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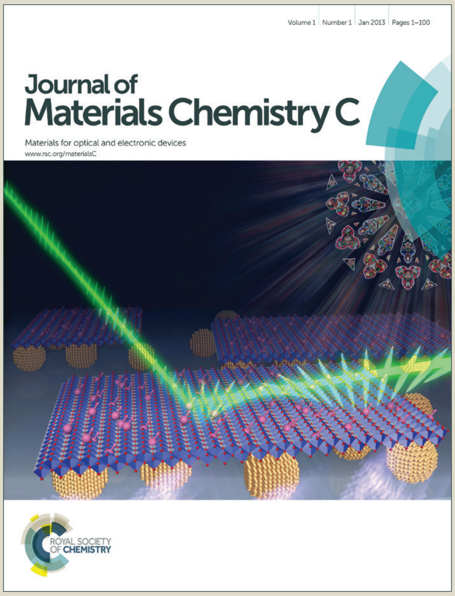

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ARTICLE

# Phenothiazine modified triphenylacrylonitrile derivates: AIE and mechanochromism tuned by molecular conformation

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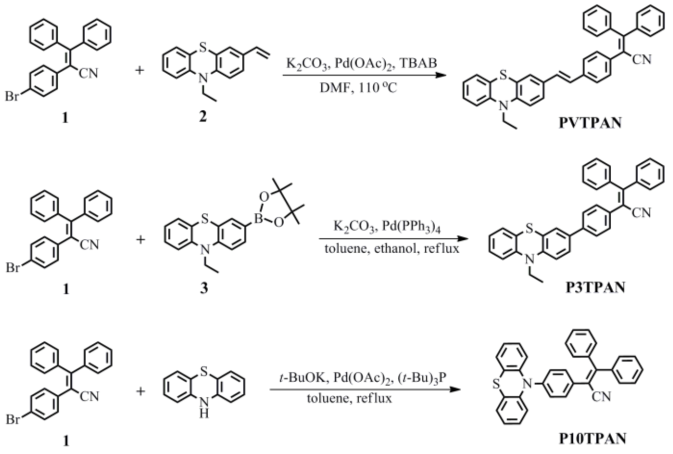
D-π-A type phenothiazine modified triphenylacrylonitrile derivatives **PVTPAN**, **P3TPAN** and **P10TPAN** have been synthesized. The three compounds exhibited AIE behaviors, and the emission enhancement of **PVTPAN** and **P3TPAN**, in which 3-position in phenothiazine was functionalized, was more significant than **P10TPAN** (10-position of phenothiazine was modified) with more twisted conformation. The single crystal structures revealed that the multiple intermolecular interactions, including π-π interactions and hydrogen bonds of C-H$\cdots\pi$ and C-H$\cdots$N, would lock the molecular conformation and reduce the energy loss via non-radiative channels, leading to enhanced emission. Interestingly, the as-synthesized crystals of **PVTPAN**, **P3TPAN** and **P10TPAN** emitting strong yellow, yellowish-orange and yellowish-green light under UV irradiation could be transferred into powders emitting red, orange-red and orange light, respectively, after grinding. Such mechanochromism was reversible upon the treatment of grinding and heating/fuming with DCM. The XRD patterns suggested that the mechanochromism was originated from the transition between the crystalline and the amorphous states. It should be noted that the recovery time of the emission of the ground powders to that of crystals for **P10TPAN** was much shorter than those for **PVTPAN** and **P3TPAN** at same temperature. Extremely, the emission of the ground powders of **P10TPAN** could recover at room temperature, but that of **PVTPAN** and **P3TPAN** could not. We suggested that such different mechanochromic behaviors of **P10TPAN** from **PVTPAN** and **P3TPAN** were coming from its more twisted conformation, which could lead to the exothermic peak appearing at lower temperature and the easier molecular rearrangement of the amorphous state into crystals. Therefore, we could prepare the dyes with stable or reversible mechanochromism via tuning the molecular conformation.

## Introduction

Luminescent materials with switchable solid-state emission in respect to mechanical stimuli, such as shearing, grinding or rubbing, have received recent attention due to their promising applications in optical memory, mechanical sensors, displacement or deformation detectors, security papers and optoelectronic devices.[1] It is known that the D-π-A type dyes usually exhibit unique fluorescent properties due to their intramolecular charge transfer (ICT) transitions, which endows them with tuned electronic states under various environments.[2] However, aggregation-caused quenching (ACQ) often takes place in the condensed phases for most D-π-A luminogens,[3] which would limit their real-world applications. Since Tang's group reported that the restriction of intramolecular rotations was favourable for the generation of highly luminescent solid organic emitters,[4-6] much effort has been made to design new dyes with AIE (aggregation-induced emission) or AIEE (aggregation-induced enhanced emission)[7]. It is interesting that the mechanochromic luminogens are mostly AIE or AIEE active.[1,2,8] For example, Tang et al suggested that the mechanochromic behaviors of tetraphenylethene and 9,10-divinylanthracene derivatives were originated from the loose molecular stacking in the crystal states, which could be easily destroyed under mechanical stimuli and led to the transformation of emitting color.[9] Therefore, the fluorescent non-planar π-conjugated compounds might be potential candidates as mechanochromic materials because of their possible loose packing.[10] It should be noted that phenothiazine with a butterfly conformation is a typical electron donor, and the non-planar D-π-A type conjugated compounds containing phenothiazine can be easily achieved.[11] Our group has found that phenothiazine functionalized benzoxazole derivates with ICT emission exhibited mechanochromism.[12] On the other hand, triphenylacrylonitrile derivatives usually showed AIE properties.[13] With these in mind, herein, we synthesized new D-π-A conjugated molecules based on triphenylacrylonitrile, which was linked to phenothiazine in its 10-position (**P10TPAN**) or 3-position (**P3TPAN**) as well as bridged by vinyl (**EPVPAN**) (Scheme 1). It was found that **PVTPAN** and

