Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Fluorinated Heptacyclic Carbazole-Based Ladder-Type Acceptors with Aliphatic Side Chains for Efficient Fullerene-Free Organic Solar Cells

Tsung-Wei Chen [a,b], Yu-Tang Hsiao [a,b], You-Wei Lin [a,b], Chia-Chih Chang[a,b], Wei-Tsung Chuang[c], Yongfang Li[d] and Chain-Shu Hsu[a,b]*

[a] *Department of Applied Chemistry, National Chiao Tung University, 1001 University Rd., Hsinchu, Taiwan 30010.*
E-mail: cshsu@mail.nctu.edu.tw
[b] *Center for Emergent Functional Matter Science, National Chiao Tung University, 1001 University Rd., Hsinchu, Taiwan 30010.*
[c] *National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu, 30076, Taiwan*
[d] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
University of Chinese Academy of Sciences, Beijing 100049, China
Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

Contents

Experimental section

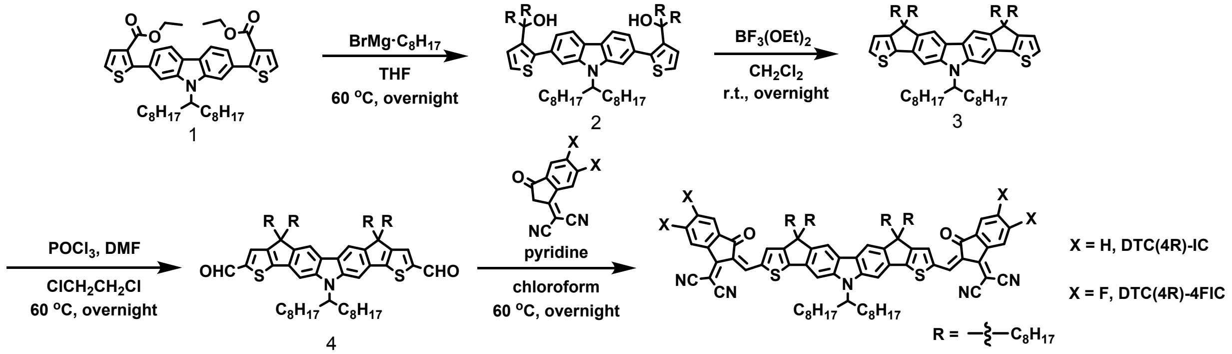

Figure S1. Synthetic route of NFAs

Synthesis of 1 to 3: Compounds **1-3** were synthesized according to our previous publication.[1]

Synthesis of 4: A mixture of compound **3** (500 mg, 0.48 mmol) and 1,2-dichloroethane (35 mL) was deoxygenated with nitrogen for 30 min and then added a solution of $POCl_3$ (0.23 mL) in DMF (3.31 mL) at 0 °C. After being stirred at 60 °C for 20 hours, the mixture was poured into $Na_2CO_{3(aq)}$ and extracted with CH_2Cl_2. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by column chromatography on silica gel using n-hexane/CH_2Cl_2 (1:1) as eluent to give product 3 as an orange solid (380 mg, 72%).^{1}H NMR (400 MHz, CDCl3): δ 9.94 (s, 2H), 8.03-8.00 (m, 2H), 7.68 (br, 3H), 7.54 (br, 1H), 4.63 (m, 1H), 2.37-2.28 (m, 2H), 2.15-1.95 (m, 10H), 1.44-1.03 (m, 64H), 0.93 (m, 8H), 0.82-0.65 (m, 18H); 13C NMR (400MHz, $CDCl_3$): δ 182.81, 156.00, 152.50, 146.23, 144.88, 142.50, 139.02, 134.94, 134.55, 130.63, 123.75, 122.33, 114.20, 113.83, 103.51, 100.96, 57.02, 53.42, 39.60, 33.64, 31.69, 31.66, 30.26, 30.02, 29.31, 29.23, 29.18, 29.07, 26.90, 24.38, 22.51, 13.96 (Multiple carbon peaks result from phenomenon of atropisomerism); HRMS (FAB) Calcd for $C_{73}H_{111}NO_2S_2$ $[M]^+$, 1097.8051; found, 1097.8042.

