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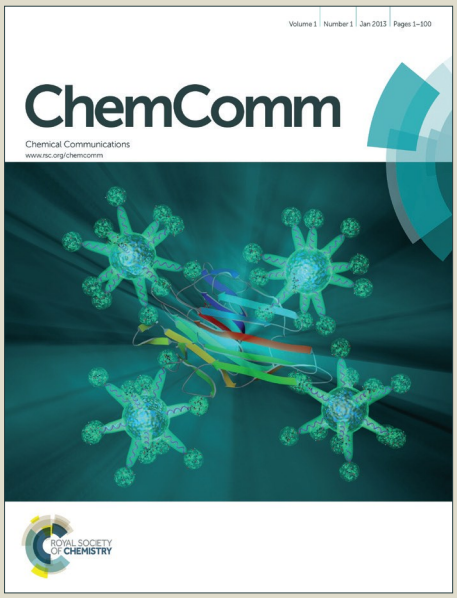

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Highly efficient blue solid emitters and tautomerization-induced ON/OFF fluorescence switching based on structurally simple 3(5)-Phenol-1*H*-pyrazoles

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Baolei Tang, Houyu Zhang, Kaiqi Ye, Hongyu Zhang* and Yue Wang

3(5)-Phenyl-1*H*-pyrazoles are employed in this study to develop highly efficient organic crystalline solids with deep-blue ESIPT fluorescence as well as provide novel experimental insight into mechanism of ESIPT fluorescence and generate an intriguing fluorescence "ON/OFF" switching.

π-Conjugated luminescent organic materials have attracted great attentions of scientists in material science due to their wide applications including organic light-emitting diodes (OLEDs)[1], organic solid-state lasers (OSLs)[2], sensors[3], bio-imaging[4], etc. Recently, great efforts have been paid to synthesize organic luminescent materials by either developing new design strategies or constructing novel π-conjugated systems.[5–8] However, the deep blue emissive organic solids with desired properties are still scarce. The typical π-conjugation framework for blue emitters such as anthracene, fluorence or pyrene takes a rigid and flat framework which readily forms face-to-face packing structures through intermolecular π–π interactions in solid states. Thus, the fluorescence of organic solids containing such π-electron units usually suffers from aggregation-caused quenching and/or bathochromic shift effects. Although some blue emissive organic solids with high fluorescence efficiency have been constructed by introducing bulk substituents into the π-system, the corresponding synthesis and purification is time-consuming and laborious. In this sense, the exploration of novel design strategy towards efficient blue emissive materials based on structurally simple and easily available organic molecules is highly important and urgently demanded.

Organic compounds that undergo excited-state intramolecular proton transfer (ESIPT) have been widely investigated recently since the photochemical process produces a tautomer with a quite different electronic structure from the original excited state.[9] The large Stokes shift of ESIPT-active organic fluorophores effectively decreases self-absorption and hence plays a positive role in emission intensity.[10] Indeed, organic materials with bright ESIPT fluorescence have been designed and some of them even perform well in optoelectronics.[11] However, most of the ESIPT-active materials are restricted to green and longer wavelength fluorophores due to the large Stokes shift (> 100 nm) and that exhibiting deep blue solid-state emission is extremely rare. Another notable feature of ESIPT fluorophores is that the proton transfer in the excited state can be blocked by perturbing the intramolecular hydrogen bond in solutions. Thus, ESIPT emitters are good candidates for sensors. However, the switching of ESIPT fluorescence in the solid state has not been developed which restrict the application of this class of fluorophores.

To achieve ESIPT-active blue solid emitters, extended π-conjugation or donor-acceptor structure should be avoided whenever possible. Taking this into account, we attempt to

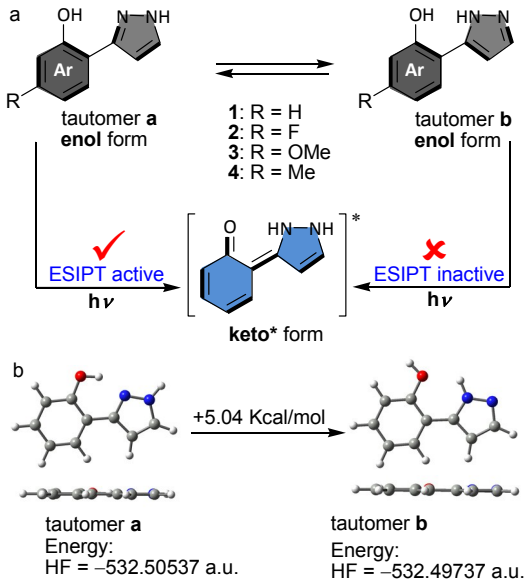

Fig. 1 Tautomeric structures and ESIPT process of **1**–**4** (a) and conformation and energy of two tautomers calculated based on **1** (b).

