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Supporting Information for the paper

Nitrofluorene-Based A-D-A Electron Acceptors for Organic Photovoltaics

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General methods

UV-Vis absorption spectra for the NFAs were recorded with a Jasco V-670 spectrophotometer in DCM solutions or in thin films. The films were prepared on quartz substrates by drop-casting from PhCN solution for **IDTBF-TeNF** and spin-coating from PhCl solutions for other NFAs and the measurements were performed in transmittance mode. Cyclic voltammograms were recorded at 0.1 V s^{-1} with a common three-electrode setup using platinum disk, platinum wire and AgCl coated silver wire as working, counter and reference electrodes, respectively. The NFAs were dissolved in DCM (except **IDTBF-TeNF** which was dissolved in PhCN due to its low solubility in DCM) with 0.1 M NBu_4PF_6 as the supporting electrolyte. The potentials measured against AgCl coated silver wire were calibrated with Fc/Fc^+ couple as an internal reference. For an oxidation process, half-wave potentials $E_{ox}^{1/2}$ were determined. Due to the irreversibility, onset potentials were used for electrochemical reductions (Table S1). Gas phase DFT calculations were performed using Gaussian 16 at B3LYP/6-31G(d) level of theory.[1] Frontier orbital energy levels of PBDB-T were calculated with two repeating units under periodic boundary conditions (PBCs). All alkyl chains were replaced with methyl groups to reduce the computational cost. Dihedral scans were performed with an interval of 2.5° and the probability distribution function was interpolated with a cubic spline function for the calculation of $\langle \cos^2\varphi \rangle$. Electronic coupling integrals were calculated for π-stacked dimers extracted from the crystal structure using ADF (2019.305) at B3LYP/TZP level of theory.[2] Scanning transmission electron microscopy (STEM) high-angle annular dark-field imaging (HAADF) was conducted on a Talos F200X G2.

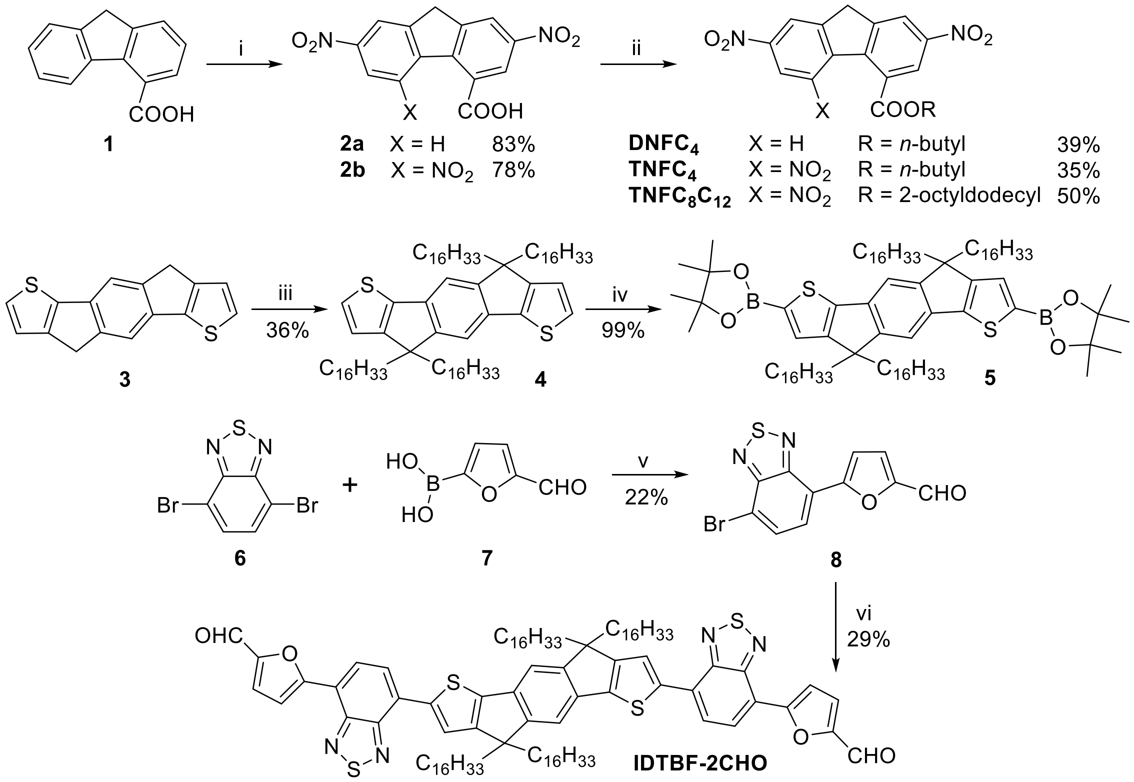
X-ray crystallography

Single crystals were grown by slow diffusion of acetone vapor into a solution of the NFA in chloroform (**IDTB-TeNF**) or toluene (**IDTBF-R**). Diffraction data were collected from shock-cooled crystals at 150 K on a Bruker Venture Metaljet k-geometry diffractometer with a metal jet using a

Helios MX Mirror Optics monochromator and a Bruker CMOS Photon III detector. The diffractometer was equipped with an Oxford Cryostream 700 low temperature device and used GaK_α radiation (λ = 1.34139 Å). All data were integrated with SAINT (2020) and a multi-scan absorption correction using SADABS 2016/2 was applied.[3] Structures were solved by dual methods with XT and refined by full-matrix least-squares methods against F^2 using XL.[4] All calculations (structural solution and refinement cycles) were performed within the graphical user interface of OLEX2.[5] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered parts were refined using a combination of restraints and constraints applied to atomic positions and thermal displacement parameters.

Synthesis of intermediates (Scheme S1)

3-Ethylrhodanine was purchased from Alfa Aesar. 4,7-Dibromobenzothiadiazole (**6**) and 5-formyl-2-furanboronic acid (**7**) were purchased from TCI. Precursors **3**, **IDTB-2CHO**, **IT-2CHO** and **O-IDTBR** were purchased from 1-Material Inc. Precursor **1**[6] and **TeNF**[7] were synthesized according to published procedures. Fuming nitric acid was prepared by distillation from a stirred mixture of KNO_3 (~150 g) and concentrated H_2SO_4 (~100 mL).



