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Graphical abstract



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mechanisms and its applications in anti-counterfeiting measures

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Abstract: In this work, a series of 2-(2-hydroxyphenyl)benzothiazole (HBT) derivatives with an aggregation-induced emission-excited state intramolecular proton transfer (AIE-ESIPT) dual mechanism was synthesized. We systematically investigated their optical properties in solution, aqueous suspension, and the solid state. The fluorescence properties of these five compounds were highly dependent on the solvent environment. Particularly, DMSO and DMF were found to significantly promote deprotonation of the phenolic hydroxyl and favor fluorescence emission from the phenolic anion. The Keto or Enol forms generally could be transformed to phenolic anions with the aid of base in solution. The results from aggregation-induced emission enhancement (AIEE) and red-shifted AIE clearly illustrated the evolution process of the fluorescence spectra, indicating that the three luminescent species in the solution were transformable. The systematic investigation demonstrated that the desired fluorescence could be generated for HBT derivatives by varying the solvents or adding additives, such as base or water, to the solution. Because of the synergistic effect of AIE and ESIPT, these fluorophores exhibited high solid-state quantum yields and large Stokes shifts. These dyes also featured high photostability and tunable emission spectra covering most of the visible light region. Single crystal studies and theoretical calculations elucidated the luminescent properties. When loaded on filter paper, the HBT-based dyes exhibited high-efficiency fluorescence visualization and reversible solid-state luminescence switching under alternating amine and acid vapor treatments. These dyes were used on banknotes for anti-counterfeiting measures, demonstrating the practical applications of these molecules as security inks.

Keywords: HBT dyes; AIE-ESIPT dual mechanism; reversible solid-state luminescence; anti-counterfeiting ink; vapor response;

1. Introduction

Fluorescent dyes based on excited state intramolecular proton transfer (ESIPT) feature a large Stokes shift, unique dual emission, and special sensitivity to the external environment [1-3]. Over the past few decades, extensive spectroscopic and theoretical research has been performed to elucidate the photophysical processes and the structure-property relationships of ESIPT molecules [4-6]. As a representative ESIPT molecule, 2-(2-hydroxyphenyl)benzothiazole (HBT) possesses an intramolecular hydrogen bond between the phenolic hydroxyl and the benzothiazole ring [7,8]. The basic four-level photophysical cycle (E-E*-K*-K) of the system is illustrated in Figure 1. In the electronic ground state, HBT exists exclusively in the enol form (Enol) as a result of stabilization of the intramolecular hydrogen bond. Upon photoexcitation, an excited enol form (Enol*) is generated. Then, a fast proton transfer reaction accompanied by a tautomeric transformation from the Enol* to the excited keto form (Keto*) occurs because of the redistribution of electronic charge. The Keto* can radiatively decay to its ground state (Keto), followed by reverse proton transfer to revert to the Enol form. This fast four-level cycle in the HBT molecule usually brings about two emission bands: a short wavelength emission caused by the decay of Enol* to Enol (normal emission, Enol FL) and a longer one resulting from the Keto* form (Keto* form (ESIPT emission, Keto FL) [1,9,10].

< Insert Figure 1>

According to the ESIPT mechanism, the fluorescence properties of the HBT skeleton are highly dependent on the solvent environment because of the alterable intramolecular hydrogen bond. Some research has demonstrated that acids or bases in the solvent can change their fluorescence [11,12]. Reportedly, luminescent phenolic anions also could be generated as the deprotonation product of the phenolic hydroxyl when some HBT derivatives were dissolved in protic solvents like ethanol or encounter bases [13,14], which means that a new emission band would be observed. Therefore, it is possible for some HBT compounds to exhibit triple fluorescence under certain conditions. According to related literature reports, it could be concluded that compounds containing an ESIPT moiety generally would be expected to have three emission patterns (single emission, dual emission, and triple emission), depending on the molecular structure, solvent, and external additives. Recognizing how the transformation of several luminescent species in the solution of HBT derivatives occurs and

understanding how to adjust the multiple fluorescence emission have not been well explored up to now [14,15].

Recently, organic solid-state fluorescent molecules based on ESIPT have drawn significant attention because of their wide applications in optoelectronic devices [16, 17], chemical sensors [18,19], and bioimaging [20]. As ESIPT molecules possess both proton donor and acceptor groups, typical ESIPT molecules can be protonated or deprotonated depending on the pH of the solution. We envisioned that alkaline vapor could also react with the hydroxyl group of the HBT derivatives, leading to a fluorescence change. Such vapor-induced fluorescence responses are useful for detection of volatile organic compounds (VOCs) [21-23], anti-counterfeiting labels [24], and rewritable printing media [25]. For HBT-based dyes, however, investigation of their fluorescent response to alkaline or acidic vapor as well as their potential applications in a solid state have been rather limited.

In developing stimuli-responsive luminescent organic materials, a series of fluorescent molecules based on the HBT scaffold was designed and synthesized (Scheme 1). The phenol ring of HBT was modified with simple substituents, including hydroxyl, chloride, and bromine. Phenylcarbazole and triphenylamine moieties were also connected on the phenol ring to afford two HBT derivatives with extended aromatic conjugated systems. By careful modification of the phenol ring of the HBT core, a broad tuning range of fluorescence emission from 450 to 700 nm was achieved. Evaluation of the solvent effect demonstrated that DMSO and DMF more significantly facilitated normal enol emission than protic solvents. DMSO and DMF also were found to markedly promote deprotonation and to favor fluorescence emission from the phenolic anion. In our experiments, we succeeded in transforming the Keto or Enol forms to phenolic anions with the aid of a base. In a tetrahydofuran (THF) solution of these compounds, the addition of water contributed to aggregation-induced emission enhancement (AIEE), whereas in the DMSO solution, an increase in the water content caused an aggregation-induced red-shift emission. Through the AIE experiments, the transformation processes among the three luminescent species in the HBT derivative solutions were clearly observed-that is, the multiple fluorescence emission was adjustable. Thus, fluorescence color adjustment of a solution of HBT derivatives could be achieved simply by varying the solvents or introducing additives such as base or water to the solution.