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 2699 Qianjin Avenue, Changchun, P. R. China, hongyuzhang@jlu.edu.cn.

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construct deep blue ESIPT fluorescent organic solids based on the structurally simple 3(5)-phenol-1*H*-pyrazole skeleton (Fig. 1a) in which the phenol ring act as proton donor and pyrazole unit serve as proton acceptor. As expected, some of these compounds produced highly efficient blue emissive crystalline solids with quantum yield as high as 0.50. Notably, the proton acceptor unit has two tautomeric forms (tautomer **a** and **b**) which essentially determine the ESIPT generation. In this sense, the present system provides a model to demonstrate the possibility of the ESIPT fluorescence switching in the solid state through tautomerization. Single crystals composed of either tautomer **a** (**1**–**3**) or **b** (**4**) with ESIPT fluorescence "ON" or "OFF", respectively, have been obtained. Optical behaviors, crystal structures, and ESIPT mechanism of these molecules were carefully studied. And the high-contrast solid-state fluorescence interconversion due to tautomerization was finally investigated.

Compound 1[12,13] is a known molecule and **2**–**4** are newly synthesized according to the literature method[12,13] to demonstrate the substituent effect. The fluorescence of compounds **1**–**4** in solution are very weak (Φ_f < 0.01), as shown in the inset of Fig. 2a. They exhibit dual-band emission spectra in dichloromethane (DCM), displaying a typical fluorescence feature of ESIPT-active molecules. The high-energy bands originated from the excited-state enol forms locate in the UV region, ranging from 323 to 334 nm. And the low-energy bands peaked at around 380 nm comes from the excited-state keto form species generated through an ESIPT process. Although the substituents don't affect the fluorescence wavelength greatly, they show certain influence on the proportion of the enol and keto emission bands in DCM solution. For instance, fluoro-substituted compound **2** displays a balanced dual-band emission while the fluorescence spectrum of **1** is dominated by the enol form emission. Similar to solution samples, the spin-coated thin films (Fig. S1) also show very weak fluorescence (Φ_f < 0.01).

As shown in Fig. 2b, the crystalline solids of **1**–**3** show intense single-band blue emissions. Crystal **1** exhibits strong fluorescence peaked at about 463 nm with Φ_f of 0.52. And crystals **2** and **3** emit slightly blue-shifted fluorescence centred at 454 (Φ_f = 0.49) and 453 nm (Φ_f = 0.49), respectively. The Stokes shifts of these crystals are about 130 nm, reflecting that the intense blue emissions of crystals originate from the ESIPT fluorescence. Enol form bands are not found in the emission spectra of crystals **1**–**3**. Surprisingly, crystals **4** exhibit totally different fluorescence compared with **1**–**3**, despite of their similar optical behaviors in solutions and thin films. Crystals **4** show much weaker emission (Φ_f < 0.01) compared with **1**–**3** (Table S1). As shown in Fig. 2c, the emission spectrum of crystal **4** shows a major band peaked at around 350 nm and a weak broad band centred at about 460 nm. In this sense, ESIPT might easily take place in crystals **1**–**3** but difficult in crystal **4**. The luminescent behaviors indicate that the excited-state enol form species of **1**–**4** have intrinsic weak emission nature and the excited-state keto emissions of **1**–**3** are significantly enhanced by crystallization. Thus, compounds **1**–**3** display a crystallization-enhanced emission (CEE) feature which

