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Strong dual-state emission of unsymmetrical and symmetrical thiazolothiazole-bridged imidazolium salts

Puhui Xie[a], Ying Zhou[b], Xiaochuan Li[c], Xiaojing Liu[a], Lijie Liu[a], Zhanqi Cao[a], Jianji Wang[c,*], Xin Zheng[a,*]

[a] *College of Sciences, Henan Agricultural University, Zhengzhou 450002, China*
[b] *Henan Institute of Advanced Technology, Zhengzhou University, Zhengzhou 450003, China*
[c] *Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China*

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ABSTRACT

A novel thiazolothiazole-bridged imidazole derivative (**1**) was found to exhibit blue fluorescence in gaseous state or in methanol and yellow fluorescence in solid state. The *N*-alkylation of imidazole subunit(s) in **1** using *n*-propyl iodide generated unsymmetrically or symmetrically alkylated thiazolothiazole-bridged imidazolium salts with good water solubility and remarkably strong emission in solution. Furthermore, the replacement of iodide counter-anion by triflate or bis(trifluoromethane sulfonyl)imide achieved remarkably strong emission in solid state and in solution as well as good water solubility. The strong fluorescence of dicationic salts with triflate and NTf_2^- counter-anions in solid state can be ascribed to their twisted and rigid structures induced by interionic C—H···F hydrogen bonding.

The exploitation of new luminescent organic materials with intense fluorescence is of great importance in fundamental studies and practical applications [1,2]. Most of the fluorescent materials, however, can emit strong fluorescence only in dilute solution but very weak fluorescence in the solid state, due to aggregation-caused quenching (ACQ). On the contrary, other luminescent materials show intense fluorescence in the aggregated or solid state but weak fluorescence in solution, which are called as aggregation-induced emission (AIE) materials [3–5]. In addition, most of the fluorescent organic molecules are inherently hydrophobic or poorly water-soluble, which would limit their applications in biosystems and water monitoring [6–8]. To address these issues, it is extremely demanding and challenging to develop materials combining strong emission in solid state and in solution (dual-state) with good water solubility.

Many design strategies, including metal complexation [9,10], molecular stacking [11], anion-π interactions and electrostatic interactions induced structural rigidifications [12], push-pull electronic effect [13], and conjugation modulation [14–16], have been proposed to achieve high fluorescence both in the solid state and in solution. Unfortunately, the rigidity beneficial for intense emission disfavors the water solubility, thus the above motioned molecular structures for dual-state emission may exhibit low water solubility. Although the introducing of charged moieties to forming organic salts may endow them with high thermal stability, and strong interactions with charged biological species [17,15], the water soluble fluorescent organic salts with dual-state emission in both solid state and in solution have been rarely reported. Recently, Suna and co-workers reported several imidazole based small organic molecules, which show combined moderately strong dual-state emission and water solubility [18]. The protonation or alkylation on thiazolothiazole (TTz) derivatives could result in dramatically enhanced water solubility and fluorescence intensity in solution [19,20]. Besides, Walter *et al.* reported the tunable fluorescence intensity and wavelength of asymmetrical TTz bridged compounds by facile one-step reactions [21].

Herein, we report a new type of TTz derivative, 2,5-bis(1-methyl-1*H*-imidazol-2-yl)thiazolo[5,4-*d*]thiazole (**1**, Scheme 1), which emits yellow fluorescence in solid state and blue fluorescence in solution or in gaseous state. *N*-Alkylation of the imidazole groups in **1** with *n*-propyl iodide at different temperature resulted in unsymmetrically or symmetrically substituted TTz-bridged imidazolium salts with good water solubility and remarkably strong emission in solution. The replacement of iodide by triflate or NTf_2^- achieved remarkably strong dual-state emission as well as good water solubility. These salts show different degree of twisting structures and push-pull electric properties between

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* Corresponding authors.
E-mail addresses: jwang@htu.cn (J. Wang), zhengxin@henau.edu.cn (X. Zheng).