HBT-based compounds, which exhibit highly emissive and photostable properties, provide a unique opportunity for solid-state sensing. The solid state of these fluorophores shows a sensitive fluorescent

response to amines and acetic acid vapor. Upon exposure of a dye-loaded filter paper strip to amine vapor, the fluorescence of the paper changed color. Removal of the amine gas or exposure to acetic acid vapor generated the original emission. The intensity ratios of the two fluorescence emission peaks remained nearly constant after at least five cycles, indicating a good fatigue resistance. HBT-based dyes have been shown to work as anti-counterfeiting fluorescent inks on banknotes. Therefore, we developed a vapor-triggered reversible luminescence-switching platform.

2. Experimental

2.1 Materials and instruments

All reagents were of analytical grade and obtained from commercial suppliers. Thin layer chromatography (TLC) silica gel plates (GF-254) and silica gel (200-300 mesh) for column chromatography were obtained from Qingdao Marine Chemicals, China. Deionized water was employed throughout all experiments. ¹H NMR and ¹³C NMR spectra were acquired on a Bruker AVANCE II 400 spectrometer (Bruker, Switzerland), respectively. High resolution mass spectra (HRMS) spectra were measured with a 6510-Q-TOF spectrometer (Agilent, USA). Single-crystal X-ray diffraction intensity data were recorded using a Bruker SMART 1000 CCD diffractometer (Bruker, Switzerland) with Mo-Ka radiation ($\lambda = 0.71073$ Å) at room temperature. The absolute fluorescence quantum yield (Φ_f) values of the solid were calculated on an Edinburgh Fluorescence Spectrometer FLS1000 using an integrating sphere (Edinburgh, England). The solid ultraviolet-visible (UV–visible) absorption spectra of the solution were recorded by a TU-1901 spectrometer (Beijing, China). Fluorescent measurements of the solution were performed on a Lengguang F97Pro FL Spectrophotometer (Shanghai, China). All spectra were recorded at room temperature. All theoretical calculations were carried out with GAUSSIAN 03 package [26].

2.2 Synthesis and characterization of compounds

Two types of HBT derivatives were synthesized. As shown in Scheme 1, three simple derivatives were prepared by directive condensation of the aromatic aldehydes with 2-aminothiophenol. Two derivatives with bulky aromatic amines, which were connected to the HBT core through a phenyl moiety, were synthesized by Suzuki coupling.

Synthesis of OHBT

OHBT was synthesized using the same procedure described in literature [27]. In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a solution of 2-Aminothiophenol (0.22 ml, 2 mmol), 2,4-dihydroxybenzaldehyde (304 mg, 2.2 mmol) and sodium metabisulfite (Na₂S₂O₅, 465 mg, 2.4 mmol) in dry DMF (10 mL) was prepared. After stirring with reflux for 2 hr, the reaction mixture was cooled and added slowly into water (20 mL). The precipitate was filtered off, washed with water (20 mL×3) and dried to give the crude product, which was further purified by recrystallization from methanol to afford a white solid (405 mg, yield 83.3%). Mp: 199-201°C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.67 (s, 1H), 10.17 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.94 (dd, *J* = 8.7 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.49 – 6.43 (m, 2H). The melting point and ¹H NMR spectrum were identical with that reported in the literature [27].

Synthesis of CHBT

CHBT was synthesized using the same method described in the literature [28]. In a round-bottomed flask (25 mL) equipped with a magnetic stirrer, a solution of 2-aminothiophenol (1.0 mmol, 126 mg) and 5-chlorosalicylaldehyde (1.1 mmol, 171 mg) in ethanol (10 mL) was prepared. Aq. 37% HCl (3 mmol, 0.5 mL) was gradually added to the mixture, followed by aq. 30% H₂O₂ (6 mmol, 0.63 mL). The mixture was then stirred at room temperature. When the starting materials had completely disappeared as monitored by TLC (eluent: petroleum ether /EtOAc = 30:1), the mixture was quenched by H₂O (10 mL), extracted with EtOAc (10 mL×3), and the combined extracts were dried over anhydrous Na₂SO₄. After removal of solvents, the crude product was purified by silica gel chromatography (eluent: petroleum ether/EtOAc = 30:1) to give the desired compound as a white solid (210 mg, yield 79.8%). Mp: 152–154 \Box . ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.69 (s, 1H), 8.25 (d, *J* = 2.4 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 1H). The ¹H NMR spectrum was identical with that reported in the literature [29].

Synthesis of DHBT

DHBT was synthesized according to a procedure similar to CHBT. White solid (270 mg, yield 63.8%). Mp: 149-151 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 12.80 (s, 1H), 8.23 (d, J = 7.9 Hz, 1H), 8.19 – 8.07 (m, 2H), 7.96 (m, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H). The ¹H NMR spectrum was identical with that reported in the literature [29].

Synthesis of HCP

In a round-bottomed flask (25 mL) equipped with a magnetic stirrer, a solution of

2-(benzo[d]thiazol-2-yl)-4-bromophenol (306 mg, 1 mmol) in THF (10 mL) was prepared. Then, K₂CO₃ (2 mM in water, 2 mL) was added under a nitrogen atmosphere. Next, [4-(9H-carbazol-9-yl)phenyl]boronic acid (288 mg, 1 mmol) was put into the mixture, and after stirring at room temperature for 10 minutes, Pd(PPh₃)₄ (58 mg, 0.05 mmol) was finally added to the solution. The mixture was stirred at 80^{\Box} for 8 hr. After completion of the reaction (monitored by TLC), the mixture was quenched by adding H₂O (5 mL). The aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. The organic layer was concentrated under vacuum and allowed to crystallize. The precipitate was collected to obtain an orange solid (270 mg, 57.6% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.75 (s, 1H), 8.63 (d, *J* = 2.2 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 2H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (dd, *J* = 9.1, 4.6 Hz, 5H), 7.38 – 7.22 (m, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 64.81, 156.53, 151.97, 140.61, 139.05, 136.24, 135.24, 131.44, 131.26, 128.41, 127.65, 126.94, 126.78, 125.57, 123.28, 122.77, 122.49, 121.04, 120.59, 119.64, 118.24, 110.22. HRMS (ESI) calcd for [M+H]⁺ 469.1375, found: 469.1370.

Synthesis of HTPA

HTPA was synthesized according to a procedure similar to HCP. The crude product was purified by silica gel chromatography (eluent: petroleum ether/EtOAc = 40:1) to give the desired compound as a yellow solid (423 mg, 90% yield): ¹H NMR (400 MHz, DMSO- d_6). δ 11.61 (s, 1H), 8.43 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 4H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.08 (t, *J* = 9.0 Hz, 8H). ¹³C NMR (100 MHz, DMSO- d_6) δ 169.52, 165.05, 155.98, 151.94, 147.62, 146.81, 135.12, 134.17, 131.91, 130.85, 130.06, 127.80, 126.92, 126.28, 125.53, 124.41, 124.31, 123.56, 122.70, 122.46, 119.37, 118.06. HRMS (ESI) calcd for [M+H]⁺471.1531, found: 471.1529.

