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ARTICLE TYPE

Phenothiazine-Based Benzoxazole Derivates Exhibiting Mechanochromic Luminescence: Effect of Bromine Atom

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Two phenothiazine-based benzoxazole derivates (**PVB** and **BPVB**) were designed and synthesized, and their photophysical properties were studied and compared. Results showed that both compounds emitted strong fluorescence in their solutions and solid states. Their emission wavelengths were also strongly affected by solvent polarity, indicating intramolecular charge transfer (ICT) transitions. Interestingly, the
10 two compounds exhibited mechanochromism that differed from each other. The ground film of **PVB** without bromine atom can self-cure and change into the original one within 15 min at room temperature. The fluorescence of ground film for **BPVB** showed no change for at least 2 weeks. Meanwhile, a higher contrast fluorescence change was observed for the solid film of **BPVB** with bromine atom under grinding, although **PVB** and **BPVB** exhibited similar spectral red shifts after grinding. Based on the spectral results
15 and single-crystal structures, mechanochromic mechanism was given.

Introduction

Organic π-conjugated molecules are gaining considerable attention because of their various functional applications, such as in field-effect transition, organic light-emitting diodes, and
20 organic film solar cell.[1] Many studies have been conducted to adjust the chemical structures of these molecules to improve performance because a slight different in chemical structure can strongly affect the molecular stacking in solid state.[2] Recently, mechanofluorochromic (MFC) emissive organic π-conjugated
25 molecules have received an increasing amount of attention both in the fundamental research field of solid photochemistry and in the applied field of optoelectronic devices.[3] These fluorescent organic molecules can show changes in their fluorescence color under mechanical stress and be restored to their original state by
30 annealing or fuming by solvent vapor. Generally, no chemical structure damage occurs during the reversible emissive color change process, and only the molecular packing model in solid state is changed under pressure stimulus.[4] Therefore, the molecular interaction in crystal state has an important function in
35 the mechanofluorochromism.[5]

As suggested by Tang and Chi, tetraphenylethene, 9,10-divinylanthracene, and their analogues always show MFC activity because of their loose molecular stacking in crystal state, which can be easily destroyed under mechanical stimuli and results in
40 emissive color transformation.[6] Therefore, nonplanar π-conjugated emissive molecules are preferentially considered to act as MFC materials.[7] Phenothiazine has a nonplanar, bowl-shaped configuration,[8] and thus, π-conjugated molecules containing phenothiazine moiety will be expected to have MFC
45 activity. In addition, halogen atoms were often introduced into functional molecules to adjust molecular interaction in crystal

state for high mobility.[9] To determine the effect of the bromine atom, two phenothiazine-based benzoxazole derivatives (**PVB** and **BPVB**, Scheme 1) were synthesized, and their photophysical
50 properties in solution and solid state were studied. The two compounds exhibited MFC behavior, but their mechanochromisms were different. The ground film of **PVB** without bromine atom can self-cure and change back to original state within 15 min at room temperature. The fluorescence of
55 ground film for **BPVB** showed no change for at least 2 weeks. Moreover, solid film of **BPVB** with a bromine atom has a higher contrast fluorescence change under grinding. Based on the spectral results and single-crystal structures, mechanochromic mechanism was given. Results suggest that phenothiazine moiety
60 is indeed an excellent module to construct MFC molecules, and the molecular MFC properties can be adjusted by introducing a halogen atom.

Experimental Section

General information

65 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 purification. Water used throughout all experiments was purified with the Millipore system. The UV-vis absorption spectra were
70 obtained using a Mapada UV-1800pc spectrophotometer. Photoluminescence measurements were taken on a Cary Eclipse Fluorescence Spectrophotometer. The fluorescence quantum yields of **PVB** and **BPVB** in solvents were measured by comparing to a standard (9,10-diphenyl anthracene in benzene,
75 $\Phi_F = 0.85$). The excitation wavelength was 395 nm. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR

MALDI-TOF (Compact) mass spectrometers. C, H, and N elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. Excitation wavelength for fluorescence microscopy measurements is 330-385 nm. XRD patterns were obtained on an Empyrean X-ray diffraction instrument equipped with graphite-monochromatized CuK$_\alpha$ radiation (λ=1.5418 Å), by employing a scanning rate of 0.026º s^{-1} in the 2θ range from 5 to 30º. The samples were prepared by casting crystal powders, ground solid and fuming samples on glass slides at room temperature. Single crystals were obtained in the mixture of CH$_2$Cl$_2$ and n-hexane by slow solvent diffusion method. The molecular configuration was used to obtained frontier orbitals of PVB and BPVB by density functional theory (DFT) calculations at B3LYP/6-31G level with the Gaussian 09W program package.[10]

Single crystals of **PVB** and **BPVB** were selected for X-ray diffraction studies in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The crystals were 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.[11] The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically. CCDC 978631 for **PVB** and 978632 for **BPVB** contains the supplementary crystallographic data for this paper.

