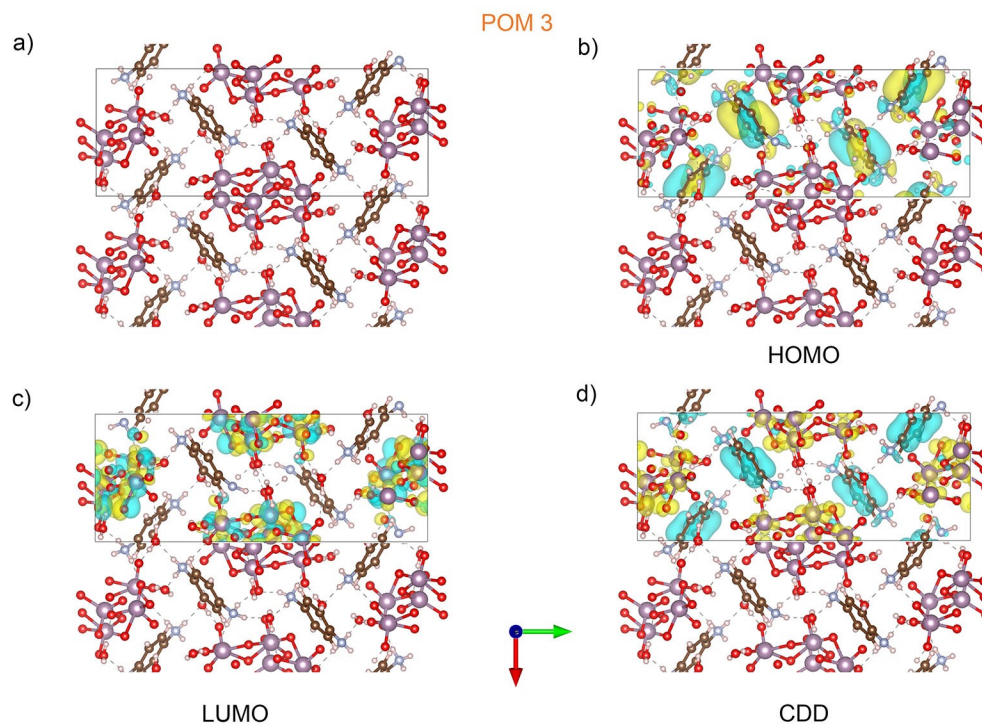


Fig. S7. For **3**. Structure (a), HOMO(b), LUMO (c) and CDD (d) map for excited state S_0 - S_1 of **3**.
Crystal axis: a, red; b, green; c, blue.

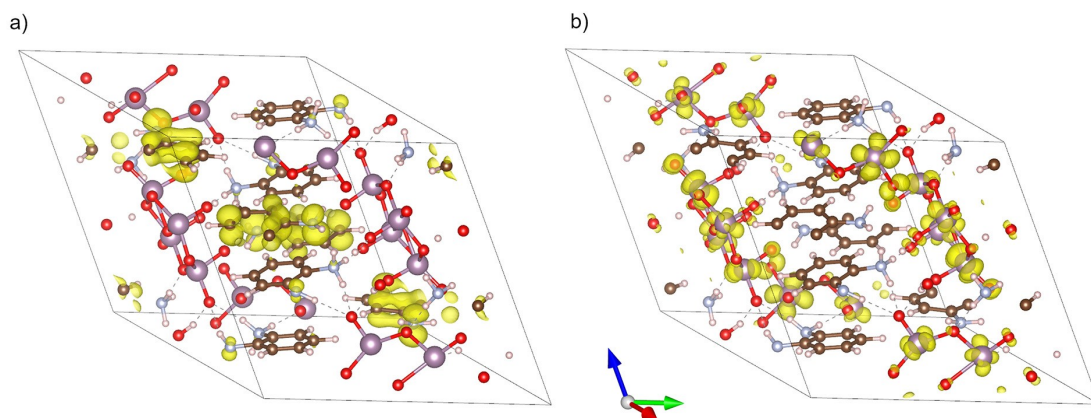


Fig. S8. Hole (a) and electron (b) map for excited state S_0-S_2 of **1**.

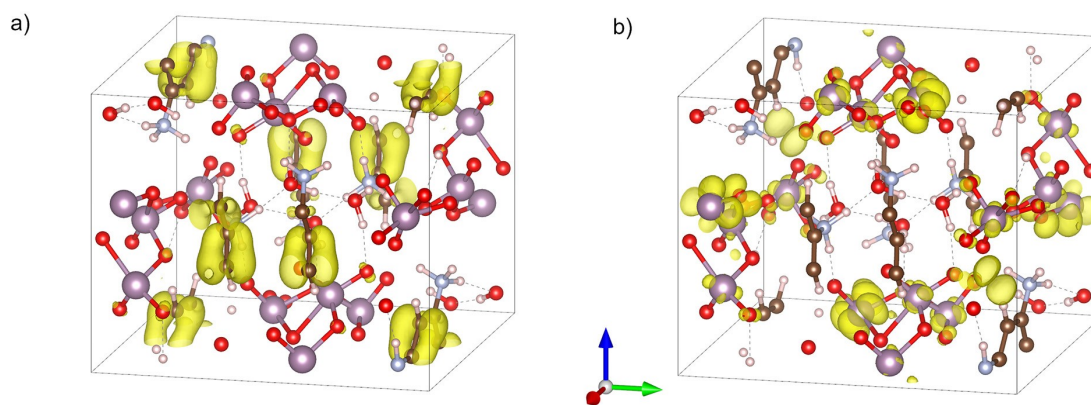


Fig. S9. Hole (a) and electron (b) map for excited state S_0-S_{12} of **2**.

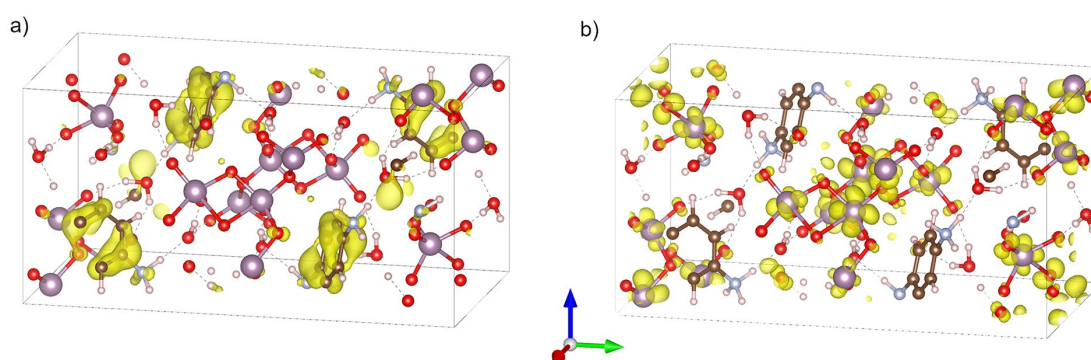


Fig. S10. Hole (a) and electron (b) map for excited state S_0-S_1 of **3**.