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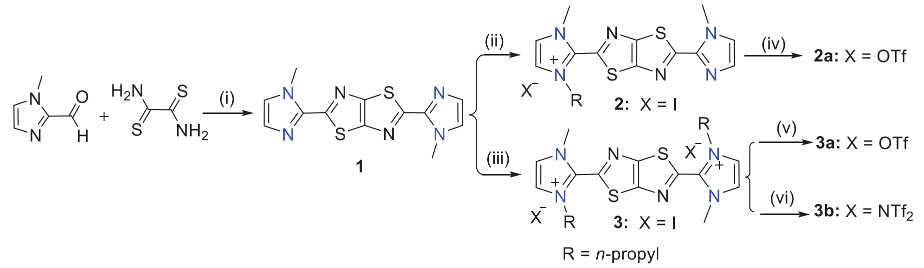

Scheme 1. Syntheses of compounds **1**, **2**, **2a**, **3**, **3a** and **3b**. Reagents and conditions: (i) DMF, 153 °C, 10 h; (ii) 1-iodopropane, CH_3CN, 75 °C, 72 h; (iii) 1-iodopropane, CH_3CN, 120 °C, 72 h; (iv) AgOTf, CH_2Cl_2, r.t., 12 h; (v) AgOTf, MeOH, r.t., 12 h; (vi) $LiNTf_2$, MeOH, r.t., 12 h.

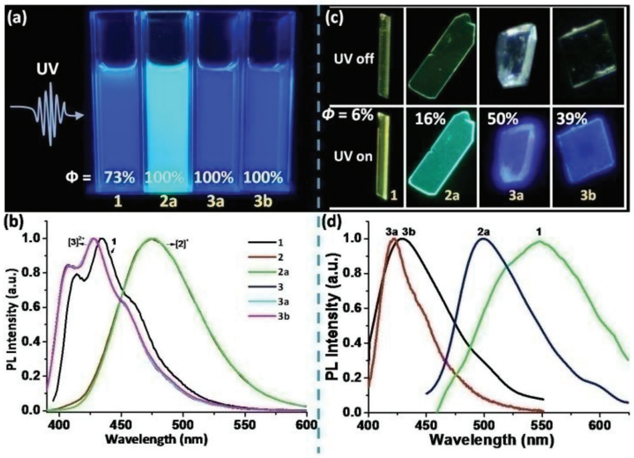

Fig. 1. (a) Photos of **1**, **2a**, **3a** and **3b** in methanol with UV on. (b) Normalized emission spectra of **1** in methanol, **2**, **2a**, **3**, **3a** and **3b** in H_2O (1.0×10^{-5} mol/L). (c) Photo images of **1**, **2a**, **3a** and **3b** in crystalline state with UV off and UV on. (d) Normalized fluorescence spectra of crystals **1**, **2a**, **3a** and **3b** in the solid state.

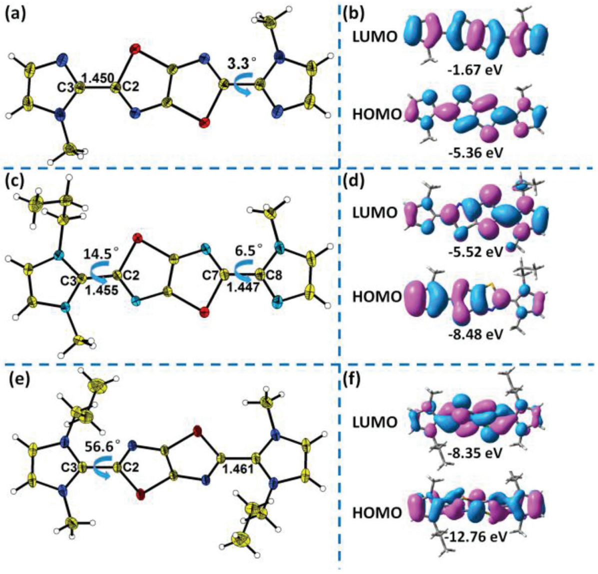

Fig. 2. (a) 30% ellipsoid drawings of structure of **1**. (b) HOMO and LUMO of **1**. (c) Structure of **2**. (d) HOMO and LUMO of **2**. (e) Structure of **3**. (f) HOMO and LUMO of **3**.

the imidazolium moieties and the TTz core. Twisted diimidazolium salts driven by interionic C—H···F hydrogen bonds in crystals were found to achieve emit remarkable fluorescence.