Scheme S1. Synthesis of nitrofluorene and **IDTBF-2CHO**. (i) HNO_3/AcOH (**2a**) or HNO_3/H_2SO_4 (**2b**), r.t, 24 h; (ii) $SOCl_2$, reflux, then ROH, 110 °C; (iii) *t*-BuOK, KI, DMSO, 80 °C, 1 h, then $C_{16}H_{33}Br$, 90 °C, 12 h; (iv) B_2pin_2, dtbpy, $[Ir(OMe)(COD)]_2$, cyclohexane, reflux, 12 h; (v) $Pd(PPh_3)_4$, K_2CO_3 (aq.), THF, reflux, 12 h; (vi) **5**, $Pd(PPh_3)_4$, TBAB, $NaHCO_3$ (aq.), PhMe, reflux, 24 h.

2,7-Dinitro-9H-fluorene-4-carboxylic acid (**2a**): **1** (2.58 g, 12.3 mmol) was added in portions to a stirred mixture of 21 mL fuming nitric acid and 15 mL AcOH at 0 °C. After storing at room temperature for 24 h, the mixture was diluted with 25 mL AcOH, stirred for an additional 2 h and poured into 150 mL cold water. The precipitate was filtered, washed with water and dried in vacuum to give a pale yellowish solid (3.07 g, 83%). The spectral characteristics are in agreement with literature data.[8]

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.73 (d, 1H, J = 2.2 Hz), 8.68 (d, 1H, J = 8.8 Hz), 8.61 (d, 1H, J = 2.3 Hz), 8.59 (d, 1H, J = 2.3 Hz), 8.37 (dd, 1H, J = 8.8 Hz, J' = 2.3 Hz), 4.33 (s, 2H).

2,5,7-Trinitro-9H-fluorene-4-carboxylic acid (**2b**):[9] **1** (2.70 g, 12.8 mmol) was added in portions to a mixture of 25 mL fuming nitric acid and 3 mL H_2SO_4 at –10 °C and stirred at this temperature for 1 h. The mixture was diluted with 14 mL H_2SO_4 and stored at room temperature for 24 h. The mixture was poured into 160 mL cold water. The precipitate was filtered, washed with water and dried in vacuum to give a pale yellowish solid (3.46 g, 78%).

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.95 (d, 1H, J = 2.1 Hz), 8.82 (d, 1H, J = 2.2 Hz), 8.72 (d, 1H, J = 2.1 Hz), 8.54 (d, 1H, J = 2.2 Hz), 4.52 (s, 2H).

Butyl 2,7-dinitro-9H-fluorene-4-carboxylate (**DNFC$_4$**): **2a** (0.254 g, 0.846 mmol) was refluxed in 4 mL thionyl chloride for 3 h. The solvent was evaporated and the residue was stirred in *n*-butanol (4 mL) at 110 °C for 3 h. After removing the solvent, the residue was purified by column chromatography ($CHCl_3$) and recrystallized three times in EtOAc/hexanes to give a white solid (0.117 g, 39%). The spectral characteristics are in agreement with literature data.[8]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.78 (d, 1H, J = 2.2 Hz), 8.74 (d, 1H, J = 8.8 Hz), 8.59 (d, 1H, J = 2.3 Hz), 8.47 (d, 1H, J = 2.2 Hz), 8.33 (dd, 1H, J = 8.8 Hz, J' = 2.3 Hz), 4.52 (t, 2H, J = 6.8 Hz), 4.20 (s, 2H), 1.86 (quint, 2H, J = 7.2 Hz), 1.53 (sext, 2H, J = 7.5 Hz), 1.03 (t, 3H, J = 7.4 Hz). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ (ppm) 165.96, 148.15, 147.72, 146.94, 146.54, 144.44, 144.23, 128.85, 127.35, 125.29, 123.14, 123.05, 120.09, 66.54, 37.41, 30.78, 19.40, 13.89.

Butyl 2,5,7-trinitro-9H-fluorene-4-carboxylate (**TNFC$_4$**): **2b** (1.01 g, 2.93 mmol) was refluxed in 10 mL thionyl chloride for 3 h. The solvent was evaporated and the residue was stirred in 10 mL *n*-butanol at 110 °C for 3 h. After removing the solvent, the residue was purified by column chromatography ($CHCl_3$) and recrystallized three times in EtOAc/hexanes to give a light yellowish solid (0.410 g, 35%). The spectral characteristics are in agreement with literature data.[8]

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.86 (d, 1H, J = 2.0 Hz), 8.73 (d, 1H, J = 2.1 Hz), 8.70 (d, 1H, J = 2.1 Hz), 8.62 (d, 1H, J = 2.2 Hz), 4.39 (t, 2H, J = 6.8 Hz), 4.35 (s, 2H), 1.82 (quint, 2H, J = 7.2 Hz), 1.51 (sext, 2H, J = 7.5 Hz), 1.01 (t, 3H, J = 7.4 Hz). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ (ppm) 165.87, 149.14, 148.01, 147.82, 147.35, 146.96, 140.48, 137.23, 131.98, 124.36, 123.67, 122.45, 119.53, 66.94, 38.14, 30.63, 19.27, 13.85.

2-Octyldodecyl 2,5,7-trinitro-9H-fluorene-4-carboxylate (**TNFC$_8$C$_{12}$**): **2b** (0.150 g, 0.435 mmol) was refluxed in 2 mL thionyl chloride for 1h. The solvent was evaporated and the residue was refluxed overnight in a mixture of in 1 mL PhMe and 2 mL 2-octyldodecanol. After removing the solvent, the residue was washed with MeOH, purified by column chromatography ($CHCl_3$) and recrystallized in hexanes to give a light yellowish solid (0.135 g, 50%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.84 (d, 1H, J = 2.1 Hz), 8.70 (d, 1H, J = 2.2 Hz), 8.69 (d, 1H, J = 2.0 Hz), 8.62 (d, 1H, J = 2.1 Hz), 4.35 (s, 2H), 4.28 (d, 2H, J = 5.9 Hz), 1.85 (sept, 1H, J = 6.0 Hz), 1.45–1.21 (m, 34H), 0.87 (t, 6H, J = 6.8 Hz). ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ (ppm) 165.94, 149.10, 148.02, 147.83, 147.35, 146.99, 140.51, 137.21, 132.08, 124.24, 123.62, 122.42, 119.53, 69.89, 38.13, 37.41, 32.06, 32.03, 31.42, 30.10, 29.80, 29.77, 29.75, 29.71, 29.49, 29.46, 26.81, 22.83, 22.82, 14.26.

