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COMMUNICATION

AIE-active Luminophore with tunable and remarkable fluorescence switching based on the piezo and protonation-deprotonation control†

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A novel luminophore TPENSOH from the building blocks of tetraphenylethylene and 6-hydroxybenzothiazole was facilely synthesized and exhibited unique AIE properties. This new dye was found to show a remarkable and reversible four-color switching based on a single molecule at solid state.

Stimuli-responsive fluorescent materials, the emissions of which can be repeatedly switched between different colors under external stimuli, are of great importance from both academic and industrial viewpoints for their promising applications in the fields of sensors, information displays and optical-recording systems.¹ To date, although dual-colored luminescence switching has been well documented, multi-colored luminescence switching based on a single luminophore in the solid state remains uncommon.^{1b,2} One of the two excellent examples reported is the mechanochromic liquid crystal studied by Kato's group, of which the tricolored switching of this crystal was realized by tuning its molecular packing architecture.³ The other example is the tetraphenylalanine derivative demonstrated by Jia's group, of which the molecule of this derivative undergoes tricolored fluorescence switching by combining the mechanisms of the chemical reactivity and force-induced transformation of assembled structures.⁴ However, similar to most conventional dyes, these two luminophores suffer from the problem of aggregation-caused quenching (ACQ), which results in low fluorescence quantum yields in the solid state.⁵ Moreover, both of these luminophores require sophisticated synthesis (> 10 steps)

by introducing different components into one molecule. This process is time-consuming and largely increases the cost. All the aforementioned drawbacks significantly limit the real-world applications of these luminophores. Therefore, the preparation of multi-colored switching luminophores with efficient solid-state emission and facile synthesis remains a challenge.

In this contribution, we attempt to design and synthesize a simple molecule that is free from the quenching effect in the solid state and shows switching for more than three colors under external stimulus. Herein, tetraphenylethylene (TPE) was employed as a building block of a new luminophore TPENSOH for its abnormal aggregation-induced emission (AIE) property.⁶ Furthermore, a few TPE derivatives found by us and Tang exhibit mechanochromism by simply changing their molecular packing mode.⁷ Meanwhile, 6-hydroxybenzothiazole was introduced as a functional group to achieve site-specific interaction with acid at the molecular level for switching.⁸

TPENSOH was prepared according to the synthetic routes depicted in Scheme S1 and the detailed procedures for the synthesis were also described in the supporting information. As depicted in Fig. S1, when 90% (v/v) of water, a poor solvent for TPENSOH, was added to the ethanol solution of TPENSOH, the corresponding photoluminescence (PL) intensity (~142 a.u.) was increased by up to ~20 times as compared with that at water fraction of 0% (~7 a.u.).

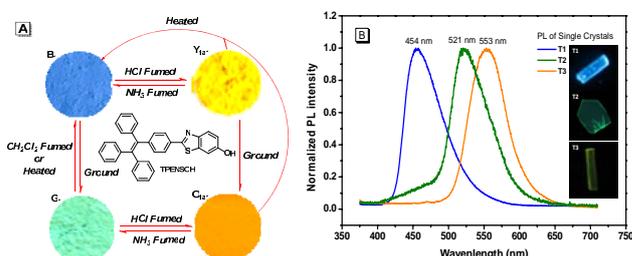


Fig. 1 A) Molecular structure of TPENSOH and fluorescence images of the powders: (B₁) as-prepared TPENSOH; (G₁) ground sample; (Y_{1a1}) B₁ in the vapor of HCl for 10 min; (O_{1a1}) G₁ in the vapor of HCl for 10 min. (Excitation wavelength: 365 nm). B) PL spectra of the three single crystals. The insets depict the fluorescence microscope images of the single crystals. (Excitation wavelength: 365 nm).

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The Mie scattering effect⁹ observed in the UV-visible absorption spectra of TPENSOH (Fig. S2) revealed that the nano-aggregates of the luminophore were formed in the mixtures with high water contents. Evidently, TPENSOH is AIE-active.

