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Reversible piezofluorochromic nature and mechanism of Aggregation-Induced Emission-Active compounds based on simple modification

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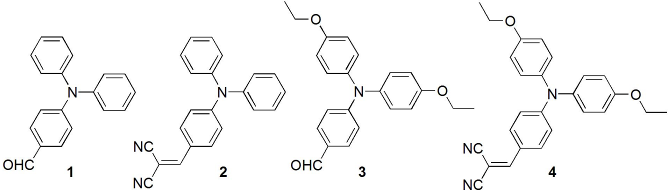
Simply modifying triphenylamine generates four luminophors with aggregation-induced emission characteristics. Three of them can be smartly switched in the fluorescence emission by various external stimuli such as grinding, annealing and solvent-fuming, which may be attributed to the transformation from the crystalline state to the amorphous state and vice versa.

Stimuli-responsive luminophors have been considered as one of the most important organic materials due to their potential applications in sensors or memory,[1] which were frequently constructed by varying the substituent groups. However, the disadvantage of irreversibility make it difficult to alter fluorescence through simply chemical modification in the solid state. One promising approach to provide the materials with reversible color transition is to control the mode of molecular packing by force. However, fluorescence efficiency of organic luminescent materials often becomes weak at high concentration or in the solid state as a result of the ACQ (aggregation-caused quenching) effect.

Several anti-ACQ materials were reported by Tang *et al*. and Park *et al*.[2] in 2001 and 2002, respectively, and these substances are termed aggregation-induced emission (AIE) and aggregation-induced emission enhancement (AIEE) materials. Some AIE or AIEE materials among these functional materials not only exhibit strong emission in solid state, but also possess stimuli-responsive switching properties. Hence, taking advantage of AIE-active materials as promising candidates to develop stimuli-responsive materials has a promising future. Although a lot of research has been carried to this area, the piezofluorochromic mechanism is still under debate. The structure-property relationships of these compounds need to be further studied to help the design and synthesis of more novel stimulus-response materials.

During our research for new AIE fluorophor based on triphenylamine,[3] we accidentally found that the reactant 4-Diphenylamino-benzaldehyde is not only AIE-active but also PIE (piezofluorochromism-induced emission)-active, which conformed with the concept of PAIE (piezofluorochromic aggregation-induced emission).[4] With this in mind, we made some simple modification to triphenylamine to further study the structure-property relationship of PAIE materials. It was found that the emission of those AIE materials could be switched between two different fluorescent colors through modulating their molecular packing pattern.[5]



Scheme 1 Chemical structure of compounds **1-4.**

The target compounds (Scheme 1) were prepared according to the synthetic routes shown in the Scheme 1S. We make a full description of the synthetic approach and the characterization of the corresponding compounds in the ESI (electronic supporting information).

Fig. 1a and Fig. 1b show the PL (photoluminescence) spectra and UV-vis absorption of **2** in solution mixtures with different water fractions. Compound **2** exhibited a very weak PL in pure DMF (dimethyl formamide). However, when the water fractions (f_w) is increased to 80%, the PL intensity was significant enhanced. The enhancement of intensity from 91 to 282 a.u. was observed as the water fraction is increased from 80% to 90%. Since water is a non-solvent of **2**, the molecules may aggregate and the free rotations were restricted, and thus the fluorescence emission was induced.

As seen in Fig. 1b, almost no change happened to the absorption curves when the water fraction is increased from 0% to 90%. However, as the water fraction is increased to 99%, a red-shift of absorption curve with a level-off tail can be obviously observed, which provided us with further evidence of nanoscale aggregation formation in aqueous mixtures with higher water fraction. The results above indicated that the emission is induced by nano-aggregation and thus **2** is AIE-active. Similar phenomena can also be observed for the other compounds (Fig. S10 and Fig. S11). Herein, **1** exhibited strong yellowish green photoluminescence when its pure solution is photoexcited, however, when the water fraction (f_w) is increased, a significant decrease in the emission intensity can be observed. This phenomenon may be attributed to an increase in the solvent polarity and energy loss in the excited state caused by the enhanced ICT (intramolecular charge transfer) process.[6] From pure