Appendix

Hole, electron and CDD map of **1**, **2** and **3**. Yellow and blue colors represent charge accumulation and depletion after electron transfer, respectively, with an iso-surface value of $0.001 \text{ e}\cdot\text{\AA}^{-3}$.

The excited state of POMo **1**: S_0-S_{109} , S_0-S_{143} , S_0-S_{193} , S_0-S_{248} , S_0-S_{451} , S_0-S_{617} , S_0-S_{620} , S_0-S_{672} , S_0-S_{759} , S_0-S_{785} , S_0-S_{806} , S_0-S_{816} , S_0-S_{821} , S_0-S_{887}

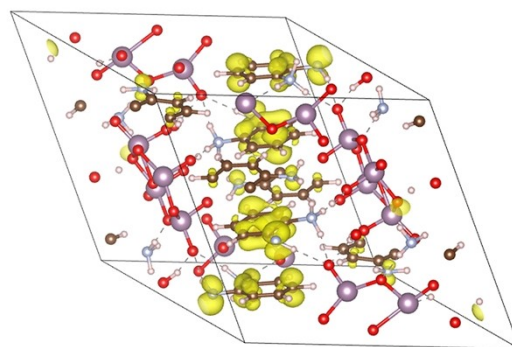
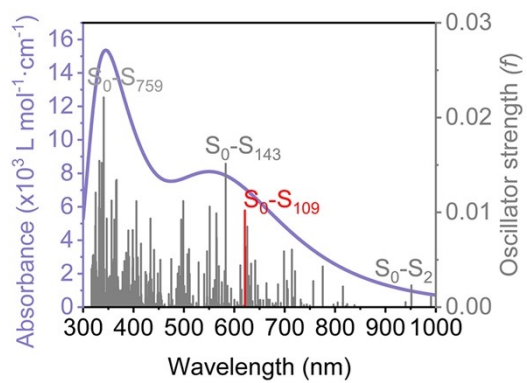
The excited state of POMo **2**: S_0-S_{77}

The excited state of POMo **3**: S_0-S_{43} S_0-S_{164}

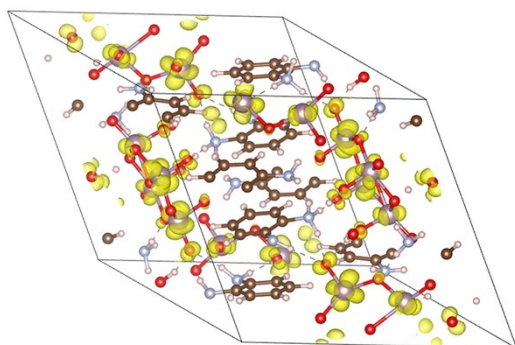
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- (1) Kuehne, T. D.; Iannuzzi, M.; Del Ben, M.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schutt, O.; Schiffmann, F.; et al. CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations. *J. Chem. Phys.* **2020**, *152*, 194103.
- (2) Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580-592.
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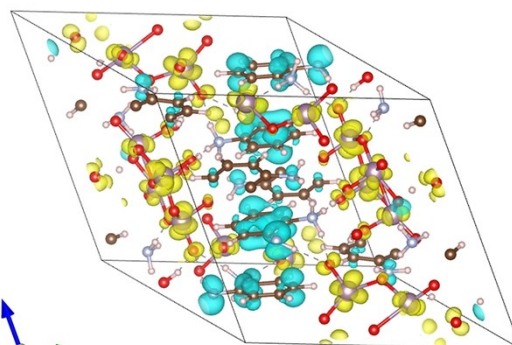
S_0-S_{109}



hole

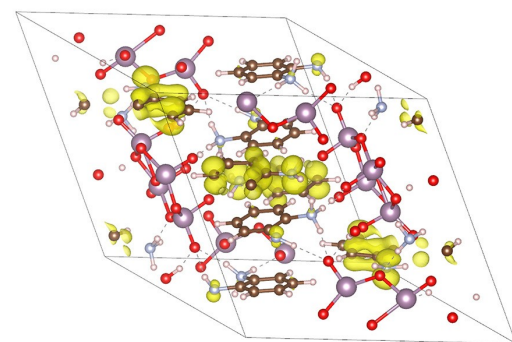
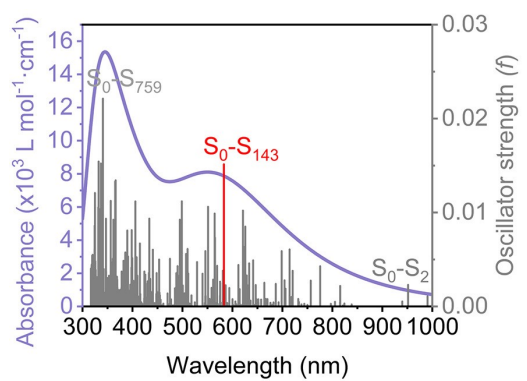


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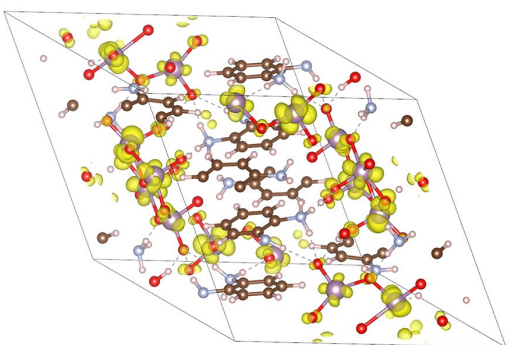


