Electronic Supplementary Information for

Solution-processible n-type and ambipolar semiconductors based on fused cyclopentadithiophenebis(dicyanovinylene) core

Xueliang Shi, Jingjing Chang and Chunyan Chi*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, 117543, E-mail: chmcc@nus.edu.sg

Table of contents

1. Experimental section ................................................................. S2
   1.1 General .............................................................................. S2
   1.2 Detailed synthetic procedures and characterization data ................. S2
2. UV-vis absorption spectra ............................................................ S6
3. Cyclic voltammograms and differential pulse voltammograms ............... S6
4. Thermogravimetric analysis curves ............................................. S7
5. Differential scanning calorimetry curves ....................................... S8
6. Variable-temperature powder X-ray diffraction data .......................... S9
7. Polarizing optical microscope (POM) images ................................ S10
8. OFET device data of FCPDT-C24 ............................................. S11
9. Additional AFM images ........................................................... S11
10. References ............................................................................. S12
11. $^1$H and $^{13}$C NMR spectra of all new compounds......................... S13
1. Experimental Section

1.1. General

All reagents were purchased from commercial sources and used without further purification. Anhydrous dichloromethane (DCM) and N,N-dimethylformaldehyde were distilled from CaH₂. Anhydrous toluene and THF were distilled from sodium benzophenone immediately prior to use. The ¹H NMR and ¹³C NMR spectra were recorded in solution of CDCl₃ on Bruker DRX 500 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution (HR) MALDI-TOF mass spectra were recorded on a Bruker Autoflex instrument. HR ACPI mass spectra were recorded on a MicrOTOF-QII instrument. The device fabrication is as following: The SiO₂/Si substrate was cleaned with acetone and isopropanol, then immersed in a piranha solution for 8 minutes. Followed by rinsing with deionized water, and then treated with octadecyltrimethoxysilane (OTMS) spin coated from 10 mM trichloroethylene solution, and treated with ammonia vapor for 7h, or octadecyltrichlorosilane (ODTS) immersed in 3 mM hexadecane solution for 16h in N₂.

Diethyl 2,5-dichlorothieno[3,2-b]thiophene-3,6-dicarboxylate ¹ and the tin complex ² were prepared by following the literature procedures. The synthetic route to FCPDT-C₁₆ and FCPDT-C₂₄ is shown as Scheme S1 (same to Scheme 1 in the main text).

Scheme S1. Synthetic route of FCPDT-C₁₆ and FCPDT-C₂₄. Reagents and conditions: (i) Pd(PPh₃)₄, toluene/DMF, 120 °C, 24h, 82~85%; (ii) NaOH, MeOH/THF, reflux, quantitative; (iii) (a) SOCl₂, dry dichloromethane, reflux; (b) AlCl₃, dry dichloromethane, 0 °C - rt., 30~50%; (iv) malononitrile, pyridine, TiCl₄ , chlorobenzene, 0 °C - rt., 60~70%.

1.2. Detailed synthetic procedures and characterization data

Compound 3 (R = 2-hexyldecyl)
A mixture of compounds 1 (706 mg, 2.00 mmol), 2 (R = 2-hexyldecyl) (4.78 g, 8.00 mmol) and catalyst Pd(PPh3)2Cl2 (231 mg, 5 mol%) in anhydrous DMF (2 mL) and toluene (10 mL) was degassed by three freeze–pump–thaw cycles. The mixture was heated at reflux under argon overnight. The mixture was cooled to room temperature and extracted with CHCl3 (30 mL×2). The combined organic phase was washed with 10% HCl (50 mL×1) and brine (50 mL×1). The organic phase was dried over anhydrous Na2SO4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane:DCM = 8:1) to afford compound 3 (1.50 g) as yellow orange oil in 84% yield. 1H NMR (500 MHz, CDCl3, ppm): δ = 7.43 (d, J = 6.0 Hz, 2H), 6.76 (d, J = 6.0 Hz, 2H), 4.40 (q, J = 12.0 Hz, 4H), 2.78 (d, J = 11.0 Hz, 4H), 1.42 (t, J = 12.0 Hz, 6H), 1.31-1.27 (m, 50H), 0.91-0.85 (m, 12H). 13C NMR (125 MHz, CDCl3, ppm): δ = 161.98, 148.41, 146.91, 136.71, 131.63, 129.70, 125.55, 118.78, 61.19, 40.00, 34.67, 34.63, 33.24, 31.91, 31.88, 31.58, 29.96, 29.62, 29.32, 26.60, 26.58, 22.68, 22.66, 22.64, 14.28, 14.09. HR MALDI-TOF MS: calcd for C52H80O4S4 (M+), 896.4939; found, 896.4934 (error: -0.56 ppm).

