

## Electronic Supplementary Information

### Photochromism of dithienylethene single crystals having anthracene substituents

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## 1. General.

$^1\text{H}$  NMR spectra were recorded on a JEOL GSX400 spectrometer. Mass spectra were taken with a Shimadzu GCMS-QP5050 gas chromatography-mass spectrometer.

Absorption and fluorescence spectra in solution were measured with a Hitachi U-4100 absorption spectrophotometer and a Hitachi F-2500 fluorescence spectrophotometer, respectively. Photoirradiation was carried out using an USHIO 500W xenon lamp as the light source. Monochromatic light was obtained by passing the light through a JOBIN YVON H-10 UV monochromator.

The cyclization quantum yields were determined using furyl flugide in *n*-hexane as a reference.<sup>S1</sup> The cycloreversion quantum yields were measured using 1,2-bis(2-ethyl-5phenyl-3-thienyl)perfluorocyclopentene in *n*-hexane as a reference.<sup>S2</sup>

The fluorescence quantum yields were determined using 9,10-diphenylanthracene in cyclohexane as a reference.<sup>S3</sup>

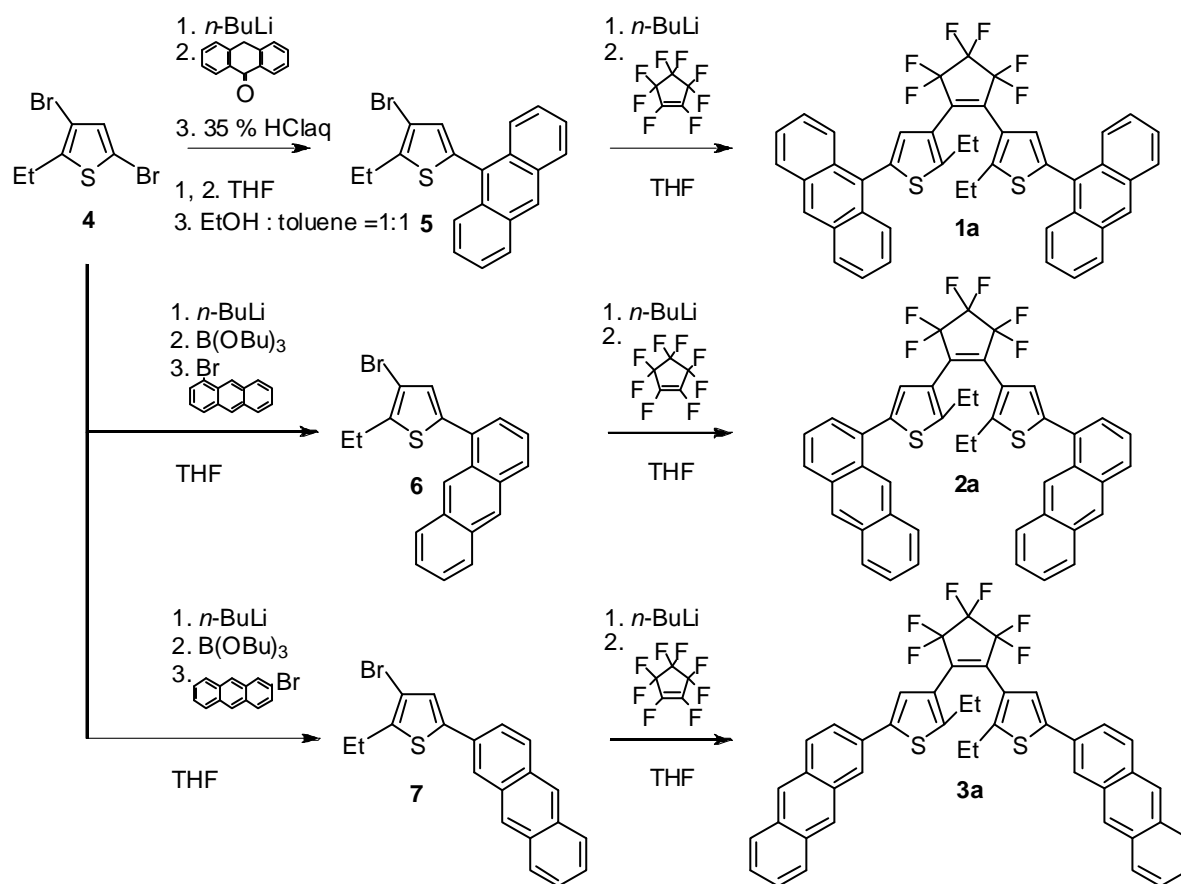
Absorption spectra in the single-crystalline phase were measured using a Leica DMLP polarizing microscope connected with a Hamamatsu PMA-12 photodetector. Polarizer and analyzer were set parallel to each other.

