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# Excited-state intramolecular single and double proton transfer emission of 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol

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ABSTRACT

In this work, excited-state intramolecular single proton transfer emission (S-PTE) and double proton transfer emission (D-PTE) are presented by employing 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol (**1**) as a prototype. **1** has been strategically designed and synthesized in an aim to explore single proton transfer and double proton transfer in the excited state. In solution **1** exhibits the lowest lying $S_0 \rightarrow S_1$ absorption at ~395 nm. Upon excitation, two large Stokes shifted emission bands maximized at 475 nm and 550 nm are resolved, which are ascribed to the tautomer emission resulting from single proton transfer and double proton transfer isomers, respectively. It is found that solvents have greatly influenced on excited-state intramolecular proton transfer emission.



## 1. Introduction

Proton transfer is one of the most important chemical reactions in chemistry and biology [1–3]. Excited state intramolecular proton transfer (ESIPT) [4] is one class of the proton transfer reactions that can be initiated by a light pulse [5,6]. Significant interest has existed in the fundamental investigation [7–10] and the application [11–15] of organic molecules exhibiting ESIPT because of their four-level photophysical scheme, spectral sensitivity to the surrounding medium and a large Stoke's shifted fluorescence. It has been demonstrated that the ESIPT process involves a photo-tautomerization reaction, the enol isomer converts to keto isomer *via* an intramolecular hydrogen bond involving the transfer of hydroxyl proton to the nitrogen atom in excited state (Scheme 1) [16,17]. The excited keto isomer relaxes radiatively to give a large Stokes shifted fluorescence or nonradiatively to the ground-state keto isomer, which then undergoes thermal re-enolization to give the original enol isomer. The transformation from enol isomer to keto isomer occurs extremely fast in the subpicosecond or the picoseconds time scale [18,19].

Most ESIPT reactions refer to the single proton transfer. Excited-state proton transfer incorporating the transfer of two or more protons is, however, of paramount interest, and attracts more attention due to its intrinsic property in mimicking proton relay in vital bio-systems. For instance, prototypes include ESIPT of green fluorescence protein, photo-induced mutation of DNA A–T and G–C base pairs with double and triple hydrogen bonds [20–22]. Unlike the ubiquitous single-proton transfer fluorescence, however, double or multiple proton-transfer fluorescence is rarely reported [23–26]. In this paper, we employ 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol (**1**) (Scheme 2) as a model compound. **1** contains two enol units, and is expected to be able to go intramolecular single and double proton transfer emission upon excitation. To better identify single and double proton transfer emission of **1**, two analogues (**2**) and (**3**) (Scheme 2) which represent none proton transfer emission and single proton transfer emission, respectively are synthesized for control experiments, and their fluorescence properties are also performed.

## 2. Experimental

### 2.1. General

$^1$H and $^{13}$C NMR spectra are recorded at 400 and 100 MHz, respectively, with TMS as an internal reference. MS spectra are recorded with TOF-MS spectrometer, respectively. All the fluorescence spectral measurements were done at $1 \times 10^{-5}$ M

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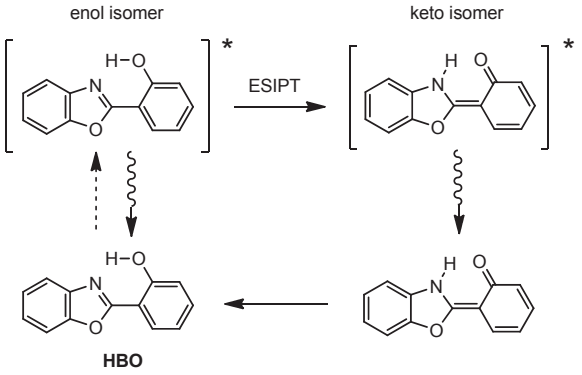
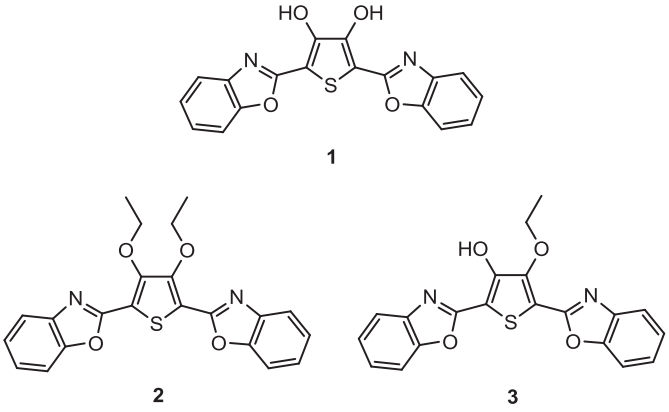



