Influence of different heteroatom, pi-expansion, and additional proton transfer site for ESIPT of the 2-(2-hydroxyphenyl)benzazoles and their derivatives relieving anti-aromaticity

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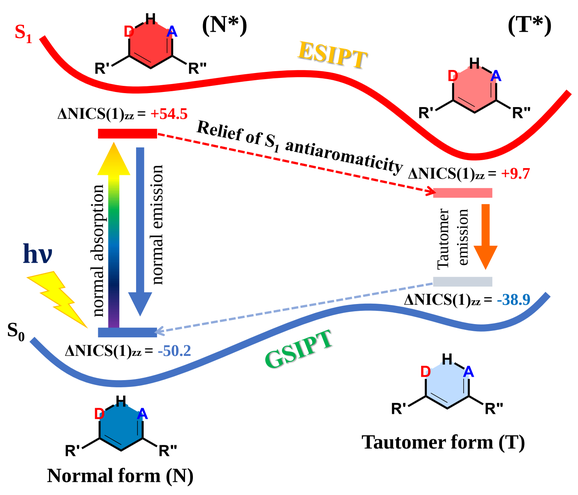
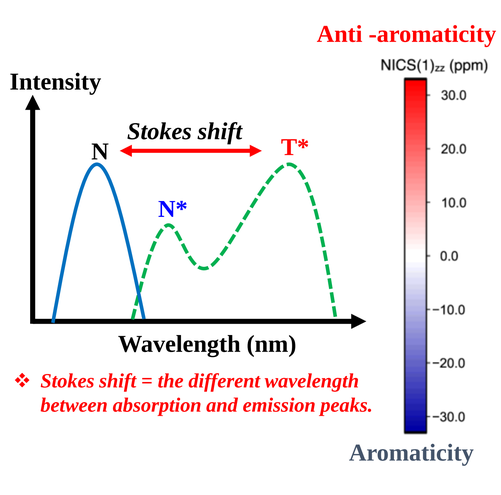
ABSTRACT

An excited-state intramolecular proton transfer (ESIPT) process is one of the most important reactions in photochemistry and photobiology. The main driving force responsible for ESIPT process has been proposed including an increase in the acidity of the proton donor and basicity of the proton transfer, a difference in the character of the wavefunction or a change in aromatic character and recently as the relief of antiaromaticity in the photoexcited state. The aim of this work is to understand the correlation of different heteroatom, pi-expansion, and addition PT sites on the ESIPT relieving antiaromaticity of the 2-(2-hydroxyphenyl)-benzazoles (HBX) and its derivatives. The correlation of such relieving antiaromaticity in term of computed nucleus-independent values in the singlet excited state with photophysical properties such Stokes shift, normal absorption and tautomer emission peaks in a longer wavelength were investigated using time-dependent density functional theory. The red-shifts of normal absorption peaks are found for all HBX derivatives regardless of chemical structures, whereas the blue-shifts or red-shifts of tautomer emission peaks are dependent on the orientation of π-expansion and the additional PT unit compared to HBX. Among designed HBX derivatives, a HBX having two PT units connected with π-expansion along the nodal plane is the best candidate for fluorescent probes because of its tautomer emission at 942 nm with the largest Stokes shift. Moreover, computed NICS values confirm that the emission of the tautomers arising from ESIPT can be related to their inherent (anti)aromatic characters depending on the antiaromaticity of the photoinduced tautomers. Based on this theoretical investigation, the tautomer emission of HBX derivatives in NIR region can be achieved by the combination of π-expansion along the nodal plane and additional PT unit.

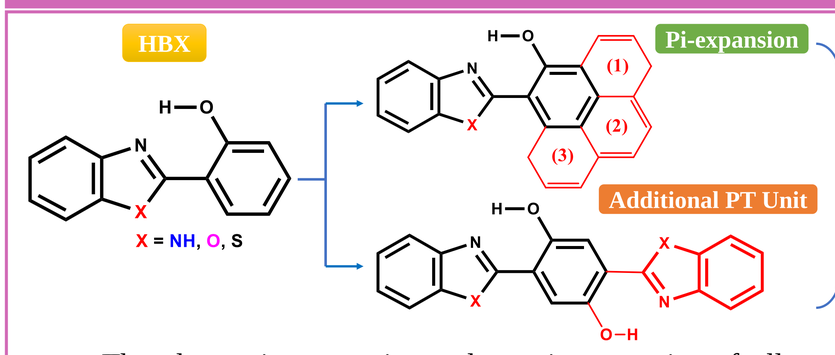
INTRODUCTION

The excited state intramolecular proton transfer (ESIPT) is an important photochemical process in biological and chemical systems [1]. The ESIPT requires a strong intramolecular hydrogen bond between proton donor (D) and proton acceptor (A) groups leading to the ultrafast PT via a four-level photocycle as shown in diagram.