X-ray diffraction data were measured using a Bruker SMART APEX CCD diffractometer (55 kV, 30 mA) with Mo  $K\alpha$  radiation. The crystals were cooled by a low temperature controller (Japan Thermal Engineering Co., Ltd. TC-190CP-CS-K). Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effect, and decay. The cell constants were determined by the global refinement. The structure was solved by direct methods using SHELXS-86<sup>S4</sup> and refined by full least-squares on  $F^2$  using SHELXL-97.<sup>S5</sup> The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

DFT calculations were performed with B3LYP functional and the 6-31G\* basis set using Gaussian 03 program.<sup>S6</sup> Molecular structures determined by X-ray crystallographic analysis were used as initial structures and only disordered structures were geometrically optimized. Molecular orbital are shown using GaussView 4.1.<sup>S7</sup>

## 2. Materials.

Synthetic procedures are shown in Scheme S1.



Scheme S1

### 2-(9-Anthryl)-3-bromo-5-ethylthiophene (5)

To a solution of 2,4-dibromo-5-ethylthiophene (**4**) (10 g, 38 mmol) in dry THF (110 cm<sup>3</sup>) was added *n*-BuLi (1.6 mol dm<sup>-3</sup>, 25 cm<sup>3</sup>, 39 mmol) under a N<sub>2</sub> atmosphere at -78 °C, and then the mixture was stirred for 1 h. A solution of anthrone (11 g, 57 mmol) in toluene (300 cm<sup>3</sup>) was added to the reaction mixture and stirred for 1 h. Subsequently, the reaction vessel was allowed warm to room temperature, and the solution was poured into a mixture of ice and water and was extracted with diethyl ether. The organic layer was washed several times with brine, and concentrated. The residue was dissolved in ethanol (80 cm<sup>3</sup>) and toluene (80 cm<sup>3</sup>) and then hydrochloric acid (35 %, 30 cm<sup>3</sup>) was added. After refluxed for 3 h, the mixture was extracted with diethyl ether, washed several times with brine, dried over MgSO<sub>4</sub>, and concentrated. The residue was purified by silica gel column chromatography (1:1 hexane/chloroform) to give compound **5** (6.8 g, 48 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 1.40 (t, *J* = 8 Hz, 3H), 2.96 (q, *J* = 8 Hz, 2H), 7.00 (s, 1H), 7.43

-7.50 (m, 4H), 7.92 (d,  $J=8\text{Hz}$ , 2H), 8.03 (d,  $J=8\text{Hz}$ , 2H), 8.53 (s, 1H); MS (70 eV, EI):  $m/z = 366$  [ $M^+$ ].

