# Theoretical study on effects of ring sizes of electron-donating groups upon photophysical properties of single benzene fluorophores

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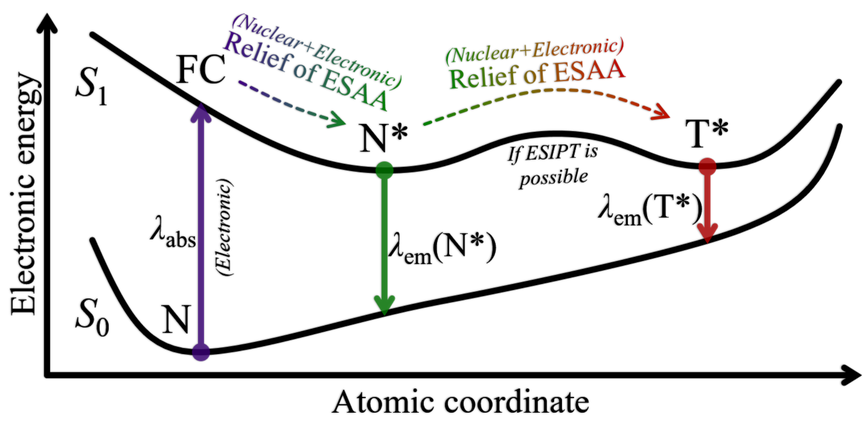
## Abstract

The conventional approach to developing fluorescent materials or molecules capable of absorbing and releasing energy in the form of light in the **visible region** has largely relied on extending the size of **π-conjugated** systems. However, modern perspectives have demonstrated that even compact molecular structures as small as **a single benzene ring** can exhibit fluorescence in the visible region with large **Stokes shifts**, provided that their electronic and geometric structures are appropriately engineered. Particularly, precise control over **electron distribution** in both the ground and excited states plays a crucial role in narrowing the **energy gaps** between these states, thereby enabling tunable fluorescence emission across the visible region. To gain fundamental understanding of the electronic properties underpinning the absorption and emission of single-benzene fluorophores, this study presents a theoretical investigation into the effect of the ring size of electron-donating substituents in derivatives of **2,5-diamino-1,4-benzenedicarbaldehyde** on **their photophysical properties**. Computational chemistry techniques are employed to calculate the energy gap between the ground and excited states and obtain the frontier molecular orbital energy levels and the changes in electronic distributions upon photoexcitation and emission. Ultimately, the authors anticipate that the insights obtained from this study will contribute to the rational design and development of **single-benzene fluorophores** for future applications in **bioimaging** and **fluorescent sensing**.

## Introduction

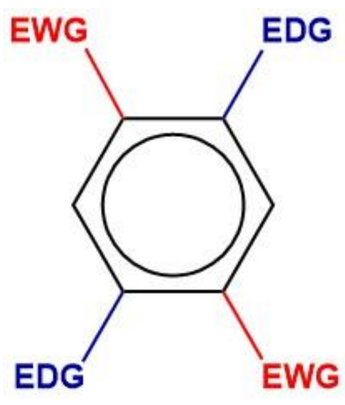
Single benzene fluorophores (SBFs) are compact molecules designed using a push–pull arrangement of electron-donating groups (EDGs) and electron-withdrawing groups (EWGs), rather than relying on conventional π-extension. Despite the absence of extended π-conjugation, SBFs exhibit tunable emission across the visible region with large Stokes shifts, making them promising for applications in bioimaging and optoelectronic devices [1].

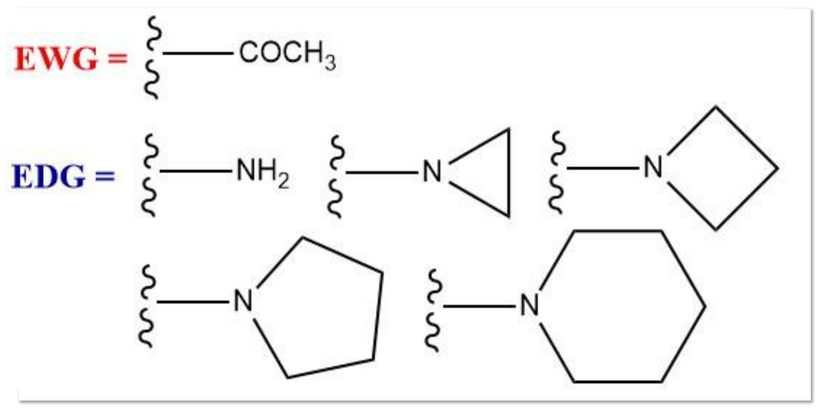
The large Stokes shifts of SBFs arise from the combination of a moderate degree of intramolecular charge transfer (ICT) upon photoexcitation to the Franck–Condon (FC) point and the relief of excited-state antiaromaticity (ESAA) during structural relaxation from FC to N* [2]. Furthermore, if a given molecule has excited-state intramolecular proton transfer (ESIPT), upon structural relaxation from FC to N*, the ESIPT on-top of ESAA could facilitate additional relief of ESAA from N* to T* [3].




