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The excited-state intramolecular proton transfer fluorescence of HBT derivative induced by solvent polarity

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ABSTRACT

In this contribution, a dye (**THBT**) with 2,5-dimethylthiophene substituted to 2-(2-hydroxyphenyl)benzothiazole was synthesized and characterized by NMR and mass spectroscopic techniques. Its emission behavior in various solvents was investigated and obvious negative solvatochromism was observed. The emission maximum of **THBT** varied from deep blue (425 nm) in DMSO to orange (550 nm) in chloroform. It is also highly emissive in polycarbonate film and solid powder with the emission peaks 546 and 554 nm, respectively. The ESIPT effect, together with the relaxation of free rotation of thiophene in the excited states, shifted the solid emission 34 nm toward longer wavelength furtherly, with respect the 520 nm (green) emission of **HBT**. Quantum calculation of frontier molecular orbitals uncovers the underlying mechanism of negative solvatochromism.



KEYWORDS

2-(2-hydroxyphenyl)benzothiazole; negative solvatochromism; highly emissive; molecular orbitals; ESIPT

Introduction

Investigation of small organic functional molecules fascinates chemists, physicists, and biochemists by its application in materials sciences and structural biotechnology. Out of various types of physical signal (electricity, light, magnetism, acoustic, etc) and variety of fascinating behavior, the signal processing of fluorescence is the most convenient way to realize the complicated logic operation [1–3]. Therefore, a series of fluorescent organic molecules were intensively investigated and developed. The typical fluorophores are the coumarins, BODIPY, naphthalimide, bisindolylmalimide, rhodamine, and perylenediimide, in which the emission color varies from deep blue to deep red with the emission maximum spanning from 440 to 750 nm [4–12].

Excited state intramolecular proton transfer (ESIPT) chromophores, highly emissive small molecules, have been applied in molecular probes, logic gates, biomarkers, and various emitting materials [13–18]. ESIPT is a photochemical tautomerization that yields an excited keto form (K^*) from the original enol form (E) in the subpicosecond time region [19, 20]. The excited-state keto form relaxes radioactively to give a fluorescence spectrum with

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a large Stokes shift or non-radioactively to the ground-state keto form, which undergoes thermal re-enolization to give the stable enol form. The large Stokes-shifted fluorescence induced by ESIPT has an attractive character of unusual emission at longer wavelength from a small molecule and therefore is not reabsorbed even in a high concentration of chromophores. Despite such a unique character, the efficiency of the large Stokes-shifted fluorescence is generally low. The typical ESIPT chromophores are those containing 2-(2-hydroxyphenyl)benzothiazole (**HBT**) or 2-(2-hydroxyphenyl)benzoxazole (**HBO**). In this contribution, an electron-rich thiophene unit was introduced to **HBT**. With such an attachment to **HBO**, the isomerization efficiency from the excited state may be diminished because a much larger volume change is required for the deactivation process. The suppression of the isomerization efficiency in ESIPT molecules may lead to an increase in the efficiency of the large Stokes-shifted fluorescence. Our intention was to achieve and understand the corresponding properties through detailed study and structural analysis, which is of significant for the application in biological science and technology [21, 22].

Experimental

General procedures and materials

The solvents used in the reaction were carefully dried according to the standard procedure and stored over 4 Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC. (South Korea) and used without further purification. Melting points were determined on a Mel-Temp® IA9200 digital melting point apparatus in a glass capillary and were uncorrected. All synthesized compounds were routinely characterized by TLC and ¹H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

¹H and ¹³C NMR spectroscopy

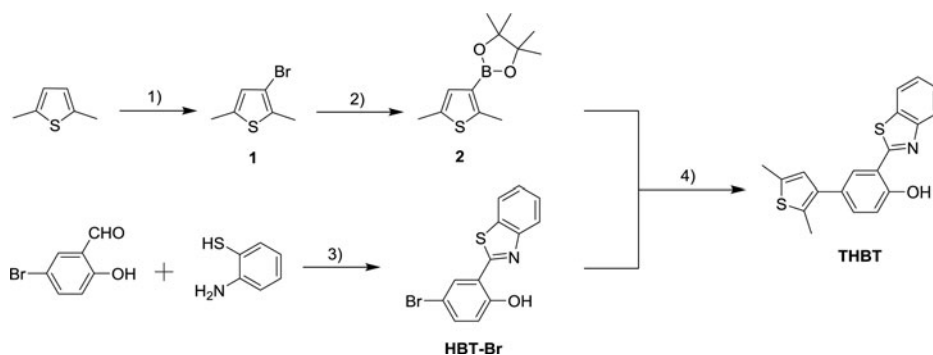
¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in CDCl₃. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz.

