Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

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

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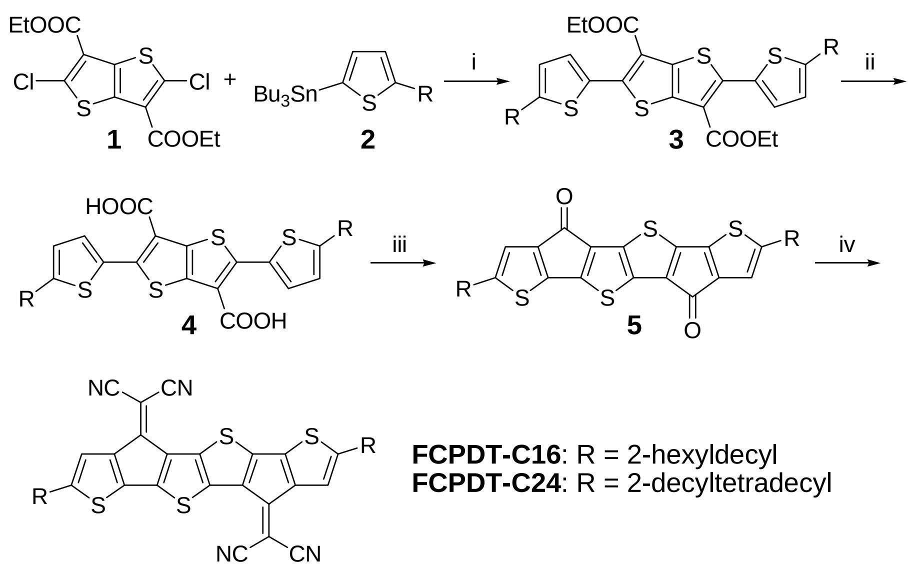
1. Experimental Section

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 CaH_2. Anhydrous toluene and THF were distilled from sodium benzophenone immediately prior to use. The ^1H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ 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-TOFmass 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 SiO_2/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 N_2.

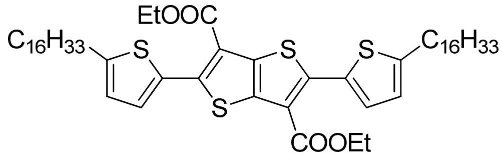
Diethyl 2,5-dichlorothieno[3,2-b]thiophene-3,6-dicarboxylate **1**[1] and the tin complex **2**[2] were prepared by following the literature procedures. The synthetic route to **FCPDT-C16** and **FCPDT-C24** is shown as Scheme S1 (same to Scheme 1 in the main text).



Scheme S1. Synthetic route of **FCPDT-C16** and **FCPDT-C24**. *Reagents and conditions*: (i) $Pd(PPh_3)_4$, toluene/DMF, 120 °C, 24h, 82~85%; (ii) NaOH, MeOH/THF, reflux, quantitative; (iii) (a) $SOCl_2$, dry dichloromethane, reflux; (b) $AlCl_3$, dry dichloromethane, 0 °C - rt., 30~50%; (iv) malononitrile, pyridine, $TiCl_4$, chlorobenzene, 0 °C - rt., 60~70%.

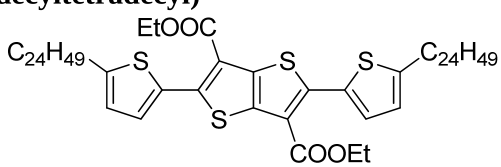
1.2. Detailed synthetic procedures and characterization data

Compound 3 (R = 2-hexyldecyl)



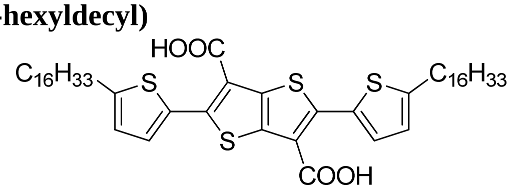
A mixture of compounds **1** (706 mg, 2.00 mmol), **2** (R = 2-hexyldecyl) (4.78 g, 8.00 mmol) and catalyst $Pd(PPh_3)_2Cl_2$ (231 mg, 5 mol%) in anhydrous DMF (2 mL) and toluene (10 mL) was degassed by three freeze–pump–thaw cycles. The mixture was heated at reflux under argon overnight. The mixture was cooled to room temperature and extracted with $CHCl_3$ (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 Na_2SO_4 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. ^{1}H NMR (500 MHz, $CDCl_3$, 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). ^{13}C NMR (125 MHz, $CDCl_3$, 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 $C_{52}H_{80}O_4S_4$ (M^+), 896.4939; found, 896.4934 (error: -0.56 ppm).

Compound 3 (R = 2-decyltetradecyl)



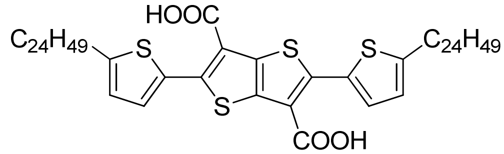
Yellow orange oil, 84% yield.
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.42 (d, *J* = 6.3Hz, 2H), 6.76 (d, *J* = 6.3 Hz, 2H), 4.40 (q, *J* = 12.0 Hz, 4H), 2.78 (d, *J* = 11.0 Hz, 4H), 1.41 (t, *J* = 11.8 Hz, 6H), 1.31-1.26 (m, 82H), 0.90-0.85 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 162.00, 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 $C_{68}H_{112}O_4S_4$ (M^+), 1120.7443; found, 1120.7438 (error: -0.45 ppm).

Compound 4 (R = 2-hexyldecyl)



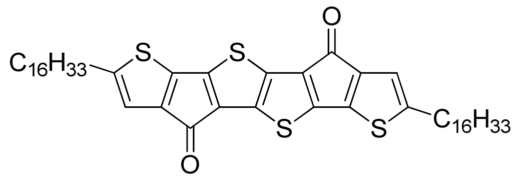
Compound **3** (R = 2-hexyldecyl) (897 mg, 1.0 mmol) was dissolved in methanol and THF (30 mL, 1:1 v/v), followed by the addition of sodium hydroxide (400 mg). This mixture was heated at reflux overnight. During this period the orange solid was formed. The solvent was removed under reduced pressure after 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-decyltetradecyl)



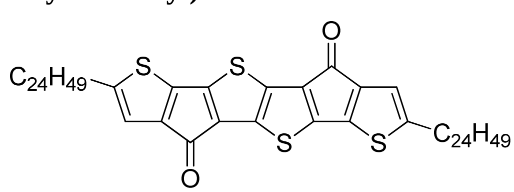
Yellow orange sticky solid 92% yield.

Compound 5 (R = 2-hexyldecyl)



Compound **4** (R = 2-hexyldecyl) (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 $AlCl_3$ (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 $CHCl_3$ (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 Na_2SO_4 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-hexyldecyl) (564 mg) as a dark blue solid in 35% yield. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 6.62 (s, 2H), 2.65 (d, *J* = 6.3Hz, 4H), 1.28-1.26 (m, 50H), 0.90-0.86 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 181.02, 151.03, 148.25, 146.97, 140.80, 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 $C_{48}H_{68}O_2S_4$ (M^+), 804.4102; found, 804.4108 (error: 0.75 ppm).

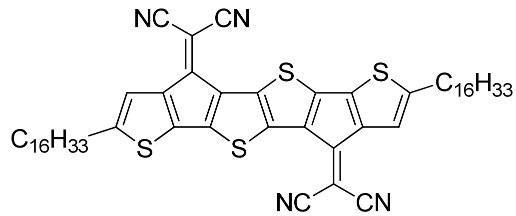
Compound 5 (R = 2-decytetradecyl)



^1H NMR (500 MHz, $CDCl_3$, 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). ^{13}C NMR (125 MHz, $CDCl_3$, 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

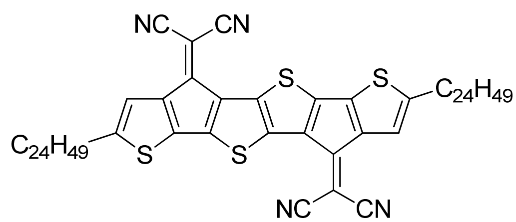
$C_{64}H_{100}O_2S_4$ (M^+), 1028.6606; found, 1028.6612 (error: 0.58 ppm).

