

Exploring the Origins of Magnetoluminescence in Triarylmethyl-Based Diradicals

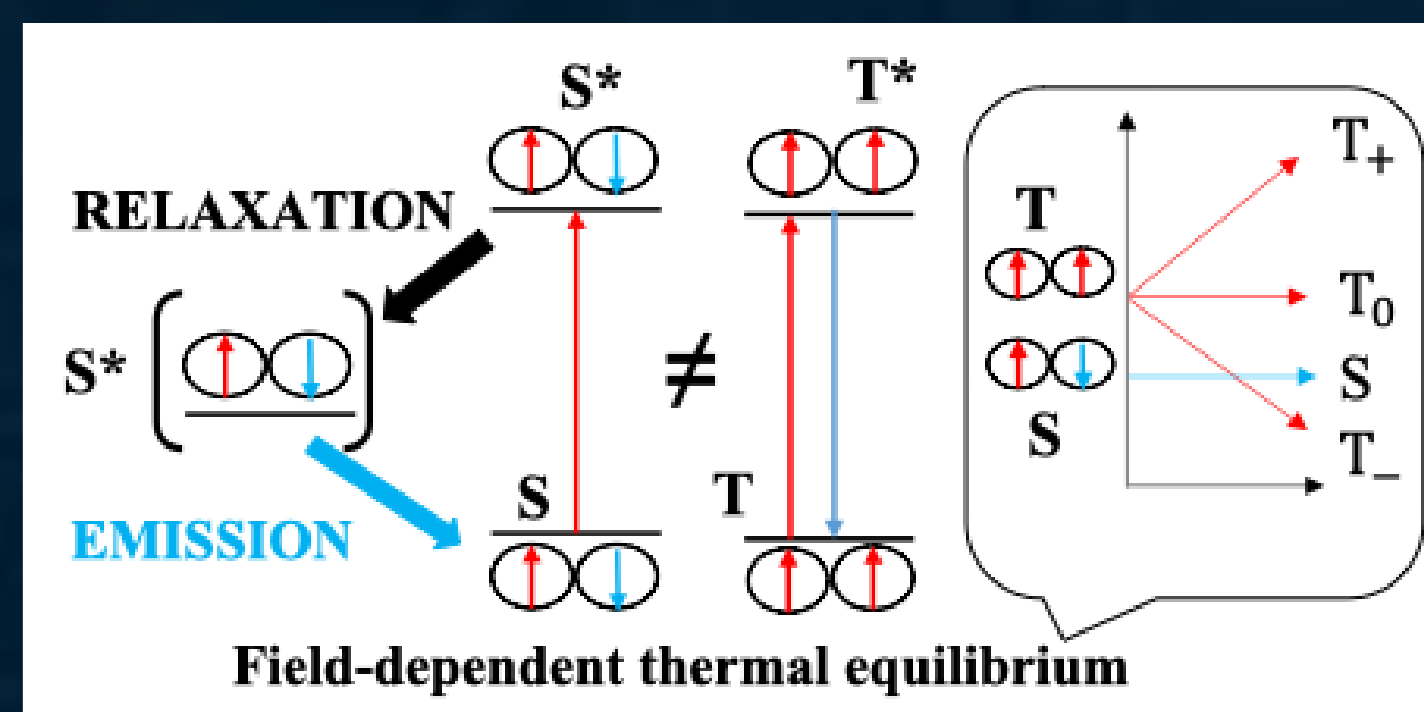
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Introduction

Magnetoluminescence, the modulation of light emission by a magnetic field^[1, 2], can be tuned in open-shell^[3] organic molecules through molecular design. A diradical with 2 luminescent