**P3TPAN** gave ICT emission, but **P10TPAN** did not show ICT feature due to large dihedral angle between the nitrogen-containing ring and nitrogen-linked benzene ring. Although the three compounds were AIE-active, the emission enhancement of **PVTPAN** and **P3TPAN** were much higher than **P10TPAN**, and the fluorescence quantum yields of **PVTPAN**, **P3TPAN** and **P10TPAN** were as high as 52.9%, 45.5% and 11.3%, respectively, in the as-synthesized crystals. Interestingly, they show significant mechanochromism. For example, the emission bands of **PVTPAN**, **P3TPAN** and **P10TPAN** in the as-synthesized crystals were located at 536 nm, 572 nm and 514 nm, and red-shifted to 608 nm, 598 nm and 568 nm, respectively, upon grinding. The mechanochromism was reversible upon the treatment of grinding and heating/fuming with DCM on account of the reversible transition between the crystalline and the amorphous states. Notably, the emission of the ground powders of **P10TPAN** could recover to that of the as-synthesized crystals at room temperature, but that of **PVTPAN** and **P3TPAN** could not. The reason might be that the more twisted **P10TPAN** led to the exothermic peak appearing at lower temperature so that the molecular rearrangement from the amorphous state into crystalline became easier. It suggested that the substitution position in phenothiazine could tune the molecular conformation and adjust the reversibility of the mechanochromism for the dyes. Thus, we could design stable or reversible mechanochromic emitters, which could be applied in different fields, including data storage, sensor, and security ink, etc.



**Scheme 1**. Synthetic routes for **PVTPAN**, **P3TPAN** and **P10TPAN**.

## Experimental section

### Measurement and characterizations

$^{1}$H NMR and $^{13}$C NMR spectra were measured with a Mercury Plus instrument at 400 MHz and 100 MHz by using DMSO-$d_6$ as the solvent in all cases. FT-IR spectra were measured with a Nicolet-360 FT-IR spectrometer by incorporation of samples in KBr disks. The UV-vis absorption spectra were obtained on Shimadzu UV-3100 spectrophotometer. Fluorescent emission spectra were obtained on a Cary Eclipse fluorescence spectrophotometer. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. XRD patterns were obtained on an Empyrean X-ray diffraction instrument, and the samples of the as-synthesized crystals, ground powders and fumed samples on glass slides were determined at room temperature. Single crystals were obtained in the mixture of CHCl$_3$ and *n*-hexane by a slow solvent diffusion method. Single crystals of **P3TPAN** and **P10TPAN** were selected for X-ray diffraction studies in a Rigaku RAXIS-RAPID diffractometer. The frontier orbitals of **PVTPAN**, **P3TPAN** and **P10TPAN** were obtained by density functional theory (DFT) calculations at B3LYP/6-31G level with the Gaussian 09W program package. Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC 204F1 at a heating rate of 10 °C/min.

### Synthesis

Toluene was dried over sodium and diphenylketone. DMF was dried over phosphorus pentoxide. The other chemicals and reagents were used as received without further purification.

The synthetic routes for **PVTPAN**, **P3TPAN** and **P10TPAN** were shown in Scheme 1. Firstly, 2-(4-bromophenyl)-3,3-diphenylacrylonitrile **1**[13], 10-ethyl-3-vinyl-10H-phenothiazine **2**[14] and 10-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H phenothiazine **3**[15] were prepared according to the reported methods. Then, the target molecule **PVTPAN** was obtained in a yield of 63% by Heck reaction between compounds **1** and **2**.[8] The Suzuki-Miyaura cross coupling reaction between **1** and **3** catalyzed by Pd(PPh$_3$)$_4$ in toluene-ethanol afforded **P3TPAN** in a yield of 62%.[16] The Buchwald-Hartwig reaction between **1** and phenothiazine yielded **P10TPAN** in a yield of 70%.[15] The new compounds were characterized by $^{1}$H NMR, $^{13}$C NMR, FT-IR and MALDI-TOF mass spectrometry. In addition, the single crystal structures of **P3TPAN** and **P10TPAN** were obtained. The target molecules showed good solubility in common organic solvents, such as THF, DCM, chloroform, DMF and DMSO.