CDD

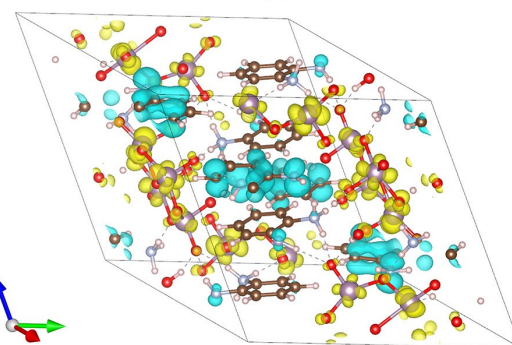
S_0-S_{143}



hole

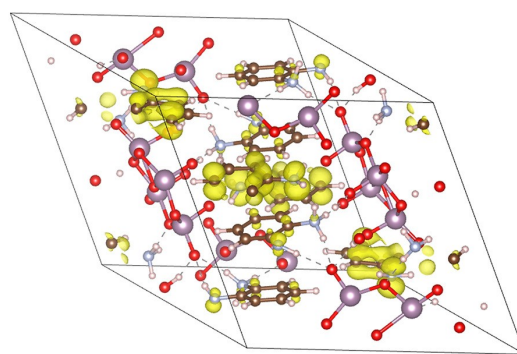
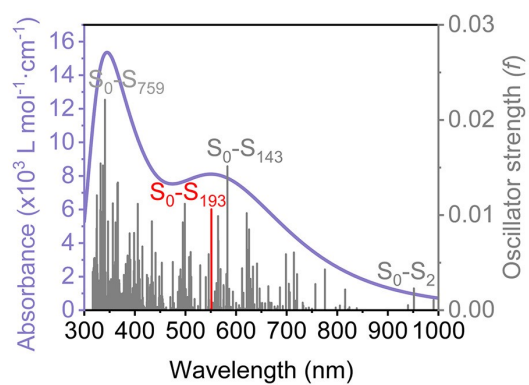


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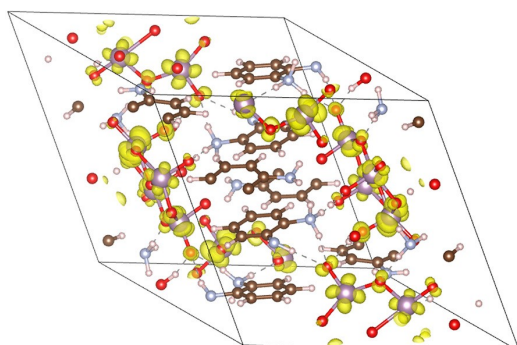


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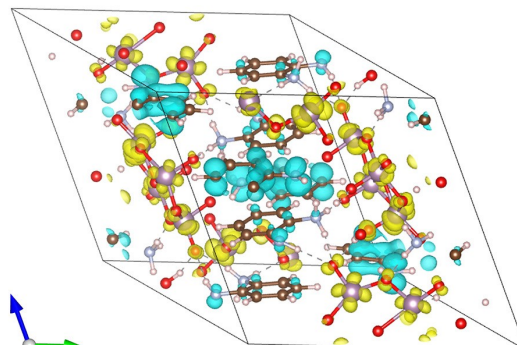
S_0-S_{193}



hole

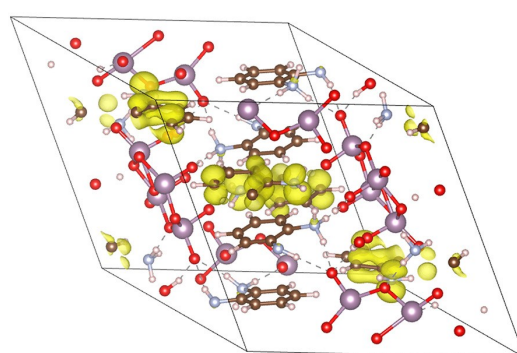
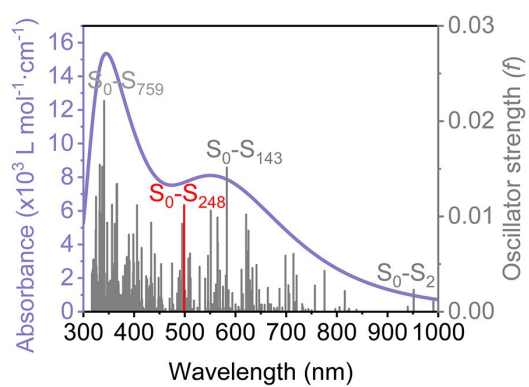


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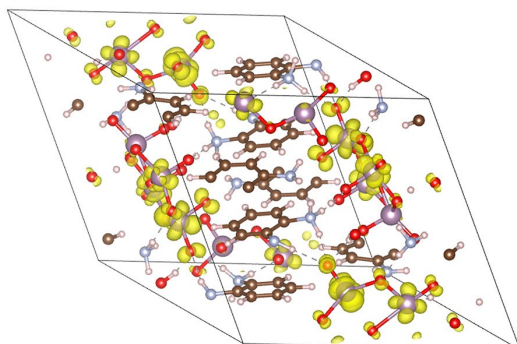


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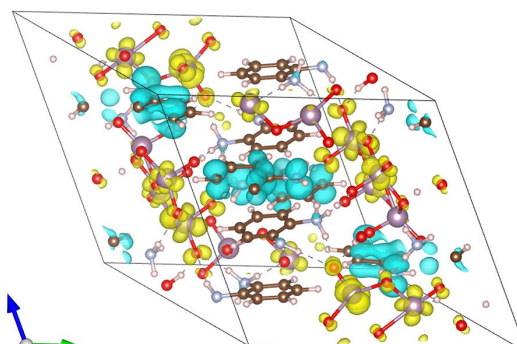
S_0-S_{248}



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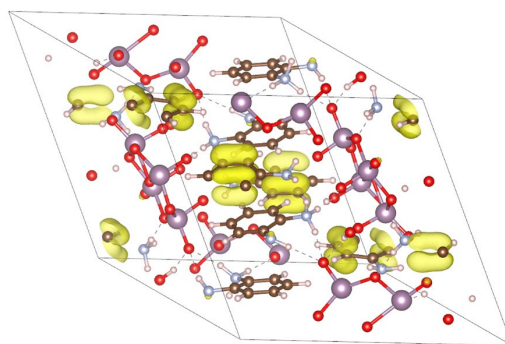
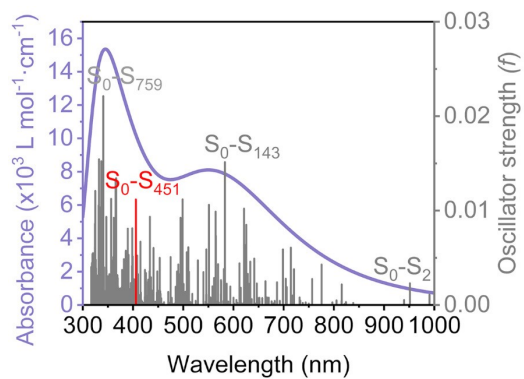