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 $TiCl_4$ (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, $CDCl_3$, 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). ^{13}C NMR (125 MHz, $CDCl_3$, 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, 31.85, 29.95, 29.60, 29.31, 26.55, 26.51, 22.67, 22.66, 14.11, 14.08. HR APCI MS: calcd for $C_{54}H_{68}N_4S_4$ (M^+), 900.4327; found, 900.4332 (error: 0.56 ppm).

Compound FCPDT-C24



^1H NMR (500 MHz, $CDCl_3$, 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). ^{13}C NMR (125 MHz, $CDCl_3$, 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 $C_{70}H_{100}N_4S_4$ (M^+), 1124.6831; found, 1124.6836 (error: 0.44 ppm).

2. UV-vis absorption spectra

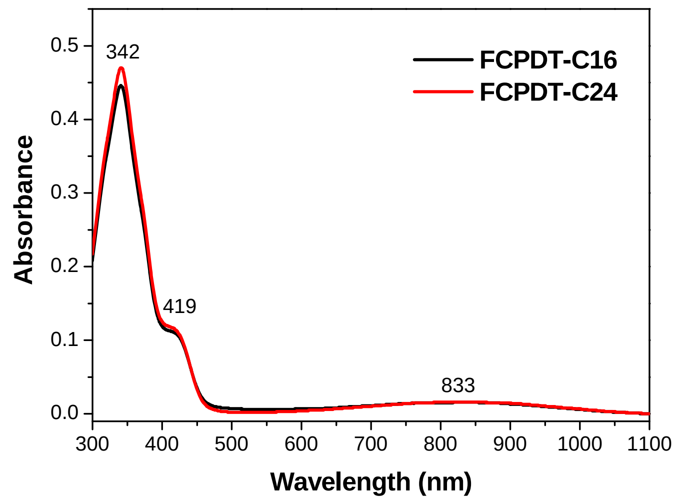


Fig. S1 UV-vis-NIR absorption spectra of **FCPDT-C16** and **FCPDT-C24** in chloroform (concentration $c = 10^{-5}$ M).

3. Cyclic voltammograms and differential pulse voltammograms

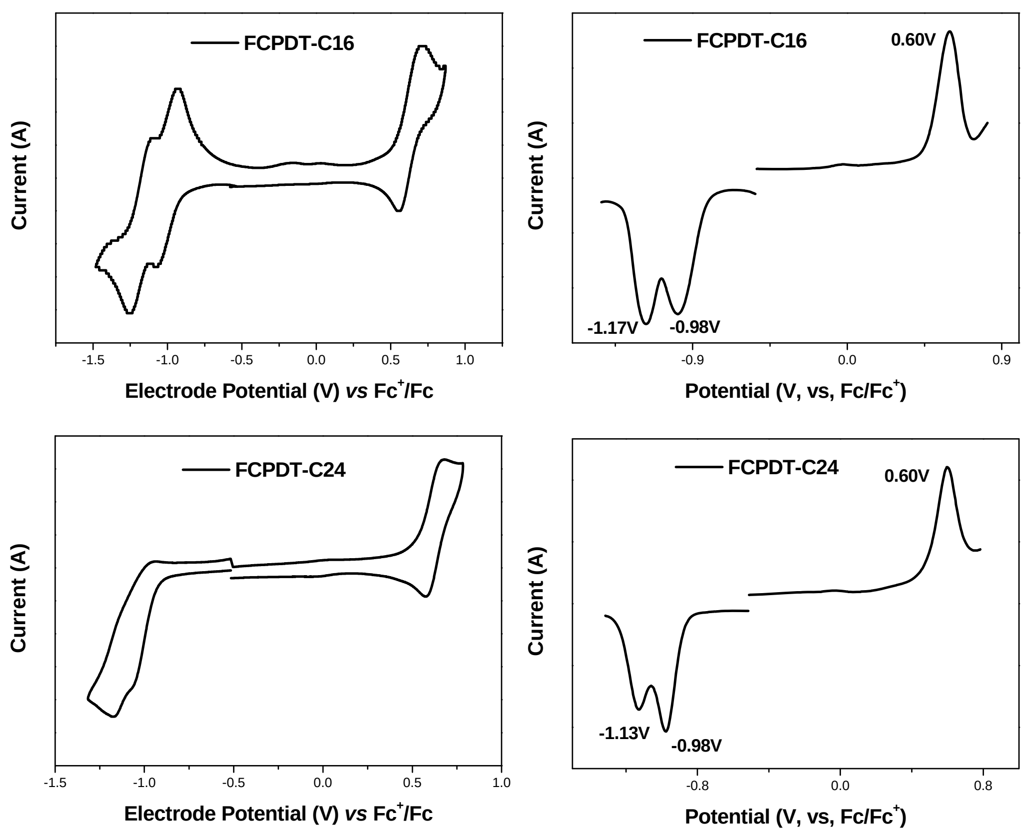


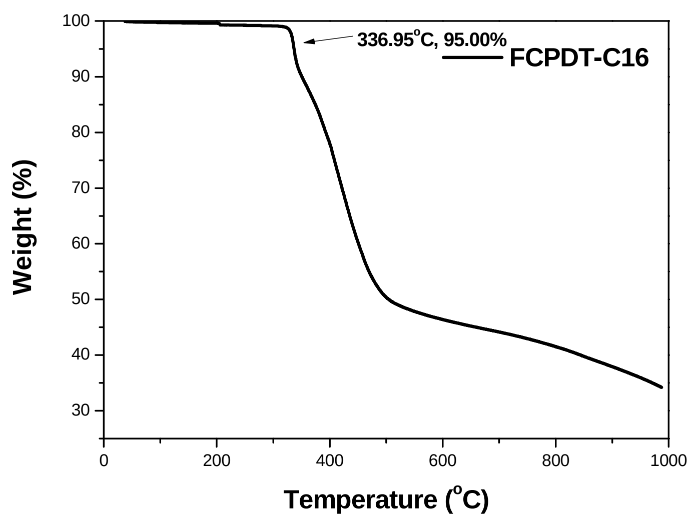
Fig. S2 Cyclic voltammograms and differential pulse voltammograms of **FCPDT-C16** and **FCPDT-C24** in dry dichloromethane containing 0.1 M Bu_4NPF_6 as the supporting electrolyte, AgCl/Ag as the reference electrode, Au as the working electrode, Pt wire as the counter electrode, and a scan rate of 50 mV s^{-1}. The potential was externally calibrated against the ferrocene/ferrocenium couple.

