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A Single 2-(2′-Hydroxyphenyl)benzothiazole Derivative Can Achieve Pure White-Light Emission

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Abstract: The synthesis and photophysics of two novel 2-(2′-hydroxyphenyl)-benzothiazole (HBT) derivatives are presented. The electron-withdrawing trifluoromethyl (CF_3) group in compound **1** facilitates the deprotonation of the phenolic hydroxy group. Well-resolved triple fluorescence from the enol, keto, and phenolic anion, which ranges from 350 to 600 nm, was detected for **1** in ethanol, which marks the first time triple fluorescence from an excited-state intramolecular proton transfer (ESIPT) molecule has been reported. Both triphenylamine and CF_3 were introduced into derivative **2**. Intramolecular charge transfer and the "red-edge effect" resulted in the bathochromic shift of dual fluorescence of **2**. Triple fluorescence was also observed for **2** in ethanol. In mixed acetonitrile and ethanol, pure white-light emission with CIE coordinates of (0.33, 0.33) and a quantum yield of 0.25 was achieved for **2**. This work provides a new avenue for the rational design of an ESIPT molecule to achieve white-light generation under mild conditions.

Keywords: charge transfer · enols · fluorescence · hydrogen bonds · photophysics

Introduction

White-light generation is drawing wide attention in both academic and industrial fields owing to its applications in constructing lighting sources, flat-panel displays, and so on.[1,2] White-light emission should ideally be composed of three primary (blue, green, and red) or two complementary (blue and yellow) colors and cover the whole visible range from 400 to 700 nm. Traditional methods to generate white light typically rely on mixing various primary-color lights emitted from different materials.[3–5] An alternative approach is to use a single-component emitter, which can have such advantages as simpler fabrication processes, higher stability, and better reproducibility.[6,7] However, for single-component emitters, the self-absorption and energy transfer between the different luminophores can inevitably quench the fluorescence intensity.[8] Thus, the development of emitting centers without an energy-transfer process would be the most ideal strategy for white-light generation.

Molecules that feature an excited-state intramolecular proton transfer (ESIPT) are usually characterized by fluorescence that covers a wide spectral range, which has considerable potential to form white light. 2-(2′-Hydroxyphenyl)-benzothiazole (HBT) derivatives are a series of well-known ESIPT compounds. As shown in Figure 1, the intrinsic four-level photocycle (N→N*→T*→T→N) is involved in the ESIPT process.[9,10] In non- or weakly polar solvents, the enol form (I) is exclusively in the ground state owing to stabilization of the intramolecular hydrogen bond. Upon photoexcitation, the redistribution of charge evokes an increasing acidity of the proton donor or the basicity of the proton acceptor. Consequently, the fast proton-transfer reaction takes place through the pre-existing intramolecular hydrogen bond to generate the keto tautomer (II), which emits fluorescence in the long-wavelength region with a large Stokes shift. Although in some strong polar solvents like

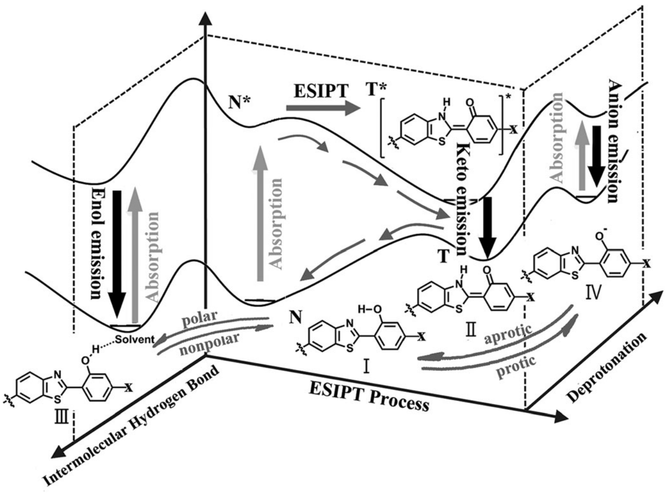

Figure 1. Schematic representation of the ESIPT mechanism of a 2-(2-hydroxyphenyl)benzothiazole derivative.