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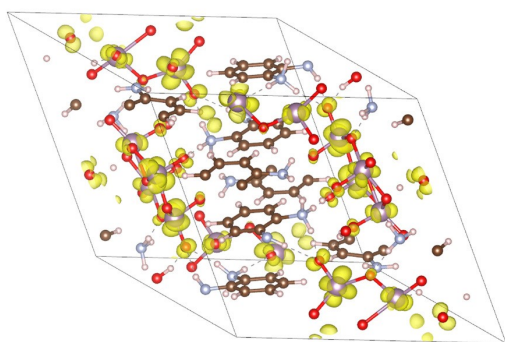


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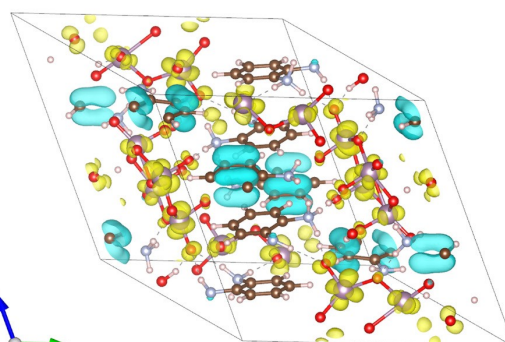
S_0-S_{451}



hole

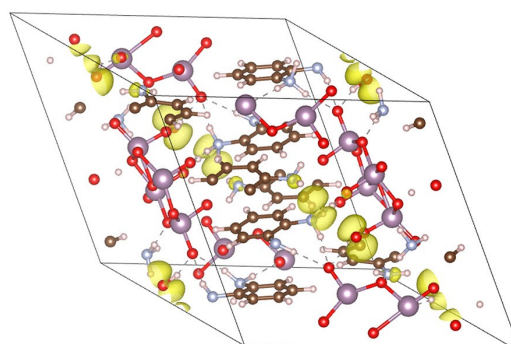
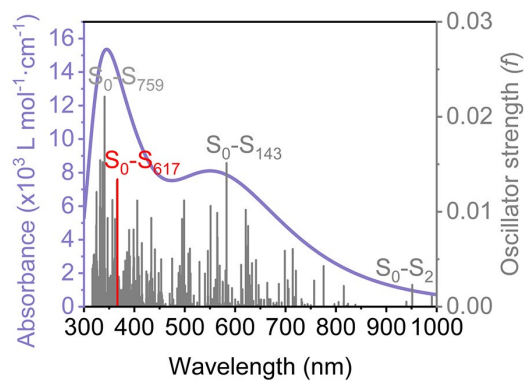


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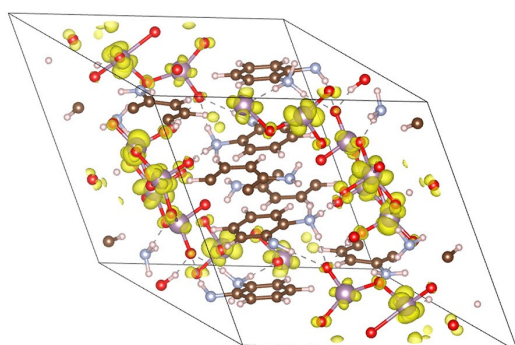


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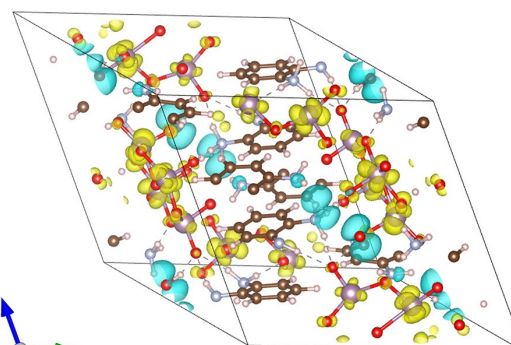
S_0-S_{617}



hole

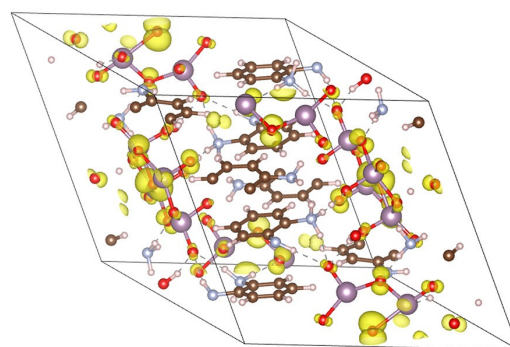
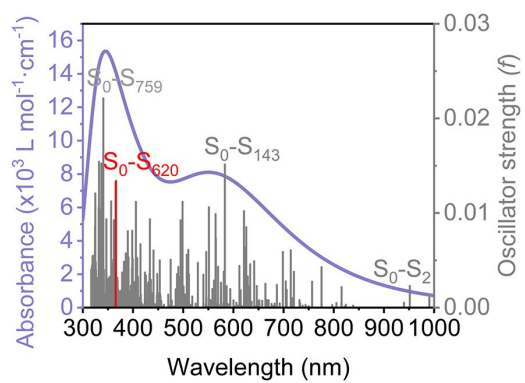


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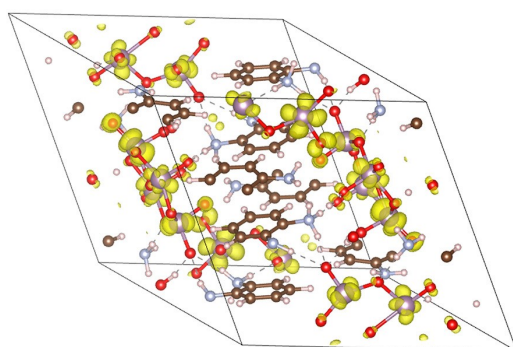


