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Synthesis and piezochromic luminescence study of a coumarin hydrozone compound†

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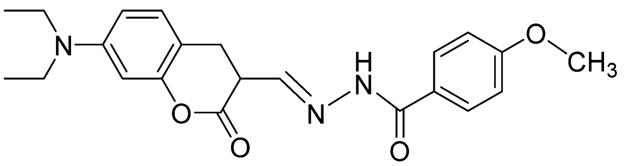
A novel coumarin hydrozone compound which exhibits piezochromic luminescence upon grinding was prepared. The piezofluorochromic properties were reversible upon fuming or heating. The intermolecular hydrogen bonds have been observed by single-crystal X-ray structural analysis, which are believed to make a major contribution to the piezofluorochromic properties.

Piezochromic luminescent materials (PLMs), a class of ''smart'' materials, have been extensively studied over the last decade due to their promising potential as rewritable optical media, pressure sensors, security inks and memory chips.[1] Araki and co-workers synthesized tetraphenylpyrene (TPPy) compounds bearing four hexyl amide groups at the *para*-position of phenyl units which showed an emission color change upon grinding.[2] Tang *et al.* and Kato *et al.* prepared various types of tetraphenylethylene (TPE)-based dyes independently, which were used as fluorescent sensors for the detection of bioactive substances.[3] Chi and co-workers reported a series of multifunctional 9,10-distyrylanthracene (DSA) derivatives, which exhibit multifunctional properties, including aggregation-induced emission (AIE), mechanochromic luminescence, vapochromism, and thermochromism.[4] In addition, other types of organic dyes exhibiting piezochromic luminescence properties have also been developed.[5]

Based on Kitaigorodoskii's close-packing principle[6] and Etter's hydrogen-bond rule,[7] π–π interaction and hydrogen bonding interaction are the two critical factors in designing tunable-state luminescent materials. For example, in the studies of Araki and co-workers, they concluded that hydrogen bond-directed interaction is the dominant factor controlling molecular packing.[2] In seeking novel versatile piezofluorochromic compounds, we design a special coumarin hydrozone derivative, which can form intermolecular hydrogen bonding in the solid state. The compound can be readily prepared by a single step condensation and shows concentration-dependent emission spectra and color change. In addition, a change in solid-state luminescence can be induced by mechanical grinding and luminescent reversion by fuming in dichloromethane (DCM). We believe that this mechanoresponsive luminescent compound will have practical application in the development of pressure sensors and security inks.

7-Diethylamino-3-(4′-methoxylbenzoylhydrazone)methylcoumarin (**DBHC**) was synthesized *via* a simple method according to Scheme S1 (see details in the ESI†). In order to verify the lowest energy spatial conformation of **DBHC**, density functional theory (DFT) calculations were performed (Scheme 1). Geometry optimizations were performed using the Gaussian 09 program. The B3LYP exchange–correlation functional[8] and the 6-31G* basis-set[9] were employed. The SMD solvation model[10] was used to represent a tetrahydrofuran (THF) solvent environment. The optimized conformation structure of compound **DBHC** can be seen in Fig. 1. The calculations also revealed an intramolecular charge transfer (ICT) trend from the *N*,*N*-diethylamino moiety to the *p*-methoxyl phenyl group in **DBHC**. The changes in the calculated electron density that can be seen from the HOMO and LUMO of **DBHC** are shown in Fig. 1.

The optical properties of **DBHC** were investigated using its photoluminescence (PL) spectra in THF solution and in the solid state. The THF solution of **DBHC** (1 μM) showed the luminescence maxima (λ_{em}) at 488 nm. Interestingly, the fluorescence emission wavelength red shifted from 488 nm to 572 nm when the concentration of **DBHC** was increased to 5 mM (Fig. 2). This concentration-dependent bathochromic luminescence shift of **DBHC** in THF could be attributed to enhanced π–π interaction and hydrogen bonding interaction.



Scheme 1 Chemical structure of **DBHC**.

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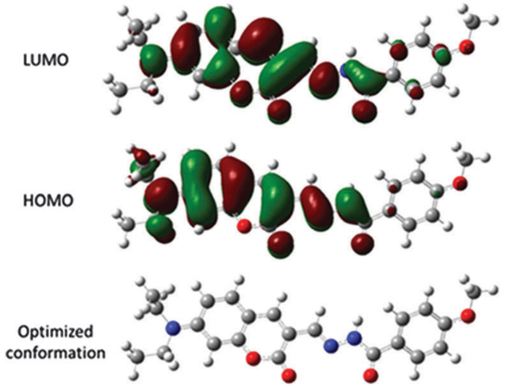

Fig. 1 Calculated spatial electron distribution of LUMO and HOMO and the optimized conformation structure of **DBHC**.