**Scheme 1.** Schematic of the ESIPT of **HBO**.




**Scheme 2.** Chemical structures of target **1** and analogues **2** and **3**.

concentrations of solute to avoid aggregation and self-quenching. The steady state absorption spectra are recorded on Hitachi U-3010 spectrophotometer. All the emission spectra are recorded on a F-2500 fluorescence spectrophotometer equipped with a 10 mm quartz cell. Fluorescence lifetimes are measured from time-resolved intensity decay by the method of time-correlated single-photon counting (TCSPC) technique.

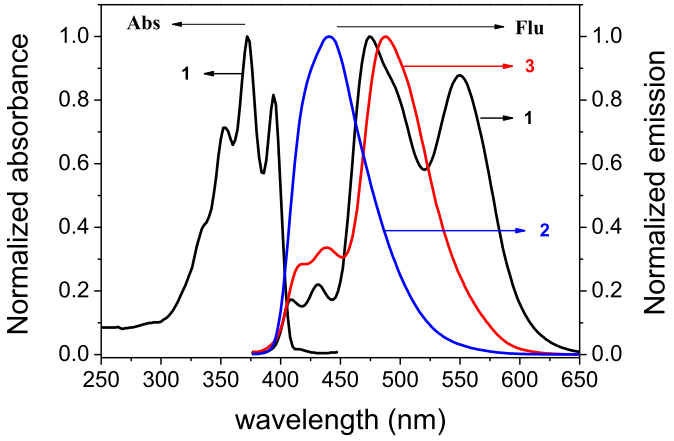
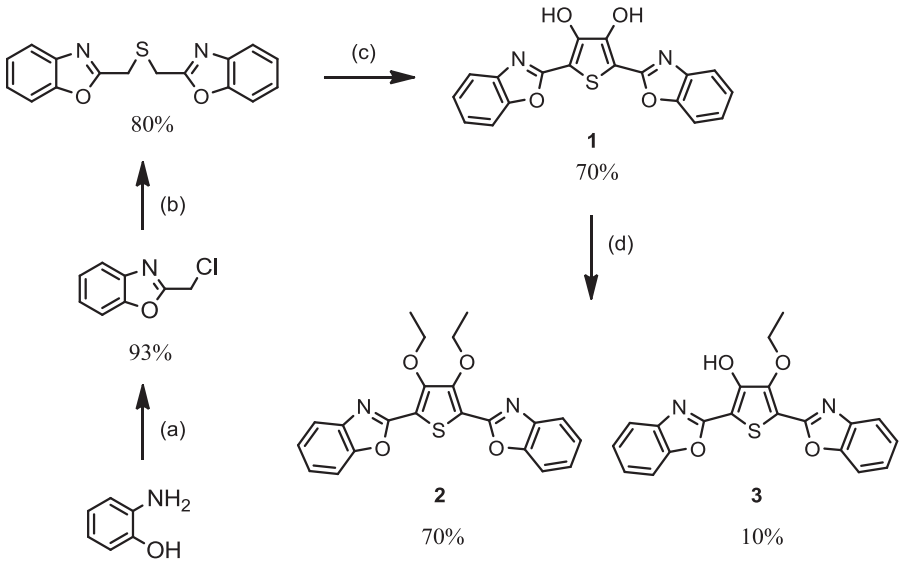



**Fig. 1.** Absorption and fluorescence spectra of **1** (black) together with fluorescence spectra of **2** (blue) and **3** (red) in solution ($CHCl_3$, 10 μM), $\lambda_{ex}$ = 394 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 2.2. Synthesis of *1, 2* and *3*

