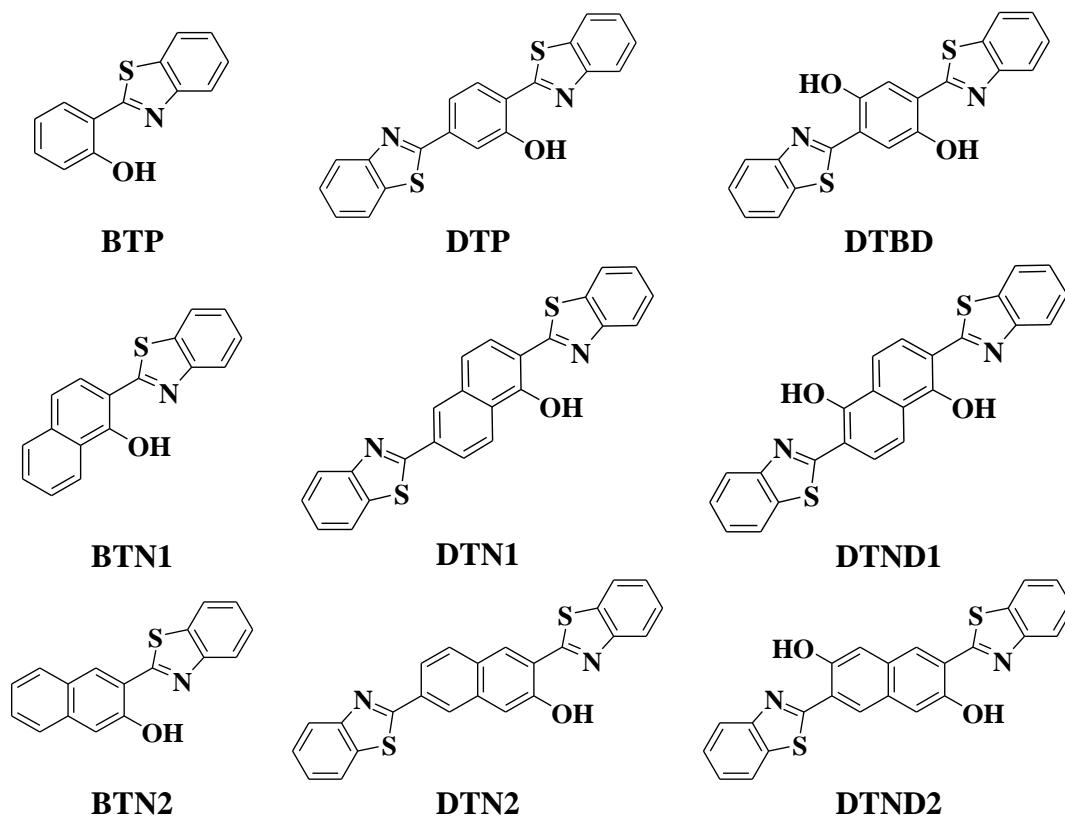


Solvent Effect of Excited-State Intramolecular Proton Transfer (ESIPT) of 2-(2-Hydroxyphenyl)-benzothiazole (HBT) derivatives: A Combined Experimental and Theoretical Study

Excited state intramolecular proton transfer (ESIPT) process is one of the most important reactions in photochemistry and photobiology.¹⁻² ESIPT occurs in bifunctional organic molecules having intramolecular hydrogen bond (intra-HB) connected by proton donor (-OH, -NH₂) and proton acceptor (=N-, -C=O) moieties. Upon photoexcitation, the proton transfer is triggered due to the charge redistribution of both proton donor and acceptor moieties, resulting in forming tautomer which is structurally different from the normal form. The tautomer is not electronically stable in the excited state (S₁), thus emitting the fluorescent with remarkable stokes shift before going down to give the ground state (S₀) and then normal form. The large stokes shift of ESIPT molecules can be applied in fluorescent probes, luminescent materials and hole transporting materials.³⁻⁴ Moreover, the ESIPT process could be affected by an intermolecular-HB with protic solvent molecules. Thus, the emission characteristics of ESIPT molecules are expected to be solvation dependent particularly with protic solvents. The aim of this work to understand the effect of different solvation of 2-(2-Hydroxyphenyl)-benzothiazole (HBT) derivatives on electronic properties.



Scheme 1. The schematic for derivatives formula of HBT.

Experimental and computational details

All compounds (as shown in Scheme 1) will be synthesized according to the protocols used in many works.³⁻⁷ Electronic absorption (UV-Vis) and steady state fluorescence spectra will be analyzed at room temperature. To obtain desirable absorption spectra, a quartz cell with optical path of 10 mm will be used for our measurement. For influence of solvation, all compounds will be prepared in solutions as methanol (MeOH), tetrahydrofuran (THF), dimethylformamide (DMF), methylene dichloride (MC), and toluene with concentration in range 10^{-5} - 10^{-4} mol L⁻¹.⁸ Moreover, fluorescence quantum yields will be also analyzed in a standard solution.

All calculations based on density functional theory (DFT) will be carried out using the Gaussian09 program suit⁹. The self-consistent field (SCF) calculations in ground state, the three-parameter hybrid functional of Becke with the correlation functional of Lee, Yang and Parr (B3LYP)¹⁰⁻¹³ with the triple- ζ valence quality with one of polarization functions (TZVP)¹⁴⁻¹⁵ basis set will be used to optimize for all compounds. Optimized structures were confirmed to be global minima on the potential energy surfaces by vibrational calculations without any imaginary frequency. The optimized structures will be further used to calculate the single point of the electronic properties.

Vertical excitation energies will be performed using time-dependent density functional theory (TD-DFT)¹⁶⁻¹⁸ both in the ground (S_0) and the first excited (S_1) geometries using B3LYP/TZVP level to give absorption and emission spectra, respectively. All optimized structures will be calculated in gas phase as well as in different solvents within the PCM framework¹⁹ which are MeOH, THF, DMF, MC, and toluene. The dipole length representation will be employed to calculate oscillator strengths which are dependent of solvents. Moreover, the molecular orbitals will be also analyzed to visualize electron density distributions.

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