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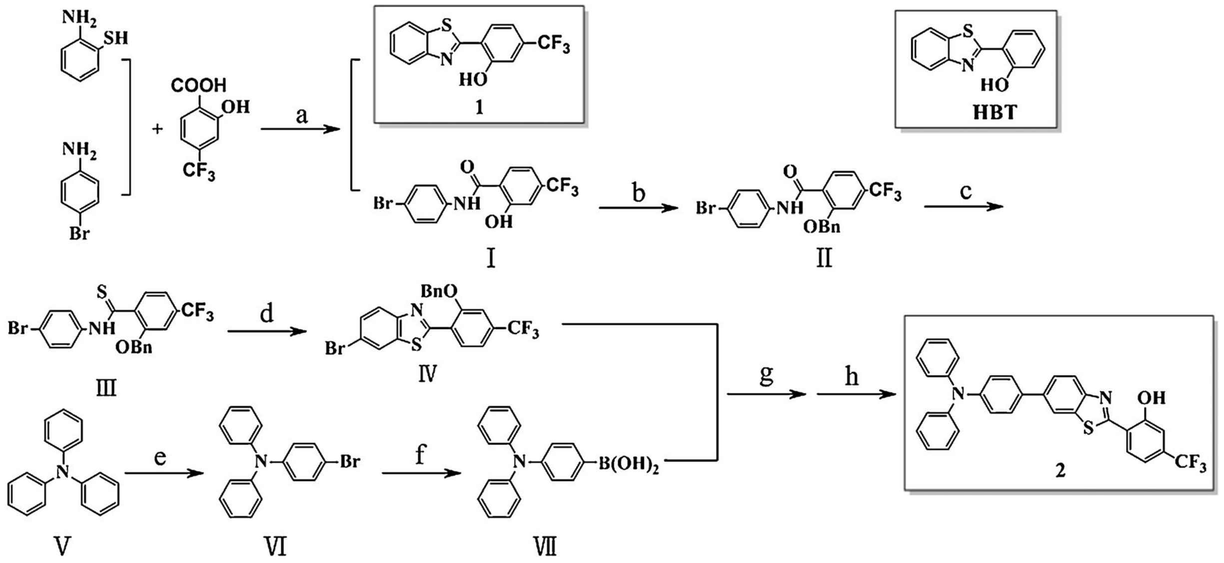

Scheme 1. Chemical structures and synthetic routes of HBT and compounds **1** and **2**. Reagents: a) PCl_3; b) benzyl chloride, K_2CO_3; c) Lawesson reagent, toluene; d) $K_3[Fe(CN)_6]$, NaOH; e) *N*-bromosuccinimide (NBS), CCl_4; f) *n*BuLi/THF, $B(OCH_3)_3$; and g) $[Pd(PPh_3)_4]$, K_2CO_3; h) HBr, acetic acid (AcOH).

acetonitrile the solvent molecules can form hydrogen bonds with the hydrogen in the hydroxyl groups and generates the enol–solvent form (III), in this case the ESIPT process is hindered. Owing to the intermolecular hydrogen-bonding effect, the radiance from the keto tautomer (II) is restricted, which consequently results in another band with a normal Stokes shift that can be observed in the short-wavelength regions. According to the previous studies, the intermolecular hydrogen bond has a great influence on the absorption and fluorescence spectra.[11] Moreover, the dual fluorescence will be disturbed in protic solvents such as alcohol because of the competition between intermolecular and intramolecular hydrogen bonding. The competition of the two kinds of hydrogen bonds will redistribute the contents of conformers I and III and might bring about the deprotonation of the phenolic hydroxyl group to generate the luminescent phenolic anions (IV). To the best of our knowledge, there has been no report of such ESIPT molecules in which the phenolic anion IV can coexist with the conformers I and III to form the triple fluorescence.

Abstract in Chinese:

本文报道了两个基于三氟甲基及三苯胺取代的2-(2′-羟苯基)苯并噻唑(即HBT)衍生物**1**和**2**的合成及光物理性质。由于分子内氢键作用，HBT分子具有典型的激发态分子内质子转移(ESIPT)特征。本文首先在HBT的苯环上引入三氟甲基得到分子**1**。三氟甲基的强吸电子性增强了酚羟基的酸性，促使化合物**1**在质子性溶剂例如乙醇中实现烯醇、酚氧负离子、ESIPT产物酮同时发光而获得三荧光。这是由ESIPT分子实现三荧光现象的首次报道，**1**的三荧光覆盖了从紫光至橙红光共250nm的宽谱带。将强吸电性的三氟甲基和强供电性的三苯胺基团同时引入到化合物**2**分子内，分子内电荷转移使得**2**的烯醇发光红移到蓝光区域，并由于“红边效应”其在乙腈中酮发光红移到红光区域。进一步调节混合溶剂中乙醇和乙腈的比例和激发波长，最终化合物**2**在该二元溶剂体系中发射出纯白光。该研究结果提供了一种通过协调分子内氢键和分子间氢键的方式，实现单一小分子化合物在如此温和条件下发射白光的简单方法。

