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Excited-state intramolecular proton transfer in 2-(2′,6′-dihydroxyphenyl)benzoxazole: effect of dual hydrogen bonding on the optical properties

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ABSTRACT

2-(2′,6′-Dihydroxyphenyl)benzoxazole (DHBO) has been synthesized by using palladium-catalyzed oxidative cyclization. The compound utilizes both *O–H⋯N* and *O–H⋯O* bonds to ensure a coplanar structure between the benzoxazole and phenol fragments. Optical comparison with the parent compound 2-(2′-hydroxyphenyl)benzoxazole (HBO) reveals that the dual hydrogen bonding in DHBO plays an essential role in raising the desirable *keto* emission for ESIPT and tuning the polarity sensitivity toward the molecular environment. DHBO also exhibits a higher quantum yield ($\phi_{\text{fl}} = 0.108$ in methanol) than HBO ($\phi_{\text{fl}} = 0.0025$) in the same solvent.

2-(2′-Hydroxyphenyl)benzoxazole (HBO) **1** has emerged to be an interesting material, due to its intrinsic property for the excited state intramolecular proton transfer (ESIPT). A distinctive feature for the HBO derivatives is that their fluorescence is well separated from their absorption maxima, leading to unusually large Stokes' shift.[1] Utilization of this feature has resulted in various applications including chemical sensors for zinc(II)[2,3] and anions,[4] and electronic devices such as organic light-emitting diodes.[5] In recent years, the HBO derivatives have been studied extensively to elucidate the ESIPT process (Scheme 1). In the ground state, the HBO derivative exists in the *enol–imine* form. Upon irradiation with photons, the HBO molecule is driven to the excited state, where a proton is transferred from the hydroxy group to an acceptor to generate the corresponding *keto–amine* tautomer. The entire process occurs in about a picosecond, making the HBO derivative an attractive candidate for optical switching.[6]

The HBO molecule is known to exist in the intramolecular hydrogen-bonded rotamers **1a** and **1b**. X-ray diffraction reveals that the two rotamers **1a** and **1b** exist in about 1:1 ratio in the crystalline state,[7] with the hydroxyl group pointing to either N- or O-atom side of the oxazole ring. It has been demonstrated that only rotamer **1b** undergoes ESIPT process,[8,9] which leads to the *keto* tautomer **2** to give the emission with large Stokes shift. The rotamer **1a** is likely the one responsible for the *enol* emission.

In the solution state, HBO can also exist as the *enol* **3**, especially when the solute molecule has strong interaction with the surrounding solvent molecules. In the extreme cases, the solvent molecules may remove the hydroxy proton to generate the anionic species. The *enol* forms (**1a, 1b**, and **3**) in solution are in equilibrium (Scheme 2), whose actual composition is dependent on the solvent properties. It should be noticed that only tautomer **1b** undergoes the ESIPT to generate the desirable *keto* emission. The effective content of **1b**, therefore, determines the optimum performance of the HBO derivatives. Previous studies have shown that the relative intensity of *keto* emission can be significantly increased by decreasing the temperature (e.g., at 77 K)[10] or solvent polarity.[11] Any environmental changes, which affect the equilibrium among **1a**, **1b**, and **3**, can ultimately influence the population of excited states and photophysical characteristics of HBO. The presence of several ground-states, in addition to their unpredictable composition in equilibrium, dilutes the effective concentration of rotamer **1b**, thereby lowering the intensity of the desirable *keto* emission and hampering a broader application of HBO. For example, the HBO **1** in ethanol[10] and methanol[12] solutions gives both *enol* ($\lambda_{\text{em}} \approx 370$ nm) and *keto* ($\lambda_{\text{em}} \approx 500$ nm) emission in about equal intensity at room temperature, while the *keto* emission is nearly exclusive in a nonpolar solvent such as 3-methylpentane.[10]

It remains a challenging task to effectively direct the equilibrium toward the useful rotamer **1b**. Decreasing temperature and using nonpolar solvents are either impractical or can only be applied to very limited situations. The known intermolecular hydrogen bond strength[13] for *O–H⋯N* ($\Delta H = -6.5$ kcal/mol, measured from phenol/pyridine) is only slightly stronger than that for *O–H⋯O* bond ($\Delta H = -5.0$ kcal/mol, measured from phenol/ether). The small energetic difference between the *O–H⋯N* and *O–H⋯O*

