Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2020

## **Supporting Information**

### Isomeric Effect of Fluorene-based Fused-ring Electron Acceptors to Achieve

### **High-Efficiency Organic Solar Cells**

Yung-Jing Xue<sup>a</sup>, Fong-Yi Cao<sup>a</sup>, Po-Kai Huang<sup>a</sup>, Yen-Chen Su<sup>a</sup> and Yen-Ju Cheng<sup>\*ab</sup>

<sup>a</sup>Department of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsinchu, Taiwan 30010. <sup>b</sup>Center for Emergent Functional Matter Science, National Chiao Tung University, 1001 University Road, Hsinchu, Taiwan 30010.

E-mail: yjcheng@mail.nctu.edu.tw

### CONTENT

- 1. TGA and DSC measurements
- 2. CV measurement
- 3. SCLC measurements
- 4. 1-dimentional GIWAXS data
- 5. General measurement and characterization
- 6. Fabrication and characterization of OPV devices
- 7. Synthetic procedures
- 8. <sup>1</sup>H and <sup>13</sup>C NMR Specta



Fig. S1. (a)TGA and (b)DSC measurement of FCTT-FIC with a ramping rate of 10 °C/min.



Fig. S2. Cyclic voltammogram of FCTT-FIC in thin films at a scan rate of 100 mV s<sup>-1</sup>.



**Fig. S3.** *J-V* curves of the (a) hole-only devices and (b) electron-only devices with FCTT-FIC contained blending films under dark condition.



**Fig. S4.** 1-Dimensional (a) in-plane and (b) out-of-plane GIWAXS patterns of FCTT-FIC, PBDB-T:FCTT-FIC, PM6:FCTT-FIC and PM6:FCTT-FIC:PC<sub>71</sub>BM films.

General Measurement and Characterization. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using Varian 400 MHz instrument spectrometer and obtained in deuterated chloroform (CDCl<sub>3</sub>) with TMS as internal reference unless otherwise stated, and chemical shifts ( $\delta$ ) are reported in parts per million. Absorption spectrum was taken on a HP8453 UV-vis spectrophotometer. DSC was conducted on a TA Q200 Instrument

under nitrogen atmosphere at a heating/cooling rate of 10 °C/min. TGA was recorded on a Perkin-Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. Electrochemical cyclic voltammetry was conducted on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and a Ag/AgCl electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was the electrolyte. CV curves were calibrated using ferrocence as the standard, whose HOMO energy level is set at -4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation  $E_{HOMO} = -(E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$  eV. The LUMO energy levels were obtained from the equation  $E_{LUMO} = -(E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$  eV. GIWAXS experiments were conducted at National Synchrotron Radiation Research Center (NSRRC) on beamline BL23A in Taiwan. The samples were irradiated with an X-ray energy of 10.09 keV ( $\lambda = 1.23$  Å) at a fixed incident angle of 0.08° through a coupled double crystal Si(111)/multilayer (Mo/B4C) monochromator, and the GIWAXS patterns were recorded on a 2D image detector (Pilatus 1M-F area detector). The thin films for GIWAXS measurement were prepared under identical conditions used for the OPV devices. Surface topography was investigated using Veeco diInnova AFM and standard tips (Tapping mode; L, 225 µm; FREQ, 75 MHz; k, 2.8 N/m).

