

Electronic Supplementary Information (ESI)

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

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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 ($\lambda_{\text{ex}} = 370$ nm, slit: 5nm/5nm, PMT Volts: 500.). $R = 0.993$, $k = 2.6 \times 10^7$ 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 ($\lambda_{\text{ex}} = 370$ nm, slit: 5nm/5nm, PMT Volts: 550.). $R = 0.992$, $k = 8.3 \times 10^6$ au/M

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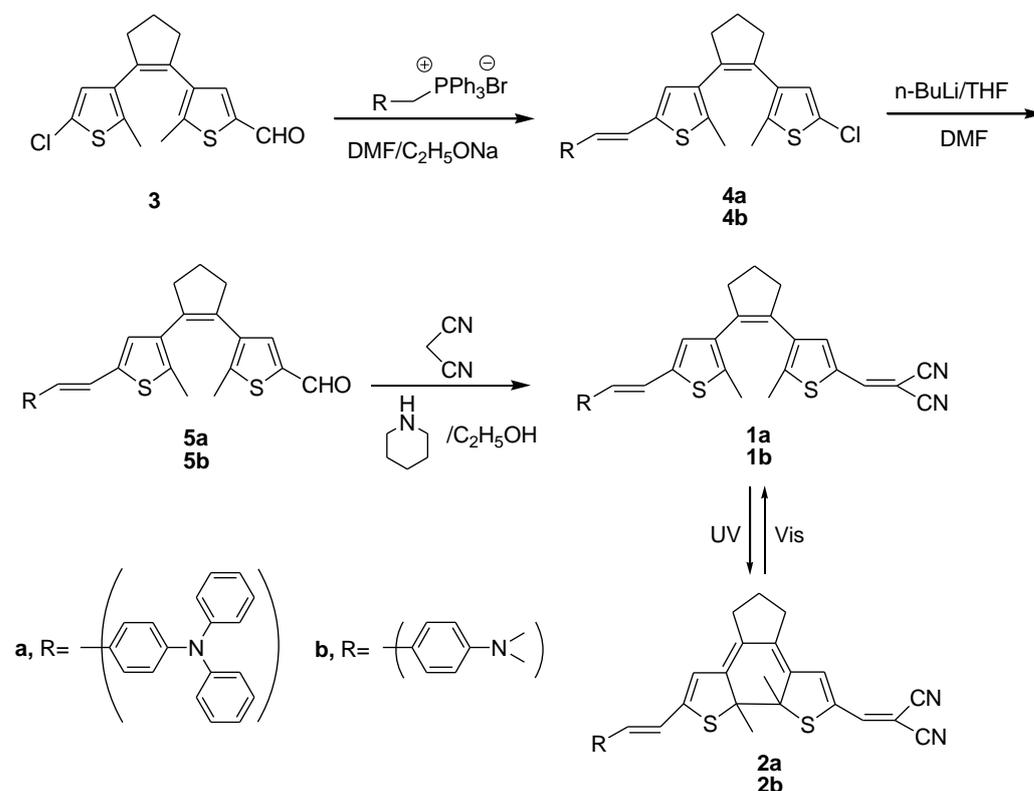
Fig. 35-37 ^1H , ^{13}C NMR spectrum and Mass spectrum of **1b**.

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 method¹⁻². All purchased chemicals and reagents were of high commercially available grade. Solvents were purified by standard procedures.

¹H and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer in CDCl₃ solutions using tetramethylsilane as the internal standard (chemical shifts in parts 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**.

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 C₂H₅ONa (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; ^1H 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 $\text{C}_{35}\text{H}_{31}\text{ClNS}_2$ (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-thienylcyclopentene (**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 °C using a syringe. The mixture was stirred for 30 min at 0 °C 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_2O . The mixture was extracted with ether. The organic layer was dried over MgSO_4 , filtrated, and concentrated. The residue was purified by column chromatography (silica gel, CH_2Cl_2 / petroleum ether 1:1) to give the compound **5a** (0.29g, 32.6%) as a yellow solid; ^1H 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 $\text{C}_{36}\text{H}_{32}\text{NOS}_2$ (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-thienylcyclopentene (**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_2Cl_2 / petroleum ether 1:1) to give the compound **1a** (75mg, 68.9%) as a purple solid; ^1H 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, 135.31, 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 $\text{C}_{39}\text{H}_{32}\text{N}_3\text{S}_2$ (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 solvent was removed in vacuum and 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 C₂₅H₂₇ClNS₂ (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 °C using a syringe. The mixture was stirred for 30 min at 0 °C and then the reaction mixture was quenched with anhydrous dimethylformamide (0.36 mL). The mixture was stirred for an additional 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 C₂₆H₂₈NOS₂ (M+H) 434.1612, found 434.1613

Synthesis of 1-(5-dicyanoethenyl-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, $J = 6.4$ 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, 125.23, 117.46, 114.32, 113.43, 112.43, 40.43, 38.50, 38.24, 22.91, 15.59, 14.50; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{N}_3\text{S}_2$ (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**: $\text{C}_{39}\text{H}_{31}\text{N}_3\text{S}_2$, $M_w=605.79$ g·mol⁻¹, $0.32 \times 0.22 \times 0.15$ mm³, *Monoclinic*, $P2(1)/c$, $a = 19.681(2)$, $b = 8.3397(9)$, $c = 21.489(2)$ Å, $\beta = 110.841(2)^\circ$, $V=3296.3(6)$ Å³, $F(000)=1272$, $\rho_{\text{calcd}}=1.221$ Mg/m³, $\mu(\text{MoK}\alpha)=0.193$ mm⁻¹, $T=293(2)$ K, 19525 data were measured on a Bruker SMART Apex diffractometer, of which 6488 were unique ($R_{\text{int}}=0.0318$); 399 parameters were refined against F_o^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**: $\text{C}_{29}\text{H}_{27}\text{N}_3\text{S}_2$, $M_w=481.66$ g·mol⁻¹, $0.30 \times 0.20 \times 0.05$ mm³, *Monoclinic*, $P2(1)/c$, $a = 24.443(4)$, $b = 8.3483(15)$, $c = 12.521(2)$ Å, $\beta = 99.817(3)^\circ$, $V=2517.6(8)$ Å³, $F(000)=1016$, $\rho_{\text{calcd}}=1.271$ Mg/m³, $\mu(\text{MoK}\alpha)=0.234$ mm⁻¹, $T=133(2)$ K, 15534 data were measured on a Bruker SMART Apex diffractometer, of which 4538 were unique ($R_{\text{int}}=0.0550$); 311 parameters were refined against F_o^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.

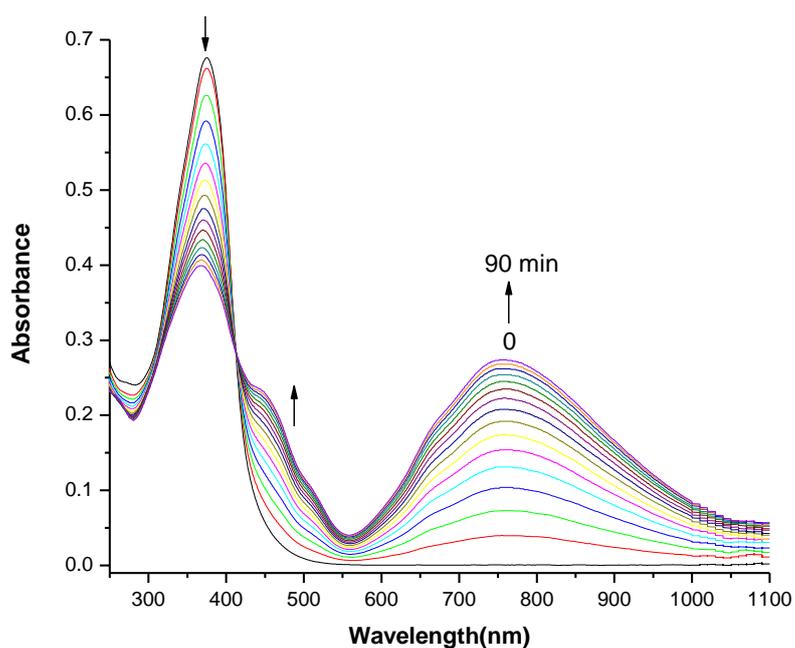


Fig. S1 UV-vis spectral changes of the **1b** (2.0×10^{-5} M) upon 365nm light irradiation in CH_2Cl_2 at 25 °C (0-90 min).

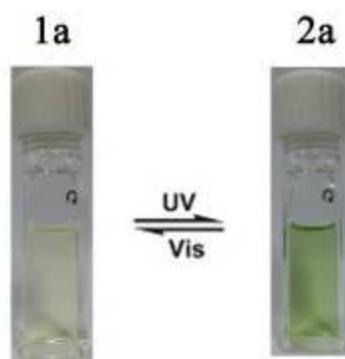


Fig. S2 Changes in graphs of color upon alternating irradiation with UV/vis light in CH_2Cl_2 for **1a** and **2a**.

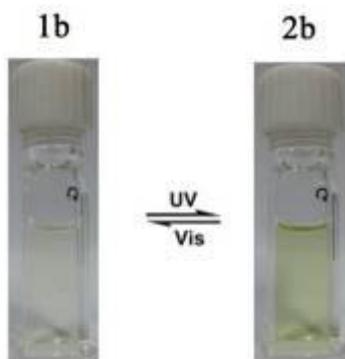


Fig. S3 Changes in graphs of color upon alternating irradiation with UV/vis light in CH_2Cl_2 for **1b** and **2b**.

