

An AEE-active Polymer Containing Tetraphenylethene and 9,10-Distyrylanthracene Moieties with Remarkable Mechanochromism^{*}

Jun-ru Chen^a, Juan Zhao^a, Bing-jia Xu^a, Zhi-yong Yang^{a**}, Si-wei Liu^a, Jia-rui Xu^a, Yi Zhang^{a**},
Yuan-chun Wu^b, Po-yen Lv^b and Zhen-guo Chi^{a**}

^a Key Laboratory for Polymeric Composite & Functional Materials of Ministry of Education, Guangdong Provincial Key Laboratory for High Performance Polymer-based Composites, Guangdong Engineering Technology Research Center for High-performance Organic and Polymer Photoelectric Functional Films, State Key Laboratory of Optoelectronic Material and Technologies, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China

^b Shenzhen China Star Optoelectronics Technology Co., Ltd, Shenzhen 518107, China

Abstract A polymer (poly(9,10-anthracenevinylene-*alt*-4,4'-(9,9-bis(4-(4'-(1,2,2'-triphenylvinyl)phenoxy)butyl)-9H-fluorene-2,7-diyl) dibenzaldehyde), **P1**) was successfully synthesized through the Wittig-Horner reaction by employing fluorene and 9,10-distyrylanthracene moieties as building blocks for backbone and tetraphenylethenes as pendant groups. Photophysical and thermal properties of the resulting polymeric emitter were fully characterized by ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). While **P1** emits an orange-light centered at 567 nm in dilute tetrahydrofuran (THF) solution, the solid powder of the polymer exhibits strong yellow emission peaked at 541 nm. It is also found that the as-synthesized polymer shows unique property of aggregation-enhanced emission (AEE). In addition, **P1** possesses high thermal stability with a decomposition temperature ($T_{d,5\%}$) of 430 °C and high morphological stability with a glass transition temperature (T_g) of 171 °C. Under the stimulus of mechanical force, the emission of **P1** can be changed from yellow to red ($\Delta\lambda_{\max} = 61$ nm), showing a remarkable mechanochromism. The results from XRD analysis suggest that such mechanochromic phenomenon of **P1** is probably caused by the destruction of crystalline structure, which leads to the conformational planarization of the distyrylanthracene moieties forming by the polymerization and the increase of molecular conjugation of the backbone.

Keywords Tetraphenylethene; 9,10-Distyrylanthracene; Aggregation-enhanced emission; High thermal stability; Mechanochromic polymer

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INTRODUCTION

Mechanochromic materials, whose emission colors change in response to external force such as grinding, rubbing, and shearing, have attracted tremendous attention recently due to their potential applications in the

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^{**} Corresponding authors: Zhi-yong Yang (杨志涌), E-mail: yangzhy29@mail.sysu.edu.cn

Yi Zhang (张艺), E-mail: ceszy@mail.sysu.edu.cn

Zhen-guo Chi (池振国), E-mail: chizhg@mail.sysu.edu.cn

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fields of stress sensing, data storage, security ink and optoelectronic devices^[1–8]. However, as conventional emitters, most of the mechanochromic compounds suffer from the notorious aggregation-caused quenching (ACQ), leading to weak fluorescence in solid state^[9–12]. As a result, color alteration of the materials under the stimulus of mechanical force is difficult to be observed, which severely limits their practical applications. Therefore, development of new mechanochromic luminophores with intense fluorescence in solid-state is highly desirable.

Recently, a general principle of creating crystalline compounds with aggregation-induced emission (AIE) or aggregation-enhanced emission (AEE) has been proposed by us for the preparation of high-performance mechanochromic materials^[13, 14]. Following this guideline, luminogens based on triphenylethene, tetraphenylethene and/or 9,10-divinylanthracene with efficient solid state emission and high contrast mechanochromism have been developed successfully^[10, 15–21]. Although a number of materials with property of dual-colored or even multi-colored luminescence switching have been well documented^[22–27], to date, single component polymer with mechanofluorochromism in solid-state remains rare. As compared to purely organic compounds and metal-organic complexes, mechanochromic polymers are more attractive because they are promising candidates for flexible fluorescent switches and optical devices. However, such polymeric emitters, especially those with AIE or AEE feature, are tough to be achieved and, to the best of our knowledge, have not yet been reported before^[28–30].

In this article, we present the detailed photophysical characterization of an AEE-active polymer that shows mechanochromic feature in solid state. Herein, fluorene and 9,10-distyrylanthracene moieties are employed as building blocks for the construction of conjugated and rigid backbone to endow the polymer with strong fluorescence and the unique mechanochromic property. Meanwhile, tetraphenylethenes are linked to the fluorene segments by alkyl chains and work as bulky pendant groups to prevent the π - π stacking of the backbone and make the polymer be AEE-active. Based on this meticulous design, the resulting polymeric emitter, namely **P1**, is thus expected to show strong fluorescence in solid state and remarkable color change under the stimulus of mechanical force.

EXPERIMENTAL

Materials

4-Hydroxybenzeneboronic acid, 1,4-dibromobutane, 1-bromine-1',2,2'-triphenylethylene, 2,7-dibromofluorene, 4-formylphenylboronic acid, 9,10-(dichloromethylene) anthracene, triethyl phosphite, tetrakis (triphenylphosphine) platinum(0), tetrabutylammonium bromide (TBAB), potassium *tert*-butoxide were purchased from Alfa Aesar Company. Ultra-pure water was used in the experiments and all other reagents and solvents were purchased from Guangzhou Dongzheng Company. Tetrahydrofuran (THF) was distilled from sodium/benzophenone.