Fabrication and Characterization of OPV Devices. The fabrication of the inverted devices follow the procedures: The ITO-coated glass substrates were cleaned by ultrasonic cleaner in detergent, DI-water, acetone and isopropyl alcohol for 10 min, respectively, and subsequently treated with UV-ozone for 45 min. The ZnO layer was prepared by the ZnO precursor (diethyl Zinc) solution in THF and spin-coated onto the pre-treated ITO-coated glass. The chlorobenzene solution of PBDB-T:FCTT-FIC, PM6:FCTT-FIC and PM6:FCTT-FIC:PC71BM in an different weight ratio with 0.5 vol% DIO as additive were prepared and stired 12 h at 80 °C. Active layers were formed by spin-coating on top of the ZnO/ITO substrate and the detailed conditions were recorded in Table S1. The molecular weight of PBDBT and PM6 determined by GPC is ca. 64 kDa and 58 kDa, respectively. Moreover, the substrates were thermally annealed at 150 °C for 10 min in the glove box. Finally, the MoO<sub>3</sub> layer (7 nm) and silver anode (150 nm) were deposited by thermal evaporation at a pressure below  $10^{-6}$ torr. The devices without encapsulation were characterized in ambient condition. Current-voltage characteristics were measured by a Keithley 2400 SMU under the irradiation of AM 1.5G San-Yi solar simulator with JIS AAA spectrum. The characteristics of the solar cells were optimized by testing approximately 25 cells. IPCE spectra were measured using a lock-in amplifier with a current preamplifier under shortcircuit conditions with illumination by monochromatic light from a 250 W quartzhalogen lamp (Osram) passing through a monochromator (Spectral Products CM110).

**Table S1.** The optimized condition of the blending solution with PBDB-T:FCTT-FIC,PM6:FCTT-FIC and PM6:FCTT-FIC:PC71BM.

Blending system [donor:acceptor]	Blending ratio	Conc.	Solvent/Additive	Thermal annealing	Spin rate [rpm]
PBDB-T: FCTT- FIC	1:1	8 mg/ml	CB/0.5 vol% DIO	150 °C 10 min	4000
PM6: FCTT-FIC	1:1	8 mg/ml	CB/0.5 vol% DIO	150 °C 10 min	1500
	1:1:0.5	8 mg/ml	CB/0.5 vol% DIO	150 °C 10 min	3500
PM6: FCTT-FIC: PC <sub>71</sub> BM	1:1:1	7 mg/ml	CB/0.5 vol% DIO	150 °C 10 min	1500
	1:1:1.5	6 mg/ml	CB/0.5 vol% DIO	150 °C 10 min	1500

#### Synthetic procedure



Synthetic procedure

Synthesis of Compound 1a



To a solution of thiophene (50.0 g, 0.60 mol) in chloroform (15 ml) was added bromine (144 ml, 2.4 mol) dropwise at 0 °C. The mixture was warmed to room temperature and additional amount of bromine (35 ml, 0.70 mol) was added dropwise. Reaction was stirred and refluxed for 5 h. The mixture was added slowly to the saturated sodium thiosulfate at 0 °C. The resultant was then filtered and washed with water. The product was obtained as orange solid (215 g, 90%).<sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>) : $\delta$  166.93, 110.27.

#### Synthesis of Compound 2a



To a solution of compound 1a (50.0 g, 0.13 mol) in glacial acetic acid-water (180 ml,

1:2, v/v) was added zinc powder (20 g, 0.30 mol) slowly at room temperature. The mixture was stirred and refluxed for 3 h. The resultant was filtered to remove excess zinc powder and the filtrate was extracted with hexane (100 ml × 2) and water (200 ml). The combined organic phase was dried over anhydrous MgSO<sub>4</sub>. Then the solvent was removed under reduced pressure and the product was obtained as light yellow oil (25.4 g, 87%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  123.67, 113.80.

### Synthesis of Compound 3a



To a solution of compound 2a (24.4 g, 0.10 mol) in dry THF (280 ml) under nitrogen was added lithium diisopropylamide (2 M in THF; 52.6 ml, 0.10 mol) dropwise at 0 °C and stirred for 1h. The mixture was added N-formylpiperidine (12.2 ml, 0.11 mol) and stirred 24 h at room temperature. The reaction was quenched by saturated NH<sub>4</sub>Cl<sub>(aq)</sub> and extracted with ethyl acetate (100 ml × 2) and water (200 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give orange solid (18.4 g, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.95 (s, 1H), 7.75 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  182.87, 137.68, 131.67, 123.48, 115.99.