Table S1 Summary of Electrochemical Properties of Compound **FCPDT**[a]

	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	HOMO (eV)	LUMO (eV)	*Eg* (eV)
FCPDT-C16	0.51	-0.92	-5.31	-3.88	1.43
FCPDT-C24	0.51	-0.91	-5.31	-3.89	1.42

[a] HOMO and LUMO energy levels were calculated according to the equations HOMO = - (4.8 + E_{ox}^{onset}) eV and LUMO = - (4.8 + E_{red}^{onset}) eV, where E_{ox}^{onset} and E_{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



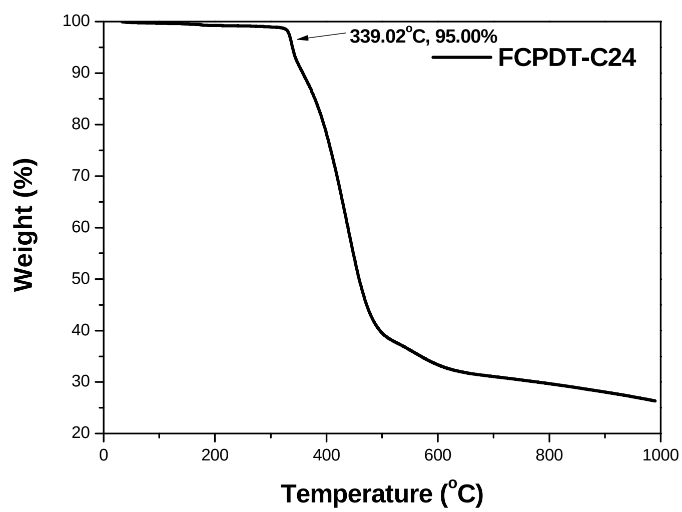
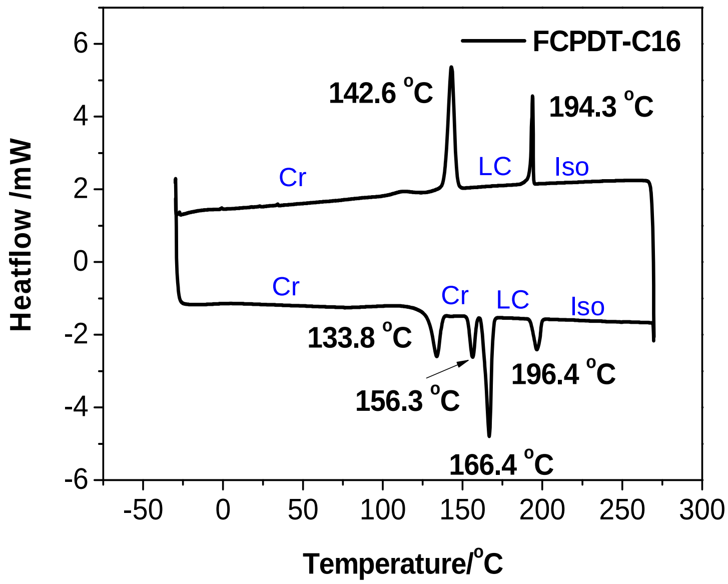


Fig. S3 Thermogravimetric analysis curves of compound **FCPDT-C16** and **FCPDT-C24** recorded under N_2 at a heating rate of 10 °C min^{-1}.

5. Differential scanning calorimetry curves



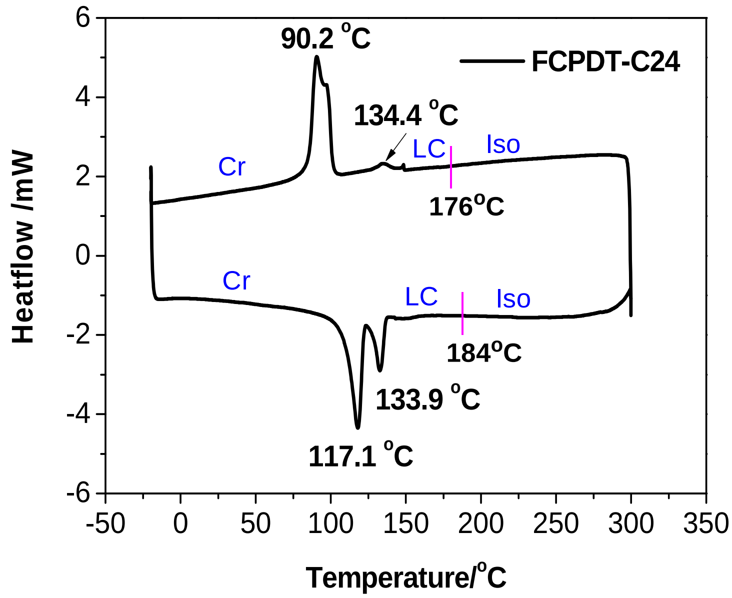


Fig. S4 Differential scanning calorimetry curves of **FCPDT-C16** and **FCPDT-C24** recorded under N_2 at a heating rate of 10 °C min^{-1} (Cr: Crystal, LC: Liquid crystal, Iso: Isotropic phase). The isotropic temperature for **FCPDT-C24** can not be observed from DSC curve, but can be determined by polarizing optical microscopy.

6. Variable-temperature powder X-ray diffraction data

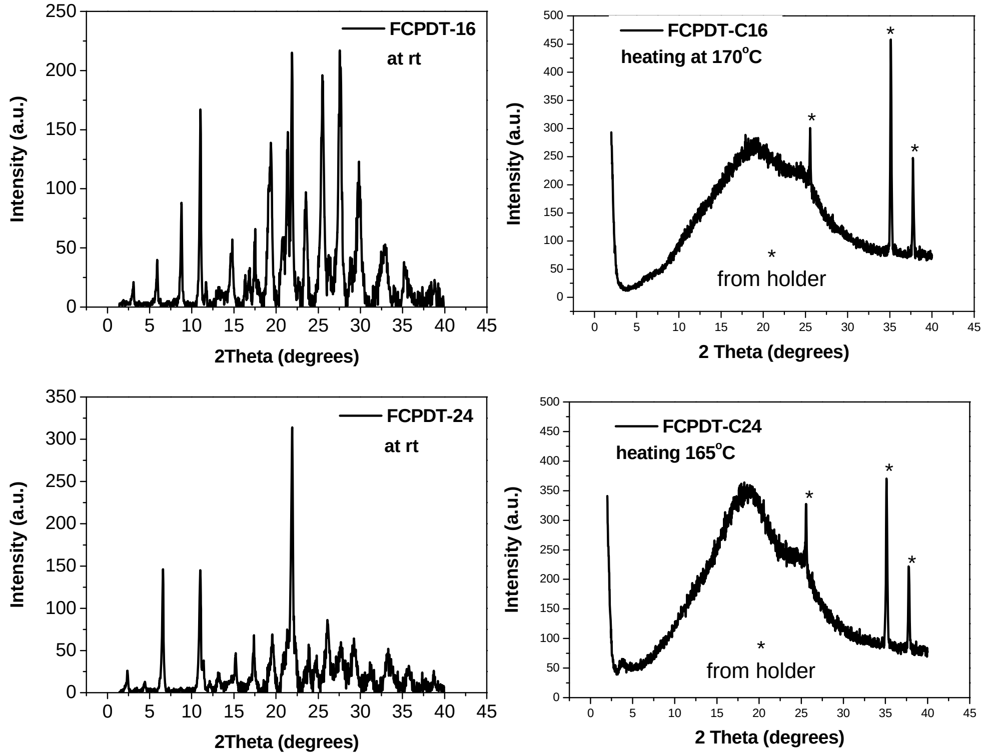


Fig. S5 Variable-temperature powder XRD patterns for **FCPDT-16** and **FCPDT-24**.

7. Polarizing optical microscope (POM) images

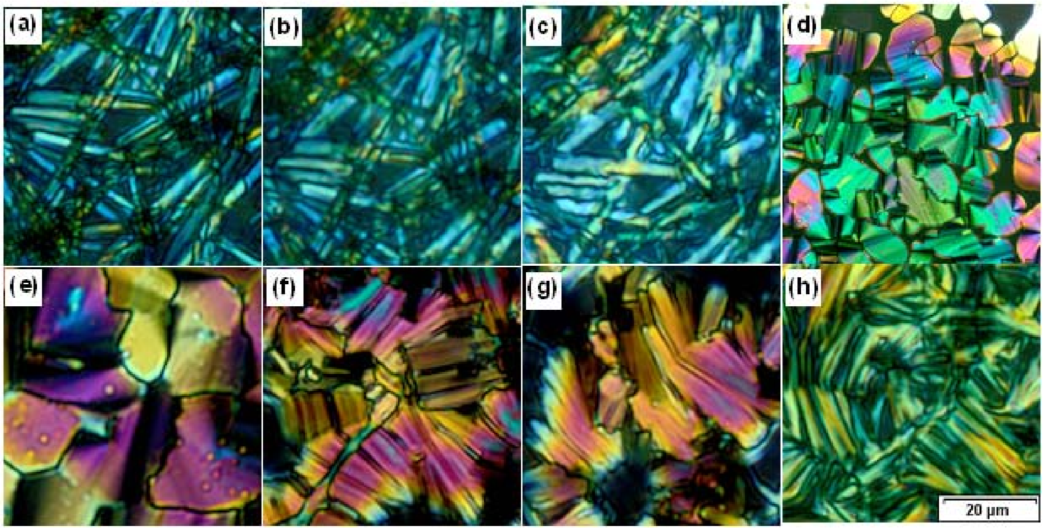


Fig. S6 POM images of **FCPDT-C16**: (a) heating at 60 °C; (b) heating at 140 °C; (c) heating at 160 °C; (d) heating at 180 °C; (e) cooling from isotropic phase at 190 °C; (f) cooling at 150 °C; (g) cooling at 120 °C; (h) cooling at 90 °C. The scale bar is same for all of images.