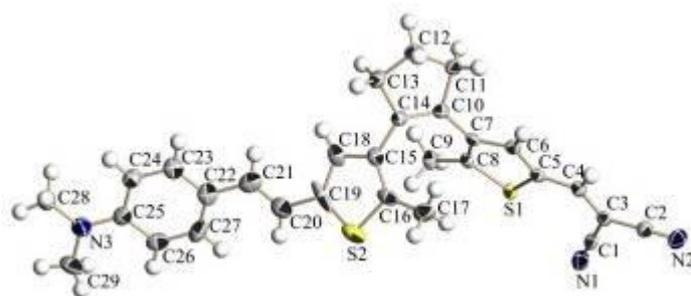


Fig. S4 Crystal structure of **1b**.

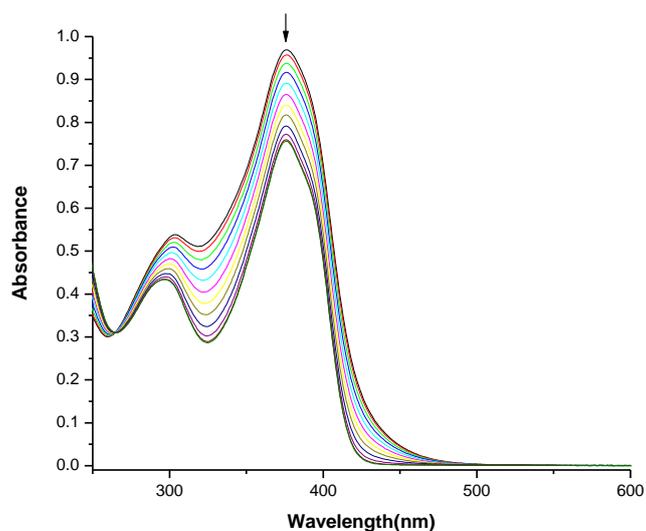


Fig. S5 UV-vis spectral changes of **1a** (2.0×10^{-5} M) upon the addition of 1.375 equiv. of cyanide anion in CH_3CN at 25°C .

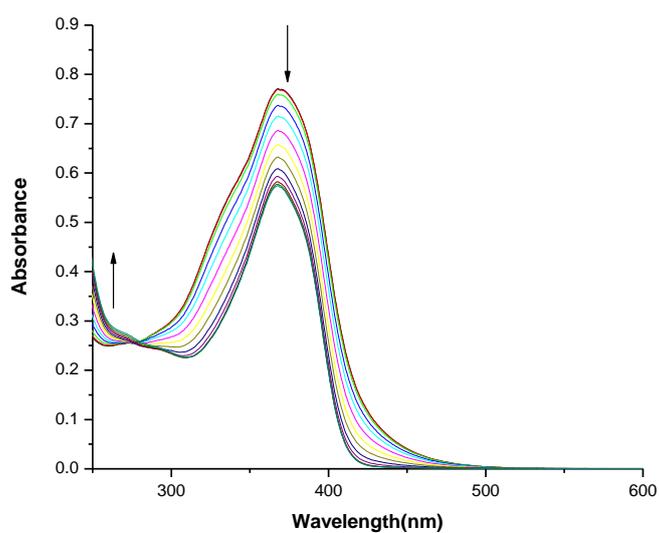


Fig. S6 UV-vis spectral changes of **1b** (2.0×10^{-5} M) upon the addition of 6.0 equiv. of cyanide anion in CH_3CN at 25°C .

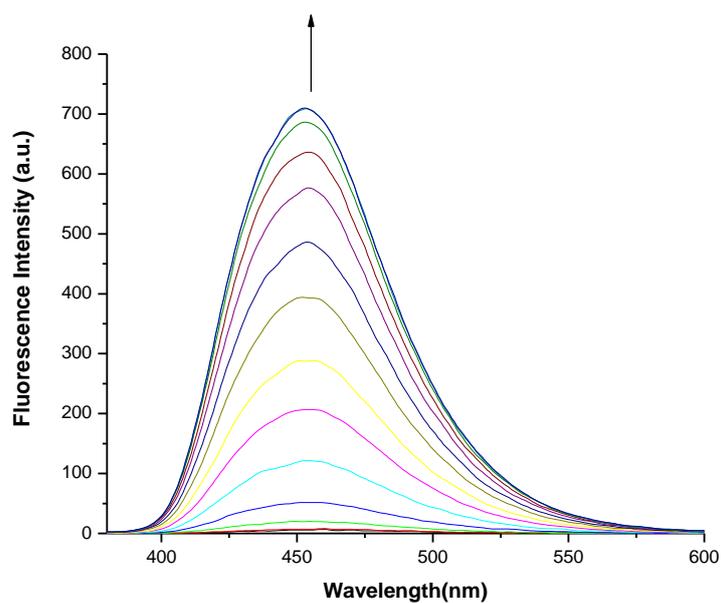


Fig. S7 Fluorescence spectral changes of **1b** (2.0×10^{-5} M) upon the addition of 6.0 equiv. of cyanide anion in CH_3CN at 25°C , $\lambda_{\text{ex}}=370$ nm.

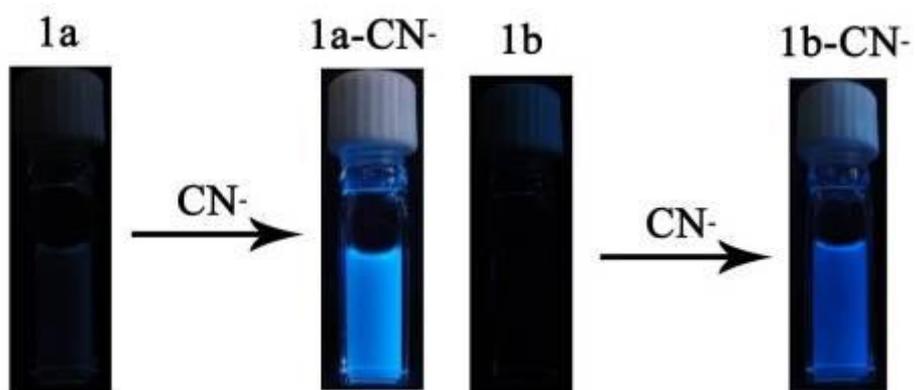


Fig. S8 Changes in graphs of fluorescence upon addition 1.5 equiv. and 6.0equiv. of CN^- in CH_3CN for **1a** and **1b** when excited 365 nm.

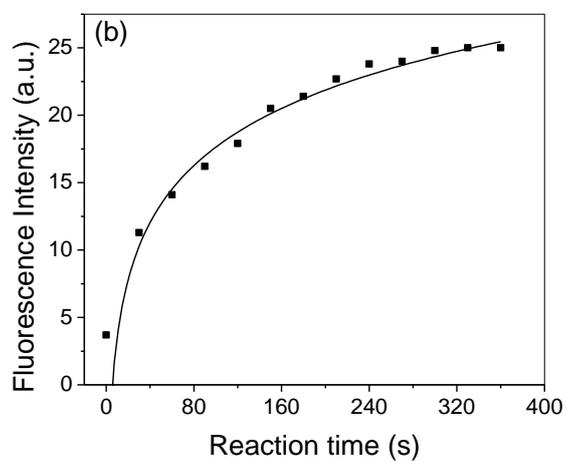
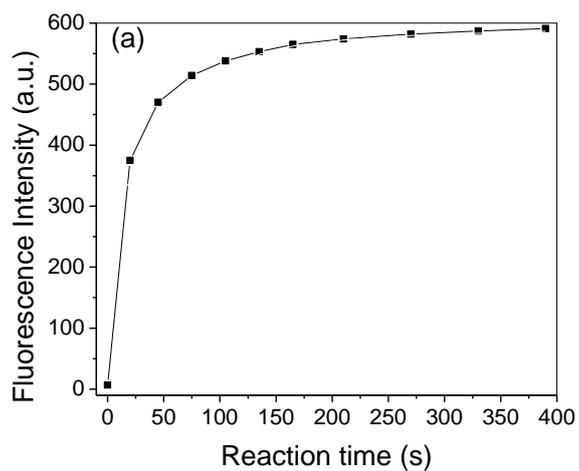


Fig. S9 Time-dependent changes in the fluorescence intensity at $\lambda = 458$ nm observed from the reaction between 1.0 equiv. **1a** (2.0×10^{-5} M) and different equiv. cyanide anion. (a) 1.375 equiv. cyanide anion. (b) 0.125 equiv. cyanide anion.