COMPUTATIONAL DETAILS



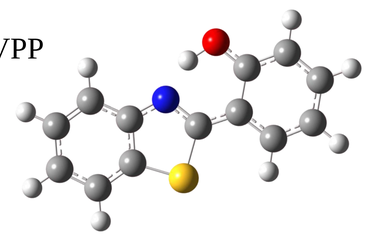
The electronic properties and reaction energies of all molecules were investigated using density functional theory (DFT) and time-dependent DFT methods [2] in DCM non-polar solvent.

- ✓Ground state (S_0) calculation : LC-B3LYP(μ=0.20)/Def2-TZVPP
- ✓Excited state (S_1) calculation : TD-LC-B3LYP(μ=0.20)/Def2-TZVPP

❖**Analysis**

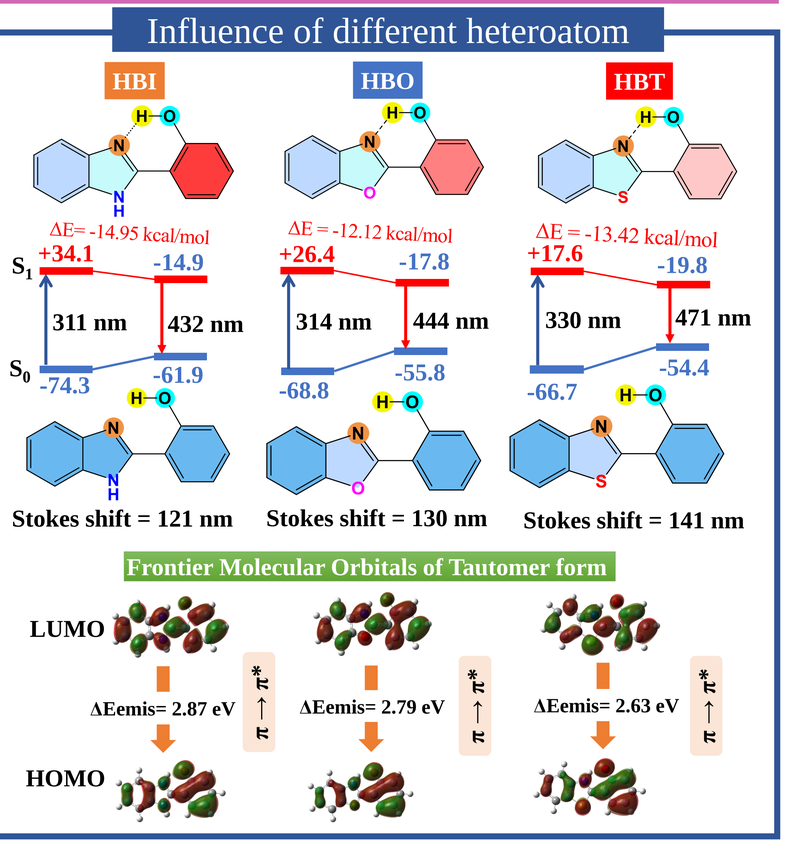
- ✓The maximum wavelengths of absorption and emission spectra
- ✓Frontier molecular orbital (MOs)
- ✓Nucleus-independent chemical shift values (NICS) [3]

All calculations were performed using Gaussian 16 program.



