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COMMUNICATION

Synthesis and Piezochromic Luminescence Study of a Coumarin Hydrozone Compound

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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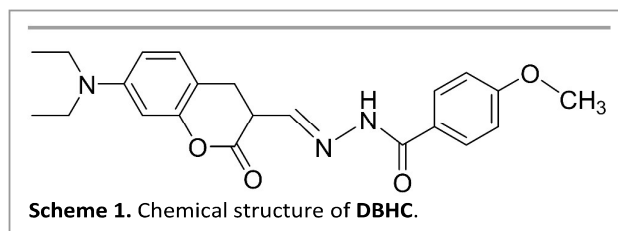
Abstract: A novel coumarin hydrozone compound which exhibits piezochromic luminescence upon grinding was prepared. The piezofluorochromic properties were reversible upon fuming or heating. The intermolecular hydrogen bonds have been observed with single-crystal X-ray structural analysis, which is believed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

Piezochromic luminescence materials (PLMs), as 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 ink 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 sensor 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 Kitaigorodskii's close-packing principle⁶ and Etter's hydrogen-bond rule⁷, π - π interaction and hydrogen bonding interaction are the two critical factors in designing tunable-state luminescent materials. For example, in Araki's

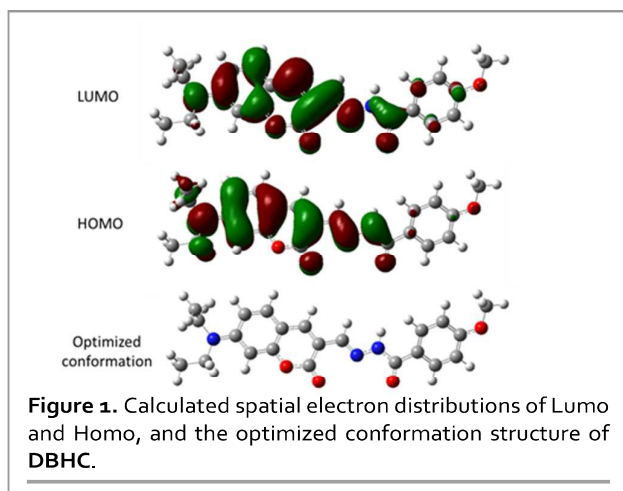
works, they concluded that hydrogen bond-directed interaction is the dominant factor controlling molecular packing.² In seeking novel versatile piezofluorochromic compounds, we design a special coumarin hydrozone derivative, which can form intermolecular hydrogen bonding at the solid state. The compound can be readily prepared by a single step condensation and shows a concentration-dependent emission spectra and color change. In addition, the solid-state luminescence changing can be induced by mechanical grinding and luminescent reversion by fuming in dichloromethane (DCM). We believe this mechano-responsive luminescent compound will have practical applications in the development of pressure sensors and security inks.

7-Diethylamino-3-(4'-methoxybenzoylhydrazone)methylcoumarin (DBHC) was synthesized via 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. Geometry optimizations were performed by Gaussian 09 program. B3LYP exchange-correlation functional⁸ and 6-31G* basis-set⁹ were employed. SMD solvation model¹⁰ was used to represent tetrahydrofuran (THF) solvent environment. The optimized conformation structure of compound DBHC can be seen in Fig. 1. The calculations also revealed that an intramolecular charge transfer (ICT) trend from the N, N-diethylamino moiety to the *p*-methoxy 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.



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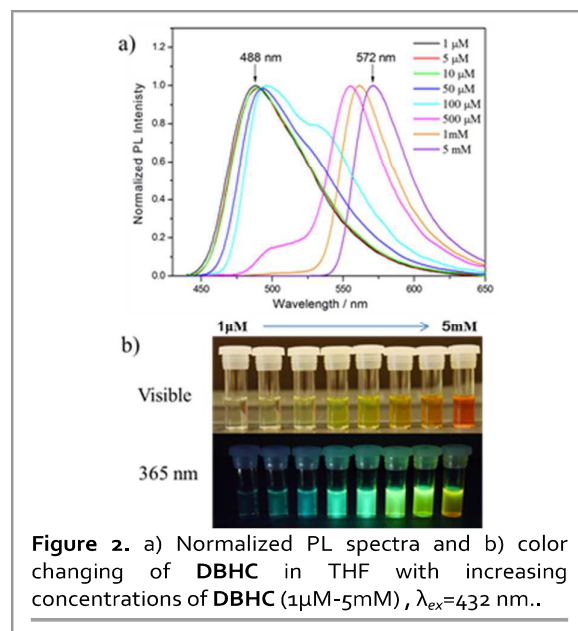
[†] Electronic Supplementary Information (ESI) available: Experimental details, DSC measurement, NMR spectra. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x