Compound **1** was synthesized by condensation of 1-methyl-2-imidazolecarboxaldehyde with dithiooxamide in DMF (Scheme 1). However, **1** is poorly soluble in water. The *N*-alkylation of **1** using 1-iodopropane in CH_3CN at 75 °C offered **2**, which is the first reported unsymmetrical TTz-bridged salt, with an electron-donating group (TTz core linked imidazole) and an electron-withdrawing imidazolium group. Upon *N*-alkylation of **1** at 120 °C, a symmetrical TTz-bridged imidazolium **3** was obtained. Using **2** or **3** as starting materials, yellow crystals of **2a**, colorless crystals of **3a** and **3b** were obtained by anion exchange reactions and recrystallizations.

Compound **1** in both MeOH solution and sublimated gaseous state can emit blue emission under 365 nm light. The gas of **1** was obtained by heating the solid at about 200 °C. We could not obtain the fluorescence spectrum of **1** in gaseous state for lack of corresponding devices. Alkylation of **1** provided charged TTz-bridged derivatives with high solubility in various polar organic solvents and water. All the salts **2**, **2a**, **3**, **3a** and **3b** could be directly prepared as solution of 1×10^{-3} mol/L in H_2O, displaying their good water solubility. In MeOH, the unsymmetrical salts of **2** and **2a** emit bright blue light, and the symmetrical salts of **3**, **3a** and **3b** emit fluorescence in deep blue under UV light (Fig. 1a, Fig. S1 in Supporting information). **1** displays a fluorescence spectrum at 434 nm with quantum yield (Φ_F) of 73% (Fig. 1b, Table S1 in Supporting information), However, the fluorescence peaks of **2** and **2a** are both red shifted to 475 nm, which is attributed to the push-pull effect across imidazole-TTz-imidazolium (D-π-A) in cations of **2** [22,23]. Whereas the fluorescence peaks of **3**, **3a** and **3b** are all blue shifted to 428 nm compared to those of **1**, **2** and **2a**. These findings indicate that the anions of I^-, OTf^- and NTf_2^- have negligible effect on fluorescence maxima for each TTz-bridged salt in MeOH.

Both the iodides of **2** and **3** are nearly non-emissive in the solid state (Fig. S2 in Supporting information). Whereas crystals of **1**, **2a**, **3a** and **3b** exhibit fluorescence in yellow, green, blue and blue under 365 nm UV light, respectively (Fig. 1c). Fig. 1d shows that the crystals **1**, **2a**, **3b** and **3a** display gradually blue-shifted fluorescence peaks at 548, 500, 429 and 423 nm, with quantum yield of 6%, 16%, 50% and 39%, respectively (Table S1). It is clear that anions of OTf^- or NTf_2^- have drastically enhanced the emission intensity among the crystals as compared to iodides.

To get insight into the fluorescence properties, single crystals of **1**, **2** and **3** (CCDC Nos. 1832311, 1864640 and 1864699, respectively) suitable for X-ray crystallographic analysis were obtained by slow solvent evaporation method (Table S2 in Supporting information). The imidazole rings and the central TTz core of **1** are almost coplanar with a torsion angle of 3.3° (Fig. 2a), indicating an effective conjugation within the molecule. The bond lengths of the C-C single bonds between imidazole subunits and the TTz core are both 1.450 Å. In addition, the centroid-to-centroid distance between the imidazole and imidazolium rings in adjacent molecular planes is 4.732 Å (Fig. S3 in Supporting information), which is longer than most reported TTz–bridged derivatives [24,25], and infers the weak intermolecular π-π interactions. The enhanced conjugation and intermolecular π-π interactions of crystal **1** result in restricted intramolecular rotation (RIR) between the imidazole rings and the central TTz core linked by single bonds **1,** which is consistent with the color transition from yellow in crystalline state to blue emission in solution. As the intermolecular distances of **1** in gaseous state are increased, the intermolecular π-π stacking interactions are greatly decreased, and the conjugation is similarly decreased compared to its crystals, which can address the phenomenon of the blue-shifted emission of **1** in gaseous state compared to its crystalline state.

