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Substituent effect on photophysical properties, crystal structures and mechanochromism of $D-\pi$ -A phenothiazine derivatives



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ABSTRACT

This study aimed to investigate the effect of substituents on the photophysical properties of four 10-ethyl-3-styryl-phenothiazine derivatives with CH₃O (PVBMA), COOMe (PVBM), CHO (PVBA), or NO₂ (NSP) moieties in solution and in crystal state. The responses of the derivatives to mechanical force stimuli were also investigated. Results suggested that the absorption and emission wavelengths of the compounds in solutions were strongly dependent on the electron-withdrawing (EW) abilities of the substituent groups. Electrochemical investigations indicated that the derivatives had identical HOMO energy levels, and the substituents only influenced the LUMO energy levels of the derivatives. The crystals of the derivatives emitted blue, green, yellow, and orange-red fluorescence. The introduction of a strong EW group resulted in the emission of wavelengths with increased length. Single-crystal structures illustrated that PVBM and PVBA crystals adopted antiparallel π -stacking, whereas NSP adopted a T-type arrangement with weak π -stacking. All four compounds could change fluorescence color under mechanical force stimuli. PVBA presented the largest spectral shift of 46 nm and PVBM exhibited the smallest shift of 27 nm after grinding. Notably, PVBM and PVBA could spontaneously recover their fluorescence within 1 h at room temperature. Meanwhile, PVBMA may retain mechanically written text for at least 1 day.

1. Introduction

Functional organic materials that respond to external stimuli have attracted immense interest given their extensive applications in chemical sensors for various analytes [1–5], field-effect transistors [6,7], solar cells [8–10], light-emitting diodes [11–13], electronic skin [14], and smart windows [15]. Among them, some luminescent organic molecules exhibit luminescent mechanochromism (MC), which is defined as alterations in emission color, intensity, or lifetime under mechanical force, such as shearing, grinding, crushing, rubbing, or hydrostatic pressure [16-21]. These smart molecules with MC may change their molecular structure [22-27] or transform their intermolecular stacking from pristine to other stacking types [28-33]. Various functional organic molecules with mechanofluorochromic (MFC) properties have been developed. These organic molecules include tetrephenylethene [34-38], 9,10-divinylanthracene [39-44], triphenylamine [45–48], β -diketone boron complexes [49–51], borondiiminates [52], and cyano-ethylene [53-58]. The phenothiazine moiety has been used as a building block of MFC molecules too because of its unique butterfly-like configuration and strong electron-donating instinct. Some D-π-A phenothiazine derivatives have been prepared, and their MFC behaviors have been investigated [59-64]. Previously obtained results have suggested that MFC properties of phenothiazine derivatives could

be strongly affected by slight modifications in molecular structure. For example, we found that a higher fluorescence color contrast could be observed through introducing an additional bromine atom [28]. Alkyl chain lengths and bridged bond differences also have substantial roles in adjusting responsive behaviors to force stimuli [40,65,66]. However, it is still lack to systematically investigate how the electron-withdrawing (EW) substituents affect MFC of phenothiazine derivatives [67].

Based on the above consideration, four D- π -A phenothiazine derivatives containing CH₃O (PVBMA), COOMe (PVBM), CHO (PVBA), or NO₂ (NSP) moieties with different EW abilities were synthesized in this work (Scheme 1), and the regulation of the MFC activities and photophysical properties of the derivatives in solid state and in solution by EW substituents was investigated. As expected, the four compounds exhibited distinct photophysical properties in solution and solid states. The introduction of a strong EW group induced absorption and emission bands with increased wavelengths. Moreover, single-crystal structure analysis illustrated that the crystal forms of the derivatives showed different stacking modes. PVBM and PVBA crystals exhibited antiparallel π -stacking, whereas NSP crystals presented T-type packing with weak π - π interaction although NO₂ had the strongest EW ability. Furthermore, all four molecules could change their fluorescence under mechanical force stimulus. This characteristic is indicative of MFC

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Scheme 1. Molecular structures of four compounds.

activity. Thermal annealing events suggested that the four amorphous solids possessed different recovery rates at the same temperature when ground. PVBM and PVBA in ground state self-recovered their fluorescence after 1 h at room temperature. NSP and PVBMA ground powder could keep their fluorescence for longer times. These results show that EW groups could not only regulate fluorescence in solid state but could also affect the responsive features of the derivatives to mechanical force.