### **1,2-Bis(2-(9-anthryl)-5-ethylthien-3-yl)perfluorocyclopentene (1a)**

To a solution of compound **5** (4.1 g, 11 mmol) in dry THF (110 cm<sup>3</sup>) was added *n*-BuLi (1.6 mol dm<sup>-3</sup>, 10 cm<sup>3</sup>, 16 mmol) under a N<sub>2</sub> atmosphere at -78 °C, and then the mixture was stirred for 1 h. Perfluorocyclopentene (1.0 cm<sup>3</sup>, 7.4 mmol) was added to the mixture and then stirred for 2 h. The reaction vessel was allowed to warm slowly to room temperature, and water was added to quench the reaction. The reaction mixture was extracted with ether, washed three times with brine, dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give compound **1a** (0.86 g, 11 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.38 (t,  $J=8\text{Hz}$ , 6H), 2.76 (q,  $J=8\text{Hz}$ , 4H), 7.17 (s, 2H), 7.29 - 7.33 (m, 4H), 7.43 - 7.47 (m, 4H), 7.82 (d,  $J=8\text{Hz}$ , 4H), 8.04 (d,  $J=8\text{Hz}$ , 4H), 8.55 (s, 2H); MS (70 eV, EI):  $m/z = 749$  [ $M^+$ ],  $\lambda_{\text{max}}$  (**1a**, cyclohexane) /nm 367( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  21 800),  $\lambda_{\text{max}}$  (**1b**, cyclohexane) /nm 569( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  10 900).

### **2-(1-Anthryl)-3-bromo-5-ethylthiophene (6)**

To a solution of compound **4** (3.2 g, 12 mmol) in dry THF (60 cm<sup>3</sup>) was added *n*-BuLi (1.6 mol dm<sup>-3</sup>, 8 cm<sup>3</sup>, 13 mmol) under a N<sub>2</sub> atmosphere at -78 °C, and then the mixture was stirred for 1 h. Tri-*n*-butylborate (4.8 cm<sup>3</sup>, 18 mmol) was slowly added to the reaction mixture at -78 °C, and the mixture was stirred for 2 h at that temperature. Subsequently, the reaction vessel was allowed warm to room temperature, and the reaction mixture was added 20 wt % Na<sub>2</sub>CO<sub>3</sub>aq (16 cm<sup>3</sup>), 1-bromoanthracene (3.2 g, 13 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1.8 g, 1.6 mmol). The mixture was refluxed for 25 h at 64 °C. The mixture was extracted with diethyl ether, dried over MgSO<sub>4</sub>, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give compound **6** (1.7 g, 38 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.39 (t,  $J=8\text{Hz}$ , 3H), 2.93 (q,  $J=8\text{Hz}$ , 2H), 7.19 (s, 1H), 7.44 - 7.51 (m, 4H), 8.02 (d,  $J=8\text{Hz}$ , 3H), 8.48 (s, 1H), 8.80 (s, 1H); MS (70 eV, EI):  $m/z = 366$  [ $M^+$ ].

### **1,2-Bis(2-(1-anthryl)-5-ethylthien-3-yl)perfluorocyclopentene (2a)**

To a solution of compound **6** (1.1 g, 3.0 mmol) in dry THF (16 cm<sup>3</sup>) was added *n*-BuLi (1.6 mol dm<sup>-3</sup>, 2 cm<sup>3</sup>, 3.2 mmol) under a N<sub>2</sub> atmosphere at -78 °C, and then the mixture was stirred for 1.5 h. Perfluorocyclopentene (0.2 cm<sup>3</sup>, 1.5 mmol) was added to the mixture and then stirred for 2.5 h. The

reaction vessel was allowed to warm slowly to room temperature, and water was added to quench the reaction. The reaction mixture was extracted with ether, dried over MgSO<sub>4</sub>, filtrated and concentrated. The residue was purified by silica gel column chromatography (20:1 hexane/ethyl acetate) to give compound **2a** (0.34 g, 31 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 1.22 (t, *J* = 8Hz, 6H), 2.63 (q, *J* = 8Hz, 4H), 7.39 (s, 2H), 7.43 - 7.51 (m, 6H), 7.55 (d, *J* = 8Hz, 2H), 7.91 (d, *J* = 8Hz, 2H), 8.04 (t, *J* = 8Hz, 4H), 8.49 (s, 2H), 8.78 (s, 2H); MS (70 eV, EI): *m/z* = 748 [M<sup>+</sup>], λ<sub>max</sub>(**2a**, cyclohexane) /nm 369(ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 17 700), λ<sub>max</sub>(**2b**, cyclohexane) /nm 600(ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 14 600).