#### Synthesis of Compound 4a



To a solution of compound 3a (8.63 g, 32.0 mmol) in THF (160 ml) was added K<sub>2</sub>CO<sub>3</sub> (8.62, 62.4 mmol) and ethyl 2-thioxoacetate (5.56 ml, 43.5 mmol) at room temperature. After stirring 72 h at room temperature, the mixture was extracted with ethyl acetate (50 ml  $\times$  2) and water (100 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under the reduced pressure, the residue was used for next reaction without purification. To a solution of the product (9.32 g, 32.0 mmol) of previous step in THF-water (180 ml, 1:1, v/v) was added lithium hydroxide monohydrate (4.04 g, 67.2 mmol). The solution was stirred and refluxed for 12 h. Then, hydrochloric acid (1M, 500 ml) was added and reaction continued for 10 minutes. The resultant was filtered. In addition, precipitate was washed with water and dried in the vacuum desiccator to give yellow solid (7.10 g, 84 %). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  8.18 (s, 1H), 8.05 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  163.08, 143.36, 138.23, 136.49, 130.56, 127.48, 101.59.

#### Synthesis of compound 5a



To a solution of compound 4a (7.89 g 30.0 mmol) in DMSO (40 ml) was added sliver carbonate (0.6 g, 3 mmol) and 3-4 drop acetic acid in sealed tube. The reaction mixture was stirred for 16 h at 130 °C. The reaction solution was extracted with ethyl acetate (50 ml) and hydrochloric acid (1M, 100 ml). The collection organic layer was dried

over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane as the eluent to give light yellow oil (4.67 g, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (dd, J = 5.2 Hz, 1H), 7.30 (d, J = 5.2 Hz, 1H), 7.28 (d, J = 1.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  140.43, 138.43, 128.11, 124.06, 120.20, 102.30.

Synthesis of compound 6a



To a solution of compound 5a (2.19 g, 10.0 mmol) in dry THF (15 ml) under nitrogen was added isopropylmagnesium chloride lithium chloride complex solution (1.3 M in THF, 10.0 ml, 13.0 mmol) dropwise at 0 °C and stirred for 3h. The reaction mixture was added ethyl chloroformate (7.7 ml, 80.0 mmol) at 0 °C and stirred for 16 h at room temperature. The reaction was quenched with water and extracted with ethyl acetate (50 ml × 2) and water (100 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure , the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give the yellow oil (1.53 g, 72 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (s, 1H), 7.47 (dd, *J* = , 1H), 7.27 (d, *J* = 5.2 Hz, 1H), 4.41 (m, 2H), 1.43 (t, *J* = 3.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.45, 138.47, 138.32, 134.17, 129.01, 125.59, 118.72, 60.74, 14.03.

Synthesis of ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate



To a solution of compound 6a (1.27 g, 6.0 mmol) in dry THF(24 ml) under nitrogen was added lithium diisopropylamide (2 M in THF, 3.9 ml, 7.8 mmol) dropwise at -78 °C and stirred for 2 h. The reaction solution was added tetrabromomethane solution (0.6 M in THF, 12 ml, 6.6 mmol) and stirred for 1h at -78 °C. After stirring for 16 h at room temperature, the reaction solution was extracted with ethyl acetate (50 ml  $\times$  2) and water (100 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give the brown oil (960.9 mg, 55 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.50 (d, J = 5.3 Hz, 1H), 7.18 (d, J = 5.3 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2 H), 1.47 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  161.07, 138.23, 136.42, 128.58, 123.93, 121.37, 118.52, 61.44, 14.25.

Synthesis of compound 1



To a solution of 2,7-dibromo-9H-fluorene (16.2 g, 0.050 mol) and 1-bromooctane (24.14 g, 0.125 mol) in THF (250 ml) was added sodium tert-butoxide (19.22 g, 0.200 mol) slowly at 0 °C. After stirring 24 h at room temperature, the reaction solution was extracted with ethyl acetate (100 ml × 2) and water (150 ml). The collection layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was distilled under the reduced pressure and gave the yellow solid (21.1 g, 77 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d, *J* = 8.1 Hz, 2H). 7.45 (d, *J* = 8.3 Hz, 4H), 1.94 – 1.87 (m, 4H), 1.26 – 1.01 (m, 24H), 0.83 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.51, 139.03, 130.11, 126.14, 121.45, 121.08, 55.66, 40.13, 31.74,

29.84, 29.16, 29.13, 23.60, 22.58, 14.06.

