Electronic Supplementary Information for

Effect of Ionic Interaction on the Mechanochromic Property of

Pyridinium Modified Tetraphenylethene

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Experimental Section

**Materials:** Diphenylmethane and 4-bromobenzophenone ketyl were purchased from Alfa Aesar. Lithium n-butyl and Pd(II)acetate were purchased from Acros. Zinc powder (99%), titanium tetrachloride, sodium, KPF$_6$, triphenylphosphine, acetonitrile, chloroform, cyclohexanone, dichloromethane (DCM), dioxane, dimethylformamide (DMF), ethylacetate, ethanol, methanol and petroleum ether (60–90 °C) were purchased from Sinopharm (Shanghai, China). Iodomethane was purchased from Advanced Technology Industry (Kowloon, Hong Kong). All these chemicals and solvents were used as received. Tetrahydrofuran (THF) was obtained from Sinopharm and it was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. 4-Vinylpyridine was purchased from Acros. It was extracted from 10% sodium hydroxide aqueous solution and dried in vacuum before using. Triethylamine was purchased from Acros and distilled under normal pressure immediately prior to use.

**Instrumentation:** $^1$H and $^{13}$C NMR spectra were measured on a Mercury plus 400 MHz NMR spectrometer in CDCl$_3$ using tetramethylsilane (TMS; $\delta =$ 0 ppm) as internal standard. $^{19}$F NMR spectra were recorded on a Bruker ARX 600 NMR spectrometer. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. UV-visible absorption spectra were measured on a Varian Cary 100 Biospectrophotometer. Fluorescence (FL) spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. Single crystal X-ray diffraction patterns were recorded on an Xcalibur, Sapphire 3, Gemini ultra diffractometer with graphite monochromated Cu-Ka X-ray radiation. Thermalgravimetric analysis (TGA) was conducted on a thermogravimetric analyzer (TAQ50) under nitrogen atmosphere at a heating rate of 20 °C/min. A Perkin-Elmer DSC 7 was employed to measure the phase transition thermograms at a scan rate of 10 °C/min under nitrogen flow. The fluorescence quantum efficiency ($\Phi$) of the samples in solutions were estimated using fluorescein in ethanol ($\Phi =$ 70%) as standard. The absorbance of the solution was kept between 0.04 and 0.06 to avoid the internal filter effect. Absolute FL quantum yield of the solid samples was tested on the instrument of Hamamatsu C11347.

**Synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethene:** The synthetic procedures of this compound was reported in literature.[1] We followed the descriptions and obtained a white solid product in a yield of 76%. The characterization data obtained by $^1$H NMR and $^{13}$C NMR spectroscope are in good agreement with the reported
results. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)), \(\delta\) (TMS, ppm): 7.19-7.25 (m, 3H), 7.06-7.13 (m, 7H), 6.96-7.03 (m, 5H), 6.85-6.90 (d, 3H). \(^{13}\)C NMR (400 MHz, CDCl\(_3\)), \(\delta\) (TMS, ppm): 142.26, 140.24, 132.94, 132.85, 131.26, 131.18, 131.07, 130.87, 130.81, 127.99, 127.79, 127.62, 126.91, 126.80, 126.61, 126.36.

Scheme S1 Synthetic route to pyridine-modified TPE (TPE-DPy).

**Synthesis of (Z/E)-1,2-diphenyl-1,2-bis{4-[(E)-2-(pyridin-4-yl)vinyl]phenyl}ethene (TPE-DPy):** Into a 50 mL reaction tube, 2-bis(4-bromophenyl)-1,2-diphenylethene 0.98 g (2 mM), Pd(II) (OAc)\(_2\) 0.045 g (0.2 mM), triphenylphosphine 0.128 g (0.48 mM) and a magnetic stirring bar were added. The tube was evacuated and filled with dry nitrogen gas (N\(_2\)) for three times. After fully recharged with N\(_2\), 4-vinylpyridine (0.56 mL, 5 mM) was injected into the reactant mixture; then 3 mL newly distilled triethylamine was injected. The reaction tube was sealed once all of the reactants and catalysts were added. The mixture was heated to 100 °C and kept for 2-3 days with continuously stirring. Then, cooling the reaction system to room temperature and dissolved the resultant mixture with DCM. The mixture solution was extracted with deionized water (5 mL) for three times to remove the water soluble inorganic components and triethylamine. The organic layer was collected and the solvents were removed on a rotary evaporator. The resultants in the residual solid were separated on a silicone gel column with a mixture of petroleum ether (60-90 °C) and THF (5:1, by volume) as eluent. Z- and E-isomers were separately obtained in yield of 23% and 37%, respectively. The resultants were characterization by using \(^1\)H NMR, \(^{13}\)C NMR and high resolution mass spectroscopic techniques (Figures S1-S3):