4,4,9,9-Tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (**4**): To a nitrogen-purged solution of **3** (0.983 g, 3.69 mmol) in 24 mL DMSO was added KI (0.165 g, 0.994 mmol) and *t*-BuOK (2.508 g, 22.4 mmol). The mixture was stirred at 80 °C for 1 h under nitrogen. 1-Bromohexadecane (6.902 g, 22.6 mmol) was injected, and the mixture was stirred overnight at 90 °C under nitrogen. After cooling to room temperature, the mixture was poured into water, extracted with $CHCl_3$, washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography (hexanes) and recrystallized in PhMe/acetone to give a light yellowish solid (1.530 g, 36%).
^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.27 (s, 2H), 7.25 (d, 2H, J = 4.8 Hz), 6.95 (d, 2H, J = 4.8 Hz), 2.00–1.80 (m, 8H), 1.32–1.04 (m, 104H), 0.91–0.75 (m, 8H), 0.87 (t, 12H, J = 6.9 Hz).

2,2'-(4,4,9,9-Tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**5**): A solution of bis(pinacolato)diboron (0.264 g, 1.04 mmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (0.026 g, 0.097 mmol) and $[Ir(OMe)(COD)]_2$ (0.030 g, 0.045 mmol) in 3 mL cyclohexane was stirred for 10 min under nitrogen. A solution of **4** (0.547 g, 0.470 mmol) in 8 mL cyclohexane was injected and the mixture was refluxed overnight under nitrogen. The solvent was evaporated, and the residue was washed for three times with MeOH to give an oily paste (0.661 g, 99%).
^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.46 (s, 2H), 7.30 (s, 2H), 2.00-1.78 (m, 8H), 1.38 (s, 24H), 1.30–1.04 (m, 104H), 0.89–0.70 (m, 8H), 0.87 (t, 12H, J = 6.9 Hz).

5-(7-Bromobenzo[c][1,2,5]thiadiazol-4-yl)furan-2-carbaldehyde (**8**): The compound was synthesized according to a procedure modified from literature.[10] To a solution of **6** (0.468 g, 1.59 mmol) and **7** (0.200 g, 1.43 mmol) in 10 mL THF was added 2.5 mL 2.5 M aqueous K_2CO_3 and $Pd(PPh_3)_4$ (0.016 g, 0.014 mmol) and the mixture was refluxed overnight under nitrogen. The solvent was evaporated, and the product was purified by column chromatography ($CHCl_3$). Starting material **6** (0.322 g, 69%) was recovered as a slightly yellowish solid and the desired product was obtained as a yellowish solid (0.096 g, 22%).
^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.75 (s, 1H), 8.16 (d, 1H, J = 7.8 Hz), 7.96 (d, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 3.7 Hz). 7.43 (d, 1H, J = 3.7 Hz).

5,5'-((4,4,9,9-Tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(furan-2-carbaldehyde) (**IDTBF-2CHO**): To a nitrogen-purged solution of **5** (0.460 g, 0.325 mmol), **8** (0.210 g, 0.679 mmol) and tetrabutylammonium bromide (0.146 g, 0.453 mmol) in 12 mL PhMe was added $Pd(PPh_3)_4$ (0.071 g, 0.061 mmol) and 3 mL 1 M aqueous $NaHCO_3$. The mixture was refluxed for 24 h under nitrogen. The solvent was evaporated, and the product was purified by column chromatography (PhMe), concentrated and precipitated with MeOH to give a dark purplish solid (0.151 g, 29%).
^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.74 (s, 2H), 8.33 (d, 2H, J = 7.8 Hz), 8.15 (s, 2H), 8.01 (d, 2H, J = 7.7 Hz), 7.91 (d, 2H, J = 3.7 Hz), 7.46 (d, 2H, J = 3.6 Hz), 7.41 (s, 2H), 2.15–1.93 (m, 8H), 1.27-1.08 (m, 104H), 1.03–0.79 (m, 8H), 0.85 (t, 12H, J = 7.1 Hz).

