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Triphenylamine-Based Benzoxazole Derivative as a High-Contrast Piezofluorochromic Material Induced by Protonation

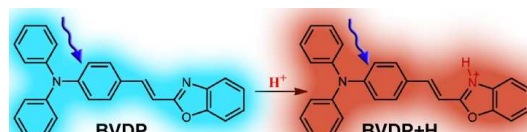
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Triphenylamine-based benzoxazole derivative exhibits a low contrast piezofluorochromic behavior under external press, and a high-contrast fluorescent change induced by protonation can be observed.

Stimulus-active organic functional materials have gained considerable attention from researchers and engineers because such materials can change their physical or chemical properties upon exposure to a particular stimulus, such as heat, electricity, light, magnet, solvent, and pH value.¹ Piezofluorochromic (PFC) organic materials have recently been developed rapidly because they are a class of smart materials with fluorescent properties that change in response to external force stimuli.² However, these smart compounds do not change their molecular structures in response to mechanical stimuli, and only intermolecular interaction or intramolecular conformation exhibit subtle changes under a press, which results in a shift in emission wavelength and causes the materials to exhibit PFC behavior.³ Tuning the molecular packing mode in a solid state is easier than altering the molecular chemical structures. Thus, these organic compounds may be widely used in sensors,⁴ memory chips,⁵ and security inks.⁶ However, fine organic PFC materials with large contrast and strong emission are rare. Numerous recent studies have focused on tetraphenylethene or triphenylethene derivatives because these compounds always exhibit excellent PFC behavior with high contrast induced by low pressure because their loose molecular stacking in a crystal state enables strong fluorescence and can be easily changed under low pressure or grinding.⁷ This fact has motivated researchers to find other efficient PFC materials with molecular loose stacking; for example, 9,10-bis-vinyl anthracene derivatives and perylene bisimide with large steric moieties.⁸ In addition, numerous works have suggested that D- π -A emissive molecules always contribute to the realization of fluorescent change under pressure.⁹

Triphenylamine (TPA) is typical nonplanar molecule that frequently serves as electron donor moiety of dyes for dye-sensitized solar cells because its nonplanar characteristic can prevent interaction or close stacking among dyes.¹⁰ Based on this idea, we synthesized a triphenylamine-based benzoxazole derivative (**BVDP**), where the triphenylimine unit serves as donor, and benzoxazole moiety serves as electron acceptor. The proposed compound is expected to change its fluorescent color with a large shift in the emission band in response to mechanical.



Scheme 1. **BVDP** chemical structure and the presentation of its emissions before and after proton binding.

stimuli. As a result, **BVDP** was found to be a PFC molecule, and the mechanically induced luminescence color can isothermally return to the original one by treatment with solvent vapors. However, grinding induced a small redshift of 32 nm in the emission band of **BVDP**, indicating a low-contrast color change observable by the naked eye. Interestingly, we found that a large redshift (76 nm) occurs after grinding when **BVDP** bound a proton to form **BVDP+H**. The corresponding emissive color reversibly changed from orange to deep red, suggesting a large contrast piezochromism. This finding suggests that piezofluorochromism can be adjusted by an additional stimulus, and more remarkable properties may be obtained.

The target compound was prepared using a one-step reaction with 2-methyl benzoxazole and 4-(diphenylamino)benzaldehyde,¹¹ as shown in Scheme S1. The compound was characterized by element analysis, NMR, and MS.

BVDP is dissolvable in many common solvents, such as THF, CH_2Cl_2 , toluene, and cyclohexane, and can form solutions with yellowish to yellow-green color depending on solvent polarity. For example, the n-hexane solution of **BVDP** has a maximal absorption peak at 392 nm, which redshifts to 395 nm in toluene and further shifts to 401 nm in CHCl_3 (Fig. 1a). This finding suggests a excited state of **BVDP** with stronger polarity than that in the ground state, as well as also implies that such absorption bands originate from intramolecular charge transfer (ICT) transition,¹² which can be confirmed by solvent-dependent fluorescent spectra and theoretical calculation. **BVDP** emits strong bluish violet fluorescence in n-hexane with two emission peaks at 427 and 448 nm (Fig. 1b) and a moderate fluorescence quantum yield ($\Phi = 18\%$, Table S1). When the polarity of the solvent increases, the fluorescence is structureless and exhibits a solvatochromic redshift (Fig. 1c) because of the dipole-dipole interactions between the solute and solvents.¹³ For instance, the fluorescence emission maximum of **BVDP** shows a remarkable redshift of 74 nm from n-hexane (434 nm) to CH_2Cl_2 (501 nm). Moreover, Lippert-Mataga plot suggests that emission maximum

energies in hexane, cyclohexane and toluene deviated from the linear relationship between other solvents (Fig. S1), suggesting a LE (locally excited) emission in nonpolar solvents and a twisted intramolecular charge-transfer (TICT) emission in polar solvents.¹⁴ The theoretical calculation has also proven the ICT transition. As shown in Fig. 1c, the electron clouds of the highest occupied frontier molecular orbital are mainly localized over the TPA unit, whereas the lowest unoccupied molecular orbitals are mainly localized over benzoxazole moiety. These results demonstrate that **BVDP** is typical D- π -A molecule.¹⁵