The structure of **2** adopts a twisted conformation with a torsion angle 14.5° between the imidazolium subunit and the TTz core, which is slightly larger than that of **1** (Fig. 2c). Compared to the corresponding parameters in **1**, the C2-C3 bond of **2** is lengthened to 1.455 Å, and C7-C8 bond of **2** is shortened to 1.447 Å, respectively. The centroid-to-centroid distances between the imidazole and imidazolium rings in adjacent molecular planes are shortened to 3.537 Å and 3.610 Å, respectively (Fig. S4 in Supporting information). The results indicate a decreased π-conjugation and an increased intermolecular interaction for **2**.

The dicationic salt **3** adopts a highly twisted conformation with two dihedral angles of 56.6° between the imidazolium and the TTz plane, and the C2-C3 single bond lengths between central TTz and the peripheral imidazolium subunits are increased to 1.461 Å (Fig. 2e), which are much longer than those in **1** and **2**. No intermolecular π-π stacking interactions was observed (Fig. S5 in Supporting information). Therefore, the *N*-alkylation increased progressively bond lengths between the imidazolium subunits and TTz core, accompanied by increased molecular twisting and decreased degree of π-conjugation, thus increased molecular flexibility and decreased fluorescence intensity in the solid state. On the other hand, iodides in crystals **2** and **3** might be the main factor for their non-emissive properties [18].

The monocationic salts **2** and **2a** show similar absorption spectra in MeOH or aqueous solution, so as the dicationic salts **3**, **3a** and **3b** (Figs. S6 and S7 in Supporting information), indicating the negligible anion effects on the electron transitions from ground state to excited state. In MeOH, the absorption maxima of **1** at 375 nm, monocationic salt **2** or **2a** at 368 nm, dicationic salt **3** or **3a** or **3b** at 345 nm exhibited blue-shifted with the increasing of *N*-alkylation (Table S1), indicating that the electron-withdrawing property of imidazolium moieties increased the transition energies from ground state to excited state in **2** or **3**. DFT calculations of **1**, **2** and **3** were performed. The HOMO of **1** is delocalized at the entire molecule, supporting its good π-conjugation (Fig. 2b). While the HOMO of **2** is mainly localized in the TTz core and linked imidazole group, and the LUMO energy level is mainly localized in the TTz core and imidazolium moiety, indicating an obvious push-pull effect (Fig. 2d). The HOMO and LUMO energy levels of **3** are mainly localized on the TTz core, indicating a weak push-pull effect and poor π-conjugation across the entire cation (Fig. 2f). The energy band gaps of **1**, **2** and **3** are calculated to be 3.69, 3.96 and 4.41 eV, respectively. Therefore, the results of DFT calculations fully support their absorption wavelengths. The Stokes shifts of monocationic salts (107 nm, 6121 cm^{-1}) and dicationic salts (83 nm, 5622 cm^{-1}) are much larger than **1** (59 nm, 3626 cm^{-1}) in MeOH, indicating that the differences in electron distributions between the excited state and ground state of these salts are more than that of **1,** as illustrated in HOMOs and LUMOs in Fig. 2.