The synthetic routes for compounds **1**–**3** are outlined in Scheme 3, and the detailed procedures are presented as follows: (a) To a solution of 2-aminophenol (16.35 g, 150 mmol) and chloroacetyl chloride (16.95 g, 150 mmol) in dry chlorobenzene (200 mL) is added pyridine (0.5 ml). The solution is stirred at ambient temperature for 2 h. To above solution is added *p*-toluenesulfonic acid (2.58 g, 15 mmol), the solution is refluxed till no water is discharged. After cooling to room temperature, the solution is washed with water (100 mL × 3) and a saturated solution of NaCl (50 mL), respectively. The organic solution is collected and dried over $Na_2SO_4$, after evaporation of the solvent, the crude 2-(chloromethyl)benzoxazole (yellow oil, 23.1 g, 93% yield) is obtained for next step without purification. (b) To a solution of 2-(chloromethyl)




**Scheme 3.** Synthesis of target compound **1** and analogues **2** and **3**. Reagents and conditions: (a) pyridine cat., dry chlorbenzene, rt, 2 h; p-toluenesulfonic acid cat., reflux, 6 h, 93%; (b) tetrabutylammonium bromide cat., DCM/$H_2O$ (v/v = 3/2), rt, 4 h, 82%; (c) Na, dry MeOH, rt, 1 h; dry DMF, reflux, 6 h, 70%; (d) $K_2CO_3$ base, KI cat., DMF, 100 °C, 5 h, 70% for **2** and 10% for **3**.

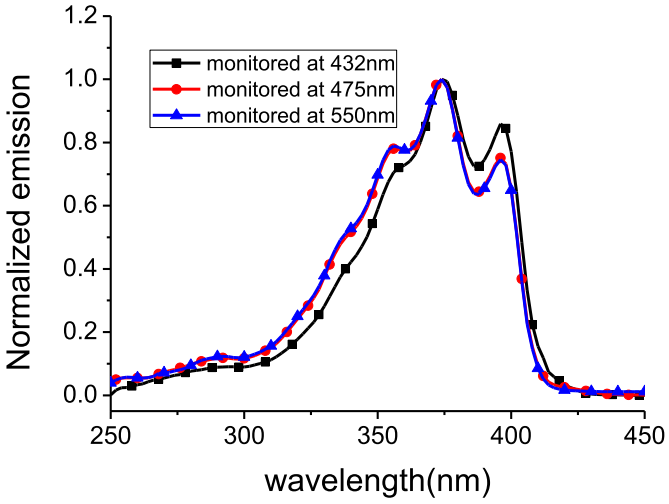



**Fig. 2.** Excitation spectra of **1** in solution ($CHCl_3$, 10 μM) at different wavelength.

**Table 1**
Optical date of **1**, **2** and **3** in $CHCl_3$ solution.

| Compd | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\Delta\nu(cm^{-1})$ |
|---|---|---|---|
| **1** | 354, 372, 394 | 412, 430, 475, 550 | 1108, 2168, 4284, 7200 |
| **2** | 356, 370, 392 | 420, 438 | 1700, 2678 |
| **3** | 358, 374, 395 | 415, 436, 485 | 1220, 2380, 4592 |

benzoxazole (23.1 g, 139.5 mmol) and tetrabutylammonium bromide (4.49 g, 13.95 mmol) in dichloromethane (150 ml) is added $Na_2S\cdot 9H_2O$ (40.2 g, 167.4 mmol) in $H_2O$ (100 ml), the mixture solution is stirred at ambient temperature for 4 h until the starting material disappeared (TLC detection). The mixture solution is washed with water (100 ml × 3), the washed organic solution is then dried over $Na_2SO_4$, after evaporation of the solvent, the crude bis(benzoxazol-2-ylmethyl) sulfane (brown oil, 33.8 g, 82% yield) is obtained for next step reaction without purification. (c) Sodium (1.15 g, 50 mmol) is added to anhydrous MeOH, the solution is stirred for 1 h at ambient temperature. To above solution is added dropwise bis(benzoxazol-2-ylmethyl)sulfane (2.98 g, 10 mmol) and diethyl oxalate (1.46 g, 10 mmol) in dry DMF (20 ml). The mixture