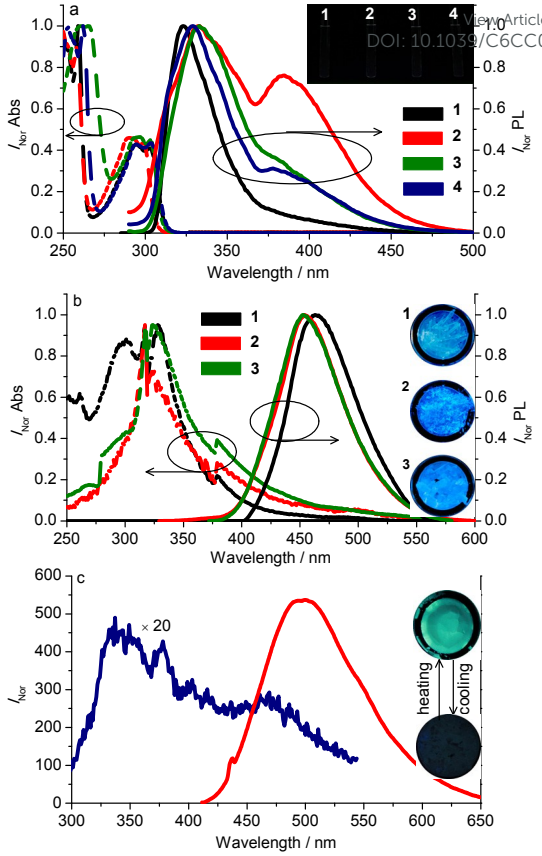

Fig. 2 a) absorption and emission spectra of **1**–**4** in DCM solution, b) absorption and emission spectra of crystals **1**–**3** and c) "ON" and "OFF" emission spectra of solid **4**. (inset: photographic images of solid samples under 254 nm UV irradiation)

together with aggregation-induced emission (AIE) has been proposed by Tang as a novel and powerful strategy for constructing organic luminescent functional materials.[14]

To disclose the CEE behaviors of crystals **1**–**3** as well as the unusual emission property of **4**, we have determined the crystal structures of all compounds. Crystals **1**–**3** hold the same space group and crystal system (P_{212121}, orthorhombic), in consistent with their similar crystalline-state emissions. As for crystal **1**, the intramolecular hydrogen bond O–H···N (distance: 1.826 Å) formed between the hydroxyl group and the nitrogen atom of the pyrazole ring generates a planar framework which not only facilitates ESIPT but also rigidifies the molecular structure (Fig. 3a). The dihedral angle between phenol and pyrazole units is 1.52°, reflecting a rather planar π-skeleton. In the packing structure, intermolecular C–H···π interactions allow the molecules to pack into a herringbone structure (Fig. 3b) which is stabilized by intermolecular C–H···O hydrogen bonds. No π···π interactions are observed in the crystal structure, despite of the planar molecular structure. As shown in Fig. S2 and Fig. 3, crystals **2** and **3** show the similar molecular structures with crystal **1**. The molecules in crystals **1**–**3** take the form of tautomer **a**, namely, 2-(1*H*-pyrazol-3-yl)phenol. In line with the unusual emission property, crystal **4** shows totally different molecular structure compared with **1**–**3**. The N–H moiety of pyrazole ring in crystal **4** is located close to the phenol group. Thus, the molecules in crystalline state take

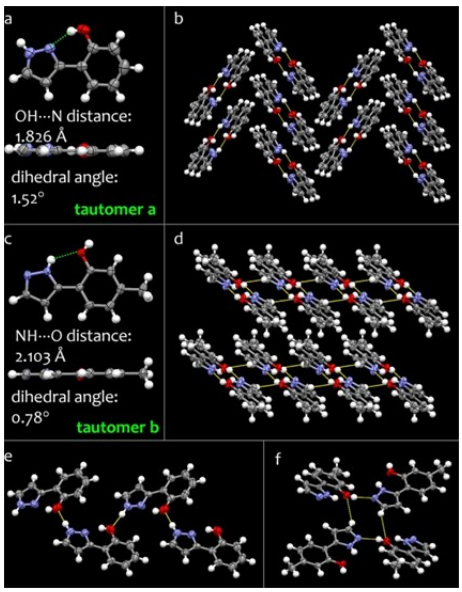

Fig. 3 Molecular (a, c), packing structures (b, d) and intermolecular hydrogen bonding interactions (e, f) of crystals **1** and **4**.

the structure of 2-(1*H*-pyrazol-5-yl)phenol (tautomer **b**) which hamper the formation of intramolecular O–H···N hydrogen bond. As a result, the ESIPT luminescence is prevented in crystal **4**. Instead of the O–H···N interaction, N–H···O hydrogen bond (distance: 2.103 Å) forms which also endows the entire molecule with a completely planar structure (Fig. 3c). Molecules **4** form a two-dimensional network in the packing structure by intermolecular hydrogen bonding and π···π interactions, as shown in Fig. 3d.