### 2-{4-[2-(10-Ethyl-10H-phenothiazin-3-yl)-vinyl]-phenyl}-3,3 diphenyl-acrylonitrile (PVTPAN)

A mixture of **1** (0.32 g, 0.89 mmol), **2** (0.25 g, 0.90 mmol), K$_2$CO$_3$ (0.5 g, 3.6 mmol), TBAB (1.2 g, 3.6 mmol), Pd(OAc)$_2$ (2 mg) and dry DMF (50 mL) was heated at 110 ℃ with stirring for 24 h under N$_2$. Then, the mixture was poured into water (400 mL) and extracted with DCM for three times. The collected organic layer was washed with water and brine twice, and then dried over anhydrous Na$_2$SO$_4$. After solvent evaporation, the crude product was purified by column chromatography (silica gel, petroleum ether/DCM, v/v = 3/2). A yellow solid was obtained in 63% yield (0.30 g). $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 7.49 (m, 4H), 7.45 (d, *J* = 6.9 Hz, 3H), 7.39 (d, *J* = 6.4 Hz, 2H), 7.30 (q, *J* = 7.2 Hz, 3H), 7.17 (m, 6H), 7.04 (m, 4H), 6.95 (t, *J* = 7.5 Hz, 1H), 3.93 (q, *J* = 6.5 Hz, 2H), 1.31 (t, *J* = 6.8 Hz, 3H) (Figure S1); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 157.71, 144.32, 140.70, 139.22, 137.94, 133.53, 131.77, 130.67, 130.37, 129.96, 129.58, 128.99, 128.17, 127.51, 126.85, 126.19, 125.05, 123.56, 122.98, 122.75, 120.12, 115.89, 111.42, 41.68, 13.06 (Figure S2); IR (KBr): ν = 700, 742, 777, 820, 866, 966, 1107, 1244, 1369, 1473, 1627, 2200 cm$^{-1}$; MALDI-TOF MS: m/z: calcd. for $C_{37}H_{28}N_2S$: 532.7; found: 534.2 $[M+H]^+$ (Figure S3).

### 2-[4-(10-Ethyl-10H-phenothiazin-3-yl)-phenyl]-3,3-diphenyl-acrylonitrile (P3TPAN)

A mixture of compound **1** (1.53 g, 3.85 mmol), compound **3** (1.36 g, 3.85 mmol), $K_2CO_3$ (5.31 g, 38.5 mmol), $Pd(PPh_3)_4$ (0.01 g, 0.87 mmol), toluene (80 mL) and ethanol (20 mL) was refluxed with stirring for 24 h under $N_2$. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The combined organic layers were washed with brine and dried over $MgSO_4$. The crude product was gained after removal of the solvent, and was purification by column chromatography (silica gel, petroleum ether/DCM, v/v = 2/1), affording a light orange solid in 62% yield (1.2 g). $^1$H NMR (400 MHz, DMSO-*d*$_6$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.50 (m, 4H), 7.44 (dd, *J* = 6.2, 2.3 Hz, 3H), 7.30 (m, 5H), 7.20 (m, 1H), 7.14 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.05 (m, 4H), 6.94 (t, *J* = 7.4 Hz, 1H), 3.94 (q, *J* = 6.9 Hz, 2H), 1.31 (t, *J* = 6.9 Hz, 3H) (Figure S4); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$) δ 157.85, 144.48, 144.45, 144.38, 140.73, 139.17, 139.15, 139.09, 133.45, 133.41, 133.26, 130.62, 130.41, 130.29, 129.94, 129.61, 129.04, 128.97, 128.19, 127.52, 126.39, 126.25, 125.21, 123.99, 123.82, 123.00, 122.86, 120.15, 116.10, 115.92, 111.32, 55.39, 41.65, 13.05 (Figure S5); IR (KBr): ν = 700, 742, 802, 1112, 1245, 1363, 1467, 1600, 2208 cm$^{-1}$; MALDI-TOF MS: m/z: calcd for $C_{35}H_{26}N_2S$: 506.7; found: 508.1 $[M+H]^+$ (Figure S6).