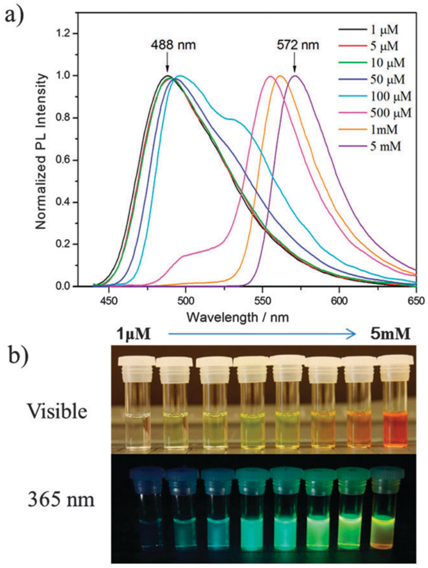

Fig. 2 (a) Normalized PL spectra and (b) color change of **DBHC** in THF with increasing concentrations of **DBHC** (1 μM–5 mM), λ_{ex} = 432 nm.

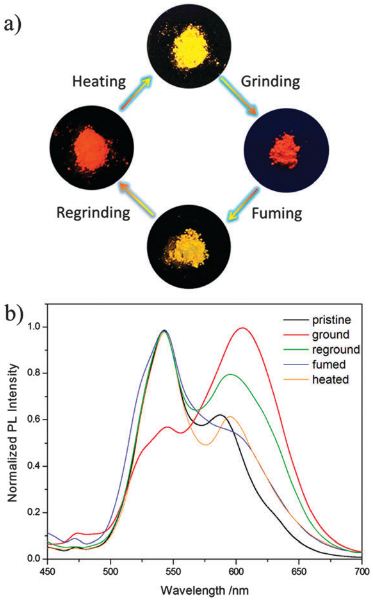

Fig. 3 (a) Images of **DBHC** taken under 365 nm UV light using different processes. The fumed sample was obtained by fuming the ground sample in DCM vapour for 5 min; the reground sample was obtained by grinding the fumed sample; the heated sample was obtained by heating the reground sample. (b) Photoluminescence spectra of **DBHC** under different treatments.

In the solid state, **DBHC** displayed red-shifted luminescence upon being ground using a pestle. Images of **DBHC** obtained under UV light, including grinding, fuming, regrinding, and heating, are shown in Fig. 3a. The pristine sample showed a luminescence color change from bright yellow to orange-red after grinding. In addition, the initial state could be recovered by fuming the ground powder with DCM vapor, which indicates that the piezofluorochromic properties of **DBHC** are reversible. Thermal annealing of **DBHC** at 170 °C also resulted in a similar luminescent reversion. Regrinding in a mortar caused a change in the luminescence color of the fumed sample from bright yellow to orange-red, and the bright yellow luminescence was recovered upon heating. These reversible switches can also be monitored by PL spectra (Fig. 3b) and diffuse reflectance absorption spectra (Fig. S2, ESI†). It was found that the PL spectra of the pristine sample exhibited a red-shift after grinding. Blue-shifts of the PL spectra were observed upon fuming and heating. The fluorescence quantum yields (Φ_f) of the corresponding states are 0.14 (pristine), 0.47 (ground), 0.10 (fumed), 0.36 (reground) and 0.08 (heated), respectively.

To study the mechanism of the piezofluorochromism of **DBHC**, wide-angle X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements were carried out. As shown in Fig. 4, the XRD curve of the pristine sample exhibited sharp diffraction peaks that indicate a well-ordered microcrystalline structure. In contrast, the diffraction peaks disappeared or decreased after grinding, showing that the structural orders of the pristine sample were disrupted. Either the intensity or the number of diffraction peaks was recovered by fuming or heating the ground sample, indicating the recovery of the microcrystalline structure. Additionally, the ground solid powder of **DBHC** showed a cold-crystallization transition peak

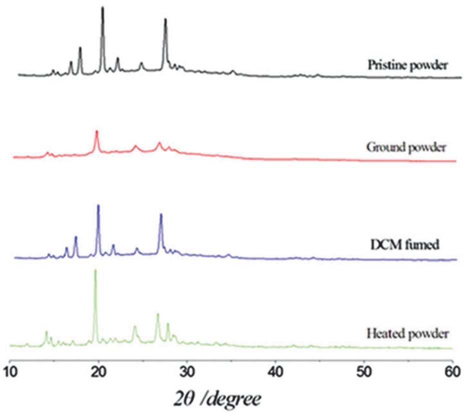

Fig. 4 XRD curves of **DBHC** as a powder with different treatments.