\((Z)\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (TMS, ppm) 8.54 (d, 4H), 7.29 (m, 4H), 7.17 (d, 2H), 7.11-7.05 (m, 18H), 6.94 (d, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (TMS, ppm) 150.08, 144.53, 144.28, 143.21, 140.84, 134.27, 132.63, 131.80, 131.28, 127.72, 126.68, 126.47, 125.64, 120.67. HRMS (MALDI-TOF): \(m/z\) = 538.2409, calcd for C\(_{40}\)H\(_{30}\)N\(_2\) = 538.2119.

\((E)\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (TMS, ppm) 8.53 (d, 4H), 7.29 (m, 4H), 7.20 (d, 2H), 7.14-7.02 (m, 18H), 6.92 (d, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (TMS, ppm)
150.01, 144.56, 144.22, 143.25, 134.12, 132.75, 131.78, 131.32, 127.87, 126.77, 126.34, 125.58, 120.67. HRMS (MALDI-TOF): \( m/z = 538.2409 \), calcd for \( C_{40}H_{30}N_{2} \) = 538.2473.

**Synthesis of \((E/Z)-1\text{-methyl-4-}(4\text{-}(1,2,2\text{-triphenylviny})\text{styryl})\text{pyridin-1-ium iodide} \ ([(E/Z)-\text{TPE-DPy-DMe}]^{2+}[\text{I}]^{2-})\):** The synthetic route is shown in Scheme S2, and the experimental procedures are described below. Into a 50 mL two-necked round-bottom flask was placed \((E)-\text{TPE-DPy} \ (217 \text{ mg, 0.5 mmol})\). The flask was evacuated under vacuum and flushed with dry nitrogen three times. After acetone (20 mL) was added and stirred for 10 min, iodomethane (1 mmol) was injected dropwise via a hypodermic syringe. The mixture was allowed to react at 45 °C for 24 h and deep red precipitate was formed. The red precipitate was collected by filtration and washed with anhydrous ethyl ether for three times, then dried under vacuum at 40 °C to a constant weight. Characterization data (Figures S4-S6):

- **(E)** ¹H NMR (400 MHz, DMSO-\( d_6 \)): \( \delta \) (TMS, ppm) 8.84 (d, 4H), 8.19 (d, 4H), 7.89 (d, 4H), 7.52 (d, 4H), 7.41 (d, 4H), 7.22-7.04 (m, 14H), 4.25 (s, 6H). HRMS (MALDI-TOF): \( m/z \) ([\( C_{42}H_{36}N_2 \])^{2+}[\text{I}]^{2-}) = 695.1923, calcd = 695.1916; \( m/z \) ([\( C_{42}H_{36}N_2 \])^{2+}) = 568.2878, calcd = 568.2939.

- **(Z)** ¹H NMR (400 MHz, DMSO-\( d_6 \)): \( \delta \) (TMS, ppm) 8.83 (d, 4H), 8.16 (d, 4H), 7.89 (d, 4H), 7.55 (d, 4H), 7.42 (d, 4H), 7.19-7.00 (m, 14H), 4.25 (s, 6H). HRMS (MALDI-TOF): \( m/z \) ([\( C_{42}H_{36}N_2 \])^{2+}[\text{I}]^{2-}) = 695.1923, calcd = 695.1910; \( m/z \) ([\( C_{42}H_{36}N_2 \])^{2+}) = 568.2878, calcd = 568.2826.