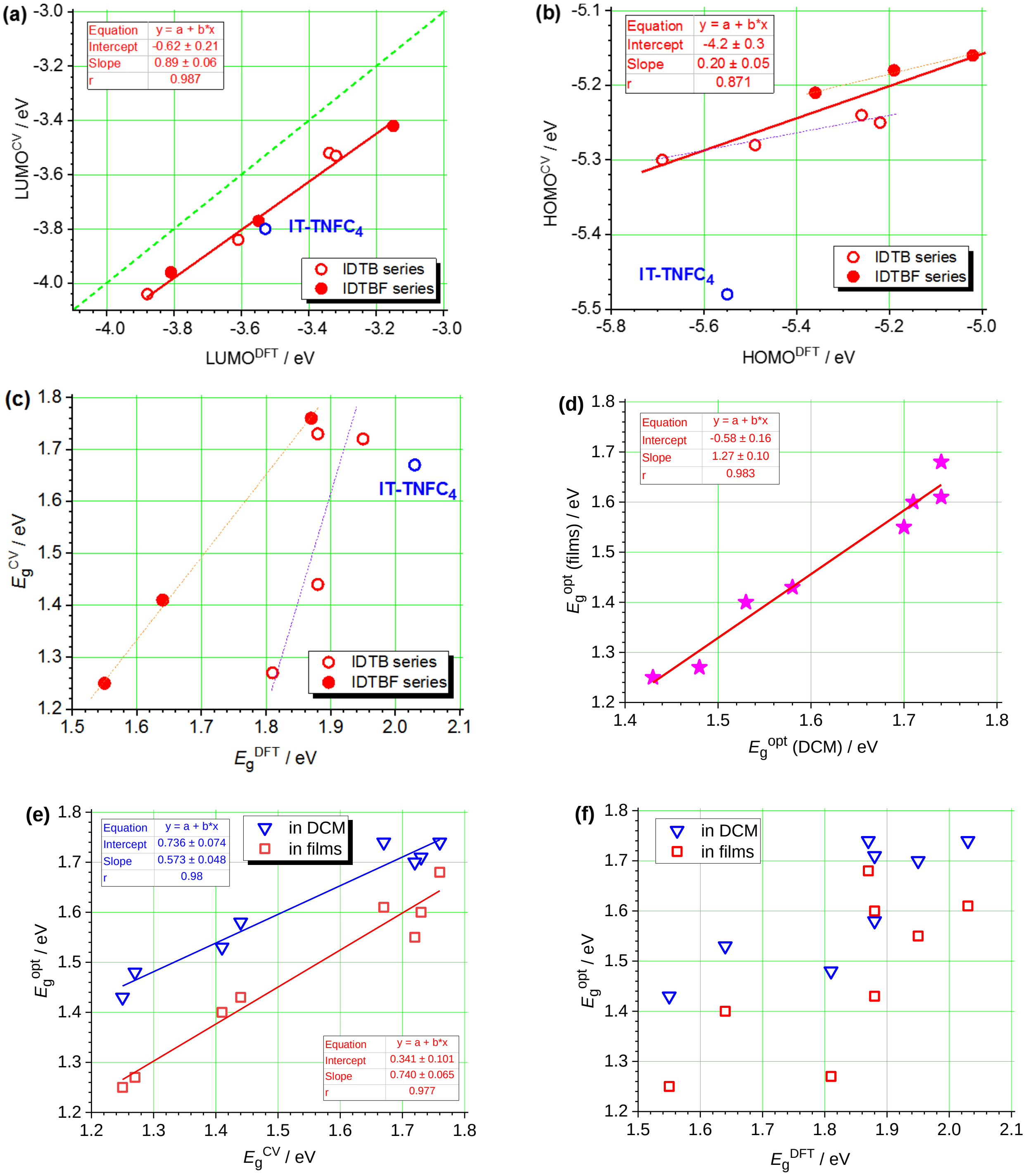


Figure S1. Correlations between HOMO/LUMO and E_g determined from cyclic voltammetry experiments, optical absorption spectroscopy and DFT calculations.

*Excellent correlation is observed between experimental (CV) and DFT-calculated LUMO energies [panel (a)]. For HOMO energies, **IT-TNFC₄** with different donor moiety (on which HOMO is mainly located) strongly deviates from a general dependency for other NFAs. Also, IDTB and IDTBF series tend to show separate linear dependence [panel (b)]. This behavior results in poor correlations between* E_g^{DFT} *and* E_g^{CV} *for the whole set [panel (c)].*

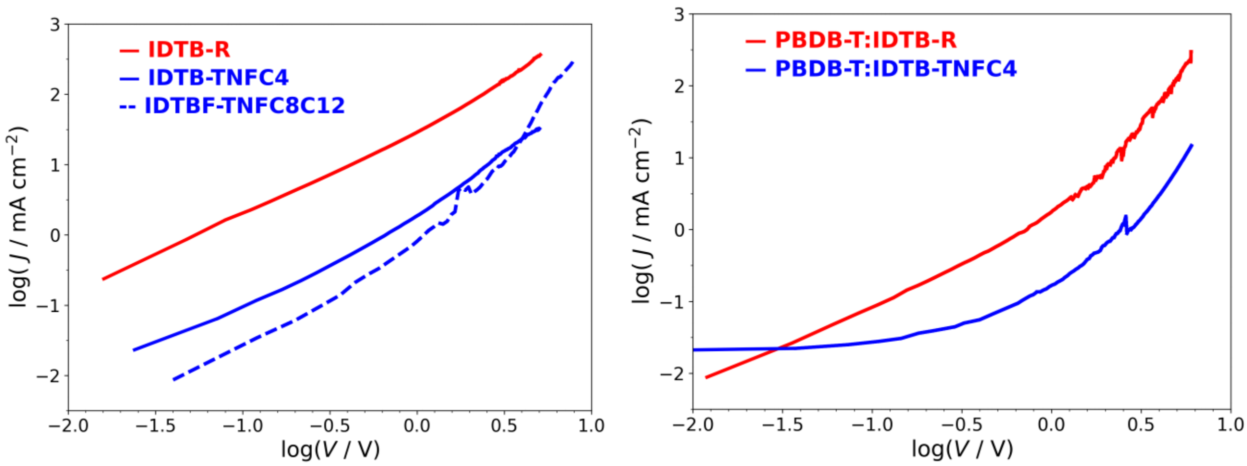


Figure S2. SCLC curves for electron-only devices with pure (left) and blend (right) films of different NFAs.

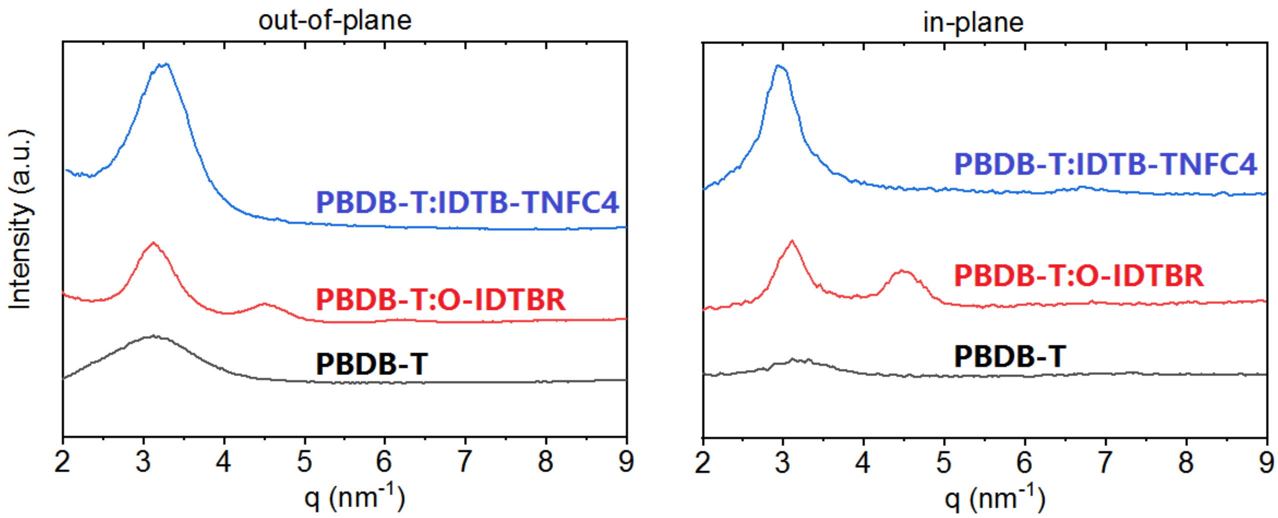


Figure S3. The out-of-plane and in-plane line cuts from the 2D GIWAXS of PBDB-T and its 1:1 blends with **O-IDTBR** and **IDTB-TNFC$_4$**.