### 2-(4-Phenothiazin-10-yl-phenyl)-3,3-diphenyl-acrylonitrile (P10TPAN)

The two-necked round bottom flask containing the mixture of compound **1** (1.0 g, 3.55 mmol), phenothiazine (0.78 g, 3.9 mmol), *t*-BuOK (0.56 g, 4.99 mmol), $Pd(OAc)_2$ (2 mg) was evacuated under vacuum and flushed with dry nitrogen for three times, and then fresh toluene (50 mL) and 2 mL of P(*t*-Bu)$_3$ (2 mL, 0.5 M in toluene) was injected. The mixture was refluxed under stirring for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The combined organic layers were washed with brine, and dried over $MgSO_4$. The crude product was gained after removal of the solvent, and was purified by column chromatography (silica gel, petroleum ether/DCM, v/v = 3/2), affording a light yellow solid in 70% yield (1.2 g). $^1$H NMR (400 MHz, DMSO-*d*$_6$) δ 7.51 (ddd, *J* = 10.2, 5.4, 2.9 Hz, 5H), 7.46 (m, 2H), 7.30 (m, 5H), 7.15 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.04 (ddd, *J* = 17.1, 8.0, 1.4 Hz, 4H), 6.94 (td, *J* = 7.5, 1.1 Hz, 2H), 6.28 (dd, *J* = 8.1, 0.9 Hz, 2H) (Figure S7); $^{13}$C NMR (100 MHz, DMSO-*d*$_6$) δ 158.83, 143.35, 141.42, 140.30, 139.89, 138.93, 134.10, 132.51, 130.81, 130.48, 130.00, 129.71, 129.07, 128.93, 128.78, 127.86, 127.45, 123.83, 121.69, 120.00, 119.94, 117.92, 110.83 (Figure S8); IR (KBr): ν = 700, 740, 918, 1047, 1126, 1255, 1303, 1463, 1504, 1589, 2210, 2362 cm$^{-1}$; MALDI-TOF MS: m/z: calcd for $C_{33}H_{22}N_2S$: 478.6; found: 480.0 $[M+H]^+$ (Figure S9).

### Preparation of the samples for AIE study

A stock solution of target molecules in THF with a concentration of $2.0 \times 10^{-4}$ M was prepared. An aliquot (1 mL) of the stock solution was transferred to a 10 mL volumetric flask. After an appropriate amount of THF was added, water was added dropwise under vigorous stirring to furnish the mixture with different water fractions. The concentration of the systems was maintained at $2.0 \times 10^{-5}$ M. The fluorescence emission spectral measurement of the mixtures was performed immediately.

### Preparation of the samples for mechanochromism study

The ground powders were prepared by grinding the as-synthesized crystals with a pestle in the mortar for 30 s. The fumed samples were obtained by fuming the ground powders with DCM for 30 s. The ground powders were heated at certain temperature until the emission was totally recovered.

## Results and discussion

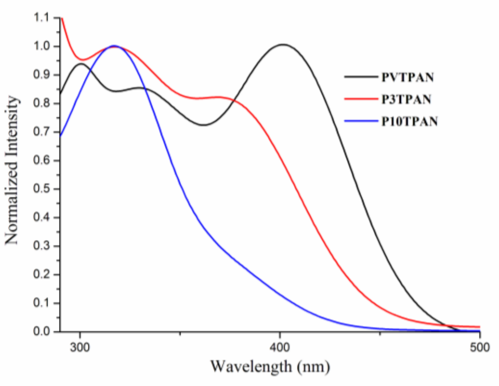


**Figure 1.** Nomalized UV-vis absorption spectra of **PVTPAN**, **P3TPAN** and **P10TPAN** in THF ($2.0 \times 10^{-5}$ M).

### UV-vis absorption spectra in THF

The UV-vis absorption spectra of **PVTPAN**, **P3TPAN** and **P10TPAN** in THF were shown in Figure 1. It was clear that **PVTPAN** gave three absorption bands located at 300 nm, 330 nm and 401 nm. The absorption bands at 300 nm and 330 nm might be attributed to the π-π* transition, and the one at 401 nm corresponded to ICT transition.[17] Two absorption bands at 317 nm and 370 nm appeared for **P3TPAN**, and could be attributed to π-π* transition and ICT transition, respectively. Because of the introduction of a spacer of vinyl between phenothiazine and triphenylacrylonitrile in **PVTPAN**, the ICT absorption band red-shifted to 401 nm compared with that of **P3TPAN** (370 nm), indicating the enlarged conjugation of **PVTPAN**. In order to confirm the occurrence of ICT transition, the solvent-dependent UV-vis absorption and fluorescence emission spectra of **PVTPAN** and **P3TPAN** were shown in Supporting Information (Figure S10 and S11). It was clear that slight red-shift of the absorption at long wavelength region was detected with increasing the solvent polarity. In the case of **PVTPAN**, the absorption at 397 nm in hexane shifted to 401 nm in THF. Additionally, we found that the emission bands of **PVTPAN** and **P3TPAN** red-shifted and broadened significantly in more polar solvents compared with those in non-polar solvents. For example, the emission of **PVTPAN** was located at 512 nm in hexane, and red-shifted to 649 nm in THF. The above electronic spectral changes with solvent polarities suggested that the absorption at 401 nm for **PVTPAN** and at 370 nm for **P3TPAN** was due to ICT transition. When triphenylacrylonitrile connected to 10-position of phenothiazine directly, only one obvious band at 317 nm for **P10TPAN** coming from π-π* transition emerged. The absence of ICT band for **P10TPAN** suggested its poor conjugation, which could be confirmed by the calculated optimized molecular structure (Figure S12). We could find that the dihedral angle between phenothiazine and the connected benzene ring in triphenylacrylonitrile for **P10TPAN** (49.85 °) was larger than those for **PVTPAN** (42.78 °) and **P3TPAN** (39.79 °). As a result, the more twisted conformation would lead to less conjugation of **P10TPAN** without ICT feature. It should be noted that in single crystals the dihedral angle of **P10TPAN** was much larger (80.93 °) than that of **P3TPAN** (29.45 °), further supporting the highly twisted conformation of **P10TPAN**, which will be discussed below.