Synthesis, Procedures, and Characterization

PVB and **BPVB** could be easily obtained by one-step reaction from 2-methylbenzoxazole and corresponding aldehydes, as shown in Scheme 1. Compounds 1, 2, 3, 4, and 5 were synthesized by the reported methods.[12] The detailed experimental procedures are as follows:
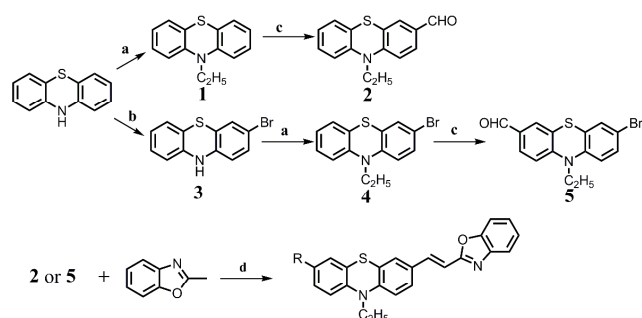
PVB R= H; **BPVB** R= Br
a. NaH, DMF, C$_2$H$_5$Br; b. NBS, DMF; c. POCl$_3$, DMF; d. t-BuOk, THF, 0 ºC.

Scheme 1. Synthesis route of **PVB** and **BPVB**.

(E)-2-(2-(10-ethyl-phenothiazin-3-yl)vinyl)benzoxazole (PVB)

To a suspension of potassium tert-butoxide (t-BuOK, 1.0 g, 8.9 mmol) was added a THF solution of 2-methyl benzoxazole (0.5 mL, 4.2 mmol) at 0 ºC and the mixture was further stirred for 30 min at this temperature. A THF solution of 4 was dropwise added into the above solution at 0 ºC. After stirred for 2 h, the mixture was poured into water (200 mL) and orange solid was collected by filtration. The crude product was purified by a silica gel column using a CH$_2$Cl$_2$/petroleum ether mixture (5:1 by vol) as the eluent. Orange powder was obtained in a yield of 86 % (1.7 g). Element analysis (%): calculated for C$_{23}$H$_{18}$N$_2$OS: C, 74.57; H, 4.90; N, 7.56; Found: C, 74.62; H, 4.91; N, 7.53. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.71 (m, 1H), 7.71 (d, J = 16.1Hz), 7.57 – 7.48 (m, 1H), 7.39 (dd, J = 8.5, 1.8 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.17 (td, J = 8.9, 1.2 Hz, 2H), 7.00 – 6.84 (m, 4H), 3.98 (d, J = 6.8 Hz, 1H), 1.47 (t, J = 7.0 Hz, 2H). MALDI-TOF MS: m/z: calcd for C$_{23}$H$_{18}$N$_2$OS: 370.1; found: 371.1 (M+H)$^+$.

### (E)-2-(2-(7-bromo-10-ethyl-phenothiazin-3-yl)vinyl) benzoxazole (BPVB)

t-BuOK (0.5 g, 4.5 mmol) was added into dry THF (20 mL) and stirred for 10 min at 0 ºC. 2-methylbenzoxazole (0.3 mL, 2.5 mmol) was dropwise added into above suspension and stirred for 10 min at 0 ºC. Then, a THF solution of 5 (0.76 g, 2.2 mmol) was dropped slowly into the above solution at 0 ºC. After stirred for 2 h, the mixture was poured into water (200 mL) and orange solid was collected by filtration. The crude product was purified by a silica gel column using a CH$_2$Cl$_2$/petroleum ether mixture (5:1 by vol) as the eluent. Yellow powder was obtained in a yield of 82 % (0.91 g). Element analysis (%): calculated for C$_{23}$H$_{17}$BrN$_2$OS: C, 61.48; H, 3.81; N, 6.23; Found: C, 61.43; H, 3.85; N, 6.20. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.68 (m, 1H), 7.66 (d, J = 16.3 Hz, 1H), 7.50 (dt, J = 7.3, 3.7 Hz, 1H), 7.36 (dd, J = 8.5, 1.7 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.25 – 7.19 (m, 2H), 6.91 (d, J = 16.3 Hz, 1H), 6.84 (d, J = 8.5 Hz, 1H), 6.70 (d, J = 9.1 Hz, 1H), 3.90 (q, J = 6.7 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H). MALDI-TOF MS: m/z: calcd for C$_{23}$H$_{17}$BrN$_2$OS: 448.0; found: 449.3 (M+H)$^+$; 451.2 (M+2+H)$^+$.