2. Results and discussion

2.1. Design and synthesis

Because those phenothiazine derivatives with EW groups always exhibited obvious spectral shift under a mechanical force stimuli [68], CHO, COOMe, NO₂ with different EW abilities were selected. In addition, to obtain a weaker EW effect than that of COOMe, an additional OCH₃ unit was introduced in PVBA to provide PVBMA. Firstly, phenothiazine was reacted with bromoethane in presence of NaH to give **1**, which further transform into **2** by a Vilsmeier-Haack reaction (Scheme 2). **3** was obtained by a Wittig's reaction of **2**. The terminal products were achieved by a Heck reaction from of **3** and corresponding bromide substrates and characterized by various spectra.

2.2. Photophysical properties in solution

First, the photophysical properties of the derivatives were investigated by using absorption and emission spectra. As shown in Fig. 1a, all four compounds have absorbance values above 400 nm. This result implies that the solutions were colored (Fig. S1). PVBMA had a wide absorption band with a maximum at 365 nm, whereas PVBM had a red-shifted band at 385 nm. The maximal absorption peak of the aldehyde analog further red-shifted to 398 nm. NSP, which had the strongest EW group, had the longest wavelength peak at 418 nm. In general, increased intramolecular charge transfer (ICT) induces long absorption wavelength [69,70]. Spectral changes suggest that the EW abilities of the four molecules with the same electron-donating group followed the order PVBMA < PVBM < PVBA < NSP. The emission spectra provided in Fig. 1b also followed the same order (Table 1). PVBMA emitted weak blue fluorescence with a maximum at 462 nm. Although PVBM and PVBA also emitted blue fluorescence, their maximal emission peaks shifted to 479 and 493 nm, respectively. NSP emitted green fluorescence, and its emission peak was located at 521 nm. Solvent-dependent absorption and emission spectra were also measured to confirm ICT transition. As shown in Fig. S2, the absorption spectra of four compounds in different solvents are similar, but gradual bathochromic shifts in emission spectra with increasing solvent polarity were observed. Moreover, stronger EW group induced more obvious red-shift in polar solvents (Fig. S1, right Fig.s), and the fluorescence quantum yields in more polar solvents are low (Table S1). These results further confirmed that their emission bands are from ICT transition.

Cvclic voltammetry measurements and quantum chemical calculations were performed to further understand the differences in the electron transition behaviors of the four compounds. The results are shown in Table 1, Fig. S1, and Table S2. As illustrated in Fig. S1, the four compounds had similar oxidation potentials. Then, their HOMO energy levels were extracted through comparison with an external reference (Fc/Fc⁺). The four compounds had almost-identical HOMO energy levels (ca. 4.83 eV) because they possess an identical electrondonating group, that is, phenothiazine. The LUMO energy levels of the derivatives could be determined through combination with the electron transition spectra. The results indicate that the presence of a strong EW group would reduce LUMO energy levels [71-73]. Quantum chemical calculations were performed to determine the origin of transition. The maximal absorption peaks of PVBA, PVBM, and NSP were mainly ascribed to the HOMO-to-LUMO transition. Although the longest wavelength transition of PVBMA was attributed to the HOMO-to-LUMO transition, its associated oscillator strength was small (Table S1). Therefore, the absorption band observed in the absorption spectrum should originate from the transition of $S_0 \rightarrow S_2$ (from HOMO to LUMO +1). The frontier orbitals in Fig. 2 illustrated that HOMO mainly distributed on phenothiazine and vinyl moieties and LUMO or LUMO+1 density is mainly observed at vinyl and electron-withdrawing moieties. indicating that these transitions should belong to the intramolecular charge-transfer transition [74–76]. This result corresponds to the D- π -A structures of the compounds.