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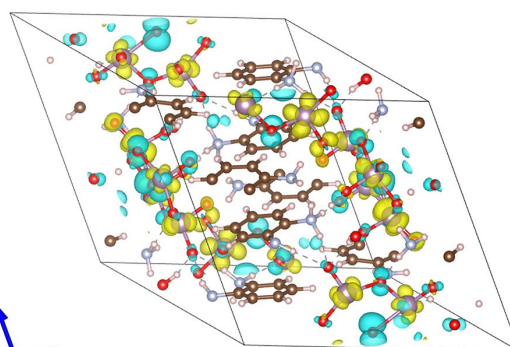
S_0-S_{620}



hole

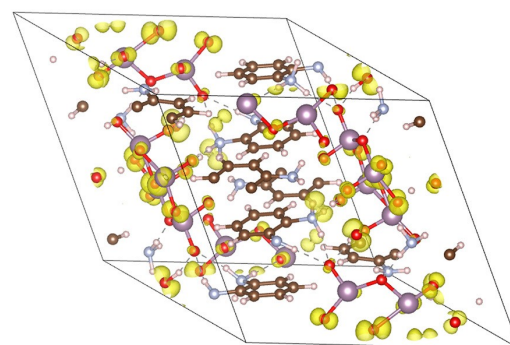
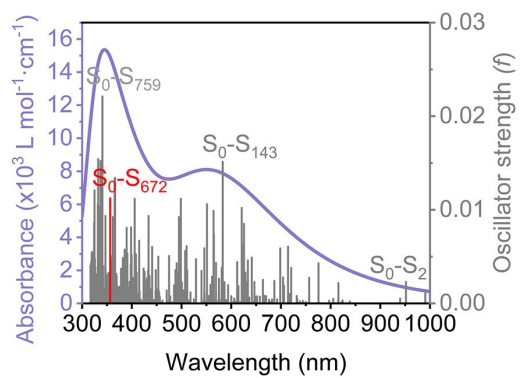


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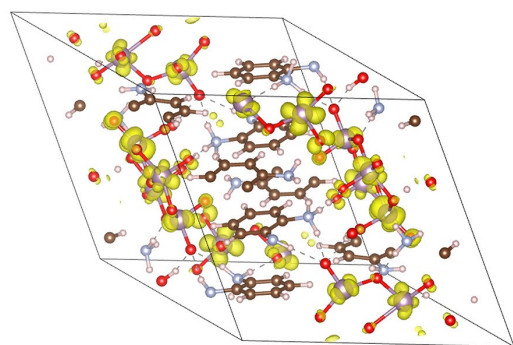


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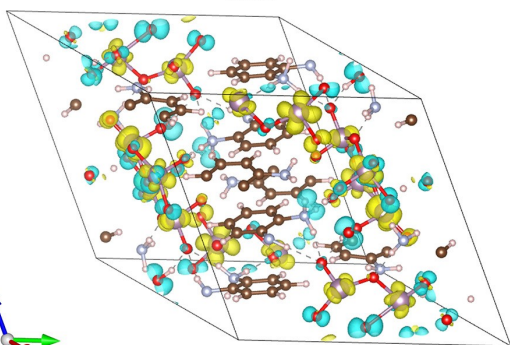
S_0-S_{672}



hole

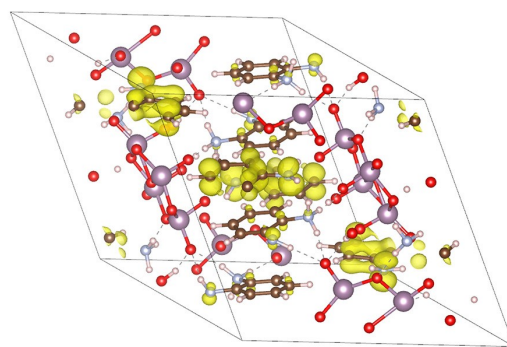
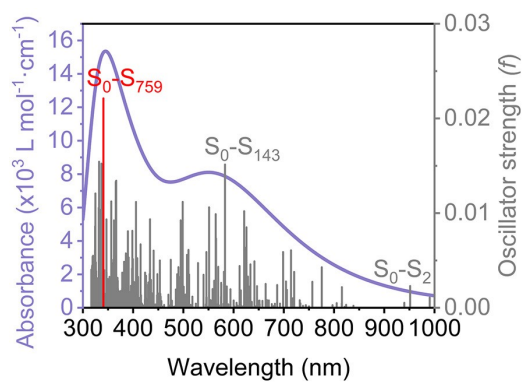


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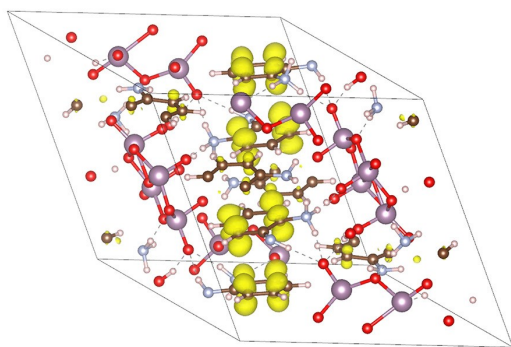


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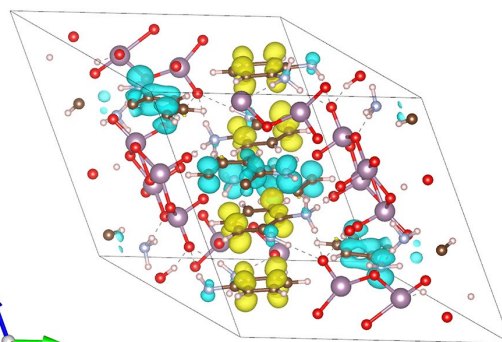
S_0-S_{759}



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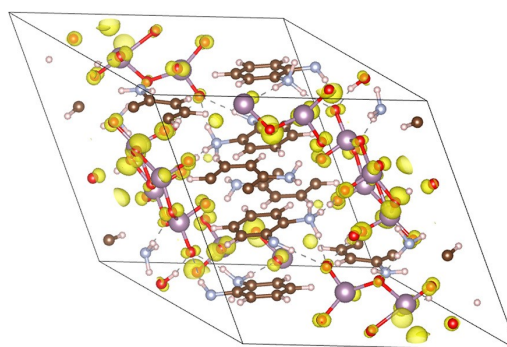
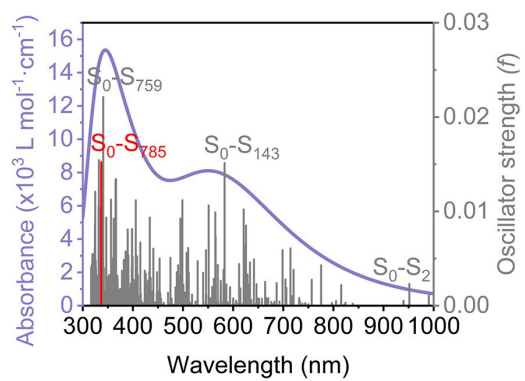