Synthesis of DTC(4R)-IC: A mixture of compound **4** (300 mg, 0.27 mmol), 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (262 mg, 1.35 mmol) in $CHCl_3$ (23 mL) was deoxygenated with nitrogen for 30 minutes. Pyridine (0.3 mL) was added and refluxed for 24 hours. After the mixture was cooled to room temperature, the mixture was poured into water (100 mL) and extracted with CH_2Cl_2. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by column chromatography on silica gel using n-hexane/CH_2Cl_2 (1:1) as eluent to give DTC(4R)-IC as a dark blue solid (110 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03-9.02 (m, 2H), 8.72-8.71 (m, 2H), 8.03-8.00 (m, 2H), 7.96-7.94 (m, 2H), 7.81-7.72 (m, 7H), 7.67 (s, 1H), 4.60 (m, 1H), 2.34-2.26 (m, 2H), 2.16-1.97 (m, 10H), 1.31-1.32 (m, 64H), 0.92 (m, 8H), 0.79 (t, J = 6.8 Hz, 18H); ^{13}C NMR (400MHz, $CDCl_3$): δ 188.61, 188.46, 162.56, 162.47, 160.84, 157.27, 147.61, 143.22, 140.35, 139.98, 139.78, 138.65, 138.46, 138.37, 136.93, 135.53, 135.08, 134.93, 134.28, 125.34, 125.24, 123.92, 123.56, 121.08, 121.00, 115.01, 114.93, 114.66, 114.31, 104.60, 102.00, 77.21, 68.16, 57.37, 53.62, 39.79, 33.57, 31.72, 30.03, 29.69, 29.30, 29.28, 29.24, 29.10, 27.10, 24.50, 22.56, 22.54, 14.00 (Multiple carbon peaks result from phenomenon of atropisomerism); HRMS (FAB) Calcd for $C_{92}H_{119}N_5O_2S_2$ $[M]^+$, 1449.8800; found, 1449.8800.

Synthesis of DTC(4R)-4FIC: A mixture of compound **4** (280 mg, 0.35 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (340 mg, 1.75 mmol) in $CHCl_3$ (25 mL) was deoxygenated with nitrogen for 30 minutes. Pyridine (1 mL) was added and then refluxed for 24 hours. After the mixture was cooled to room temperature, the mixture was poured into water (100 mL) and extracted with CH_2Cl_2. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. After removal (1:2) as eluent to give DTC(4R)-4FIC as a dark blue solid (120 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01-9.00 (m, 2H), 8.58-8.54 (m, 2H), 8.04-8.00 (m, 2H), 7.82 (br, 1H), 7.75-7.68 (m, 5H), 4.60 (m, 1H), 2.32-2.28 (m, 2H), 2.16-1.97 (m, 10H), 1.35-1.13 (m, 64H), 0.90 (m, 8H), 0.79 (t, J = 7.0 Hz, 18H); ^{13}C NMR (400MHz, $CDCl_3$): δ 186.23, 186.06, 163.65, 163.56, 158.65, 157.62, 155.74, 155.61, 153.13, 152.99, 147.82, 143.34, 140.27, 139.90, 139.00, 138.90, 138.82, 136.49, 135.46, 135.01, 134.49, 125.63,124.21, 120.10, 115.09, 114.79, 114.55, 114.44, 112.57, 112.38, 104.81, 102.23, 77.21, 68.67, 57.44, 53.71, 53.66, 39.78, 33.58, 31.71, 30.00, 29.69, 29.30, 29.28, 29.23, 29.10, 27.09, 24.51, 22.57, 22.54, 14.02, 14.00 (Multiple carbon peaks result from phenomenon of atropisomerism); HRMS (FAB) Calcd for $C_{97}H_{115}N_5O_2F_4S_2$ $[M]^+$, 1521.8423; found, 1521.8420.