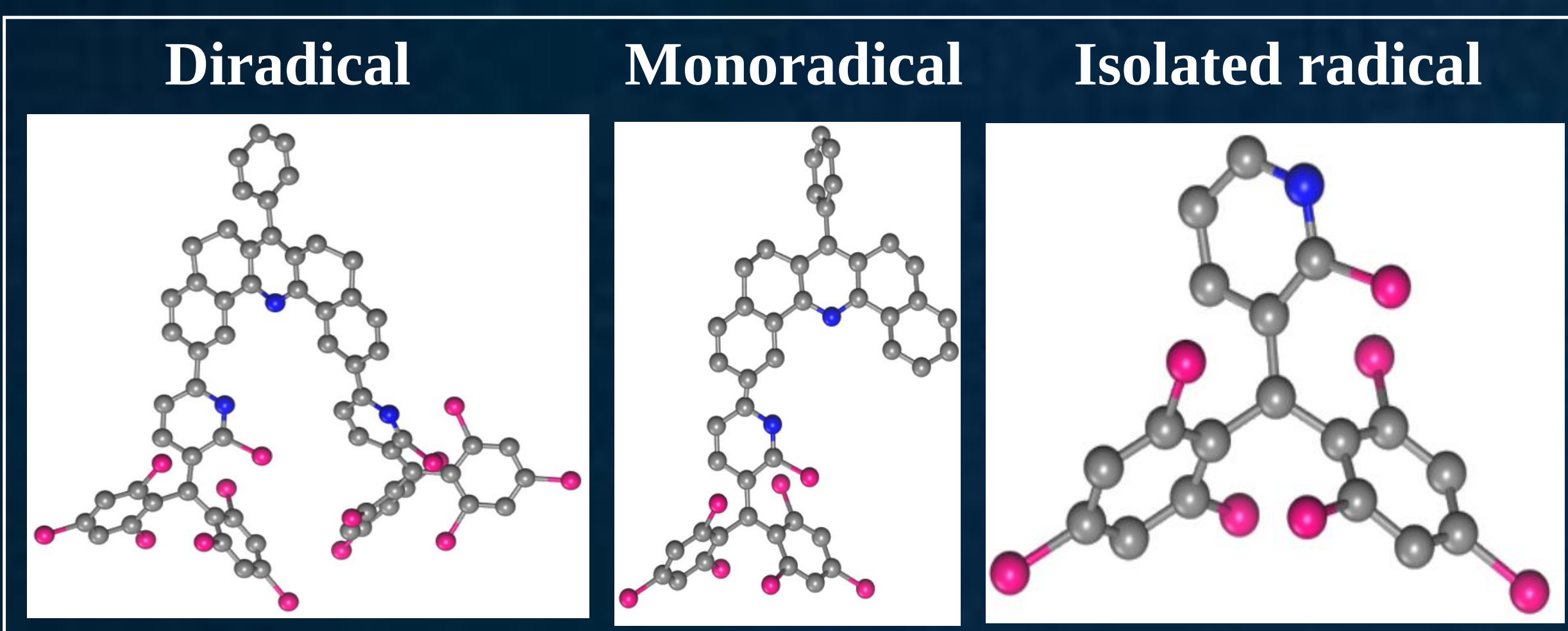
PyBTM (3,5-dichloro-4-pyridyl)bis(2,4,6trichlorophenylmethyl) radicals is the 1st organic system with magnetoluminescence at the molecular level^[4].