The optical properties of DBHC were investigated using its photoluminescence (PL) spectra in THF solution and at the solid state. The THF solution of DBHC (1 μ M) 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 enhancement of π - π interaction and hydrogen bonding interaction.

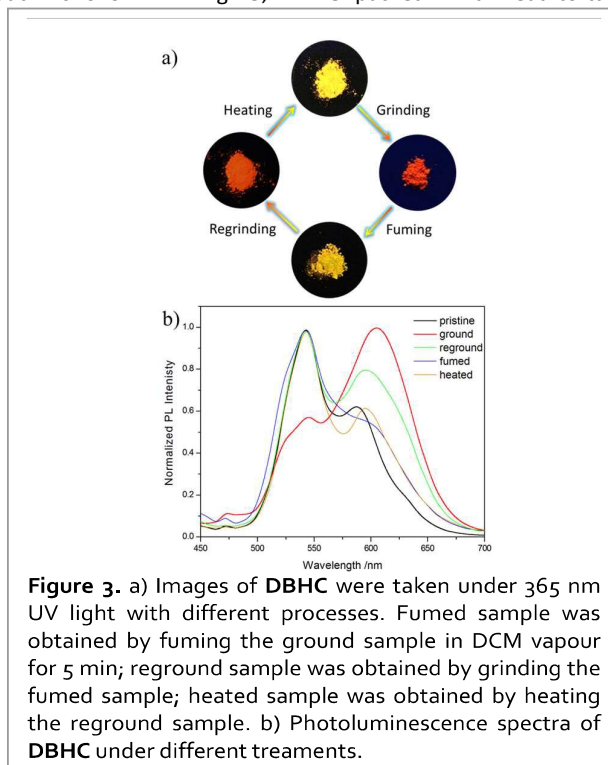
At the solid state, DBHC displayed the red-shifted luminescence upon being ground with a pestle. Images of DBHC obtained under UV light, including grinding, fuming, regrinding, and heating, are shown in Fig. 3a. The pristine sample showed a luminescence color changing from bright yellow to orange-red 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 $^{\circ}$ C also resulted in a similar luminescent reversion. Regrinding in a mortar caused a change in luminescence color of 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). It was found that the PL spectra of pristine sample exhibited red-shift after grinding. Blue-shifts of the PL spectra were observed upon fuming and heating. The fluorescence quantum yields (Φ_f) of corresponding state 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 pristine sample were disrupted. Either the intensity or number of the diffraction peaks were recovered by fuming or heating the ground sample, indicating the recovery



of microcrystalline structure. Additionally, the ground solid of DBHC showed a cold-crystallization transition peak at 112 $^{\circ}$ C prior to melting at 268 $^{\circ}$ C, indicating an exothermal recrystallization process of the ground powder in a metastable amorphous phase converting to a stable crystalline phase. The DSC curves for 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



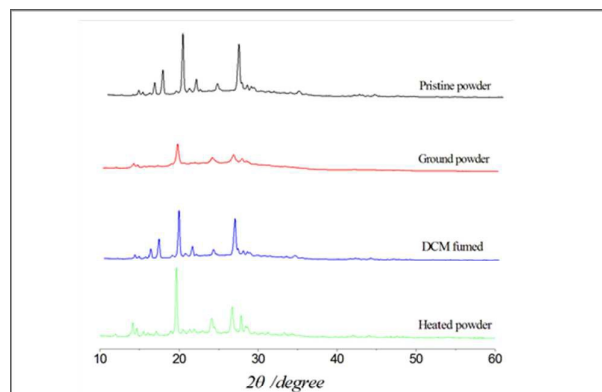


Figure 4. XRD curves of DBHC as a powder with different treatments.