#### Synthesis of compound 2



To a solution of compound 1 (5.46 g, 10.0 mmol) in THF (110 ml) under nitrogen was added n-Butyllithium (2.5 M in hexane, 10.40 ml, 26.0 mmol) dropwise at -78 °C and stirred for 2 h. The mixture was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.50 ml, 26.0 mmol) dropwise at -78 °C and stirred for 1.5 h. After stirring 16 h at room temperature, the reaction solution was extracted with ethyl acetate (50 ml × 2) and water (100 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was washed by methanol to give the white solid ( 4.24 g, 66 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.80 (d, *J* = 7.5 Hz, 2H), 7.74 (s, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 2.06 – 1.91 (m, 4H), 1.38 (s, 24H), 1.31 – 0.95 (m, 24H), 0.80 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.44, 143.89, 133.62, 128.69, 119.34, 83.69, 55.16, 40.07, 31.76, 29.91, 29.18, 29.13, 24.92, 23.58, 22.57, 14.05.

Synthesis of compound 3



To a degassed toluene-water (26.5 ml, 5:1, v/v) solution of compound 2 (642.6 mg, 1.0

mmol) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (115.6 mg, 0.1 mmol), potassium carbonate (1.38 g, 10.0 mmol), compound 7a (698.8 mg, 2.4 mmol), and Aliquat 336 (2 drop). The mixture was stirred for 5 h under refluxing. The reaction solution was extracted with ethyl acetate (25 ml × 2) and water (50 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give the brown sticky oil (616.5 mg, 76 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.53 (s, 2H), 7.47 (d, *J* = 5.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 2.07 – 1.93 (m, 4 H), 1.34 – 1.00 (m, 30 H), 0.80 (t, *J* = 6.8 Hz, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  162.20, 153.89, 150.88, 141.15, 140.75, 135.84, 132.84, 129.08, 128.40, 124.66, 120.77, 119.35, 118.75, 60.81, 55.38, 40.12, 31.78, 30.04, 29.68, 29.25, 29.21, 23.87, 22.58, 14.18, 14.05;HRMS (FD, C<sub>47</sub>H<sub>54</sub>O<sub>4</sub>S<sub>4</sub>): calcd, 810.28994; found 810.29015.

### Synthesis of FCTT



A Grignard reagent was prepared by the following procedure. To a suspension of magnesium turnings (195 mg, 8.0 mmol) and 3-4 drops of 1,2-dibromoethane in dry THF (9 ml) was slowly added 1-bromo-4hexylbenzene (2.3 g, 9.4 mmol), and the mixture was stirred for 1 h under refluxing. To a solution of compound 3 (542.4 mg, 0.67 mmol) in dry THF (25 ml) under nitrogen was added 4-hexylbenzene 1-

magnesium bromide (5.0 ml 5.2 mmol) dropwise at room temperature. The mixture was refluxed for 16 h. The reaction solution was quenched by water and extracted with dichloromethane (50 ml  $\times$  2) and water (100 ml) and then dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was used for next reaction without purification. To a solution of the product (mg, 0.67 mmol) of previous step in octane (60 ml) was added acetic acid (0.4 ml) and sulfuric acid (0.4 ml, 7.45 mmol) slowly. The mixture was stirred for 2 h at 65 °C. After removing the octane under the reduce pressure, the residue was extracted with dichloromethane (50 ml  $\times$  2) and water (100 ml) The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane as the eluent to give the yellow solid FCTT (402 mg, 45 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.59 (s, 2H), 7.38 (s, 2H), 7.31(d, J =5.1 Hz, 2H), 7.27 (d, J = 4.8 Hz, 2H), 7.16 (d, J = 8.0 Hz, 8H), 7.06 (d, J = 8.0 Hz, 8H), 2.60 - 2.50 (m, 8H), 2.06 - 1.99 (m, 4H), 1.63 - 1.51 (m, 12H), 1.39 - 1.25 (m, 28H), 1.25 - 1.08 (m, 16H), 0.86 (t, J = 6.4 Hz, 12H), 0.80 (t, J = 6.7 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 152.39, 151.24, 146.12, 143.41, 141.47, 141.42, 140.60, 139.43, 136.92, 133.86, 128.34, 128.10, 126.18, 120.30, 117.13, 113.53, 62.91, 54.52, 40.58, 35.57, 31.80, 31.68, 31.18, 29.23, 29.19, 23.97, 22.59, 22.57, 14.06;HRMS (FD,  $C_{91}H_{11}S_4$ ): calcd, 1330.74849; found 1330.74983.

