Electronic Supplementary Information (ESI)

Modulation of the Near-Infrared Photochromic Behavior in a Donor-Acceptor Diarylethene by a Cyanide Anion

Jiayu Jin, Junji Zhang, Lei Zou and He Tian*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, China

E-mail: tianhe@ecust.edu.cn (He Tian);
Fax: +86 21-64252288; Tel: +86-21-64252756

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**Fig. S11** (a) Plot of fluorescence intensity changes of 1a (2.0×10^{-5} M) against varied concentrations of CN^{-} from 0.25×10^{-5} M to 2.5×10^{-5} M ($\lambda_{ex}$=370 nm, slit: 5nm/5nm, PMT Volts: 500.). R=0.993, k=2.6×10^{7} au/M, (b) Plot of fluorescence intensity changes of 1b (2.0×10^{-5} M) against varied concentrations of CN^{-} from 2.0×10^{-5} M to 1.1×10^{-4} M ($\lambda_{ex}$=370 nm, slit: 5nm/5nm, PMT Volts: 550.). R=0.992, k=8.3×10^{6} au/M

**Fig. S12** Relative fluorescence intensities of the free 1b (2.0 × 10^{-5} M) upon the addition of 6.0 equiv. of various anions in CH$_3$CN. Each spectrum was obtained after addition of various analytes at 25 °C for 2 min.

**Fig. S13** ^1H NMR spectral changes seen upon the addition of cyanide anion (as its tetrabutylammonium salts) to 1b in CDCl$_3$ at 25 °C.

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**Fig. S16** Changes in graphs of color upon addition CN^{-} in CH$_3$CN for 2a.

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**Fig. S18** Changes in graphs of color upon addition CN^{-} in CH$_3$CN for 2b.

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**Fig. 20-22** ^1H, ^13CNMR spectrum and Mass spectrum of 4a.

**Fig. 23-25** ^1H, ^13CNMR spectrum and Mass spectrum of 5a.

**Fig. 26-28** ^1H, ^13CNMR spectrum and Mass spectrum of 1a.

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Experimental section

Materials and instrumentations

The synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-formyl-2-methyl-3-thienyl)cyclopentene and phosphonium salt were based on the literature method\textsuperscript{1,2}. All purchased chemicals and reagents were of high commercially available grade. Solvents were purified by standard procedures.

\( ^{1} \)H and \( ^{13} \)C NMR spectra were recorded on a Bruker AM-400 spectrometer in CDCl\(_{3}\) solutions using tetramethylsilane as the internal standard (chemical shifts in departs per million). High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions (ESI, 70eV). All UV-Vis absorption and fluorescence emission spectrum were recorded with a Varian Cray 500 and a Varian Cary Eclipse, respectively.

![Scheme S1 Synthetic routine of compounds 1a and 1b.](image)

Synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-(triphenylamine-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (4a)

To a stirring solution of 3 (1.4g, 4.5mmol) and phosphonium salt (3.0g, 5mmol) in DMF (25 mL), was added C\(_{2}\)H\(_{5}\)ONa (0.34g, 5mmol). The mixture was then refluxed for overnight. After cooling, water (50 mL) was added to the reaction mixture. The resulting mixture was extracted by dichloromethane (3 times) and the organic solvent
was removed in vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give the compound 4a (0.92g, 36.2%) as a yellow solid; 
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 - 7.23 (m, 5H), 7.09 (d, 4H, $J = 7.6$ Hz), 7.00-7.04 (m, 5H), 6.97 (d, 1H, $J = 16.0$ Hz), 6.69 (d, 1H, $J = 16.0$ Hz), 6.68 (s, 1H), 6.61 (s, 1H), 2.79 – 2.69 (m, 4H), 2.07 – 1.99 (m, 2H), 1.96 (s, 3H), 1.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.56, 147.11, 139.11, 135.90, 135.15, 135.12, 133.80, 133.70, 133.28, 131.34, 129.30, 127.01, 126.88, 126.82, 126.77, 125.00, 124.47, 123.64, 123.01, 120.43, 38.42 (s, 5H), 22.91 (s, 3H), 14.62 (s, 2H), 14.23 (s, 3H); HRMS (ESI) calcd for C$_{35}$H$_{31}$ClNS$_2$ (M+H) 564.1586, found 564.1585.