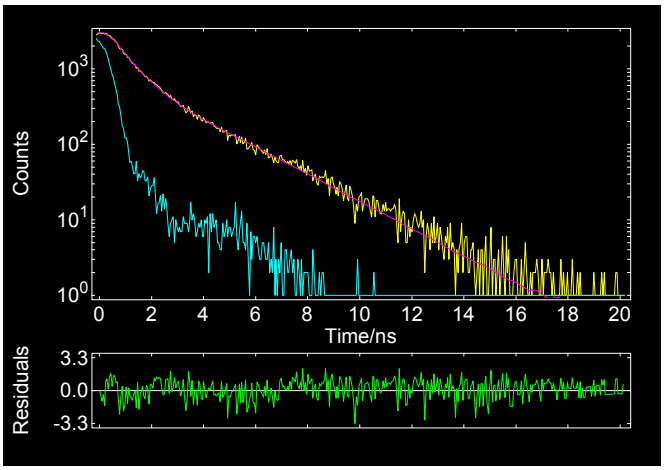



**Fig. 3.** The fluorescence decay of **1** at 474 nm emission in $CHCl_3$.

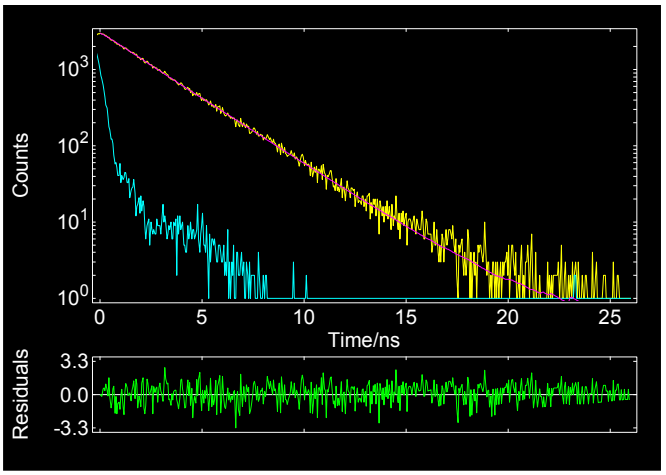



**Fig. 4.** The fluorescence decay of **1** at 550 nm emission in $CHCl_3$.

solution is refluxed for 6 h until no starting material is detected (TLC detection). After cooled to room temperature, the solution is acidified with HCl (12 N, 50 ml) till pH = 3, the solid is filtered off and washed successively with EtOH (30 ml), saturation $NaHCO_3$ (30 ml) and $H_2O$ (30 ml). After dried in vacuo, the target compound **1** is obtained (yellow solid, 2.45 g). **1.** Yield: 70%. $^1$H NMR (DMSO-$d_6$): $\delta$ (ppm) 7.45–7.40 (m, 4H), 7.82–7.75 (m, 4H), 5.01 (s, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 157.7, 151.6, 149.2, 142.7, 127.3, 126.5, 120.8, 116.5, 111.8. MS (EI) $C_{18}H_{10}N_2O_4S$. calcd. 350.0361, found: 350.0368. Anal. Calcd for $C_{18}H_{10}N_2O_4S$: C, 61.71; H, 2.88. Found: C, 61.68; H, 2.91. (d) To a solution of **1** (1.05 g, 3 mmol) in DMF (10 ml) is added bromoethane (0.98 g, 9 mmol), $K_2CO_3$ (1.24 g, 9 mmol) and KI (0.15 g, 0.9 mmol). The mixture solution is heated at 100 °C for 5 h, after cooled to room temperature, the solution is acidified with HCl (12 N, 50 ml) till pH = 3. The product is extracted with DCM, the combined organic phase is dried with anhydrous $Na_2SO_4$. After evaporation of the solvent, the crude product is purified by flash column chromatography with petroleum/ethyl acetate (1:2) as eluent to afford compound **2** and **3**.