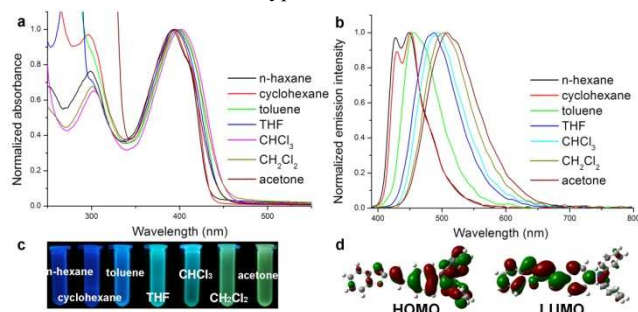


Fig. 1 Solvent-dependent absorption (a) emission (b) spectra of **BVDP**. (c) Photos of solutions under 365 nm UV light, and frontier orbitals of **BVDP**. The excitation wavelength is 370 nm.

BVDP may function as a sensory material to detect H^+ because the benzoxazole moiety can be protonated to form a cation (**BVDP+H**, Scheme 1).¹⁶ As shown in Fig. S2, the absorption of **BVDP** in $CHCl_3$ has a bathochromic shift upon the addition of TFA, such that a new peak at 498 nm appears, which results in a color change of the solution from yellowish to red. Upon excitation at 400 nm, the emission band at 492 nm gradually decreases upon the addition of TFA, and a weak emission peak at 602 nm appears and gradually enhances. NMR spectra also confirmed the formation of **BVDP+H**. As shown in Fig. S3, an evident downfield shift was observed for the phenyl protons of benzoxazole ring and vinyl group upon the addition of TFA, suggesting the proton binding of **BVDP** attributed to the protonation of nitrogen atom in the benzoxazole unit reduces the electron density around these protons.¹⁷ These results imply that fluorescent **BVDP** may respond to proton in a solid state, consequently affecting its piezofluorochromism.

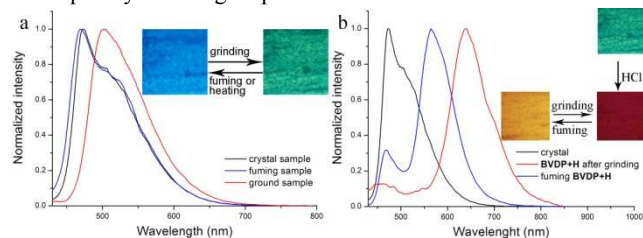


Fig. 2 Normalized fluorescence spectra (a) of **BVDP** and **BVDP+H** under external stimuli. Inset: Solid films on glass slides under 365 nm UV light.

In what follows, the PFC characteristic of D- π -A fluorescent **BVDP** is described. We can obtain a good single crystal that such crystal emits strong blue-green fluorescence under 365 nm UV light using the slow solvent diffusion method (Fig. 3c). The microcrystal of **BVDP** had an emissive maximum at 473 nm, accompanied by a shoulder peak at 510 nm, which causes the crystal to exhibit blue-green fluorescence (B-form) discernible by

the naked eye. Mechanical shearing to the yellow B-form film was applied, such that a yellow-green ground film that exhibited green fluorescence (G-form) was obtained. One wide emission peak located at 502 nm was observed, indicating a spectral redshift of 29 nm. The G-form can be retained for more than one week at room temperature. However, exposure of the G-form film to organic vapors of THF, CH_2Cl_2 , or $CHCl_3$ for several seconds induced the structural transition from the G-form to the B-form. Such recovery was also achieved by annealing at 70 °C for less than 30 s.

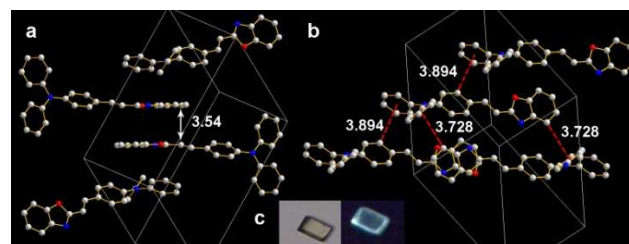


Fig. 3 Crystal packing of **BVDP** with different intermolecular interactions, (a) π - π interaction for dimer, and (b) CH - π hydrogen bonds. For clarity, the hydrogen atoms were not showed. (c) Single crystal under natural and 365 nm UV light.

