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Reversible and hydrogen bonding-assisted piezochromic luminescence for solid-state tetraaryl-buta-1,3-diene†

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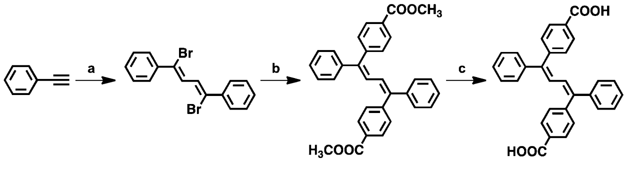
Reversible piezochromic luminescence and aggregation induced emission properties of 4,4′-((*Z*,*Z*)-1,4-diphenylbuta-1,3-diene-1,4-diyl)-dibenzoic acid are reported. The photoluminescent color of it changes from blue to yellow-green upon grinding, which can be restored upon exposure to a solvent. Intermolecular hydrogen bonding plays a key role in the altered emission.

Piezochromic materials, which change the color of their luminescence in response to mechanical stimuli, are of practical importance for mechano-sensors, optical recording, security papers and optoelectronic devices.[1] They possess significance in fundamental research to establish the remarkable influence of the subtle interplay of molecular and supramolecular level structures on the tuning and altering of the luminescence of fluorophores in the solid state (SS).[2] Although a variety of mechano-sensitive organic molecules,[3] metal complexes[4] and polymers[5] have been developed recently, the rational molecular design of such materials and an effective mechanism explanation still need to be explored.

In order to access piezochromic materials with high performance, chromophores that can emit high fluorescence in the solid state with stimuli-responsive units are expected to be incorporated. Aggregation induced emission (AIE) molecules, discovered in 2001 by Tang's group,[6] are a class of materials that show no emission or little emission in dilute solutions but are brightly fluorescent in their aggregation state.[7] Unlike typical luminophores that usually quench their fluorescence in SS resulting from undesirable intermolecular interactions (*e.g.* π–π stacking, the formation of excimers), AIE luminophores generally contain short intermolecular interactions (*e.g.* C–H···π) in SS, which can not only prevent the formation of π–π stacking interactions, but can also efficiently obstruct the rotation of the phenyl groups and permit deactivation by fluorescence in the aggregation state.[8] On the other hand, although the atoms within crystals can move, the movement is severely constrained. We suppose that the introduction of another stimuli-responsive part is preferred to produce some remarkable changes by mechanical force.

Herein, we designed and synthesized a novel piezochromic material 4,4′-((*Z*,*Z*)-1,4-diphenylbuta-1,3-diene-1,4-diyl)dibenzoic acid (TABD–COOH), which exhibits high solid-state fluorescence quantum yield (69.60%) with characteristic AIE properties as well as reversible mechano-responsive abilities. A drastic change in fluorescence of TABD–COOH occurred upon grinding and can be fully restored to its original color upon exposure to solvents or their vapors. The destruction of intermolecular hydrogen bonding (H-bonding) interactions by applying high pressure, leading to the state where close packing is the overriding factor governing molecular packing, is responsible for the altered emission of the ground samples.

TABD–COOH was prepared in three simple steps with an overall yield of 51% (Scheme 1). A full description of the synthetic approach and the characterization of the corresponding compounds are provided in the ESI.† Compared with iconic AIE-fluorophores, tetraphenylethylene (TPE) derivatives, that were synthesized through McMurry coupling reaction,[7d] the product of which is commonly a mixture of *E* and *Z* stereoisomers, TABD derivatives can be easily obtained symmetrically with high stereoselectivities. Meanwhile, TABD–COOH is thermally



DBDABD **TABD-COOCH$_3$** **TABD-COOH**

Scheme 1 Synthesis route of TABD–COOH. (a) PdCl$_2$, CuBr$_2$, r.t.; (b) 4-methoxycarbonylphenylboronic acid, Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (aq), reflux; (c) (1) NaOH (aq), reflux (2) HCl (aq).

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stable up to 320 °C as indicated by thermal gravimetric analysis (Fig. S1, ESI†), which is important for further device applications.

AIE features of TABD–COOH were indicated by a 55-fold increase in quantum yield when going from its THF solution (Φ_F = 1.28%) to SS (Φ_F = 69.60%). It was further verified by the trajectory of the change in its fluorescence intensity in the THF–hexane mixtures (Fig. 1). The fluorescence intensities of its solutions with a hexane fraction (f_H) lower than 60% were negligibly small. This contributes to the non-radiative de-excitation caused by the free rotation of the σ bonds. The emission started to drastically increase until the f_H reached 70%, at which point, the aggregates started to form (Fig. S2, ESI†) and the free rotations were restricted. With a f_H of 90%, the Φ_F value increased to 43.1%.