In this paper, we report the design and synthesis of novel HBT derivatives that are capable of emitting white light in a simple solvent system. First the strong electron-withdrawing trifluoromethyl group (CF_3) was introduced into the *para* position of the hydroxyphenyl ring of the parent HBT to form derivative **1** (Scheme 1). The well-resolved triple fluorescence that covers a wide spectral range from 350 to 600 nm was easily achieved in protic solvents. By attaching an electron-donating triphenylamine (TPA) group into the benzothiazole ring of molecule **1**, we synthesized derivative **2**, the emission spectrum of which can cover the whole visible-light region. In addition, derivative **2** can emit pure white light in mixed acetonitrile and ethanol solvents.

Results and Discussion

Preparation of Compounds

Scheme 1 illustrates the synthetic procedure of compounds **1** and **2**. Compound **1** was prepared by the one-step cyclization reaction between 2-aminothiophenol and 4-trifluoromethylsalicylic acid at high yield of 80 % according to the literature method.[12] Compound **2** was synthesized through multistep reactions according to the literature method.[13] Condensation of 4-bromoaniline with 4-trifluoromethylsalicylic acid in the presence of PCl_3 generated the amide (I). After treatment with benzyl chloride to protect the phenolic hydroxy, the amide was converted by Lawesson's reagent into the thiobenzamide (III). Jacobsen reaction of this thiobenzamide with potassium ferricyanide resulted in the important intermediate 2-[2′-(benzyloxy)-4′-(trifluoromethyl)phenyl]-6-bromobenzothiazole (IV). Finally, the Suzuki coupling reaction of IV with [4-(diphenylamino)phenyl]boronic acid (VI) followed by deprotection of the hydroxy group generated the target compound **2**.

Triple Fluorescence

Figure 2 illustrates the absorption and emission spectra of the parent molecule HBT and derivative **1** in different solvents. Similar to the parent HBT, compound **1** in toluene and tetrahydrofuran (THF) displays two major absorption bands. In protic ethanol, one additional absorption band centered at 390 nm is observed, which implies that a novel chemical species is formed in the ground state in addition to conformers I and III. As can be seen in Figure 2, upon photoexcitation the emission evolution of **1** from single, via dual, to triple fluorescence was easily achieved only by varying the solvent. In nonpolar toluene, **1** emits single fluorescence with an emission peak at 520 nm (Figure 2b; fluorescence quantum yield $\Phi_F=0.444$). In THF with increased polarity, a short-wavelength band at 380 nm was detected along with the original band around 520 nm, thus leading to the formation of the dual fluorescence (Figure 2c; $\Phi_F=0.028$ for dual emission). According to the typical spectral features of the general HBT derivatives, it is reasonable to ascribe the above 380 and 520 nm emission bands of compound **1** to the corresponding conformer III and tautomer II, respectively.[9,13,14] If **1** is dropped into protic ethanol, a third emission band at 455 nm can be simultaneously detected, accompanied with the former purple and green bands (Figure 2d; $\Phi_F=0.183$ for all three bands). Triple fluorescence with a wide spectrum is generated.

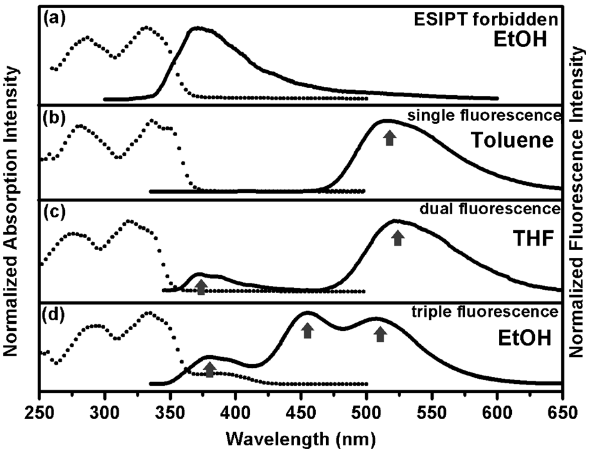

Figure 2. UV/Vis absorption (dashed lines) and emission spectra (solid lines) for parent compound HBT and derivative **1**. a) The spectra of HBT in ethanol; b–d) the emission evolution of **1** from single via dual to triple fluorescence in different solvents (3×10^{-5} mol L^{-1}, $\lambda_{exc}=330$ nm).