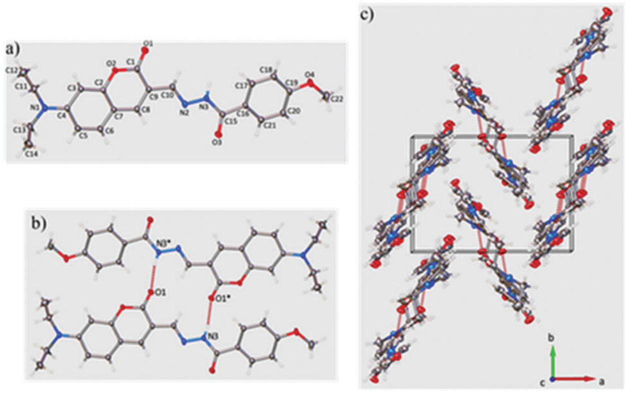

Fig. 5 (a) Displacement ellipsoid plot of the molecular structure. (b) Molecules associate into dimers by NH···O hydrogen bonding (red dotted bond) across an inversion center. (c) Molecular packing pattern of hydrogen-bonded dimers.

at 112 °C prior to melting at 268 °C, indicating an exothermal recrystallization process of the ground powder in a metastable amorphous phase converting to a stable crystalline phase. The DSC curves of **DBHC** are shown in Fig. S1 (see details in the ESI†).

To obtain further insights into the piezochromic mechanism of **DBHC**, a single-crystal X-ray structural analysis was carried out. As shown in Fig. 5, **DBHC** packed in a head-to-tail orientation to form J-aggregates. Intermolecular hydrogen bonds N3–H···O1* (2.93 Å) and N3*–H···O1 (2.93 Å) were found. Compared with the lowest energy spatial conformation of **DBHC** in THF solution, N3–H inverted to the same orientation as C1═O1 in a single crystal and formed intermolecular hydrogen bonds. Upon the bonding of intermolecular hydrogen bonds, two molecules constructed the slipped packing pattern. The free rotation of N2–N3 and N2*–N3* bonds was locked, and stable hydrogen-bonded dimers were obtained.

Based on these results, we postulate that the red-shifts of photoluminescence spectra in THF solution and in the solid state were caused by the non-covalent interaction (Fig. 6). Upon increasing the concentration of **DBHC** in THF from 1 μM to 5 mM, more hydrogen-bonded dimers formed. The larger π-conjugated electron system induced the red-shift of emission spectra and color change of solution. In addition, a stable hydrogen bond-directed structure promoted intramolecular charge transfer (ICT) from the electron-donating group (*N*,*N*-diethylamino) to the hydrazone moiety, resulting in the luminescence bathochromic shift.[5b] In the solid powder state, hydrogen-bonded dimers converted to a slightly disordered state induced by grinding, and this structural change is accompanied by a luminescence color change from bright yellow to orange-red.[2b] The ordered hydrogen bond-directed packing can be reversed by thermal treatment or DCM fuming of the ground solid powder. All these indicated that **DBHC** was a piezochromic compound.

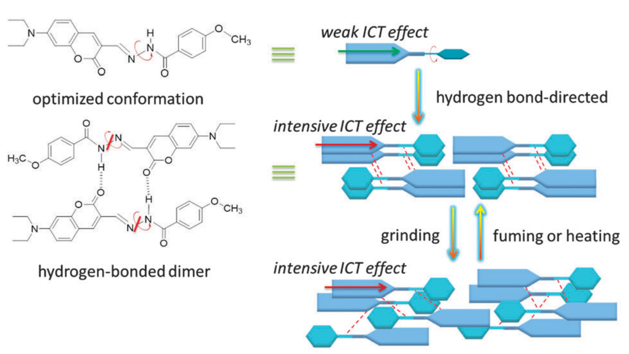

Fig. 6 Proposed mechanisms of piezofluorochromic properties of **DBHC**.

In summary, a new coumarin benzoyl hydrazone compound has been synthesized, which showed interesting piezochromic luminescence properties. The spectroscopic properties and luminescence color change in the solid state were reversible upon grinding and fuming or heating. The hydrogen bond-directed structure showed slight disorder that was caused by mechanical grinding, which could be restored by fuming or heating. These results provide a design method to use new hydrogen-bonding sites as dominant factors for designing piezochromic luminescent materials. We believe that these studies can help researchers obtain a deep insight into the piezofluorochromic mechanism and develop rewritable media, pressure sensors and security inks in the future.

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