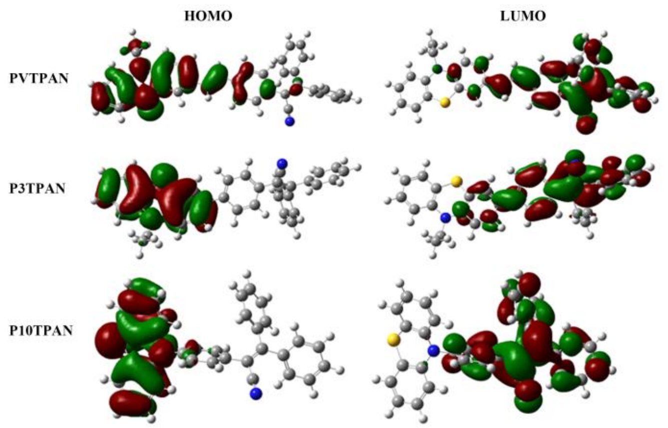


**Figure 2**. The frontier orbital plots of the HOMO and LUMO for **PVTPAN**, **P3TPAN** and **P10TPAN**.

## Theoretical Calculation

We carried out the density functional theory (DFT) calculations for **PVTPAN**, **P3TPAN** and **P10TPAN** by Gaussian 09W program[18] using DFT/B3LYP/6-31G method to reveal their electronic structures. The frontier orbital plots of the HOMO and LUMO were shown in Figure 2. In the cases of **P10TPAN** and **P3TPAN**, the LUMO was mainly distributed at the acceptor of triphenylacrylonitrile unit and HOMO was mainly located at phenothiazine unit. Upon introduction of a spacer of vinyl between phenothiazine and triphenylacrylonitrile moieties, we found that the HOMO of **PVTPAN** was not only mainly located at phenothiazine but also partially distributed on triphenylacrylonitrile unit, while the LUMO was mainly located at triphenylacrylonitrile and partially distributed on phenothiazine. It meant that conjugation degree of **PVTPAN** was better than **P3TPAN** and **P10TPAN**, which was consistent with their absorption spectra.

## AIE Properties

Triphenylacrylonitrile is a typical building block in AIE compounds,[19] so it is envisioned that the synthesized triphenylacrylonitrile derivates might exhibit AIE properties. As shown in Figure 3, **PVTPAN** gave quite weak emission in dilute THF and in the mixture solvents of THF/water with water fraction ($f_w$) ≤ 80%. However, when $f_w$ was increased to 90%, the emission at ca. 610 nm was boosted swiftly and its intensity was ca. 14.0-fold higher than that in THF. It illustrated that **PVTPAN** was a kind of AIE dye. In other words, **PVTPAN** molecules tended to aggregate when a large amount of non-solvent of water ($f_w > 80\%$) was added in the mixture, in which the encapsulated **PVTPAN** molecules were located in a non-polar environment and the ICT process was limited. Thus, the fluorescence was lightened.[2d] We found that the formed aggregates of **PVTPAN** emitted strong orange light (Figure 3b) in THF/water with high $f_w$ and emitted strong yellow light in the as-synthesized crystals (Figure 4d) under UV irradiation. Similarly, the emission of **P3TPAN** was also very weak in THF, and was intensified significantly in THF/water ($f_w > 80\%$). Around 13.8-fold of emission enhancement was observed for **P3TPAN** when $f_w$ reached 90% in THF/water systems, and orange light (centered at 608 nm) emitting was observed for the aggregates (Figure S13). However, **P10TPAN** exhibited poor AIE behaviors compared with **PVTPAN** and **P3TPAN**. As shown in Figure S14, the non-emissive **P10TPAN** in THF emitted weak fluorescence at 580 nm in THF/water with high $f_w$ of 98%. The reason of weak AIE of **P10TPAN** might be ascribed to its less conjugation and absence of ICT transition. We deemed that the non-emissive nature of the three compounds in THF/$H_2O$ systems with low $f_w$ might be ascribed to the intramolecular rotation of the isolated molecules, which would effectively consume the energy of the excitons non-radiatively. However, the intramolecular rotations would be restricted at high $f_w$ in THF/water, and the non-radiative relaxation channels would be restricted, leading to high emission.[1] To quantitatively evaluate AIE, the fluorescence quantum yields of the target compounds in solutions ($\Phi_{F,s}$) and in the as-prepared solids ($\Phi_{F,aps}$) were determined. The $\Phi_{F,aps}$ values for **PVTPAN**, **P3TPAN** and **P10TPAN** (52.9%, 45.5% and 11.3%) were much higher than $\Phi_{F,s}$ (1.50%, 1.30% and 1.80%), further suggesting AIE behaviors. We could get the AIE factors ($\alpha_{AIE} = \Phi_{F,aps}/\Phi_{F,s}$) of **PVTPAN**, **P3TPAN** and **P10TPAN** were 35.3, 35.0 and 6.3, respectively.[1]