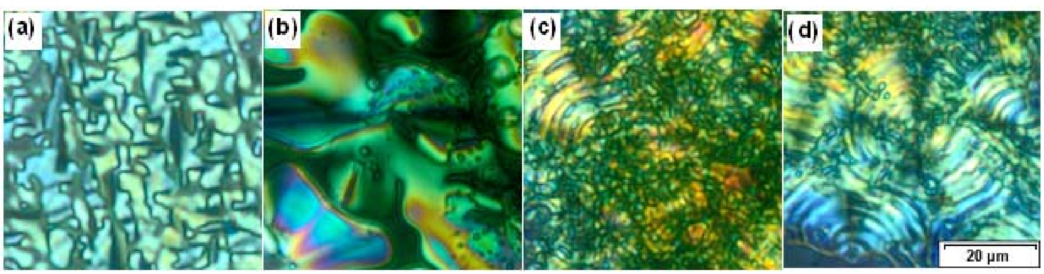


Fig. S7 POM images of **FCPDT-C24**: (a) heating at 160 °C; (b) cooling from isotropic phase at 140 °C; (c) cooling at 120 °C; (d) cooling at 45 °C. The scale bar is same for all of imgaes.

8. OFET device data of FCPDT-C24

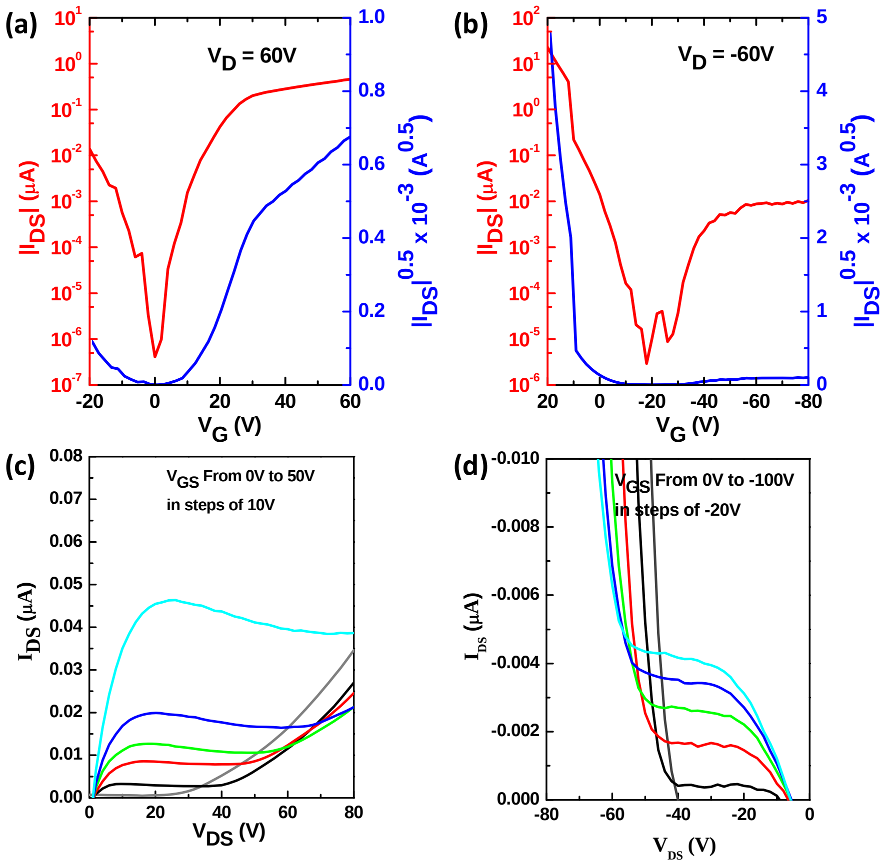


Fig. S8 The transfer (a, b) and output (c, d) curves of **FCPDT-C24** thin film (45 nm) on ODTS modified substrates measured in nitrogen.

9. Additional AFM images

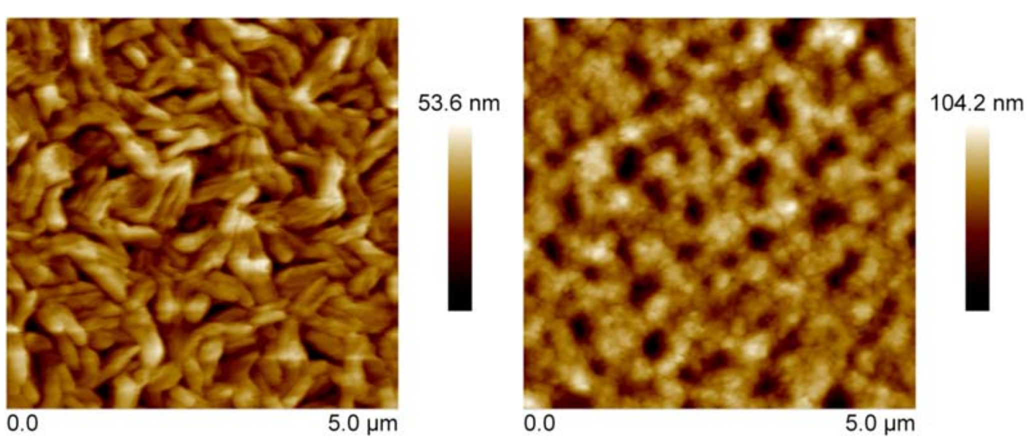


Fig. S9 AFM images (height image) of the thin films of **FCPDT-C16** (left) and **FCPDT-C24** (right) deposited by spin-coating on the OTMS treated substrates.