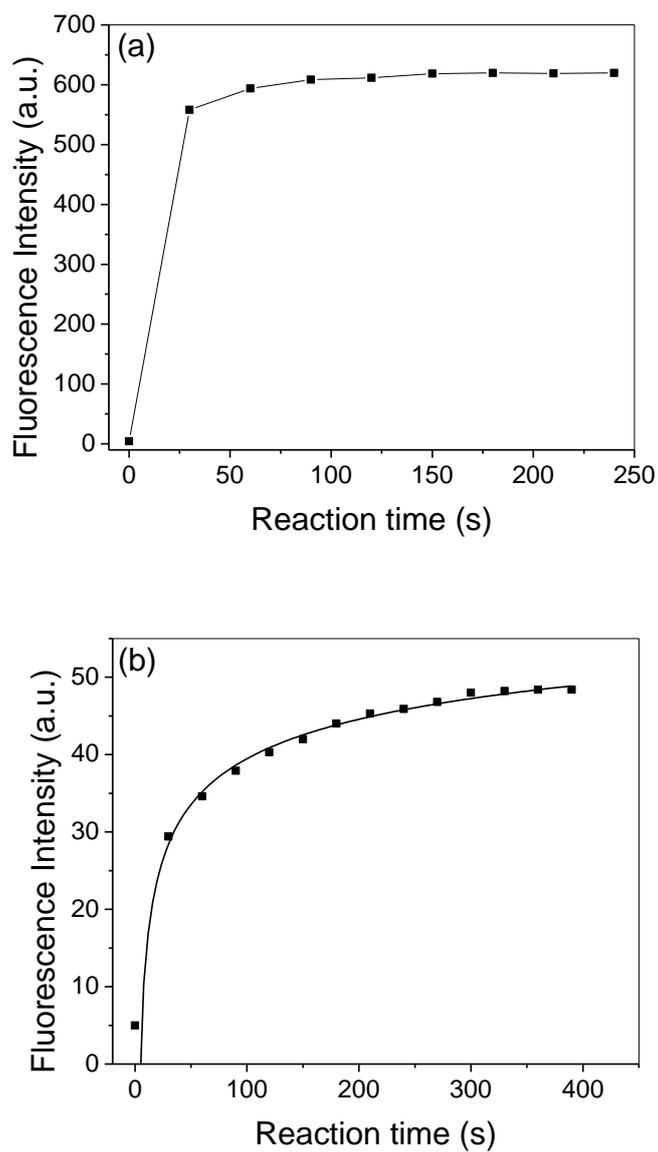


Fig. S10 Time-dependent changes in the fluorescence intensity at $\lambda = 458$ nm observed from the reaction between 1.0 equiv. **1b** (2.0×10^{-5} M) and different equiv. cyanide anion. (a) 6.0 equiv. cyanide anion. (b) 1.0 equiv. cyanide anion.

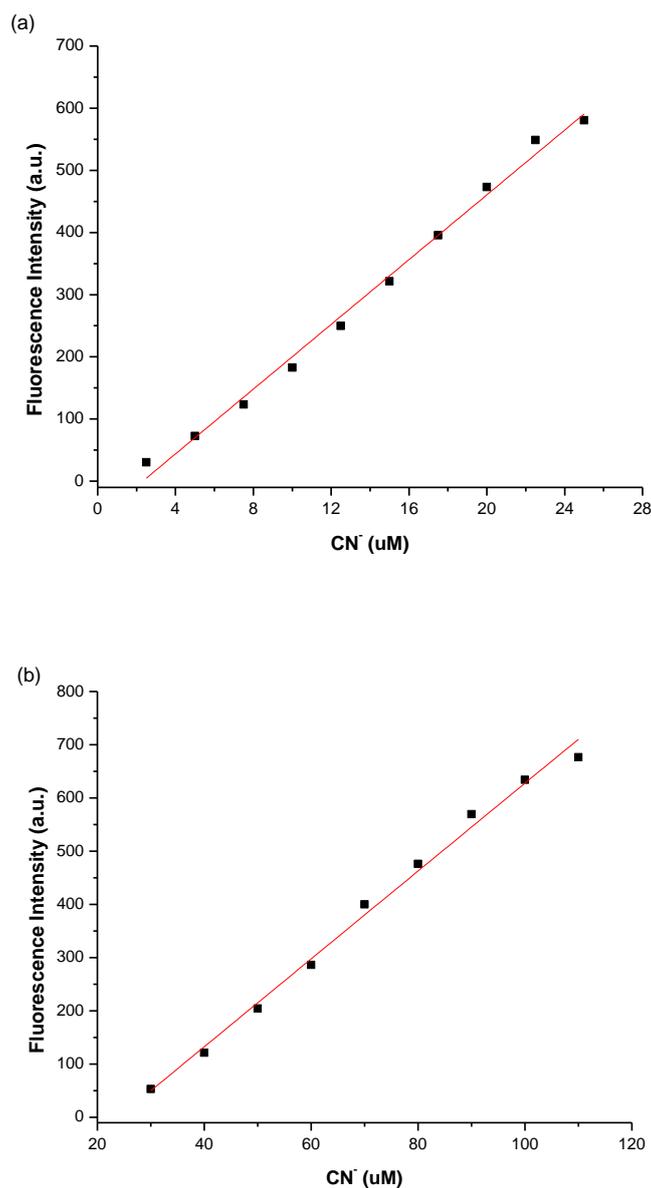


Fig. S11 (a) Plot of fluorescence intensity changes of **1a** (2.0 × 10⁻⁵ M) against varied concentrations of CN⁻ from 0.25 × 10⁻⁵ M to 2.5 × 10⁻⁵ M (λ_{ex} =370 nm, slit: 5nm/5nm, PMT Volts: 500.). R=0.993, k=2.6 × 10⁷ au/M, (b) Plot of fluorescence intensity changes of **1b** (2.0 × 10⁻⁵ M) against varied concentrations of CN⁻ from 2.0 × 10⁻⁵ M to 1.1 × 10⁻⁴ M (λ_{ex} =370 nm, slit: 5nm/5nm, PMT Volts: 550.). R=0.992, k=8.3 × 10⁶ 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 σ /k) and gave the results as 1.73 × 10⁻⁸ M and 4.36 × 10⁻⁸ M.

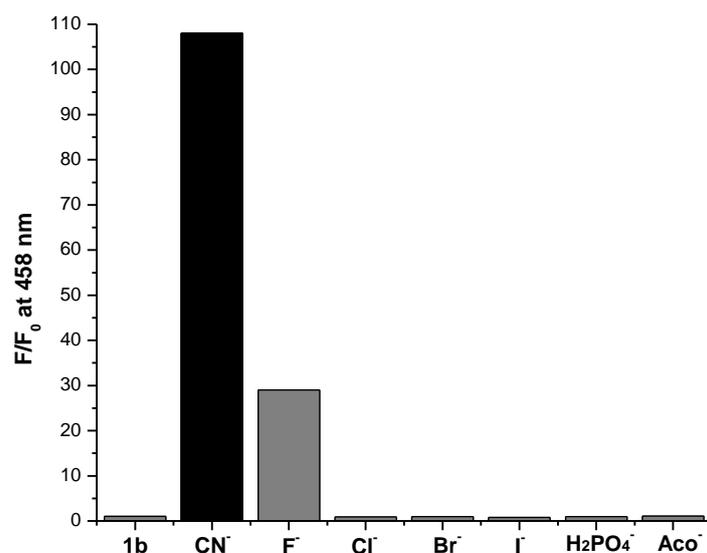


Fig. S12 Relative fluorescence intensities of the free **1b** (2.0×10^{-5} M) upon the addition of 6.0 equiv. of various anions in CH_3CN . Each spectrum was obtained after addition of various analytes at 25°C for 2 min.

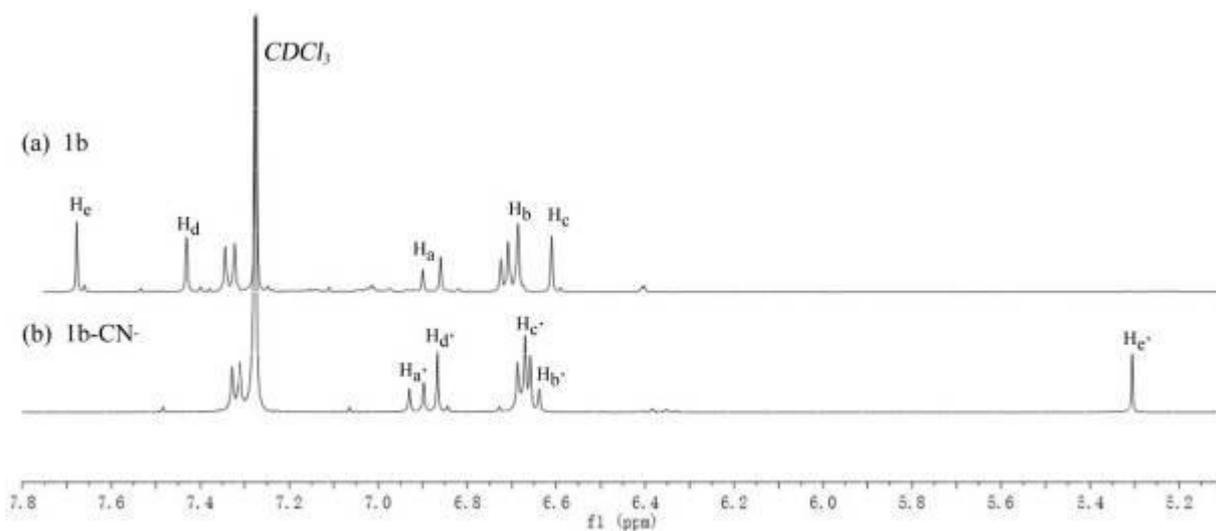


Fig. S13 ^1H NMR spectral changes seen upon the addition of cyanide anion (as its tetrabutylammonium salts) to **1b** in CDCl_3 at 25°C .

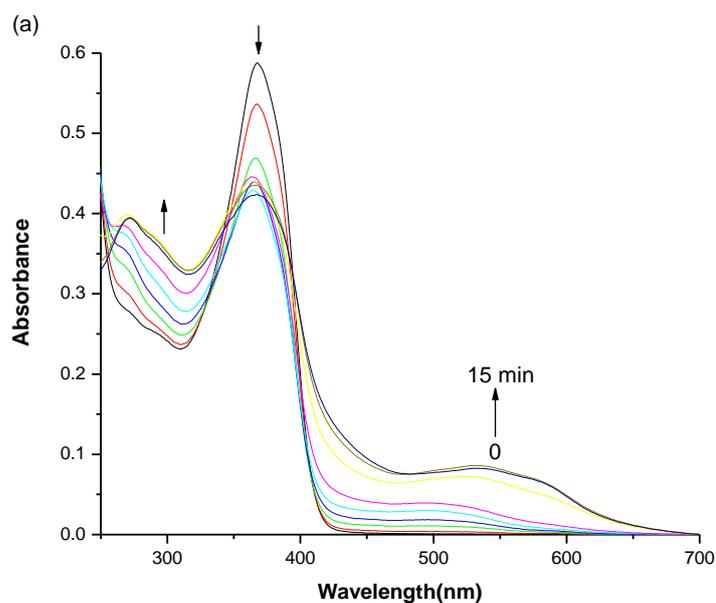


Fig. S14 UV-vis spectral changes of the $1b-CN^-$ ($2.0 \times 10^{-5} M$) upon 254 nm light irradiation in CH_3CN (0-15 min) at 25 °C.