orientation to form J-aggregates. Intermolecular hydrogen bonds $N3-H\cdots O1^*$ (2.93 Å) and $N3^*-H\cdots O1$ (2.93 Å) were found. Comparing with the lowest energy spatial conformation of DBHC in THF solution, N3-H inverted to the same orientation with C1=O1 in 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 were 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 the concentration of DBHC in THF increased 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, stable hydrogen bond-directed structure promoted intramolecular charge transfer (ICT) from electron-donating group (N, N-diethylamino) to hydrazone moiety, resulting in the

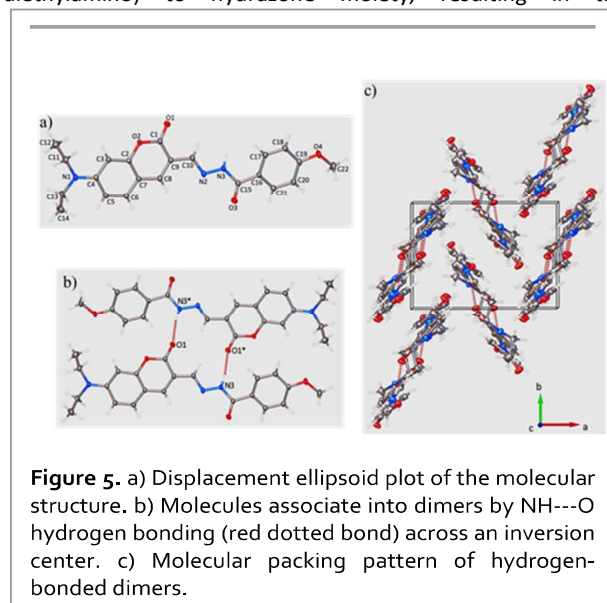


Figure 5. a) Displacement ellipsoid plot of the molecular structure. b) Molecules associate into dimers by $NH\cdots O$ hydrogen bonding (red dotted bond) across an inversion center. c) Molecular packing pattern of hydrogen-bonded dimers.

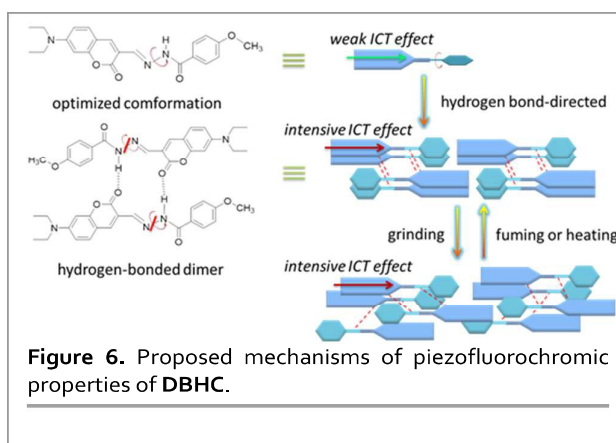


Figure 6. Proposed mechanisms of piezofluorochromic properties of DBHC.

luminescence bathochromic shift.^{5 b} In the solid powder state, hydrogen-bonded dimers converted to slight disordered state induced by grinding, and this structural change is accompanied by a luminescence color change from bright yellow to orange-red.^{2 b} The ordered hydrogen bond-directed packing can be reversal by thermal treatment or DCM fuming of the ground solid powder. All these indicated that DBHC was piezochromic compound.

In summary, a new coumarin benzoyl hydrazone compound has been synthesized, which showed interesting piezochromic luminescence properties. The spectroscopic properties and luminescence color changing 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 researches obtain a deep insight to the piezofluorochromic mechanism and develop rewritable media, pressure sensors and security ink in the future.

We are grateful for funding from the National Natural Science Foundation of Tianjin (No. 14JCTPJC00549). We thank Dr Q. Wang (University of South Carolina, UA) for the single crystal and PL spectra measurements. We would also like to acknowledge the support of National Training Program of Innovation and Entrepreneurship for Undergraduates.

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