Methods

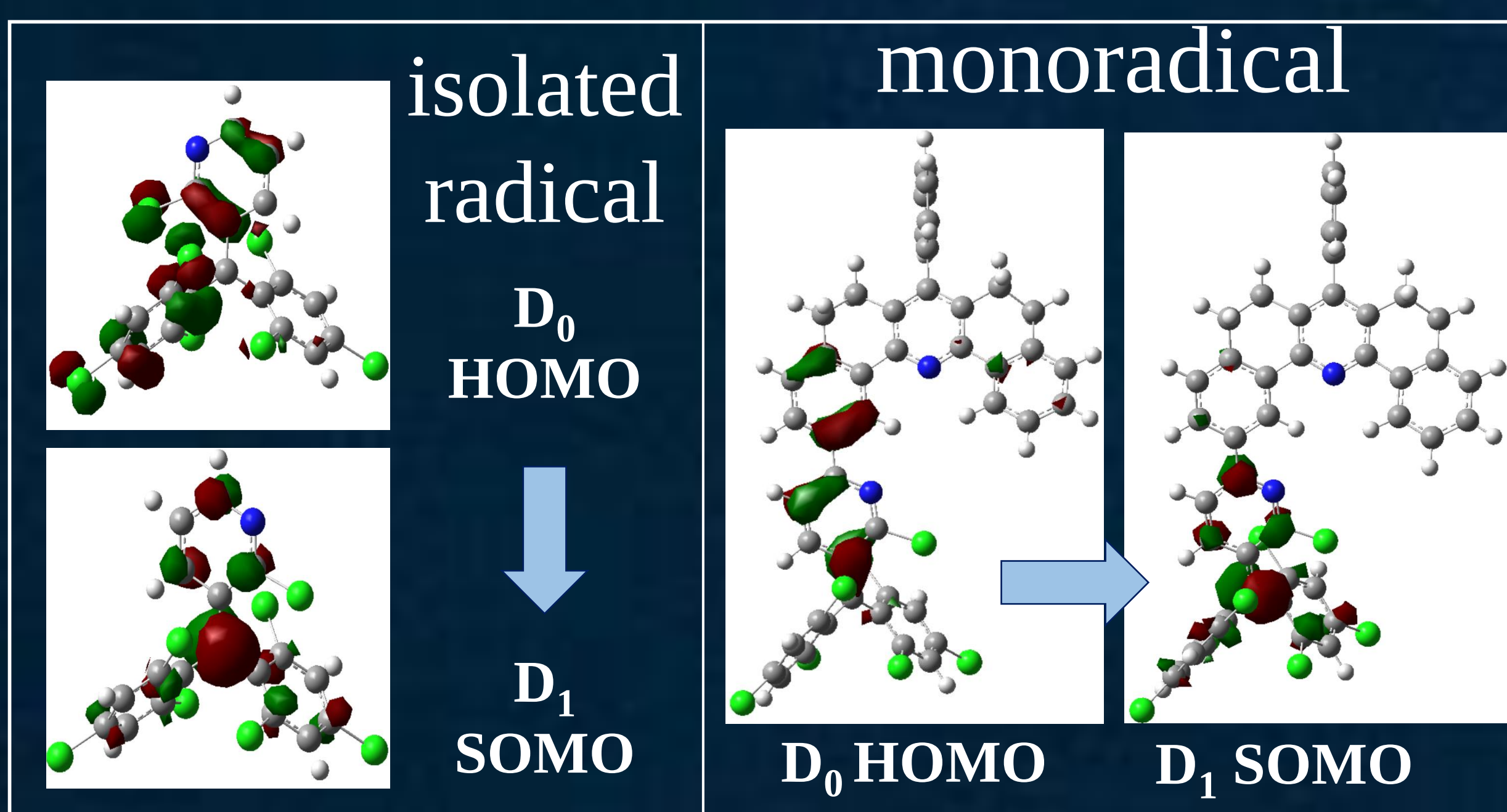
- Ground and excited states are characterized with DFT/TDDFT at ω B97XD/6-31g(d) level using ORCA software including CH_2Cl_2 solvent with CPCM.
- Optimally-tuned ω value for our system is 0.13.
- CASSCF/NEVPT2 in gas phase have validated ω B97XD data

Results and Discussion

In our study, optical properties of the diradical molecule as well as the monoradical and isolated radical are investigated



1. ISOLATED RADICAL : lowest $D_0 \rightarrow D_1$ excitation corresponds to electron transfer from aromatic ligands (HOMO) to central carbon radical (SOMO); reverse transition occurs for $D_1 \rightarrow D_0$ emission predicted at 525 nm