The AIE characteristics of TPENSOH prompted us to apply the material in the solid state. Compared with the emissive nanoaggregates, the as-prepared TPENSOH solid powder (B_1) exhibited even a stronger blue-light emission centered at 454 nm [$\Phi_F=0.25$, $\tau_1=0.90$ ($A_1=0.98$). Data for fluorescence lifetime and fractional contribution shown in Fig S3 and Table S1]. Interestingly, when B_1 was exposed to HCl vapors (37% concentrated hydrochloric acid vapors), the PL spectrum of this solid powder changed remarkably, passing from an initial blue to yellow light at 550 nm [$\Phi_F=0.19$, $\tau_1=0.96$ ($A_1=0.29$), $\tau_2=2.28$ ($A_2=0.57$), $\tau_3=3.95$ ($A_3=0.14$)], which indicates a significant acid-stimuli response (Figs. 1A and S4). After subsequent exposure to NH_3 vapors (25% concentrated ammonium hydroxide vapors), the resulting yellow powder (Y_{fa1}) fully recovered its initial blue-light emission (Fig. S5). The strong bathochromic shift of 96 nm in fluorescence and the recovery toward the initial state demonstrated the attractive fluorescence switching properties of the as-prepared TPENSOH powder under protonation-deprotonation stimuli. Meanwhile, after grinding with a pestle or shearing with a spatula, the PL spectra of the pristine TPENSOH solid powder shifted to 492 nm [$\Phi_F=0.15$, $\tau_1=0.53$ ($A_1=0.69$), $\tau_2=1.42$ ($A_2=0.28$)], exhibiting a notable emission wavelength change of 38 nm. The emission color and quantum yield of the ground sample (G_1) can be entirely restored upon heating or solvent fuming, which suggests that the piezochromic fluorescence process is completely reversible (Fig. S6). As observed above, the original TPENSOH solid powder was responsive to the protonation-deprotonation process. If sample G_1 retains this attractive property, the photophysical characteristics of TPENSOH upon acid-alkali stimulation would be tuned by pressure *via* simply altering the mode of molecular packing. To verify this hypothesis, the PL spectrum of G_1 was monitored after exposure to HCl vapors (hereinafter referred to as O_{fa1}). Intriguingly, the fumigation of acid vapors also significantly affected the fluorescence of G_1 powder, turning it from bluish green to orange with a peak at approximately 565 nm [$\Phi_F=0.27$, $\tau_1=0.87$ ($A_1=0.52$), $\tau_2=2.19$ ($A_2=0.44$)]. Similar to the Y_{fa1} powder, the deprotonation of O_{fa1} with the aid of NH_3 could result in completely recovered emission toward G_1 (Fig. S7). In addition, when Y_{fa1} powder was ground, its fluorescence changed from yellow to orange (G_Y), which was similar to that of O_{fa1} powder (Fig. S4). Evidently, both of the protonated samples, Y_{fa1} and O_{fa1} , were easily restored to the pristine B_1 solid powder upon heating, suggesting a lossless switching. Therefore, a four-color switching was achieved under protonation-deprotonation stimuli from a single molecule of TPENSOH, which could be facilely tuned by pressure.

Single crystals of T1 (constituted by unprotonated TPENSOH molecules) and T2 (constituted by TPENSOH molecules protonated with HCl), and T3 (constituted by tetrahydrofuran molecules and TPENSOH molecules protonated with HCl) with highly ordered molecular packing structures were obtained by using the solvent evaporation method. As illustrated in Fig. 1B, T1, T2, and T3 emitted intense blue (454 nm), green (521 nm) and yellow (553 nm) light with quantum yields of 64%, 34% and 29%, respectively. Notably, the emission spectra of T1 and T3 agreed well with those of solid powders before and after protonation of pristine TPENSOH, which suggests that the molecular packing modes of B_1 and Y_{fa1} were possibly similar to those of T1 and T3, respectively. Systematic analysis revealed that the chemical structures of the three single crystals were completely different (Fig. S8). All the single crystals belonged to the monoclinic system (Table S2) and

