



# Reversible piezochromic luminescence of coumarin hydrozone derivatives and the influence of substituents



Yanan Liang, Ping Wang, Hongguang Lu, Fan Wang, Lei Huang, Qiusheng Wang\*

Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China

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## ABSTRACT

Four benzoyl hydrazone coumarin derivatives with different substituents at the phenyl moiety, namely, BHC-*OCH*<sub>3</sub>, BHC-*H*, BHC-*Br*, and BHC-*CF*<sub>3</sub>, respectively, were synthesized and characterized via photoluminescence, wide-angle X-ray diffraction, differential scanning calorimetry, and other techniques. The results indicate that the compounds exhibit piezofluorochromic properties which are reversible upon fuming or heating. The fluorescence emission peaks show red shift upon grinding and the degrees of the red-shift are dependent on the electronic effect and steric size of the substituents. Based on the results, the roles of the intermolecular hydrogen bonds and the molecular charge transfer process were discussed in detail. This study will help researchers understand the piezofluorochromic mechanism and design new piezofluorochromic materials.

## 1. Introduction

Piezochromic luminescence materials (PLMs) have drawn considerable attention because of the potential in the application of rewritable optical media, pressure sensors, security ink, photonic and photoelectronic devices [1–7]. Araki and co-workers reported piezofluorochromism (PFC) phenomenon of 1, 3, 6, 8-tetraphenylpyrene (TPPy) compounds bearing four hexyl amide groups at the *para*-position of phenyl units [8]. TPPy compounds exhibited the emission color change which was caused upon mechanical grinding and reversible change upon heating. Chi et al. and Tian et al. synthesized Tetraphenylethylene (TPE)-based derivatives, which showed aggregation-induced emission (AIE) and PFC properties [9,10]. Zhang and co-workers and Yang et al. reported a series of 9, 10-distyrylanthracene (DSA) derivatives, which exhibited multifunctional properties, including aggregation-induced emission (AIE), mechanochromic luminescence, vapochromism and thermochromism [11–15]. In addition, other types of solid-state organic molecules that show a reversible color change by their luminescence have also been developed [16–18].

In a previous communication [19], we reported that a coumarin hydrozone (BHC-*OCH*<sub>3</sub>) compound showed piezochromic luminescence, of which emission color change was caused upon mechanical grinding and reversion to the original color upon fuming or heating. We have demonstrated that piezochromic luminescence properties were attributed to a reversible slight disordered hydrogen bond-directed structure.

In this study, benzoyl hydrazone coumarin (BHC) derivatives with methoxyl, hydrogen, bromide, and trifluoromethyl groups at the phenyl moiety were synthesized respectively and their piezofluorochromic properties were characterized. Piezofluorochromic activity can be changed by the introduction of different groups into the molecular. Structure-property relationships were studied in detail with emission spectra, wide-angle X-ray diffraction (XRD), differential scanning calorimetry (DSC), and other techniques. The obtained results will offer more insight into piezofluorochromic mechanism and enable the development of pressure sensors and security inks in the near future.

## 2. Results and discussion

### 2.1. Synthesis and characterization

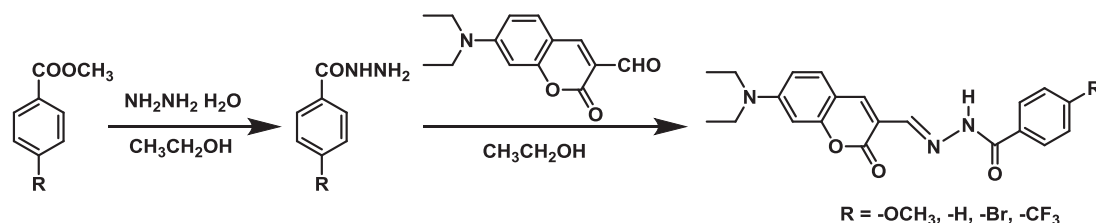
Four BHC derivatives named BHC-*OCH*<sub>3</sub>, BHC-*H*, BHC-*Br*, and BHC-*CF*<sub>3</sub>, respectively, were successfully synthesized according to the routes shown in Scheme 1. The chemical structures of all compounds were characterized via nuclear magnetic resonance, elemental analysis and mass spectrometry.