DMF to mixture of 10% $f_{w,}$ the solvation and ICT process are dominant, which may contribute to the non-radiative excitation caused by the free rotation of the σ bonds, and thus no light emission can be observed. However, the PL intensity was swiftly promoted with a water fraction of 80%. Although water was further added, solvent polarity may no longer have a considerable influence on the optical properties. A positive solvatochromism of **1** can be observed in Fig. S12 and the maximum emission wavelength in polar solvents red shift compared to those in apolar solvents. Indeed, according to the molecular simulation, the electron distribution in the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels are located around the triphenylamine and aldehyde/malononitrile groups (Fig. S13), respectively, which is indicative of ICT process and demonstrate our previous inference.

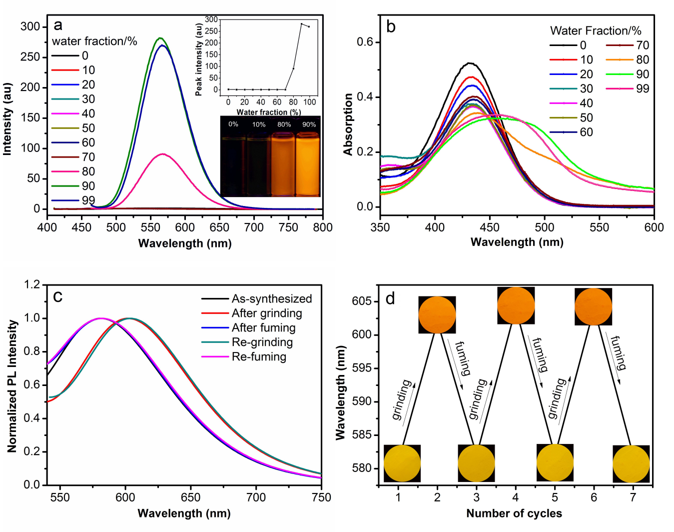


Fig. 1 (a) PL spectra of **2** in the DMF/H_2O mixture with different water fractions. Concentration of **2**: 10 μM; excitation wavelength: 365 nm. The top inset shows the changes in the PL peak intensity. The bottom inset shows the emission photos of compound **2** in pure DMF as well as solvent mixtures with 10%, 80% and 90% water fractions taken under 365 nm UV illumination; (b) UV-vis absorption spectra of **2** in DMF/ H_2O mixtures with different water fractions; (c) Normalized PL spectra of **2** powder upon repeated fuming and grinding; (d) Maximum emission wavelength change versus repeating cycles (auxiliary photos: luminescence of solids for **2** taken at room temperature under UV light after grinding and after initializing by fuming process).

The as-synthesized compound **2** exhibited strong yellow luminescence (581 nm) in the solid state. After grinding, the sample showed a strong orange emission (602 nm) with a red-shift of 21 nm (Fig. 1c and Fig. 1d, others in Fig. S15 and Fig. S16), which is a typical mechanochromic phenomenon. Upon further fuming with DCM (dichloromethane) vapor for 5 minutes or annealing at 80℃ for 10 minutes, the original color can be restored. The conversion between yellow and orange emission colors can be repeated many times without fatigue.

Fig. 2 shows the real time pictures of evaporation procedure of drops of **1-4** solution in dichloromethane placed on a filter paper. At the early development, the wet spots could scarely be visualized under irradiation at 365 nm by a UV lamp (Fig. 2a). As the solvent evaporated, all the spots except **4** changed to brighter color (Fig. 2b) and finally reaching full-size brightness (Fig. 2c) after the solvent completely volatilized, which further indicating that compounds **1-3** are AIE-active and have potential for application as security inks. Herein, no obvious change of **4** in fluorescence emission intensity can be observed, which correspond with the weak AIE properties as shown in Fig. S10.