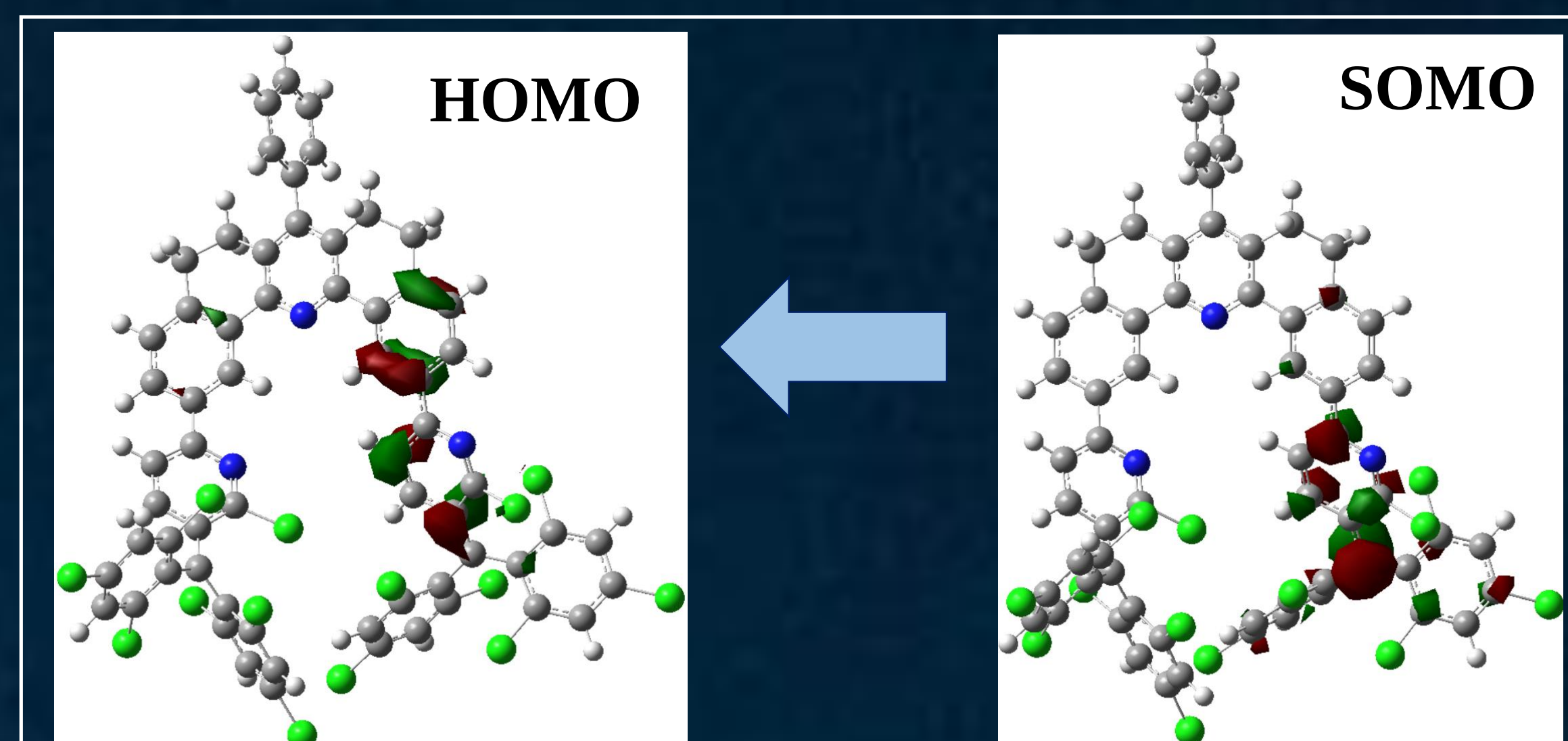


2. MONORADICAL : lowest excitation mainly localized in PyBTM radical but HOMO has non-negligible participation of attached ring of bridge => emission energy is slightly shifted to 554 nm.