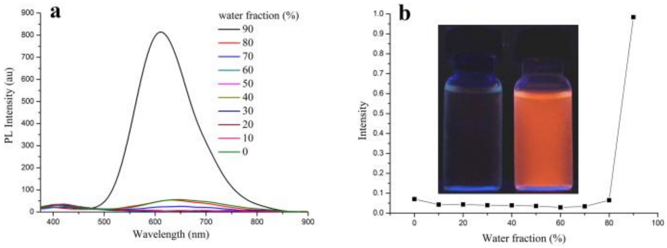


**Figure 3.** (a) Fluorescent emission spectra of **PVTPAN** in THF/water with different water fractions ($f_w$). (b) Normalized fluorescent emission intensities of **PVTPAN** in THF/water with different $f_w$. Concentration: $2.0 \times 10^{-5}$ M; $\lambda_{ex}$ = 365 nm. Photographs in (b) are **PVTPAN** in THF and THF/water ($f_w = 90\%$) under 365 nm illumination.

## Mechanochromism Properties

Considering AIE dyes with ICT emission usually gave tuned emission in response to mechanical stimuli, we investigated the mechanochromic properties of **PVTPAN**, **P3TPAN** and **P10TPAN**. It was clear from the insets of Figure 4 that **PVTPAN**, **P3TPAN** and **P10TPAN** in the as-synthesized crystals emitted intense yellow, yellowish-orange and yellowish-green light under UV irradiation, and their emitting colors changed into red, orange-red and orange light, respectively, after grinding. It meant obvious mechanochromic behaviors of phenothiazine modified triphenylacrylonitrile derivates. As shown in Figure 4a, the emission of **PVTPAN** in the as-synthesized crystals was located at 536 nm, and red-shifted to 608 nm in the ground powders. Moreover, the red emitting ground powders of **PVTPAN** could be transferred into yellow emitting solids, similar to the as-synthesized crystals, after fuming with DCM for 2 s, suggesting the reversibility of the mechanochromic fluorescence (Figure S15). Furthermore, other vapors of organic solvents were employed to fume the ground powders of **PVTPAN** at room temperature. It was found that the emitting color of **PVTPAN** changed from red to yellow within 2 s upon exposed to $CHCl_3$ and THF. 10 s and 20 s were needed for the emission recovery when treated with acetone and toluene. The recovery time was prolonged to 120 s upon fuming the ground powders of **PVTPAN** with *n*-hexane and DMF. Although we could not find the relationship between solvent polarity and recovery time, the higher saturated vapor pressure and the good solubility of the solvent for **PVTPAN** were favorable to the emission recovery process because the permeation of the solvent molecules into the ground powders would lead to the rearrangement of **PVTPAN** and the emitting color recovery.[20] Similarly, the emission of **P3TPAN** and **P10TPAN** also red-shifted in the ground powders (598 nm and 568 nm) compared with those in the as-synthesized crystals (572 nm and 514 nm) upon UV irradiation (Figure 4b-c), and the mechanochromism was also reversible upon fuming-grinding treatment (Figure S16-S17). In addition, we found that the fluorescence quantum yields ($\Phi_f$) of **PVTPAN**, **P3TPAN** and **P10TPAN** in the as-synthesized crystals (52.9%, 45.5% and 11.3%) were higher than those in the ground powders (28.9%, 36.0% and 10.2%), which will be explained below. It suggested that the synthesized phenothiazine modified triphenylacrylonitrile could be used as solid emitting materials.

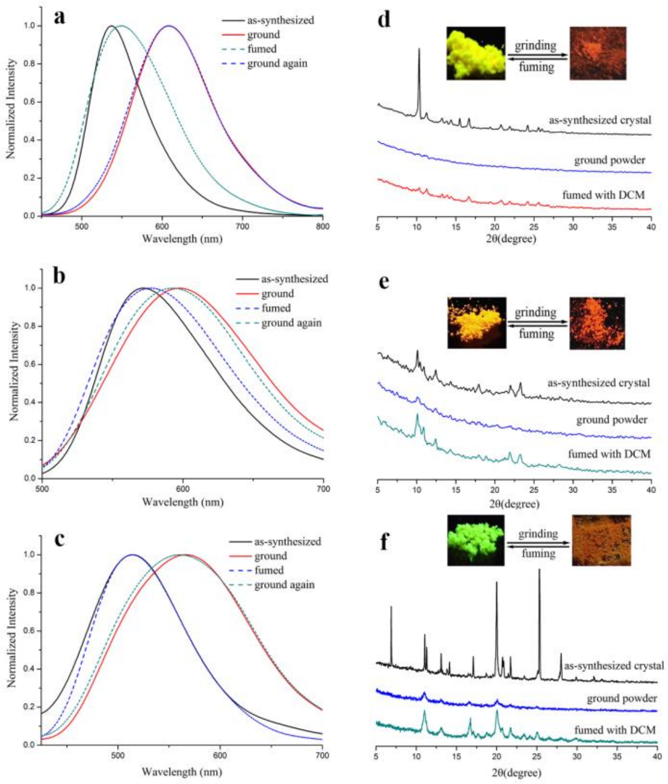


**Figure 4.** Normalized fluorescent emission spectra of **PVTPAN** (a), **P3TPAN** (b) and **P10TPAN** (c) ($\lambda_{ex}$ = 400 nm) and XRD patterns of **PVTPAN** (d), **P3TPAN** (e) and **P10TPAN** (f) in different solid states. Insets are photographs of **PVTPAN**, **P3TPAN** and **P10TPAN** in different solid states under UV illumination.