Crystal structure analysis has unambiguously confirmed that the tautomeric form of molecules **1**–**4** decides the fluorescence nature of the solids. The geometry optimizations of two tautomers were performed with the density functional theory using the B3LYP functional and 6–31G (d, p) basis set, as implemented in Gaussian 09 package.[15] Both of tautomers form flat structures because of the existence of an intramolecular hydrogen bond (Fig. 1b), consistent with the crystal structure analysis. Tautomer **a** is more stable than **b** by 0.008 a.u (5.04 Kcal/mol), indicating that these compounds exist as the structure of 2-(1*H*-pyrazol-3-yl)phenol in solution. Indeed, there are only one set of proton signals, corresponding to tautomer **a**, in the NMR spectra of compounds **1**–**4**. Although the reason why compound **4** prefer the structure of tautomer **b** in solid form is not clear at the current state, the intermolecular hydrogen bonding interactions (Fig. 3e and f) demonstrate that tautomer **b** can stably survive in crystal **4**. The O(OH) in **1**–**3** acts as intermolecular hydrogen bond acceptor and the H(OH) approaches to nearest of two nitrogen atoms. In sharp contrast, H(OH) in crystal **4** is away from the adjacent N atom due to the formation of intermolecular hydrogen bond with a neighbor molecule. As a result, H(N) is located on the N atom close to phenol ring and form a N–H···O intramolecular hydrogen bond. In addition, the rich inter/intramolecular hydrogen bonds facilitate the formation of a tetramer which greatly stabilizes tautomer **b**.

In DCM solution, tautomer **a** is energetic more favourable than tautomer **b**. The energy difference between tautomer **a** and **b** (ΔE) is in the order of **4** < **1** < **2** < **3** (Table S2). Thus, compound **4** has the greatest possibility to undergo isomerization during crystallization since **4** has the smallest energy barrier between tautomer **a** and **b**. For the better understanding of the different behaviors of **4** in solid state, it had better compare both **a** and **b** form in their crystal state, unfortunately, we only obtained the crystal states of **1**–**3** in their tautomer **a** form and crystal state of **4** in its tautomer **b** form, so we could not compare the conformation and energy of its tautomers directly. The calculated energies of compounds in their crystal states are higher than those in solution (Table S2). Such higher energy states in crystal need the strong intermolecular interaction to stabilize their conformation. It is the easiest for compound **4** to occur such tautomer transformation from **a** to **b** and once compound **4** in its tautomer **b** is formed, it will be stabilized by the surrounding intermolecular interactions as demonstrated by the crystal structure analysis. So only **4** belongs to different space group and crystal system, significantly different from **1**–**3**. Though short of direct comparison of **a** and **b** in solid state, the existence of **4** in **b** form seems reasonable from our calculation results.

Molecule **4** underwent isomerization while **1**–**3** did not during crystallization. Thus, N–H switching might take place in the solids of **4** and lead to fluorescence change. Indeed, the reversible heating-cooling controlled "ON/OFF" fluorescence switching of solid **4** has been realized (Fig. 4a). The faint emissive crystals **4** (tautomer **b**) converted into the melt state when heated over 130 °C. During natural cooling, the sample exhibited bright ESIPT fluorescence immediately after solidification, indicating a certain amount of tautomer **a** molecules existed in the deformed solid. The freshly generated ESIPT fluorescence gradually diminished during cooling and disappeared after standing in air for several hours. When the crystalline solids were heated to melt, molecules underwent isomerization from tautomer **b** to **a**. After solidified at about 130 °C, the reverse isomerization took place right away. This tautomerization in solid form takes a relatively long time and some ESIPT-active molecules could retain to several hours. Therefore, the just solidified sample exhibited bright emission which became weaker and weaker due to the on-going reverse isomerization of ESIPT-active molecules. It is worthy to note that the ESIPT fluorescence could recover when the cooled sample was heated to melt and followed by the cooling again. Thus, the reversible fluorescence "ON/OFF" switching due to the interconversion between ESIPT and local emissions which are CEE-active and faint emissive, respectively, has been obtained.