2.3 UV-visible absorption and fluorescence measurements

Stock solutions of HBT derivatives (10 mM) were prepared in analytical grade tetrahydrofuran (THF). The test solutions (50 μ M) were prepared by adding aliquots (50 μ L) of the stock solution to 10 mL volumetric flasks, followed by filling volumetric flasks with different solvents. All spectra were

recorded at room temperature.

2.4 Aggregation-induced emission enhancement (AIEE) measurements

Stock solution of HBT derivatives (10 mM) were prepared in analytical grade THF. Aliquots (50 μ L) of the stock solution were added to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under shaking to give 5 \times 10⁻⁵ M solutions with different water contents (0-99 vol %). The UV-visible and photoluminescent measurements of the resultant solutions were then performed immediately at room temperature.

2.5 Measurement of the fluorescence switching on a filter paper strip loaded with fluorescence dyes

2.5.1 Preparation of the filter paper strip loaded with fluorescence dyes

The dye-loaded filter paper was prepared by dropping 15 μ L of a pre-mixed THF solution of tested compounds (50 μ M) on a small piece of filter paper and drying under air for 24 hr.

2.5.2 Measurement of fluorescence switching

The amine vapors were prepared by charging amines $(15 \ \mu L)$ in a quartz cell (O.D = 1 cm, height = 4 cm), and then saturating the cell with a tightly closed lid over 0.5 hr. The acetic acid (AcOH) vapor was prepared according to the same procedure.

The dye-loaded filter strips were fastened on a small glass plate that was put in a quartz cell. The cell with the plate was positioned on a solid sample holder of the fluorescence spectrometer. The strips were fumed in amine vapor for 30 s and then their fluorescence spectra were measured. The filter strips were taken out, dried for 1 min with a hair dryer, and then put in the AcOH vapor for 30 s. The fluorescence spectra were then recorded and this procedure was repeated several times.

< Insert Scheme 1>

3. Results and discussion

3.1 Ultraviolet-visible absorbance properties and fluorescence characteristics

The optical properties of the five HBT derivatives in the solid state and in solvents of different polarities were investigated by ultraviolet-visible (UV-visible) and fluorescence spectroscopy. All of the compounds showed a strong absorption band between 280 and 370 nm in various solvents. In the

solid state, compounds **HCP** and **HTPA** exhibited absorption maxima at 396 and 418 nm, respectively, which were red shifted compared with the absorption peaks in solvents (Table 1 and Figure S1 in the Supporting Information).

After studying the absorption properties of the HBT derivatives, their emission behaviors in the solid state were examined. All of the compounds were highly emissive in the solid state (Table 1). Figure 2a illustrates the emission spectra of these compounds in the solid state. The emission maxima of **OHBT**, **CHBT**, and **DHBT** were located at 502, 526, and 536 nm, respectively. As expected, **HCP** and **HTPA** showed red shifts in the emission spectra because of the extended aromatic conjugation system and the emission maxima appeared at 560 nm for **HCP** and 588 nm for **HTPA**. The emission spectra of these solid samples covered the visible light region from 450 nm to 700 nm. Figure 2a presents the solid-state luminescence images of the crystalline powders illuminated under UV light ($\lambda_{ex} = 365$ nm). These samples have emission colors ranging from cyan to orange red.

The photostability of the solid HBT derivatives were then evaluated by time-progression fluorescence measurements. As shown in Figure 2b, the fluorescence intensity of these five compounds remained almost constant under continuous in situ UV irradiation (1 hr), which was indicative of the good solid-state photostability exhibited by these compounds.

< Insert Figure 2>

As mentioned, the ESIPT process is quite sensitive to the solvent environment. In a preliminary test, **HTPA** had a highly solvent-dependent fluorescence and single, dual, or triple emission could be achieved by varying the solvent. For compounds containing an ESIPT moiety, having two emission patterns (single broad emission and dual emission) generally was expected. A few HBT derivatives also have been reported to show the triple fluorescence phenomenon, which has indicated the coexistence of the enol, keto, and phenolic anions. The spectral evolution process of the multiple fluorescence, as well as the solvent effect on the generation of phenolic anions, have not been explored very well [13, 14]. Therefore, a thorough fluorescence spectral investigation of **HTPA** in various solvents was first performed to obtain a detailed elucidation of the process (Figures 3, Figure S2 and Figure S3). As shown in Figures 3a and 3b and Figure S2, **HTPA** showed weak fluorescence emission in all of the organic solvents except DMSO and DMF. **HTPA** exhibited dual fluorescence at ~408 nm

and ~585 nm in non- and weakly polar solvents (hexane, toluene, and dichloromethane), which were ascribed to the Enol FL and Keto FL, respectively; the Keto forms were more prominent in the spectra in these solvents. In THF, two fluorescence peaks at 440 nm and 580 nm could be attributed to the Enol FL and Keto FL, respectively, and the Enol form was dominant. A triple fluorescence (centered at ~412, ~500, and ~583 nm) phenomenon was observed for HTPA in ethyl acetate, acetonitrile, methanol, and ethanol; the two emission peaks at ~412 and ~583 nm were attributed to the corresponding Enol and Keto forms, respectively. In sharp contrast, HTPA emitted a very strong bluish green fluorescence around 507 nm in polar aprotic solvents, such as DMSO and DMF. With increased solvent polarity, generally, the fluorescence spectral profiles gradually evolved from dual fluorescence (at ~420 and ~580 nm) to triple fluorescence (at ~412, ~500, and ~583 nm), and finally a strong single fluorescence at 507 nm dominated the entire emission spectrum. Compared with the other solvents, DMSO and DMF showed high stabilization ($\epsilon \sim 47$ for DMSO; $\epsilon \sim 36.7$ for DMF). The basic natures of DMSO and DMF are also beneficial to the deprotonation process. Therefore, we believe that the strong emission around 507 nm for HTPA originated from the phenolic anion form of HTPA that was generated because of the deprotonation induced by the intermolecular H-bond between the phenolic hydroxy and the solvent molecules. To present solid evidence of the generation of the anion, the ultraviolet absorption and fluorescence emission spectra of HTPA when titrated with piperidine (from 0 to 3 equiv.) in DMSO were monitored. As shown in Figures 4a and 4b, with the addition of the base, the very weak original absorption band at 440 nm became strong and gradually moved to 431 nm, which could be assigned to the absorption of the phenolic anion. Meanwhile, in the fluorescence spectra, the emission peak at 507 nm increased significantly and reached its maximum intensity when the amount of piperidine was 3 equivalents. The changes in the fluorescence spectra indicated that the presence of base was favorable for phenolic anion formation. Based on the experimental results and related literature, it would be reasonable to assign the fluorescence emission at 507 nm to the phenolic anion of HTPA.