It is known that the emission behaviors of solid emitters usually depended on the molecular packings.[1] Thus, the X-ray diffraction (XRD) patterns for **PVTPAN**, **P3TPAN** and **P10TPAN** in different solid states were shown in Figure 4d-f. We found that the as-synthesized crystals of **PVTPAN**, **P3TPAN** and **P10TPAN** gave strong and sharp diffraction peaks, indicative of the crystalline forms. However, the corresponding ground powders showed very weak or no diffraction peaks, indicating disordered molecular packing or amorphous states. Upon fuming the ground powders with DCM vapor, diffraction peaks emerged again due to the rearrangement of the molecules into ordered aggregates. As a result, we deduced that the mechanochromism of phenothiazine functionalized triphenylacrylonitrile was due to the transition between the ordered crystalline and the disordered amorphous states.

As discussed above, the permeation of solvent vapors into the ground powders would increase the molecular mobility and then lead to the blue-shift of the emission bands on account of the molecular rearrangement. Accordingly, the heating would also accelerate the molecular thermal motion and play similar role in tuning the emission of the mechanochromic dyes.[20] We found that it took 2 s, 20 s and 90 s for the ground powders of **P10TPAN, PVTPAN** and **P3TPAN** to restore to their original states (as-synthesized crystals) when the temperature was maintained at 100 ℃ (Figure S18). The lower was the temperature, the more time was needed for the recovery of the emission. For example, the orange emitting ground powders of **P10TPAN** converted into yellowish-green emitting solids upon heated at 60 ℃ for 20 s, and more than 20 min was needed for the emission recovery of the ground powders of **PVTPAN** and **P3TPAN**. Notably, the emitting colors of the ground powders of **PVTPAN** and **P3TPAN** could not change if they were put at room temperature (20 ℃) for more than one week, but the ground powders of **P10TPAN** could gradually turn into yellowish-green emitting solids when aging at 20 ℃ for one day. These findings suggested that varying the coupling positions of phenothiazine could yield the emitting dyes with stable or self-recovering mechanochromic behaviors, which would find applications in data storage and mechanosensors, etc.

To further reveal the effect of the heating on the mechanochromic properties, the differential scanning calorimetry (DSC) curves were shown in Figure S19-S21. It was found that the ground samples (first heating-cooling cycle) of **PVTPAN**, **P3TPAN** and **P10TPAN** exhibited clear exothermic peaks, whereas no peak was observed for the corresponding as-synthesized crystals (second heating-cooling cycle). We deduced that the broad exothermic peak for each compound was ascribed to the cold-crystallization (crystallizing from glass state) of ground solids upon heat annealing,[21] illustrating that the amorphous state was metastable. It should be noted that the exothermic peaks for the amorphous powders of **PVTPAN** and **P3TPAN** appeared at the temperature as high as 106 °C and 98 °C, respectively, which resulted in their stable mechanochromic behaviors at room temperature. The ground powders of **P10TPAN** could cold-crystallize at room temperature since the exothermic peak appeared at lower temperature (51 ℃),[9f,22] so that the emission of the amorphous solids of **P10TPAN** induced by grinding could recover even at room temperature. The reason why the phase-transition temperature for **P10TPAN** was lower than that of **PVTPAN** and **P3TPAN** was due to its highly twisted conformation, which would lead to loose packing and easier molecular rearrangement.

In order to well understand the different AIE and mechanochromic behaviors of the synthesized compounds we intended to gain the single crystals, but only single crystals of **P3TPAN** and **P10TPAN** were obtained. Firstly, from Figure S22-S23 we could find that the dihedral angles between the benzene ring in triphenylacrylonitrile and the phenothiazine were 29.45 ° and 80.93 ° for **P3TPAN** and **P10TPAN** in single crystals, illustrating more twisted conformation of **P10TPAN**. The different molecular conformation would affect the molecular packing modes in crystals.