The addition of hexane to a THF solution of TABD–COOH resulted in precipitation of a white powder (F-form, Fig. S3a, ESI†), which exhibited strong blue luminescence under irradiation of UV-light (Fig. S3d, ESI†). Upon gentle grinding of TABD–COOH using a spatula or mortar, this blue-emitting white solid was converted to a yellowish solid (G-form, Φ_F = 34.76%, Fig. 2a and Fig. S3c in ESI†) showing yellow-green luminescence (Fig. 2b and Fig. S3f in ESI†), and this change occurred only at the pressed area (Fig. 2a and b). Attractively, it can be reverted to its original color upon adding a drop of polar solvent (*e.g.* MeOH, EtOH, THF, Fig. 2c). Absorption and emission spectra of TABD–COOH in two forms are shown in Fig. S4 in ESI† and Fig. 3(a), respectively. A red shift of 11 nm in UV-vis absorption spectra was observed from the F-form powder (λ = 363 nm) to the G-form powder (λ = 374 nm), whereas the maximum emission wavelength shifted from 448 to 478 nm. This remarkable change in fluorescence upon grinding is a characteristic piezochromic effect. Meanwhile, TABD–COOCH$_3$ exhibits a similar AIE phenomenon, but its piezochromic change is not as significant as that of TABD–COOH.

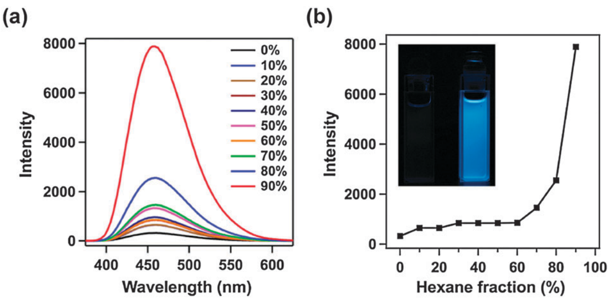

Fig. 1 (a) FL spectra of TABD–COOH in the THF–hexane mixture with different f_H. TABD–COOH concentration: 10 μM; excitation wavelength: 360 nm. (b) Plot of maximum intensity *vs.* f_H. Inset picture: image of TABD–COOH in THF–hexane mixtures with f_H of 0 (left) and 90 (right) under illumination using a hand-held UV lamp at 365 nm.

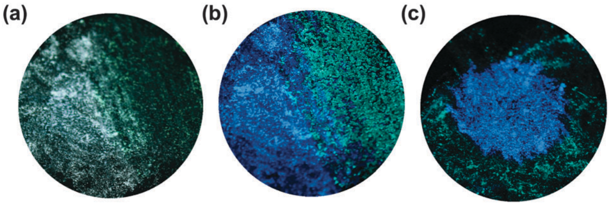

Fig. 2 (a) Photograph of the half-ground powder of TABD–COOH under ambient light. (b) Photograph of the half-ground powder under UV irradiation (365 nm). (c) Photograph of the entire-ground sample after treatment with a drop of MeOH.

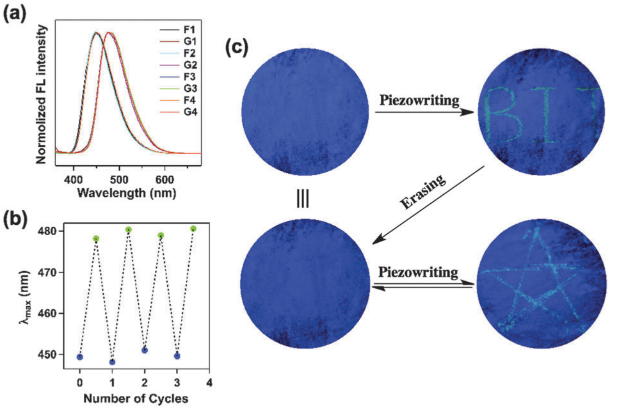

Fig. 3 (a) Normalized FL spectra of the TABD–COOH powder upon fuming–grinding. (b) Maximum emission wavelength change *versus* repeating cycles. (c) Photographs of TABD–COOH cast filter paper upon piezowriting–erasing under UV-light (365 nm).