**2.** Yield: 70%. $^1$H NMR ($CDCl_3$): $\delta$ (ppm) 7.80–7.77 (m, 2H), 7.60–7.58 (m, 2H), 7.38–7.36 (m, 4H), 4.46–4.41 (q, 4H), 1.52 (t, $J_1$ = 6.8 Hz, $J_2$ = 7.2 Hz, 6H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 159.8, 153.4, 152.6, 149.7, 127.3, 124.5, 120.8, 116.5, 112.8, 65.6, 14.9. HRMS (EI) $C_{22}H_{18}N_2O_4S$, calcd. 406.0987 found: 406.0973. Anal. Calcd for $C_{22}H_{18}N_2O_4S$: C, 65.01; H, 4.46. Found: C, 65.07; H, 4.42.

**3.** Yield: 10%. $^1$H NMR (DMSO-$d_6$): $\delta$ (ppm) 7.82–7.76 (m, 4H), 7.45–7.40 (m, 4H), 5.31 (s, 1H), 4.37–4.32 (q, 2H), 1.43 (t, $J_1$ = 7.2 Hz, $J_2$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 159.8, 157.4, 153.2, 152.3, 149.5, 127.3, 124.4, 120.5, 116.3, 112.4, 65.9, 14.9. HRMS (EI) $C_{20}H_{14}N_2O_4S$, calcd. 378.0674 found: 378.0693. Anal. Calcd for $C_{20}H_{14}N_2O_4S$: C, 63.48; H, 3.73. Found: C, 63.51; H, 3.69.

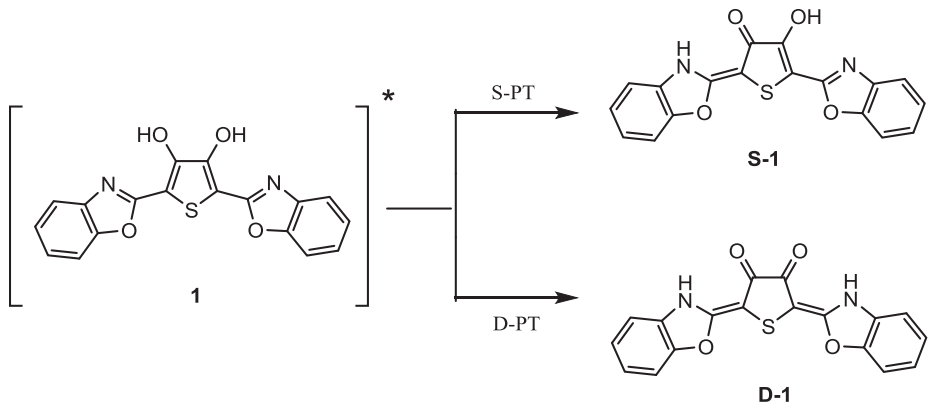
## 3. Results and discussion

### 3.1. Synthesis

Target compound **1** and analogues **2** and **3** are prepared from

**Table 2**
Fluorescent lifetime of **1** and **2** in DCM solution.

| Compd | $\lambda_{em}$ (nm) | $\tau_f$ (ns) | $\chi^2$ |
|---|---|---|---|
| **1** | 475 | 0.67, 2.40 | 0.971 |
| **1** | 550 | 2.44, 3.63 | 0.969 |
| **2** | 438 | 0.68 | 1.237 |




**Scheme 4.** Schematic of the single and double proton transfer of **1**.

commercially available starting material 2-aminophenol following the depiction in Scheme 3. Bis(benzoxazol-2-ylmethyl) sulfane is produced by the condensation of 2-aminophenol with 2-chloroacetyl chloride in chlorobenzene (93% yield), followed by the reaction with $Na_2S$ in $H_2O$-DCM (v/v = 1:1) using tetrabutylammonium bromide (TBAB) as catalyst (80% yield). Condensation of bis(benzoxazol-2-ylmethyl) sulfane with diethyl oxalate in EtOH using sodium methanolate ($NaOCH_3$) as base affords 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol (**1**) in 70% yield. Treatment of **1** with bromoethane in the ratio of 1:2 equiv. in EtOH gives **2** (70% yield) and **3** (10% yield), respectively.