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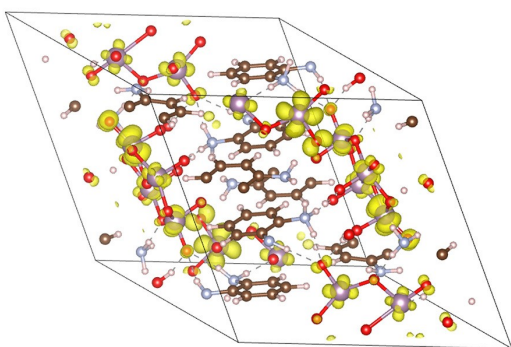


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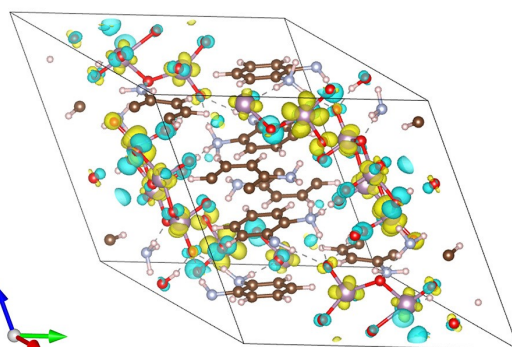
S_0-S_{785}



hole

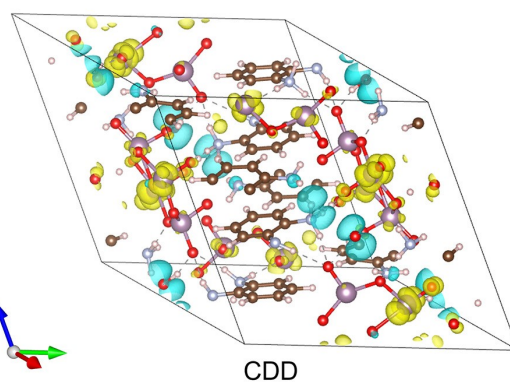
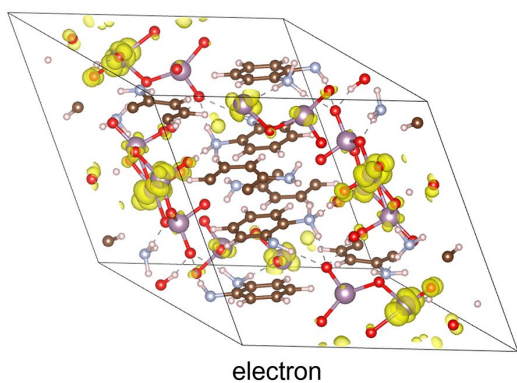
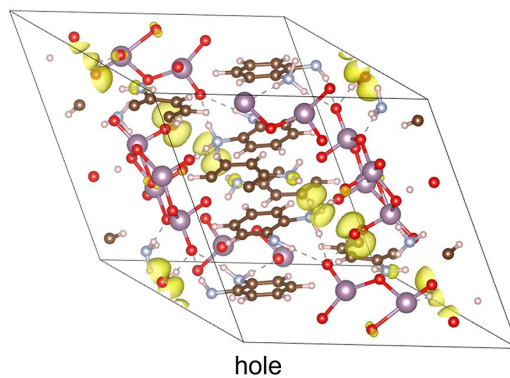
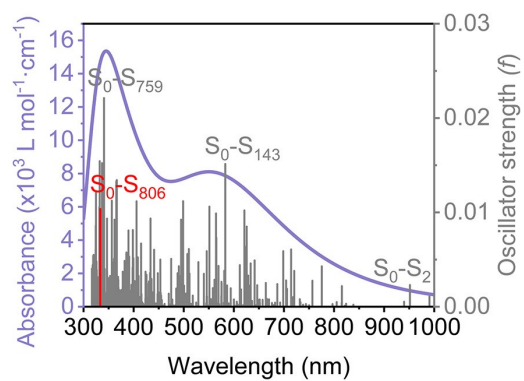


electron

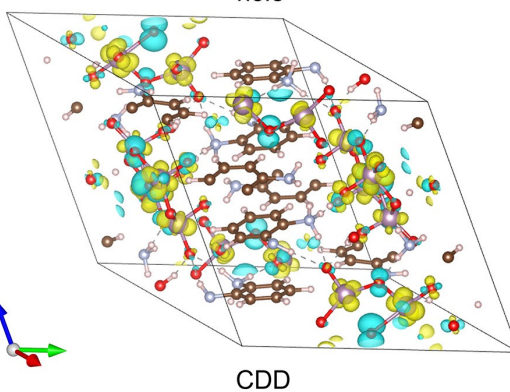
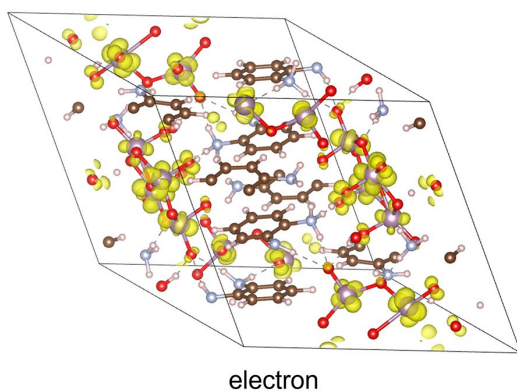
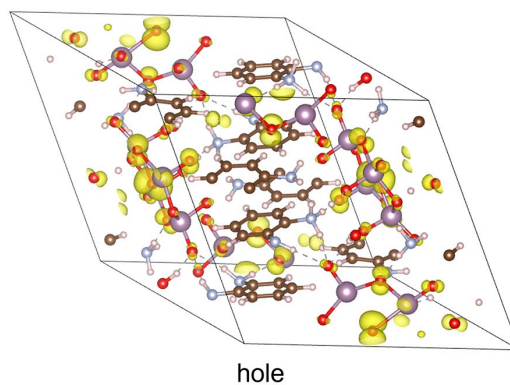
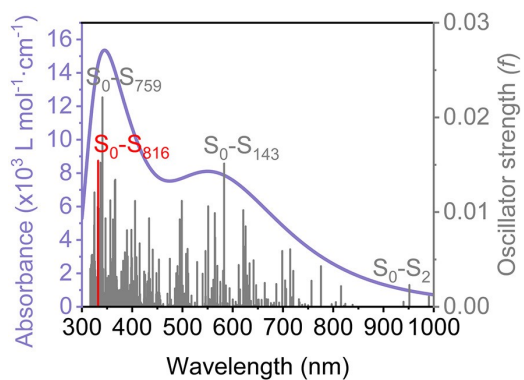