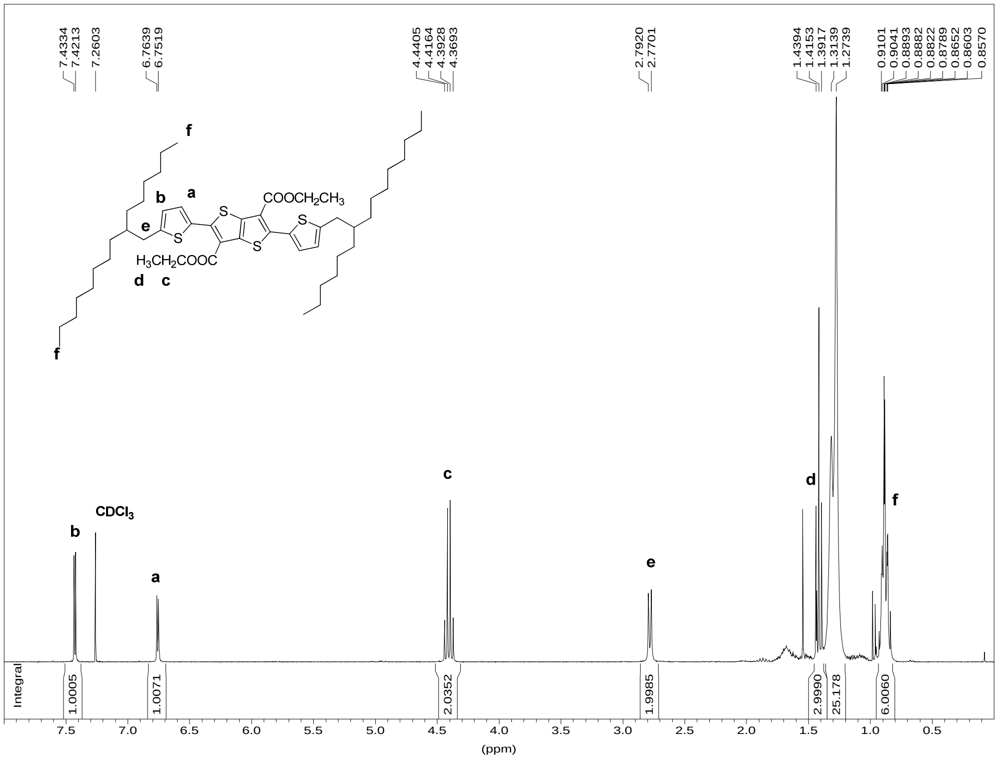
10. References

(1) S. Ellinger, U. Ziener, U. Thewalt, K. Landfester and M. Möller, *Chem. Mater*. 2007, **19**, 1070.

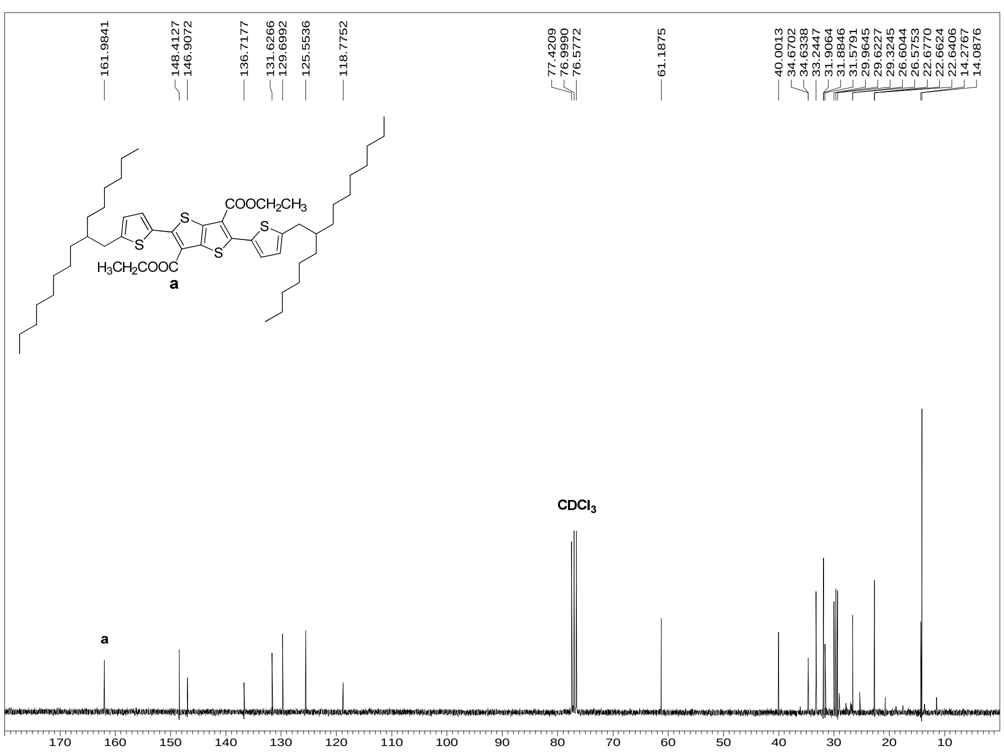
(2) T. Kunz and P. Knochel, *Chem. Eur. J.* 2011, **17**, 866.

(3) (a) A. J. Bard, L. R. Faulkner, Electrochemical Methods: *Fundamentals and Applications*, Wiley, New York, 1984; (b) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bassler, M. Porsch, J. Daub, *Adv. Mater*. 1995, **7**, 551.

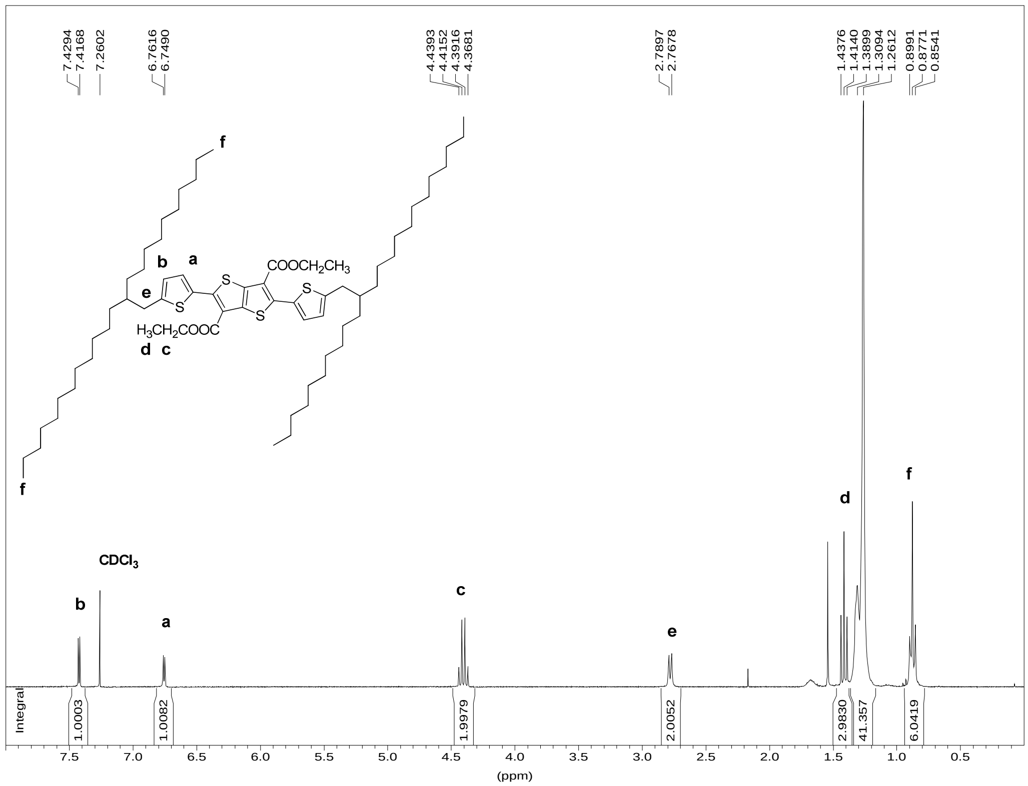
11. ^{1}H and ^{13}C NMR spectra of all new compounds