**Compound 3 (R = 2-decyltetradecyl)**

Yellow orange oil, 84% yield.

1H NMR (500 MHz, CDCl3, ppm): δ = 7.42 (d, J = 6.3 Hz, 2H), 6.76 (d, J = 6.3 Hz, 2H), 4.40 (q, J = 12.0 Hz, 4H), 2.78 (d, J = 11.0 Hz, 4H), 1.41 (t, J = 11.8 Hz, 6H), 1.31-1.26 (m, 82H), 0.90-0.85 (m, 12H). 13C NMR (125 MHz, CDCl3, ppm): δ = 162.00, 148.44, 146.92, 136.72, 131.63, 129.70, 125.56, 118.78, 61.20, 40.00, 34.65, 33.24, 31.93, 29.98, 29.70, 29.68, 29.63, 29.36, 26.62, 22.69, 22.67. HR MALDI-TOF MS: calcd for C68H112O4S4 (M+), 1120.7443; found, 1120.7438 (error: -0.45 ppm).

**Compound 4 (R = 2-hexyldecyl)**

Compound 3 (R = 2-hexyldecyl) (897 mg, 1.0 mmol) was dissolved in methanol and THF (30 mL, 1:1 v/v), followed by the addition of sodium hydroxide (400 mg). This mixture was heated at reflux overnight. During this period the orange solid was formed. The solvent was removed under reduced pressure after the reaction was finished. To the residue then concentrated hydrochloric acid was added. The precipitate formed was collected by filtration and washed with water and a little...
amount of DCM, then dried in vacuo to afford product 4 as a yellow orange sticky solid (800 mg, 95%). The material is carried forward without further purification and characterization.

**Compound 4 (R = 2-decytetradeyle)**

![Chemical structure of Compound 4](image)

Yellow orange sticky solid 92% yield.

**Compound 5 (R = 2-hexydecy)**

Compound 4 (R = 2-hexydecy) (1.68 g, 2.00 mmol) was dissolved in anhydrous DCM (20 mL), followed by the addition of thionyl chloride (952 mg, 8.00 mmol). To this mixture anhydrous DMF (1-2 drops) was added at room temperature. The resultant mixture was heated at reflux overnight. The solvent was removed under reduced pressure to afford crude acid chloride. This intermediate compound was dissolved in anhydrous DCM (20 mL) then anhydrous AlCl₃ (1.067 g, 8.00 mmol) was added carefully at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight, then slowly quenched by 10% HCl solution, extracted with CHCl₃ (30 mL × 2). The combined organic phase was washed with 10% HCl (50 mL × 1) and brine (50 mL × 1). The organic phase was dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane : DCM = 5:1) to afford compound 5 (R = 2-hexydecy) (564 mg) as a dark blue solid in 35% yield. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 6.62 (s, 2H), 2.65 (d, J = 6.3 Hz, 4H), 1.28-1.26 (m, 50H), 0.90-0.86 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 181.02, 151.03, 148.25, 146.97, 146.97, 134.67, 131.32, 119.53, 39.90, 34.77, 33.05, 31.91, 29.93, 29.71, 29.69, 29.67, 29.65, 29.37, 26.60, 22.68, 14.09. HR APCI MS: calcd for C₄₈H₆₈O₂S₄ (M⁺), 804.4102; found, 804.4108 (error: 0.75 ppm).