CDD

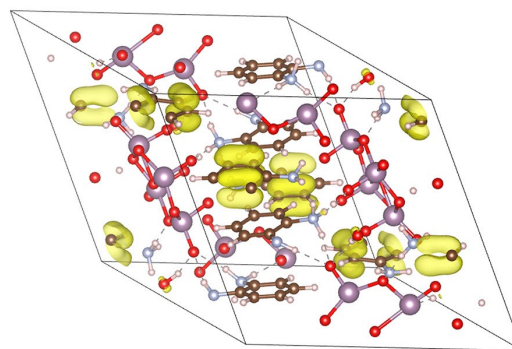
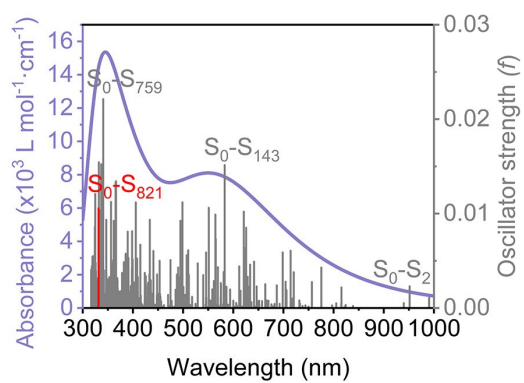
S_0-S_{806}



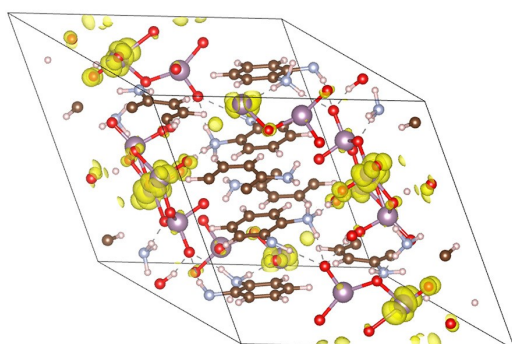
S_0-S_{816}



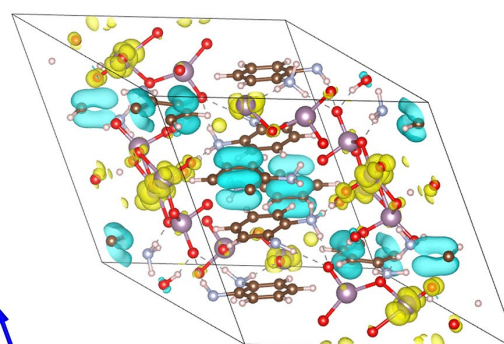
S_0 - S_{821}



hole

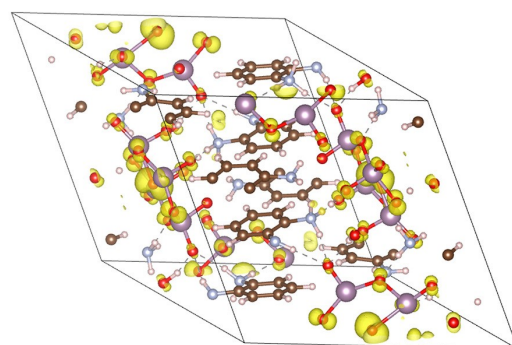
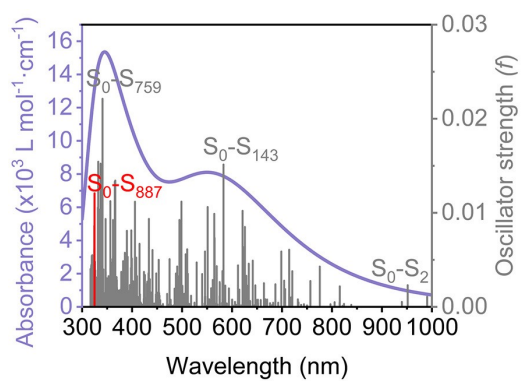


electron

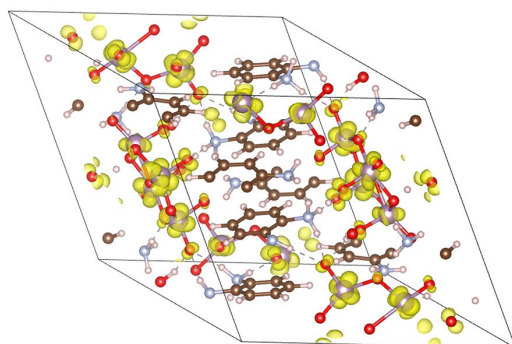


CDD

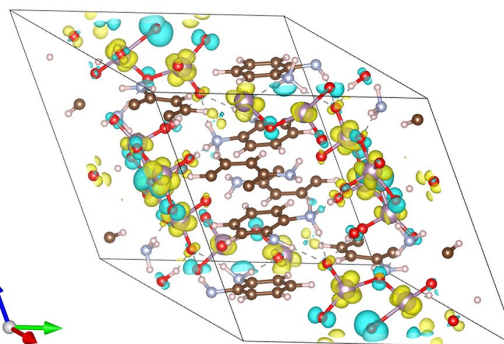
S_0 - S_{887}



hole

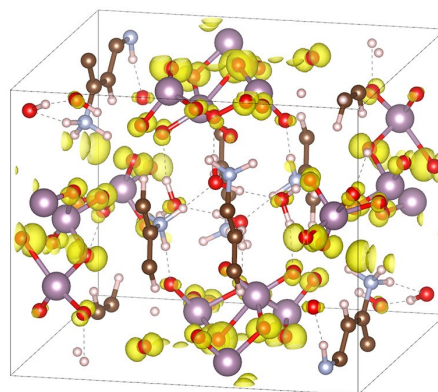
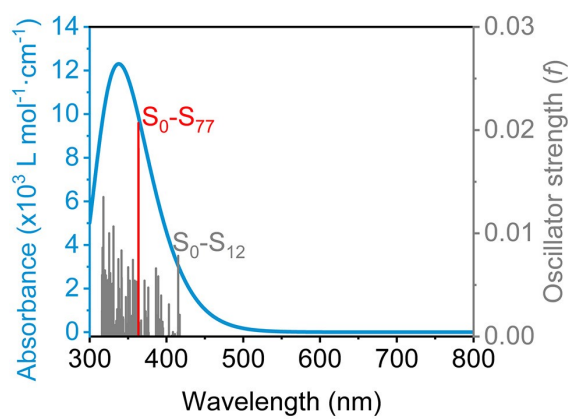