For **DHBT**, a moderate emission at ~535 nm in hexane, toluene, dichloromethane, and acetonitrile was observed, which was attributed to the Keto FL of **DHBT** (Figure 3e). In THF, a dual fluorescence at 410 nm and 540 nm appeared; the fluorescence peak at 540 nm was attributed to the Keto FL and the very weak emission at 410 nm was ascribed to the Enol FL. In ethanol and DMSO, **DHBT** exhibited a dual fluorescence at ~462 nm and ~535 nm, which originated from the phenolate anion and Keto forms,

respectively. **DHBT** emitted a single fluorescence at ~462 nm in methanol and DMF, which arose from the phenolic anion form. To verify the generation of the phenolic anion, the emission spectra of **DHBT** when titrated with piperidine (from 0 to 5 equiv.) in acetonitrile (CH₃CN) was recorded. As shown in Figure 4c, upon the addition of the base, the peak at 530 nm decreased gradually and a new fluorescence band centered at 470 nm emerged and increased progressively with a well-defined isosbestic point at ~520 nm. When 3 equivalents of piperidine were added, the emission intensity at 470 nm reached its maximum value and a single fluorescence peak was formed.

For **HCP**, an emission band at ~550 nm was observed in hexane, toluene, and dichloromethane, which was assigned to the Keto FL (Figure 3f). For the ethanol solution of **HCP**, a strong emission at 417 nm appeared, accompanied by a weak peak at 540 nm, and the peak at 417 nm belonged to the Enol FL of **HCP**. **HCP** exhibited intense dual fluorescence at ~417 nm and ~483 nm in DMSO and DMF, which were attributed to the Enol and phenolic anion forms, respectively. Furthermore, titration experiments with piperidine in DMSO were conducted to demonstrate the generation of the phenolic anion. As the amount of base increased, the peak at 418 nm consistently decreased and, simultaneously, the peak at 483 nm gradually was enhanced with a clean isosbestic point at 460 nm. Finally, a strong emission band centered at 487 nm dominated the entire spectrum (Figure 4d).

OHBT showed almost no fluorescence in the visible region in all solvents. A weak emission band appeared at around 500 nm in dicholoromethane and toluene (Figure 3c). In DMSO and DMF, a strong single fluorescence peak was observed at ~383 nm. The two emissions were ascribed to Enol FL and Keto FL, respectively. The generation of the phenolic anion was also verified by titration experiments in DMSO (Figure S4a). A new peak at ~447 nm emerged and became stronger at the expense of the band at 384 nm upon the addition of piperidine. Because of the weak acidic property of **OHBT**, the band at 384 nm could not be transformed completely to the new band, even if a large amount of base was added. As a result, the dual fluorescence was retained.

For **CHBT** in hexane, toluene, and dichloromethane, an emission was observed at ~530 nm, which could be attributed to Keto FL. **CHBT** exhibited dual fluorescence at ~390 nm and ~470 nm in polar solvents (DMSO, DMF, methanol, and ethanol), which was ascribed to the Enol and phenolic anion forms, respectively (Figure 3d). The generation of the phenolic anion was also demonstrated by titration experiments in DMF (Figure S4b). As the amount of piperidine was raised, the peak at 390 nm showed a consistent decrease; meanwhile, the peak at 470 nm was gradually elevated and a

well-defined isosbestic point at 451 nm was observed. When 60 equivalents of piperidine were added, the band at 390 nm was almost totally consumed and a strong emission band centered at 473 nm dominated the whole spectrum.

< Insert Figure 3>

< Insert Figure 4>

< Insert Figure 5>

The systematic investigation of the luminescent properties of the five compounds in a variety of solvents showed that non- or weakly polar solvents favored the ESIPT process and long-wavelength emission from the Keto form, which agreed with literature reports [13]. Most of the compounds dissolved in DMSO and DMF were found to exhibit a much more significant hindering of the ESIPT process, facilitating normal emission from the Enol form. DMSO and DMF also significantly enhanced deprotonation, promoting the phenolic anion fluorescence. For example, the fluorescence emission originating from the phenolic anion of **HTPA** contributed to strong single peaks in DMSO and DMF. In our experiments, the alkaline additive facilitated the dissociation of the phenolic hydroxyl group and consequently gave rise to a remarkable enhancement of the emission from the phenolate form. Notably, we succeeded in transforming Keto or Enol forms to phenolic anions with the aid of a base. A possible mechanism is proposed in Figure 5, which shows the excited state structures generating different emission wavelengths.

In contrast to the very solvent-dependent fluorescence properties in solution, these compounds all exhibited a strong emission in the solid state, which was assigned to the Keto form fluorescence. As shown in Table 1, the solid-state samples showed higher fluorescence quantum yields than those in solution. To understand the relationship between the aggregated state and the fluorescence quantum efficiencies, aggregation-induced emission (AIE) studies were performed.

3.2 Aggregation-induced emission enhancement properties

Normally, AIE luminophores exhibit stronger emission in the aggregated state than in the dispersed state. Because all of these HBT derivatives showed weak fluorescence in pure THF, the AIE features in

a THF/H₂O mixture were examined first. The fluorescence characteristics of **OHBT** in the mixed water/THF solvents (water fraction (f_w) ranging from 0% to 99%, v/v) were studied (Figure 6a). In pure THF, **OHBT** had very weak fluorescence at 375 nm. When water was added, the emission intensity increased rapidly, accompanied with gradual red shifts, which reached its maximum at 70% water content. When the $f_w \ge 80\%$, the emission peak at 385 nm weakened continually and, simultaneously, a new emission at ~438 nm emerged and consequently dominated the spectra, thus resulting in a dual fluorescence (385 and 438 nm). Based on the previous conclusions about the solution phase, the two peaks (385 and 438 nm) were ascribed to the Enol and phenolic anion forms, respectively.