Results and Discussion

Photophysical properties in solution

As suggested by Harima etc, the design of D-π-A fluorescent dye molecules with a large dipole is a better choice for developing MFC dyes.[13] Thus, we initially studied their spectral characteristics in solution to understand their donor-acceptor π-conjugation systems. As shown in Fig. 1a, **PVB** has an absorption band with a maximum of 393 nm in nonpolar n-hexane and cyclohexane, which red shifted to 400 nm in tetrahydrofuran (THF) and CH$_2$Cl$_2$, to 403 nm in CHCl$_3$, and to 398 and 399 nm in acetone and dimethylformamide (DMF). The red-shifted absorption peaks in polar solvents suggest that **PVB** has a larger dipole moment in the excited state than that in the ground state,[14] which can be confirmed by solvent-dependent fluorescence spectra. The abnormal blue-shifted absorption peaks in acetone and DMF relative to those in THF, CH$_2$Cl$_2$ and CHCl$_3$ may be induced by increasing dihedral angle between vinyl unit and aromatic rings, which weakened the π-conjugation. An emission peak at 483 nm for **PVB** n-hexane solution was observed along with a shoulder peak at 508 nm (Fig. 2a and Table 1). In cyclohexane, **PVB** has a similar fluorescence spectrum with two emissive peaks, exhibiting vibrational structures. This result indicates that two separated close-lying excited states exist. Thus, the excited-state contribution to the emission in n-hexane and cyclohexane is the locally excited one. With further increase in the polarity of the solvent, the fluorescence becomes structureless and exhibits a solvatochromic red shift because of the dipole–dipole interactions between the solute and solvents.[15] For example, the fluorescence emission maximum of PVB shows a remarkable red shift of 97 nm from hexane (483 nm) to DMF (580 nm). The maximum of the emission bands shifts

significantly to low energy, accompanied by an obvious broadening of the emission bands in polar solvents, which indicates an intramolecular charge-transfer (ICT) characteristic for the excited state.[16] Results shown in the absorption and
5 fluorescence spectra imply that **PVB** is a typical D-π-A molecule and the absorption bands around 400 nm are from ICT transition. Therefore, a mechanochromic activity was expected for **PVB** in solid state.
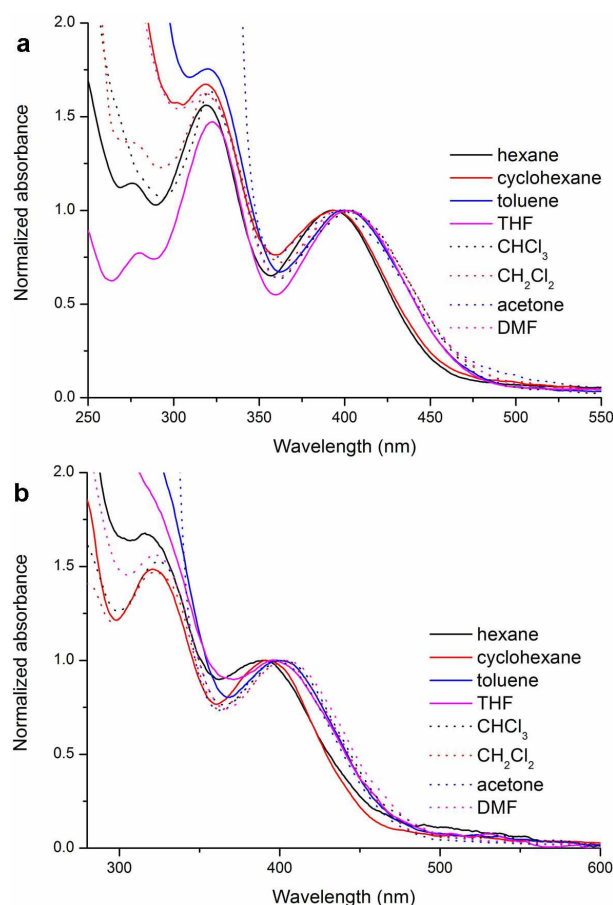

10 **Fig. 1** Normalized solvent-dependent UV-vis absorption spectra of **PVB** (a) and **BPVB** (b). Concentration for all samples is 10^{-6} M.

Table 1. Absorption, emission peaks and fluorescence quantum yields (Φ) in different solvents for **PVB** and **BPVB**.

	PVB			**BPVB**		
	λ_{abs} (nm)[a]	λ_{max} (nm)[a]	Φ[b]	λ_{max} (nm)[a]	λ_{abs} (nm)[a]	Φ[b]
hexane	393	483	0.46	388	480	0.42
cyclohexane	393	486	0.53	392	483	0.52
Toluene	400	525	0.56	400	517	0.56
THF	400	549	0.37	400	541	0.51
CHCl$_3$	403	554	0.47	401	543	0.50
CH$_2$Cl$_2$	400	568	0.33	401	550	0.53
Acetone	398	572	0.22	398	562	0.45
DMF	399	580	0.21	403	576	0.34

[a] Spectra were measured at a concentration of 10^{-5} M. [b] Fluorescence quantum yields were obtained by comparing with a standard (9,10-diphenyl anthracene in benzene, Φ = 0.85).