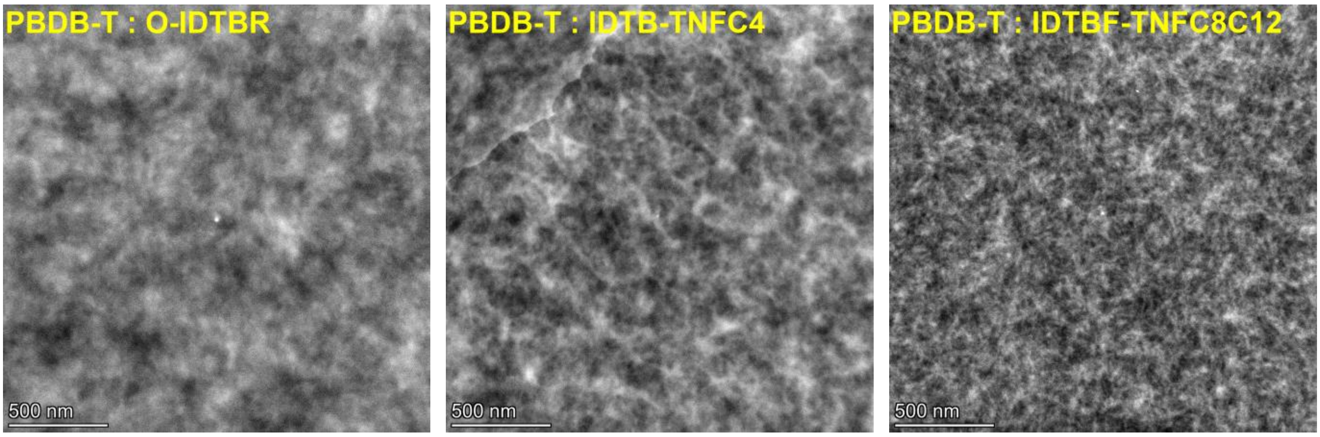
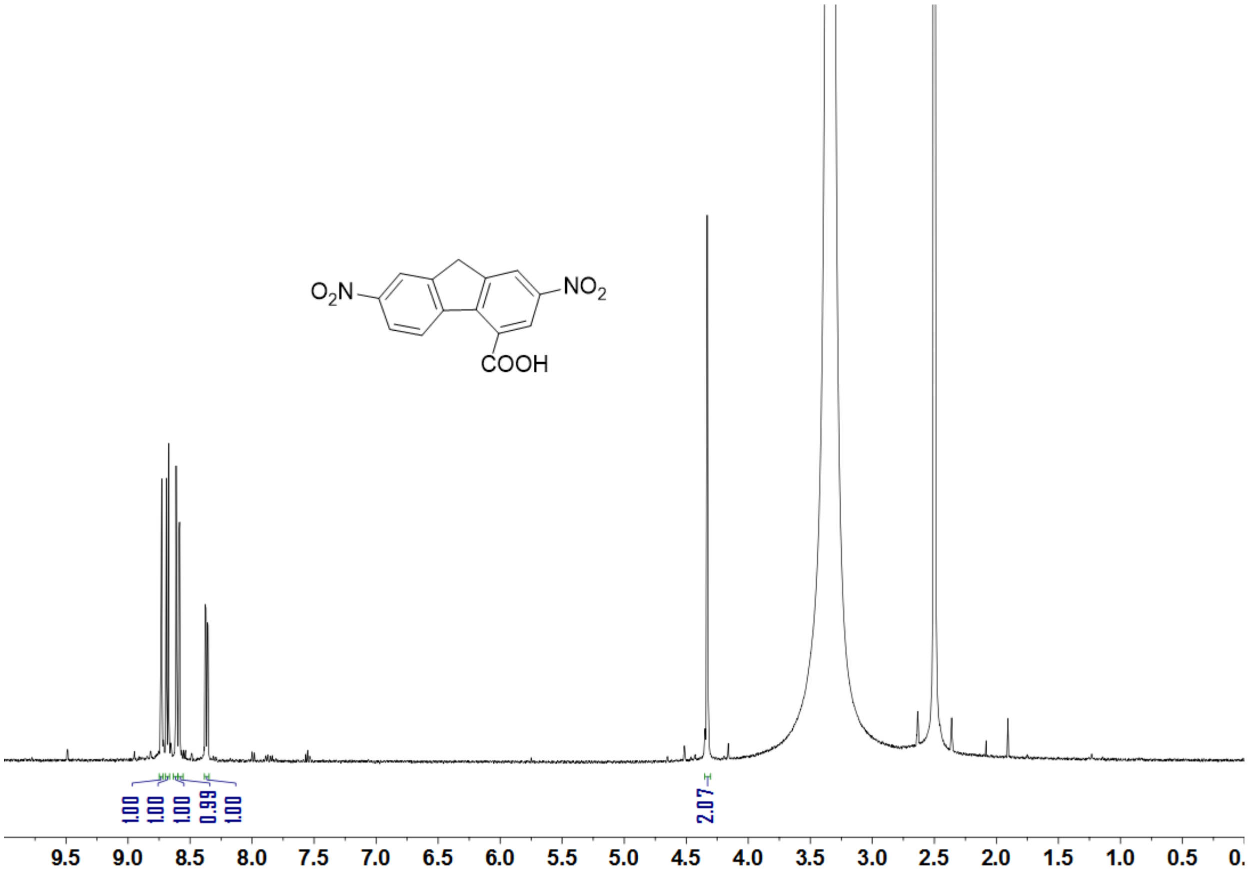