Characterization

Proton and carbon nuclear magnetic resonance (¹H-NMR and ¹³C-NMR) spectra were recorded on a Mercury-Plus 300 spectrometer and an AVANCE AV 400 spectrometer (CDCl₃, tetramethylsilane (TMS) as the internal standard). Mass spectra (MS) were collected from a Thermo DSQ EI-mass spectrometer and a MAT95XP-HRM spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 670 spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Hitachi UV-Vis spectrophotometer (U-3900). Photoluminescence (PL) spectra were measured on a Shimadzu RF-5301pc spectrometer with 3.0 nm slit widths for both excitation and emission. The fluorescence quantum yields of **P1** in solution, aggregation and solid states were measured on an integrating sphere of HORIBA FluoroLog-3. Time-resolved emission decay behavior was studied on an Edinburgh combined fluorescence lifetime and steady-state spectrometer (FLSP920). Thermogravimetric analysis (TGA) curves were obtained with a Shimadzu thermal analyzer (TGA-50H) at a heating rate of 20 K/min under N₂ atmosphere. Differential scanning calorimetry (DSC) curves were collected

with a NETZSCH thermal analyzer (DSC 204 F1) at a heating and cooling rate of 10 K/min under N₂ atmosphere. Wide-angle X-ray diffraction (WAXD) was performed by using a Bruker X-ray diffractometer (D8ADVANCE, Germany) with an X-ray source of Cu K α (λ = 0.15406 nm) at 40 kV and 40 mA with scan rates of 4° (2 θ)/min or 0.6° (2 θ)/min.

The ground samples were prepared by grinding using a mortar and pestle. The annealing experiments were carried on a hot plate with an automatic temperature control system. The tetrahydrofuran (THF)/water mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature.

Preparation of P1

The compounds P₄A^[31], P₄MBr^[32] and Anpho₂^[32] were synthesized according to the methods described in previous literature.

Diethyl(4-(1,2,2'-triphenylvinyl)benzyl)phosphonate (P₄pho)

P₄MBr (0.30 g, 0.71 mmol) was dissolved in triethylphosphite (0.38 g, 2.29 mmol) and the mixture was heated to 150 °C and stirred for 8 h under argon atmosphere. After cooling to room temperature, the residue was purified through silica-gel column chromatography with acetone/CH₂Cl₂ (1/3, *V/V*) to give P₄pho as a light yellow powder (0.19 g, 56% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 7.10–6.96 (m, 19H); 3.99–3.83 (m, 2H); 3.17–2.91 (d, 2H); 1.25–1.17 (m, 6H); ¹³C-NMR (100 MHz, CDCl₃, δ): 145.11, 144.99, 144.94, 143.83, 143.79, 142.42, 141.92, 132.81, 132.63, 131.00, 130.91, 130.60, 130.53, 128.99, 127.79, 127.73, 63.58, 63.51, 35.65, 34.28, 31.05; FTIR (KBr, ν , cm⁻¹): 3053, 3022, 2977, 2926, 2853, 1600, 1500, 1192, 854, 747, 700; EI-MS, *m/z*: [M]⁺ 482, Calcd for C₃₁H₃₁O₃P 482; Anal. Calcd for C₃₁H₃₁O₃P: C 77.16, H 6.48, O 9.95; Found: C 77.14, H 6.51.

4-(1,2,2'-Triphenylvinyl)phenol (TPEOH)

1-Bromine-1',2,2'-triphenylethylene (8.00 g, 23.86 mmol) and 4-hydroxybenzeneboronic acid (3.95 g, 28.64 mmol) were dissolved in THF (50 mL), then K₂CO₃ aqueous solution (2 mol/L, 15 mL) and TBAB (0.30 g) were added. The solution was stirred at room temperature under argon atmosphere for 40 min. After adding Pd(PPh₃)₄ (0.10 g), the mixture was heated to 75 °C and stirred for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure, the residue was purified through silica-gel column chromatography with acetone/*n*-hexane (1/3, *V/V*) as eluent to give TPEOH as a yellow powder (8.16 g, 98% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 7.10–6.93 (m, 15H), 6.87–6.81 (d, 2H), 6.59–6.48 (d, 2H), 4.67–4.55 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃, δ): 153.68, 143.69, 143.59, 140.13, 139.89, 136.07, 132.45, 131.07, 127.43, 127.34, 126.11, 126.00, 114.34; FTIR (KBr, ν , cm⁻¹): 3520, 3053, 3022, 1600, 1500, 1260, 828, 747, 700; EI-MS, *m/z*: [M]⁺ 348, Calcd for C₂₆H₂₀O 348; Anal. Calcd for C₂₆H₂₀O: C 89.62, H 5.79, O 4.59; Found: C 89.24, H 5.82.

(2-(4-(4'-Bromobutoxy)phenyl)ethene-1,1',2'-triyl)tribenzene (EBuBr)

TPEOH (8.00 g, 23.00 mmol) and 1,4-dibromobutane (19.80 g, 91.70 mmol) were dissolved in dry *N,N*-dimethyl formamide (DMF) (10 mL), and K₂CO₃ was added (6.35 g, 46.01 mmol). Then the solution was heated to 85 °C and stirred at this temperature for 20 h. After cooling to room temperature, the mixture was filtered. The filtrate was collected and the solvent was removed under reduced pressure. The residue was purified through silica-gel column chromatography with *n*-hexane as eluent to give EBuBr as a white powder (8.23 g, 74% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 7.14–6.95 (m, 15H), 6.93–6.86 (d, 2H), 6.62–6.56 (d, 2H), 3.93–3.87 (t, 2H), 3.48–3.43 (t, 2H), 2.08–1.98 (m, 2H), 1.92–1.82 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃, δ): 157.06, 143.68, 140.21, 139.82, 135.91, 132.26, 131.08, 127.33, 125.98, 113.32, 66.47, 33.40, 29.43, 27.85; FTIR (KBr, ν , cm⁻¹): 3053, 3022, 2939, 1600, 1500, 1240, 822, 747, 614; EI-MS, *m/z*: [M]⁺ 482, Calcd for C₃₀H₂₇BrO 482; Anal. Calcd for C₃₀H₂₇BrO: C 74.53, H 5.63, O 3.31; Found: C 74.39, H 5.67.