Although the conventional crystallization of **4** produces weak emissive solids, the rapid evaporation gives rise to different results. As shown in Fig. 4b, when the DCM solution was rapidly volatilized by hot air, the freshly obtained solids exhibited bright ESIPT fluorescence which became weaker and weaker and finally disappeared in air. The molecules have enough time to undergo isomerization (tautomer **a**→**b**) during

the routine slow crystallization, leading to faint emissive crystals. However, in the rapid evaporation and solidification process, some ESIPT-active molecules retained and gradually underwent tautomerization, leading to the observed fluorescence change. Thus, the same fluorescence "ON/OFF" switching due to the solid phase tautomerization as mentioned above was realized in another way.

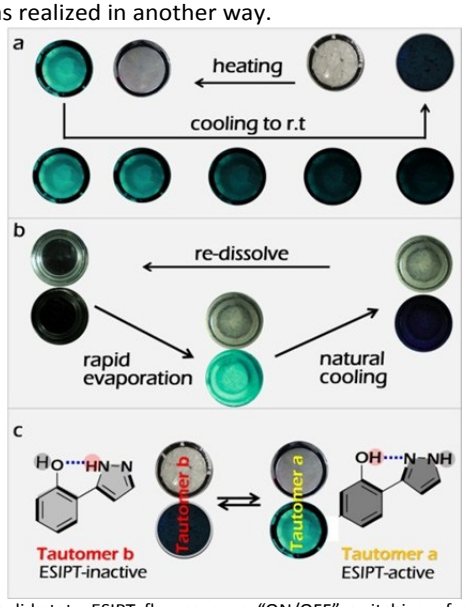

Fig. 4 The solid-state ESIPT fluorescence "ON/OFF" switching of compound **4** realized through two different processes (a and b) and Switching mechanism (c).

To experimentally verify the ESIPT fluorescence nature of an organic compound, replacing the hydroxyl group by methoxyl substituent followed by the comparison of emission properties is one of the routine ways. In that case, the additional synthesis is required and the spectral difference that supports ESIPT comes from different molecules. The solid-state fluorescent chromism of compound **4** offers a novel evidence for the ESIPT fluorescence. This compound produces ESIPT-active and inactive tautomers in solid phase by controlling physical conditions. Both emission color and intensity of the solids depend on the ratio of ESIPT-active tautomer. Thus, the mechanism of ESIPT process has been verified in a new way by the comparison of emission properties between two tautomeric forms of one single organic compound.

Conclusions

In summary, 3(5)-phenol-1*H*-pyrazole derivatives **1**–**3** were employed in this study to construct organic crystalline solids with intense deep blue ESIPT fluorescence. Despite of the similar structure as **1**–**3**, compound **4** produced crystals with faint ultraviolet emission. The tautomer form of molecules in crystals **1**–**3** facilitates ESIPT reaction whereas that in crystal **4** hampers the generation of ESIPT, which endow the similar organic molecules with quite different solid-state emission properties. The high-contrast "ON/OFF" fluorescence switching of solids **4** based on the reversible isomerization between two tautomeric forms has been realized through two convenient procedures. The present study not only gives a rare example of blue solid-state ESIPT fluorescence but also has scientific significance in disclosing the ESIPT fluorescence mechanism. In addition, the reversible luminescent chromism of compound **4** suggests the potential application of this material in sensors or memory devices.

Acknowledgements

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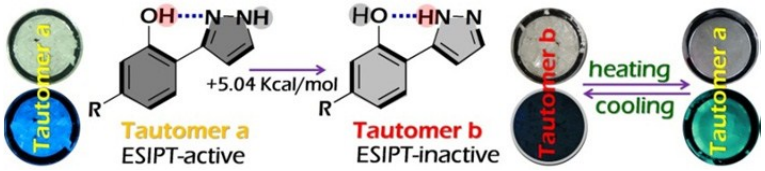

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