Investigation of Organic Radicals Electronic Structure: A Multi-Methodological Study

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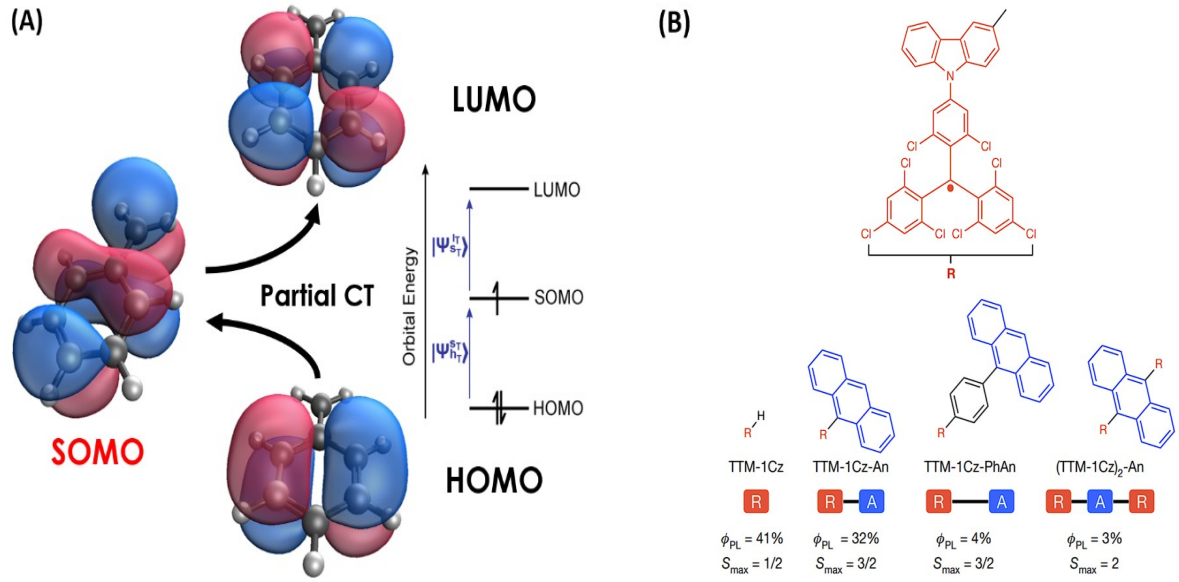
Organic radicals are gaining attention in optoelectronics and quantum information science (QIS), driven by their unique ability to exhibit near-infrared luminescence with a potential 100% internal quantum efficiency (IQE)[1] and access to high spin excited states (S > 1) that satisfy the DiVincenzo criteria for quantum computing.[2] However, modeling the excited states of open-shell systems remains challenging, particularly due to spin contamination issues that arise when single-reference methods, such as TD-DFT, are employed. While several spin-pure methods have been developed in recent years, not all of them adequately capture the nature and energetics of electronic excitations in organic radicals, particularly those involving short-range or partial charge-transfer (CT) character.

To address this, spin-pure multireference approaches like CASSCF could be considered, but dynamic correlation must be incorporated through, for example, second-order perturbation theory corrections (e.g., CASPT2, NEVPT2). While these methods are accurate, they are computationally demanding, and selecting an appropriate active space is non-trivial. More affordable alternatives, such as multiconfigurational pair-density functional theory (MC-pDFT) and its multi-state variants (MC-MS-pDFT)[3], provide a compromise between cost and accuracy, although they are sensitive to the CAS component used in the exchange–correlation functional. Others promising approach are a machine-learning–parametrized semiempirical method (ExROPPP)[4], currently in development, as well as a spin-purified extension of TD-DFT (X-TD-DFT), which has shown encouraging results, at least for doublet systems.[5]

Using the benzyl radical as a benchmark and extending the analysis to TTM-based chromophores, we evaluated a range of available spin-pure methods—ExROPPP, X-TD-DFT, CAS-QD-NEVPT2, and MS-MC-pDFT —highlighting their respective strengths and limitations in capturing excited-state character and energetics.



(A) HOMO→SOMO and SOMO→LUMO short-range partial CT transitions of the benzyl radical. **(B)** TTM-1Cz derivates that show spin addressable excited states with multiplicity greater than one (S >1), with their PLQE (φ_{PL}) in toluene solution.[2]

References:

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