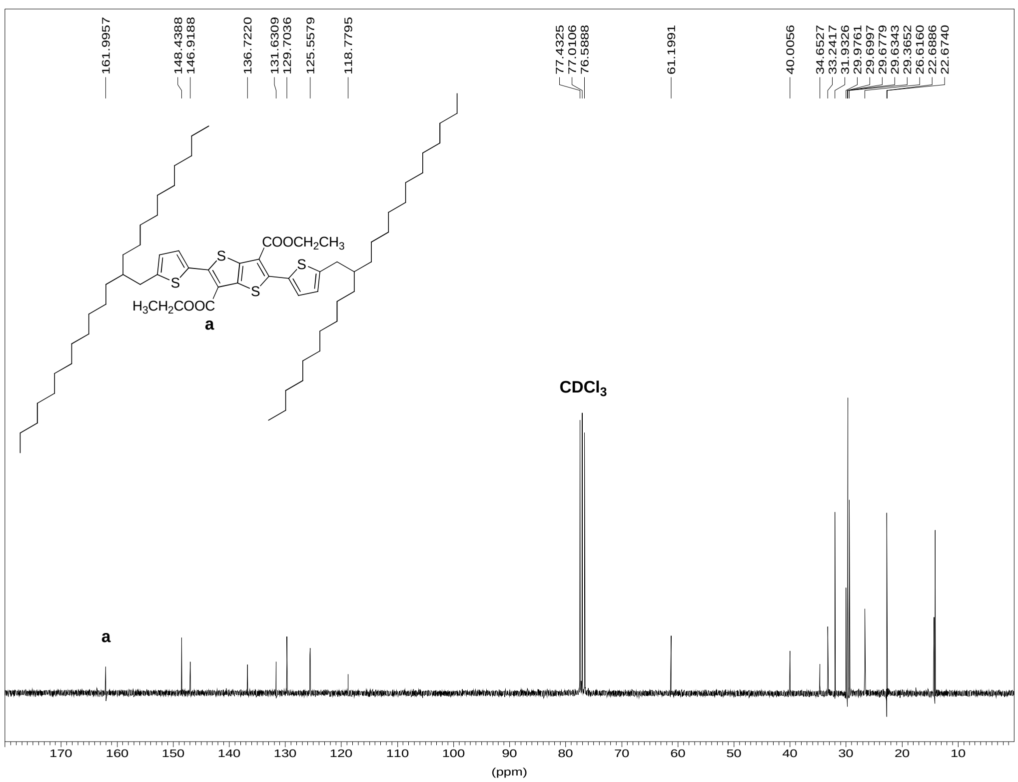
^{1}H NMR spectrum of compound **3** (R = hexyldecyl) (500 MHz, $CDCl_3$, RT)



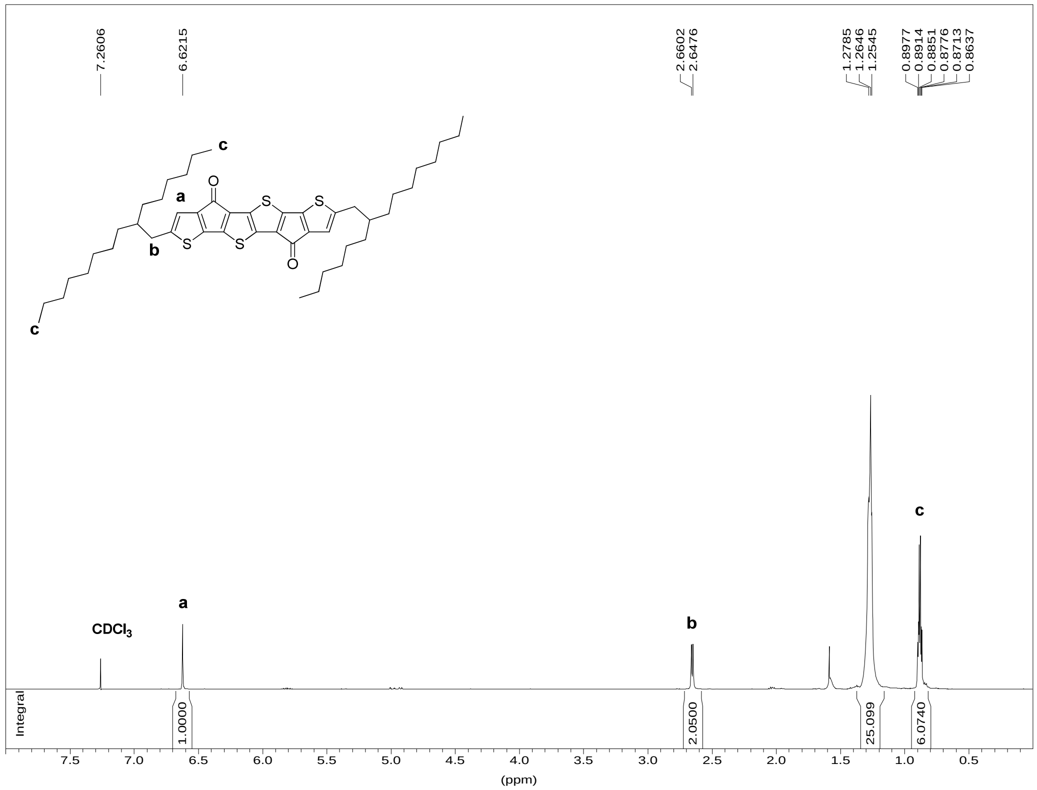
^{13}C NMR spectrum of compound **3** (R = hexyldecyl) (125 MHz, $CDCl_3$, RT)



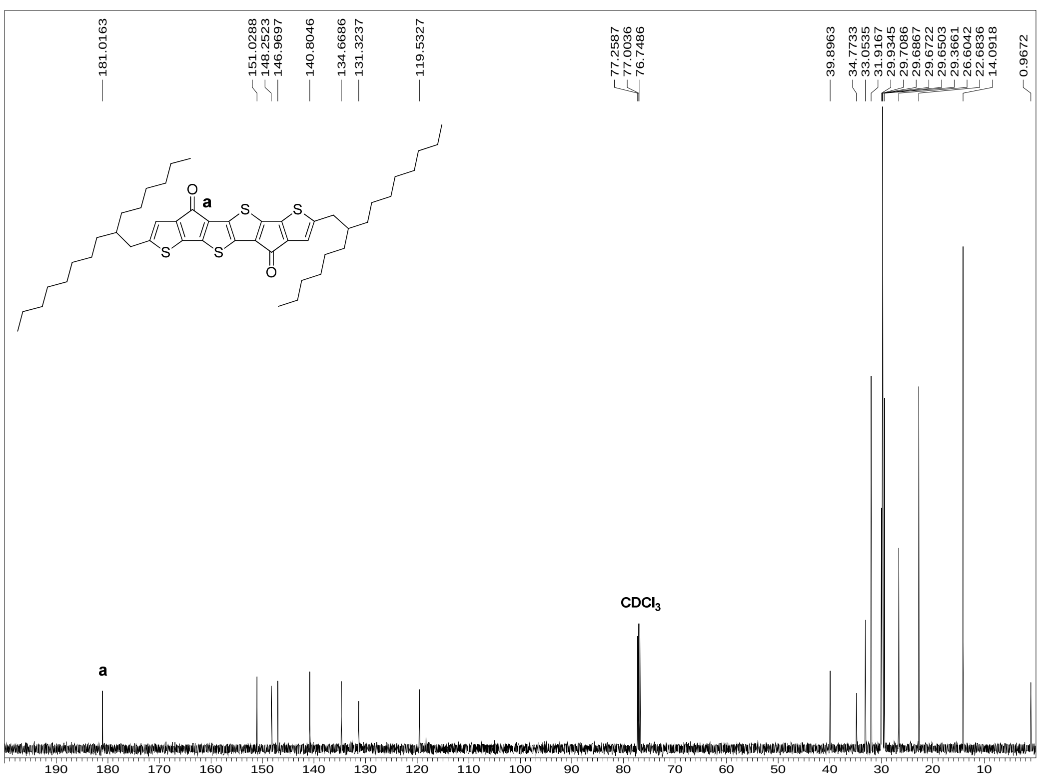
^{1}H NMR spectrum of compound **3** (R = decyltetradecyl) (500 MHz, $CDCl_3$, RT)