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\text{Scheme S2 Synthetic route to the target pyridinium modified TPE-based organic salt.}
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**Synthesis of 4,4’-\{((1E, 1’E)-[\((E)-1,2\text{-diphenylethene-1,2-diyl}])\text{bis(1-methylpyridin-1-ium hexafluorophosphate} \ ([(E)-\text{TPE-DPy-DMe}]^{2+}[\text{PF}_6]^{2-})\):** Into a 50 mL round-bottom flask was placed compound \([(E)-\text{TPE-DPy-DMe}]^{2+}[\text{I}]^{2-}) \ (240 \text{ mg, 0.3 mM})\). After 100 mL acetone added, potassium...
hexafluorophosphate (KPF₆, 552 mg in 7 mL water) was added into the reactant mixture and the system was stirred for 2 h at room temperature. Yellow solid was obtained in a yield of 96%. Characterization data (Figures S7-S9): ¹H NMR (400 MHz, DMSO-d₆): δ (TMS, ppm) 8.83 (d, 4H), 8.156 (d, 4H), 7.88 (d, 4H), 7.52 (d, 4H), 7.41 (d, 4H), 7.19-7.06 (m, 14H), 4.24 (s, 6H). ¹³C NMR (400 MHz, CDCl₃): δ (TMS, ppm) 152.31, 145.07, 142.59, 140.94, 139.99, 133.49, 131.42, 130.77, 128.11, 127.63, 127.04, 123.38. ¹⁹F NMR (600 MHz, acetone-d₆): δ (TMS, ppm) -90.00 (d, 6F), -71.77 (d, 12F). HRMS (MALDI-TOF): m/z ([C₄₂H₃₆N₂]²⁺[PF₆]⁻) = 713.2520 ([M]+); calcd = 713.2500; m/z ([C₄₂H₃₆N₂]³⁺) = 568.2878; calcd = 568.2759; m/z ([PF₆]⁻) = 144.9642, calcd. 144.9.

Reference

Figure S1. $^1$H NMR spectra of (E/Z)-TPE-DPy in CDCl$_3$. The solvent peaks are marked with asterisks.

Figure S2. $^{13}$C NMR spectra of TPE-DPy isomers in CDCl$_3$. 
Figure S3. HRMS spectra of (Z)-TPE-DPy (upper) and (E)-TPE-DPy (lower).
Figure S4. $^1$H NMR spectra of $[(E)$-TPE-DPy-DMe$]^{2+}$ $[I]_2^{2-}$ (upper) and $[(Z)$-TPE-DPy-DMe$]^{2+}$ $[I]_2^{2-}$ (lower) in DMSO-$d_6$. 
Figure S5. HRMS spectra of [(Z)-TPE-DPy-DMe]$_2^{2+}$ [I]$_2^{2+}$(upper) and [(E)-TPE-DPy-DMe]$_2^{2+}$[I]$_2^{2+}$(lower).
Figure S6. HRMS spectra of [(E)-TPE-DPy-DMe]^{2+}[PF_6]^{2-}.
Figure S7. $^{13}$C NMR spectrum of [(E)-TPE-DPy-DMe]²⁺ [PF₆]²⁻ in DMSO-$d_6$.

Figure S8. $^1$H NMR spectrum of [(E)-TPE-DPy-DMe]²⁺ [PF₆]²⁻ in DMSO-$d_6$. 
**Figure S9.** $^{19}$F NMR spectrum of [(E)-TPE-DPy-DMe]$^{2+}$[PF$_6$]$_2$$^-$ in acetone-$d_6$.

Figure S11. Normalized absorption and emission spectra of [(E)-TPE-DPy-DMe]$^{2+}$[PF$_6$]$^{2-}$ in acetone. Concentration: $1 \times 10^{-5}$ M; $\lambda_{ex} = 395$ nm.

**Figure S13.** TGA curve of [(E)-TPE-DPy-DMe]$^{2+}$[PF$_6$]$_{22}^-$ in nitrogen atmosphere at a heating rate of 20 °C/min.

**Figure S14.** DSC curves of [(E)-TPE-DPy-DMe]$^{2+}$[PF$_6$]$_{22}^-$ in nitrogen atmosphere at a heating rate of 10 °C/min.
Figure S15. Schematic illustration of the irreversible mechanochromic process occurring for the [(E)-TPE-DPy-DMe]^{2+}[PF_6]_2^{2-} salt. The ionic interaction holds the luminogens together and bestows the amorphous solid robustness to endure the solvent vapor fuming and thermal annealing treatments.