Synthesis of 1-(5-formyl-2-methyl-3-thienyl)-2-(5-(triphenylamine-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (5a)

Compound 4a (0.90g, 1.60 mmol) was dissolved in anhydrous THF (15 mL) and n-butyl lithium (1.5 mL of 1.6 M solution in hexane) was added dropwise under nitrogen at 0 ºC using a syringe. The mixture was stirred for 30 min at 0 ºC and then the reaction mixture was quenched with anhydrous dimethylformamide (0.62 mL).

The mixture was stirred for an addition hour at room temperature, before it was poured into H$_2$O. The mixture was extracted with ether. The organic layer was dried over MgSO$_4$, filtered, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether 1:1) to give the compound 5a (0.29g, 32.6%) as a yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.74 (s, 1H), 7.46 (s, 1H), 7.29-7.23 (m, 5H), 7.10 (d, 5H, $J = 7.7$ Hz), 7.02 (t, 4H, $J = 8.0$ Hz), 6.95 (d, 1H, $J = 15.9$ Hz), 6.69 (d, 1H, $J = 16.0$ Hz), 6.67 (s, 1H), 2.81 (t, 4H, $J = 7.5$ Hz), 2.12 – 2.04 (m, 2H), 2.08 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 182.62, 147.52, 147.20, 146.65, 139.80, 139.54, 138.11, 137.77, 136.37, 135.54, 133.74, 133.05, 131.14, 129.30, 127.08, 127.03, 126.53, 124.49, 123.56, 123.05, 120.17, 38.46, 38.33, 23.02, 15.51, 14.55; HRMS (ESI) calcd for C$_{35}$H$_{32}$N$_2$S$_2$ (M+H) 558.1925, found 558.1923.

Synthesis of 1-(5-dicyanoethenyl-2-methyl-3-thienyl)-2-(5-(triphenylamine-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (1a)

A mixture of malonitrile (24mg, 0.36mmol), 5a (100mg, 0.18mmol) and a catalytic amount of piperidine (2 drop of a stock solution of 1 drop of amine in 2 mL of absolute ethanol) in absolute ethanol (7 mL) was heated to reflux. After 17 h, the solution was cooled to room temperature and solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, CH$_2$Cl$_2$/ petroleum ether 1:1) to give the compound 1a (75mg, 68.9%) as a purple solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (s, 1H), 7.44 (s, 1H), 7.32-7.26 (m, 5H), 7.15-7.11 (m, 5H), 7.07-7.03 (m, 4H), 6.97 (d, 1H, $J = 16.0$ Hz), 6.72 (d, 1H, $J = 16.1$ Hz), 6.66 (s, 1H), 2.82 (dd, 4H, $J = 11.3, 5.9$ Hz), 2.16 (s, 3H), 2.13 – 2.07 (m, 2H), 1.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.76, 149.56, 147.51, 140.35, 139.88, 138.72, 137.57, 135.51, 133.74, 132.11, 131.71, 131.03, 129.33, 127.36, 127.09, 126.33, 124.54, 123.52, 123.12, 120.02, 114.32, 113.44, 38.50, 38.25, 22.94, 15.61, 14.59; HRMS (ESI) calcd for C$_{39}$H$_{32}$N$_3$S$_2$ (M+H) 606.2038, found 606.2032.
Synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-(dimethylphenylamine-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (4b)

To a stirring solution of 3 (0.85g, 2.64mmol) and phosphonium salt (1.38g, 2.90mmol) in DMF (20 mL), was added C2H5ONa (0.20g, 2.90mmol). The mixture was then refluxed for overnight. After cooling, water (40 mL) was added to the reaction mixture. The resulting mixture was extracted by dichloromethane (3 times) and the organic layer was dried over MgSO4, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether) to give the compound 4b (0.48g, 41.4%) as a yellow solid; 1H NMR (400 MHz, CDCl3) δ 7.32 (d, 2H, J = 8.7 Hz), 6.89 (d, 1H, J = 16.0 Hz), 6.70 (d, 2H, J = 2.3 Hz), 6.67 (d, 1H, J = 4.8 Hz), 6.64 (s, 1H), 6.61 (s, 1H), 2.97 (s, 6H), 2.78 – 2.70 (m, 4H), 2.05 – 2.00 (m, 2H), 1.94 (s, 3H), 1.87 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 149.93, 139.76, 135.74, 135.31, 135.20, 133.45, 133.28, 132.88, 127.59, 127.28, 126.86, 125.83, 125.56, 124.92, 117.90, 112.50, 40.51, 38.41, 22.91, 14.58, 14.27; HRMS (ESI) calcd for C25H22ClNS2 (M+H) 440.1273, found 440.1273.