For the relationship between the additional absorption band at 390 nm and the fluorescence emission at 455 nm in ethanol to be explored, **1** was excited at 390 nm, and the band at 450 nm was detected as the exclusive emission band (see the Supporting Information). This indicates that the 390 nm absorption band and the 455 nm emission band indeed originate from the same chemical species. Furthermore, when **1** was titrated with Bu$_4$NOH in ethanol, the original green and purple emission bands collapsed into the blue emission at 450 nm (see the Supporting Information). Hence, it is reasonable to ascribe the concurrent appearance of the blue emission band at 455 nm and the 390 nm absorption band to the corresponding phenolic anions IV that are formed in the ground state and the excited state. The excitation spectra of **1** (see the Supporting Information) further confirm these assignments. No such blue emission was detected for the parent HBT in ethanol (Figure 2a). As shown by the calculation results in the Supporting Information, incorporation of the electron-withdrawing CF$_3$ group extends the O−H bond length and increases the charge density on the O atom for **1**, which results in the increased acidity of the hydroxyl group and facilitates its deprotonation. The incorporation of the CF$_3$ group into HBT causes the appearance of the 455 nm emission; hereafter, the triple fluorescence of **1** in ethanol has a wide spectral range from 350 to 600 nm, as shown in Figure 2d. Further structural modification of **1** might redshift this broad spectrum to cover the whole visible-light region.

White-Light Emission of a Single HBT Molecule

By introducing an electronic-donating triphenylamine (TPA) group into **1**, we designed and synthesized **2** with the expectation that its broad spectrum would cover the entire visible-light region. As can be seen from the Supporting Information, **2** exhibits a broad absorption band centered at 380 nm in various solvents, which is attributed to the overlap between the phenolic anion absorption band and the charge-transfer absorption band. The complete separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) shown in Figure 3 confirms the intramolecular charge-transfer feature for **2**.[15] Figure 4 illustrates the fluorescence spectra of **2** in different solvents. Compound **2** exhibits the single fluorescence with a peak at 475 nm ($\Phi_F=0.889$) in nonpolar toluene, which should be due to the emission from the corresponding keto tautomer. This deduction was confirmed by time-dependent (TD) DFT calculations, in which the bandgap and emission wavelength of the keto form of **2** in toluene are calculated to be 2.80 eV and 443 nm, respectively (Figure 3). Dual emission at 435 and 605 nm from the corresponding conformer III and the keto tautomer was detected in strong polar acetonitrile ($\Phi_F=0.0594$), and triple emission peaks (435, 480, and 525 nm) in protic ethanol ($\Phi_F=0.24$). The fluorescence quantum yields are much higher than