**Compound 5 (R = 2-decytetradeyle)**

¹H NMR (500 MHz, CDCl₃, ppm): δ = 6.64 (s, 2H), 2.66 (d, J = 7.0 Hz, 4H), 1.28-1.25 (m, 82H), 0.89-0.86(m, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 181.44, 151.19, 148.42, 147.06, 140.88, 134.70, 131.45, 119.64, 39.92, 34.82, 33.07, 31.91, 29.90, 29.68, 29.65, 29.64, 29.35, 26.60, 22.68, 14.10. HR APCI MS: calcd for C₄₈H₆₈O₂S₄ (M⁺), 804.4102; found, 804.4108 (error: 0.75 ppm).

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
C_{64}H_{100}O_{2}S_{4} (M^+), 1028.6606; found, 1028.6612 (error: 0.58 ppm).

**Compound FCPDT-C16**

Compound 5 (R = 2-hexyldecyl) (403 mg, 0.50 mmol) and malononitrile (0.13 mL, 2.00 mmol) were dissolved in chlorobenzene (10 mL) under nitrogen atmosphere and then TiCl₄ (0.23 mL, 2.00 mmol) and pyridine (0.33 mL, 4.00 mmol) were slowly added at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. After adding methanol (10 mL) the crude compound formed as a green precipitate. This crude product was further purified by column chromatography (silica gel, DCM) to give a green solid (305 mg, 68%). ¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.04 (s, 2H), 2.72 (d, J = 11.2 Hz, 4H), 1.28-1.26 (m, 50H), 0.90-0.86 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 153.28, 150.38, 148.58, 142.82, 140.63, 135.97, 129.61, 121.68, 113.66, 112.47, 39.91, 35.15, 33.12, 31.90, 29.95, 29.60, 29.31, 26.55, 26.51, 22.67, 22.66, 14.11, 14.08. HR APCI MS: calcd for C_{54}H_{68}N_{4}S_{4} (M⁺), 900.4327; found, 900.4332 (error: 0.56 ppm).

**Compound FCPDT-C24**

¹H NMR (500 MHz, CDCl₃, ppm): δ = 7.05 (s, 2H), 2.71 (d, J = 11.2 Hz, 4H), 1.27-1.26 (m, 82H), 0.90-0.85 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 153.59, 150.18, 148.62, 142.85, 140.60, 135.99, 129.71, 121.67, 113.71, 112.53, 39.91, 35.14, 33.08, 31.92, 29.93, 29.70, 29.67, 29.64, 29.37, 29.35, 26.54, 22.68, 14.11. HR APCI MS: calcd for C_{70}H_{100}N_{4}S_{4} (M⁺), 1124.6831; found, 1124.6836 (error: 0.44 ppm).
2. UV-vis absorption spectra

![UV-vis absorption spectra](image)

Fig. S1 UV-vis-NIR absorption spectra of FCPDT-C16 and FCPDT-C24 in chloroform (concentration $c = 10^{-5}$ M).

3. Cyclic voltammograms and differential pulse voltammograms

![Cyclic voltammograms](image)

Fig. S2 Cyclic voltammograms and differential pulse voltammograms of FCPDT-C16 and FCPDT-C24 in dry dichloromethane containing 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte, AgCl/Ag as the reference electrode, Au as the working electrode, Pt wire as the counter electrode, and a scan rate of 50 mV s$^{-1}$. The potential was externally calibrated against the ferrocene/ferrocenium couple.
Table S1 Summary of Electrochemical Properties of Compound FCPDTa