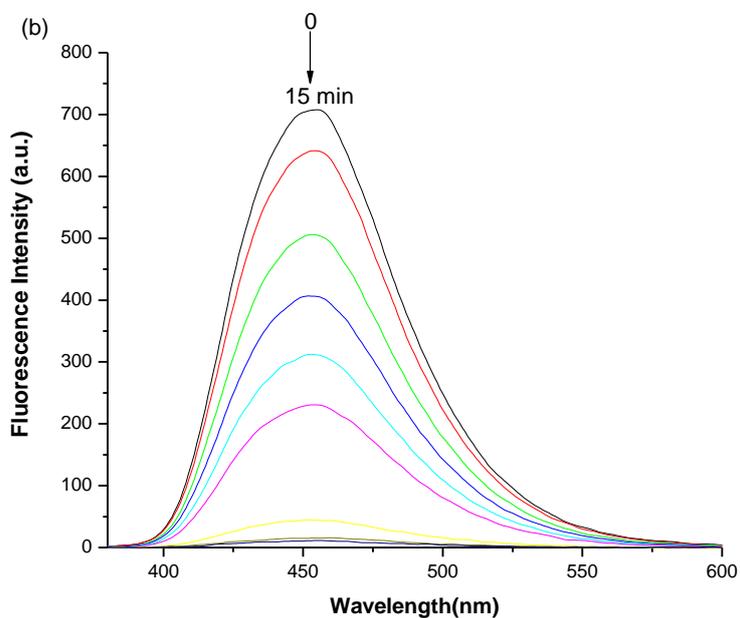


Fig. S15 Fluorescence spectral changes of the $1b-CN^-$ ($2.0 \times 10^{-5} M$) upon 254 nm light irradiation in CH_3CN (0-15 min) at 25 °C.

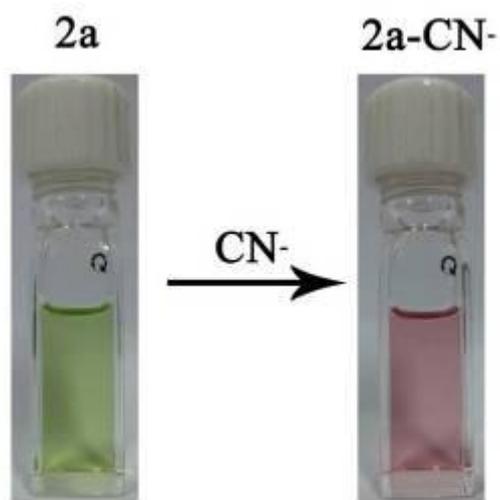


Fig. S16 Changes in graphs of color upon addition CN^- in CH_3CN for **2a**.

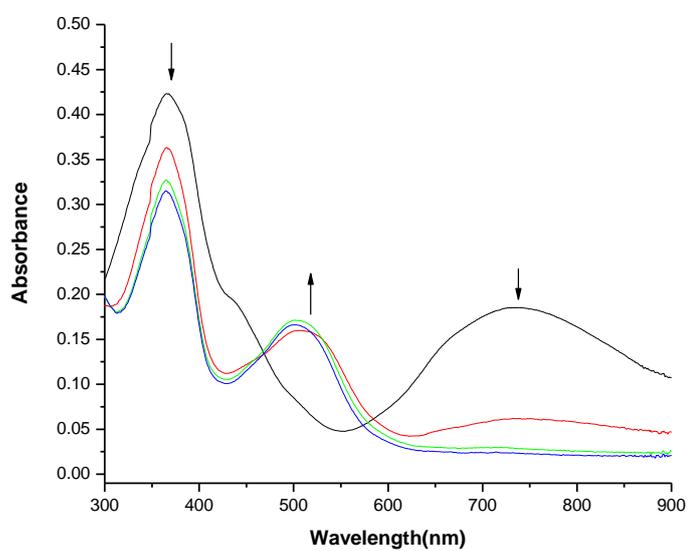


Fig. S17 UV-vis spectral changes of **2b** ($2.0 \times 10^{-5} \text{ M}$) upon the addition of 3.0 equiv. of cyanide anion in CH_3CN at 25°C .



Fig. S18 Changes in graphs of color upon addition CN^- in CH_3CN for **2b**.

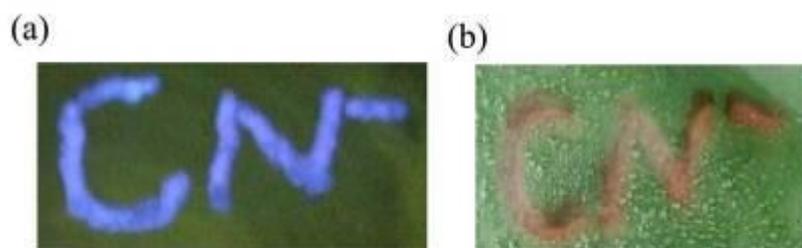


Fig. S19 Image patterns of word “CN⁻” with a PMMA on a quartz plate: (a) Fluorescence images of **1b**/PMMA in the presence of cyanide. (b) Color images of **2b**/PMMA in the presence of cyanide.

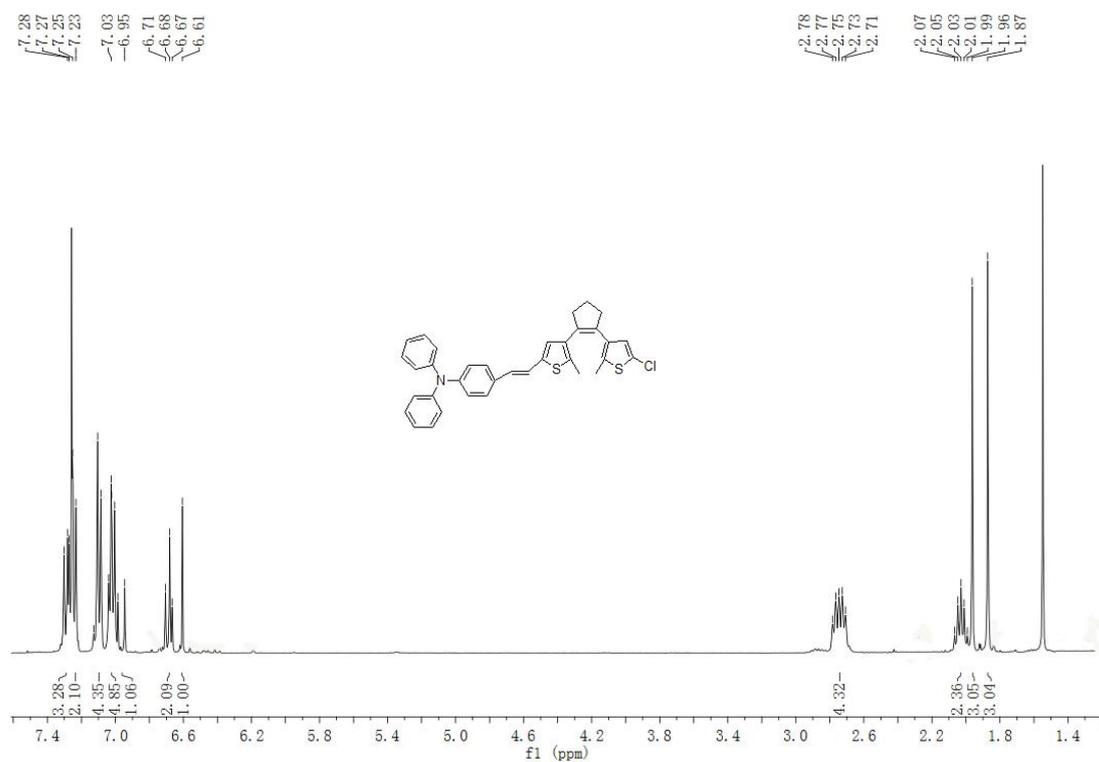


Fig. S20 ^1H NMR (CDCl_3 , 400 MHz) spectrum of **4a**.