### 3.2. Absorption spectra of *1*.

Fig. 1 depicts the steady-state absorption and emission spectra of **1** in chloroform ($CHCl_3$) at room temperature. Solution absorbance study of **1** is performed to determine the appropriate excitation wavelength for fluorescence studies. According to Fig. 1, **1** is characterized by virtually identical features, the absorption spectra exhibits three well-defined vibronic peaks at 354 nm ($\varepsilon = 3.45 \times 10^4$ cm L $M^{-1}$), 372 nm ($\varepsilon = 4.84 \times 10^4$ cm L $M^{-1}$), and 394 nm ($\varepsilon = 3.95 \times 10^4$ cm L $M^{-1}$), respectively, which are assigned to both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ type of electronic transition.

### 3.3. Fluorescence of *1*

As shown in Fig. 1, four emission peaks are observed upon excitation of **1**. Two small Stokes shifted emission maximized at 412 nm ($\Delta\nu = 1108$ $cm^{-1}$) and 432 nm ($\Delta\nu = 2168$ $cm^{-1}$), and two large Stokes shifted emission maximized at 475 nm ($\Delta\nu = 4284$ $cm^{-1}$), and 550 nm ($\Delta\nu = 7200$ $cm^{-1}$), respectively, are resolved versus the lowest lying absorption (394 nm). The identical excitation and absorption spectra (Fig. 2) conclude the same ground-state origin for the emission. Both small and large difference in Stokes shift indicates that not only occurred normal electron transition from $S_0 \rightarrow S_1$ but also proton transfer in the excited state.

### 3.4. Control experiments

To identify the correspondence of emission peaks and to elucidate the proton transfer in **1**, control experiments have been carried out. First, we probe this issue *via* chemical modification. Compounds **2** (used for none proton transfer emission) and **3** (used for single proton transfer) as prototypes are employed. Both **2** and **3** exhibit similar absorption profile and absorption bands (Table 1) with that of **1**. However, fluorescence spectra show distinct difference among them. As shown in Fig. 1, **2** exhibits a normal Stokes shifted emission ($\lambda_{em} = 438$ nm, $\Delta\nu = 2678$ $cm^{-1}$) versus the lowest lying absorption (394 nm), and no large Stokes shifted emission is observed. **3** exhibits, however, both normal Stokes shifted emission ($\lambda_{em} = 436$ nm, $\Delta\nu = 2380$ $cm^{-1}$) and a large Stokes shifted emission ($\lambda_{em} = 485$ nm, $\Delta\nu = 4592$ $cm^{-1}$) versus the lowest lying