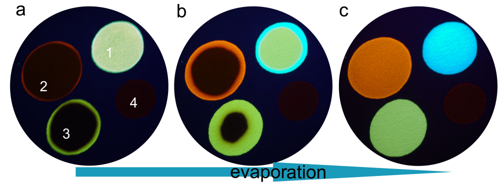


Fig. 2 Photographs of several drops of **1-4** solution in CH_2Cl_2 taken on a filter paper under irradiation at 365 nm (time: a = 2 s, b = 5 s, c = 9 s).

The as-synthesized sample of **2** was outspread on filter papers and labeled as "AHU" with a metal spatula in contrast to the yellow surrounding regions. Under a hand-held UV lamp, the letter "AHU" emits orange light, which can be erased by either vapor fuming or thermal annealing treatment (Fig. 3a). Thus, various kinds of pattern can be recorded simply by hand-writing and be erased by annealing or fuming, which makes **1-3** promising candidates for optical recording and pressure-sensing systems.

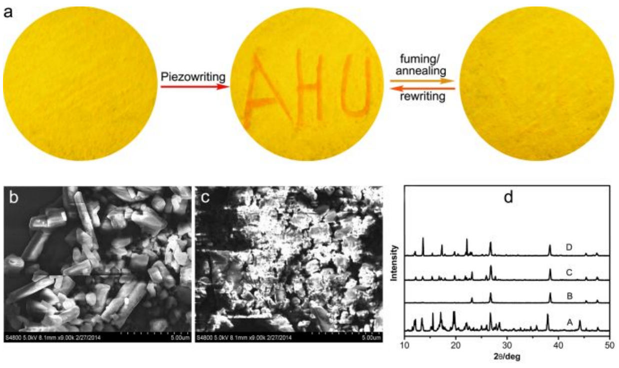


Fig. 3 (a) Photographs of **2** in filter paper upon piezowriting-erasing by fuming, annealing and grinding under UV-light (365 nm); (b) SEM of the as-synthesized sample; and (c) the ground sample of **2**; (d) WXRD of **2**: A) as-synthesized sample, B) ground sample, C) fuming B in CH_2Cl_2 vapor for 5 minutes, D) annealing B at 80 ℃ for 10 minutes.

Fig. 3b and Fig. 3c show the scanning electron microscope (SEM) images of the as-synthesized and ground sample of **2**, respectively. As shown, the as-synthesized sample shows a rectangular shape with different lengths. After it was ground, the crystal particles was destroyed and broke up into amorphous pieces, resulting in a crude surface. This process leads to the red-shift of emission of **2** from yellow to orange. To gain further insight into the mechanism of the piezofluorochromic effect, we also carried out the wide-angle X-ray diffraction (WAXD) measurement. According to the WAXD data of the as-prepared **2** solid (Fig. 3d-A), the diffraction pattern exhibited multiple strong and sharp diffraction peaks, indicating of its crystalline structure. In contrast, no noticeable diffraction peak can be observed in the profiles of the ground sample (Fig. 3d-B), which implying that most of the crystalline structures were destroyed and transformed to amorphous state. However, the WXRD curve diffraction peaks reemerged after simple fuming or annealing treatments (Fig. 3d-C and Fig. 3d-D), which realized the reversible conversion of piezofluorochromism. This interesting phenomenon can also be observed for other compounds except for **4**. With regard to **4**, no diffraction peaks can be observed in the profiles of either as-synthesized sample or ground sample. Meanwhile, no obvious change can be observed in the change of maximum emission wavelength (Fig. S15-4) and SEM images (Fig. S17) when as-synthesized or ground, which indicating that **4** is amorphous even when as-synthesized.[7] These results demonstrate that the change of molecules from crystalline state to amorphous state can indeed induce a significant PIE properties.[8]

