Photophysical Properties and Relief of Excited-State Antiaromaticity upon Proton Transfer of 2-(2'-Hydroxyphenyl)benzothiazole and its Derivatives

Thanapat Charoenkitkaset[1], Nawee Kungwan[1]

[1]*Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

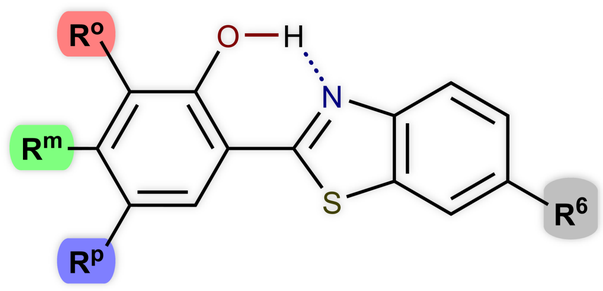
E-mail: naweekung@gmail.com

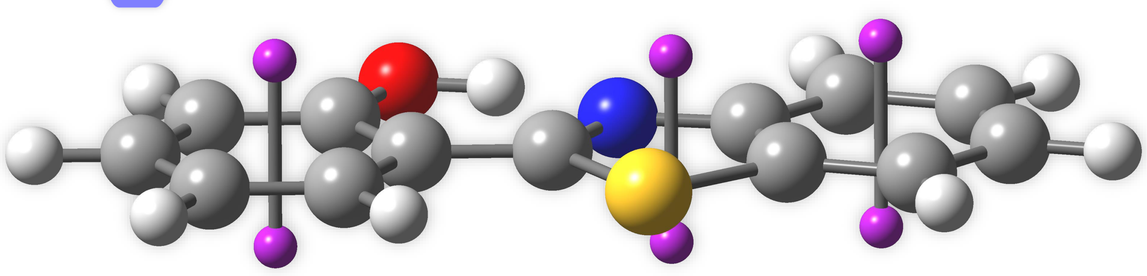
Abstract

Fluorophores undergoing **excited-state intramolecular proton transfer (ESIPT)** are known to exhibit notably redshifted emission wavelength with respect to their absorption wavelength. Consequently, they suffer less from self-absorption and are of interest in applications requiring photon down-conversion, such as fluorescent probes, sensors, and organic light-emitting diodes. In addition, ESIPT is driven by excited-state aromatization, which manifests as **relief of excited-state antiaromaticity** for Hückel-aromatic fluorophores. In this work, effects on photophysical properties, ESIPT exothermicity, and excited-state antiaromaticity arising from strategic mono-substitutions upon 2-(2'-hydroxyphenyl)benzothiazole (HBT) were theoretically investigated. In addition, correlation between **exothermicity and barrier height,** and between **exothermicity and relief of excited-state antiaromaticity** were observed and highlighted. The author hopes this study will provide insights towards data generation and screening for machine-learning-based approaches on theoretical studies of ESIPT-based fluorophores.