Changes in the fluorescence spectra of **CHBT** in the THF/H₂O mixture were also recorded (Figure 6b). **CHBT** exhibited very weak green fluorescence in THF. When water was added, the intensity of blue fluorescence emission at 471 nm increased rapidly and reached its maximum at 60% water content. Once the f_w was beyond 70%, the peak at 471 nm decreased sharply, a new emission around 521 nm emerged and, finally, green fluorescence dominated the spectrum. The two peaks (471 and 521 nm) were attributed to the phenolic anion and Keto forms, respectively.

DHBT showed a medium fluorescence emission at 538 nm in THF. As shown in Figure 6c, when water was added, the emission peak at 538 nm blue shifted slightly (521 nm), and a new fluorescence emission around 471 nm appeared. Thus, a dual fluorescence (471 and 521 nm) was observed. When the $f_w > 50\%$, the emission peak at 471 nm was dramatically elevated. Interestingly, as the water fraction increased to 80%, the fluorescence peak at 538 nm was recovered, accompanied by a decrease of the emission band at 471 nm. As the water content increased further, the yellow green fluorescence was obviously enhanced, and a single peak was formed. The two peaks (471 and 538 nm) were attributed to the phenolic anion and Keto forms, respectively.

For **HCP**, there was a weak dual fluorescence (402 and 556 nm) in THF (Figure 6d). When the $f_w =$ 10%, the emission at 402 nm increased significantly and red shifted to 411 nm; meanwhile, the peak at 556 nm was replaced by a new strong emission band at 480 nm. With an increase in the water fraction (20% to 50%), the peak at 411 nm gradually decreased. Simultaneously, the peak at 480 nm was continually enhanced, and a well-defined isosbestic point at 440 nm was observed. When the f_w increased further (60% and 70%), the fluorescence peak at 556 nm reappeared, yielding a triple fluorescence (411, 480 and 556 nm). The three peaks (411, 480, and 556 nm) were attributed to the Enol, phenolic anion, and Keto forms, respectively. When the f_w ranged from 80% to 99%, a strong

single emission at 556 nm was obtained.

HTPA exhibited a weak dual fluorescence (440 and 580 nm) in THF (Figure 6e). In the mixtures with a low water fraction (0 to 20%), the emission at 440 nm red shifted to 480 nm and increased dramatically. Then, the peak continued to decrease as the water content was increased further (30 to 60%). Once the f_w was beyond 70%, the mixture exhibited a consistent increase in the peak at 580 nm and, finally, a strong single emission around 580 nm was observed. The two peaks (480 and 580 nm) were attributed to the phenolic anion and Keto forms, respectively. When the $f_w = 99\%$, the fluorescence intensity decreased because of aggregate precipitates.

In the THF/H₂O mixtures, the addition of water caused the fluorescence emission intensity of the tested solutions to increase significantly. When the f_w was higher than 70%, the aggregated states of the HBT derivatives typically were preferred because of their insolubility in water, in which the intramolecular hydrogen bonds were stable. As a result, an ESIPT process occurred, leading to a fluorescence emission from the Keto form (i.e., an AIE emission). During the AIE process, all of the compounds experienced a dual or triple fluorescence process and the emission bands gradually red shifted with the elevation of water content. Finally, the aggregation of dye molecules in the aqueous solution resulted in emission spectra similar to that in the solid state, except for **OHBT**.

More evidence for the aggregation of HBT derivatives in aqueous solution was obtained from the absorption spectra. As shown in Figure S5, level-off tails can be observed in the UV absorption spectra as the f_w values increase, which were due to light scattering of the aggregated suspensions.

The AIE study was also carried out in DMSO/H₂O mixtures. All of the compounds exhibited aggregation-induced red-shift emission. For **OHBT**, with the increase of the water fraction, a strong single fluorescence at 384 nm (Enol FL) gradually decreased and a new emission at ~440 nm (phenolic anion form) emerged. Then, a third emission band at ~480 nm (Keto FL) was detected. Finally, triple fluorescence with a wide spectrum was generated (Figure S6a). Thus, in DMSO/H₂O mixtures, **OHBT** exhibited red-shift AIE emission and simultaneously experienced an emission evolution from single, to dual, and finally to triple fluorescence as the water content increased. The evolution processes among the enol, phenolic anion, and Keto forms were also observed for **CHBT**, **DHBT**, and **HCP** (Figure S6b, Figure S6c, and Figure S6d) and, finally, a strong single emission in the long wavelength region was obtained with high water content. **HTPA** showed a strong single fluorescence at 507 nm (phenolic anion form) in DMSO. For **HTPA**, the complete transformation from the phenolic anion to the Keto

form was attained by progressively increasing the water content in DMSO, thus resulting in a single emission at 580 nm (Figure S6e).

The AIEE and aggregation-induced red-shift emission indicated that the three luminescent species in the solutions of the HBT derivatives were transformable—that is, the multiple fluorescence emission was adjustable. Based on this inspiring phenomenon, it would be very convenient to generate the desired fluorescence simply by adding a certain amount of water to a solution of the HBT derivatives.

< Insert Figure 6>

3.3 Structural analysis

To understand the relationship between the solid-state fluorescence properties and the structural characteristics, single-crystal studies were performed. A single crystal of **OHBT** was obtained by slow evaporation of an **OHBT** solution in a petroleum ether/ethyl acetate mixture at room temperature. Suitable **CHBT** and **HTPA** single crystals were produced through a crystallization process in a refrigerator in a similar solvent system. Several attempts were made to develop single crystals of the other two compounds, but suitable samples for X-ray analysis could not be obtained.

The single-crystal X-ray diffraction studies showed that **OHBT** and **CHBT** were almost planar with small dihedral angles (1.33° and 1.20°) between the benzothiazole heterocycle and phenol ring (Figure 7a and Figure 8a). Both compounds had strong intramolecular H-bond interactions with the same distance (1.88 Å), which accounted for the coplanar conformation. In contrast to **OHBT** and **CHBT**, **HTPA** had a larger dihedral angle (15.04°) between the benzothiazole and phenol ring. In the **HTPA** crystal, the length of the intramolecular H-bond between the hydroxyl and the benzothiazole ring was 1.92 Å, which was slightly longer than that of **OHBT** and **CHBT** (Figure 9a). The strong hydrogen bonding was beneficial to the stabilization of the enol form in the ground state. In the ESIPT process, the excited enol form transformed to the excited keto tautomer.