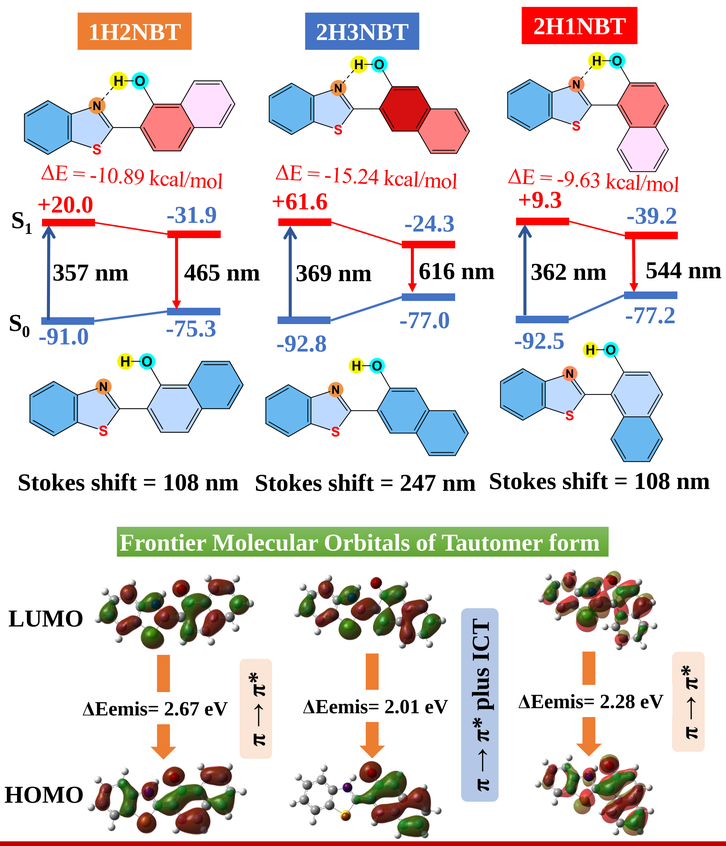
RESULTS AND DISCUSSION

Influence of different heteroatom

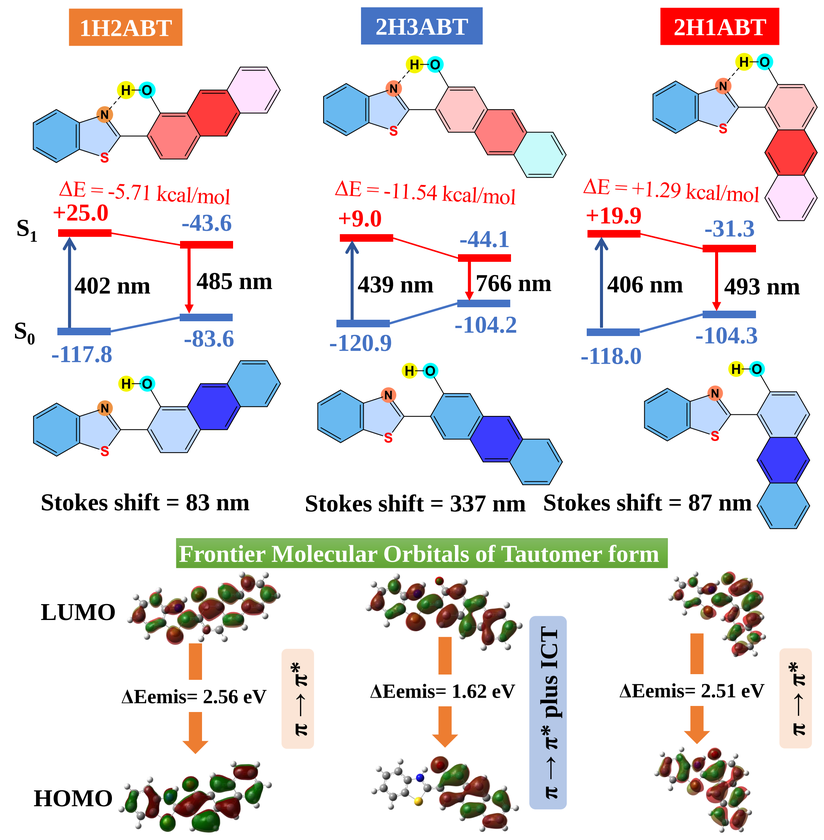


Frontier Molecular Orbitals of Tautomer form

Influence of pi-expansion

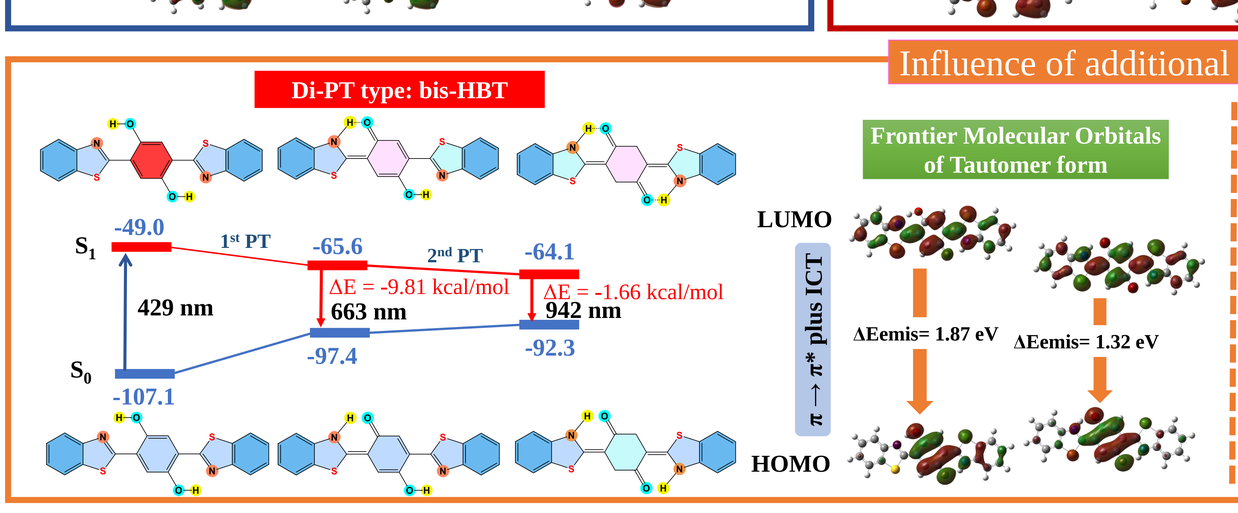


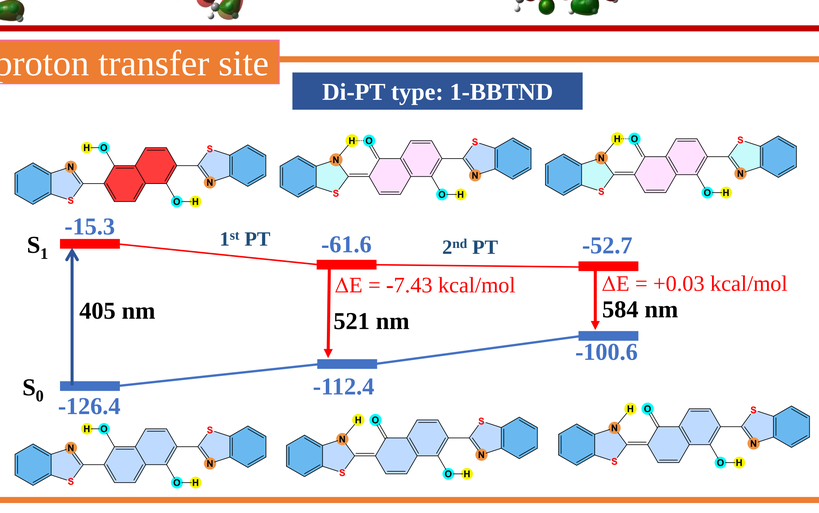
Frontier Molecular Orbitals of Tautomer form

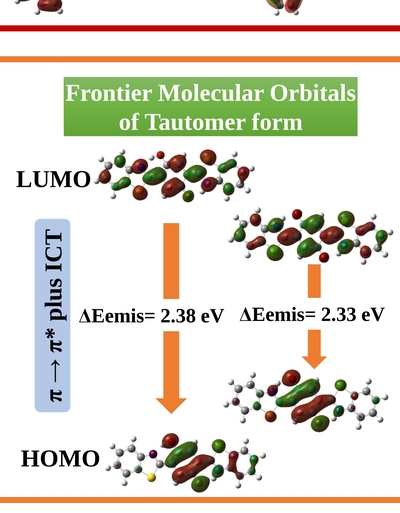


Frontier Molecular Orbitals of Tautomer form

Influence of additional proton transfer site







CONCLUSION

- ✓Influence of different heteroatom does not significantly affect different photophysical properties and the S_1 antiaromaticity relief for HBX.
- ✓The HBX derivatives with π-expansion along the nodal plane show emission peaks close to NIR region with large stokes shifts.
- ✓The HBX derivatives with a combination of π-expansion and addition PT unit along the nodal plane show emission peaks at NIR region with much larger stokes shifts than those with only π-expansion.
- ✓The HBX derivatives with higher relief of S_1 antiaromaticity through PT result in more ESIPT exothermicity.

ACKNOWLEDGEMENTS

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[1] J. Zhao, et al., *Physical Chemistry Chemical Physics*, 14 (2012) 8803-8817.
[2] K. Chaihan, et al., *Journal of Photochemistry and Photobiology A: Chemistry*, 419(2021) 113450.
[3] C.-H. Wu, et al., *Proceedings of the National Academy of Sciences*, 116(2019) 20303–20308.