Synthesis of 1-(5- formyl -2-methyl-3-thienyl)-2-(5-(dimethylphenylamine-1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (5b)

Compound 4b (0.43g, 1.0 mmol) was dissolved in anhydrous THF (9 mL) and n-butyl lithium (0.93 mL of 1.6 M solution in hexane) was added dropwise under nitrogen at 0 ºC using a syringe. The mixture was stirred for 30 min at 0 ºC and then the reaction mixture was quenched with anhydrous dimethylformamide (0.36 mL). The mixture was stirred for an addition hour at room temperature, before it was poured into H2O. The mixture was extracted with ether. The organic layer was dried over MgSO4, filtrated, and concentrated. The residue was purified by column chromatography (silica gel, CH2Cl2/ petroleum ether 1:1) to give the compound 5b (0.15g, 34.7%) as a yellow solid; 1H NMR (400 MHz, CDCl3) δ 9.74 (s, 1H), 7.47 (s, 1H), 7.32 (d, 2H, J = 8.8 Hz), 6.88 (d, 1H, J = 16.0 Hz), 6.70 (d, 2H, J = 3.9 Hz), 6.67 (d, 1H, J = 3.2 Hz), 6.63 (s, 1H), 2.97 (s, 6H), 2.80 (t, 4H, J = 7.5 Hz), 2.11 – 2.04 (m, 2H), 2.08 (s, 3H), 1.89 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 182.66, 150.00, 146.69, 140.19, 139.75, 138.21, 137.86, 136.52, 135.39, 132.81, 129.82, 127.91, 127.31, 125.48, 125.35, 117.63, 112.44, 40.46, 38.34, 23.09, 15.54, 14.51; HRMS (ESI) calcd for C26H26ClNS2 (M+H) 434.1612, found 434.1613.

Synthesis of 1-(5- dicyanoethyl -2-methyl-3-thienyl)-2-(5-(dimethylphenylamine -1-yl)vinyl-2-methyl-3-thienyl)cyclopentene (1b)

A mixture of malonitrile (27mg, 0.40mmol), 5b (87mg, 0.2mmol) and a catalytic amount of piperidine (2 drop of a stock solution of 1 drop of amine in 2 mL of absolute ethanol) in absolute ethanol (7 mL) was heated to reflux. After 17 h, the solution was cooled to room temperature and solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, CH2Cl2/ petroleum ether 1:1) to give the compound 1b (70mg, 72.9%) as a purple solid; 1H NMR (400 MHz, CDCl3) δ 7.66 (s, 1H), 7.42 (s, 1H), 7.32 (d, 2H, J = 8.7 Hz), 6.87 (d, 1H, J = 16.0 Hz, 6.70 (d, 2H, J = 3.9 Hz), 6.67 (d, 1H, J = 3.2 Hz), 6.63 (s, 1H), 2.97 (s, 6H), 2.80 (t, 4H, J = 7.5 Hz), 2.11 – 2.04 (m, 2H), 2.08 (s, 3H), 1.89 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 182.66, 150.00, 146.69, 140.19, 139.75, 138.21, 137.86, 136.52, 135.39, 132.81, 129.82, 127.91, 127.31, 125.48, 125.35, 117.63, 112.44, 40.46, 38.34, 23.09, 15.54, 14.51; HRMS (ESI) calcd for C26H26ClNS2 (M+H) 434.1612, found 434.1613.
Hz), 6.70 (d, 2H, J = 6.4 Hz), 6.67 (s, 1H), 6.60 (s, 1H), 2.98 (s, 6H), 2.80 (dd, 4H, J = 12.7, 5.4 Hz), 2.14 (s, 3H), 2.11 – 2.06 (m, 2H), 1.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.75, 150.07, 149.59, 140.52, 140.37, 138.80, 137.72, 135.12, 132.80, 131.85, 131.66, 128.18, 127.33, 117.46, 114.32, 113.43, 40.43, 38.50, 38.24, 22.91, 15.59, 14.50; HRMS (ESI) calcd for C$_{29}$H$_{28}$N$_3$S$_2$(M+H) 482.1725, found 482.1727.