The reversibility of piezochromic behaviour was confirmed (Fig. 3). The yellow-green emission color obtained after grinding (G-form) could be fully restored to its initial state (F-form) upon simply wetting or fuming with polar solvents, such as MeOH, EtOH and THF, and this piezochromic change could be repeated many times without any deterioration (Fig. 3a and b). As a practical fast-responding demonstrator for piezochromic luminescence tuning, we prepared a blue-emitting film by casting THF solution of TABD–COOH on a filter paper. As shown in Fig. 3c, three distinct yellow-green luminescent letters "BIT" were written on the filter paper with a spatula in contrast to the blue surrounding regions. This piezowriting could be erased upon exposure to organic vapor (several minutes) as well as upon adding polar solvents on it (within 1 second). Thus, various kinds of patterns can be recorded simply by handwriting and subsequently be erased with solvents.

FT-IR, single crystal X-ray diffraction, powder X-ray diffraction (PXRD) and differential scanning calorimetry (DSC) measurements were applied to gain insight into the origin of the piezochromic properties of TABD–COOH.

A broad absorption peak near 3430 cm^{-1} arising from H-bonding interactions was observed in the FT-IR spectrum of the F-form TABD–COOH, whereas a relatively sharp peak at 3423 cm^{-1} resulting from "free" O–H bands in the G-form solid was detected (Fig. S5, ESI†). In addition, compared with the G-form solid, the C–O stretching band shifted from 1205 to 1267 cm^{-1} and the out-of-plane O–H band appeared at 932 cm^{-1} for the F-form solid. These results indicated that H-bonding interactions in TABD–COOH were generated upon fuming and suffered a different extent of deformation by the applied pressure.

Upon crystallization from the THF–hexane mixture, a transparent single crystal of TABD–COOH was obtained. The structure solved from the diffraction data confirmed that multiple H-bonding interactions occurred (Fig. 4), for example, O–H···O interactions between the carboxylic acid group in TABD–COOH and oxygen atoms in THF, C–H···π interactions between TABD–COOH

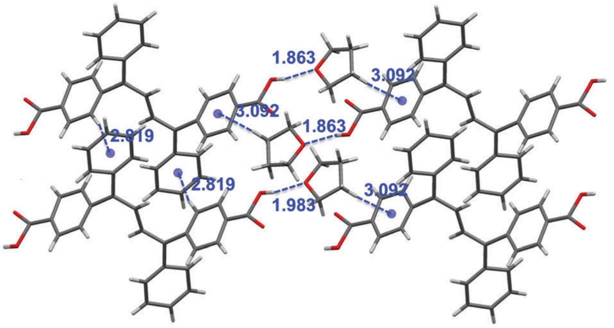

Fig. 4 Illustration of H-bonding interactions (O–H···O and C–H···π) in the TABD–COOH single crystal.

and THF and C–H···π interactions between two adjacent TABD–COOH molecules. With the aid of all of these H-bonding interactions, the free rotation of σ bonds was obstructed and the close π–π interactions were avoided.

The PXRD pattern of the F-form solid showed clear reflection peaks, which suggested the formation of ordered structure. It should be noted that this pattern is not similar to the diffraction data simulated from single crystal structure. This is because unlike the single crystal structure, for the F-form solid, dimeric and even "polymeric" structures could be formed due to strong H-bonding interactions between carboxylic acid groups in two adjacent TABD–COOH molecules. On the other hand, the PXRD intensity of the G-form solid was strongly weakened (Fig. S6, ESI†), which is an indication of partial deformation of the ordered structure. Meanwhile, although the heating profile of the F-form solid showed no peak up to 250 °C, two clear exothermic peaks at 133 and 151 °C were observed only in the first heating curve of the G-form solid (Fig. S7, ESI†). These two peaks were supposed to contribute to crystallization and crystal transformation temperatures, respectively. It is observed that after annealing, the sample can also convert to its original color due to the formation of highly ordered structures (Fig. S6, ESI†).

Thus, these results confirmed the piezochromic nature of the TABD–COOH solid. It originated from the changes in the molecular packing. That is, the molecular arrangement in the F-form solid is overridden by H-bonding interactions. Applying high pressure can destroy these interactions and lead to the formation of the G-form solid, where close packing governs the molecular packing. Furthermore, the permeation of vapors of polar solvents into the powder or film promotes the regeneration of H-bonds and the rearrangement of TABD–COOH molecules from the G-form state to the F-form state.

In summary, we have demonstrated AIE features and reversible piezochromic behavior of TABD–COOH, which was easily prepared symmetrically with high stereoselectivity. The photoluminescent color of TABD–COOH can be altered upon gentle grinding and simply recovered upon exposure to solvents within 1 s. It is shown to be effective in introducing both the AIE core and hydrogen bonding sites for the design of piezochromic material with high fluorescence quantum yield in the solid state.

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