High resolution mass spectra (HRMS)

The mass spectra measured on a LC-MS (Waters UPLC-TQD) mass spectrometer. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II Focus instrument.

UV-Vis and emission spectra

The absorption spectra were measured with a PERSEE TU-1900 and an Agilent 8453 spectrophotometer. Emission spectra were measured with Shimadzu RF-5301PC fluorescence spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds (2×10^{-3} M) was prepared in THF, and a fixed amount of these concentrated solutions were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were



Scheme 1. Synthesis of 4-(2,5-dimethylthiophen-3-yl)-2-(2-hydroxyphenyl)benzothiazole (**THBT**). 1) NBS, dichloromethane, r.t.; 2) -78°C , $n\text{-BuLi}$, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF; 3) Ethanol, reflux; 4) N_2 , $\text{Pd}(\text{PPh}_3)_4$, 2 M Na_2CO_3 , THF, reflux 48 h.

obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.

Theoretical calculations

For the theoretical study of the excited state photo-physics of the dye, the *DMol*³ program, which is available as part of *Material Studio* (Accelrys Inc., San Diego, California, United States), was used. Both the ground state geometries and the frontier molecular orbital of the dye were calculated using the density function theory (DFT) with the B3LYP hybrid functional and the double numerical plus *d*-functions (DND) atomic orbital basis set.

Synthesis

Synthetic routes of the ESIPT dye, 4-(2,5-dimethylthiophen-3-yl)-2-(2-hydroxyphenyl)benzothiazole (**THBT**), are outlined in Scheme 1. The 2,5-dimethylthiophene was conveniently brominated with NBS in dichloromethane to give **1** [23, 24]. And it was treated with $n\text{-BuLi}$ and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and yielded **2** (2-(2,5-dimethylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) [25]. HBT-Br was obtained by condensation of 5-bromo-2-hydroxybenzaldehyde and 2-aminobenzenethiol [22, 26, 27]. Finally, HBT-Br and **2** was coupled under standard Suzuki coupling conditions and yielded **THBT**.

4-(2,5-dimethylthiophen-3-yl)-2-(2-hydroxyphenyl)benzothiazole (THBT)

Under nitrogen atmosphere, HBT-Br (153 mg, 0.5 mmol), Na_2CO_3 (1.06 g, 10 mmol), $\text{Pd}(\text{PPh}_3)_4$ (28.9 mg), and H_2O (5 mL) were charged in a 100 mL flame dried Schlenk tube. **2** (143 mg, 0.6 mmol) in THF (50 mL) was added by syringe. Next, the mixture was heated to reflux for 48 h and monitored by TLC. After HBT-Br was fully reacted, as confirmed by TLC, the reaction mixture was cooled to room temperature and poured in to distilled water (60 mL). The mixture was stirred for 30 m, then it was extracted with dichloromethane (25 mL \times 3). The organic phase was combined and washed with brine (75 mL). Next, the solvent was dehydrated over anhydrous MgSO_4 and evaporated in a vacuum. The residue was purified by silica gel (200–300 mesh) column chromatography with hexane and afforded **THBT** (168 mg, 60%).

Table 1. Optical data of the **THBT** in various solvents.