**Preparation of the PMMA films**

To prepare the PMMA thin film sensors, 1a, 1b, 2a or 2b (2mg) was dissolved in dichloromethane and added PMMA (50mg) in the solution standing until the PMMA was resolved. The solution was poured onto a clean glass surface and evaporated to dryness, and a homogeneous, nonfluorescence polymer sensor film was obtained. This thin film was covered with a shadow mask including the CN- fingerprint. A solution containing tetrabutylammonium cyanide in dichloromethane (1 mM) was sprayed onto the film, and the solvent was evaporated in air.

**Crystallography**

Single crystals of 1a and 1b suitable for X-ray analyses were obtained by slow evaporation of their corresponding solutions at room temperature. Crystal data for 1a: C$_{39}$H$_{31}$N$_3$S$_2$, $M_w$=605.79 g·mol$^{-1}$, 0.32×0.22×0.15 mm$^3$, Monoclinic, $P2(1)/c$, $a = 19.681(2)$ Å, $b = 8.3397(9)$ Å, $c = 21.489(2)$ Å, $\beta = 110.841(2)^\circ$, $V = 3296.3(6)$ Å$^3$, $F(000) = 1272$, $\rho_{calcd} = 1.221$ Mg/m$^3$, $\mu(MoK\alpha) = 0.193$ mm$^{-1}$, $T = 293(2)$ K, 19525 data were measured on a Bruker SMART Apex diffractometer, of which 6488 were unique ($R_{int} = 0.0318$); 399 parameters were refined against $F_2^2$ (all data), final $wR_2 = 0.1393$, $S = 1.026$, $R_1(I>2\sigma(I)) = 0.0542$, largest final difference peak/hole = +0.314/−0.154 eÅ$^{-3}$. Structure solution by direct methods and full-matrix least-squares refinement against $F^2$ (all data) using SHELXTL.

Crystal data for 1b: C$_{29}$H$_{27}$N$_3$S$_2$, $M_w$=481.66 g·mol$^{-1}$, 0.30×0.20×0.05 mm$^3$, Monoclinic, $P2(1)/c$, $a = 24.443(4)$ Å, $b = 8.3483(15)$ Å, $c = 12.521(2)$ Å, $\beta = 99.817(3)^\circ$, $V = 2517.6(8)$ Å$^3$, $F(000) = 1016$, $\rho_{calcd} = 1.271$ Mg/m$^3$, $\mu(MoK\alpha) = 0.234$ mm$^{-1}$, $T = 133(2)$ K, 15534 data were measured on a Bruker SMART Apex diffractometer, of which 4538 were unique ($R_{int} = 0.0550$); 311 parameters were refined against $F_2^2$ (all data), final $wR_2 = 0.1568$, $S = 1.038$, $R_1(I>2\sigma(I)) = 0.0637$, largest final difference peak/hole = +1.438/−1.089 eÅ$^{-3}$. Structure solution by direct methods and full-matrix least-squares refinement against $F^2$ (all data) using SHELXTL.
**Fig. S1** UV-vis spectral changes of the 1b (2.0 × 10⁻⁵ M) upon 365nm light irradiation in CH₂Cl₂ at 25 °C (0-90 min).

**Fig. S2** Changes in graphs of color upon alternating irradiation with UV/vis light in CH₂Cl₂ for 1a and 2a.

**Fig. S3** Changes in graphs of color upon alternating irradiation with UV/vis light in CH₂Cl₂ for 1b and 2b.
**Fig. S4** Crystal structure of 1b.

**Fig. S5** UV–vis spectral changes of 1a (2.0×10⁻⁵ M) upon the addition of 1.375 equiv. of cyanide anion in CH₃CN at 25°C.

**Fig. S6** UV–vis spectral changes of 1b (2.0×10⁻⁵ M) upon the addition of 6.0 equiv. of cyanide anion in CH₃CN at 25°C.
**Fig. S7** Fluorescence spectral changes of 1b (2.0×10^{-5} M) upon the addition of 6.0 equiv. of cyanide anion in CH$_3$CN at 25°C, λ$_{ex}$=370 nm.