2,7-Dibromo-9,9'-bis(4-(4'-(1,2,2'-triphenylvinyl)phenoxy)butyl)-9H-fluorene (FBuE₂Br₂)

EBuBr (8.00 g, 16.55 mmol), 2, 7-dibromofluorene (2.14 g, 6.60 mmol) and TBAB (0.20 g) were dissolved in

THF/dimethyl sulfoxide (DMSO) (1/4, *V/V*) mixture. The solution was stirred at 60 °C for 8 h after adding NaOH aqueous solution (50 wt%, 7 mL). After cooling to room temperature, most of the solvent was removed under reduced pressure. Then the mixture was poured into water (150 mL) and extracted with CH₂Cl₂ three times. The combined organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified through silica-gel column chromatography with CH₂Cl₂/*n*-hexane (1/2, *V/V*) as eluent to give FBU₂Br₂ as a light-green powder (6.04 g, 81% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 7.51–7.47 (d, 2H), 7.45–7.39 (m, 4H), 7.12–6.92 (m, 30H), 6.87–6.82 (d, 4H), 6.51–6.45 (d, 4H), 3.66–3.60 (t, 4H), 2.03–1.94 (m, 4H), 1.52–1.45 (m, 4H), 0.79–0.66 (m, 4H); ¹³C-NMR (100 MHz, CDCl₃, δ): 157.30, 152.02, 143.73, 140.32, 139.69, 138.79, 135.60, 132.19, 131.09, 130.02, 127.43, 127.30, 126.04, 125.92, 121.29, 120.95, 113.32, 67.48, 55.51, 40.03, 34.61, 29.53, 29.09, 25.65, 23.59; FTIR (KBr, ν, cm⁻¹): 3053, 3027, 2941, 2864, 1600, 1500, 1241, 813, 750, 700, 614. FAB-MS, *m/z*: [M+H]⁺ 1128, Calcd for C₇₃H₆₀Br₂O₂ 1127; Anal. Calcd for C₇₃H₆₀Br₂O₂: C 77.66, H 5.36, O 2.83; Found: C 77.61, H 5.38.

4,4'-(9,9'-Bis(4-(4'-(1,2,2'-triphenylvinyl)phenoxy)butyl)-9H-fluorene-2,7-diyl)dibenzaldehyde (FBU₂A₂)

FBU₂Br₂ (1.00 g, 0.89 mmol) and 4-formylphenylboronic acid (0.33 g, 2.21 mmol) were dissolved in toluene, then K₂CO₃ aqueous solution (2 mol/L, 2 mL) and TBAB (0.10 g) were added. The solution was stirred at room temperature under argon atmosphere for 40 min. After adding Pd(PPh₃)₄ (0.10 g), the mixture was heated to 85 °C for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified through silica-gel column chromatography with CH₂Cl₂/*n*-hexane (1/1, *V/V*) as eluent to give FBU₂A₂ as a light-green powder (0.85 g, 81% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 10.04–9.99 (s, 2H), 7.96–7.89 (d, 4H), 7.84–7.75 (t, 4H), 7.67–7.58 (dt, 4H), 7.10–6.90 (m, 30H), 7.96–7.89 (d, 4H), 6.45–6.39 (d, 4H), 3.68–3.60 (t, 4H), 2.20–2.08 (m, 4H), 1.55–1.47 (m, 4H), 0.89–0.85 (m, 4H); ¹³C-NMR (100 MHz, CDCl₃, δ): 191.48, 191.45, 157.06, 151.08, 147.03, 143.72, 143.67, 143.63, 140.63, 140.16, 139.77, 138.86, 135.68, 134.92, 132.18, 132.10, 131.05, 130.67, 127.49, 127.34, 126.60, 125.94, 121.43, 120.46, 113.30, 113.22, 67.12, 55.29, 40.04, 29.43, 20.47; FTIR (KBr, ν, cm⁻¹): 3051, 3022, 2936, 2864, 1700, 1600, 1504, 1243, 815, 750, 700; FAB-MS, *m/z*: [M+H]⁺ 1179, Calcd for C₈₇H₇₀O₄ 1178; Anal. Calcd for C₈₇H₇₀O₄: C 88.59, H 5.98, O 5.43; Found: C 88.62, H 5.96.

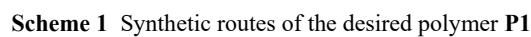
Poly(9,10-anthracenevinylene-alt-4,4'-(9,9-bis(4-(4'-(1,2,2'-triphenylvinyl)phenoxy)butyl)-9H-fluorene-2,7-diyl)dibenzaldehyde) (P1)