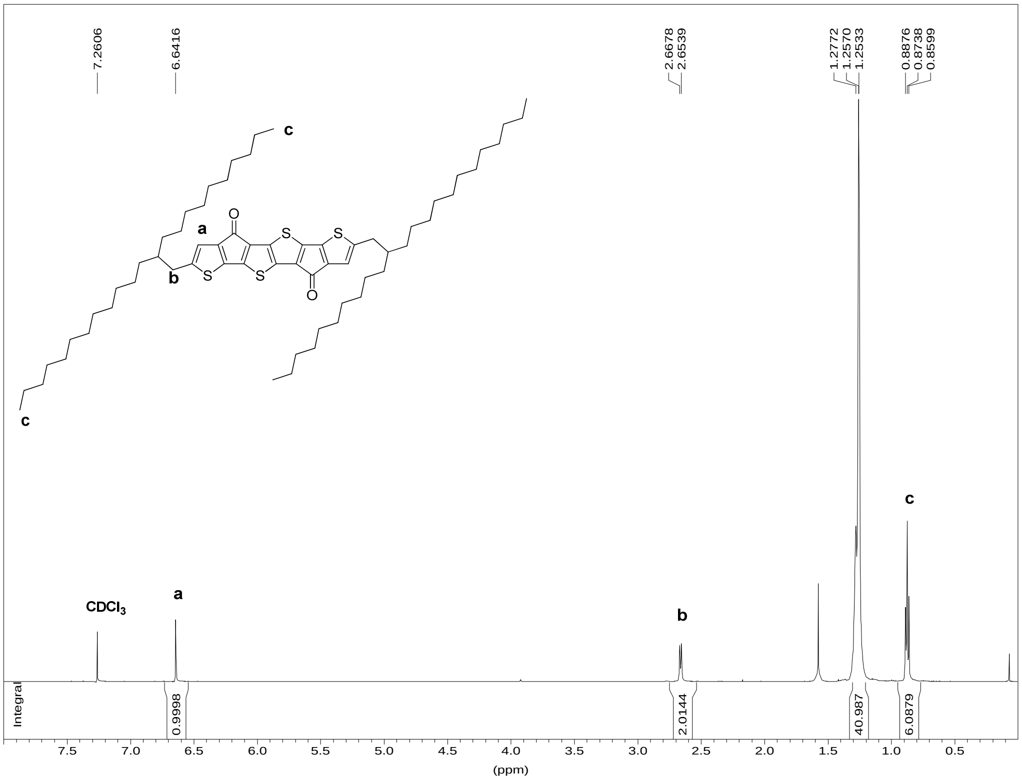
^{13}C NMR spectrum of compound **3** (R = decyltetradecyl) (125 MHz, $CDCl_3$, RT)



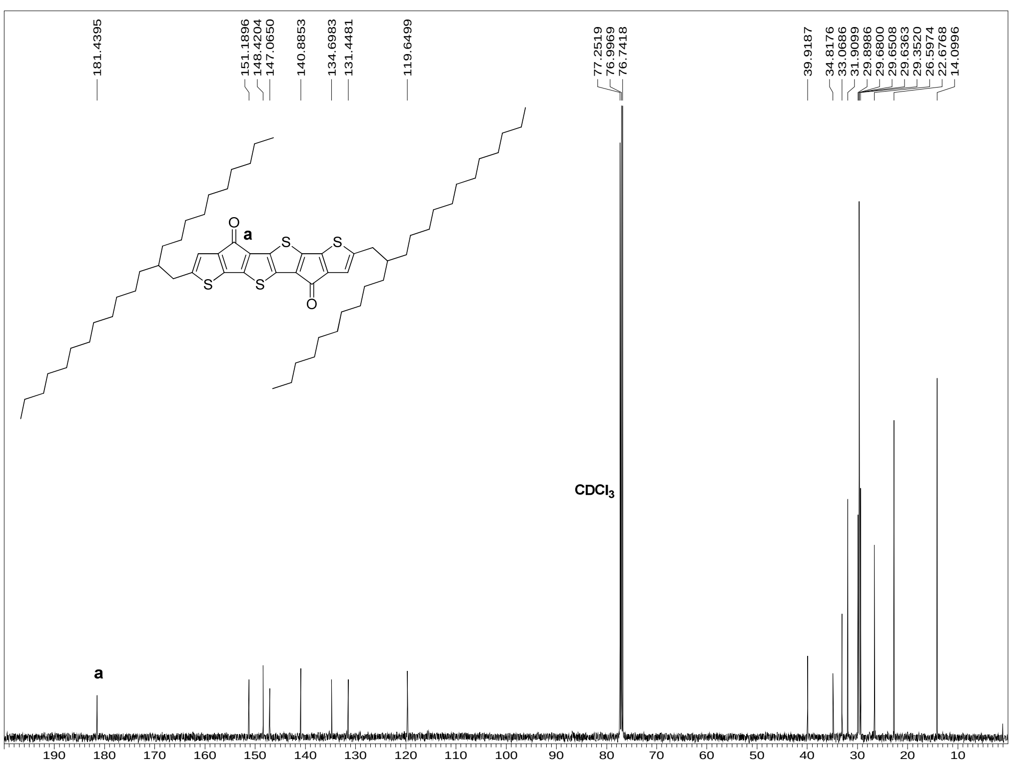
^{1}H NMR spectrum of compound **5** (R = hexyldecyl) (500 MHz, $CDCl_3$, RT)



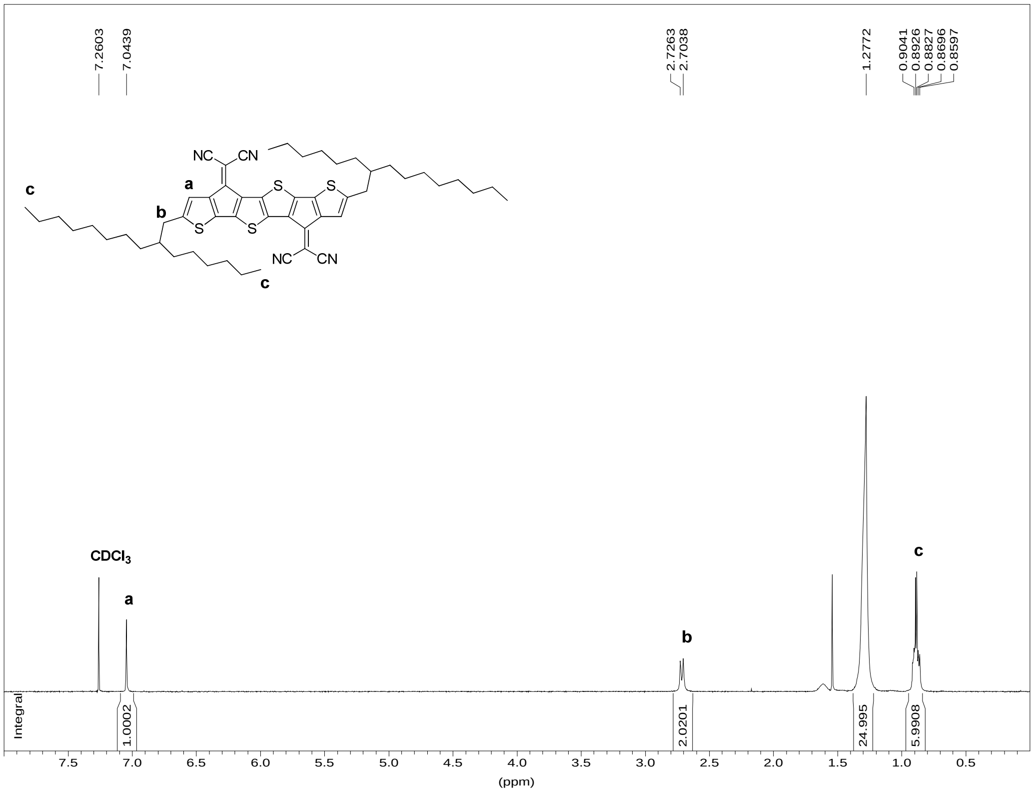
^{13}C NMR spectrum of compound **5** (R = hexyldecyl) (125 MHz, $CDCl_3$, RT)