When a bromine atom was introduced as weak electron-
15 withdrawing group into the 7-positon of phenothiazine to obtain **BPVB**, blue-shifted absorption bands with maximum of 388 and
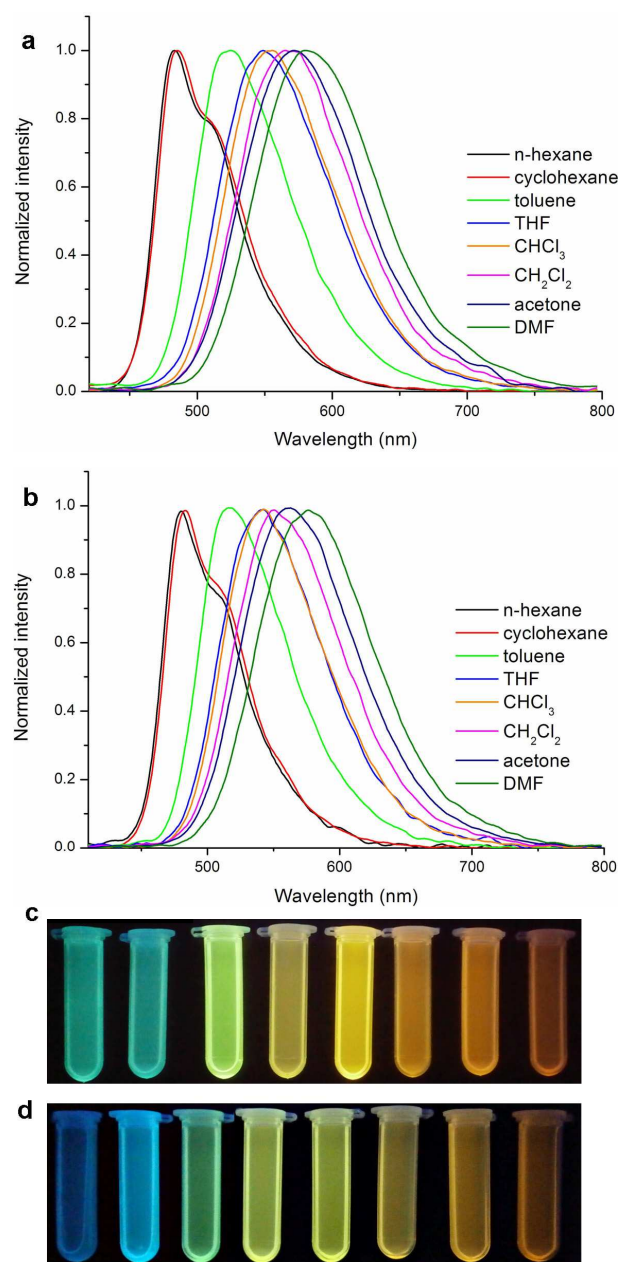
Fig. 2 Normalized fluorescence spectra and photos under 365 nm light for **PVB** (a and c) and **BPVB** (b and d). Concentration for all samples is 10^{-6}
20 M. λ_{ex} = 400 nm.

392 nm were observed in n-hexane and cyclohexane, respectively. The existence of bromine atom may be responsible for the blue-shift of absorption band because bromine atom as a weak electron-withdrawing group weakens the electron-donating
25 ability of phenothiazine. With further increase in the polarity of solvents, the absorption and emission peaks gradually show red shifting, similar to those of **PVB**. The fluorescence colors for the two compounds can change from blue, green, and yellow to orange with increasing solvent polarity (Fig. 2c and 2d). **PVB** has
30 a relatively longer emission wavelength than **BPVB** in the samesolvent because **BPVB** is a weaker donor-acceptor molecule compared with **PVB**.

To further clarify the ICT transition, quantum chemical

calculations were performed on **PVB** and BPVB by density functional theory calculations at the B3LYP/6-31G(d) level. Fig. 3 shows that the HOMO state density for the two compounds is mainly distributed at the phenothiazine and vinyl units. By
5 contrast, the electron density of LUMO at phenothiazine unit decreases and benzoxazole and vinyl moieties possess large electron density. The stimulated absorption spectrum of **PVB** and **BPVB** showed a strong absorption band with a maximum of ca. 458 nm (Fig. S1) because of the HOMO→LUMO transition
10 (Table S1). Therefore, light excitation will clearly induce electron transfer from the donor unit to acceptor. This result further proves that the maximum absorption and the emission are due to ICT transition.[17]
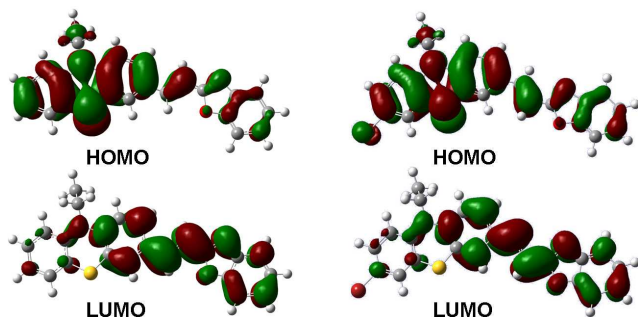

15 **Fig. 3** HOMO and LUMO electron densities of **PVB** (left) and **BPVB** (right).