Introduction

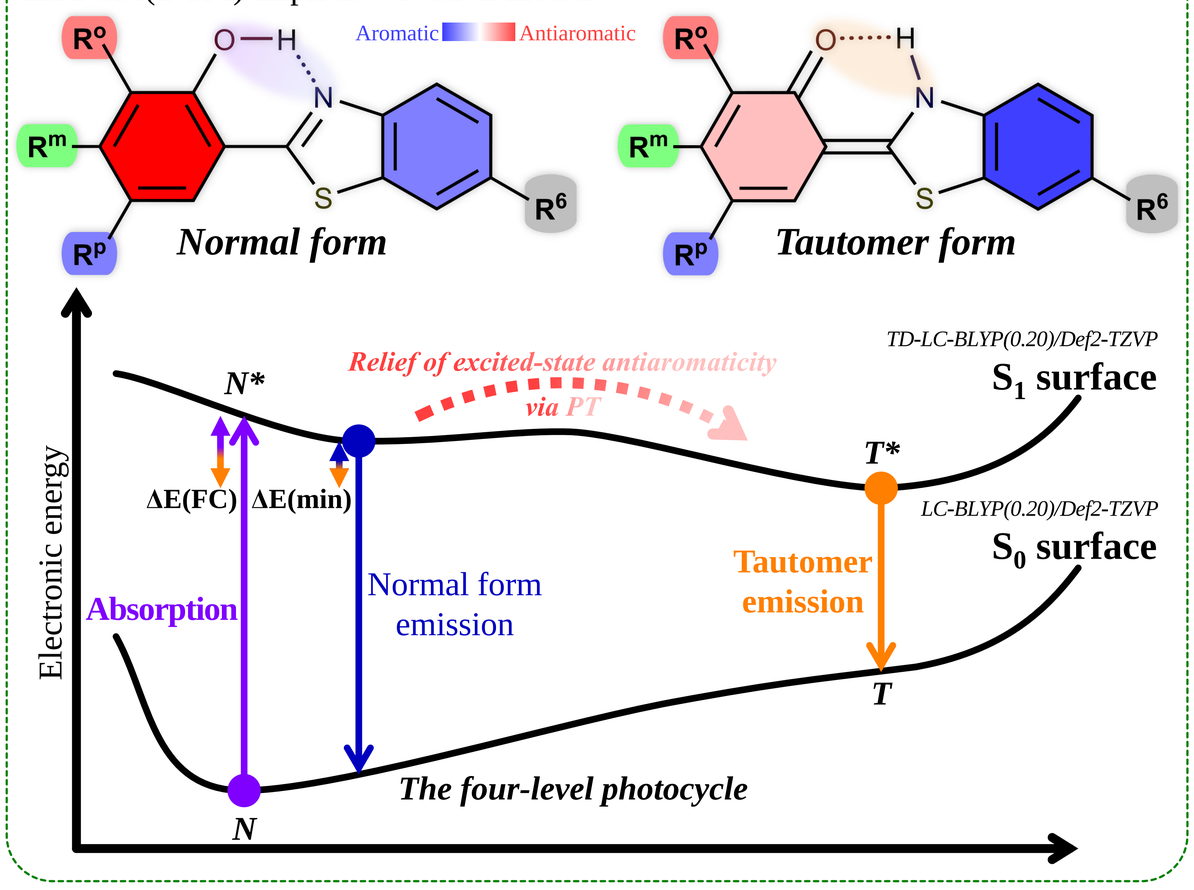
ESIPT occurs in bifunctional molecules having an intramolecular hydrogen bond connecting a proton donor and a proton acceptor moiety. A prominent feature of ESIPT fluorophores is the down-conversion of the absorbed photon [1] through **the four-level photocycle**. Consequently, ESIPT fluorophores show promising applications in natural sciences [2]. Moreover, ESIPT is driven by relief of excited-state antiaromaticity [3,4], which occurs when the proton jumps from the donor to the acceptor. Antiaromaticity is quantified via the axial component of the nucleus-independent chemical shift tensors probed at 1Å above and below each molecular ring [5], denoted **$NICS_{zz}$(1Å)**.