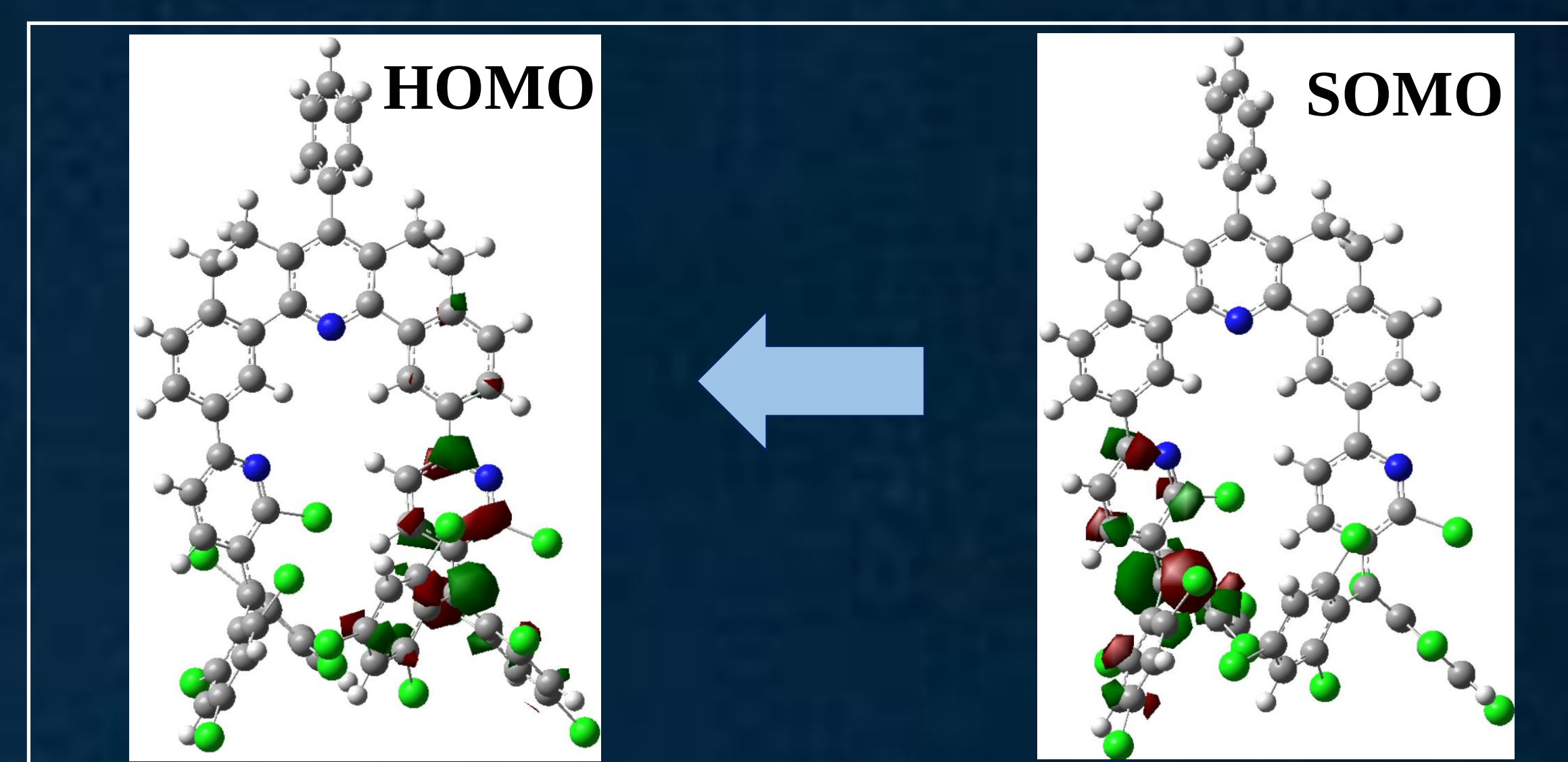
References

- 1) Murto, P. et al. J. Mat. Chem. C, 2022, 10, 7368-7403.
- 2) Mizuno, A. et al. Chem. Rev. 2024.
- 3) Kusamoto, T. et al.. Chem. Lett., 2021, 50, 1445-1459.
- 4) Matsuoka, R. et al. J. Am. Chem. Soc., 2023, 45, 13615-13622.