2.3. Photophysical properties in crystals

First, the crystal forms of the four compounds were obtained through slow solvent volatilization at room temperature. Subjecting PVBMA solutions (CH₂Cl₂/hexane, CH₂Cl₂/methanol, or THF/hexane) to solvent volatilization yielded thin and long yellowish fibers that emitted strong blue fluorescence under 365 nm light (Fig. 3) and presented the maximum emission at 467 nm (Fig. 4). Solvent removal provided yellow PVBM bulk crystals with green emission. The emission band of PVBM crystals was broad and had a peak at 517 nm. The obtained PVBA crystals were orange, needle-like, and emitted strong yellow fluorescence. A narrow emission band with a maximum at 545 nm emerged when PVBA crystals were excited. Numerous red



Scheme 2. Synthesis route of four compounds.



Fig. 1. (a) Absorption and (b) fluorescence spectra of four compounds in cyclohexane $(10^{-5} M)$.

Table 1 Photophysical data of four compounds.

		-			
Compound	λ_{abs}^{a} (nm)	$\lambda_{em}^{\ \ b}$ (nm)	HOMO (eV) ^c	LUMO (eV) ^d	E _g (eV) ^e
PVBMA	365	462	-4.84	-1.93	2.91
PVBM	385	479	-4.83	-2.05	2.78
PVBA NSP	398 418	493 521	- 4.83 - 4.82	-2.13 -2.28	2.70 2.54

^a Maximal absorption peak in cyclohexane.

^b Maximal emission peak in cyclohexane.

 $^{\rm c}$ Electrochemical method was used to obtain the HOMO energy levels by comparing with an external reference, the ferrocene/ferrocenium (Fc/Fc^+, 4.8 eV relative to vacuum).

 d The LUMO energy level was estimated by the equation: $E_{\rm LUMO}=E_{\rm HOMO}$ + $E_{\rm g}.$

 e E_g was determined from the edge of the absorption spectrum.

sheet-like crystals of NSP were acquired from its CH_2Cl_2 /hexane solution. These crystals emitted weak red fluorescence after UV light excitation. The emission peak of NSP crystals was located at 579 nm. This result indicates that similar to solutions, crystals with a strong EW group possessed long emission wavelengths. Thus, crystals with full-color fluorescence from blue to red were easily obtained by adjusting the EW groups.

Single-crystal structures were resolved to determine the relationship between the EW group and intermolecular stacking in crystals. PVBMA crystals were frail and had an unknown single-crystal structure. The single crystals of the other three compounds were sufficient for X-ray



Fig. 3. Photos of crystals in natural light and 365 nm light.

structural analysis. The crystal systems of PVBA and NSP were orthorhombic and had a Z value of 8. As expected, the phenothiazine moiety adopted a V-shaped configuration in three crystals. The twisted angles between vinyl and two adjacent phenyl rings in PVBM crystals were 6.14° and 6.97° , and the dihedral angle between A and B rings (Fig. 5a) was 12.61°. These results suggest that phenothiazine and methyl benzoate moieties were almost coplanar. Moreover, one-dimensional (1D) π -stacking was observed (Fig. 5b). Two kinds of antiparallel arrangements existed in 1D stacking (Fig. 5c): One consisted of two molecules and is indicative of a dimer. Two molecules extensively overlapped. The interplanar distance was 3.25 Å. The proximity between the EW ester group and electron-donating phenothiazine moiety



Fig. 2. Energy levels, band gap and corresponding frontier orbitals (HOMO and LUMO) of four compounds.



Fig. 4. Fluorescence spectra of four compounds in cyclohexane.

observed from the top view of the structure (Fig. 5d) indicates that the electrostatic attraction between donor and acceptor groups may be responsible for antiparallel packing [77–81]. The other antiparallel arrangement was formed through stacking between two dimers and had an interplanar distance of 3.40 Å.

Fig. 6 shows the molecular configuration and stacking of PVBA in crystals [82]. A small dihedral angle of 18.37° suggests improved π -conjugation. An isolated antiparallel dimer was found, and the interplanar distances between the two phenyl rings of phenothiazine moieties and two benzaldehyde units were the same and were as high as 4.22 Å (Fig. 6d). The shortest C–C distance between two molecules was 3.29 Å (Fig. S3). Indeed, the electrostatic attraction between phenothiazine and aldehyde moieties may also be responsible for the formation of the antiparallel dimer. Many dimers were first arranged in 1D column, and then two columns stacked together in a T-type order (Fig. 6c).