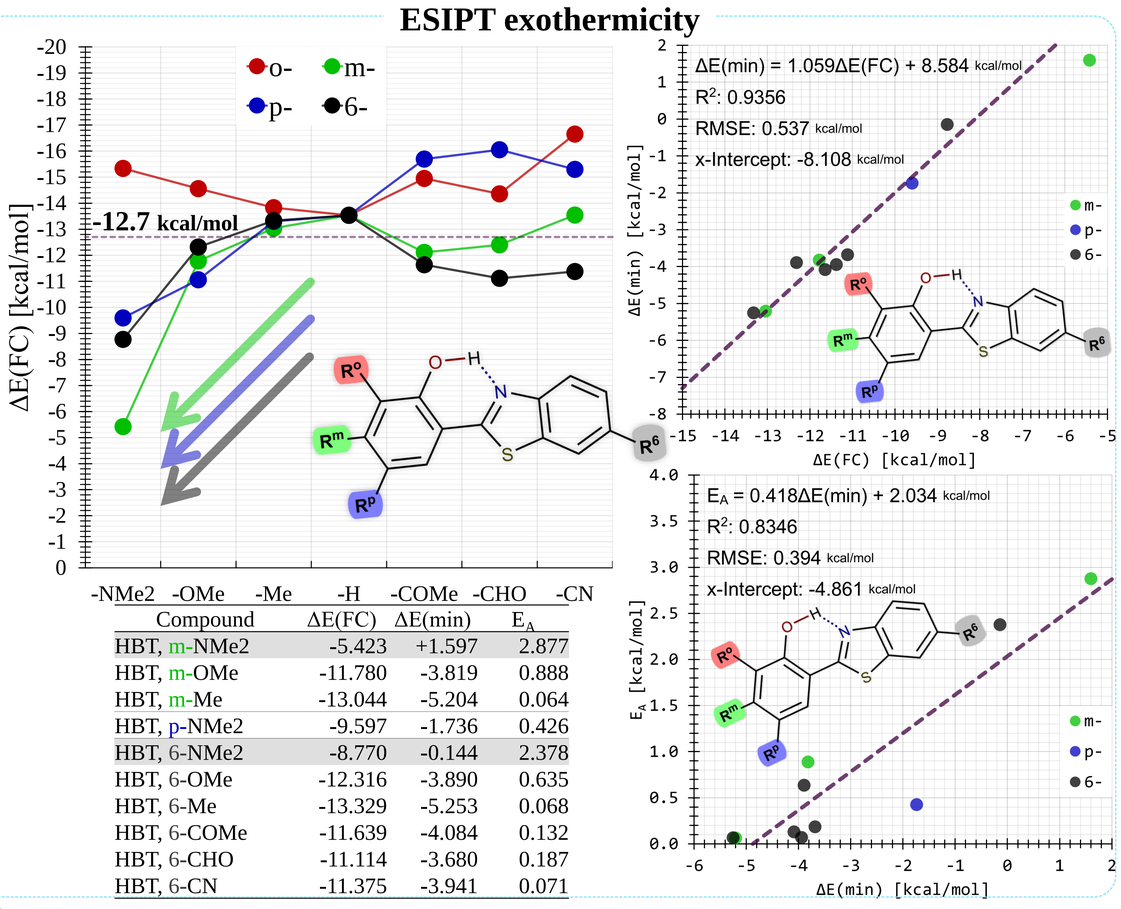
Computational details

All calculations were performed using Gaussian 16 B.01 software package with IEFPCM(DCM) implicit solvation model.