electron

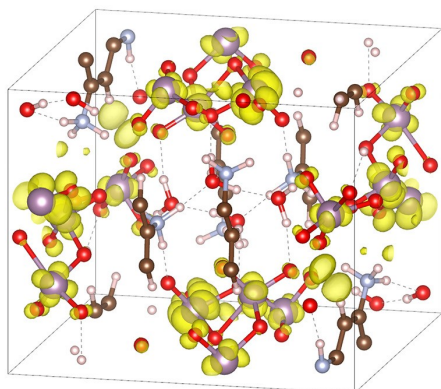


CDD

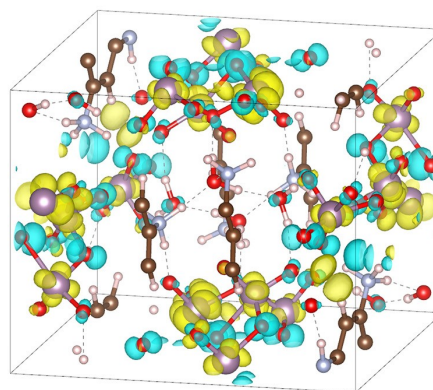
S_0-S_{77}



hole

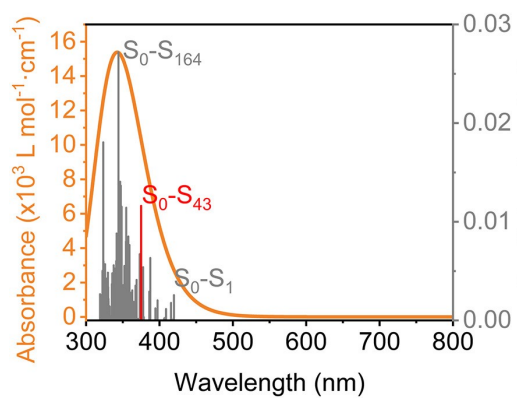


electron

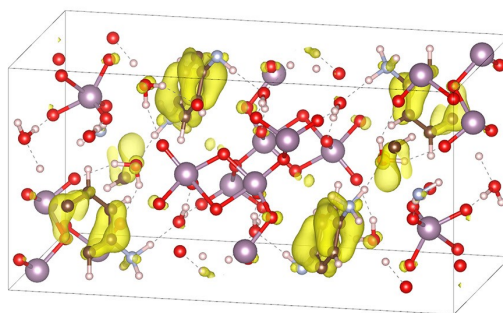


CDD

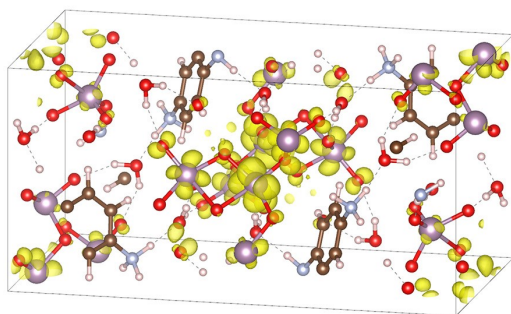
S_0-S_{43}



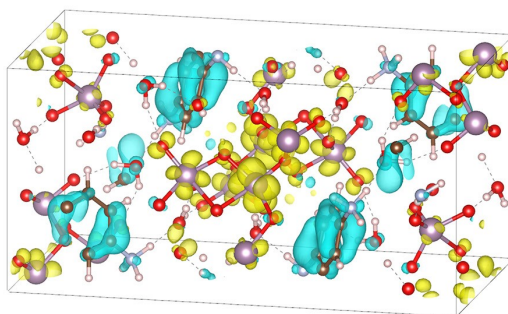
Oscillator strength (f)



hole

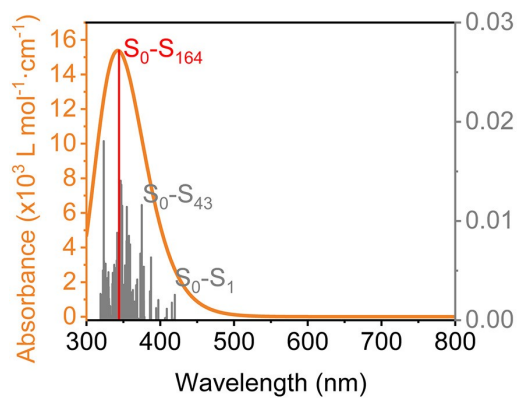


electron

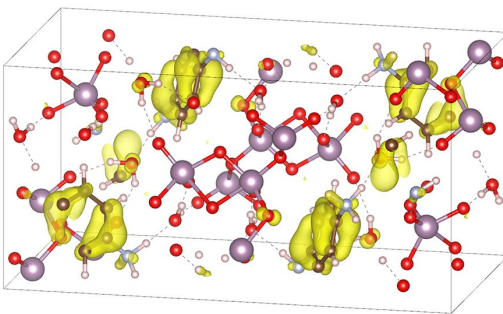


CDD

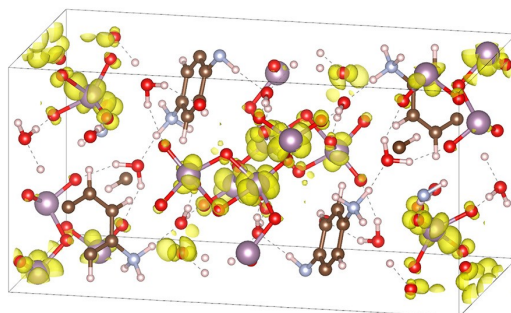
S_0-S_{164}



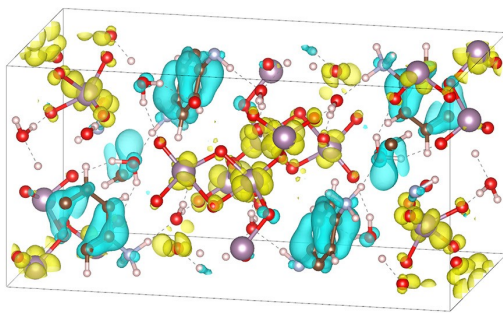
Oscillator strength (f)



hole



electron



CDD