## Computational Details

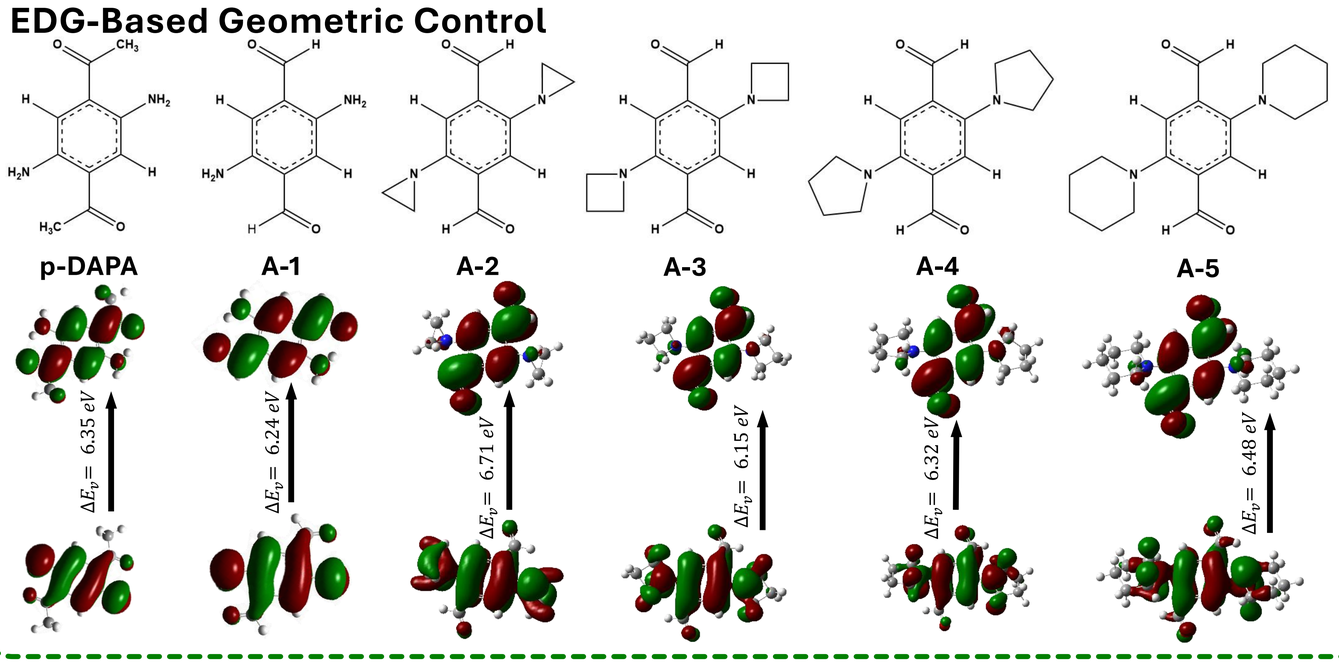
All electronic structure calculations were performed using Gaussian 16 (B.01) with the IEFPCM (DCM) implicit solvation model. Ground- and excited-state properties were investigated using LC-BLYP/Def2-TZVP and TD-LC-BLYP (μ = 0.25 $bohr^{-1}$)/Def2-TZVP. Vertical absorption energies were obtained from single-point TD-DFT calculations on optimized $S_0$ geometries under non-equilibrium solvation conditions, while $S_1$ geometries, ESIPT transition states, and vibrational frequency analyses were optimized under equilibrium solvation. In this work, the results obtained from the molecular structure construction and calculations are presented as the **$S_1$ minimum structure**.

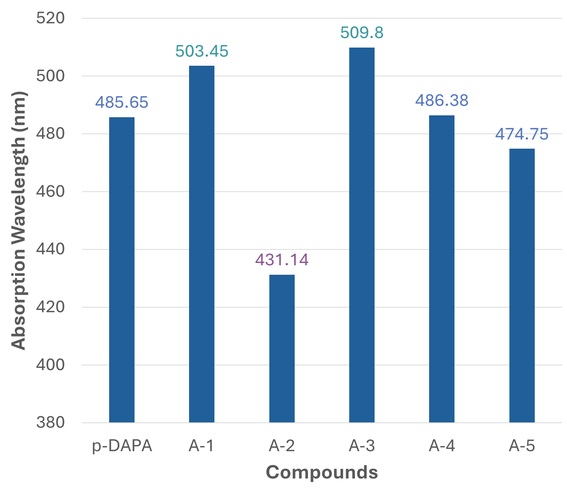


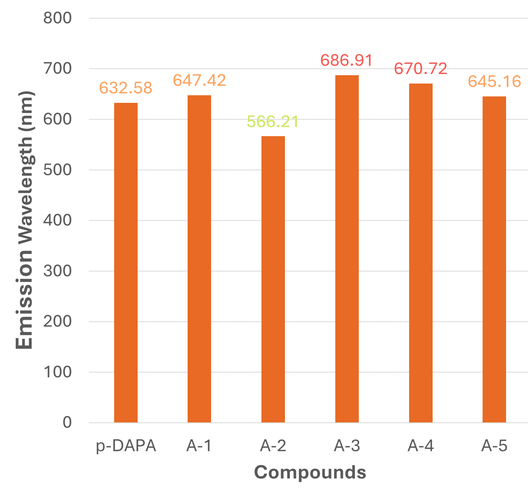




## Results and Discussion

### EDG-Based Geometric Control




## Conclusion

Structural modulation of X-shaped SBFs by varying the ring size of electron-donating groups (EDGs) and introducing steric constraints enhances intramolecular charge transfer (ICT) and narrows the HOMO–LUMO energy gap, thereby facilitating charge transfer from the EDG to the electron-withdrawing group (EWG). During excited-state relaxation, the molecule releases energy as fluorescence at longer wavelengths, producing a large Stokes shift (~4800–5500 $cm^{-1}$) and enabling the development of red-to-near-infrared (NIR) emitting fluorophores without relying on hydrogen-bonding interactions.

## References

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[3] Wu, C.-H. et al. *Proc. Natl. Acad. Sci. U. S. A.* 2019, *116* (41), 20303.
[4] Lu, T. *J. Chem. Phys.* 2024, *161* (8).
[5] Stanger, A. *Chem. Phys. Chem.* 2023, *24* (10), e202300080.