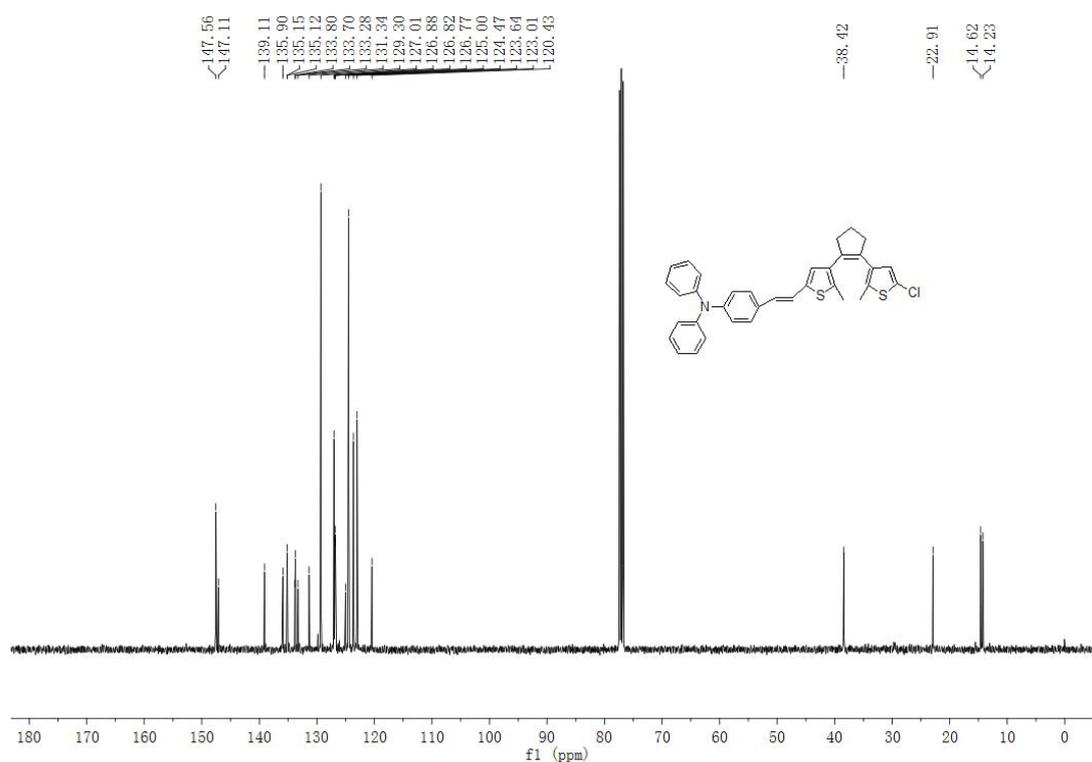


Fig. S21 ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **4a**.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

207 formula(e) evaluated with 16 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-50 H: 0-60 N: 0-4 S: 0-3 Cl: 0-1

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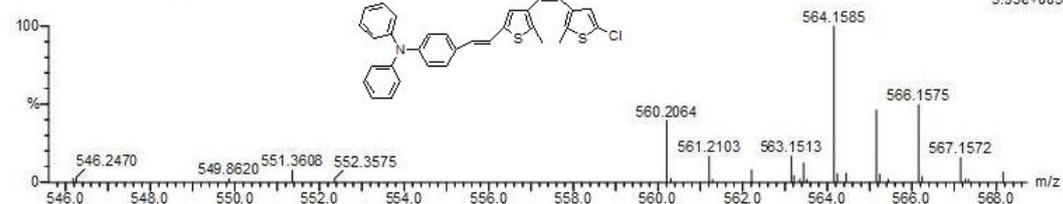
13-May-2012

19:24:20

1: TOF MS ES+

3.93e+003

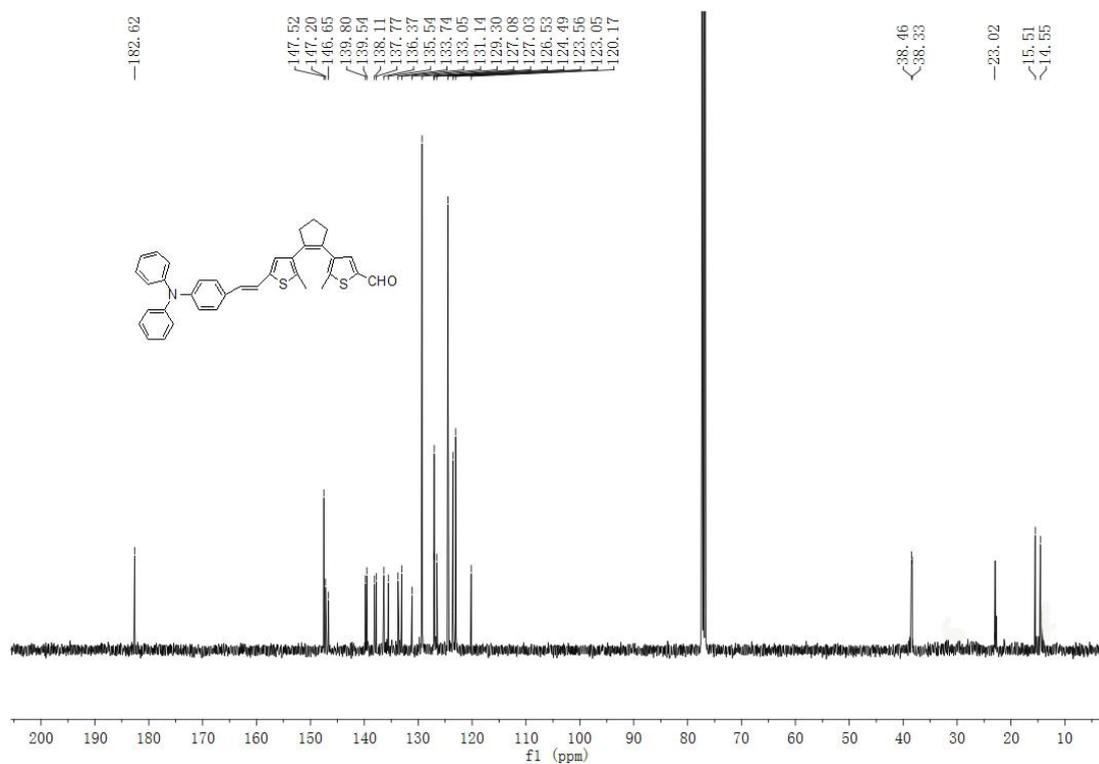
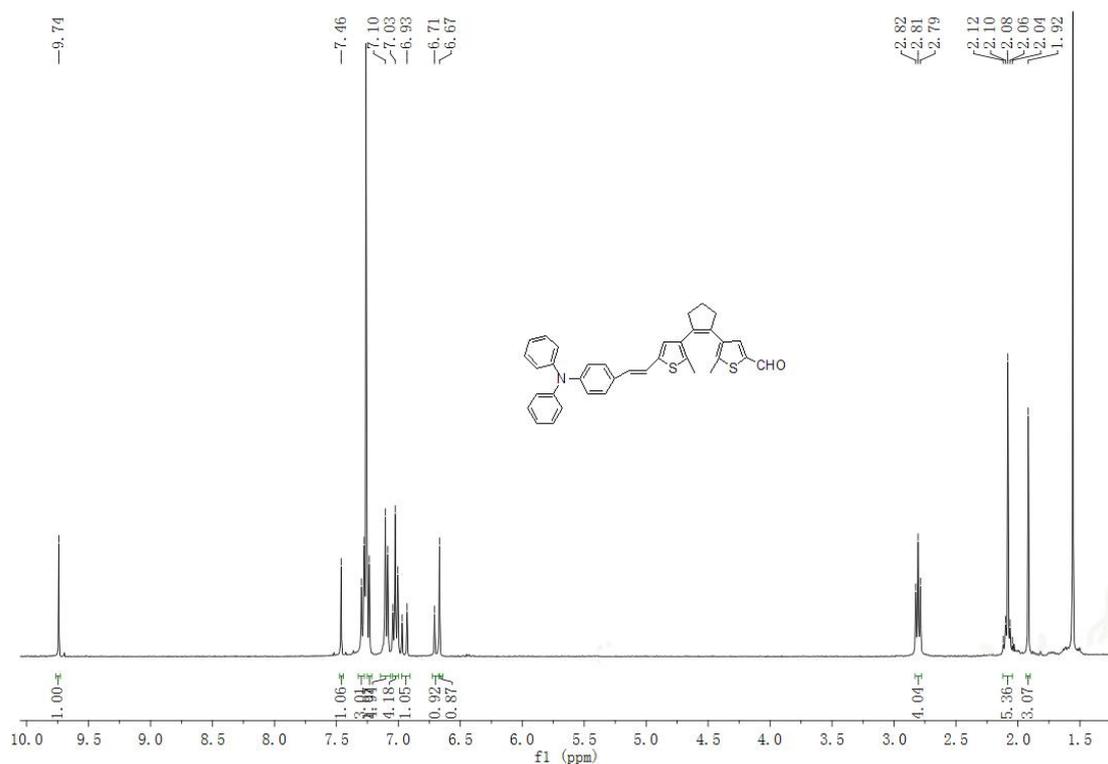
TH-JY-21 41 (1.358) Cm (35.44)



Minimum: -1.5
 Maximum: 50.0 50.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|----------|------------|------|------|------|-------|--------------|-----------------|
| 564.1585 | 564.1586 | -0.1 | -0.2 | 20.5 | 52.9 | 0.0 | C35 H31 N S2 Cl |

Fig. S22 HRMS (ESI) spectrum of compound **4a**.



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

921 formula(e) evaluated with 74 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-50 H: 0-60 N: 0-4 O: 0-8 S: 0-3

H-TIAN

TH-JY-22 17 (0.619) Cm (14:23)

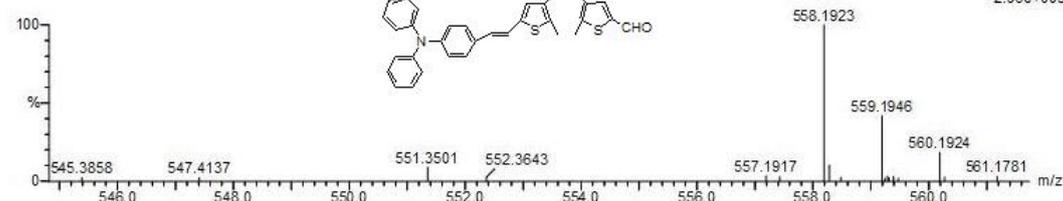
ECUST institute of Fine Chem

13-May-2012

19:35:30

1: TOF MS ES+

2.96e+003



| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|----------|------------|------|------|------|-------|--------------|--|
| 558.1923 | 558.1925 | -0.2 | -0.4 | 21.5 | 69.5 | 0.0 | C ₃₆ H ₃₂ N O S ₂ |

Fig. S25 HRMS (ESI) spectrum of compound 5a.