**Fig. S8** Changes in graphs of fluorescence upon addition 1.5 equiv. and 6.0equiv. of CN$^-$ in CH$_3$CN for 1a and 1b when excited 365 nm.
Fig. S9 Time-dependent changes in the fluorescence intensity at $\lambda = 458$ nm observed from the reaction between 1.0 equiv. 1a ($2.0 \times 10^{-5}$ M) and different equiv. cyanide anion. (a) 1.375 equiv. cyanide anion. (b) 0.125 equiv. cyanide anion.
**Fig. S10** Time-dependent changes in the fluorescence intensity at \( \lambda = 458 \) nm observed from the reaction between 1.0 equiv. 1\( \text{b} \) (2.0\( \times \)10\(^{-5} \) M) and different equiv. cyanide anion. (a) 6.0 equiv. cyanide anion. (b) 1.0 equiv. cyanide anion.
**Fig. S11** (a) Plot of fluorescence intensity changes of 1a (2.0×10^{-5} M) against varied concentrations of CN\(^-\) from 0.25×10^{-5} M to 2.5×10^{-5} M (\(\lambda_{ex}\)=370 nm, slit: 5nm/5nm, PMT Volts: 500.). R=0.993, k=2.6×10^7 au/M, (b) Plot of fluorescence intensity changes of 1b (2.0×10^{-5} M) against varied concentrations of CN\(^-\) from 2.0×10^{-5} M to 1.1×10^{-4} M (\(\lambda_{ex}\)=370 nm, slit: 5nm/5nm, PMT Volts: 550.). R=0.992, k=8.3×10^6 au/M. The Standard Deviation of 1a and 1b were 0.15 and 0.12 by fluorescence responded (7-time of consecutive scanning on the Varian Cray 500 spectrophotometer.). Therefore, the detection limits of 1a and 1b were calculated by the formula (3\(\sigma/k\)) and gave the results as 1.73×10^{-8} M and 4.36×10^{-8} M.
**Fig. S12** Relative fluorescence intensities of the free 1b (2.0 × 10⁻⁵ M) upon the addition of 6.0 equiv. of various anions in CH₃CN. Each spectrum was obtained after addition of various analytes at 25 °C for 2 min.

**Fig. S13** ¹H NMR spectral changes seen upon the addition of cyanide anion (as its tetrabutylammonium salts) to 1b in CDCl₃ at 25 °C.
**Fig. S14** UV-vis spectral changes of the 1b-CN (2.0 × 10^{-5} M) upon 254 nm light irradiation in CH₃CN (0-15 min) at 25 °C.

**Fig. S15** Fluorescence spectral changes of the 1b-CN (2.0 × 10^{-5} M) upon 254 nm light irradiation in CH₃CN (0-15 min) at 25 °C.
**Fig. S16** Changes in graphs of color upon addition CN⁻ in CH₃CN for 2a.

**Fig. S17** UV–vis spectral changes of 2b (2.0x10⁻⁵ M) upon the addition of 3.0 equiv. of cyanide anion in CH₃CN at 25 °C.
Fig. S18 Changes in graphs of color upon addition CN− in CH3CN for 2b.

Fig. S19 Image patterns of word “CN” with a PMMA on a quartz plate: (a) Fluorescence images of 1b/PMMA in the presence of cyanide. (b) Color images of 2b/PMMA in the presence of cyanide.
Fig. S20 $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 4a.

Fig. S21 $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 4a.

Fig. S22 HRMS (ESI) spectrum of compound 4a.
**Fig. S23** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 5a.

**Fig. S24** $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 5a.
Fig. S25 HRMS (ESI) spectrum of compound 5a.

Fig. S26 $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 1a.
Fig. S27 $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 1a.

Fig. S28 HRMS (ESI) spectrum of compound 1a.
Fig. S29 $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 4b.

Fig. S30 $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 4b.
**Fig. S31** HRMS (ESI) spectrum of compound 4b.

**Fig. S32** $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 5b.
Fig. S33 $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 5b.

Fig. S34 HRMS (ESI) spectrum of compound 5b.
Fig. S35 $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 1b.

Fig. S36 $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 1b.
Fig. S37 HRMS (ESI) spectrum of compound 1b.

References