General Measurement and Characterization : All chemicals were purchased from Aldrich or Acros and used as received unless otherwise specified. Compound 1 was synthesized in accord to our previous publications. ^{1} H and ^{13} C NMR spectra were measured using a Varian 300 MHz instrument spectrometer. Fourier transform infrared (FTIR) spectra were obtained on a Perkin-Elmer One Instrument by preparing KBr Pellets. Differential scanning calorimeter (DSC) was measured on a TA Q200 Instrument and thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C min $^{-1}$. Absorption spectra were collected on a HP8453 UV-vis spectrophotometer. The molecular weight of polymers was measured by the GPC on a Viscotek VE2001GPC, and polystyrene was used as the standard (THF as the eluent). The electrochemical cyclic voltammetry (CV) was conducted on a CH Instruments Model 611D. A carbon glass coated with a thin polymer film was used as the working electrode and Ag/Ag^+ electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dichloromethane was used as the electrolyte. CV curves were calibrated using ferrocene as the standard, whose oxidation potential is set at –4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO = $-(E_{ox}^{onset} - E_{ferrocene}^{onset} + 4.8)$ eV. The LUMO levels of polymer were obtained from the equation LUMO = $-(E_{red}^{onset} - E_{ferrocene}^{onset} + 4.8)$ eV. We respectively performed GIWAXS at TLS13A beamilne and GISAXS at the end stations of the TLS 23A and TPS 25A SWAXS beamlines at the National Synchrotron Radiation Research Center (NSRRC). GISAXS data were obtained from X-rays (15 keV energy, 0.8265 Å wavelength) at an incident angle of 0.2°. All GISAXS data were collected with an area detector (Pilatus) that was rigorously corrected for electronic noise, sample transmission, background scattering, and detector sensitivity. We calibrated the area detector for absolute scattering intensity by using a sample of high-density polyethylene, and with silver behenate for the scattering wavevector (q, defined by $4 \pi \lambda^{-1} \sin\theta$ and the scattering angle 2θ). In-plane scattering profiles were integrated line cuts along the direction q_{xy} at $q_z \approx 0$ nm^{-1} from the corresponding GISAXS patterns. The mapping PL images were performed by laser scanning confocal microscope (SouthPort, JadeMAT) equipped with 532 CW laser and galvo-based scanner. The objective is 100x with NA0.9, for this objective confocal pinhole is set to 50 μm in diameter. The detector is a multialkali photomultiplier tube (Hamamatsu) with photon counting module. The laser source is set to 0.1 mW range on the samples for measurement.

Fabrication and Characterization of OSC Devices: The photovoltaic devices were fabricated as followed: The ITO-coated glass was sequentially sonicated in detergent, DI water, acetone, isopropyl alcohol for 15 minutes, respectively. Next, the substrate was dried with a stream of N_2 flow and treated with UV-ozone for 30 minutes. A thin film of ZnO was deposited by spin-coating followed by thermal annealing at 170 °C in air for 30 min. The chloroform solution with 0.1 v% CN additive in optimal ratio of donor: acceptor =1: 1.3 by weight was spin-coated at 3000rpm for 30 seconds on top of ZnO layer and then thermal-annealed at 140°C for 3 minutes. Finally, the MoO_3 layer (7 nm) and silver anode (150 nm) were deposited by thermal evaporation at a pressure around 10^{-7} torr.