FBU₂A₂ (0.40 g, 0.34 mmol) and Anpho₂ (0.16 g, 0.34 mmol) were dissolved in THF (50 mL) under argon atmosphere. Then, a THF solution of potassium *tert*-butoxide (0.11 g, 1.02 mmol) was slowly added into the above system. After the mixture was stirred at room temperature for 24 h, the end capping agent P₄A (15 mg, 0.03 mmol) was added. While another end-capping agent P₄pho (15 mg, 0.03 mmol) was added after additional stirring for 24 h. After most of the solvent was removed by reduced pressure distillation, 200 mL of anhydrous ethanol was added. The filtered solid was extracted by Soxhlet extraction using ethanol and acetone for 72 h, respectively. The residual solid was dried under vacuum to give **P1** as an orange powder (0.28 g). Molecular weight (gel permeation chromatography, GPC): *M_n* = 1.41 × 10⁴, *M_w* = 3.38 × 10⁴, *M_p* = 2.92 × 10⁴; *M_w*/*M_n* = 2.39; *T_{d,5%}* = 430 °C; *T_g* = 171 °C. ¹H-NMR (300 MHz, CDCl₃, δ): 8.48–8.40 (C₆H₄), 8.08–7.96 (C₆H₄), 7.88–7.62 (C₆H₄), 7.56–7.44 (C=C–H), 7.14–6.91 (C₆H₄), 6.90–6.80 (C₆H₄), 6.56–6.46 (C₆H₄), 3.76–3.67 (–O–CH₂–), 2.40–2.00 (–CH₂–), 1.90–1.30 (–CH₂–); 1.15–0.75 (–CH₂–); ¹³C-NMR (100 MHz, CDCl₃, δ): 157.21, 150.91, 143.75, 143.70, 140.28, 139.71, 135.64, 132.20, 131.06, 129.41, 127.42, 127.29, 126.86, 126.06, 125.94, 125.12, 113.39, 67.29, 55.15, 40.17, 29.54; FTIR (KBr, ν, cm⁻¹): 3051, 3022, 2926, 2853, 1600, 1504, 1243, 817, 754, 700.

RESULTS AND DISCUSSION

Synthesis

The polymer **P1**, which contains tetraphenylethene units at its side chain and 9,10-distyrylanthracene unit at its backbone, was prepared through a Wittig-Horner polymerization reaction (Scheme 1) at room temperature by



Scheme 1 Synthetic routes of the desired polymer **P1**

using two monomers, 2,7-bis(4-aldehyde group phenyl) fluorene derivative with two alkyl chain linked tetraphenylethene units (FBuE₂A₂) and 9,10-bis(methyl phosphonic acid diethyl ester)anthracene (Anpho₂), respectively. The purified intermediates and final product were characterized by standard spectroscopic techniques, including mass spectrum (MS), nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared spectroscopy (FTIR), from which satisfactory analysis data corresponding to their chemical structures were obtained. Details are provided in the Experimental and the Supporting Information.

Photophysical Properties

The UV-Vis absorption spectrum of the product **P1** was measured in a THF solution, as shown in Fig. 1(A)-a. Three absorption bands centered at 314, 343 and 420 nm, respectively, were observed in the UV-Vis absorption spectrum. The first two bands can be assigned to be the absorption from the 2,7-diphenylfluorene unit in the main chain and the tetraphenylethene side group of the polymer, and the latter was associated with the intramolecular charge transfer (ICT) transition in the polymer's backbone. In dilute THF solution, **P1** exhibits an orange-light emission that peaks at 567 nm ($\Phi_{\text{F,sl}} = 0.12$) (Fig. 1A-b). However, in solid powder, the emission of the polymer is obviously blue-shifted ($\lambda_{\text{max}} = 541$ nm, $\Phi_{\text{F,s}} = 0.90$), showing a strong yellow-light (Fig. 1B-a). Solid thin film of **P1** with intense fluorescence is also facile to be prepared by spin-coating, indicating that the polymer is promising for solution processing in device fabrication (Fig. 1B-b).

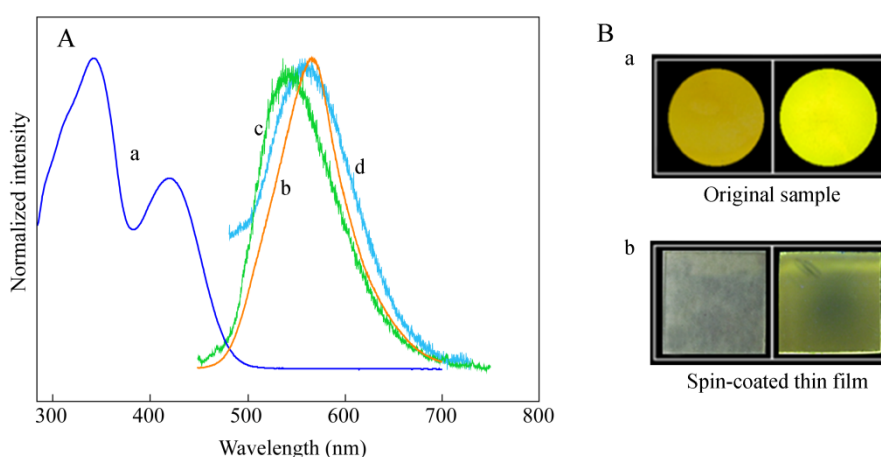


Fig. 1 Photophysical properties and images of **P1** in different states: (A) UV-Vis absorption and PL spectra of **P1** in different states: a, UV-Vis absorption spectrum; b, PL spectrum in THF solution (concentration: 0.1 mg/mL); c, PL spectrum in solid powder; d, PL spectrum in solid thin film; (B) Images of **P1** in different states: a, without (left) and with (right) the illumination of UV light in original solid powder; b, without (left) and with (right) the illumination of UV light in solid thin film

AIE Properties

The polymer **P1** is soluble in common organic solvents such as tetrahydrofuran (THF), dichloromethane, chloroform, and *N,N*-dimethylformamide (DMF) because of its flexible alkyl chains and the twisted tetraphenylethene units. As depicted in Figs. 1(B)-a and 2(a), while strong yellow emission is observed for the as-prepared solid powder, the dilute THF solution of **P1** exhibits weak orange-light when illuminated by 365 nm UV lamp. The enhanced fluorescence of the polymer in the aggregated state suggests that **P1** is most likely AEE-active.