Solvent	UV-Vis		Fluorescence		Stokes shift (nm)
	λ_{abs} (nm)	$\log \varepsilon_{\text{max}}$	λ_{em} (nm)	Φ_{F}	Stokes shift (nm)
DMSO	348	4.05	425	0.51	77
	440	3.71			
DMF	350	4.12	475	0.47	125
	438	3.38			
THF	354	4.47	495	0.23	141
Acetonitrile	351	4.43	505	0.18	154
	450	4.16			
Dioxane	354	4.47	553	0.43	199
	455	4.40			
Dichloromethane	355	4.33	550	0.33	195
Chloroform	350	4.21	550	0.58	200
	458	4.30			
Hexane	356	4.18	548	0.55	192
Methanol	350	4.14	— ^a	— ^a	— ^a
Polycarbonate film	355	4.15	546	0.36	191
	456	4.33			

^a The data was not shown due to the weak emission.

Mp: 225–228°C; ¹H NMR (400 MHz, CDCl₃) δ : 8.00 (*d*, 1 H, *J* = 8.0 Hz), 7.90 (*d*, 1 H, *J* = 8.0 Hz), 7.68 (*s*, 1 H), 7.51 (*t*, 1 H, *J* = 8.0 Hz), 7.40 (*m*, 3H), 7.14 (*d*, 1 H, *J* = 8.0 Hz), 6.73 (*s*, 1 H), 2.48 (*s*, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 156.7, 151.9, 137.1, 135.9, 133.1, 132.6, 131.5, 128.6, 128.2, 127.1, 126.8, 125.6, 122.2, 121.6, 117.8, 116.6, 15.2, 14.1. HRMS (ESI): [M+H]⁺ C₁₉H₁₆NOS₂ requires 338.0673; found [M+H]⁺ 338.0680.

Result and discussion

The spectra properties of **THBT** was investigated in various solvents, such as DMSO, DMF, THF, acetonitrile, dioxane, dichloromethane, chloroform, hexane, and methanol. It was found that the solubility of **THBT** in organic media was enhanced due to the attachment of thiophene unit to **HBT**. At the same time, the photostability of **THBT** in solvents is robust. Long time exposure to the room light does not decompose the compound. However, the attachment of thiophene to **HBT** makes it sensitive to the external environment. Negative solvatochromism was induced by the variation of solvent polarity. The basic absorption/emission peaks, absorption coefficients, quantum yields, and Stokes shifts of **THBT** are presented in Table 1. The absorption spectra of **THBT** in various solvents were recorded in Figure 1. In dioxane, chloroform, and acetonitrile, the longest absorption maximum was positioned around 400–500 nm. In other tested solvents, including polar and nonpolar media, the absorption was very weak in visible region. In all the solvents, the stronger absorptions were in the UV region (~350 nm).

The emission of **THBT** is significantly environment dependent, which is different from that of **HBT**. In most of the organic solvents, **THBT** is highly emissive. However, the fluorescence was almost totally quenched in protonic solvent, such as methanol. In aprotic solvents, **THBT** exhibits various emission characters irregularly. Detailed emission properties are listed Table 1. Figure 2 shows the emission spectra in various aprotic solvents, by which highly emission was induced. Interestingly, a negative solvatochromism was observed. In DMSO, the emission maximum of **THBT** is shortest (425 nm, deep blue) among all the tested solvents. It was shifted to 475 nm (light blue) with the solvent displaced by DMF. With the polarity

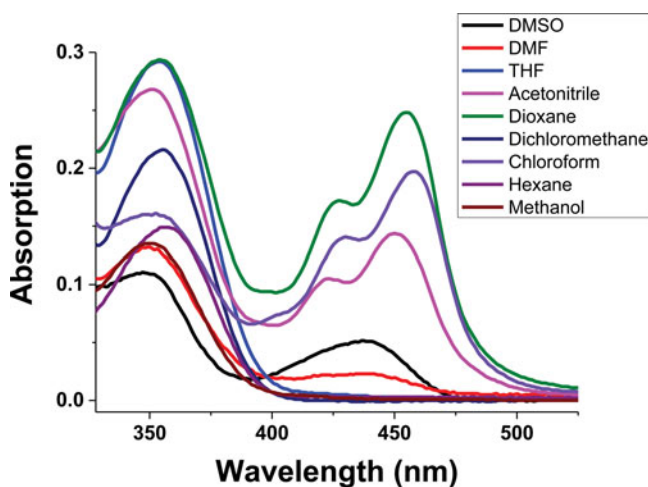


Figure 1. Absorption spectra of **THBT** in various solvents (1.0×10^{-5} M).