#### **Synthesis of FCTT-CHO**



POCl<sub>3</sub> (0.4 ml, 4 mmol) was added in DMF (2 ml) and stirred for 30 min at 0 °C. FCTT (266.4 mg, 0.20 mmol) was dissolve in 1,2-dichloroethane (16 ml) was added in the mixture slowly and stirred for 16 h at 85 °C. The reaction solution was extracted with dichloromethane (50 ml × 2) and water (100 ml). The collection organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 10:1) to give the light yellow solid of FCTT-CHO (247 mg, 89 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.98 (s, 2H), 7.96 (s, 2H), 7.64 (s, 2H), 7.46 (s, 2H), 7.11 (d, *J* = 8.3 Hz, 8H), 7.07 (d, *J* = 8.4 Hz, 8H), 2.58 – 2.50 (m, 8H), 2.08 – 2.01 (m, 4H), 1.36 – 1.21 (m, 20H), 1.20 – 1.05 (m, 26H), 0.85 (t, *J* = 6.8 Hz, 12H), 0.78 (t, *J* = 6.9 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  182.81, 153.64, 151.80, 146.32, 143.97, 142.01, 141.30, 140.64, 140.46, 139.63, 136.29, 128.61, 127.89, 117.64, 114.61, 63.01, 54.72, 40.50, 35.55, 31.78, 31.66, 31.19, 29.19, 29.15, 23.97, 22.58, 22.55, 14.05;HRMS (FD, C<sub>93</sub>H<sub>110</sub>O<sub>2</sub>S<sub>4</sub>): calcd, 1386.73882; found 1386.73889.

Synthesis of FCTT-FIC



2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inded-1-ylidene)malononitrile (115 mg, 0.5 mmol) was added to the solution of FCTT-CHO (139 mg, 0.1 mmol) in the degassed chloroform (20 ml) with pyridine (1-2 drop). The reaction mixture was stirred for 6 h under refluxing. After cooling to room temperature, the reaction was poured into water. The precipitate was filtered off and washed with methanol. The crude product was purified by column chromatography on silica gel using DCM as the eluent to give a dark blue solid FCTT-FIC (149 mg, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.85 (s, 2H), 8.52 (dd, J = 9.6, 6.4 Hz, 2H), 8.22 (s, 2H), 7.72 - 7.63 (m, 4H), 7.53 (s, 2H), 7.19 (d, 2H), 7.1J = 7.9 Hz, 8H), 7.12 (d, J = 8.0 Hz, 8H), 2.61 – 2.48 (m, 8H), 2.14 – 2.01 (m, 4H), 1.68 - 1.54 (m, 16H), 1.41 - 1.23 (m, 24H), 1.24 - 1.01 (m, 22H), 0.85 (t, J = 6.2 Hz, 12H), 0.79 (t, J = 6.5 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  185.77, 158.26, 154.85, 154.78, 152.38, 148.20, 147.18, 143.51, 142.28, 141.65, 139.26, 139.00, 138.47, 137.62, 136.25, 128.77, 127.91, 121.21, 117.99, 115.30, 115.01, 114.79, 114.32, 114.21, 69.41, 63.13, 54.84, 40.49, 35.58, 31.77, 31.67, 31.18, 30.00, 29.21, 24.03, 22.58, 22.56, 14.05; HRMS (FD, C<sub>117</sub>H<sub>114</sub>N<sub>4</sub>O<sub>2</sub>F<sub>4</sub>S<sub>4</sub>): calcd, 1810.7755; found 1810.7752.