Similar to that in PVBM and PVBA, π -conjugation may be present in NSP because of the small dihedral angle of 19.5°. Given that NO₂ groups have the strongest EW ability, NSP should possess the largest polarity, which will induce the molecule to adopt an antiparallel arrangement.

However, face-to-face antiparallel stacking, similarly to in PVBM and PVBA was not observed in NSP crystal, and two kinds of T-type stacking emerged (Fig. 7b–d). One consisted of a parallel array, which only contained weak C–H···H–C interaction. The other is in an antiparallel arrangement in which short C–H···H–C, C–H···C, C–H···N, and C···C contacts existed between nitrobenzene and phenothiazine units. Thus, only weak exciton couple within two antiparallel NSP molecules may be present. Therefore, the EW group may regulate π -stacking types.

2.4. Response to mechanical force

The four compounds were expected to approach MFC given their Vshaped configuration and D- π -A electron characteristics. As expected, all four pristine crystals showed changes in their fluorescence color after breakage through mechanical crushing. The detailed MFC behaviors were investigated through absorption, emission, and XRD spectroscopy. The data for absorption and fluorescence spectral peaks before and after grinding are listed in Table 2. Fig. 8a shows the fluorescence spectra of PVBMA solids in different states. Pristine PVBMA crystals emitted strong blue fluorescence with a maximum at 467 nm. The emission peak red-shifted to 512 nm after grinding and the ground solid showed green emission under 365 nm light. The spectral shift value was 45 nm. Fluorescence recovered to its original blue color and the emission band was restored when the ground powder was exposed to common solvent vapors, such as THF, CH₂Cl₂, CHCl₃, and toluene, for 1 min (Fig. 8a). Moreover, fluorescence color conversion could be repeated numerous times (Fig. S4). This behavior implies that MC is reversible [30,53,83-88].

The XRD and absorption spectra of pristine and ground solids were acquired to further understand the MC mechanism of the compounds. As shown in Fig. 9a, pristine PVBMA crystals exhibited several strong and sharp diffraction peaks. This characteristic is suggestive of good crystallinity [89,90]. The weakening of some diffraction peaks and the almost disappearance of the peak at 5.23° indicate that the crystals are in amorphous state [91–94]. Strong and sharp peaks re-emerged after fuming and were similar to those of pristine solids. However, the diffraction peak at 5.23° remained weak. This result implies that the directional growth along the crystal plane that corresponds to 5.23° was suppressed. The reversible conversion of diffraction peaks also confirms that MFC was reversible and was accompanied by a reversible phase



Fig. 5. (a) Molecular conformation of PVBM in crystal, (b) 1D stacking, (c) π -stacking with interplanar distances in front view, (d) face-to-face dimer in top-view and (c) heat-to-tail stacking in top view.



Fig. 6. Molecular conformation of PVBA in crystal in (a) front view and (b) top view, (c) herringbone stacking, antiparallel π -stacking with interplanar distances in (d) front and (e) top view.



Fig. 7. (a) Molecular conformation of NSP in crystal, (b) T-type stacking, and four molecules in 1D direction in (c) front (d) left views.

 Table 2

 Absorption and fluorescence data of four compounds before and after mechanical force stimuli.

	λ_{abs} (nm)		$\Delta\lambda_{abs}$ (nm)	λ_{em} (nm)		$\Delta \lambda_{em}$ (nm)
	pristine	ground		pristine	ground	
PVBMA	360	378	18	467	512	45
PVBM	387	404	17	517	544	27
PVBA	422	432	18	545	591	46
NSP	446	462	16	579	616	37

transition between crystalline and amorphous states. The absorption peak of pristine crystals was located at 360 nm. Face-to-face *H*-aggregates may have formed as indicated by the presence of an absorption peak at 365 nm in cyclohexane solution [95]. The shifting of this absorption peak to 378 nm after grinding suggests that mechanical force stimuli induced head-to-tail *J*-aggregation [96]. Thus, MFC originates from the transition of π -stacking from *H*- to *J*-aggregate.