MFC properties of PVB and BPVB

As discussed above, **PVB** and **BPVB** have nonplanar phenothiazine moiety and D-π-A structure, and thus, their MFC
20 behavior is anticipated. **PVB** is an orange solid showing orange emission after running the column. The crystal obtained by mixing CH_2Cl_2 and n-hexane is yellow and emits yellow fluorescence. By simply grinding the crystal with a mortar and pestle, an orange powder with orange emission is obtained. When
25 the ground powder was exposed to CH_2Cl_2 vapor for several seconds, the orange powder rapidly changed to the yellow one, which showed yellow fluorescence. This process of fluorescence color change can be repeated many times. An obviously reversible MFC behavior is suggested.[18] Fluorescence and UV-
30 Vis absorption spectra were used to monitor such a color transformation under grinding and fuming stimuli. As shown in Fig. 4a, the crystal from the mixture of CH_2Cl_2 and n-hexane has a maximum emission peak at 537 nm with a shoulder peak at 560 nm and exhibits a structural emission band. The fluorescence
35 color of the crystal is yellow (Y-form) as observed by the naked eye because of the presence of the shoulder peak at 560 nm. Applying mechanical grinding to the crystal resulted in an emissive wavelength change from 537 nm to 567 nm, inducing the orange fluorescence (O-form) of the ground powder. When
40 the ground powder was exposed to the vapor of CH_2Cl_2 for several seconds, orange solid transferred rapidly into a yellow one, which had the same emission spectrum as that of the crystal. Moreover, the yellow solid can change to the O-form again under mechanical stimulus, and such process can be reversibly repeated
45 many times. The nuclear magnetic resonance spectrum of the Y-form solid after five grinding-fuming cycles is consistent with original one, which suggests that mechanical pressure did not

damage the chemical structure.

As discussed above, grinding can induce the color change, and
50 thus, UV-vis spectra before and after grinding were compared. As shown in Fig. 5a, the crystal of **PVB** has wide absorption in visible region with a maximum of 475 nm, which is a red-shifted absorption band when compared with those in solutions. For example, the toluene solution of **PVB** has an absorption peak at
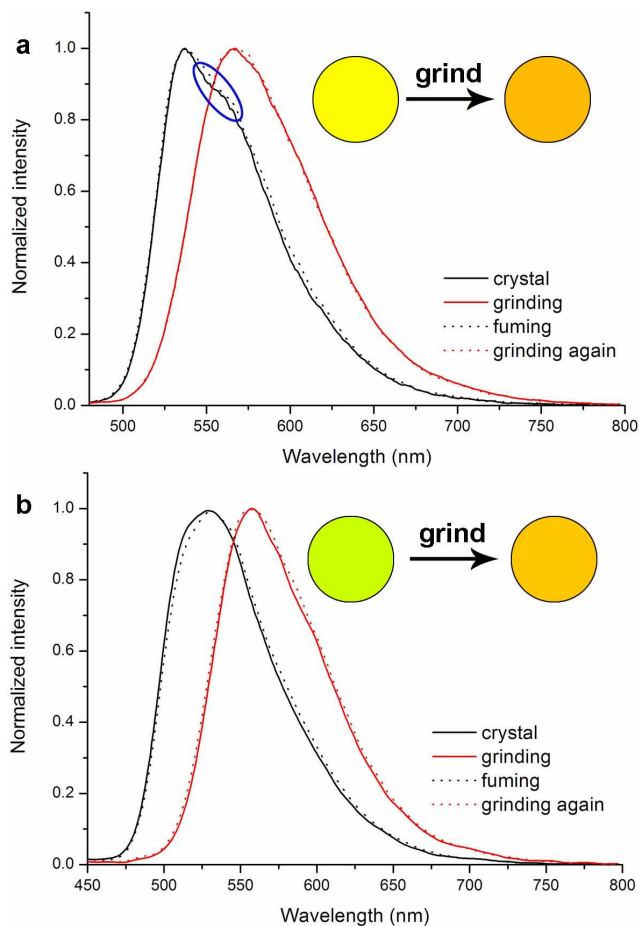

Fig. 4 Normalized fluorescence spectra of **PVB** (a) and **BPVB** (b) in solid state under external stimuli. Inset: schematic diagrams after grinding for the two compounds. Excitation wavelength is 400 nm. Blue mark indicates the shoulder peak.

60 400 nm, which means a red shift of 75 nm. This result suggests that **PVB** molecules stack together to form *J*-aggregate (head-to-tail),[19] which can be confirmed by crystal structure (vide infra). The O-form solid obtained after grinding has a blue-shifted (53 nm) absorption band with a maximum of 422 nm compared with
65 that of Y-form crystal, indicating that grinding can change the packing model of **PVB**. The absorption wavelength of O-form is also longer than those in solutions, indicating the existence of the π-π interaction between **PVB** molecules during grinding of sample even if grinding always induces an amorphous state. After
70 fuming, the absorption spectrum of O-form can be restored to that of the Y-form, and such an absorption spectral conversion is repeatable. Therefore, **PVB** exhibits mechanochromic behavior not only for fluorescence spectra, but also for absorption spectra. To determine the MFC mechanism of **PVB**, X-ray diffraction

