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Ab initio investigation of the electronic structure of Sn(IV) and Sb(V) tris(dmit) complexes

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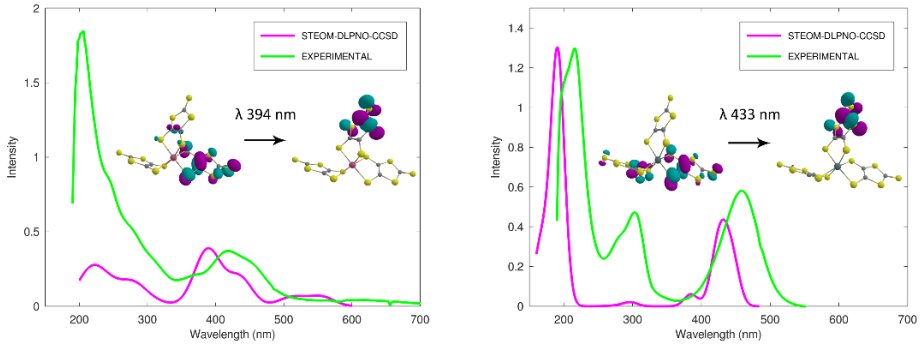
1,3-dithiole-2-thione-4,5-dithiolate (dmit) complexes are versatile substances known for their applications in semiconductors and capacitors [1]. This study investigated the tris(dmit) complexes of Sn(IV) and Sb(V) using advanced computational methods. The study employed high-level methodologies such as Local Energy Decomposition (LED) analysis, similarity transformed equations of motion (STEOM-DLPNO-CCSD), and state-averaged complete active space Self-consistent field/N-electron valence second-order perturbation theory (SA-CASSCF/NEVPT2) with spin-orbit coupling correction, using Def2-TZVP basis set in ORCA 5 software [2-5]. The LED analysis evaluated interactions and stability of the metal-thiolate sulfur bonds in two geometries for both systems. The energy released upon the bond formation between the cation and ligands, compared to isolated fragments, was approximately 834 kcal/mol for Sn(IV) and 1424 kcal/mol for Sb(V) tris(dmit) complexes. The STEOM-DLPNO-CCSD results were taken in the most stable geometry and are in excellent agreement with the experimental UV-Vis spectra in acetonitrile. There were identified 3 main types of electronic transitions: $\pi(pS_{thiolate})\rightarrow\sigma^*(M\text{-}S)$, $\pi(pS_{thione})\rightarrow\pi^*(C{=}S)$, and $\pi(pS_{thiolate})\rightarrow\pi^*(C{=}S)$. The SA-CASSCF/NEVPT2 results report a multireferential nature to the tris(dmit) complexes' excited states with several singlet-triplet coupled states.



$[Sb(dmit)_3]^-$ $[Sn(dmit)_3]^{2-}$

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References

[1] V. H. da Silva *et al.*, J. Mol. Struct. **1223**, 129219 (2021).
[2] A. Altun *et al.*, J. Chem. Theory Comput., **15(3)**, 1616–1632 (2019).
[3] S. Ranga *et al.*, J. Chem. Theory Comput., **17(12)**, 7428–7446 (2021).
[4] C. Angeli *et al.*, J. Chem. Phys., **114**, 10252–10264 (2001).
[5] F. Neese, WIREs Comput Mol Sci. **12**, e1606 (2022).