Yellow-green PVBM crystals were transformed into yellow powder after grinding. The fluorescence color of the crystals changed from green to yellow after grinding. The maximal emission peak had a small red-shift of 27 nm from 517 nm to 544 nm. Fuming the ground solid with saturated CH_2Cl_2 vapor for 5 s rapidly restored the yellow fluorescence to the original green fluorescence. This spectral change could be repeated many times and is suggestive of a reversible MFC process. XRD patterns were used to investigate phase transition under mechanical force stimuli. As shown in Fig. 9, pristine PVBM crystals exhibited sharp diffraction peaks that disappeared or weakened after grinding. Strong peaks also emerged after fuming. In addition, the



Fig. 8. Fluorescence spectra of (a) PVBMA, (b) PVBM, (c) PVBA and (d) NSP in different states.

diffraction peaks at 6.26° and 12.53°, which corresponded to the 002 and 004 crystal planes, respectively, of fumed PVBM solid were weaker than those of pristine crystals. Thus, preferred growth along the 001 plane during fuming was not observed. As shown in Fig. 3b, PVBM in the absorption spectra also had a red-shift of 17 nm from 387 nm to 404 nm after grinding. Crystal structure resolution revealed the presence of antiparallel π -stacking in pristine crystals; thus, the red-shift observed in the absorption spectra of the ground crystals may originate from the change in slipped angle and the formation of *J*-aggregates.

The MC behavior of PVBA was also examined. The yellow needlelike PVBA crystals emitted yellow fluorescence and were converted into orange-red crystals after grinding. The maximal emission peak was located at 591 nm (Fig. 8c). Fuming and regrinding the solid resulted in the recovery of yellow fluorescence and the reappearance of orange-red fluorescence. These results indicate that PVBA exhibited reversible MFC. XRD measurements proved that PVBA underwent phase transition from crystalline to amorphous states after mechanical force stimulus. The red-shifted absorption peak (422 nm) of pristine PVBA crystals relative to that (398 nm) of PVBA in cyclohexane solution confirmed that the antiparallel π -packing ascribed to *J*-aggregation. The further red-shift of an absorption band after grinding proved that the packing mode had changed (Fig. S5c).

Similar to the other three compounds, NSP exhibited a fluorescence spectral redshift. Its emission peak shifted by 37 nm from 579 nm to 616 nm. The XRD patterns of pristine, ground, and fumed solids also indicate that the MFC of NSP occurred after the phase transition from crystal to amorphous powder (Fig. 9d). The maximal absorption peak of pristine NDP crystals was located at 446 nm and further shifted to 462 nm (Fig. S5d).

The π -stacking transformation that occurred during MFC is illustrated in Fig. 10 on the basis of the above results. Considering that PVBMA had a weak EW group, antiparallel π -stacking may be present in

its crystals. The bathochromic shift in the absorption spectra of the three compounds under mechanical force stimuli is indicative of *J*-aggregate formation. Hence, the application of mechanical force to PVBM and PVBA crystals promotes the reduction in sliding angle that results in the formation of metastable *J*-aggregates (Fig. 10a). After solvent fuming, molecules were rearranged into a crystal-state structure with increased stability. The close proximity of molecules (Fig. 10b) in NSP crystals after grinding implies loose T-type packing and close-packed T-type array. This metastable close packing will transform into loose T-type stacking after fuming.

The four compounds have potential applications in the security field given their excellent MFC properties. The solid films were used as writing paper to demonstrate their potential applications. As shown in Fig. 11, the four solid films emitted blue, green, yellow, and orange red fluorescence before mechanical force application. Text, for example "TJ," could be written on the films by using a ballpoint pen and then erased through solvent fuming. The written text on PVBM film gradually disappeared within 10 min at room temperature. The self-erasure of the text on PVBA film lasted for 50 min. The text on the NSP film had almost disappeared after 6 h. Meanwhile, the text on the PVBMA film remained visible after 1 day. These results indicate that the compounds have different fluorescence thermal recovery speeds at the same temperature. Thus, the thermal recoveries of the four compounds at different temperatures were investigated. As shown in Fig. S6, PVBA had the shortest recovery times at the same temperature. A high temperature consistently resulted in rapid fluorescence recovery. For example, text on the PVBA film immediately disappeared within 1 s. Considering that high temperatures may accelerate molecular thermal motion, molecules can gradually form highly stable crystals through weak intermolecular interactions within a short duration. PVBMA required the longest time to recover its fluorescence at the same temperature. This result indicates that the substituent influences not only emission color



Fig. 9. XRD patterns of four compounds in different states.