(XRD) patterns and infrared (IR) spectra were investigated. Fig. 6a shows the XRD patterns of crystal, and grinding and fuming solid films. The crystal film showed many sharp and strong peaks. In contrast, the ground O-form film was amorphous because of very weak diffraction peaks.[20] After fuming by CH_2Cl_2 vapor, sharp and strong diffraction peaks similar to those of the crystal film appeared again, suggesting the regeneration of the Y-form crystal phase. This result confirms that the reversibility of MFC behavior for **PVB** is based on the reversible phase transformation of molecular stacking. The IR spectra also showed a similar result. Sharp stretching vibration peaks of aromatic and aliphatic C-H from 3100 cm^{-1} to 2800 cm^{-1} for Y-form crystal changed to wide and structureless absorption peaks after grinding, which suggests an amorphous phase.[21]
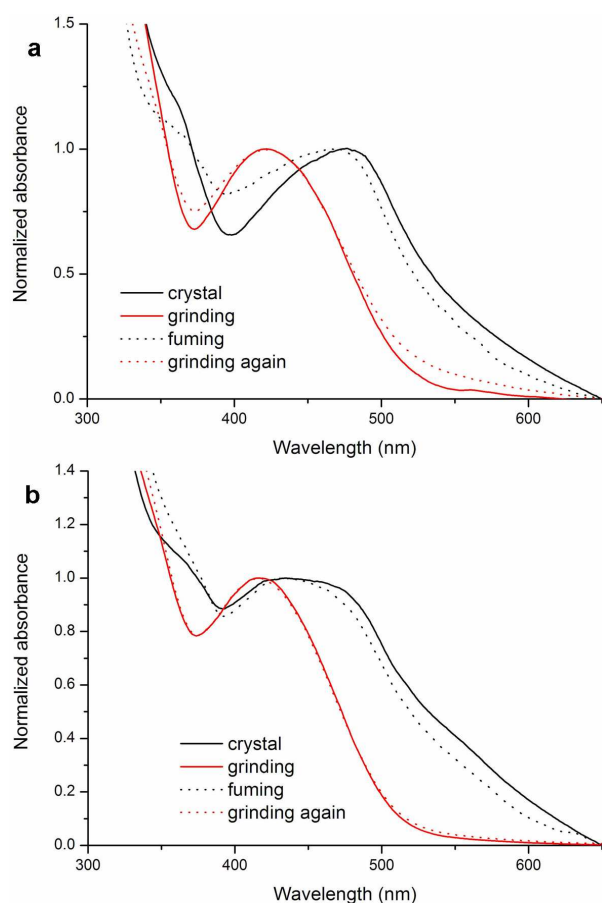

Fig. 5 UV-vis absorption spectra of **PVB** (a) and **BPVB** (b) under external stimuli.

To further understand the relationship between MFC behavior and intermolecular interaction, we prepared and analyzed a single crystal of **PVB**. Fig. 7a and 7b depict the molecular stacking of **PVB** in a crystal obtained by solvent diffusion. In the crystal, a one-dimensional π-π molecular packing occurred, in which the distance between two adjacent **PVB** molecules was 3.53 Å and the sliding angle, which is the angle between the line-to-center of two molecules and the long axes of any one of the parallel molecules, was 34.4°. This result clearly indicates the formation of a *J*-aggregate in the crystal and also explains why the large, red-shifted absorption band in the crystal is present in comparison

with those in solutions.[22] In addition, a kind of S···S interaction[23] and two classes of weak hydrogen bonds including C-H···π and C-H···N interactions are present. As shown in Fig. 7b, central **PVB** molecule links to upper molecule by the two same C-H···N hydrogen bonds, and another two adjacent molecules participate in C-H···π hydrogen bond and S···S interaction with the central molecule. Therefore, one **PVB** molecule is involved in two π-π interactions with two adjacent molecules and four weak intermolecular interactions with three adjacent molecules, by which **PVB** molecules adopt a J-aggregate with a small sliding angle.
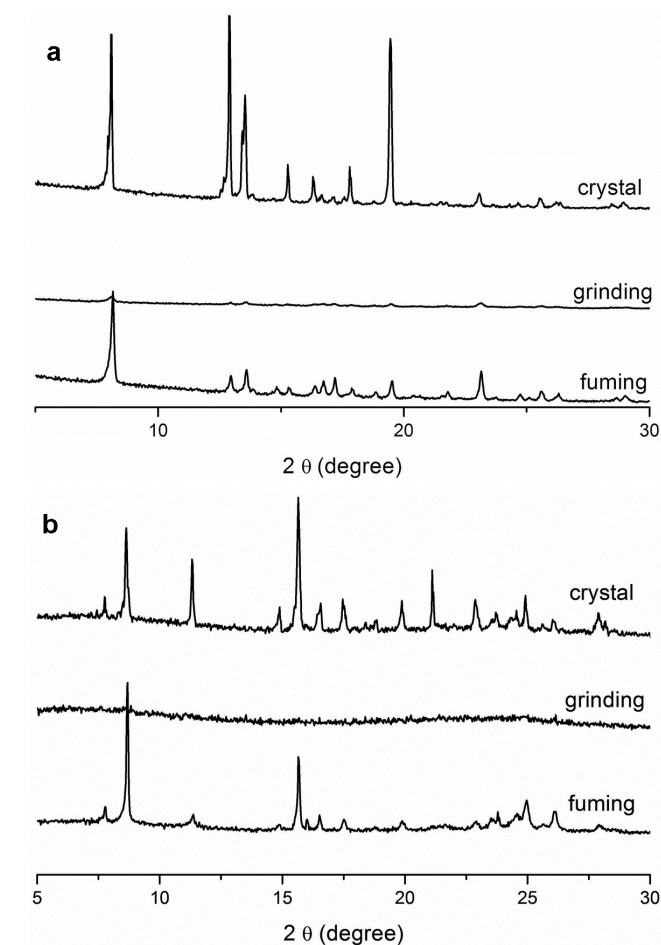

Fig. 6 XRD patterns of **PVB** (a) and **BPVB** (b) in different states.