decreasing, the emission maximum was shifted to 495/505 nm (green) in THF and acetonitrile, respectively. Further decreasing of solvent polarity, the emission maximum of **THBT** was red-shift to about 550 nm (yellow). In medium and weak polar solvent, the emission of **THBT** was sensitive enough to the polar environment. Except the difference of emission intensities, the emission peaks are almost identical to each other. It can be seen that **THBT** solvatochromic shift from chloroform to DMSO is 125 nm toward the shorter wavelength, comparable to the largest solvatochromic effects observed in heavily studied merocyanine derivatives. It is known to all that the solvatochromism depends on the difference in dipole moment between the ground state and the excited states of the chromophore. Within the conventional interpretation of solvatochromic interactions, the negative solvatochromism indicates that the value of the dipole moment in the excited electronic state (μ_e) is smaller than in the ground state (μ_g). The attaching of electron rich heterocycle thiophene to **THBT** enhances the total electron density of molecules, which facilitates the enlargement of ground state dipole moment.

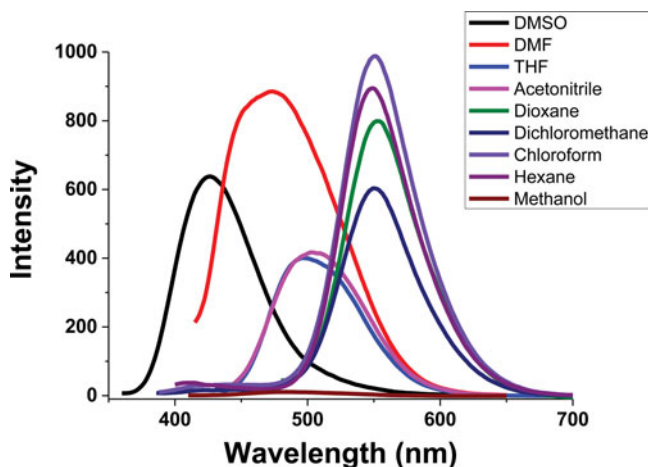


Figure 2. Emission spectra of **THBT** in various solvents (1.0×10^{-5} M).

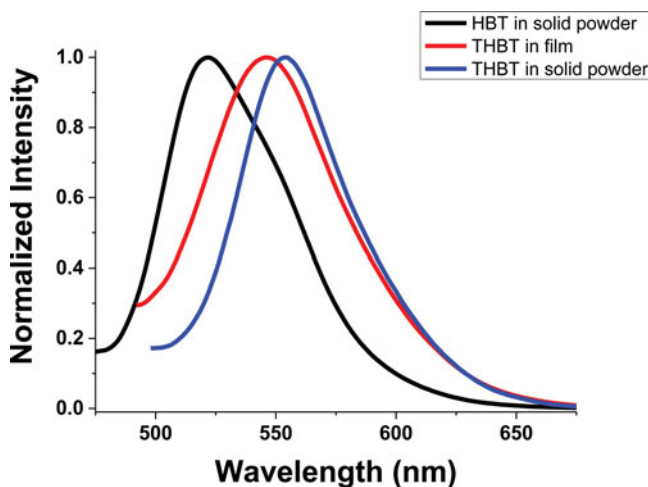


Figure 3. Emission spectra of **THBT/HBT** in solid powder and **THBT** in film at with 5 wt.% blended in polycarbonate.

The Stokes shift of **HBT** derivatives is generally larger than conventional dyes due to the ESIPT. The emission maximum in aggregate state shifted to green region due to the mechanism of ESIPT. For the unsubstituted **HBT** fluorophore, the molecular framework is rigid due to the intramolecular hydrogen bonding, and thus leads to small geometry relaxation. With thienyl substitution to **HBT**, the molecular flexibility was increased; that is, the dihedral angle between the thienyl and the benzene ring may be changed upon excitation. This enhanced geometry relaxation will radiationlessly consume absorption energy, then lower the emission energy correspondingly, red shift the emission wavelength. This was fully verified by the emission behavior of **THBT** in chloroform (200 nm Stokes shift). The quantum yields of **THBT** in different solvents varied in the range of 0.18–0.58. There seems to be no regular trend for the quantum yield variation in different polarity solvents. The emission efficiency in chloroform and hexane is higher than other tested solvents. In contrary, it was significantly lowered in acetonitrile/dichloromethane, and totally quenched in protonic solvent, such as methanol.