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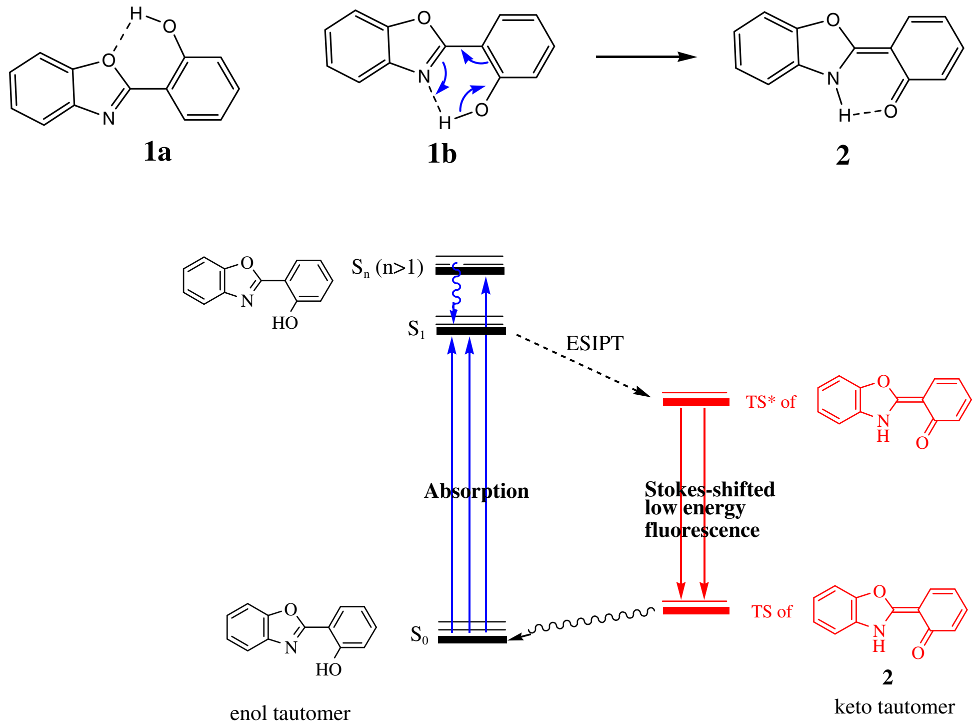
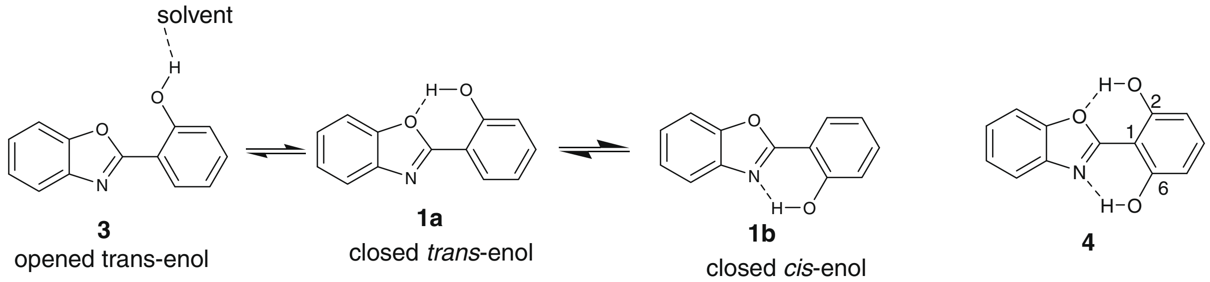
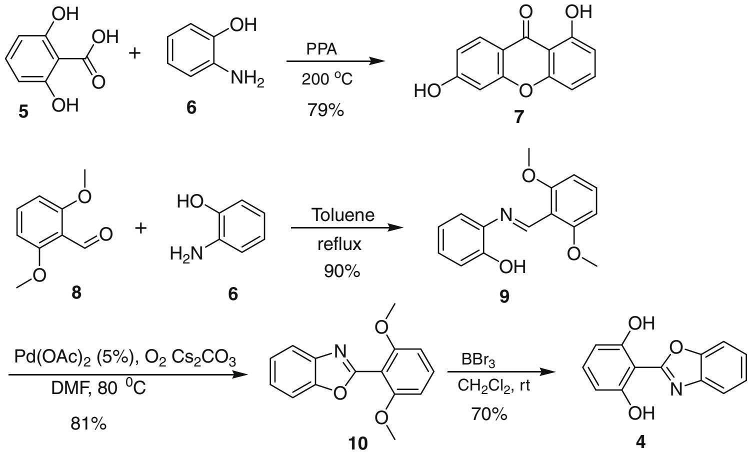


Scheme 1. Schematic illustration for ESIPT of HBO **1**.



Scheme 2. Enol isomers of HBO in the ground state.

bonds only renders a limited control to minimize the amount of the tautomer **1a**, which is incapable of undergoing ESIPT to give *keto* emission. A rational design to maximize the ESIPT signal demands new strategies to minimize the content of **1a** and **3**, while preserving the valuable optical characteristics of HBO. Herein, we report the synthesis of 2-(2′,6′-dihydroxyphenyl)benzoxazole (DHBO) **4**, in which the second hydroxy group is introduced at the 6-position of the phenol segment. The dual hydrogen bondings



Scheme 3. Synthesis of compound **4**.