#### <sup>1</sup>H and <sup>13</sup>C NMR spectrum

# <sup>13</sup>C spectrum of compound 1a









<sup>13</sup>C spectrum of compound 3a





# <sup>13</sup>C spectrum of compound 4a



## <sup>1</sup>H spectrum of compound 5a





<sup>13</sup>C spectrum of compound 5a

<sup>1</sup>H spectrum of compound 6a



<sup>13</sup>C spectrum of compound 6a





<sup>1</sup>H spectrum of ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate



<sup>13</sup>C spectrum of ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate



<sup>1</sup>H spectrum of compound 1



# <sup>13</sup>C spectrum of compound 1

# <sup>1</sup>H spectrum of compound 2

10 0-7		
10.0-1	-	
00'0		
10.0		
10.0-		
75.0 <sup>7</sup>		
62.0		
08.0-		
- 78'0		
00.1-	± ∠8.5-8	
70.1 <del>.</del>	- 10 G	
80.1-	- 22-	
OF P	24   24	
4[ <sup>1</sup> ]-		
9111-		
81.1-		
61'1-	[	
12.1-	-4.0	
52.1-		
82.1-	- 4	
S8'I-		
85.1-	5.0 5.0 11 (ppm)	freed.
25°1-		× .
<u>79.1</u>		
861-	- 52	
661-		
001	- <sup>9</sup>	
2.00 2.01		
10.6	6.5	
77.26		
0/:/-1		
02.7 07.7 27.7 27.7 18.7 18.7 18.7		
7/./-		
61.11		
18.17	/ 00.S - 🕱	
10 1		
	- 8	
	-0.6	
	-6	
01	10.0	
ION	10-	
PROTON_01	2	



## <sup>13</sup>C spectrum of compound 2



<sup>1</sup>H spectrum of compound 3





<sup>1</sup>H spectrum of compound FCTT





### <sup>1</sup>H spectrum of FCTT-CHO

5



### <sup>13</sup>C spectrum of FCTT-CHO

<sup>1</sup> H spectrum of FCTT-FIC	
00.01	-
44.01	
62.01	
08.0	0.5
78.0√	
S8.0-1	
78.0 <sup>7</sup>	
1112	
1014	10 %6
SIT	
SIT	LU 7-
21°14 =	
6111	
72.1 <del>.</del>	30-
82.1-	
621-	- 2
62.1-	
18.1-	- 07
Z8.1-	-12
25.1-	7
82.1-	FI (mm)
<u>88.</u> !-	212
<u>/</u> 5')-	- 25
6S'I-	
09.1-	- 09
90°Z-	
80.2-	65
80'Z-	
80.5-	₹ <u>1/: /</u> -?:
01' Z- 75' Z-	
75 61	
9S'Z- <i>L</i> S'Z-	00 7
65 67	- 00
11°2- 81°2-	
01.7	F 92.2- 🕾
81 <sup>°</sup> L-	2.22 ¥ 2.20 ×
06.6	-06
DZ'L- 9Z'L- 2S'L- 2Z'8- 8'8-	1.0
10.1-	- 5.0
57.0-	10.0
50.0 200 0	[0]
Cin n	2

# <sup>13</sup>C spectrum of FCTT-FIC

L	
רול־20	
J22.56	- 10
85.221	
20.420	- 92
12.62	
/30.00	 30-
81.18	 
19'18'r	40-
1 <sup>2</sup> 31'31 32'28	 4
64.04	- 20
₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩	- <u>-</u>
/ P3 13	
07.697	- 99
89.977	
00.17	- 6
07.17.20	
ZE.TT	- 8
1Z.411	7004
28.411-	- 8
64.411-	
10'SII-	- 00
CII2'30	
66'ZII'	110
IS.ISI	
16.7212	 -
LL'8217	-
52.981 <sup>1</sup>	 -
7-137.62	
14.881-2	140
00'681	
96 98 -	150
59'lbl-t	 -
82.241	 160
15.241-	-
81.741- 02.041-	170
02.841- 152.81-	
82.421-	-180
<u>58.421</u>	
97.8 CI	- 06
97.851 2.1.581	-
en la companya de la comp	Q