In order to demonstrate the AEE behavior, we studied the photophysical properties of **P1** in water/THF mixtures with different water fractions (f_w). The UV-Vis absorption spectra are shown in Fig. 2(b). When f_w is increased from 0% to 70%, the absorption of **P1** at 420 nm shows a continuous decrease. Meanwhile, no trailing phenomenon is observed in the spectrum, indicating that nano-**P1** aggregates haven't formed in the mixtures at $f_w \leq 70\%$. Therefore, the variation of absorption at 420 nm may result from the increase of solvent polarity,

leading to the reduction of ICT absorption. When the f_w is further increased, the whole absorption profile started to rise and trailing effect is also detectable, which is caused by light scattering of the nanoaggregates^[33].

Figure 2(a) shows the PL spectra of **P1** in the water/THF mixtures at different water contents. Both of the solutions with 0% and 5% water fraction exhibit weak orange emission peaked at 568 nm. Considering that tetraphenylethene is a typical AIE emitter with blue-light emission and is almost non-emissive when dissolved in dilute solution, the light of the mixtures would mainly originate from the conjugated backbone of **P1**. By further increasing the f_w to 30% and then to 70%, the mixtures show a significant emission enhancement, followed by a slight decrease in PL intensity. Accompanied with these changes, the maxima of the spectra display a hypochromic shift from 568 nm to 546 nm. These results might be caused by a combined effect of the entanglement of the polymeric backbones and the increase of solvent polarity, which is beneficial for and is detrimental to emission enhancement, respectively. Subsequently, further enhancement in luminescence is observed in water/THF mixtures at $f_w > 70\%$ and strong yellow light peaked at around 541 nm could be recorded. In the solvent mixture with 95% water ($\Phi_{F,a} = 0.70$), the PL intensity of **P1** rises to 741 a.u., which is nearly 5-fold higher than that in pure THF solution (158 a.u.). The PL behaviors are also corresponding well to those of the UV-Vis absorptions. Obviously, the emission enhancement of the polymer is induced by the formation of nanoaggregates, thus suggesting that **P1** is AEE-active^[34].

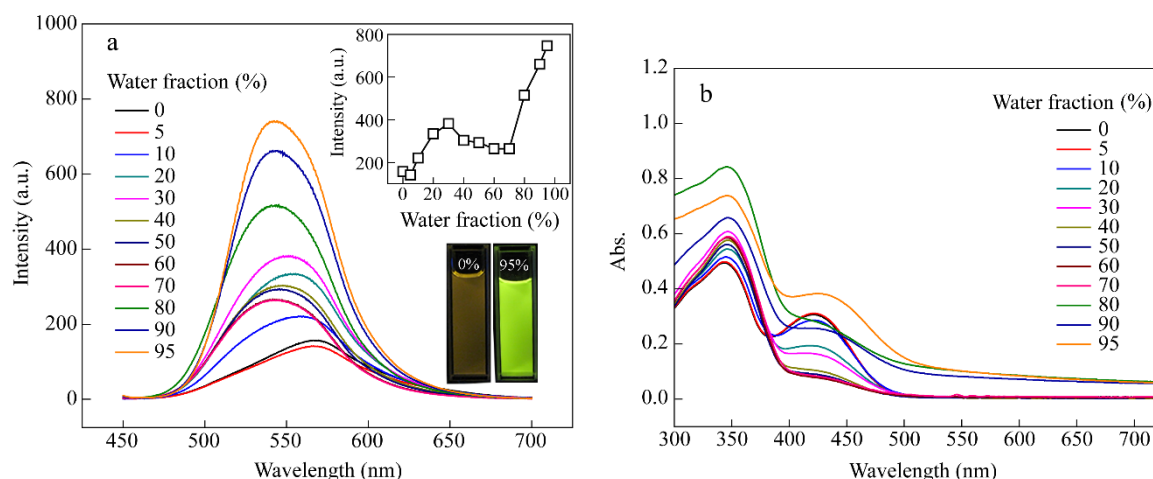


Fig. 2 UV-Vis absorption (a) and PL (b) spectra of **P1** in water/THF mixtures with different water fractions (Excitation: 440 nm; concentration: 0.1 mg/mL)

The insets in (a) are the changes of PL peak intensity (upper) and the fluorescent images of the mixtures with 0% and 95% water fractions under the illumination of 365 nm UV lamp (bottom).

Thermal and Morphological Properties

As depicted in Fig. 3(a), the decomposition temperature of the emitting polymer with 5% weight loss ($T_{d,5\%}$) under N_2 atmosphere was determined to be 430 °C, indicating that **P1** is highly thermal stable. Further observation reveals that the TGA curve of **P1** exhibits two main stages in weight loss. Obviously, the former one at lower temperature and the latter one at higher temperature should be attributed to the decomposition of the pendant group and the backbone, respectively. In addition, differential scanning calorimetry (DSC) was carried out and the glass transition temperature (T_g) of **P1** was determined to be 171 °C (Fig. 3b), which is much higher than most of the reported polymeric emitters. The impressive morphological stability of **P1** should be ascribed to its rigid backbone and bulky pendants. Such high T_d and T_g values thus meet the requirements of real-world applications making **P1** promise for the fabrication of optoelectronic devices.