### **2-(2-Anthryl)-3-bromo-5-ethylthiophene (7)**

To a solution of compound **4** (4.2 g, 16 mmol) in dry THF (80 cm<sup>3</sup>) was added *n*-BuLi (1.6 mol dm<sup>-3</sup>, 10 cm<sup>3</sup>, 17 mmol) under a N<sub>2</sub> atmosphere at -78 °C, and then the mixture was stirred for 1 h. Tri-*n*-butylborate (6.5 cm<sup>3</sup>, 18 mmol) was slowly added to the reaction mixture at -78 °C, and the mixture was stirred for 2 h at that temperature. Subsequently, the reaction vessel was allowed warm to room temperature, and the reaction mixture was added 20 wt % Na<sub>2</sub>CO<sub>3</sub> aq (22 cm<sup>3</sup>), 2-bromoanthracene (3.6 g, 9.8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (3.3 g, 2.8 mmol). The mixture was refluxed for 37 h at 64 °C. The mixture was extracted with diethyl ether, dried over MgSO<sub>4</sub>, and concentrated. The residue was purified by silica gel column chromatography (hexane) to give compound **7** (1.8 g, 35 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 1.36 (t, *J* = 8Hz, 3H), 2.87 (q, *J* = 8Hz, 2H), 7.29 (s, 1H), 7.46 - 7.48 (m, 2H), 7.65 (dd, *J* = 1.8 and 8Hz, 1H), 7.98 - 8.02 (m, 3H), 8.12 (s, 1H), 8.40 (d, 2H); MS (70 eV, EI): *m/z* = 367 [M<sup>+</sup>].

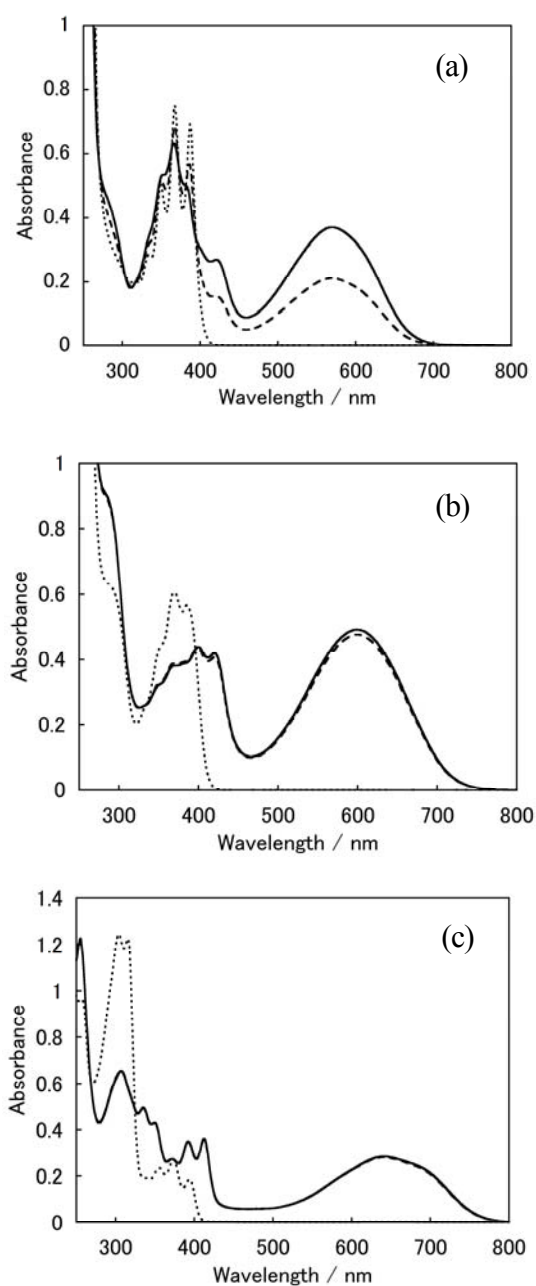
### **1,2-Bis(2-(2-anthryl)-5-ethylthien-3-yl)perfluorocyclopentene (3a)**