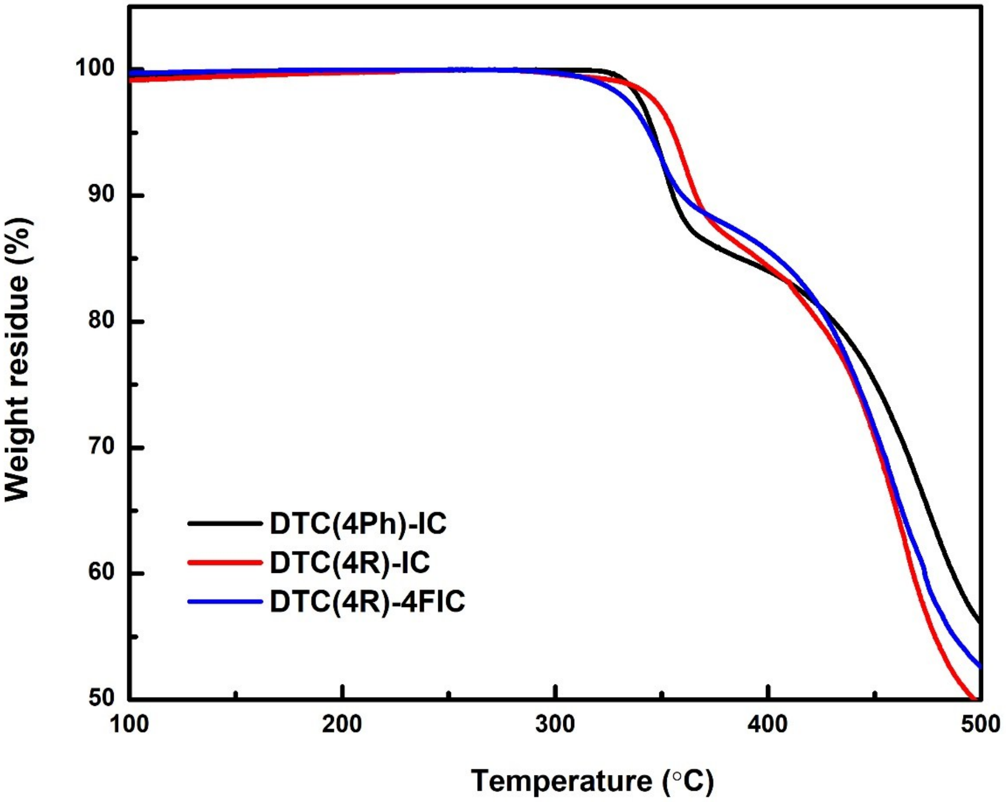

Figure S2. TGA traces of NFAs. The T_d values of DTC(4Ph)-IC, DTC(4R)-IC and DTC(4R)-4FIC were determined to be 346°C, 355°C and 344°C, respectively.

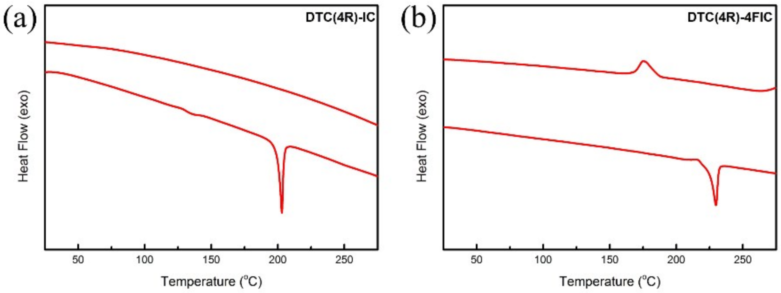

Figure S3. DSC diagrams of NFAs. The T_m values of DTC(4R)-IC and DTC(4R)-4FIC are 203°C and 230°C, respectively.

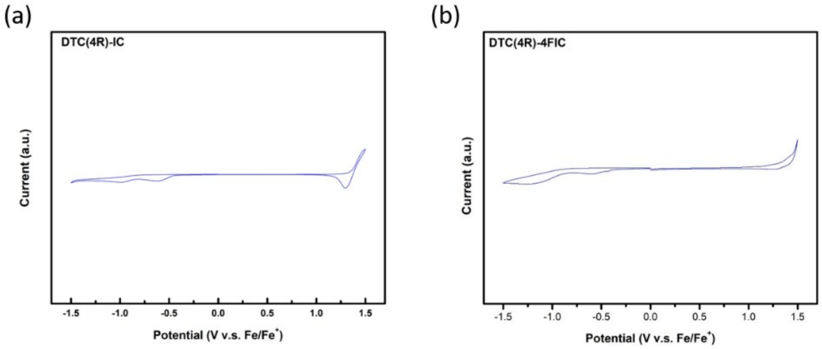

Figure S4. CV diagrams of NFAs. The HOMO/LUMO values of DTC(4R)-IC and DTC(4R)-4FIC are -5.69/-3.63 and -5.79/-3.99.