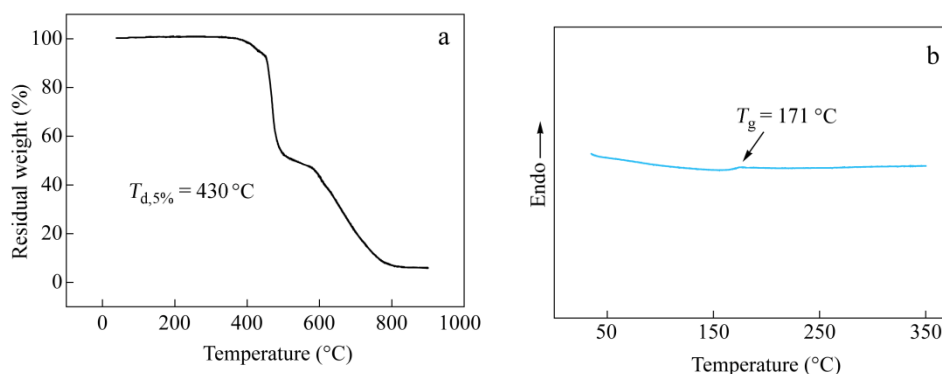


Fig. 3 Thermal and morphological stabilities of **P1**: (a) TGA curve; (b) DSC curve (2nd heating run)

Mechanochromism

To specify the mechanochromic characteristic of **P1**, the PL spectrum of the as-prepared polymer was investigated. As shown in Fig. 4(A), the emission maximum of the pristine sample for **P1** locates at 541 nm, exhibiting a strong yellow light. However, by grinding with a pestle or shearing with a spatula, the emission color of the polymer changes from an initial yellow to red light (Fig. 4B). The PL maximum of the sample also shifts bathochromically by 61 nm to 602 nm, showing a remarkable mechanochromism. These results fully demonstrate that **P1** is an AIE-active mechanoluminescent polymer.

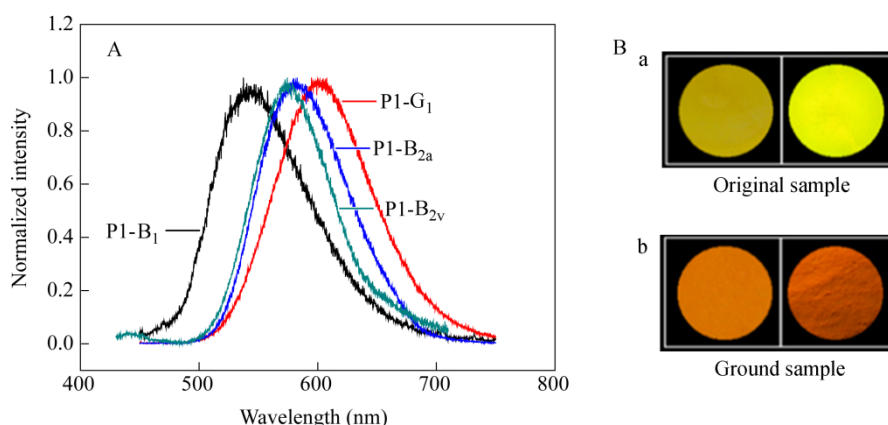


Fig. 4 PL spectra (A) and images (B) of **P1** in different states: (A) PL spectra of **P1** in different states: (B₁) original sample; (G₁) ground sample; (B_{2v}) fumed sample from G₁ (ground sample of **P1** in the vapor of THF for 30 min); (B_{2a}) annealed sample from G₁ (Ground sample of **P1** was heated at 200 °C for 30 min, and then, cooled down to room temperature); (B) Images of **P1** in different states: a, without (left) and with (right) the illumination of UV light on original solid powder; b, without (left) and with (right) the illumination of UV light in ground solid powder

The phase characteristics for the original and ground samples of **P1** were then measured by X-ray diffraction to gain insight into the origin of this phenomenon (Fig. 5). Some intense and sharp diffraction peaks were observed in the pattern of the pristine powder of **P1**, suggesting that the polymer is partially crystalline. In contrast, after grinding, all of the diffraction peaks disappeared, verifying that the ground sample is amorphous. On the other hand, although the polymer showed remarkable mechanochromism, similar phenomena were not observed for the monomers of FBU₂A₂ and Anpho₂. As noted above, the light of the **P1** mainly comes from the conjugated backbone. Accordingly, the mechanochromism of **P1** is believed to be correlated with the destruction of the crystalline structure, which leads to the conformational planarization of the distyrylanthracene moieties forming by the polymerization and the increase of molecular conjugation of the backbone^[10, 35]. Time-resolved

emission decay was also carried out and the results are presented in Fig. 6 and Table 1. For the original yellow powder, the species in the excited-state decay mainly through the first ($\tau_1 = 1.15$, $A_1 = 0.82$) and second ($\tau_2 = 6.58$, $A_2 = 0.13$) pathways with a mean lifetime of 3.56 ns. Nevertheless, such a mean lifetime of **P1** decreases to 2.18 ns upon grinding, which is most likely caused by the stronger interactions of the polymer chains in the amorphous state^[36].

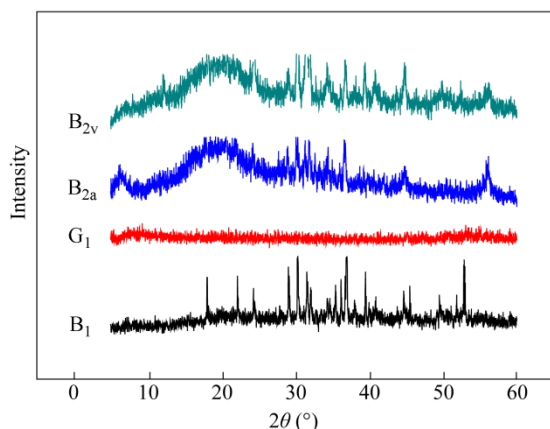


Fig. 5 XRD patterns of **P1** at different treatment conditions: (B₁) original sample; (G₁) ground sample; (B_{2v}) fumed sample from G₁ (ground sample of **P1** in the vapor of THF for 30 min); (B_{2a}) annealed sample from G₁ (Ground sample of **P1** was heated at 200 °C for 30 min, and then, cooled down to room temperature)