Fig. 10. Changes of $\pi\mbox{-stacking model}$ for (a) PVBMA, PVBM and PVBA, and (b) NSP.

but also thermal recovery time. In addition, it was found that four compounds emitted similar fluorescence colors to corresponding ground solids when they were heated to melt and cooled to room temperature (Fig. S7). It suggested that intermolecular π -stacking models in such cooled solids were similar to those in ground solids.

3. Conclusions

Four D- π -A phenothiazine derivatives were synthesized. The effect of substituents on the photophysical properties of the derivatives in solution and crystal state was investigated. The response of the derivatives to mechanical force stimuli was also studied. Absorption and emission spectra and electrochemical measurements suggest that the



Fig. 11. Photographic images of (a) PVBMA, (b) PVBM, (c) PVBA and (d) NSP films on pieces of weighing paper in response to grinding, fuming under 365 nm light.

EW abilities of substituent groups may determine the photophysical properties of the compounds in solution by regulating molecular LUMO energy levels. The crystals of the compounds emitted fluorescence that ranged in color from blue to orange-red, and the results of their π -packing models differed on the basis of their strong EW groups. MFC measurements suggest that all four compounds exhibited reversible fluorescence conversion after grinding and solvent fuming. The compounds exhibited different fluorescence recovery times under thermal annealing. PVBM and PVBA could spontaneously recover their fluorescence within 1 h at room temperature. PVBMA and NSP may retain mechanically written information for long durations. The obtained results indicate that molecular MFC features can be easily regulated through mild substituent adjustment.

4. Experiment sections

4.1. Measurements and instruments

¹H and ¹³C NMR spectrum was recorded using a Bruker Avance 400 MHz spectrometer at 400 MHz and 100 MHz in DMSO-d₆. FT-IR spectra were recorded using a Nicolet-360 FT-IR spectrometer by casting samples into a KBr crystal. UV-Vis spectra were obtained on a Mapada UV-1800pc spectrophotometer. Fluorescence emission spectra were obtained on a FL-3 fluorescence spectrophotometer. C, H, and N elemental analyses were performed on a PerkinElmer 240C elemental analyzer. XRD patterns were obtained on a Bruker D8 Advance X-ray diffraction instrument equipped with graphite-mono-chromatized CuK α radiation ($\lambda = 1.5418$ Å), by employing a scanning rate of $0.0261^{\circ} \text{ s}^{-1}$ in the 2 θ range from 5° to 30°. Heating recovery of ground solids was employed using a temperature-controlled heating board. Cyclic voltammetry was employed using a three-electrode cell and an electrochemistry work station (CHI 604) at room temperature at a scan rate of 50 mV s^{-1} . The working electrode was a glass carbon disc, the auxiliary electrode was a Pt wire, and Ag/Ag⁺ was used as reference electrode. Tetrabutylammonium tetrafluoroborate (TBABF₄, 0.1 M) was used as the supporting electrolyte in dry CH₂Cl₂ and the ferrocenium/ ferrocene (F_c/F_c^+) redox couple was used as an internal potential reference. Geometrical optimization was performed by density functional theory (DFT) calculations at B3LYP/6-31G(d) level with the Gaussian 09W program package. Electronic transition data of PVBMA, PVBM, and PVBA were obtained by the TD/DFT-mpw1pw91/6-31G(d) calculation based on the configuration at ground state. Electronic transition of NSP is from TD/DFT-b3lyp/6-311G(d) calculation.

Single crystals of two compounds were obtained by slowing solvent evaporation (CH₂Cl₂ and n-hexane mixture) and selected for X-ray diffraction analysis on in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ 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. The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically. CCDC 1906762 and 1906792 contain the supplementary crystallographic data for PVBM and NSP.