formed packed molecular layers with the aid of weak C-H $\cdots\pi$ interactions. In the case of T1, the molecules adopted antiparallel coupling and established efficient tail-to-tail interaction with adjacent molecules through O-H $\cdots\pi$ and C-H \cdots O hydrogen bonds in each layer (Fig. S9). Such strong interactions helped solidify the molecular conformation and blocked non-radioactive pathways, resulting in a high quantum yield of T1. After protonation of benzothiazole moieties with the chloride ion as the counter-ion, a different stacking mode was observed in T2, the intermolecular interactions of which were mainly composed of O-H \cdots Cl⁻ (II) and N-H \cdots Cl⁻ (III) interactions in the layers (Fig. S10). The unit cell consisted of four crystallographically independent protonated TPENSOH molecules and four chloride ions, which were filled in the heart-shaped channels. Additionally, the H-type aggregation occurred along the long axis of the molecules in both of the crystals (Fig. 2). The centroid distances between two benzothiazole planes in T1 and T2 were measured to be approximately 3.639(2) Å and 3.771(1) Å, respectively, which corresponded to the formation of weak π - π interaction (Table S3). The π - π overlap of the benzothiazole planes between the adjacent molecules increased significantly from T1 to T2, which could enhance exciton coupling and then strongly red shift the emission of the chromophores in crystal T2.¹⁰ Meanwhile, the quantum chemical calculations based on the density functional theory were conducted at the B3LYP/6-31G(d) and B3LYP/6-31G+(d) levels using Gaussian 09 to investigate the effect of protonation of benzothiazole on luminescent properties. The theoretical calculation results suggested that TPENSOH in T1 and TPENSOH-HCl in T2 had ICT characteristics: the electronic transitions (mainly from HOMO to LUMO for TPENSOH in T1 and from HOMO-3 to LUMO for TPENSOH-HCl in T2) from occupied orbitals delocalized over the TPE (donor) moiety to the benzothiazole (acceptor) moiety made major contributions to the excited states (Table S4). Benzothiazole is electron-withdrawing compared with the TPE moiety. The electron-withdrawing character of benzothiazole was intensified upon protonation with HCl, which strengthened the push-pull effect and further promoted the ICT process from the TPE unit to the benzothiazole-H⁺ moiety, resulting in a remarkable red shift of the spectrum.

In the case of T3, solvent molecules were found to fill in the heart-shaped channels accompanied by the chloride ions (Fig. S11). Moreover, specific intermolecular interactions observed in T2, such as the π - π stacking and H-aggregation, were ruled out by X-ray analysis data, and the molecules were bound together mainly by N-H \cdots Cl⁻ (I), O-H \cdots Cl⁻ (II), and C-H \cdots Cl⁻ (III) interactions, which might have resulted from the insertion of solvent molecules in the

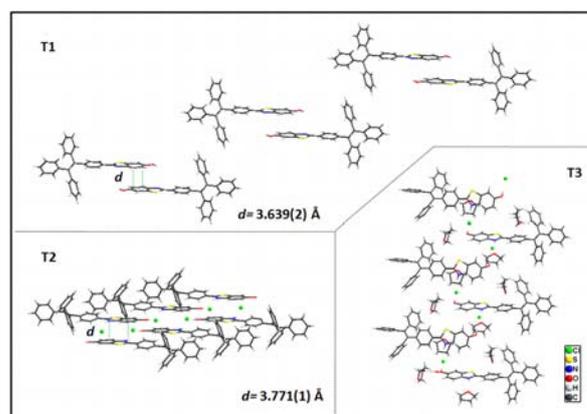


Fig.2 Stacking modes of the three single crystals.

