



Crystallization-induced emission of styrylbenzoxazole derivate with response to proton



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ABSTRACT

A benzoxazole derivative called **BVDA** was synthesized. **BVDA** exhibited an AIE effect although there was H-aggregated dimer in the crystal. According to the spectral results and crystal structure, the presence of excimer and the restriction of intramolecular rotation are responsible for the AIE phenomenon. Moreover, **BVDA** could respond to proton in solution and to volatile acid vapours in film. **BVDA** exhibited three colours because its binding sites to proton have different basicities. These binding sites can then be protonated in turn. These results indicate that AIE fluorophores with H-aggregated dimer is possible. Furthermore, these fluorophores can exhibit stimuli-responsive characteristics through the introduction of functional moieties.

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1. Introduction

Highly efficient emission of organic molecules in solid state is essential in optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic light-emitting field-effect transistors, organic solid-state lasers, and organic fluorescent sensors [1]. However, achieving strong emission for organic molecules in solid or crystal state is extremely difficult. One cause of the quenching process is mechanistically associated with “aggregation-caused quenching” because of the quick de-excitation of excited fluorophores through internal conversion, intersystem crossing, intramolecular charge transfer, intermolecular electron transfer, excimer or exciplex formation, or isomerization. In fact, there are some reports to disclose organic fluorophores with strong emission in solid [2]. More importantly, the group of Tang discovered a silole derivative in 2001, exhibiting dramatically enhanced emission in solid state, and named this phenomenon aggregation-induced emission (AIE) or aggregation-induced enhanced emission [3]. Many AIE molecules have been developed and applied in OLEDs, piezochromism, fluorescent sensors and probes, bioimaging, and fluorescent switch [4]. Generally, AIE molecules have twisted configurations and freely rotated single bonds, such as silole, tetraphenylethene, 9,10-

distyrylanthracene, and cyano-diphenylethene derivatives [5]. In solid or crystal state, intramolecular rotation is suppressed, and the twisted configuration leads to loose stacking, which promotes strong emission relative to the solutions. The formation of J-aggregates can also activate radiative transition and cause fluorophores to exhibit AIE properties [6]. However, fluorescent H-aggregates that exhibit AIE behaviour are rarely reported, although some emissive dyes in H-aggregate have been observed [7].

As we know, **BVDA** is one fluorescent molecule and have been applied in fluorescence probe for cell, solvent polarity, and PH [8]. In the present study, we found that **BVDA** exhibited weak emission in solutions but emitted strong fluorescence in crystal state. Spectral result and single-crystal structure suggest that the presence of anti-parallel H-aggregated dimer should be responsible for emission enhancement. Moreover, **BVDA** exhibited dual-mode response to proton and to volatile acid vapour in the solution and crystal state, respectively.

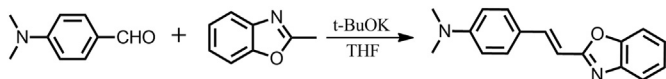
2. Experimental section

2.1. General information

All the raw materials were used without further purification. All the solvents as analytical reagent were purchased from Beijing Chemical Works (Beijing, China), and were used without further

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Scheme 1. Synthesis route of **BDVA**.

purification. Water used throughout all experiments was purified with the Millipore system. The UV–vis absorption spectra were obtained using a Mapada UV-1800pc spectrophotometer. Photoluminescence measurements were taken on a Cary Eclipse Fluorescence Spectrophotometer. The fluorescence quantum yields of **BVDA** in solvents were measured by comparing to a standard (9,10-diphenyl anthracene in benzene, $\Phi_F = 0.85$). The excitation wavelength was 375 nm. The absolute fluorescence quantum yield of **BVDA** crystal was measured on an Edinburgh FLS920 steady state fluorimeter using an integrating sphere. Fluorescence decay experiment was measured on an Edinburgh FLS920 steady state fluorimeter equipped with an nF900 ns flash lamp. Mass spectra were obtained with AXIMA CFR MALDI-TOF (Compact) mass spectrometers. C, H, and N elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. Single crystal was obtained in the mixture of CH_2Cl_2 and n-hexane by slow solvent diffusion method. The molecular configuration in crystal was used to obtain frontier orbitals of **BVDA** by density functional theory (DFT) calculations at B3LYP/6-31G level with the Gaussian 09W program package [9].

Single crystal of **BVDA** was selected for X-ray diffraction analysis on in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was kept at room temperature during data collection. The structures were solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program [10]. The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically. CCDC 994905 contains the supplementary crystallographic data for this paper.