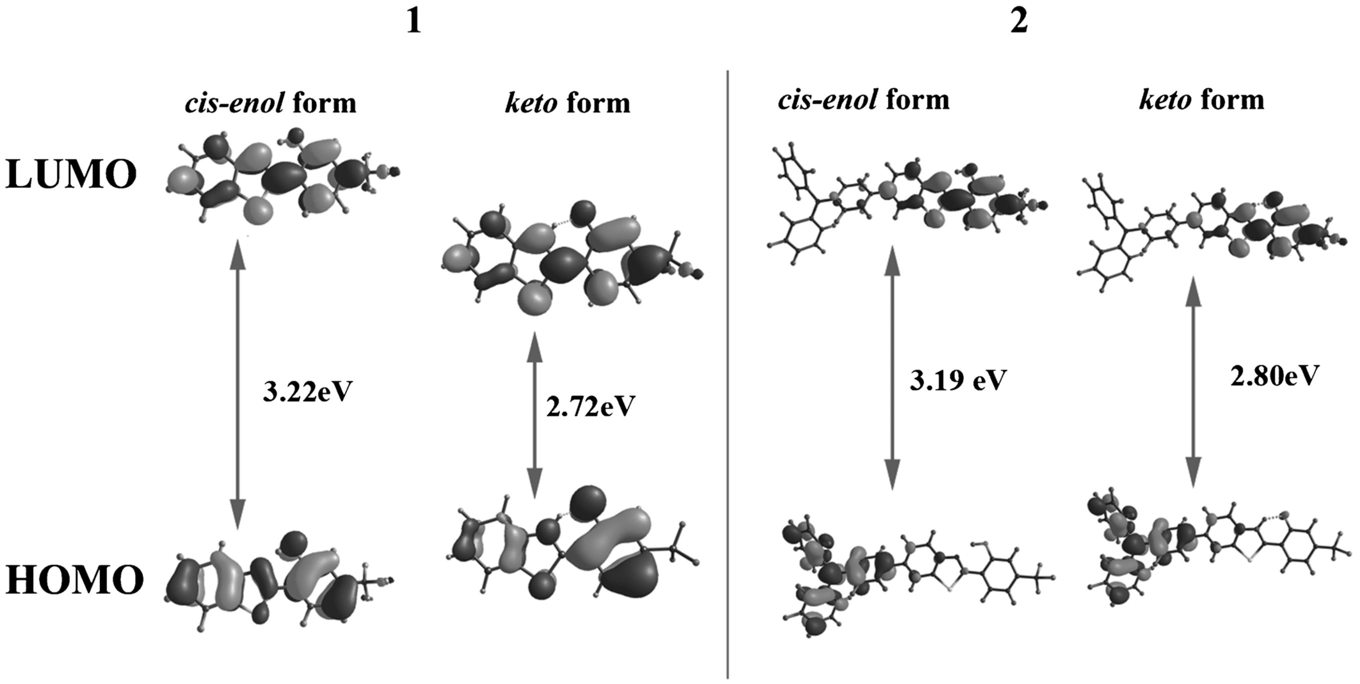

Figure 3. The frontier molecular orbitals of enol forms and keto forms for compounds **1** and **2** at the optimized geometries and corresponding energies. Toluene was used as solvent in these calculations. The fluorescence wavelength of the keto form of **2** was calculated to be 1240/2.80 = 443 nm.

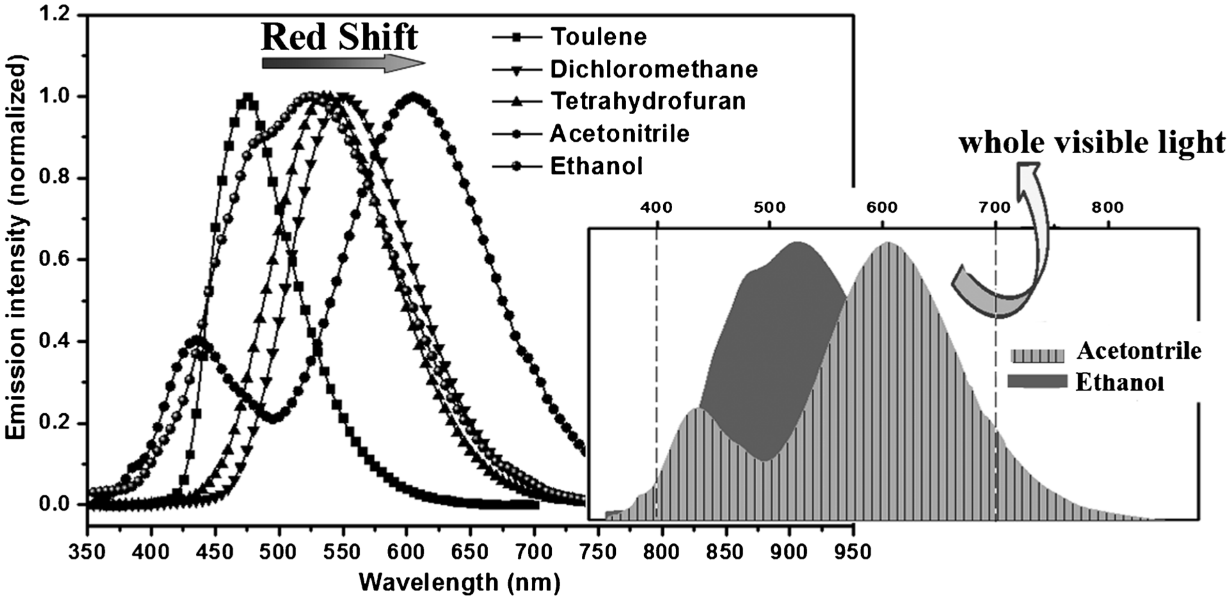

Figure 4. Fluorescence spectra of compound **2** in different solvents with excitation at 345 nm. The inset describes the spectra by simply integrating the emission spectra in acetonitrile and ethanol.