To gain an insight into the PFC behavior of **BVDP**, we analyzed the absorption spectra and XRD pattern before and after grinding, as well as its single crystal (details are provided in Table S2). As previously described, grinding induces a color change from yellow to yellow-green, which can be confirmed by the absorption spectra. Microcrystal film has a wide absorption band with the maximum at 441 nm (Fig. S4), which exhibited an obvious redshifted peak compared with those in the solvents. This finding indicates that **BVDP** molecules adopt the J-aggregation mode in crystal. Ground G-form film possesses a similar absorption band with a maximum at 400 nm compared with those in solvents, implying no or weak π - π intermolecular interaction in the grinding film. Moreover, polarizing microscopy observation has proven the disappearance of the birefringence patterns of B-form after grinding to form G-form (Fig. S5). The casting disorder film of **BVDP** from CH_2Cl_2 has absorption and emission bands similar to those of G-form film (Fig. S6). In addition, many sharp peaks of B-form in the XRD pattern disappeared under a mechanical stimulus (Fig. S7). These results indicate that the molecules in the ground G-form film are stacked together in a disorderly manner.¹⁸

Fig. 3 depicts the molecular structures and intermolecular interaction of neighboring molecules. The molecule adopts a nonplanar conformation, which induces an anti-parallel arrangement with weak π - π interaction attributed to the slight overlap between adjacent molecules (Fig. 3a). Such packing indicates a J-aggregate, being consistent with the result of absorption spectra. In addition, one **BVDP** molecule intends four weak CH - π hydrogen bonds with adjacent three molecules, which clearly explains the reason why the molecular packing of **BVDP** in crystal can be easily changed by external mechanical stimulus.¹⁹

When the ground G-form film was heated or fumed by organic solvents, the yellow-green film changed into a yellow film, the absorption band of which is consistent with that of a microcrystal. Moreover, fuming of the ground G-form film resulted in the re-

appearance of the same refraction peaks as those of the crystal in the XRD patterns and the birefringence patterns upon polarizing microscopy observation (Figs. S7 and S5). These results suggest that the permeation of vapors of solvents in the ground film or heating film increases the mobility of **BVDP** molecules, which promotes the rearrangement of molecules from a metastable amorphous structure to a more stable crystalline B-form state.²⁰

As previously described, **BVDP** exhibited PFC behavior, but its fluorescence change, with a small spectral shift of 29 nm, was not evident. Given the significant alteration in the fluorescence spectrum after **BVDP** bound a proton to form the **BVDP+H** complex, we expected that proton could modulate its PFC properties. When the ground G-form film was exposed to HCl vapor, the yellow-green film immediately turned into a dark red film (R-form), which emitted weak red fluorescence with a maximum at 639 nm (Fig. 2b) and had three absorption peaks at 507, 534, and 595 nm (Fig. S4), suggesting that **BVDP** bound proton. No birefringence patterns can be observed, indicating a disordered film. Interestingly, this red film can transfer into an orange film (O-form), emitting strong orange fluorescence with a maximal emission peak at 564 nm, having three absorption peaks at 445, 491, and 530 nm, and exhibiting birefringence patterns. The result illustrates that the treatment of solvent promotes the phase transition from a disordered to a crystal structure, linking above the case without HCl vapor steaming. Moreover, the O-form film can retransfer into the R-form by mechanical shearing, accompanied by a large emission spectral redshift of 75 nm. Such transformation of fluorescence color is reversible by grinding-fuming circulation. Thus, a large contrast piezofluorochromism can be realized by the protonation of **BVDP**. Notably, the O-form film can turn into B-form by annealing at 70 °C for 10 min. Moreover, the inverse transition from B-form to O-form was achieved upon exposure of HCl vapor.

In summary, a nonplanar triphenylamine-based benzoxazole derivative called **BVDP** was designed and synthesized. This compound exhibited typical ICT characteristics and luminescence mechanochromism. However, only low-contrast fluorescent color change (a spectral shift of 29 nm) was observed. When **BVDP** bound a proton to form **BVDP+H** complex, a high contrast piezofluorochromism with a large spectral change of 75 nm was achieved. This finding suggests that additional external stimuli can significantly affect and enhance the PFC properties of materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [detailed synthesis experiment, titration absorption and emission spectra of **BVDP** in solutions, NMR spectra of **BVDP** before and after adding trifluoroacetic acid, absorption spectra, polarizing microscopy images and XRD patterns of films, and the cif file for **BVDP** crystal]. See DOI: 10.1039/b000000x/

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