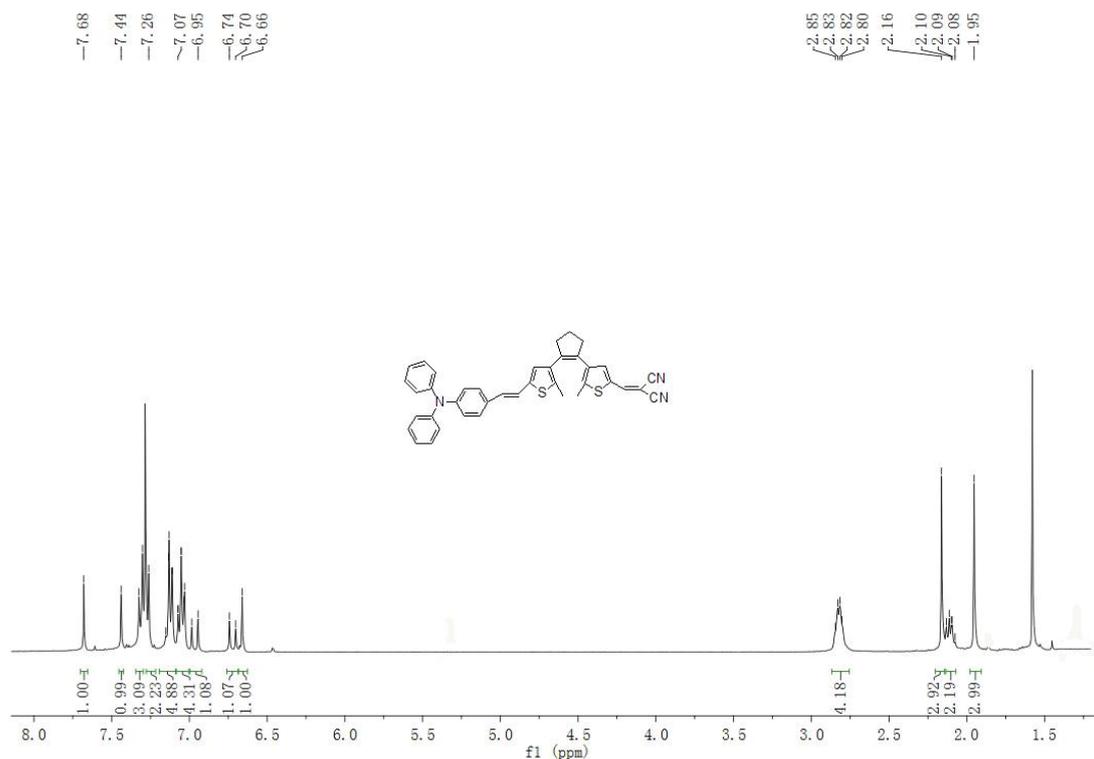


Fig. S26 ¹H NMR (CDCl₃, 400 MHz) spectrum of 1a.

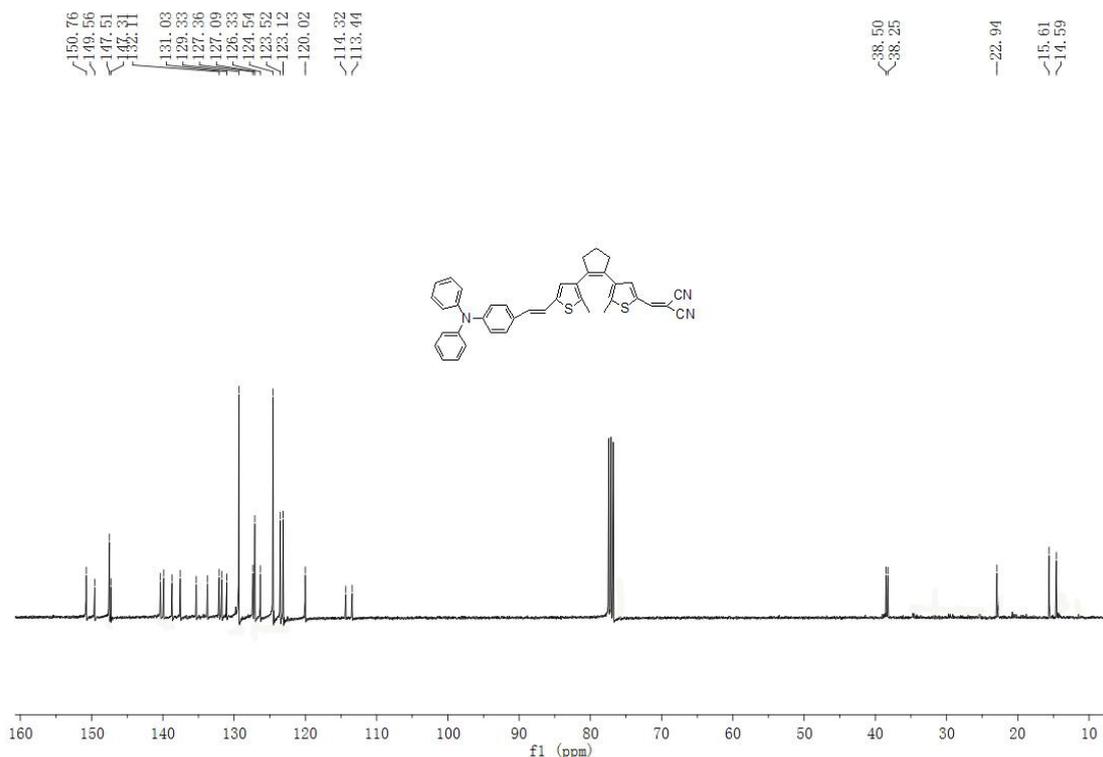


Fig. S27 ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **1a**.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

90 formula(e) evaluated with 9 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-40 H: 0-60 N: 0-5 S: 0-4

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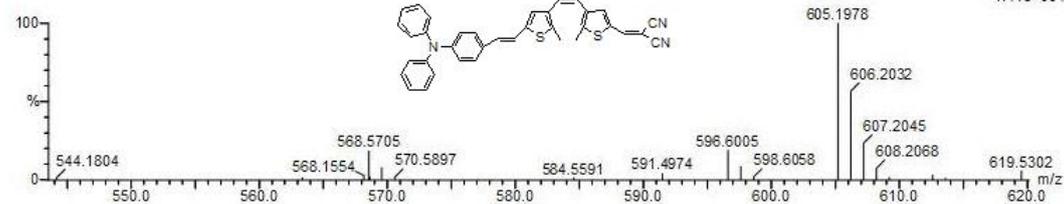
19-Apr-2012

18:16:30

1: TOF MS ES+

1.41e+004

TH-JY-12 20 (0.692) Cm (10:24)



Minimum:

Maximum: 50.0 50.0 -1.5 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|----------|------------|------|------|------|-------|--------------|---------------|
| 606.2032 | 606.2038 | -0.6 | -1.0 | 25.5 | 13.2 | 0.0 | C39 H32 N3 S2 |

Fig. S28 HRMS (ESI) spectrum of compound **1a**.

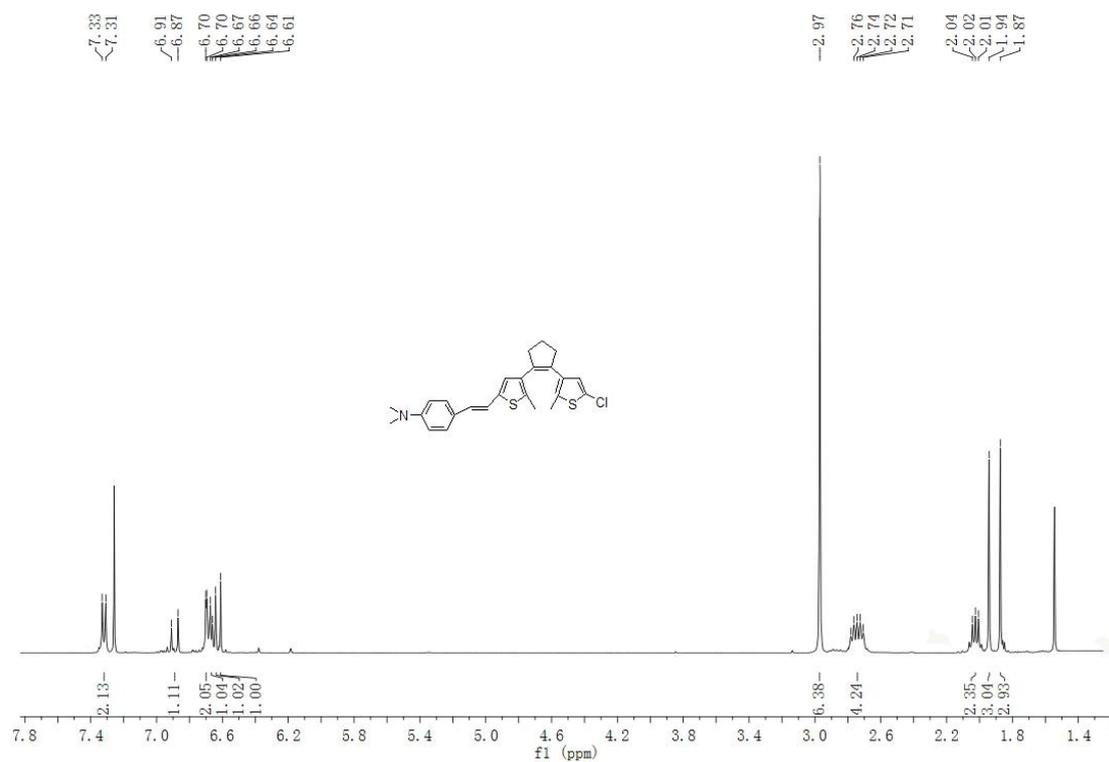


Fig. S29 ^1H NMR (CDCl_3 , 400 MHz) spectrum of **4b**.