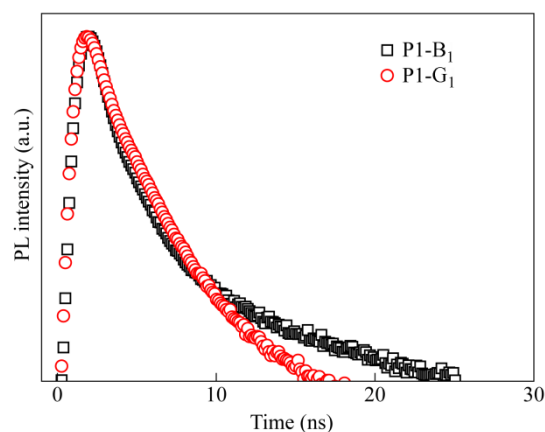


Fig. 6 Time-resolved emission decay curves of **P1** at different treatment conditions: (B₁) original sample; (G₁) ground sample

Table 1 Emission decay parameters of **P1** in different states

Sample	τ_1 (ns)	A_1 ^d	τ_2 (ns)	A_2	τ_2 (ns)	A_2	$\langle \tau \rangle$ ^e (ns)
B ₁ ^a	1.15	0.82	6.58	0.13	35.30	0.05	3.56
G ₁ ^b	1.28	0.90	4.08	0.08	35.1	0.02	2.18

^a Original sample; ^b Ground sample; ^c Fluorescence lifetime; ^d Contribution ratio; ^e Mean lifetime

Although some of the diffraction peaks recover by heating the ground sample at 200 °C or fuming it in dichloromethane vapor for 30 min, the crystallinity of the annealed sample and the fumed sample are obviously lower than the pristine powder because of their diffuse patterns (Fig. 5). As a result, the emission of the ground sample for **P1** can merely shift back to 580 and 574 nm, respectively. In other words, the ground polymer is hard to reverse back to the pristine one. This might be attributed to the difficulty of recovering the destroyed crystalline (ordered) structure of the polymer limited by the high molecular weight and the motion of its chain segments.

CONCLUSIONS

In summary, an AEE-active polymer, **P1**, with 9,10-distyrylanthracene unit at the backbone and side tetraphenylethene unit was successfully synthesized by a Wittig-Horner polymerization reaction with the two designed monomers. This AEE polymer exhibits mechanochromic property with an obvious red-shifted fluorescence from 541 nm to 602 nm in solid state when the sample is ground with an external pressure/force. It is revealed that the destruction of the crystalline structure of the polymer, which leads to the planarization of the molecular conformation and the increase of molecular conjugation in the polymer chain segments, is the reason for such red-shifted emission. The fluorescent color of the ground polymer could not restore completely by thermal annealing or solvent fuming, due to the difficulty of recovering the destroyed crystalline (ordered)

structure of the polymer limited by the motion of its chain segments, which is the main difference between polymer and small molecules. These results demonstrate that the mechanochromic property is a common feature of the crystalline AEE materials, including not only small molecules but also polymers. The structure-property relationships of **P1** established in this study would provide an idea to identify and synthesize new mechanochromic polymers with AEE property.