To a solution of compound **7** (1.0 g, 2.8 mmol) in dry THF (20 cm<sup>3</sup>) was added *n*-BuLi (1.6 mol dm<sup>-3</sup>, 1.8 cm<sup>3</sup>, 3.0 mmol) under a N<sub>2</sub> atmosphere at -78 °C, and then the mixture was stirred for 15 min. Perfluorocyclopentene (0.2 cm<sup>3</sup>, 1.5 mmol) was added to the mixture and then stirred for 2 h. The reaction vessel was allowed to warm slowly to room temperature, and water was added to quench the reaction. The reaction mixture was extracted with ether, dried over MgSO<sub>4</sub>, filtrated and concentrated. The residue was purified by silica gel column chromatography (20:1 hexane/ethyl acetate) to give compound **3a** (0.36 g, 34 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 1.07 (t, *J* = 8Hz, 6H), 2.44 (q, *J* = 8Hz, 4H), 7.44 (s, 2H), 7.45 - 7.48 (m, 4H), 7.70 (dd, *J* = 1.8 and 8Hz, 2H), 7.96 - 8.01 (m, 6H), 8.03 (d, 2H), 8.15 (s, 2H), 8.40 (s,

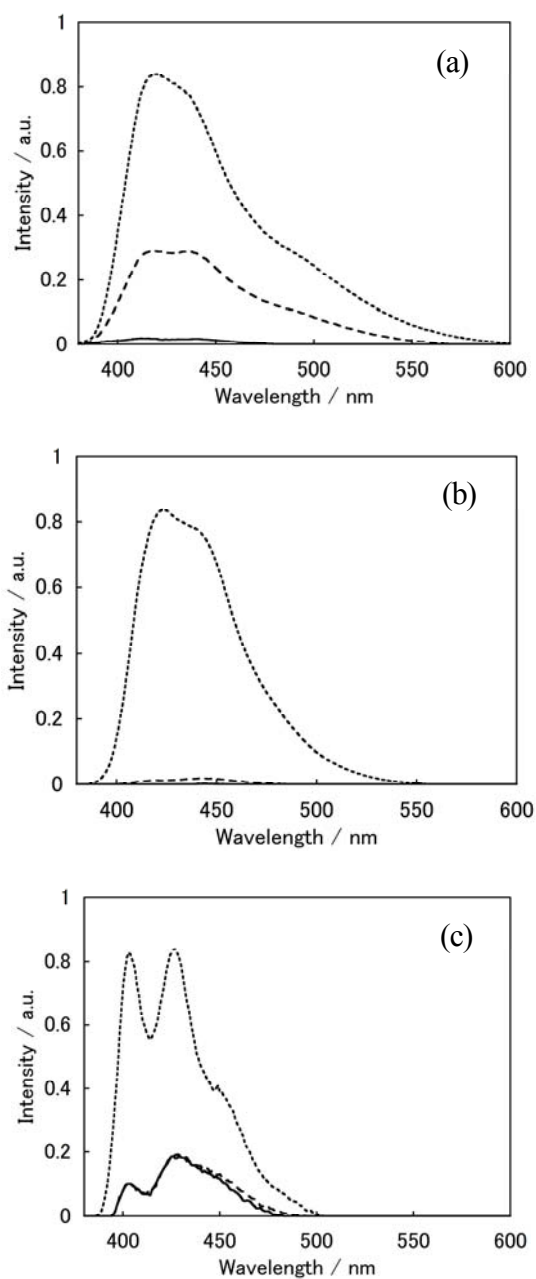
4H); MS (70 eV, EI):  $m/z = 748 [M^+]$ ,  $\lambda_{\max}(\mathbf{3a}, \text{cyclohexane}) / \text{nm}$  373 ( $\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  23 600),  $\lambda_{\max}$  ( $\mathbf{3b}, \text{cyclohexane}) / \text{nm}$  640 ( $\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  24 700).