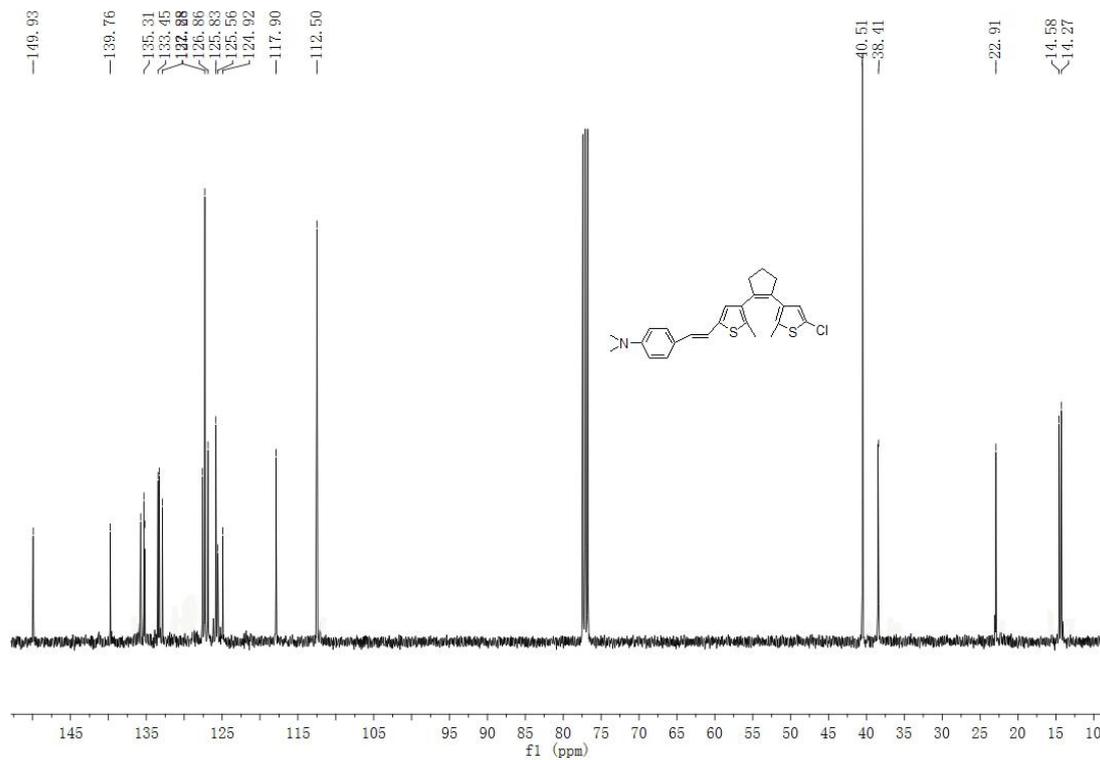


Fig. S30 ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **4b**.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

199 formula(e) evaluated with 16 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-50 H: 0-60 N: 0-4 S: 0-3 Cl: 0-1

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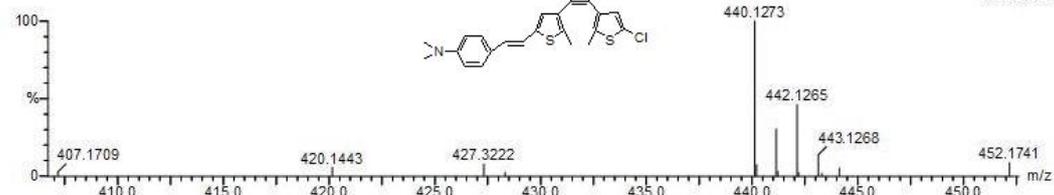
13-May-2012

19:31:13

1: TOF MS ES+

1.50e+004

TH-JY-11 25 (0.865) Cm (21:31)



Minimum: -1.5
Maximum: 50.0 50.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|----------|------------|-----|-----|------|-------|--------------|-----------------|
| 440.1273 | 440.1273 | 0.0 | 0.0 | 12.5 | 34.7 | 0.0 | C25 H27 N S2 Cl |

Fig. S31 HRMS (ESI) spectrum of compound **4b**.

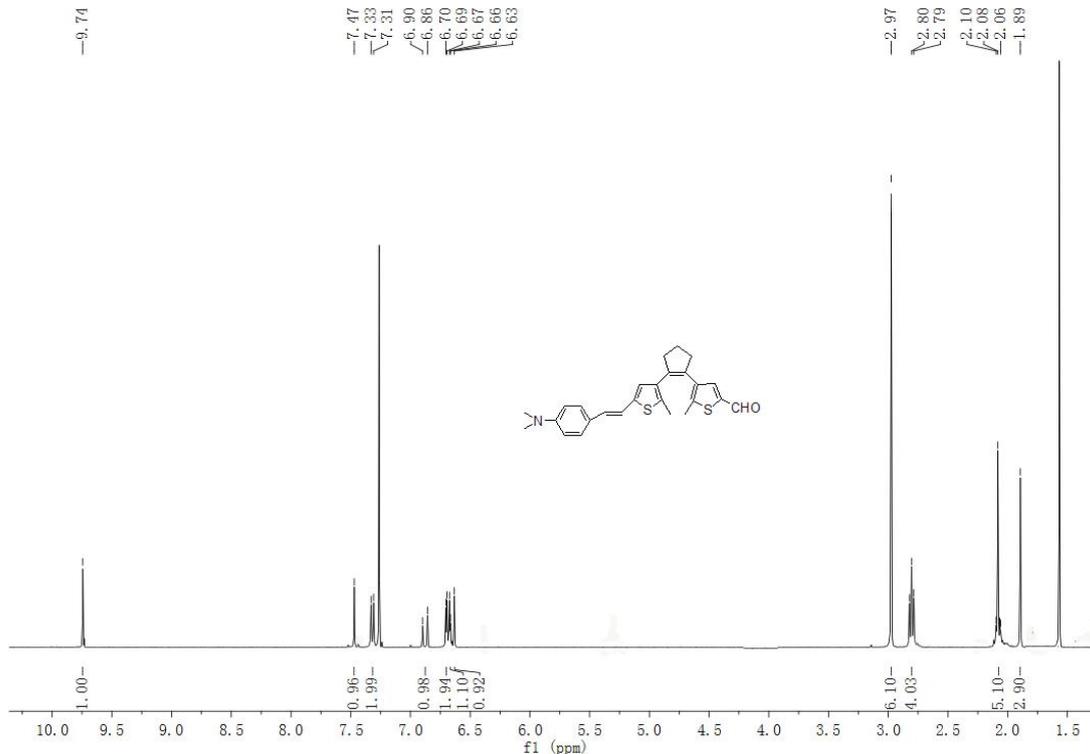


Fig. S32 ¹H NMR (CDCl₃, 400 MHz) spectrum of **5b**.

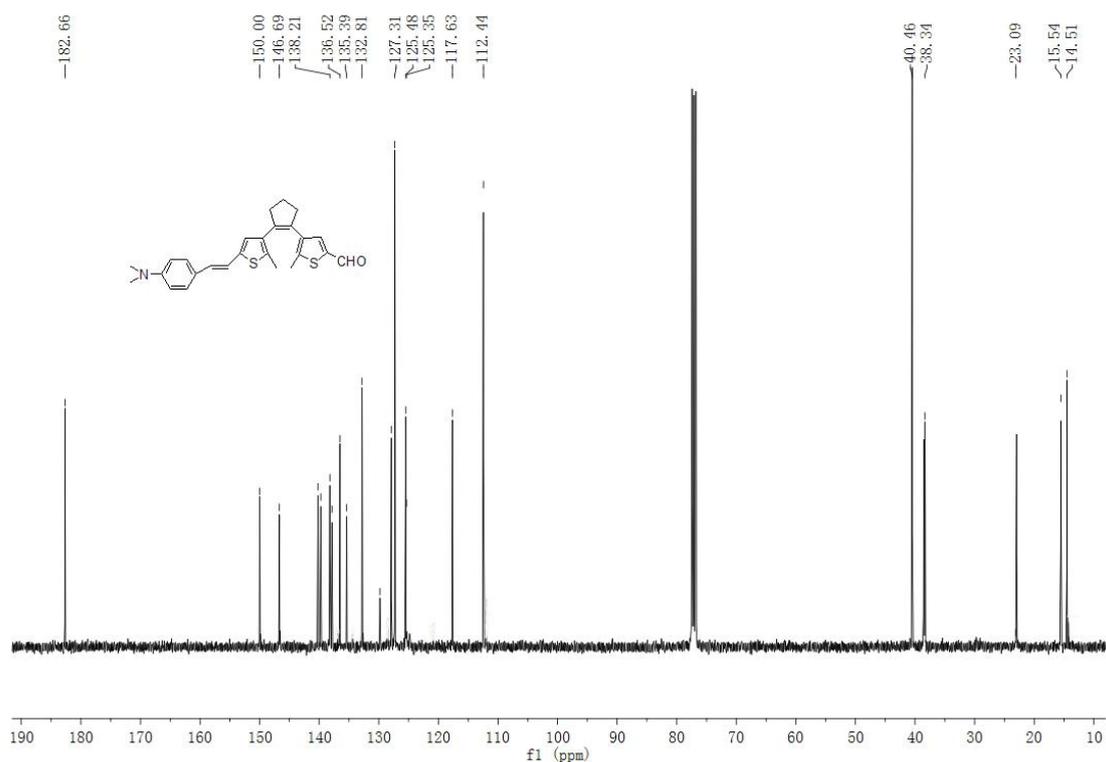


Fig. S33 ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **5b**.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