Phenothiazine moiety is nonpolar in crystal (Fig. 7a). Therefore, the sliding angle in *J*-aggregate can possibly be transformed under mechanical stimuli if the four weak intermolecular interactions disappear. Based on the experimental results of IR and XRD, weak intermolecular interactions, including hydrogen bond and S···S interaction, can be destroyed under grinding. Thus, we consider that the difference in fluorescence colors before and after grinding comes from the change of sliding angle. A blue-shifted absorption band relative to the Y-form was observed after grinding, and thus, we speculate that the large *J*-aggregate was divided into smaller aggregates, in which **PVB** molecules stacked together with a large sliding angle (Fig. 8a), generating a small red-shifted absorption band relative to those in solutions. Consequently, the fluorescence color changes from

yellow to orange. O-form is not an energy maximized state or is a metastable state, and thus, solvent fuming leads to an increase in mobility of molecules and promotes rearrangement from a metastable amorphous structure to a more stable crystalline Y-form state.[24]
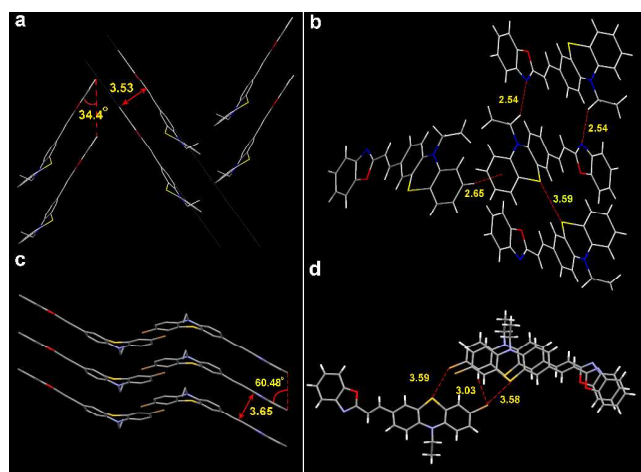

Fig. 7 Molecular stacking in crystal for **PVB** (a and b) and **BPVB** (c and d).

The slight difference in molecular structure can induce differences in the packing of π-conjugated organic molecules in crystal,[25] inducing a large difference in emission spectra. Therefore, the distinct MFC behavior for **BPVB** is expected. Yellow-green crystal state (G-form) of **BPVB** emitted a strong green fluorescence under 365 nm light. The application of mechanical shearing to the G-form solid resulted in an obvious fluorescence color change from green to orange (O-form). Fluorescence restoration from O-form to G-form can be performed by solvent-fuming (CH_2Cl_2, THF, and $CHCl_3$) for a few seconds. The color change indicates a larger contrast than that observed in **PVB** case and fluorescence spectra can confirm this phenomenon. G-form crystal has a single emission band at 529 nm, and a red-shifted emission band with a maximum of 557 nm exists after grinding. The grind-induced spectral red shift for **BPVB** (28 nm) is slightly smaller than that of **PVB** (30 nm), but no shoulder peak exists in the G-form of **BPVB**, which results in a large contrast mechanofluorochromism. Introducing a bromine atom can alter molecular MFC behavior.
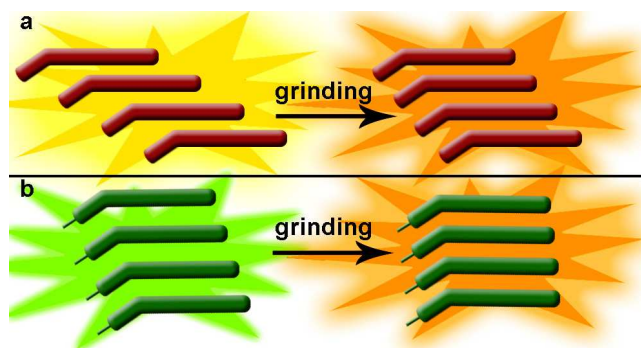

Fig. 8 Schematic diagram of MFC mechanism for **PVB** (a) and **BPVB** (b).