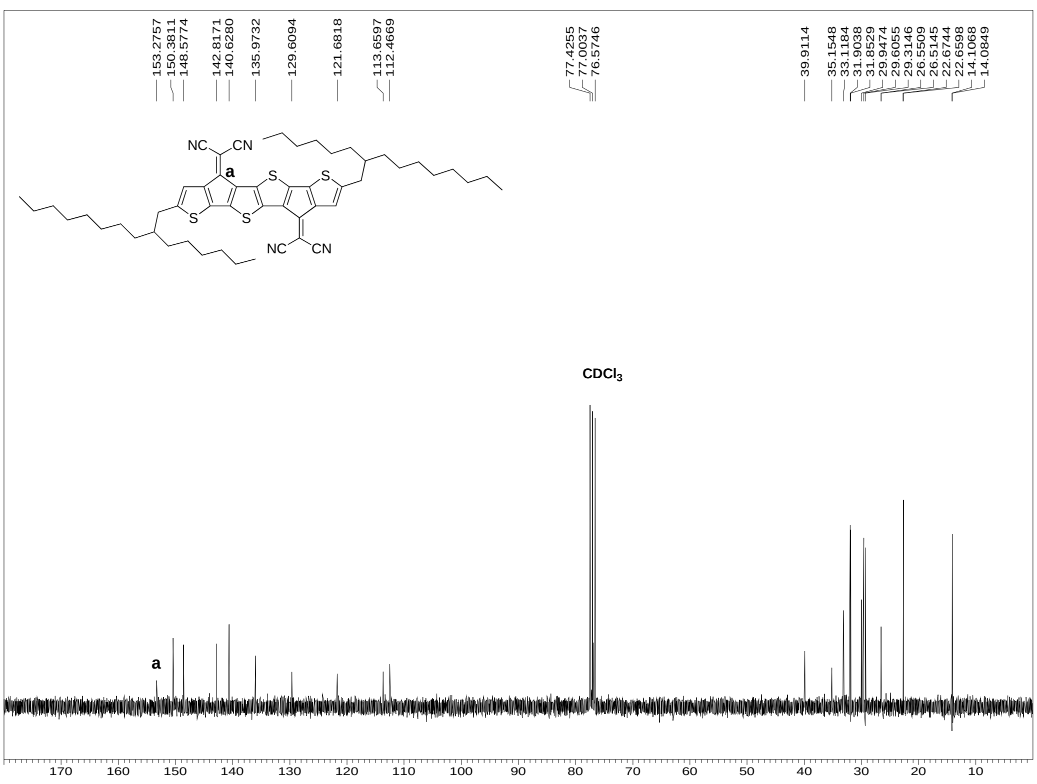
^{1}H NMR spectrum of compound **5** (R = decyltetradecyl) (500 MHz, $CDCl_3$, RT)



^{13}C NMR spectrum of compound **5** (R = decyltetradecyl) (125 MHz, $CDCl_3$, 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)

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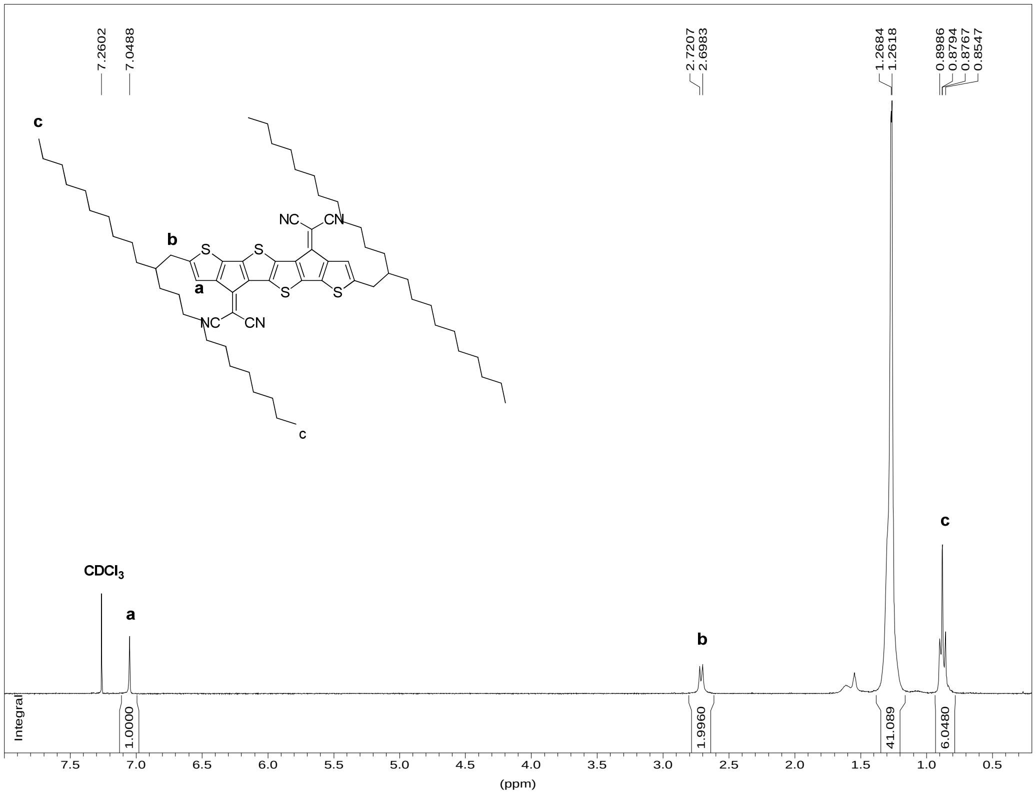
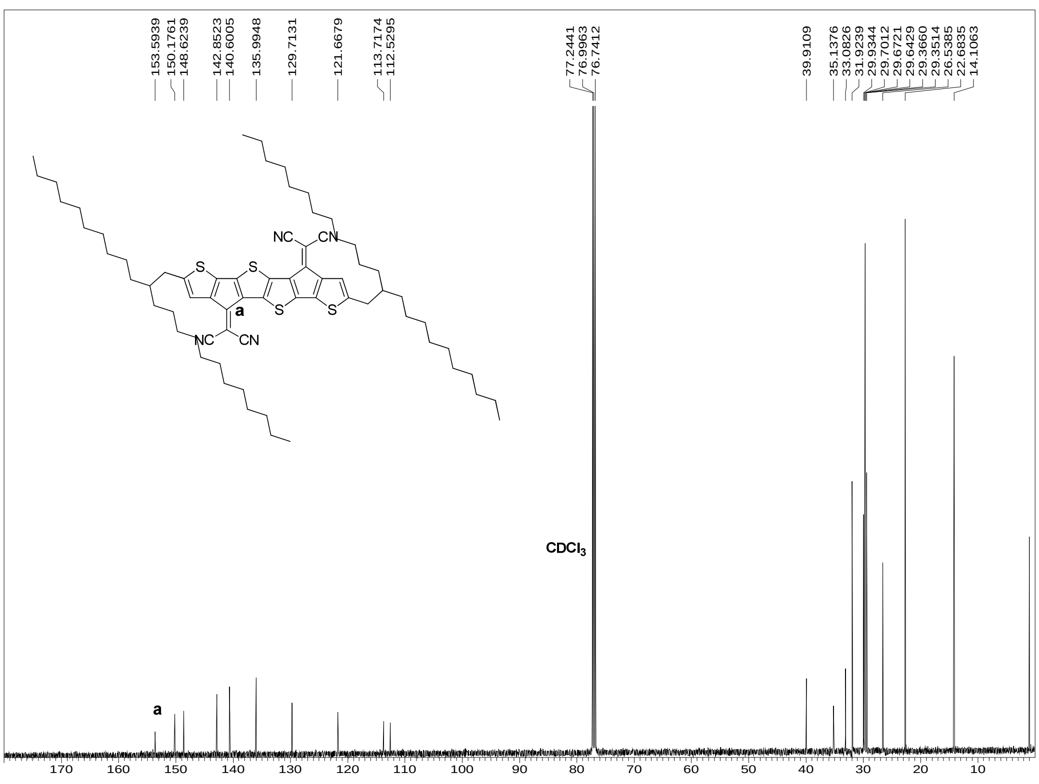


^{1}H NMR spectrum of compound **FCPDT-C24** (500 MHz, $CDCl_3$, RT)



^{13}C NMR spectrum of compound **FCPDT-C24** (125 MHz, $CDCl_3$, RT)