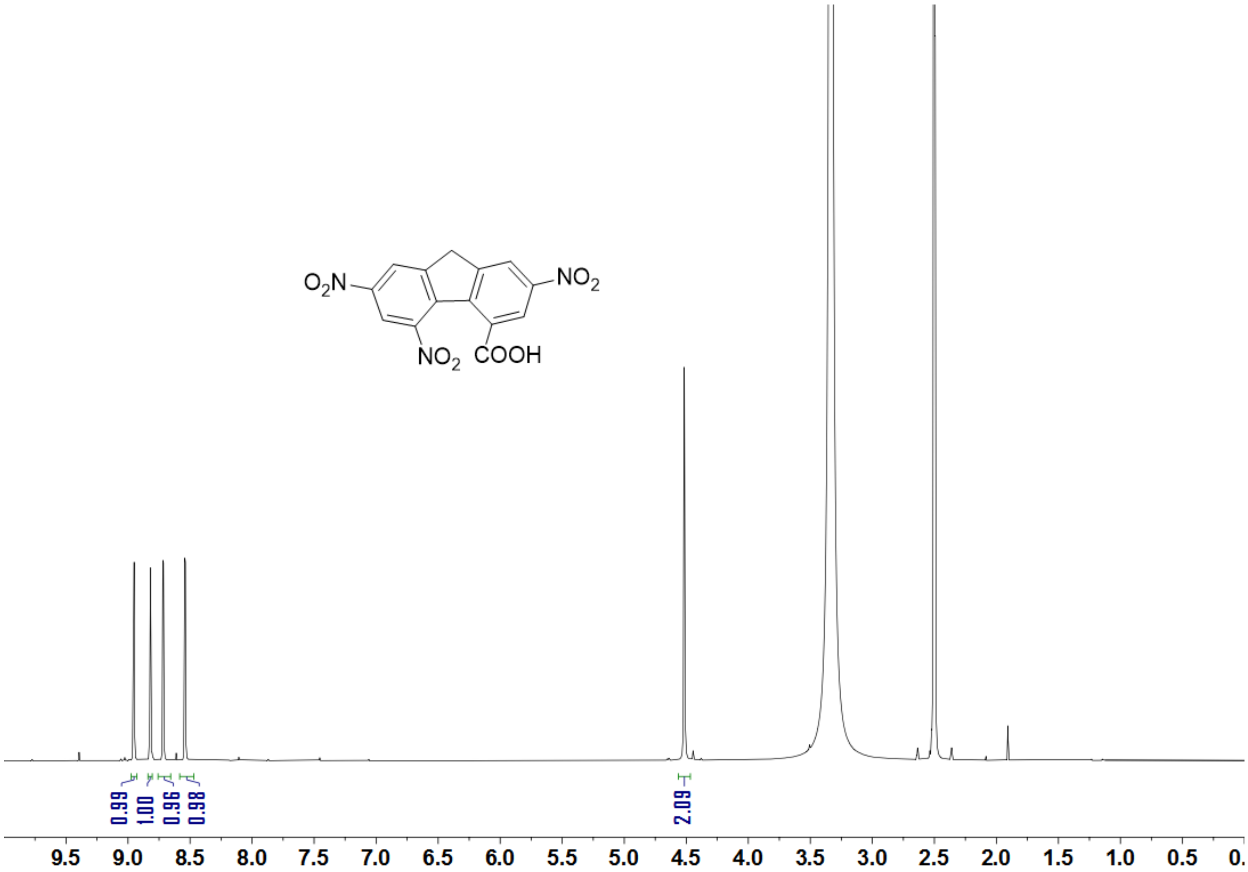
Figure S4. TEM images of the blend film of PBDB-T with **O-IDTBR**, **IDTB-TNFC$_4$** and **IDTBF-TNFC$_8$C$_{12}$**. The differences in morphology are qualitatively similar to those observed in AFM.

Table S1. Redox potentials extracted from the cyclic voltammogram of the studied NFAs.

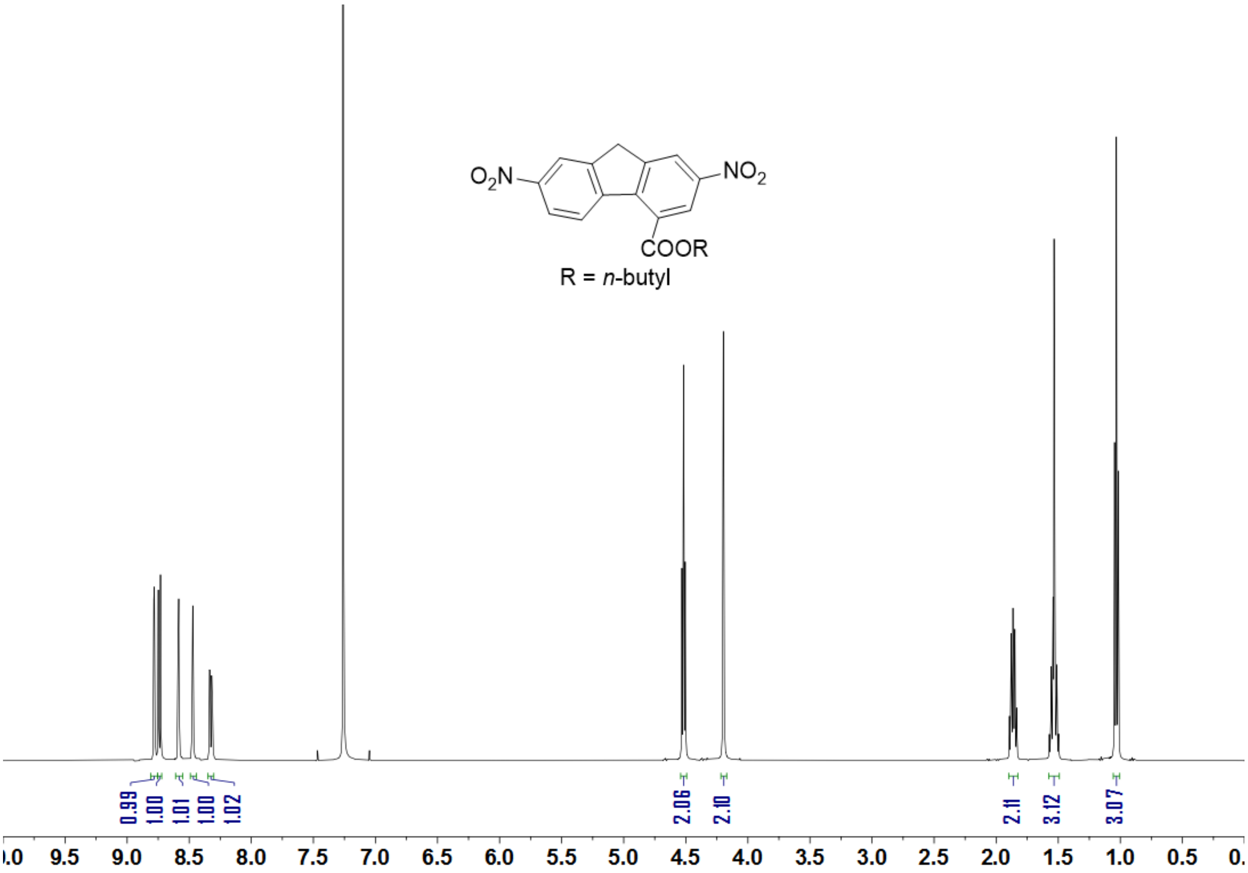
	$E_{\mathrm{ox}}^{1/2}$ (V)	$E_{\mathrm{red}}^{\mathrm{onset}}$ (V)
O-IDTBR	0.45	–1.28
IDTB-DNFC$_4$	0.44	–1.27
IDTB-TNFC$_4$	0.48	–0.96
IDTB-TeNF	0.50	–0.76
IDTBF-R	0.36	–1.38
IDTBF-TNFC$_8$C$_{12}$	0.38	–1.03
IDTBF-TeNF	0.41	–0.84
IT-TNFC$_4$	0.68	–1.00