2.2. Synthesis of **BVDA**

(E)-4-(2-(benzo[d]oxazol-2-yl)vinyl)-N,N-dimethylaniline (**BVDA**)

t-BuOK (2.2 g, 19.6 mmol) was added into dry THF (20 mL) and stirred for 10 min at 0 °C. 2-methylbenzoxazole (0.3 mL, 10.8 mmol)

was dropwise added into above suspension and stirred for 10 min at 0 °C. Then, a THF solution of 4-(dimethylamino)benzaldehyde (1.47 g, 9.8 mmol) was dropped slowly into the above solution at 0 °C. After stirred for 2 h, the mixture was poured into water (200 mL) and yellow solid was collected by filtration. The crude product was purified by a silica gel column using CH_2Cl_2 as the eluent. Yellow platy crystal was obtained in a yield of 81% (2.1 g), mp: 181–182 °C. FT-IR: 3091, 3064, 3054, 3010, 2982, 2982, 2894, 2816, 1635, 1603, 1555, 1537, 1455, 808, and 746 cm^{-1} . Element analysis (%): calculated for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}$: C, 77.25; H, 6.10; N, 10.60; Found: C, 77.20; H, 6.30; N, 10.68. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (t, $J = 16.2 \text{ Hz}$, 1H), 7.72–7.67 (m, 1H), 7.56–7.49 (m, 3H), 7.36–7.30 (m, 2H), 6.88 (d, $J = 16.2 \text{ Hz}$, 1H), 6.76 (d, $J = 8.6 \text{ Hz}$, 2H), 3.06 (s, 6H). MALDI-TOF MS: m/z : calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}$: 264.1; found: 265.1 ($\text{M} + \text{H}$) $^+$.

3. Results and discussion

BVDA as yellow platy crystal was synthesized through a one-step reaction (Scheme 1) with a yield of 81%. **BVDA** easily dissolved in CH_2Cl_2 , CHCl_3 , benzene, toluene, THF, DMF, and so on, but exhibited low solubility in cyclohexane and hexane. Moreover, **BVDA** solutions have different absorption and emission spectra (Table S1). The maximal absorption peak was observed at 378 nm in cyclohexane, a red-shifted peak (389 nm) for toluene solution appeared, and the DMF solution possessed an absorption band ($\lambda_{\text{ab}} = 394 \text{ nm}$) with the lowest energy (Fig. 1a). A structured emission band with a maximum absorption peak at 434 nm and a shoulder peak at 456 nm was observed in cyclohexane. With an increase in solvent polarity, the emission wavelength of the solutions shifted to the low energy region, and the emission bands became structureless. A red shift in the emission wavelength indicates the excited state of **BVDA** with stronger polarity than that in ground state [11], and absorption and emission bands in different solvents could be ascribed to intramolecular charge transfer (ICT) transition. The quantum-chemical calculation confirmed the ICT transition. Fig. 1c shows that the dimethylaniline group has a larger density than benzoxazole in the highest occupied frontier molecular orbital (HOMO). As the electron density of the lowest unoccupied molecular orbital (LUMO) of the dimethylaniline unit decreases, the benzoxazole and vinyl moieties achieve large

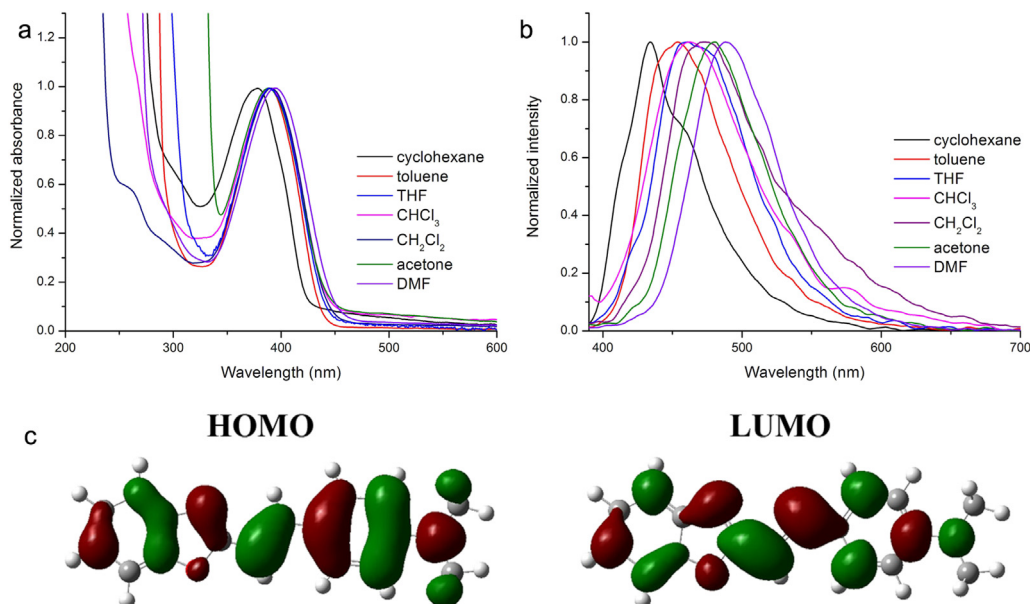


Fig. 1. (a) Absorption and (b) fluorescence spectra of **BVDA** in different solvents, and (c) frontier orbitals of **BVDA**.

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