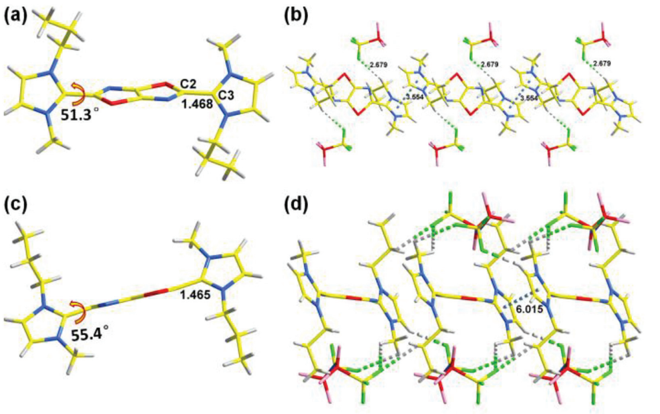

Fig. 3. (a) Molecular structure of **3a**. (b) *J*-stack and hydrogen bonding in **3a**. (c) Molecular structure of **3b**. (d) Networks around **3b** connected by hydrogen bonding.

To further understand the remarkable enhanced quantum yields of **2a**, **3a** and **3b** in the solid state, single crystals of **3a** and **3b** (CCDC Nos. 1864702 and 1866650, respectively) suitable for X-ray crystallographic analysis were provided. The crystalline information of **2a** could not be obtained because its crystals were too thin and brittle. In structure of **3a**, the imidazolium planes were twisted from the TTz core with a dihedral angle of 51.3° (Fig. 3a), and the adjacent planes of imidazolium rings were *J*-type stacked with a centroid-to-centroid distance of 3.554 Å (Fig. 3b). In addition, strong C−H···F hydrogen bondings (2.679 Å) between the α-H atoms of *n*-propyl and OTf^- were observed, the synergistic effect of π-π stacking and hydrogen bonding endows **3a** with rigid structure, which greatly enhances its fluorescence quantum yield. In structure of **3b** with anion of $NTf_2{}^-$, the dihedral angle of 55.4° and the C-C single bonds of 1.465 Å (Fig. 3c) are approached to those in **3**. And the imidazolium planes are aligned parallel to each other with a centroid-centroid distance of 7.347 Å (Fig. 3d and Fig. S8 in Supporting information), indicating there were no intermolecular interactions [26]. But strong C−H···F hydrogen bondings with distances of 2.584−2.818 Å between cations in **3** and $NTf_2{}^-$ can be observed. Some of them are shorter than the van der Waals hydrogen bonding (2.6 Å) [27]. These hydrogen bondings formed a complex network around cations in **3**, thus endowing remarkable molecular rigidity of **3b**. Therefore, the great increased Φ_F and blue-shifted fluorescence maxima of crystals **3a** and **3b** compared to **1** could be ascribed to their twisted and rigid structures by *N*-alkylation and hydrogen bonding interactions [28]. As the amount of OTf^- around **2a** is less than those around **3a**, we inferred that the green fluorescence with lower Φ_F of crystal **2a** than **3a** and **3b** was ascribed to a moderately twisted structure and fewer hydrogen bondings compared to **3a** and **3b**. Overall, the degree of distortion between the imidazole rings and the central TTz core decreases in order of **3**, **3a**, **3b** > **2**, **2a** > **1**, corresponding to the bathochromic shift of their fluorescence spectra.

The strong C−H···F hydrogen bondings in **3a** and **3b** were further supported by Raman and ^1H NMR spectroscopy analyses. The Raman spectrum at 1406 cm^{-1} in **3**, ascribed to the N−C−N stretch in the imidazolium ring, split into two bands at 1393 and 1407 cm^{-1} in **3a**, and two bands at 1392 and 1412 cm^{-1} in **3b**. And the band at 1492 cm^{-1} assigned to the stretching of imidazole ring in **3** is upshifted to 1500 and 1502 cm^{-1} in **3a** and **3b**, respectively (Fig. 4a). As well, the chemical shifts in partial ^1H NMR spectra for **3a** and **3b** compared to **3** in DMSO-d_6 solution were downfield shifted due to the effect of hydrogen bonding (Fig. 4b).