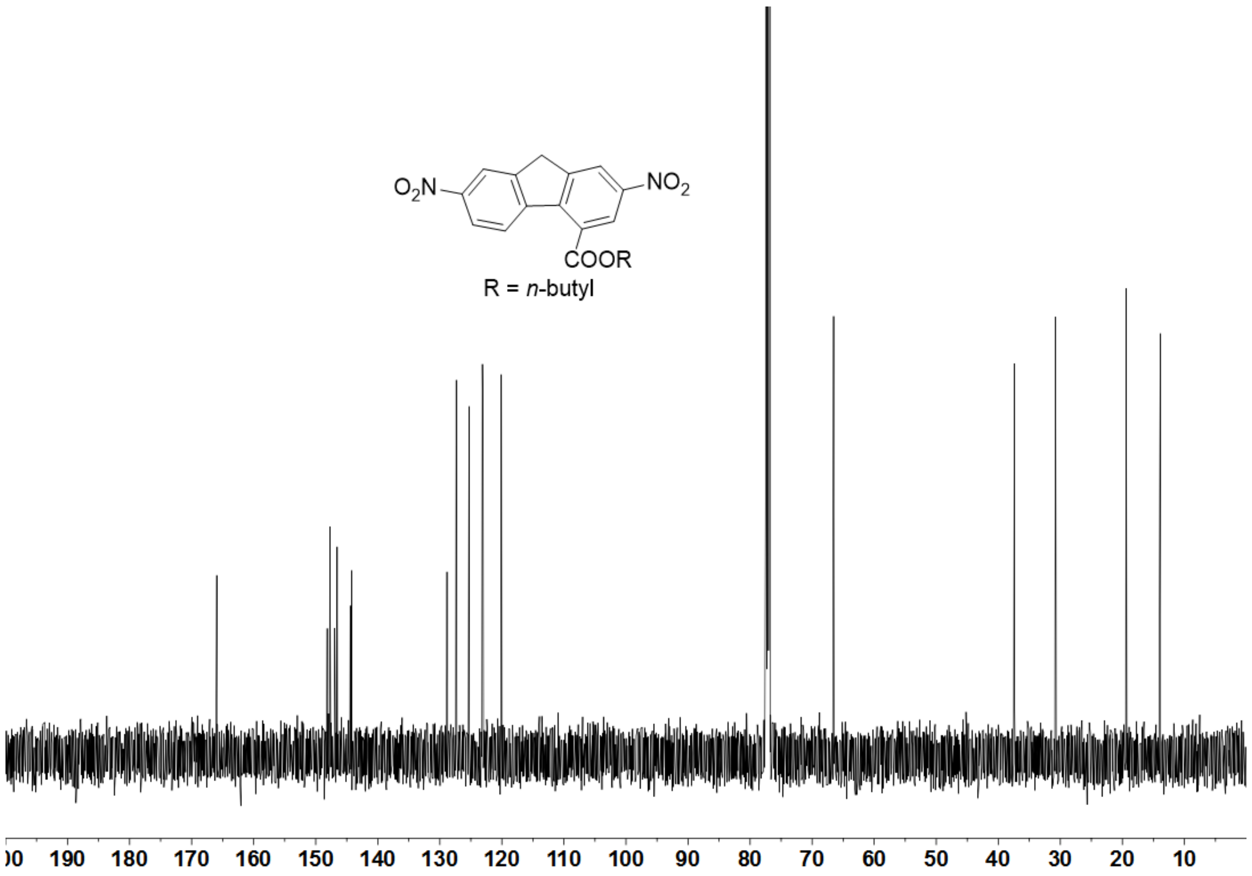
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **2a**.