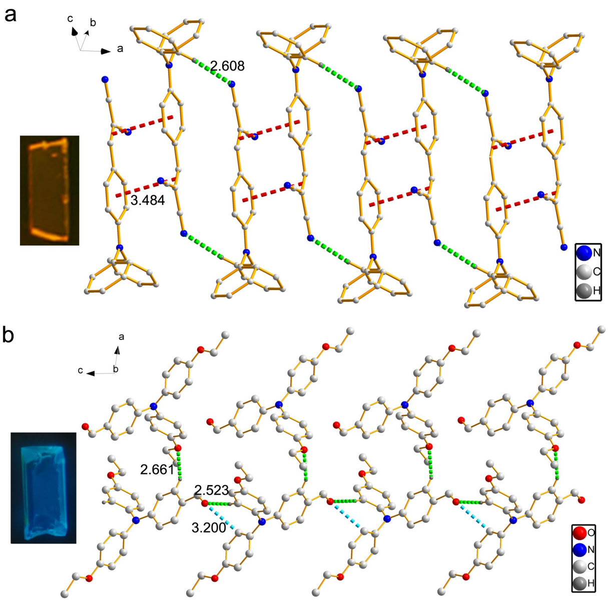


Fig. 4 (a) Molecular packing of **2** in single crystals with π···π (3.484 Å), C-H···N (2.608 Å) hydrogen bonds indicated; (b) Molecular packing of **3** in single crystals with O···C (3.200 Å), C-H···O (2.523 Å) and C-H···O (2.661 Å) hydrogen bonds. The left insets show the photographs of single crystal of **2** (yellow) and **3** (blue) irradiated under UV-light (365 nm).

The single crystals of compounds **2** and **3** (Fig. 4, single crystal of **1** in Fig. S19) are easy to be obtained by recrystallization with ethanol. The highly twisted conformations, which support for the active intramolecular rotations in good solutions, can effectively consume the energies of excitation state and subsequently make **2** molecules non-luminescent. However, when the molecules aggregate as nanoparticles or solid, such rotation can be restricted. The crystalline structure shows that the molecules of **2** are packed in antiparallel pattern with weaker interactions (π-π, 3.484 Å) and hydrogen bonds (C-H···N, 2.608 Å), which can help to rigidify the conformations of molecules, thereby generating the enhanced emissions.[9] The highly twisted benzene rings in this crystal molecules can also prevent the formation of exciplex or excimer, which could further favor the boosted emissions. Fortunately, such twist can be released when the conformation was planarized upon facile mechanical stimuli, which could also be restored upon thermal annealing or solvent fuming. The high twisted stacking architectures could result in shorter effective conjugation lengths and bluer emissions, while the planar conformation could result in increased effective lengths and redder emissions.[10] Similar twisted conformation can also be observed in the single crystals of **1** and **3**. Obviously, aromatic rings of one molecule in crystals of **3** are all restricted by the weak interactions or hydrogen bonds, which provide more twisted and compressible space than that of **2**. Thus a redder shift of emission wavelength (nearly 50 nm) can be observed in contrast to **2** (nearly 20 nm) after grinding.

In summary, we have easily synthesized and fully characterized a class of triphenylamine-derivatives. In spite of very simple molecular structure, all the compounds except **4** show excellent AIE activities. Besides, compounds **1-3** exhibit reversible off/on fluorescent switching feature to organic solvent and showed significant piezofluorochromic properties, which can be switched via external stimulation including grinding, annealing and fuming with organic vapor. Morphological change from crystalline phase to amorphous phase may account for the phenomenon. Obviously, taking advantage of triphenylamine as a core to develop PAIE materials may be feasible and effective. Meanwhile, further modification by enlarging the substituent is also underway.

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Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis and characterization of compounds **1-4**; HOMO and LUMO energy levels; change in the PL spectrum of **1-3** by repeated grinding-heating cycles, XRD profiles of **1-3** in different states; change in the PL spectrum, TEM images and XRD profile of as-synthesized sample and ground sample of **4**; CCDC: 994493, 990297, 990298 for **1**, **2** and **3**.

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