THBT is highly emissive not only in solution but also in the film blended with polycarbonate and in the solid powder state. The emission spectra are shown in Figure 3. Without the attaching of thiophene, the solid powder emission of **HBT** is greenish with the emission peak 522 nm. With the attaching of thiophene unit, the film emission of **THBT** blended in polycarbonate (5 -wt.%) red-shifted to 546 nm due to the effect of ESIPT and aggregation in the polymer matrix. Further red-shift of **THBT** was observed in solid powder (554 nm), which is closer to that in film. Additionally, the emission behavior in the film/solid powder is similar to that in chloroform/hexane. The full width at half maximum (FWHM) of **THBT** in the solid powder was estimated to be 57 nm, which is narrower than that in chloroform. Generally, tightly packing in the solid powder will broaden the FWHM of emission. Therefore, the ESIPT effect plays a major role in the solid powder emission of **THBT**. The variation of emission in solution/film/solid (blue to orange) was characterized by CIE coordinates (Figure 4). Notable CIE coordinate change exhibits the fluorescence color variation induced by solvent polarity (Figure 4a). With the polarity decreasing, the CIE coordinates crowded in orange region. The CIE coordinates of film and solid emission is adjacent to each other, which facilitates to the future application in device (Figure 4b).

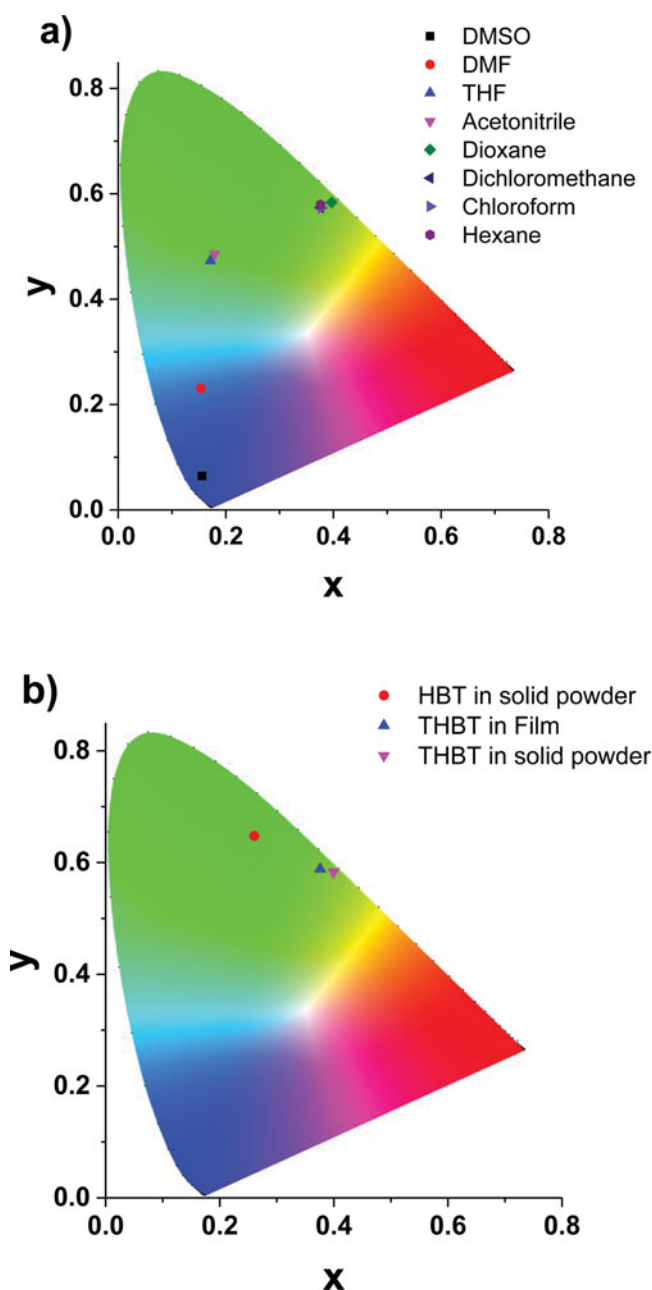


Figure 4. CIE 1931 chromaticity diagram of the emissions of **THBT** in solution (a), and **HBT** (in polycarbonate film), **THBT** (in polycarbonate film and solid powder).