MFC mechanism of **BPVB** was also investigated. A wide absorption band with a maximum of 433 nm was observed (Fig. 5b). Compared with the toluene solution, crystallization induced a red shift of 33 nm, which was smaller than that of **PVB** (97 nm). An obvious blue-shifted absorption peak (17 nm) appeared at 416 nm after the application of mechanical shearing to the G-form. Similar to **PVB**, the maximum absorption wavelength of grinding O-form is longer that those in the solutions. Thus, π-π interaction still exists in the grinding sample. IR spectra and XRD patterns of **BPVB** exhibited results that are similar to those of **PVB**, which illustrate that mechanical shearing leads to the formation of amorphous state, and the G-form crystal state can be restored by solvent fuming. Fig. 7b shows the molecular stacking of **BPVB** in crystal state. In crystal state, a one-dimensional π-π packing with a distance of 3.65 Å exists, and is larger than that (3.53 Å) of **PVB** in crystal. However, the sliding angle (60.48°) between **BPVB** is larger that of **PVB**, which may cause a small red shift of absorption peak from the solution to crystal state. Besides the π-π interaction, one weak C-H···Br and two Cl···Br interaction were found in the crystal of **BPVB**. We assume that MFC mechanism of **BPVB** is the same as that of **PVB**. As shown in Fig. 8b, application of mechanical shearing to the G-form crystal promotes the increase in sliding angle to form a metastable O-form solid. After solvent fuming, molecules were rearranged to construct a more stable crystal state structure.
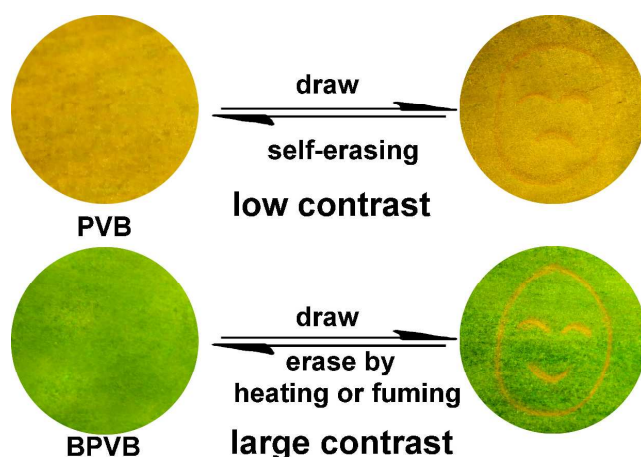

Fig. 9 Photographic images of **PVB** and **BPVB** films on pieces of weighing paper in response to grinding, fuming and heating under UV light (365 nm).

As discussed above, the grinding solid can be rapidly restored to original crystal state after solvent fuming for a few seconds because solvent vapors increase the molecular mobility, leading to the formation of a more stable crystal phase. Annealing is a good method to obtain stable crystal state, and has been widely used to increase the performance of polymer film solar cell because high temperature may increase molecular thermal motion.[26] To study the thermal reversibility of MFC behavior, three temperatures (20 °C, 70 °C, and 110 °C) were chosen. Two films for **PVB** and **BPVB** on pieces of weighing paper were prepared in a pattern and placed on a heating plate (Fig. 9). At 20 °C, orange fluorescence pattern on **PVB** Y-form film disappeared after 15 min, but the orange fluorescence smiling face on **BPVB** G-form film was retained for more than two

weeks. On one hand, **PVB** showed an isothermally reversible fluorescence switching of an MFC material because of its short restoration time at room temperature. On the other hand, **BPVB** is able to save information because of the isothermal irreversibility of MFC behavior at room temperature.[27] At 70 °C, the O-form pattern of **PVB** film required 10 s to change to Y-form, and the pattern of **BPVB** film can be retained for 10 min. With a further increase of temperature to 110 °C, the pattern of **PVB** film can disappear for less than 1 s, but **BPVB** required a minute and a half to erase the pattern. The thermally induced phase transition from amorphous to crystal state occurs in the solid state because the melting points of **PVB** and **BPVB** are 131 °C and 138 °C, respectively. We determined why **PVB** has a short restoration time at the same temperature. As described above, the absorption spectra for **PVB** showed a larger red shift (53 nm) than that of **BPVB** (17 nm) under mechanical shearing, which may suggest that the metastable O-form of **PVB** is more unstable compared with that of **BPVB**. Additional, **PVB** molecules may intend more weak intermolecular interactions to obtain the crystal with lower energy. Consequently, O-form **PVB** has a greater tendency to convert into the Y-form crystal state. The results clearly indicate that one bromine atom can affect the fluorescence color contrast of MFC behavior and thermal reversibility.

Conclusions

Two phenothiazine-based benzoxazole derivates (**PVB**, and **BPVB**) were designed and synthesized and their photophysical properties were studied and compared. Spectral result and theory computation indicate that two compounds are D-π-A molecules. Interestingly, two compounds exhibited mechanochromism. However, their mechanochromism were different. **BPVB** has a higher contrast fluorescence color change than that of **PVB** under mechanical stimuli. More interestingly, the ground film of **PVB** could self-cure and change into original one within 15 min at room temperature. The fluorescence of **BPVB** ground film showed no change for at least two weeks. The result of this work suggests that the introducing bromine atom can adjust the MFC behaviors of materials.

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Notes and references

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*† Electronic Supplementary Information (ESI) available: Electronic transition data and UV spectra obtained by the TD/DFT-B3LYP/6-31G calculation for **PVB** and **BPVB**; crystal data of two compounds; IR spectra before and after grinding. See DOI: 10.1039/b000000x/*

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