3. DIRADICAL TRIPLET / SINGLET: The same SOMO and HOMO localized in one PyBTM, so charge transfer is LOCAL => emission energy is slightly shifted to 558/557 nm very close to the monoradical in agreement with experiments

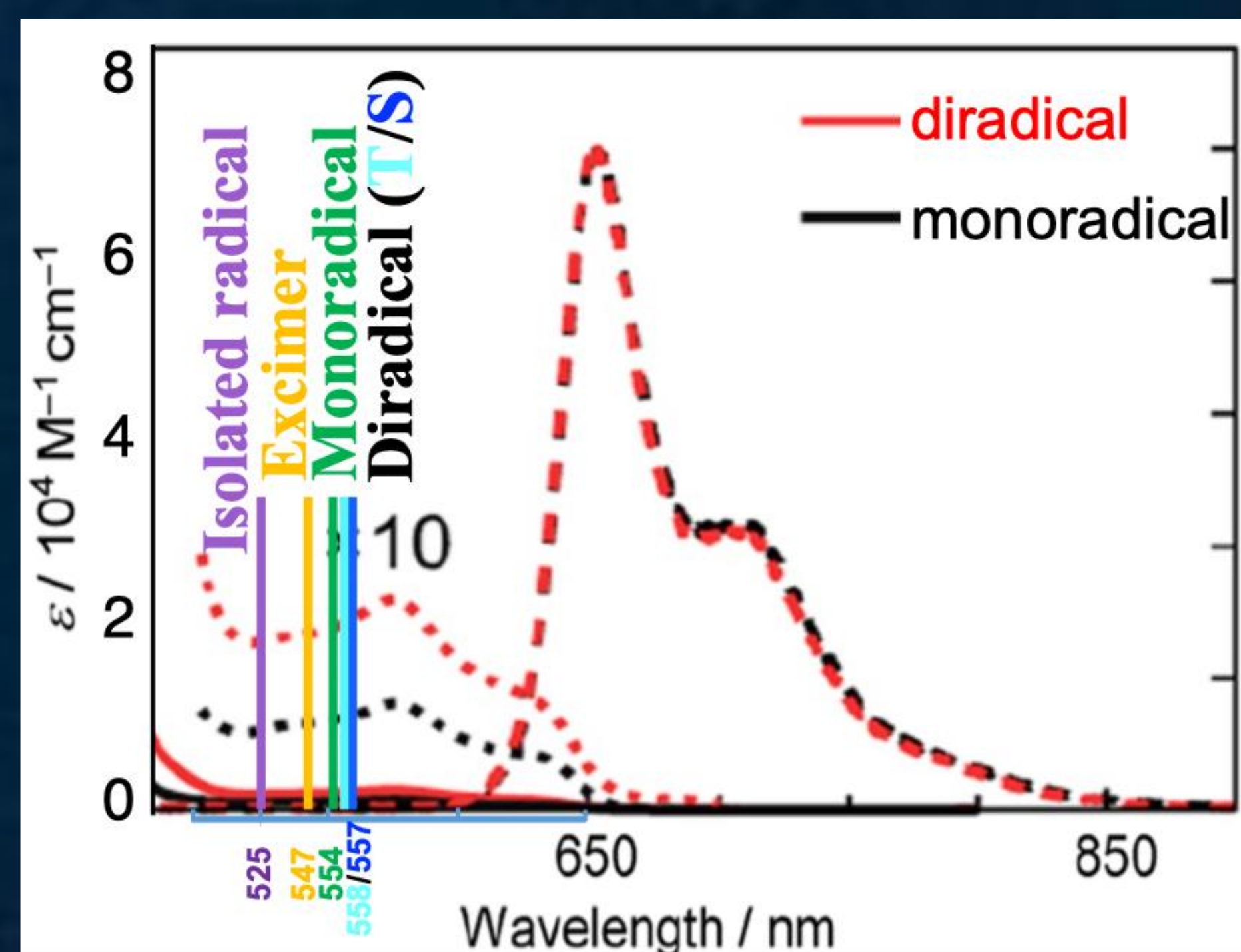


4. EXCIMER: lowest excited state localized in PyBTM radical corresponds to the charge transfer to the other PyBTM => emission energy is slightly shifted to 547 nm



Conclusion

- 1) Our results show that the bridge has a non-negligible effect on the monoradical and diradical triplet/singlet emission with respect to the isolated PyBTM radical.
- 2) The broad emission peak in the experimental spectra of the diradical attributed to the excimer has been now characterized as a charge transfer state from one PyBTM to the other.



Acknowledgements



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