To better comprehend the geometrical, electronic, and optical properties of **HBM**, we undertook a comprehensive computational investigation using Material Studio. To reduce the run times in the first instance, the ground-state energy-minimized structures were calculated using DFT and LDA/DN basis set [28, 29]. Further refinement and optimization on structures were undertaken using DND/B3LYP basis set.

The size and signs of frontier molecules orbitals are illustrated in Figure 5. Distinctive contributions of each atomic orbital are discernible in the HOMO and LUMO diagrams, which

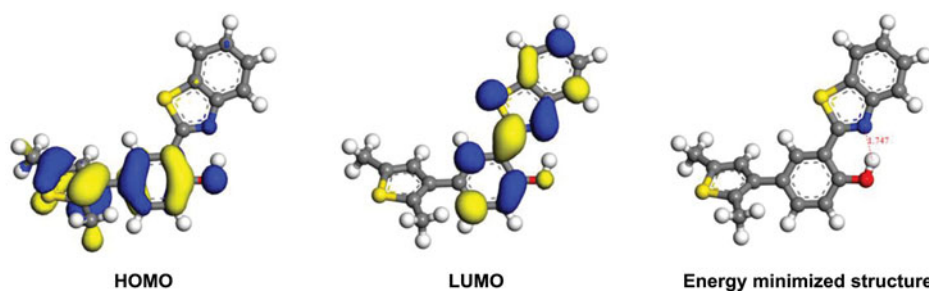


Figure 5. HOMO and LUMO diagrams of **THBT** obtained from $Dmol^3$ calculations and the energy minimized structure.

dominated the strong absorption band in UV-Visible region [8, 30, 31]. In HOMO, the electron density is well distributed over the thiophene and phenolic rings, reflecting the electron-rich character. However, the LUMO distribution moved away from thiophene ring to benzothiazole ring. While the phenolic rings contribute always to the HOMO and LUMO distribution. The enhanced electron density due to the attaching of thiophene ring was easy to induce the ground state charge separation in polar environment. The higher electron density location at nitrogen in LUMO indicates the interaction between hydrogen and nitrogen atoms. The distance also can be estimated to be 1.747 Å by calculation, which limits the free rotation of benzothiazole ring around the single covalent bond. The enhanced rigidity of molecular framework contributes mainly to its solid powder emission. While, the rotation of thiophene ring around the single covalent bond is free. The energy dissipation of excited states shifts the emission spectra to orange, which was supported by the calculated dipole moment of ground/excited state ($\mu_e = 3.623D$, $\mu_g = 3.196D$). According to the optimized excited state, the absorption and emission energy can be estimated to be 2.53 eV and 2.21 eV, respectively. The absorption and emission wavelength could be calculated to be 490 and 561 nm, which is in agreement with the experimental value mentioned above.

Conclusions

In summary, a 2,5-dimethylthiophene attached dye (**THBT**) was synthesized under Suzuki conditions and fully characterized. The electron rich nature of substituent leads to higher electron density in the molecular system. An obvious negative solvatochromism was observed for the emission behavior of **THBT** in different polarity solvent. The emission color varied from deep blue in DMSO (425 nm) to orange in hexane/chloroform (~550 nm). Increase of solvent polarity blue shifts the emission maximum. Additionally, **THBT** is also highly emissive in polycarbonate film and solid powder with the emission peaks 546 and 554 nm respectively. The emission color of **THBT** in solution/film/solid powder was characterized by CIE coordinates in detail. The calculated HOMO distribution indicates that the higher electron density in thiophene and phenolic rings. It is the higher dipole moment in ground state induced by polar solvent results in the negative solvatochromism.

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