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{ox , onset}}$ (V)</th>
<th>$E_{\text{red , onset}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCPDT-C16</td>
<td>0.51</td>
<td>-0.92</td>
<td>-5.31</td>
<td>-3.88</td>
<td>1.43</td>
</tr>
<tr>
<td>FCPDT-C24</td>
<td>0.51</td>
<td>-0.91</td>
<td>-5.31</td>
<td>-3.89</td>
<td>1.42</td>
</tr>
</tbody>
</table>

a HOMO and LUMO energy levels were calculated according to the equations HOMO = - (4.8 + $E_{\text{ox \, onset}}$) eV and LUMO = - (4.8 + $E_{\text{red \, onset}}$) eV, where $E_{\text{ox \, onset}}$ and $E_{\text{red \, onset}}$ are the onset potential of the first oxidation and reduction wave, respectively. 4.8 eV in these equations is the energy level of ferrocene/ferrocenium (Fc+/Fc) below the vacuum level.3

4. Thermogravimetric analysis curves

Fig. S3 Thermogravimetric analysis curves of compound FCPDT-C16 and FCPDT-C24 recorded under N2 at a heating rate of 10 °C min⁻¹.
5. Differential scanning calorimetry curves

Fig. S4 Differential scanning calorimetry curves of FCPDT-C16 and FCPDT-C24 recorded under N₂ at a heating rate of 10 °C min⁻¹ (Cr: Crystal, LC: Liquid crystal, Iso: Isotropic phase). The isotropic temperature for FCPDT-C24 can not be observed from DSC curve, but can be determined by polarizing optical microscopy.
6. Variable-temperature powder X-ray diffraction data

**Fig. S5** Variable-temperature powder XRD patterns for FCPDT-16 and FCPDT-24.
7. Polarizing optical microscope (POM) images

**Fig. S6** POM images of FCPDT-C16: (a) heating at 60 °C; (b) heating at 140 °C; (c) heating at 160 °C; (d) heating at 180 °C; (e) cooling from isotropic phase at 190 °C; (f) cooling at 150 °C; (g) cooling at 120 °C; (h) cooling at 90 °C. The scale bar is same for all of images.

**Fig. S7** POM images of FCPDT-C24: (a) heating at 160 °C; (b) cooling from isotropic phase at 140 °C; (c) cooling at 120 °C; (d) cooling at 45 °C. The scale bar is same for all of images.
8. OFET device data of FCPDT-C24

Fig. S8 The transfer (a, b) and output (c, d) curves of FCPDT-C24 thin film (45 nm) on ODTS modified substrates measured in nitrogen.

9. Additional AFM images

Fig. S9 AFM images (height image) of the thin films of FCPDT-C16 (left) and FCPDT-C24 (right) deposited by spin-coating on the OTMS treated substrates.
10. References


11. $^1$H and $^{13}$C NMR spectra of all new compounds

$^1$H NMR spectrum of compound 3 (R = hexyldecyl) (500 MHz, CDCl$_3$, RT)

$^{13}$C NMR spectrum of compound 3 (R = hexyldecyl) (125 MHz, CDCl$_3$, RT)
$^1$H NMR spectrum of compound 3 \((R = \text{decyltetradecyl})\) \((500 \text{ MHz, CDCl}_3, \text{RT})\)

$^{13}$C NMR spectrum of compound 3 \((R = \text{decyltetradecyl})\) \((125 \text{ MHz, CDCl}_3, \text{RT})\)
$^1$H NMR spectrum of compound 5 (R = hexyldecyl) (500 MHz, CDCl$_3$, RT)

$^{13}$C NMR spectrum of compound 5 (R = hexyldecyl) (125 MHz, CDCl$_3$, RT)
1H NMR spectrum of compound 5 (R = decyltetradecyl) (500 MHz, CDCl3, RT)

13C NMR spectrum of compound 5 (R = decyltetradecyl) (125 MHz, CDCl3, RT)
$^1$H NMR spectrum of compound **FCPDT-C16** (500 MHz, CDCl$_3$, RT)

$^{13}$C NMR spectrum of compound **FCPDT-C16** (125 MHz, CDCl$_3$, RT)
$^1$H NMR spectrum of compound **FCPDT-C24** (500 MHz, CDCl$_3$, RT)

$^{13}$C NMR spectrum of compound **FCPDT-C24** (125 MHz, CDCl$_3$, RT)