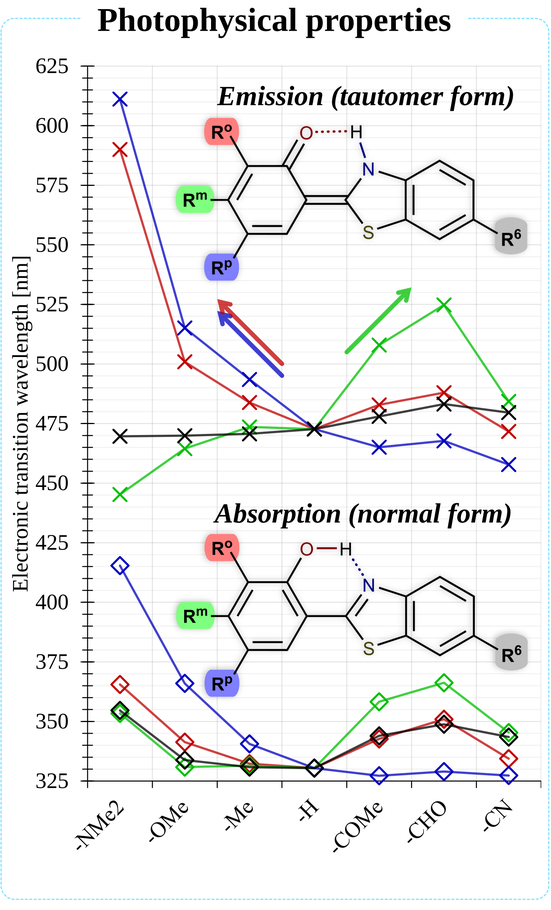
Results and discussion

ESIPT exothermicity

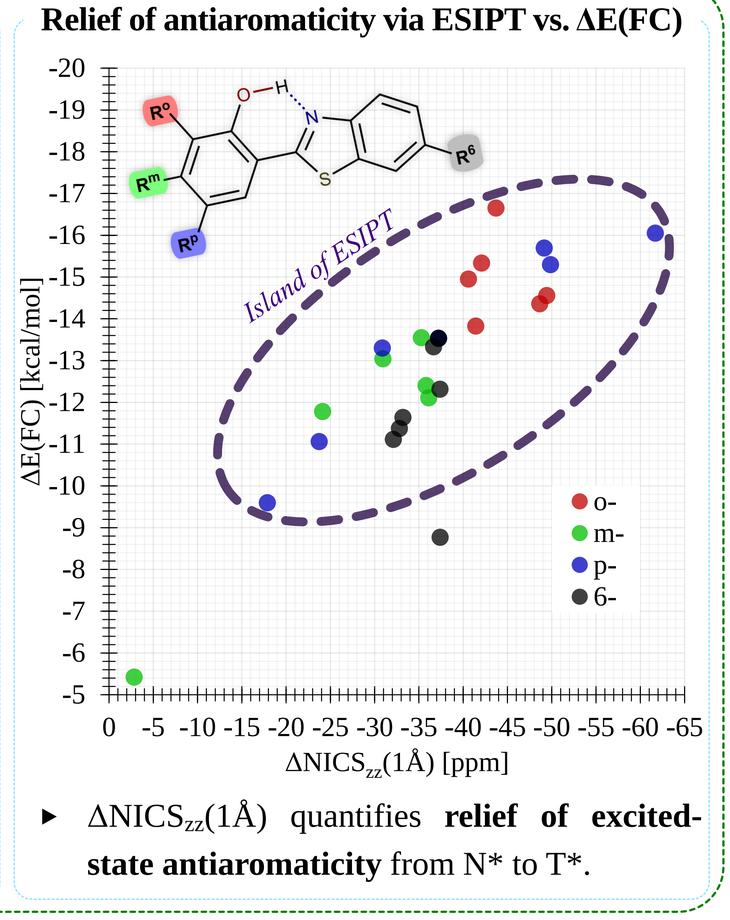


Compound	ΔE(FC)	ΔE(min)	E_A
HBT, m-NMe2	-5.423	+1.597	2.877
HBT, m-OMe	-11.780	-3.819	0.888
HBT, m-Me	-13.044	-5.204	0.064
HBT, p-NMe2	-9.597	-1.736	0.426
HBT, 6-NMe2	-8.770	-0.144	2.378
HBT, 6-OMe	-12.316	-3.890	0.635
HBT, 6-Me	-13.329	-5.253	0.068
HBT, 6-COMe	-11.639	-4.084	0.132
HBT, 6-CHO	-11.114	-3.680	0.187
HBT, 6-CN	-11.375	-3.941	0.071

Photophysical properties



Relief of antiaromaticity via ESIPT vs. ΔE(FC)



- $\Delta NICS_{zz}$(1Å) quantifies **relief of excited-state antiaromaticity** from N* to T*.

Conclusion

- Mono-substitutions with EDGs at the m-, p-, and 6- position **reduce ESIPT exothermicity**.
- ΔE(FC) is **linearly correlated** to ΔE(min) and E_A.
- ESIPT barriers **emerge** at roughly ΔE(FC) = -12.7 kcal/mol.
- Mono-substitutions with EDGs at the o- and p- position, and EWGs at the m- position result in **tautomer emission redshift**.
- Exothermicity upon ESIPT **correlates with** relief of excited-state antiaromaticity.

References

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