those of its parent molecule HBT and compound **1** (see the Supporting Information). The fluorescence lifetimes of compounds **1** and **2** are summarized and compared with the parent HBT in the Supporting Information. It should be noted that the fluorescence of conformer III of **2** in acetonitrile (at 435 nm) was successfully redshifted relative to that of **1** (at 380 nm) owing to the intramolecular charge-transfer (CT) effect, which is discussed in the Supporting Information. In addition, an extra shift of the keto emission toward longer wavelength, which corresponds to the increase in polarity of the solvent, indicates the existence of a red-edge effect.[16] The origin of the red-edge effect lies in the change in fluorophore–solvent interactions in the ground and excited states, which is brought about by a change in the dipole moment of the fluorophore upon excitation. The D–π–A structure allows the creation of a large dipole moment in the excited state that allows for the stabilization of the excited-state intramolecular charge transfer (ESICT) state in the polar solvents. As a result, we can observe that the emission shows a large bathochromic shift with increasing solvent polarity. The bathochromic shift of the keto emission of compound **2** from 475 nm in toluene (with orientation polarizability Δf of 0.03) to 525 nm in ethanol (with Δf of 0.29) and further to 605 nm in acetonitrile (with Δf of 0.31) remains in line with the above rule. Most likely, it can be speculated that compound **2** undergoes ESIPT prior to the ESICT reaction. Compound **2** displays the largest Stokes shift with the long-wavelength keto emission centered at 605 nm in acetonitrile, and its redshifted triple fluorescence in ethanol encouraged us to simply combine the emission spectra in acetonitrile and ethanol so that a broad spectrum that covers the whole visible-light range from 400 to 750 nm can be obtained (shown in the inset of Figure 4).

To realize pure white-light emission, we adopted the strategy of mixing acetonitrile and ethanol in various proportions as the solvents for compound **2**. Owing to the perturbation of intermolecular hydrogen bonds between ethanol and **2**, the efficiency of the ESIPT process would be restrained, as shown by the transient fluorescence decay spectra and the potential-energy curves in the Supporting Information. As a result, the incorporation of ethanol in acetonitrile will strengthen the intensity of the phenolic anion (IV) at the expense of the keto (II) emission. Hence, there is one optimal proportion of the mixed solvents to balance the multiple emission bands for white-light generation. In the mixed solvents of acetonitrile and ethanol with a volume ratio of 5:1, the fluorescence is located in the white region as the excitation wavelength changes from 340 to 370 nm (Figure 5c–e). In addition, a pure white emission is realized when the excitation wavelength is 350 nm. And its CIE coordinates of (0.33, 0.33) fall well within the white region of the 1931 CIE diagram (Figure 5 and the Supporting Information; for pure white $x = 0.33$, $y = 0.33$).[17] In our case, the quantum yield of the white emission that spans the entire visible spectrum is 0.245. As far as we know, this novel compound is the first example of a single ESIPT dye that can emit pure white light under mild conditions without the help of low temperature or high pressure. Based on the easy realization of ideal white light, we propose that compound **2** can find potential applications as a white-light lighting or decorative source for long-term usage, especially in deep-sea exploration or in swimming pools, when a violet light is available as an excitation source.

Conclusion

In summary, a single type of HBT derivative has been designed and synthesized to realize pure white-light emission composed of enol, keto, as well as phenolic anion emission. The mechanism for white-light generation is based on interactions of the electron-donating/-withdrawing framework with the solvents, which involve the intermolecular hydrogen bond, the ESIPT process, as well as deprotonation. In particular, deprotonation was demonstrated to be capable of tuning the emission spectrum. By properly modulating the content ratio of the binary solvents, we utilized compound **2** to achieve white-light emission with CIE coordinates of (0.33, 0.33). This compound is the first example of a single ESIPT dye that can emit pure white light under mild conditions.