### 3. Absorption spectra of 1, 2 and 3 in cyclohexane



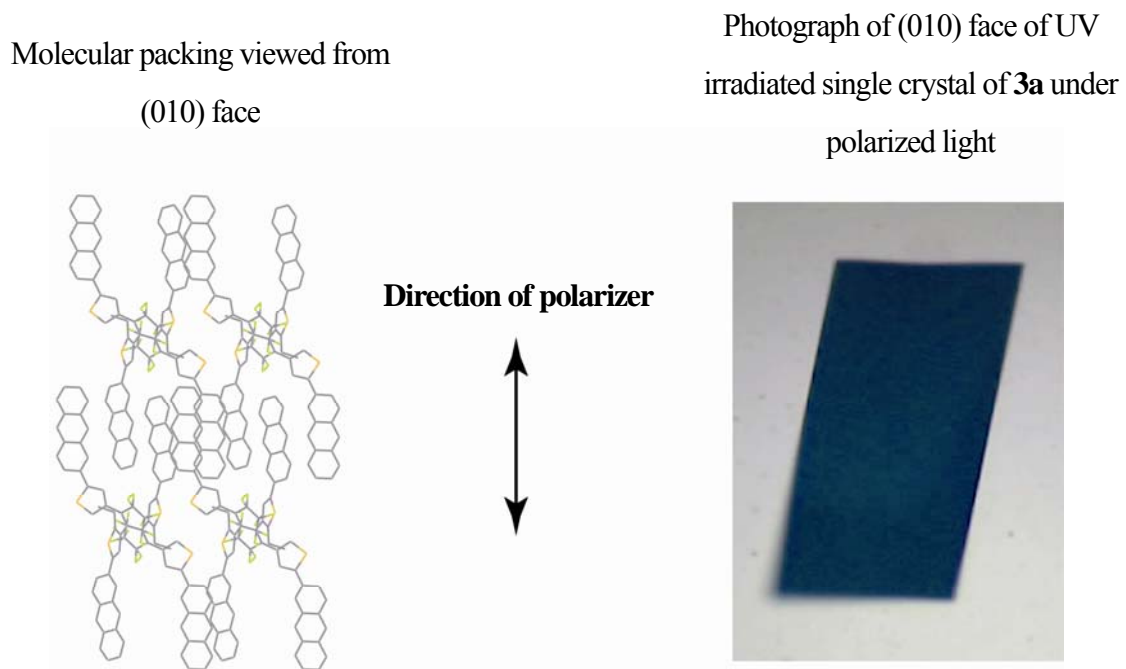
**Fig. S1** Absorption spectra of **1** (a), **2** (b) and **3** (c) in cyclohexane. Dotted lines: open-ring isomers **1a**, **2a** and **3a**, solid lines: closed-ring isomers **1b**, **2b** and **3b**, dashed lines: photostationary states under irradiation with 365 nm light.

#### 4. Fluorescence spectra of **1**, **2** and **3** in cyclohexane



**Fig. S2** Fluorescence spectra of **1** (a), **2** (b) and **3** (c) in cyclohexane. Dotted lines: open-ring isomers **1a**, **2a** and **3a**, solid lines: closed-ring isomers **1b**, **2b** and **3b**, dashed lines: photostationary states under irradiation with 365 nm light.