In the **OHBT** crystal, the molecules aggregated into molecular chains based on a strong intermolecular H-bond (2.29 Å) (Figure 7b) between the 4-hydroxy groups on the benzenes of two molecules. The chains were connected into a molecular sheet by C-H…O interactions (2.60 Å) (Figure 7c), along with π - π stacking interactions with a contact distance of 3.67 Å (Figure 7d). The molecular

sheets were held together by three strong C-H $\cdots \pi$ interactions (2.67 Å, 2.77 Å and 2.95 Å) to form the 3D structure (Figures 7e and 7f, and Figure S7).

< Insert Figure 7>

< Insert Figure 8>

The planar **CHBT** molecules was arranged into molecular columns through three weak intermolecular face-to-face π - π stacking interactions with contact distances of 3.82 Å, 3.75 Å, and 3.70 Å (Figure 8b). In the columns, molecules were parallel with slight twisting and the orientations of adjacent molecules were essentially opposite. The benzothiazole moieties of adjacent molecules did not completely overlap. The molecular columns were linked together by C-H…O (2.73 Å) and C-H…Cl (2.89 Å) interactions, resulting in the formation of a 3D structure (Figure 8c and Figure S8).

The noncovalent intermolecular interactions could be a factor affecting the low fluorescence quantum efficiency. **OHBT** and **CHBT** exhibited different packing modes in the single crystals. In **OHBT** crystals, various types of intermolecular interactions existed (O-H···O, C-H···O, C-H···· π and π - π) and the O-H···O (2.29 Å) and C-H···O (2.60 Å) interactions were particularly strong. The three C-H··· π interactions played an essential role in linking the two-dimensional molecular sheets together. As compared with **OHBT**, the molecular packing structure feature of **CHBT** was based on weak π - π stacking and modest intermolecular H-bonds. The orientations of neighboring molecules avoided maximum face-to face overlap, causing the quenched emission. These observations could be responsible for the higher quantum efficiency ($\Phi_f = 82\%$) of **CHBT** in the solid state.

< Insert Figure 9>

Two strong C-H··· π interactions (2.89 Å) between H15 and the benzothiazole cycle were observed in the crystal lattice of **HTPA** that led to the formation of a dimer with exactly opposite dipoles (Figure 9c). The terminal benzene of the triphenylamine unit formed two C-H··· π interactions (2.91 Å and 3.20 Å) with two neighboring molecules from different dimers, which played an important role in holding the adjacent molecules together (Figures 9c and 9d).

Incorporation of a triphenylamine moiety on the HBT core triggered a marked effect on the molecular structure. In the **HTPA** molecule, the dihedral angle between the triphenylamine moiety and the HBT plane was 41.56° in the aggregated state (Figure 9b). As noted previously, **HTPA** exhibited a large dihedral angle (15.04°) between the benzothiazole and phenol ring, while it was close to 0° for **OHBT** and **CHBT**. The twisted structure of **HTPA** led to a lower fluorescence quantum yield ($\Phi_f = 21\%$) as compared with **OHBT** and **CHBT**.

3.4 Computational studies

To gain further insights into the luminescent behaviors of the compounds, density functional theory calculations were performed at the B3LYP/6-31G (d, p) level [26]. The molecular orbitals of the compounds are shown in Figure 10 (only HOMO and LUMO are presented). The LUMO distributions of the five compounds were very similar, whereas those of the HOMO were different as a result of the different substituents and substituted positions on the phenol ring. **OHBT**, **CHBT**, and **DHBT** were molecules with simple substituents on the phenol ring. Compared with **OHBT**, which had a hydroxyl group, the halogen-substituted molecules showed smaller energy gaps, resulting in a red shift of the emission spectra.

For **HCP** and **HTPA**, incorporation of the phenylcarbazole and triphenylamine moieties to the 4-position of benzene extended the length of the π -conjugation system, which gave rise to significantly increased HOMO energy levels. Consequently, the energy gaps decreased, and the emission spectra exhibited a red shift compared with the three simpler compounds.

< Insert Figure 10>

3.5 Tunable solid-state emission by external stimuli

The fact that the deprotonation products of the HBT derivatives are highly emissive in solution has been demonstrated. However, the response of the solid-state HBT compounds to alkali vapor, thus far, has received little attention [20]. The products were exposed to amine vapor and the fluorescence of the solid sample blue shifted and emitted another color. The vapor-fumed samples could regain their original emission state when exposed to ambient air as the vapors volatized. The strong solid state and switchable fluorescence prompted us to conduct vapor-responsive experiments using a filter

paper-supported sample to explore the practical applications. **OHBT** was investigated first. The dye-loaded filter paper strip was prepared by dropping the **OHBT** solution on filter paper and air-drying. The change and recovery of the **OHBT** fluorescence spectra are shown in Figures 11a and 11b. **OHBT** on filter paper emitted cyan light centered at 485 nm under UV illumination (365 nm), which arose from the Keto form. Upon exposure to piperidine vapor for 30 s, the emission color of the paper strip changed to blue centered around 430 nm, which was close to that of the phenolic anion formed in the alkaline solution, thus replicating the solution behavior. When exposed to ambient air, the blue-shifted fluorescence returned to its original state within 4–6 hr. Note that fuming with acetic acid vapor could reduce the recovery time to 30 s. The peak wavelength difference of the two emission spectra was about 55 nm. The fatigue resistance of the sample-loaded filter papers was evaluated by repeatedly switching between the cyan and blue emissive states. The fluorescence intensity ratios remained nearly unaltered, without obvious degradation after five cycles, demonstrating a good fatigue resistance (Figures 11a and 11b).

The other HBT derivatives displayed similar four vapor-responsible reversible fluorescence-switching behavior on the filter paper strips. The peak wavelength differences of the two emission spectra ranged from 60 nm to 85 nm. For all compounds, the fluorescence changes provided clear signal and high contrast (insets in Figure 12b to Figure 15b). Such vapor-induced fluorescence switching also could be reproduced without apparent fatigue (Figures 12-15). Notably, the HTPA-loaded on filter paper exhibited a clear selectivity in response to a variety of amine vapors. As can be seen in Figure 16, under the same conditions, only piperidine and pyrrolidine triggered the blue shift of the initial fluorescence. Other common aliphatic amines, aniline, pyridine, and ammonia only caused quenching of the fluorescence intensity at 585 nm, indicating its potential for use in basic vapor sensors owing to the obvious fluorescence visualization recognition.