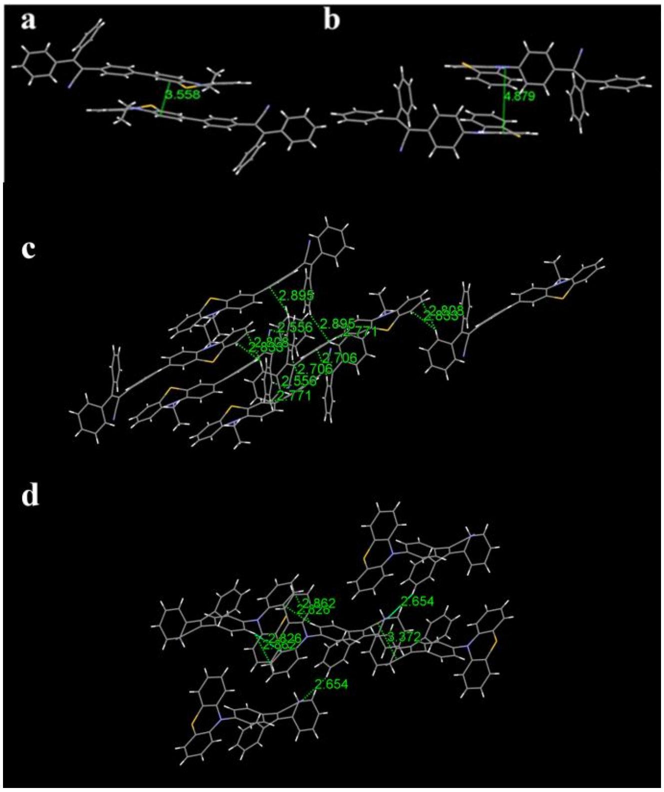


**Figure 5**. Molecular packing in crystals of (a) **P3TPAN**, (b) **P10TPAN** in single crystals, and the intermolecular interactions in single crystals of (c) **P3TPAN**, (d) **P10TPAN**.

As shown in Figure 5a, we could find a face to face stacking mode between two phenothiazines in **P3TPAN**, in which the distance between two adjacent molecular planes was 3.558 Å, indicating the π-π interaction. Moreover, in the single crystal of **P3TPAN**, the intermolecular hydrogen bonds of C-H···π (2.808 Å, 2.833 Å, 2.706 Å, 2.771 Å, 2.895 Å) and C-H···N (2.556 Å) were observed (Figure 5c). These multiple interactions would rigidify the molecular conformation and prohibit the intramolecular rotation, so that high fluorescence quantum yields would be afforded for the crystals of **P3TPAN**. In the case of single crystal of **P10TPAN**, a similar face-to-face stacking with a distance of 4.879 Å between two phenothiazines was observed (Figure 5b). The distance corresponding to π-π stacking in single crystal of **P10TPAN** was longer than that in **P3TPAN** meant that the π-π interactions were weaker between **P10TPAN** than **P3TPAN**, which was originated from the highly twisted conformation of **P10TPAN**. Besides, the multiple hydrogen bonds of C-H···π (2.862 Å, 2.826 Å) and C-H···N (2.654 Å), as well as the interaction of N≡C···C≡N (3.372 Å) appeared in the crystal of **P10TPAN** (Figure 5d). These kinds of intramolecular interactions would lock the molecular conformation and reduce the energy loss via non-radiative channels, leading to highly emissive of the crystals. Upon grinding, some of the interactions were destroyed, and the molecules would be forced to adopt less twisted conformation, thus giving red-shifted and relative weak emission.[1]

## Conclusions

In summary, we synthesized D-π-A luminogens based on phenothiazine modified triphenylacrylonitrile derivatives **PVTPAN**, **P3TPAN** and **P10TPAN** with AIE and mechanochromism. It was interesting that **P10TPAN** exhibited weaker AIE and better reversibility of mechanochromism than **PVTPAN** and **P3TPAN**. On the one hand, the weak AIE of **P10TPAN** might originate from its twisted conformation, less conjugation and weak intermolecular interactions. On the other hand, the single crystal structures of **P3TPAN** and **P10TPAN** suggested that the π-π interactions as well as the hydrogen-bonds of C-H···π and C-H···N would lock the molecular conformation and restrain the intramolecular rotation, yielding intense emission in crystals. As a result, the as-synthesized crystals of **PVTPAN**, **P3TPAN** and **P10TPAN** could emit intense yellow, yellowish-orange and yellowish-green light, respectively, under UV irradiation. Moreover, the emitting colors of **PVTPAN**, **P3TPAN** and **P10TPAN** would change into red, orange-red and orange, respectively, after grinding the crystals. The mechanochromism was reversible upon the treatment of grinding and heating/fuming with DCM on account of the transition between the crystalline and the amorphous states. However, the reversibility of mechanochromism for **P10TPAN** was better than **PVTPAN** and **P3TPAN** on account of its lower phase-transition temperature and more easy transformation from amorphous to crystalline states. It provided a strategy for designing new dyes with controllable mechanochromism behaviors via tuning molecular conformation.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: $^1$H NMR, $^{13}$C NMR and MALDI/TOF MS of target molecules; Fluorescent emission spectra of **PVTPAN**, **P3TPAN** and **P10TPAN**; Emission changes upon ground and fumed with DCM for target compounds; Reversible switch of the emission upon grinding/fuming or heating; DSC curves of the as-synthesized crystals and ground powders; The preferred conformations of all molecules; The crystal structures of **P3TPAN** and **P10TPAN**. Deposition numbers of the single crystals of **P3TPAN** and **P10TPAN** are CCDC 1026368 and CCDC 1026377, respectively. See DOI: 10.1039/b000000x/

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# Graphic Abstract for:

## Phenothiazine modified triphenylacrylonitrile derivates: AIE and mechanochromism tuned by molecular conformation

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The substituted position in phenothiazine can tune the mechanochromic and AIE properties of phenothiazine modified triphenylacrylonitrile derivates.