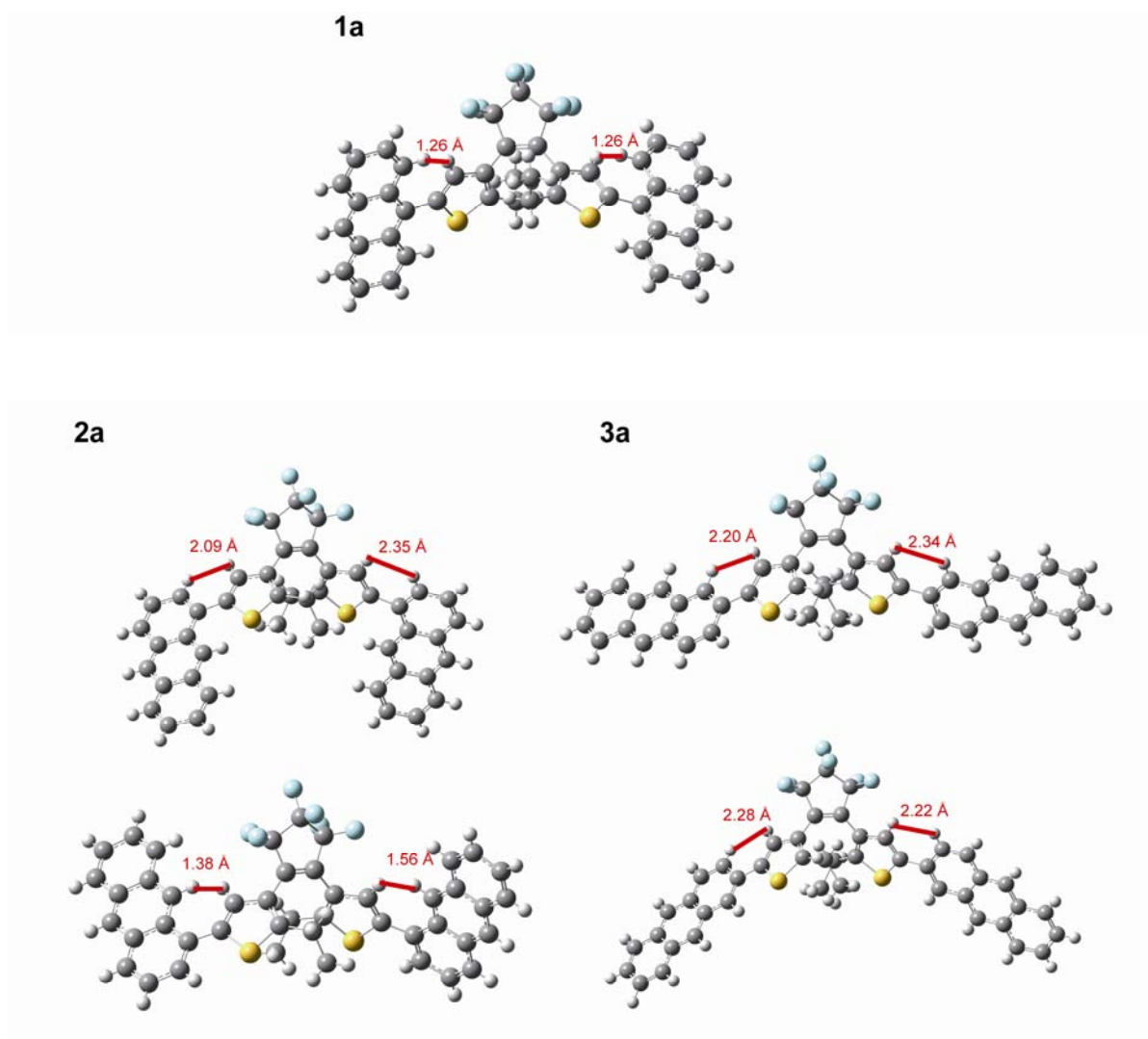
## 5. The relationship between the polarization direction and the molecular packing



**Fig. S3** The relationship between the molecular packing viewed from (010) face and the photograph of (010) face of UV irradiated single crystal **3a** under polarized light.