Unlike their non-emitting properties in crystals, **2** and **3** exhibited fluorescence with Φ_F of 93% and 95% in H_2O, at 467 nm with lifetime (τ) of 2.6 ns and at 425 nm with lifetime of 1.9 ns, respectively (Fig. S9 in Supporting information). They exhibited bright blue fluorescence upon 365 nm light irradiation in aqueous solution (insert in Fig. S9). As the fluorescence decay rates ($k_F = \Phi_F/\tau_F$) of 3.58×10^8 s^{-1} and 5.0×10^8 s^{-1} for **2** and **3** in H_2O, respectively, were enormously large, we concluded that there was little non-

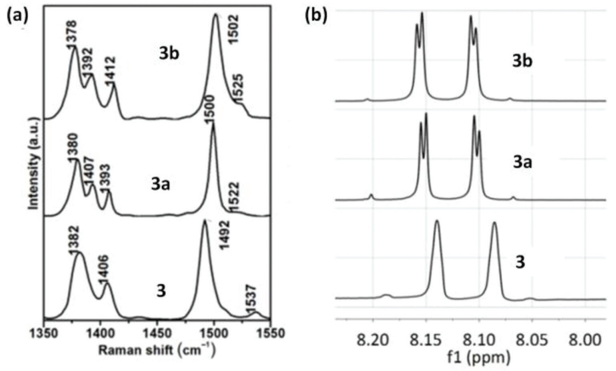

Fig. 4. (a) Raman spectra of **3**, **3a** and **3b** in solid state excited at 532 nm. (b) Partial ^{1}H NMR spectra of **3**, **3a** and **3b**.

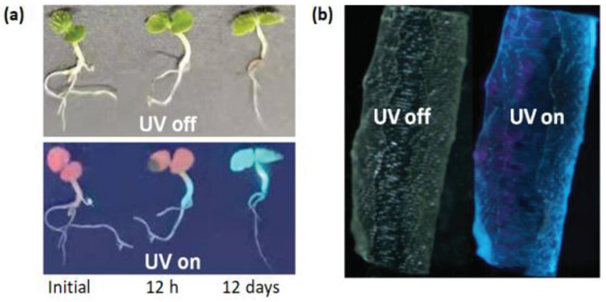

Fig. 5. (a) Photographs of paulownia sprouts cultivated with **2a** (10 µmol/L) in H_2O for 12 h and 12 days. (b) Onion tissues cultivated with **2a** (10 µmol/L) in H_2O for 8 h.

emissive decay during the fluorescence process in aqueous solution. In addition, **2** and **2a** exhibited slightly variable absorption and fluorescence bands in different solvents (Table S1 and Figs. S10-S12 in Supporting information). But the fluorescence maxima of **3a** were little affected by solvents (Fig. S13 in Supporting information). The high fluorescence quantum yields suggest that these salts have stable excited states in solution, and little electron transfer or few extra non-emissive relaxation pathways [29].

The water solubility of such fluorescent salts enables their application in illuminating plants such as paulownia sprouts and onion tissues under UV irradiation of 365 nm. Blue fluorescence was observed in the stem of paulownia sprouts (Fig. 5a) after cultivated with **2a** for 12 h and onion tissues (Fig. 5b) for 8 h. The red fluorescence coming from chlorophyll in leaves of paulownia sprouts was covered by blue fluorescence from **2a** after cultivated for 12 days. The blue fluorescence in both the leaves and stems means the uptake and transporting ability in root of paulownia sprouts toward **2a** and potential applications in illuminating plants.

In conclusion, a novel TTz-bridged imidazole derivative (**1**) was found to exhibit blue fluorescence in gaseous state or in methanol and yellow fluorescence in solid state. The *N*-alkylation of imidazole subunit(s) in **1** generated unsymmetrical or symmetrical TTz-bridged imidazolium salts with good water solubility and remarkably strong emission in solution. The replacement of iodide counter-anion by triflate or NTf_2^- achieved remarkably strong, blue-shifted, dual-state emission as well as good water solubility. The strong fluorescence of dicationic salts **3a** and **3b** in solid state can be ascribed to their twisted and rigid structures induced by interionic C—H···F hydrogen bonding. The results indicate that the twisted and rigid cationic structures with suitable counter-anions may play a critical role in developing high dual-state emissive materials and good water solubility.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.06.005.

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