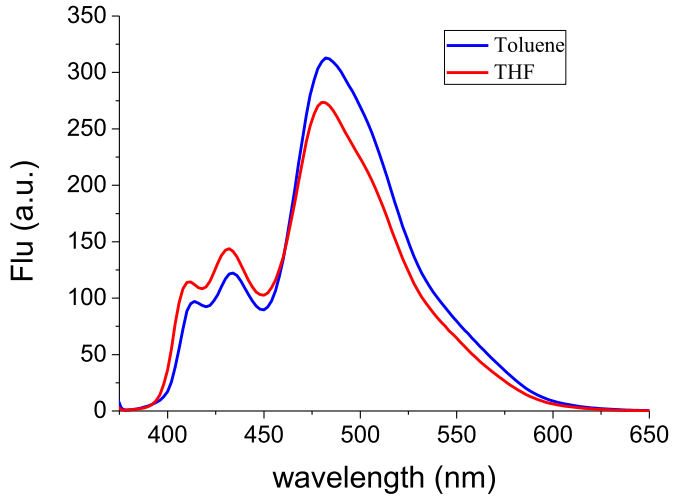



**Fig. 5.** Fluorescence of **1** in non-polar solution (10 μM), $\lambda_{ex} = 394$ nm.

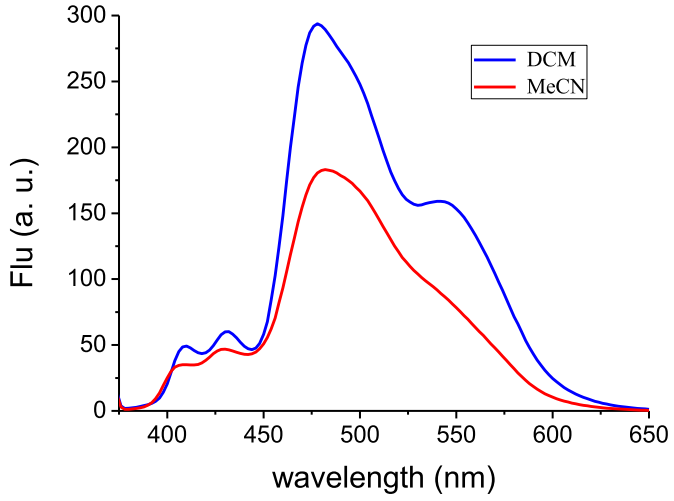



**Fig. 6.** Fluorescence of **1** in polar solution (10 μM), $\lambda_{ex} = 394$ nm.

absorption (394 nm) (Fig. 1). The large Stokes shifted emission suggests the occurrence of proton-transfer tautomer in **3**.

Second, fluorescence lifetime of **1** is also performed. It is found that the decay curves of both 474 nm and 550 nm are well fitted by biexponential decay pattern (Fig. 3 and Fig. 4). The decay at 474 nm exhibits two lifetimes $\tau_1 = 0.67$ ns and $\tau_2 = 2.40$ ns (Table 2), which indicates that there are two decay components. As compared to the fluorescence lifetime of **2** ($\tau = 0.69$ ns), it can be assumed that the short lifetime of **1** ($\tau_1 = 0.67$ ns) corresponds to normal Stokes shifted emission, and the long lifetime ($\tau_2 = 2.40$ ns) attributes to proton transfer emission. Measurement of fluorescence decay at 550 nm exhibits two long lifetimes $\tau_1 = 2.44$ ns and $\tau_2 = 3.63$ ns, the similar lifetime ($\tau_1 = 2.44$ ns) makes it reasonable to ascribe the $\tau_1 = 2.44$ ns to single proton transfer emission, and $\tau_2 = 3.63$ ns to double proton transfer emission.

The above spectroscopic results led to the suggestion that excited-state intramolecular proton transfer takes place in **1**, resulting in two types of proton transfer tautomers (Scheme 4) corresponding to emission maximized at 475 and 550 nm. The molecular structure of each isomer can be inferred from the control compound. Single and double proton transfer may proceed *via* synchronous or asynchronous types of double proton-transfer or even more complicated multiple pathways. Unfortunately, because of the lack of ultrafast time-resolved spectrometer, the mechanism of double proton transfer which undergoes one-step or stepwise process is unclear.

### 3.5. The effect of solvents on S-PT emission and D-PT emission

It is well known that excited state proton transfer emission is of great sensitivity to the surrounding medium [27–29]. The fluorescence of **1** in different solvents is conducted. It is found that **1** exhibits both S-PT emission and D-PT emission in either non-polar solvents such as THF and toluene (Fig. 5) or polar solvents such as DCM and MeCN (Fig. 6). Comparing the spectra in Fig. 5 with that in Fig. 6 finds that the D-PT emission in Fig. 5 is not as significance as that in Fig. 6, which suggests that the D-PT emission is influenced by solvents. In addition, it is also found that no or very weak emission is detected when **1** is in protic solvents such as MeOH, the quenched emission of **1** in MeOH probably results from the intermolecular H-bond between **1** and MeOH.

## 4. Conclusions

In summary, a symmetric molecule 2,5-bis(benzoxazol-2-yl) thiophene-3,4-diol which contains two enol units to explore single proton transfer and double proton transfer in the excited-state has been strategically designed and synthesized. It has demonstrated that 2,5-bis(benzoxazol-2-yl)thiophene-3,4-diol exhibits excited-state intramolecular single and double proton transfer emission. It has also demonstrated that solvents play a role in excitied-stated intramolecular proton transfer emission.

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