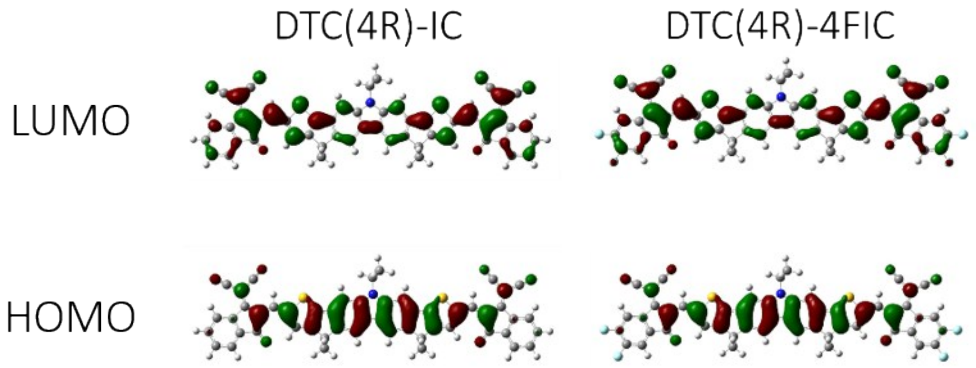

Figure S5. Energy level simulation through B3LYP/6-31G DFT calculation

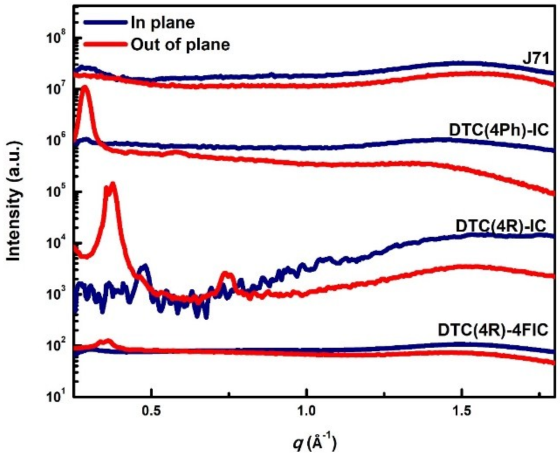

Figure S6. 1D GIWAXS profiles of J71 and NFAs neat films

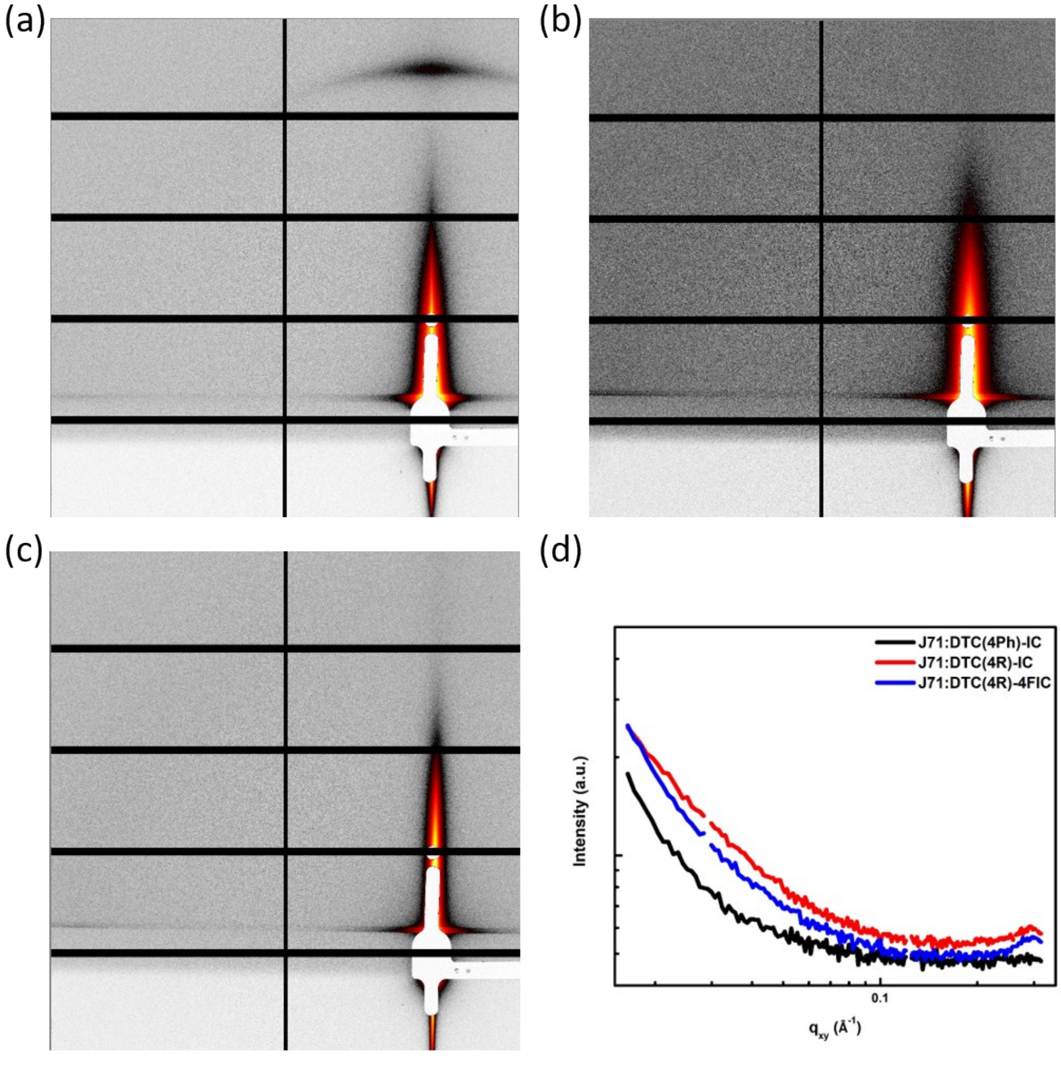

Figure S7. 2D GISAXS patterns of (a)J71:DTC(4Ph)-IC; (b)J71:DTC(4R)-IC and (c)J71:DTC(4R)-4FIC, and (d)their in-plane 1D linecuts.