811 formula(e) evaluated with 71 results within limits (up to 1 closest results for each mass)

Elements Used:

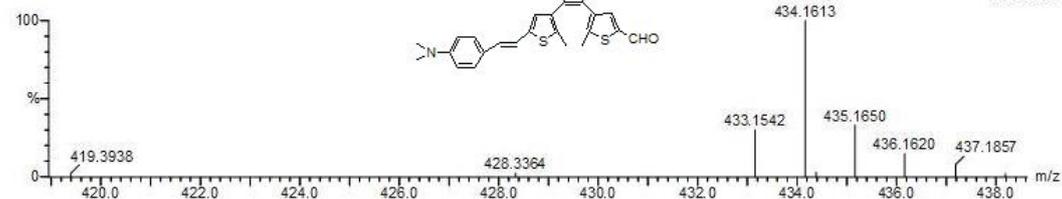
C: 0-50 H: 0-60 N: 0-4 O: 0-8 S: 0-3

H-TIAN

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13-May-2012
 19:13:50
 1: TOF MS ES+
 2.04e+004

TH-JY-12 43 (1.404) Cm (38:48)



Minimum: -1.5
 Maximum: 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|----------|------------|-----|-----|------|-------|--------------|--|
| 434.1613 | 434.1612 | 0.1 | 0.2 | 13.5 | 22.9 | 0.0 | C ₂₆ H ₂₈ N O S ₂ |

Fig. S34 HRMS (ESI) spectrum of compound **5b**.

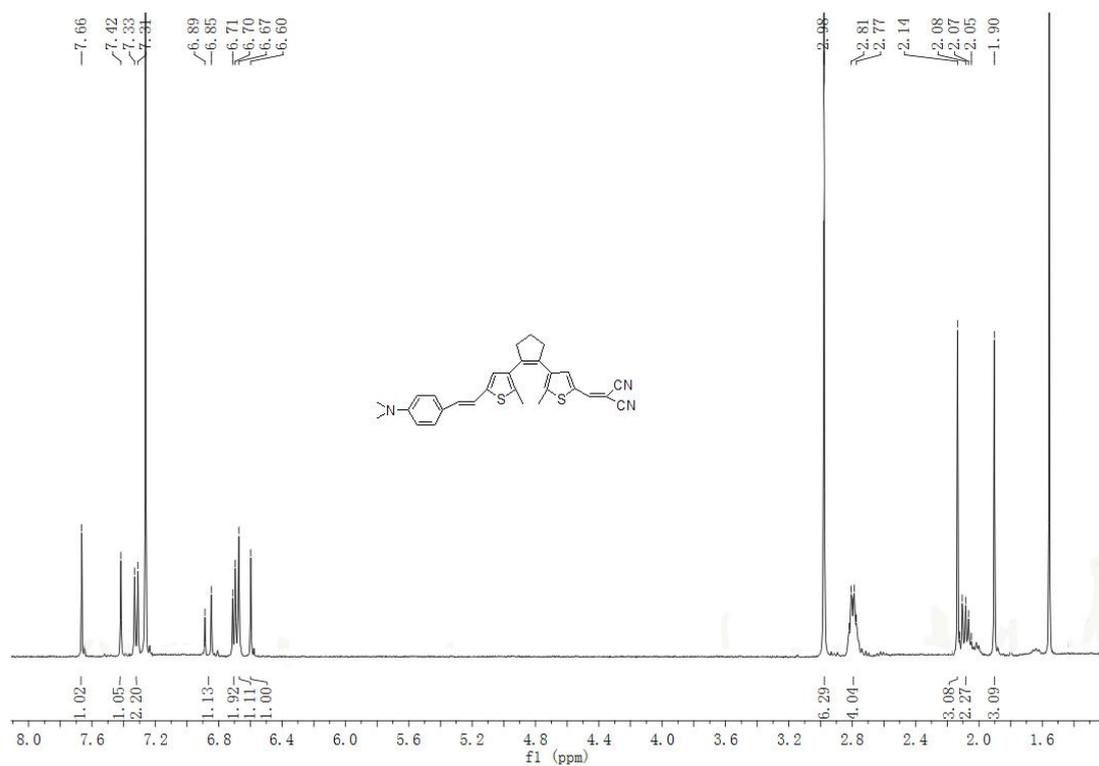


Fig. S35 ^1H NMR (CDCl_3 , 400 MHz) spectrum of **1b**.

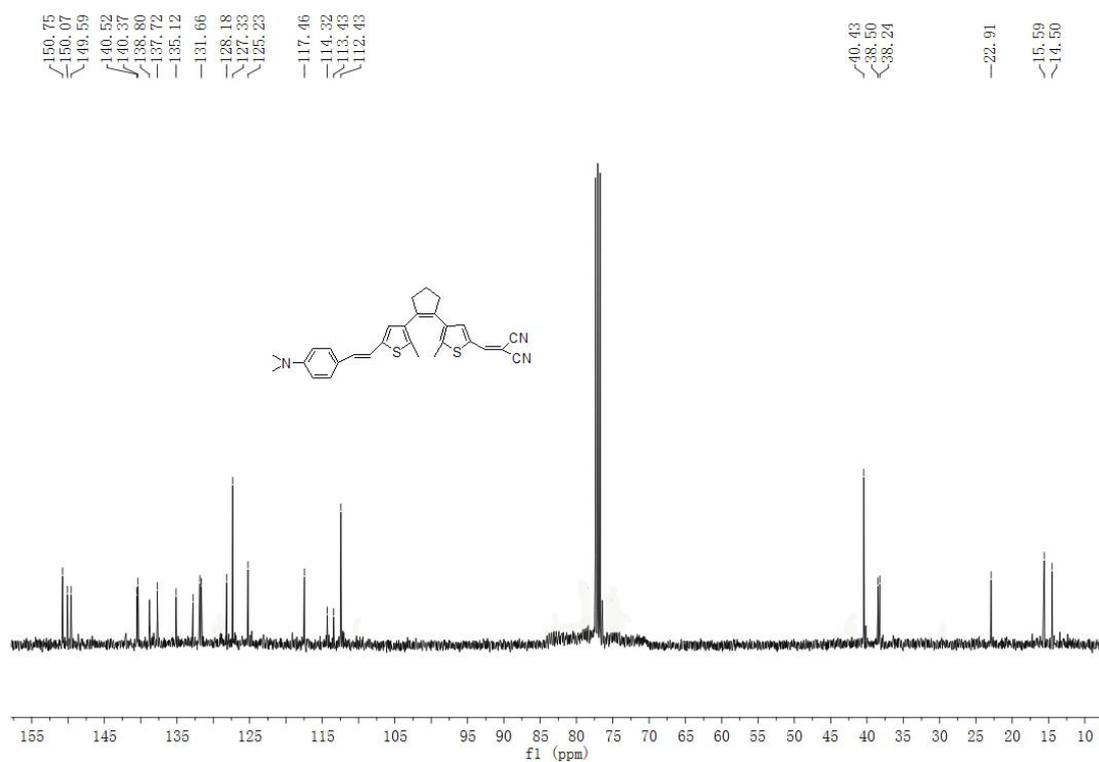


Fig. S36 ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **1b**.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

152 formula(e) evaluated with 15 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-40 H: 0-60 N: 0-5 S: 0-4

H-TIAN

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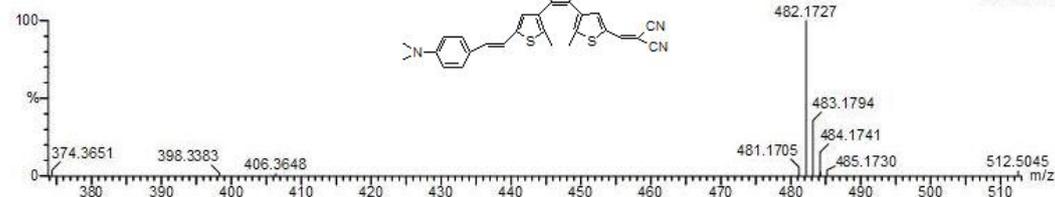
19-Apr-2012

18:20:27

1: TOF MS ES+

3.31e+003

TH-JY-11 94 (2.979) Cm (93:94)



Minimum: -1.5
Maximum: 50.0 50.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|----------|------------|-----|-----|------|-------|--------------|---------------|
| 482.1727 | 482.1725 | 0.2 | 0.4 | 17.5 | 10.5 | 0.0 | C29 H28 N3 S2 |

Fig. S37 HRMS (ESI) spectrum of compound **1b**.

References

1. Q. Zou, J. Y. Jin, B. Xu, L. Ding and H. Tian, *Tetrahedron*, 2011, **67**, 915-921.
2. J. Heo, J. -W. O, H. -I. Ahn, S. -B. Lee, S. -E. Cho, M. -R. Kim, J. -K. Lee and N. Kim, *Synthetic Metals*, 2010, **160**, 2143-2150.