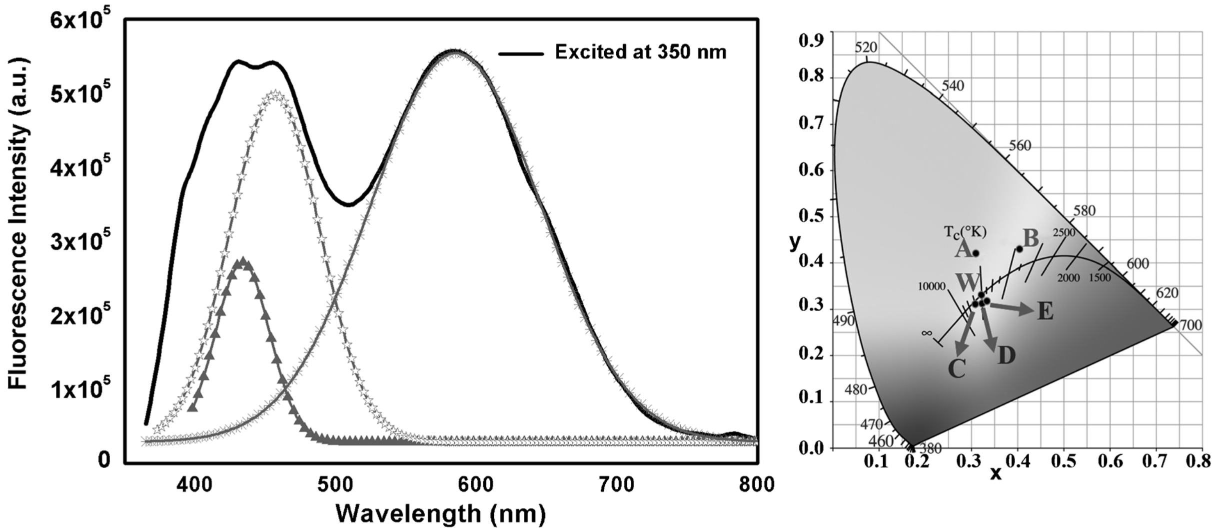

Figure 5. Fluorescence spectra of compound **2** (black solid line) in mixed acetonitrile and ethanol (5:1) ($\lambda_{ex} = 350$ nm) and the deconvolution curves (left), and the CIE 1931 chromaticity coordinates of the fluorescence of **2** (right): A) in ethanol, $\lambda_{ex} = 360$ nm; B) in acetonitrile, $\lambda_{ex} = 360$ nm, W) in mixed acetonitrile and ethanol (5:1), $\lambda_{ex} = 350$ nm; and C–E) in mixed acetonitrile and ethanol (5:1), $\lambda_{ex} = 340, 360, 370$ nm, respectively.

Experimental Section

Instruments and Methods

^{1}H NMR spectra were recorded with a 400 MHz Varian Unity Inova spectrophotometer without any peak frequencies referenced versus an internal standard (TMS) shift. Mass spectra were recorded with a Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray). The UV/Vis absorption spectra were recorded with an HP 8453 spectrophotometer. Both the steady-state fluorescence and time-resolved fluorescence decays were measured with a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. The time-resolved fluorescence decays were obtained using the time-correlated single photon counting (TCSPC) method and the data analysis was performed by means of commercial software provided by Horiba Instruments. The fluorescence quantum yields were measured and calculated relative to quinine sulfate in 0.1 N sulfuric acid as standard ($\Phi = 0.55$).

Theoretical Calculations

The ground-state (S_0) structures of these molecules were optimized by using density functional theory (DFT) with the B3LYP hybrid functional and the 6-31G(d,p) basis set. To evaluate the solvent effect, toluene, acetonitrile, and ethanol were employed as the solvent in the self-consistent reaction field (SCRF) calculations by using the polarized continuum model (PCM). The Coulomb-attenuated time-dependent DFT with the CAM-B3LYP functional and 6-31G(d,p) basis sets was used to calculate the vertical excited energies. It has been said that the CAM-B3LYP functional is in better agreement with the experimental results than results using the B3LYP hybrid functional when dealing with the situation as a long-range correction process. The ground-state potential-energy surfaces along the proton-transfer coordinates were calculated by using the energies of the B3LYP/6-31G(d,p) fully optimized geometry for the minimum-energy conformer at fixed O−H distances over the range 0.93–1.70 Å. The first excited state (S_1) potential-energy curves (PECs) were obtained by adding the Franck–Condon transition energies for the optimized ground-state structures at fixed O−H distances to the corresponding ground-state intramolecular proton transfer (GSIPT) curves. All these calculations were performed with Gaussian 09.[18]

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