Table S1. Lattice parameters of J71:DTC-based NFA blends

Composition	(100)		(010)
	Grain size (D_{J71}, D_{NFA}) * (Å)	d-spacing ($d(100)_{J71}$, $d(100)_{NFA}$) (Å)	d-spacing d(010) (Å)
J71:DTC(4Ph)-IC	174.53, 110.23	20.27, 19.64	3.49
J71:DTC(4R)-IC	112.20, na.	20.27, na.	4.30
J71:DTC(4R)-4FIC	157.08, 224.40	20.27, 16.54	3.45

*Grain size was calculated from peak width of (100) by using Scherrer equation.

Table S2. Lattice parameters of neat films of J71 and DTC-based NFAs

Composition	(100)		(010)
	Grain size* (Å)	d-spacing (Å)	d-spacing (Å)
J71	76.62	21.67	4.03
DTC(4Ph)-IC	241.66	20.94	4.30
DTC(4R)-IC	190.40	13.09	4.22
DTC(4R)-4FIC	161.11	20.27	4.22

*Grain size was calculated from peak width of (100) by using Scherrer equation.

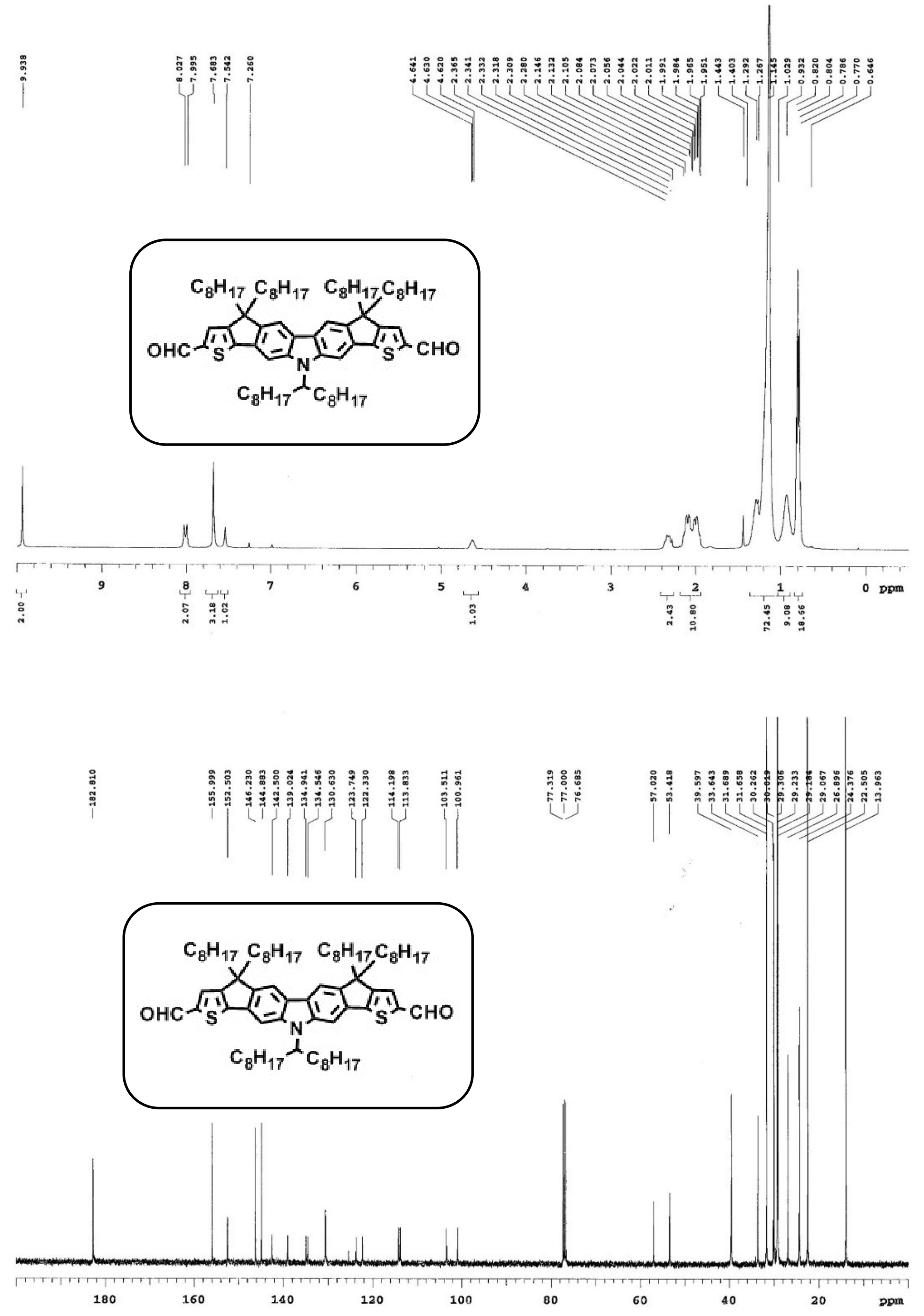

Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound **4**

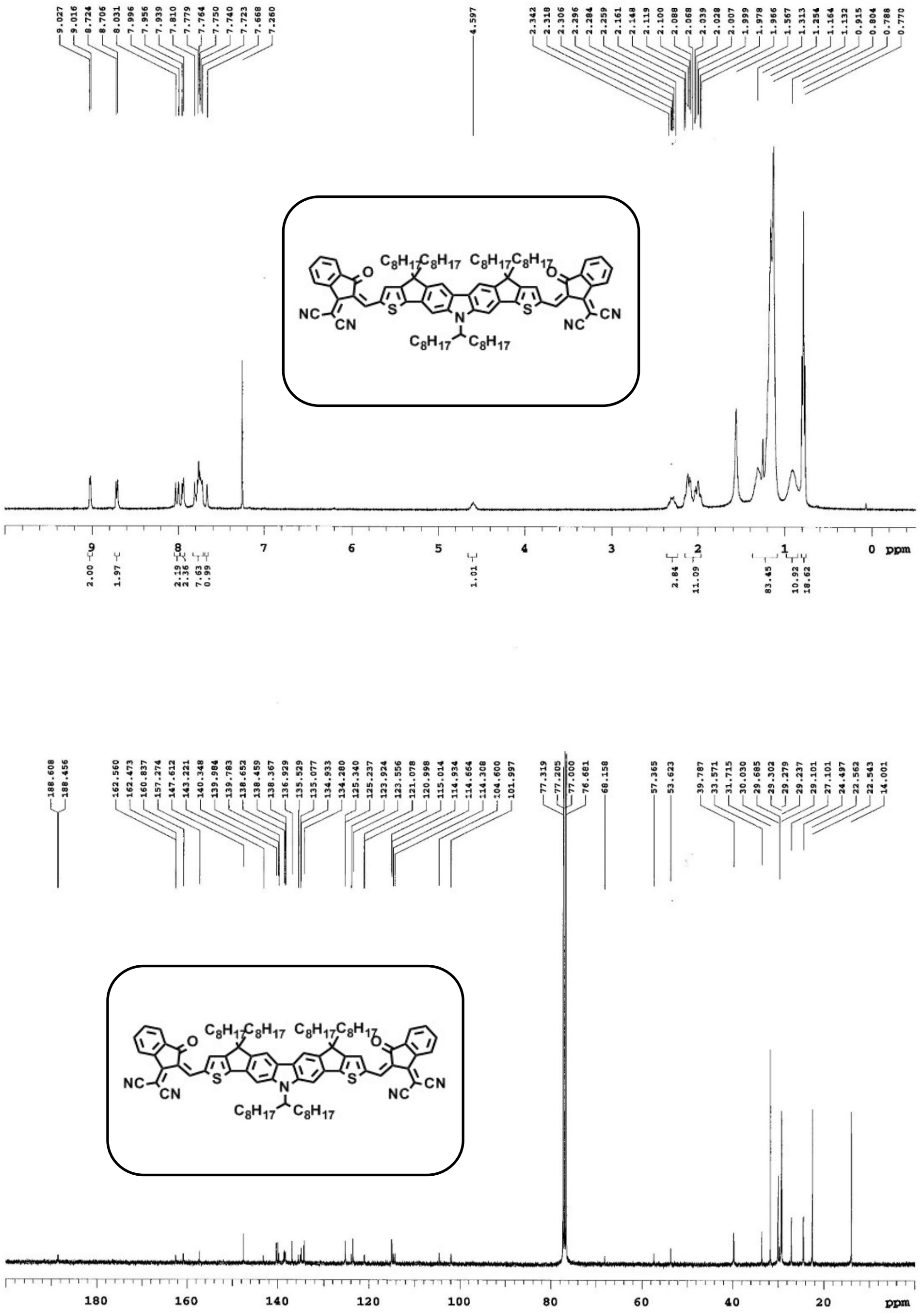

Figure S9. ^{1}H NMR and ^{13}C NMR spectra of DTC(4R)-IC

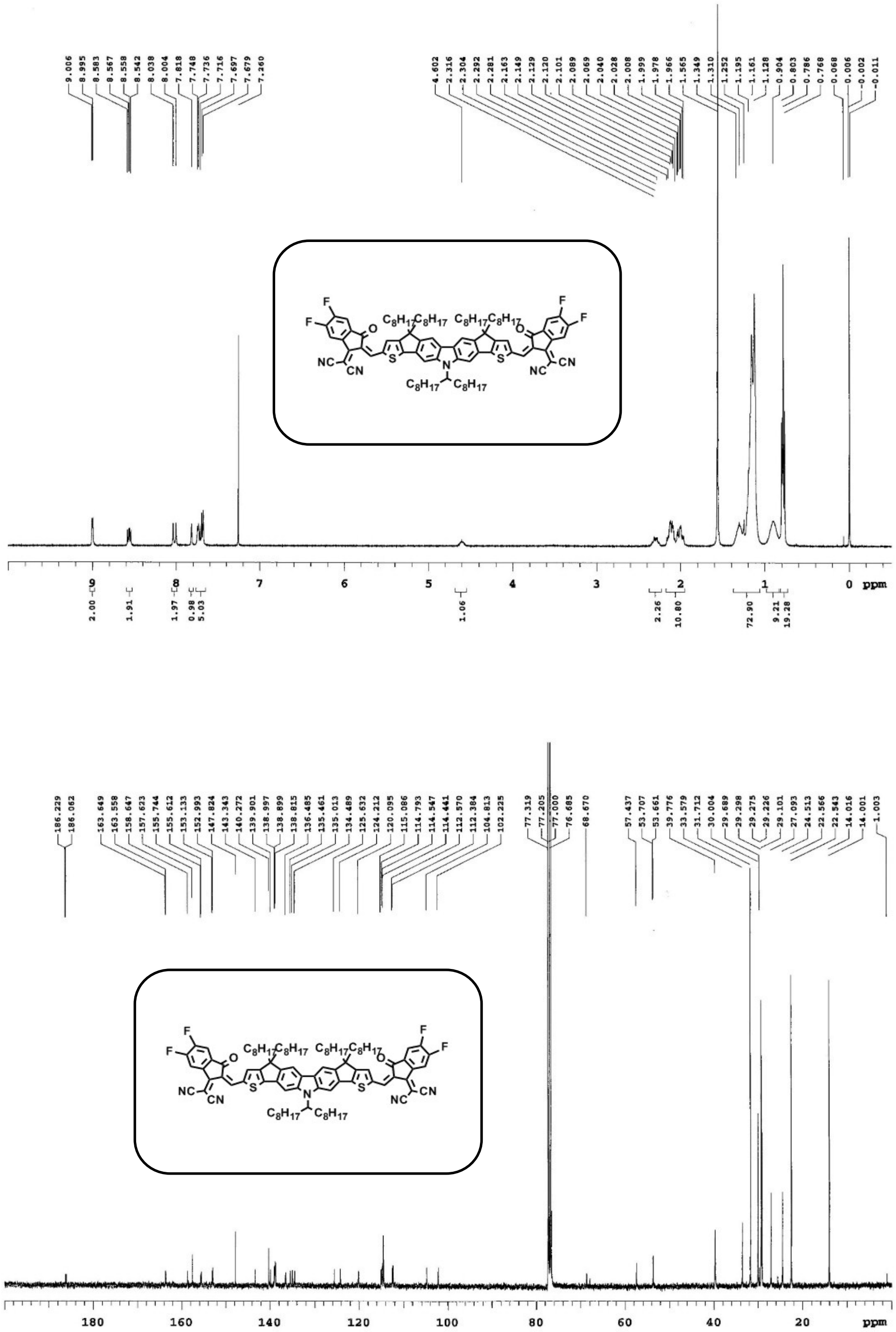

Figure S10. ^1H NMR and ^{13}C NMR spectra of DTC(4R)-4FIC

Reference

1. J. S. Wu, Y. J. Cheng, M. Dubosc, C. H. Hsieh, C. Y. Chang and C. S. Hsu, *Chem Commun*, 2010, **46**, 3259-3261.