### 2.2. Photophysical properties in solution

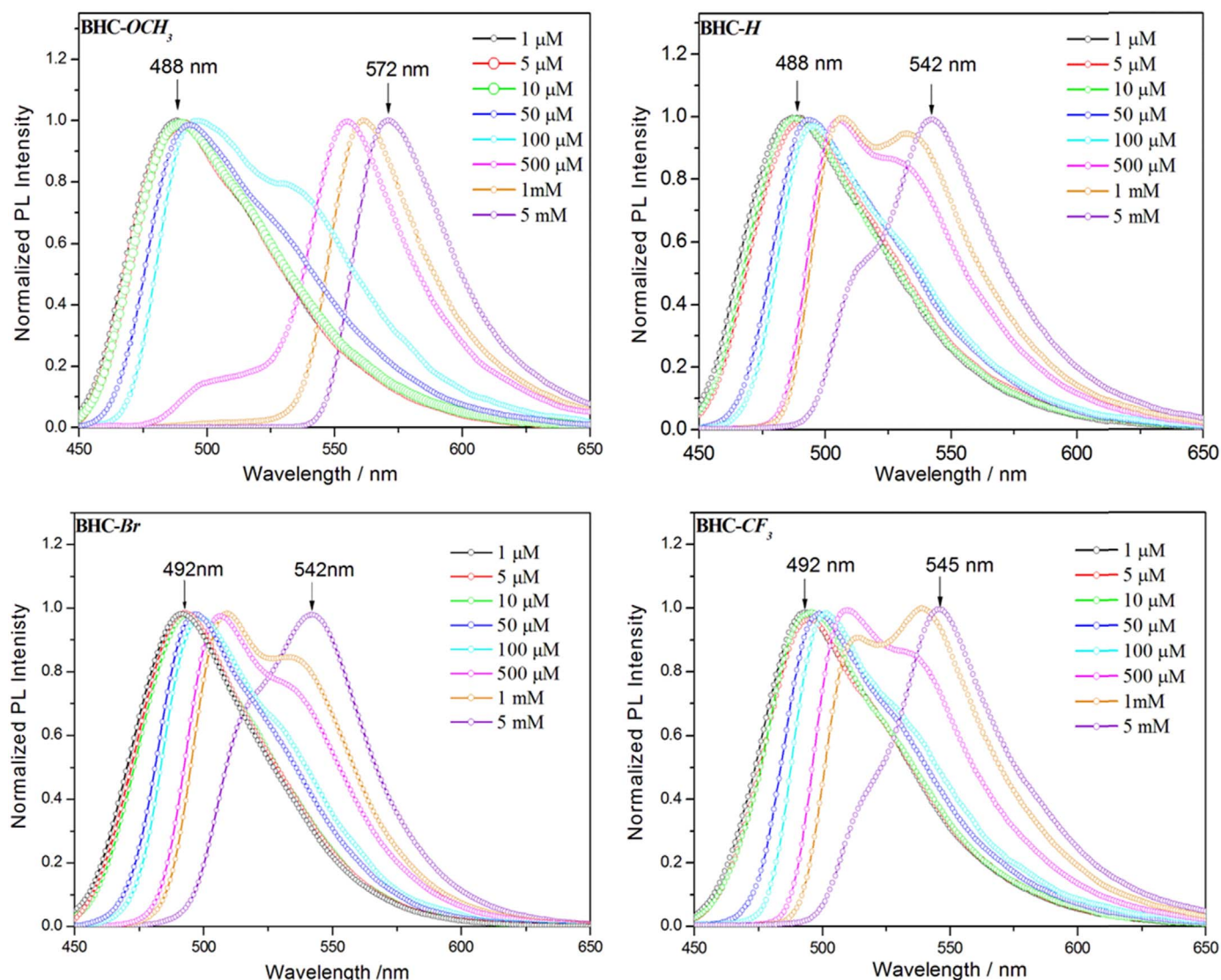
The BHC derivatives showed absorption maxima at around 435 nm in tetrahydrofuran (THF) solution (Fig. S1, Supporting information). The concentration dependence photoluminescence (PL) spectra of the

\* Corresponding author.

E-mail address: [wangqsh@tjut.edu.cn](mailto:wangqsh@tjut.edu.cn) (Q. Wang).



Scheme 1. Synthetic routes for BHC derivatives.

Fig. 1. Normalized PL spectra of BHC derivatives in THF with increasing concentrations of BHC derivatives (1  $\mu$ M–5 mM),  $\lambda_{\text{ex}} = 435$  nm.

compounds are shown in Fig. 1. Upon excitation, BHC derivatives (1  $\mu$ M) showed the luminescence maxima ( $\lambda_{\text{em}}$ ) at around 490 nm. The fluorescence emission wavelength red shifted when the concentrations of BHC derivatives were increased to 5 mM. The maximum emission wavelength of the derivatives in THF solution are listed in Table S1 (Supporting information). Although all the derivatives showed dramatic red shift, the introduction of electron donating group at 4'-position in phenyl moiety led to a larger shift in solution. This concentration-dependent bathochromic luminescence shift of BHC derivatives in THF solution could be attributed to enhanced  $\pi$ - $\pi$  interaction in hydrogen-bonded dimers.

### 2.3. Photophysical properties in the solid-state

As reported in the previous communication [19], BHC-OCH<sub>3</sub> showed bright yellow luminescence at 542 nm in solid state. The luminescence color changed to orange-red upon grinding in a mortar and returned to bright yellow again upon heating above 170 °C or fuming in dichloromethane (DCM). The BHC derivatives BHC-H, BHC-Br, and BHC-CF<sub>3</sub> powders were obtained from their ethanol solutions and they showed bright yellow luminescence. The pristine samples showed luminescence color changes upon being ground using a pestle. In addition, the initial states could be recovered upon fuming the ground powders with DCM vapor, which suggests that the piezofluorochromic properties of the compounds are finely reversible. Thermal annealing of

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