crystal structure. Nevertheless, most of the dihedral angles of the molecules in T3 between the neighboring phenyl rings notably decreased as compared with the ones in T2 (Table S5). The planarization of molecular configuration may result in a large increment of electronic conjugation and a more efficient ICT process, thus shifting the emission of TPENSOH-HCl in the single crystals from green to yellow. Given that the TPENSOH-HCl chromophores in T3 were surrounded by solvent molecules, the solvent relaxation process might emerge and contribute to the remarkable red shift of fluorescence. In fact, the emission of T3 can recover spontaneously toward T2 at room temperature in about half a month (not shown here), which should be attributed to the gradual escape of solvent molecules from the channels and the recovery of molecular configuration.

As previously mentioned, the emission of pristine B₁ powder under the stimuli of HCl vapors exhibited a large red shift of 96 nm from 454 nm to 550 nm, which totally covered the corresponding spectra of the three crystals T1 (454 nm), T2 (521 nm) and T3 (553 nm). In this acid-stimuli-responsive process, pristine B₁ powder is believed to undergo a transformation between the molecular aggregation states of the three crystals. That is, external HCl-stimuli induced the molecular aggregation state of TPENSOH powder to transform from channel-rich microcrystals, such as T1, to the benzothiazole protonated aggregation, as found for T2, and further to the solvent molecule (*i.e.* H₂O from the concentrated hydrochloric acid or the moisture in the air) encaged arrangement, as in the case of T3. Meanwhile, the ICT process gradually strengthened, accompanied by the enhancement of excitonic coupling or the solvent relaxation, thus inducing the fluorescence of the original powder to change from blue to yellow. Similarly, the ground sample G₁ probably underwent the same process, changing its emission from bluish green to orange when exposed to HCl vapors.

The phase characteristics of TPENSOH powder were investigated by powder X-ray diffraction to obtain more insight into the origin of the piezochromic properties of TPENSOH. As depicted in Fig. S12A, the pristine B₁ solid powder clearly showed intensive and sharp reflection peaks, suggesting a well-ordered microcrystalline-like structure. By contrast, although some resolvable peaks of the ground sample were consistent with those of the pristine solid powder, most of the original peaks became weaker or even disappeared, which reveals that the ground sample was partially in a metastable amorphous state. Additionally, differential scanning calorimetry (DSC) was also performed for the samples of before and after grinding, and the results are shown in Fig. S12B. Compared with B₁, an additional exothermal peak at approximately 132 °C was observed in the DSC thermogram of G₁, fully demonstrating that the microcrystals of B₁ were partially destroyed and converted to the amorphous state by grinding treatment. The theoretical calculation results shown in Table S5 revealed that the dihedral angles between any of two neighboring phenyl rings in the simulated free molecule were significantly lower than that for the corresponding ones in T1. Thus, the twist stress of the molecules in crystals is believed to be greater and is therefore readily released when triggered by external pressure, leading to the planarization of molecular conformation. In other words, the amorphization of microcrystals in B₁ resulted in an extension of molecular conjugation, and a bathochromic shift of fluorescent emission then occurred. The red shift of O_{fa1} powder relative to that of Y_{fa1} should be attributed to the same reason.

In summary, we have developed an AIE-active luminophore with remarkable four-colored switching based on the piezo and protonation-deprotonation control. The investigation on the single crystals with distinctly different fluorescent emissions indicated that

the process for the acid-stimuli-response of TPENSOH underwent a two-step transformation, *i.e.* protonation of benzothiazole moiety, and then planarization as well as solvent relaxation of the resultant TPENSOH-HCl. The results of WXR and DSC, as well as the theoretical calculation show that the piezochromic luminescence of the pristine TPENSOH powder upon grinding originated from the amorphization of microcrystals and the extension of molecular conjugation. Such multicolored-switching features of TPENSOH may enable this novel AIE dye to promise an array of potential applications in the fields of chemosensors, optical displays and rewritable optical media.

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