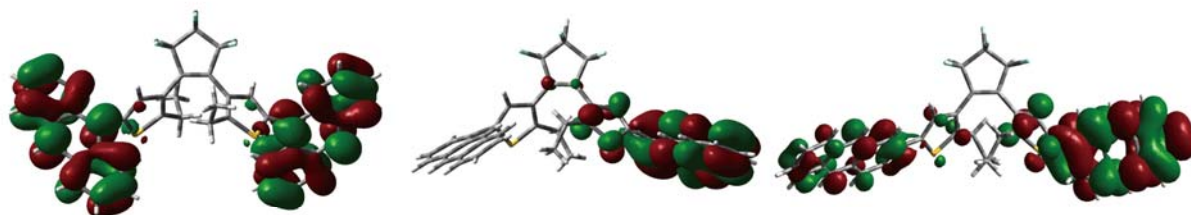
## 6. Steric hindrance between anthracene and thiophene rings



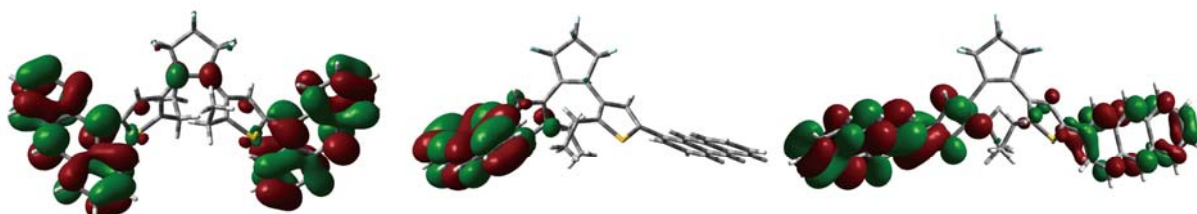
**Fig. S4** Coplanar conformations of **1a**, **2a** and **3a** in which the dihedral angles between the anthracene and thiophene rings are  $0^\circ$ . The red lines indicate the distances between the anthracene-H and thiophene-H. The steric hindrance between the H atoms in **3a** is smaller than that in **1a** and **2a**.

## 7. DFT calculation

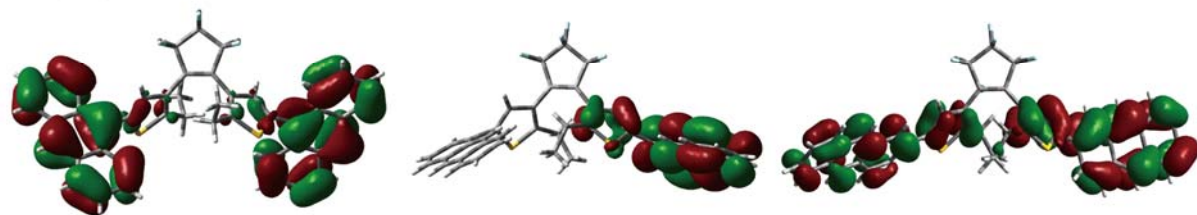
LUMO+1



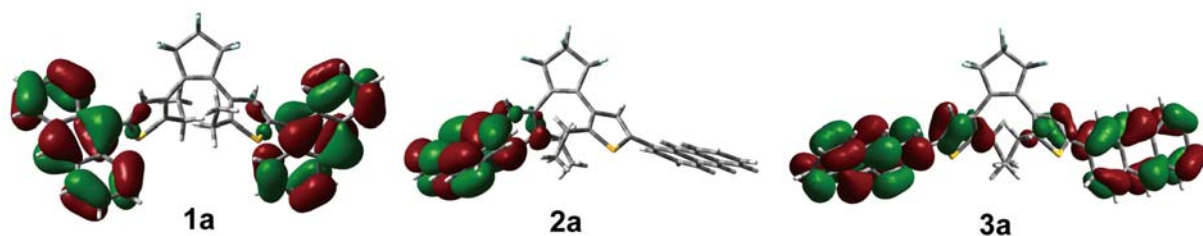
LUMO



HOMO



HOMO-1



**Fig. S5** Orbital shapes of the HOMO-1, HOMO, LUMO and LUMO+1 of **1a**, **2a** and **3a** molecular structure determined by X-ray crystallographic analysis.

## References

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