REFERENCES

- 1 Chi, Z.G., Zhang, X.Q., Xu, B.J., Zhou, X., Ma, C.P., Zhang, Y., Liu, S.W. and Xu, J.R., *Chem. Soc. Rev.*, 2012, 41(10): 3878
- 2 Gong, Y.Y., Tan, Y.Q., Liu, J., Lu, P., Feng, C.F., Yuan, W.Z., Lu Y.W., Sun, J.Z., He, G.F. and Zhang, Y.M., *Chem. Commun.*, 2013, 49(38): 4009
- 3 Gautam, P., Maragani, R., Mobin, S.M. and Misra, R., *RSC Adv.*, 2014, 4(94): 52526
- 4 Park, S.K., Cho, I., Gierschner, J., Kim, J.H., Kim, J.H., Kwon, J.E., Kwon, O.K., Whang, D.R., Park, J.H. and An, B.K., *Angew. Chem.*, 2016, 128(1): 211
- 5 Wu, J., Cheng, Y.Y., Lan, J.B., Wu, D., Qian, S.Y., Yan, L.P., He, Z., Li, X.Y., Wang, K., Zou, B. and You, J.S., *J. Am. Chem. Soc.*, 2016, doi:10.1021/jacs.6b03890
- 6 Zeng, S.S., Zhang, D.Y., Huang, W.H., Wang, Z.F., Freire, S.G., Yu, X.Y., Smith, A.T., Huang, E.Y., Nguon, H. and Sun, L.Y., *Nat. Commun.*, 2016, 7: 1
- 7 Sagara, Y. and Kato, T., *Nat. Chem.*, 2009, 1(8): 605
- 8 Mei, J., Leung, N.L.C., Kwok, R.T.K., Lam, J.W.Y. and Tang, B.Z., *Chem. Rev.*, 2015, 115(21): 11718
- 9 Sagara, Y., Mutai, T., Yoshikawa, I. and Araki, K., *J. Am. Chem. Soc.*, 2007, 129(6): 1520
- 10 Yuan, W.Z., Tan, Y.Q., Gong, Y.Y., Lu, P., Lam, J.W.Y., Shen, X.Y., Feng, C.F., Sung, H.H.Y., Lu, Y.W. and Williams, I.D., *Adv. Mater.*, 2013, 25(20): 2837
- 11 Yang, J., Huang, J., Li, Q.Q. and Li, Z., *J. Mater. Chem. C*, 2016, 4(14): 2663
- 12 Li, Q.Q. and Li, Z., *Sci. China Chem.*, 2015, 58(12): 1800
- 13 Li, H.Y., Zhang, X.Q., Chi, Z.G., Xu, B.J., Zhou, W., Liu, S.W., Zhang, Y. and Xu, J.R., *Org. Lett.*, 2011, 13(4): 556
- 14 Xu, B.J., Chi, Z.G., Zhang, J.Y., Zhang, X.Q., Li, H.Y., Li, X.F., Liu, S.W., Zhang, Y. and Xu, J.R., *Chem. Asian J.*, 2011, 6(6): 1470
- 15 Dong, Y.J., Xu, B., Zhang, J.B., Tan, X., Wang, L.J., Chen, J.L., Lv, H.G., Wen, S.P., Li, B. and Ye, L., *Angew. Chem. Int. Ed.*, 2012, 51(43): 10782
- 16 Misra, R., Jadhav, T., Dhokale, B. and Mobin, S.M., *Chem. Commun.*, 2014, 50(65): 9076
- 17 Wang, J., Mei, J., Hu, R.R., Sun, J.Z., Qin, A.J. and Tang, B.Z., *J. Am. Chem. Soc.*, 2012, 134(24): 9956
- 18 Zhao, N., Yang, Z.Y., Lam, J.W.Y., Sung, H.H.Y., Xie, N., Chen, S.J., Su, H.M., Gao, M., Williams, I.D. and Wong, K.S., *Chem. Commun.*, 2012, 48(69): 8637
- 19 Tong, J.Q., Wang, Y.J., Mei, J., Wang, J., Qin, A.J., Sun, J.Z. and Tang, B.Z., *Chem. Eur. J.*, 2014, 20(16): 4461
- 20 Zhang, J.B., Chen, J.L., Xu, B., Wang, L.J., Ma, S.Q., Dong, Y.J., Li, B., Ye, L. and Tian, W.J., *Chem. Commun.*, 2013, 49(37): 3878
- 21 Qi, Q.K., Liu, Y.F., Fang, X.F., Zhang, Y.M., Chen, P., Wang, Y., Yang, B., Xu, B., Tian, W.J. and Zhang, S.X.A., *RSC Adv.*, 2013, 3(21): 7996
- 22 Kim, H.J., Whang, D.R., Gierschner, J., Lee, C.H. and Park, S.Y., *Angew. Chem. Int. Ed.*, 2015, 54(14): 4330
- 23 Ma, Z.Y., Teng, M.J., Wang, Z.J., Yang, S. and Jia, X.R., *Angew. Chem. Int. Ed.*, 2013, 52(47): 12268
- 24 Gong, Y., Zhang, Y., Yuan, W.Z., Sun, J.Z. and Zhang, Y., *J. Phys. Chem. C*, 2014, 118(20): 10998
- 25 Wang, L., Wang, K., Zou, B., Ye, K., Zhang, H. and Wang, Y., *Adv. Mater.*, 2015, 27(18): 2918
- 26 Mao, Z., Yang, Z.Y., Mu, Y.X., Zhang, Y., Wang, Y.F., Chi, Z.G., Lo, C.C., Liu, S.W., Alan, L. and Xu, J.R., *Angew. Chem. Int. Ed.*, 2015, 54(21): 6270

- 27 Xu, B.J., Mu, Y.X., Mao, Z., Xie, Z.L., Wu, H.Z., Zhang, Y., Jin, C.J., Chi, Z.G., Liu, S.W., Xu, J.R., Wu, Y.C., Lu, P.Y., Alan, L. and Martin, R.B., *Chem. Sci.*, 2016, 7(3): 2201
- 28 Hu, R.R., Leung, N.L.C. and Tang, B.B., *Chem. Soc. Rev.*, 2014, 43(13): 4494
- 29 Ciardelli, F., Ruggeri, G. and Pucci, A., *Chem. Soc. Rev.*, 2013, 42(3): 857
- 30 Kwok, R.T. K., Leung, C.W.T., Lam, J.W.Y. and Tang, B.B., *Chem. Soc. Rev.*, 2015, 44(13): 4228
- 31 Zhang, X.Q., Chi, Z.G., Li, H.Y., Xu, B.J., Li, X.F., Zhou, W., Liu, S.W., Zhang, Y. and Xu, J.R., *Chem. Asian J.*, 2011, 6(3): 808
- 32 Wang, Z.K., Chen, S.J., Lam, J.W.Y., Qin, W., Kwok, R.T.K., Xie, N., Hu, Q.L. and Tang, B.Z., *J. Am. Chem. Soc.*, 2013, 135(22): 8238
- 33 Tong, H., Hong, Y.N., Dong, Y.Q., Matthias, H., Jacky, W.Y., Li, Z., Guo, Z.F., Guo, Z.H. and Tang, B.Z., *Chem. Commun.*, 2006, (35): 3705
- 34 Chen, M., Li, L.Z., Nie, H., Tong, J.Q., Yan, L.L., Xu, B., Sun, J.Z., Tian, W.J., Zhao, Z.J. and Qin, A.J., *Chem. Sci.*, 2015, 6(3): 1932
- 35 Xu, B.J., He, J.J., Mu, Y.X., Zhu, Q.Z., Wu, S.K., Wang, Y.F., Zhang, Y., Jin, C.J., Lo, C.C. and Chi, Z.G., *Chem. Sci.*, 2015, 6(5): 3236
- 36 Xu, B.J., He, J.J., Liu, Y., Xu, B., Zhu, Q.Z., Xie, M.Y., Zheng, Z.B., Chi, Z.G., Tian, W.J. and Jin, C.J., *J. Mater. Chem. C*, 2014, 2(17): 3416