> < Insert Figure 11> < Insert Figure 12> < Insert Figure 13> < Insert Figure 14> < Insert Figure 15> < Insert Figure 16> 17

3.6 Application as an anti-counterfeiting ink

Fluorescent materials have been incorporated onto banknotes and trademarks and are used widely as anti-counterfeiting labels. Because of the light color, high fluorescent brightness, and photostability of the HBT derivatives, developing these dyes into anti-counterfeiting fluorescent inks is attractive. To illustrate that HBT-based dyes can be used as fluorescent inks, the letters "HBT" were written on a practice banknote with a THF solution of HCP (10 mM), which was invisible under daylight but highly emissive under UV light (Figure 17). Reversible fluorescence-switchable dyes further increased security. Amine vapors have long been employed to reveal anti-counterfeiting ink by inducing fluorescence or color formation [24,30]. Exposure to the amine vapor triggered an obvious fluorescence color change on the practice banknote, which could be distinguished with the naked eye. Leaving the banknote under ambient air for several minutes allowed the original fluorescent color to be recovered. There were no obvious color changes in the letters "HBT" in daylight after the recovery. The amine vapor-induced fluorescence switching was quick and could be reproduced many times, which increased the complexity of the anti-counterfeiting performance compared with the common single-color fluorescence dyes. Recently, biluminescent or multicolor luminescent materials have been developed for anti-counterfeiting measures [31-33]. Two or three excitation sources, however, were required for these materials. Thus, the cost of excitation sources and the complexity of the preparation process limited the scope of their potential applications. To the best of our knowledge, amine vapor-responsive reversible fluorescence-switchable anti-counterfeiting dyes seldom exist in the literature. In addition to HCP, the other molecules showed similar fluorescence-switchable behavior on practice banknotes (Figures S9-S12). These experiments demonstrated that HBT-based dyes as fluorescent inks have significant potential for use in high-security anti-counterfeiting labels.

< Insert Figure 17>

4. Conclusions

A series of AIE-ESIPT dual mechanism-based HBT derivatives were synthesized. A systematic comparison in a variety of solvents showed that the fluorescence properties of these compounds were

quite sensitive to the solvent environment. DMSO and DMF greatly influenced the deprotonation of the phenolic hydroxyl, thus favoring fluorescence emission from the phenolic anion. In solution, the Keto or Enol forms could generally be transformed to the phenolic anion with the aid of a base. These molecules exhibited high solid-state quantum yields and large Stokes shifts, and the emission spectra of these solids covered most of the visible light region. The HBT-based dyes showed AIEE in THF/H₂O mixtures, as well as aggregation-induced red-shift emission in DMSO/H₂O mixtures. Through the AIEE and red-shift AIE experiments, the fluorescence spectral evolution process was clearly observed. Based on these results, we concluded that the three luminescent species in the HBT derivative solutions were transformable and, therefore, the fluorescence emission was adjustable. Single crystal studies and theoretical calculations were conducted to elucidate the luminescent properties. HBT-based dyes exhibited vapor-responsible reversible fluorescence-switching behavior on filter paper strips. Upon exposure to amine and acid vapors, the distinct fluorescence color changes were clear enough to be recognized by the naked eye. Finally, we successfully demonstrated the applications of these molecules as anti-counterfeiting fluorescent inks on banknotes.

Acknowledgement

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Table

	Tuore I. Buillin	ary or the	optical p	operates	011121 0	0111 441 1 05	
Compounds	Medium	λ_{Abs}	λ_{ex}	λ_{em}	Stokes	Stokes	Quantum
		[nm]	[nm]	[nm]	shift	shift	efficiency
					[nm]	[cm ⁻¹]	$arPsi_f$ [%]
OHBT	Solid	377	350	502	125	6604	25 ^[a]
	Toluene ^[b]	291	325	505	214	14562	2.8 ^[c]
	EtOH ^[b]	344	325	385	41	3095	17.3 ^[c]
		291			94	8390	
	DMSO ^[b]	292	325	385	93	8273	68 ^[c]
СНВТ	Solid	340	360	526	130	10400	82 ^[a]
	Toluene ^[b]	396	360	532	136	6456	6.2 ^[c]
	EtOH ^[b]	288	360	534	246	15995	9.7 ^[c]
		345			189	10259	
	DMSO ^[b]	294	360	474	180	12917	65 ^[c]
		342			132	8142	
DHBT	Solid	378	355	536	148	7798	31 ^[a]
	Toluene ^[b]	299	355	538	239	14857	
		356			182	9503	24.1 ^[c]
	EtOH ^[b]	294	355	534	240	15287	12.9 ^[c]
		346			188	10175	
	DMSO ^[b]	295	355	471	176	12667	11.8 ^[c]
		348			123	7504	
НСР	Solid	396	365	560	164	7395	70 ^[a]
	Toluene ^[b]	295	365	553	258	15815	9.6 ^[c]
	EtOH ^[b]	295	365	403	108	9084	
				552	257	15782	18.1 ^[c]
	DMSO ^[b]	292	365	420	128	10437	65 ^[c]
				483	191	13542	
HTPA		418	360	588	170	6916	21 ^[a]

Table 1. Summary of the optical properties of HBT derivatives

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	Solid	319	360	449	130	9076							
	Toluene ^[b]			585	266	14254	7.4 ^[c]						
		318	360	582	264	14264	7.5 ^[c]						
	EtOH ^[b]	321	360	505	184	11350	53 ^[c]						
	DMSO ^[b]												

[a] Absolute quantum yields in the solid state. [b] Measured from 5×10^{-5} M solution. [c] Quantum

yields measured by relative method using quinine sulphate standard (10^{-5} M) .

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A reversible vapor-responsive fluorochromic molecular platform based on coupled AIE-ESIPT

mechanisms and its applications in anti-counterfeiting measures

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Figures and Schemes

Figure 1 Schematic representation of four-level ESIPT photocycle of HBT.

Figure 2 (a) Fluorescence-emission spectra of HBT derivatives in their crystalline states and images of the corresponding crystals under 365 nm UV light. (b) Photostability evaluation of HBT derivatives in their crystalline states.