4.1.1. (E)-5-(2-(10-ethyl-10H-phenothiazin-3-yl)vinyl)-2methoxybenzaldehyde (PVMBA)

10-ethyl-3-vinyl-10H-phenothiazine (1.5 g, 5.92 mmol), 5-bromo-2methoxybenzaldehyde (1.27 g, 5.92 mmol), K₂CO₃ (1.8 g, 13 mmol), and tetrabutylammonium bromide (4.0 g, 12.4 mmol) were dispersed in dry DMF (20 mL) and then 1.0 mg PdCl₂ was added. The mixture was heated at 120 °C under N₂ for 12 h, and poured into 200 mL water. The crude product was obtained by suction. Product was achieved by column chromatography on silica gel using CH₂Cl₂/petroleum ether (V/V = 1:2) as eluent. Yield: 89%. m.p: 177–178 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.47 (s, 1H), 7.95 (d, *J* = 2.4 Hz, 1H), 7.63 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.23 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.18–7.09 (m, 2H), 6.97 (d, J = 8.7 Hz, 1H), 6.94–6.79 (m, 5H), 3.94 (s, 5H), 1.42 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 189.74, 189.70, 161.09, 144.49, 144.25, 133.68, 131.67, 130.49, 127.37, 127.30, 127.07, 125.86, 125.81, 125.24, 124.87, 124.75, 124.60, 123.83, 122.44, 115.06, 112.01, 55.87, 55.83, 41.96, 12.97. Elemental Analysis: C, 74.39; H, 5.46; N, 3.61; found: C, 74.45; H, 5.66; N, 3.57.

4.1.2. (E)-methyl 4-(2-(10-ethyl-10H-phenothiazin-3-yl)vinyl)benzoate (PVBM)

PVBM was obtained through the same procedure as that of PVBMA. Yield: 88%. m.p: 133–135 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04–7.95 (m, 2H), 7.56–7.45 (m, 2H), 7.30–7.22 (m, 2H), 7.18–7.10 (m, 2H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.95 (d, *J* = 16.8 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 5H), 1.41 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.91, 144.78, 144.32, 142.02, 131.24, 130.03, 129.97, 128.60, 127.38, 127.35, 126.29, 126.10, 125.81, 125.11, 124.64, 123.71, 122.57, 115.12, 115.00, 52.06, 52.01, 41.99, 12.98. Elemental Analysis: C, 74.39; H, 5.46; N, 3.61; found: C, 74.40; H, 5.62; N, 3.54.

4.1.3. (E)-4-(2-(10-ethyl-10H-phenothiazin-3-yl)vinyl)benzaldehyde (PVBA)

PVBA was obtained through the same procedure as that of PVBMA. Yield: 91%. m.p: 165–166 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.91–7.78 (m, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.37–7.27 (m, 2H), 7.20–7.08 (m, 3H), 7.06–6.79 (m, 4H), 3.95 (s, 2H), 1.44 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 191.54, 143.64, 135.10, 131.11, 131.04, 131.03, 130.24, 127.38, 125.54, 125.19, 124.71, 123.66, 122.66, 115.16, 115.01, 42.04, 13.05. Elemental Analysis: C, 77.28; H, 5.36; N, 3.92; found: C, 77.21; H, 5.46; N, 3.99.

4.1.4. (E)-10-ethyl-3-(4-nitrostyryl)-10H-phenothiazine (NSP)

PVBA was obtained through the same procedure as that of PVBMA. Yield: 91%. m.p: 165–166 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 8.9 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H), 7.28 (s, 1H), 7.27 (dd, J = 8.2, 2.4 Hz, 1H), 7.15 (td, J = 8.0, 1.6 Hz, 1H), 7.11 (dd, J = 8.0, 1.6 Hz, 1H), 7.09 (d, J = 16.8, 1H), 6.94 (d, J = 16.8, 1H), 6.92 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 3.92 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 146.47, 145.27, 144.07, 132.05, 130.64, 130.62, 127.45, 127.39, 126.70, 126.56, 125.28, 124.72, 124.69, 124.43, 124.14, 123.52, 123.49, 122.76, 115.23, 115.02, 42.17, 42.12, 12.94, 12.92. Elemental Analysis: C, 70.57; H, 4.85; N, 7.48; found: C, 70.67; H, 4.81; N, 7.41.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107692.

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