Figure 3 Fluorescence spectra and image of HBT derivatives (50 μ M) in different solvents. (a) **HTPA**, $\lambda_{ex} = 360 \text{ nm.}$ (b) Fluorescence image of **HTPA**, $\lambda_{ex} = 360 \text{ nm.}$ (c) **OHBT**, $\lambda_{ex} = 325 \text{ nm.}$ (d) **CHBT**, $\lambda_{ex} = 360 \text{ nm.}$ (e) **DHBT**, $\lambda_{ex} = 355 \text{ nm.}$ (f) **HCP**, $\lambda_{ex} = 365 \text{ nm.}$

Figure 4 Changes of (a) UV-vis absorption of **HTPA** in DMSO, (b) fluorescence spectra of **HTPA** in DMSO, (c) fluorescence spectra of **DHBT** in CH₃CN and (d) fluorescence spectra of **HCP** in DMSO with the addition of piperidine. The concentrations are 5×10^{-5} mol/L.

Figure 5 Excited state structures proposed for the multifluorescence emissions of HBT derivatives in different solvents.

Figure 6 Fluorescence spectra of (a) **OHBT** ($\lambda_{ex} = 325 \text{ nm}$), (b) **CHBT** ($\lambda_{ex} = 360 \text{ nm}$), (c) **DHBT** ($\lambda_{ex} = 355 \text{ nm}$), (d) **HCP** ($\lambda_{ex} = 355 \text{ nm}$) and (e) **HTPA** ($\lambda_{ex} = 360 \text{ nm}$) in THF/H₂O mixtures with different water fractions (f_w). The concentrations of compounds are 5 × 10⁻⁵ mol/L. Insets: Fluorescence images of HBT derivatives in THF/H₂O mixtures with different water fractions (f_w) ($\lambda_{ex} = 365 \text{ nm}$).

Figure 7 Views of the intra- or intermolecular interactions and packing modes in single crystal **OHBT**: (a) intramolecular H-bonding interaction, (b) a molecular chain connecting with hydrogen bonds, (c) and (d) a molecular sheet connecting by intermolecular hydrogen bonds and π - π stacking, (e) 3D structure connected by C-H··· π interactions and (f) cross stacked molecules connected by C-H··· π interactions. The non-covalent interactions are indicated by dashed lines.

Figure 8 Views of the intra- or intermolecular interactions and packing modes in single crystal **CHBT**: (a) intramolecular H-bonding interaction, (b) a molecular column connected by π - π stacking and (c) 3D structure formed by columns connected by hydrogen bonds. The non-covalent interactions are indicated by dashed lines.

Figure 9 Views of the intra- or intermolecular interactions and packing modes in single crystal **HTPA**: (a) intramolecular H-bonding interaction, (b) dihedral angle of triphenylamine unit and HBT, (c) cross stacked molecules connected by C-H $\cdots \pi$ interactions and (d) 3D structure of **HTPA**. The non-covalent interactions are indicated by dashed lines. Hydrogen atoms except H23 are omitted for clarity.

Figure 10 Frontier molecular orbitals analysis for HBT derivatives in the ground and excited states.

Figure 11 (a) The change and recovery of fluorescence spectra and (b) fluorescence ratio changes of **OHBT**-loaded filter paper by fuming with piperidine and AcOH vapors repeatedly. Inset: Fluorescence images of **OHBT**-loaded filter paper upon piperidine and AcOH fuming ($\lambda_{ex} = 365$ nm).

Figure 12 (a) The change and recovery of fluorescence spectra and (b) fluorescence ratio changes of **CHBT**-loaded filter paper by fuming with piperidine and AcOH vapor repeatedly. Inset: Fluorescence images of CHBT-loaded filter paper upon piperidine and AcOH fuming ($\lambda_{ex} = 365$ nm).

Figure 13 (a) The change and recovery of fluorescence spectra and (b) fluorescence ratio changes of **DHBT**-loaded filter paper by fuming with isopropylamine and AcOH vapor repeatedly. Inset: Fluorescence images of **DHBT** on a filter paper upon isopropylamine and AcOH fuming ($\lambda_{ex} = 365$ nm).

Figure 14 (a) The change and recovery of fluorescence spectra and (b) fluorescence ratio changes of HCP-loaded filter paper by fuming with isopropylamine and AcOH vapor repeatedly. Inset: Fluorescence images of HCP-loaded filter paper upon isopropylamine and AcOH fuming ($\lambda_{ex} = 365$ nm).

Figure 15 (a) The change and recovery of fluorescence spectra and (b) fluorescence ratio changes of **HTPA**-loaded filter paper by fuming with piperidine and AcOH vapor repeatedly. Inset: Fluorescence images of **HTPA**-loaded filter paper upon piperidine and AcOH fuming ($\lambda_{ex} = 365$ nm).

Figure 16 Changes of fluorescent spectra of HTPA loaded on filter papers after fumed by different amines.

Figure 17 Illustration of **HCP** as an anti-counterfeiting ink on a practice banknote with letters of "HBT". Images taken (a) under daylight, (b) under 365 nm UV light, (c) under daylight after fumed

with piperidine, (d) under 365 nm UV light after fumed with piperidine, (e) image of (c) under daylight

after exposed to the ambient air for 5 mins, (f) image of (e) under 365 nm UV light.

Scheme 1 Chemical structures and synthetic routes for HBT derivatives: (i) EtOH, reflux; (ii) 30% H₂O₂. 37% HCl, EtOH, rt; (iii) Pd (PPh₃)₄, K₂CO₃, THF/H₂O, reflux.

Figure 1

200

0

400

500 550

Wavelength (nm)

450



DMSO

DME

650

600

DMSO

700







Figure 6



5

Journal Pre-proof























Figure 12





Figure 13





Figure 15



Scheme 1





Highlights

- A series of HBT derivatives with AIE-ESIPT dual mechanism were synthesized.
- The fluorescence properties of these dyes are highly dependent on the solvent environment.
- These dyes exhibit reversible solid-state luminescence switching under alternating amine and acid vapors treatment.
- These dyes can be used as anti-counterfeiting fluorescent inks on banknotes.

Journal Prevention

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conflict of interest

- 1. The authors declare that no conflict of interest exists in the submission of this manuscript.
- 2. We declare that the supporting source had no effects on the study design, data analysis and paper writing.
- 3. The manuscript is approved by all authors for publication.
- 4. We declare that the supporting source had no such involvement when we submit the manuscript.

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