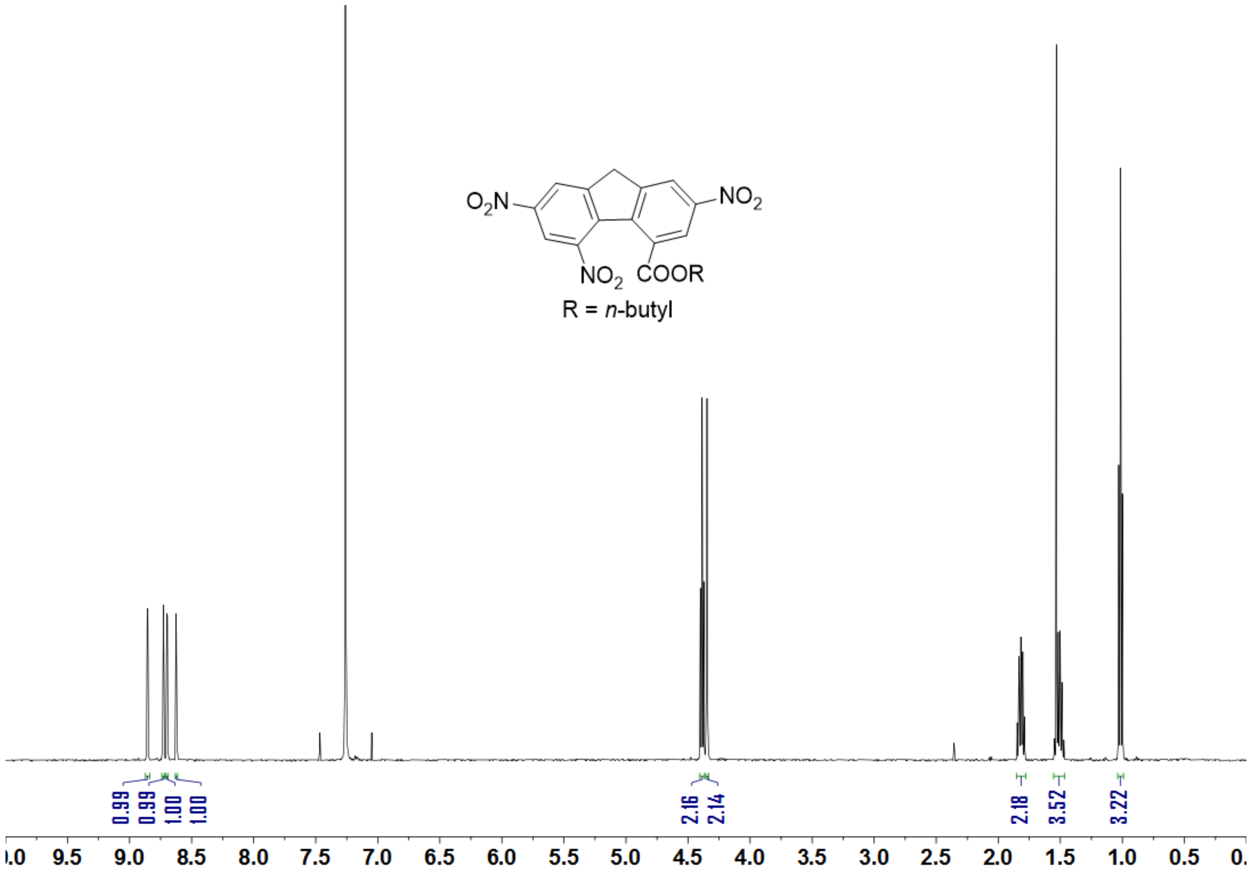
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **2b**.



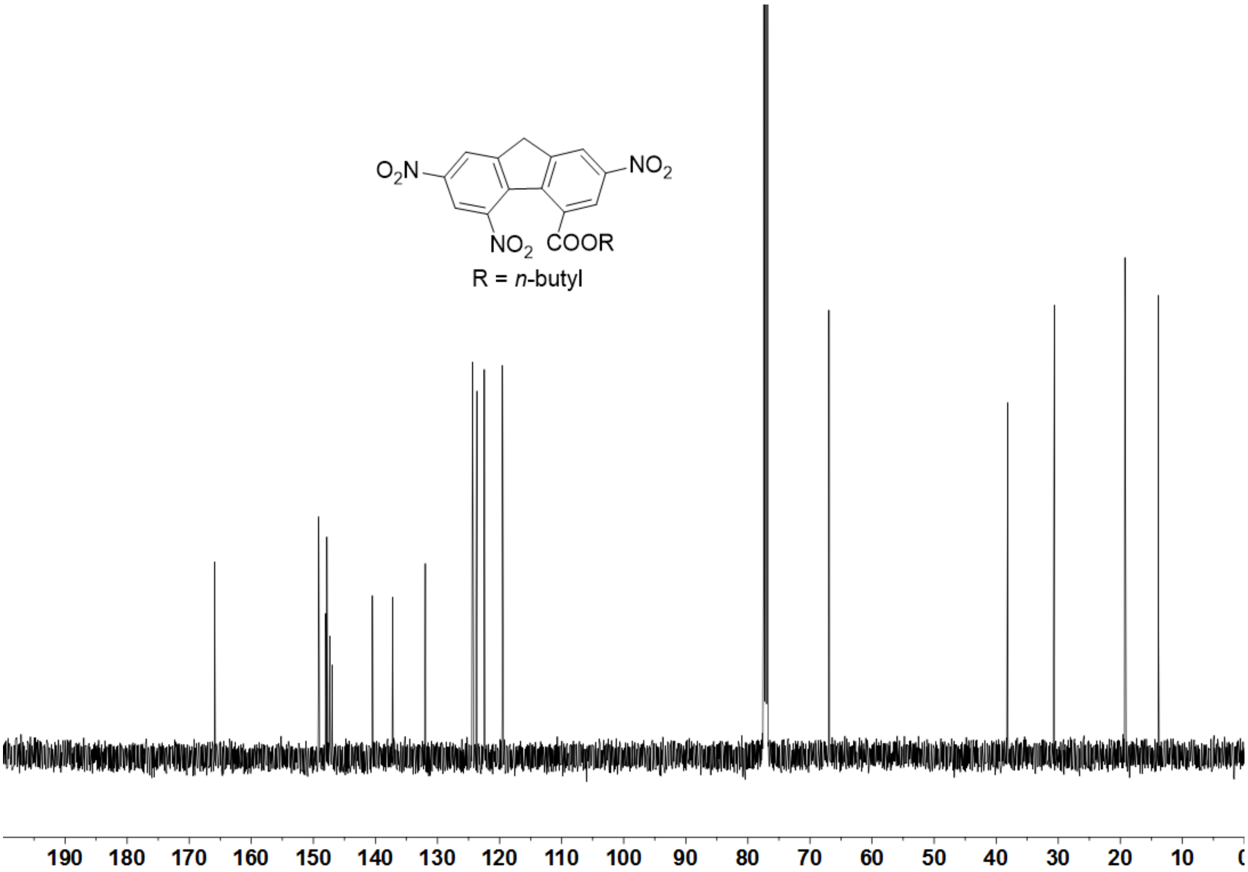
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **DNFC$_4$**.



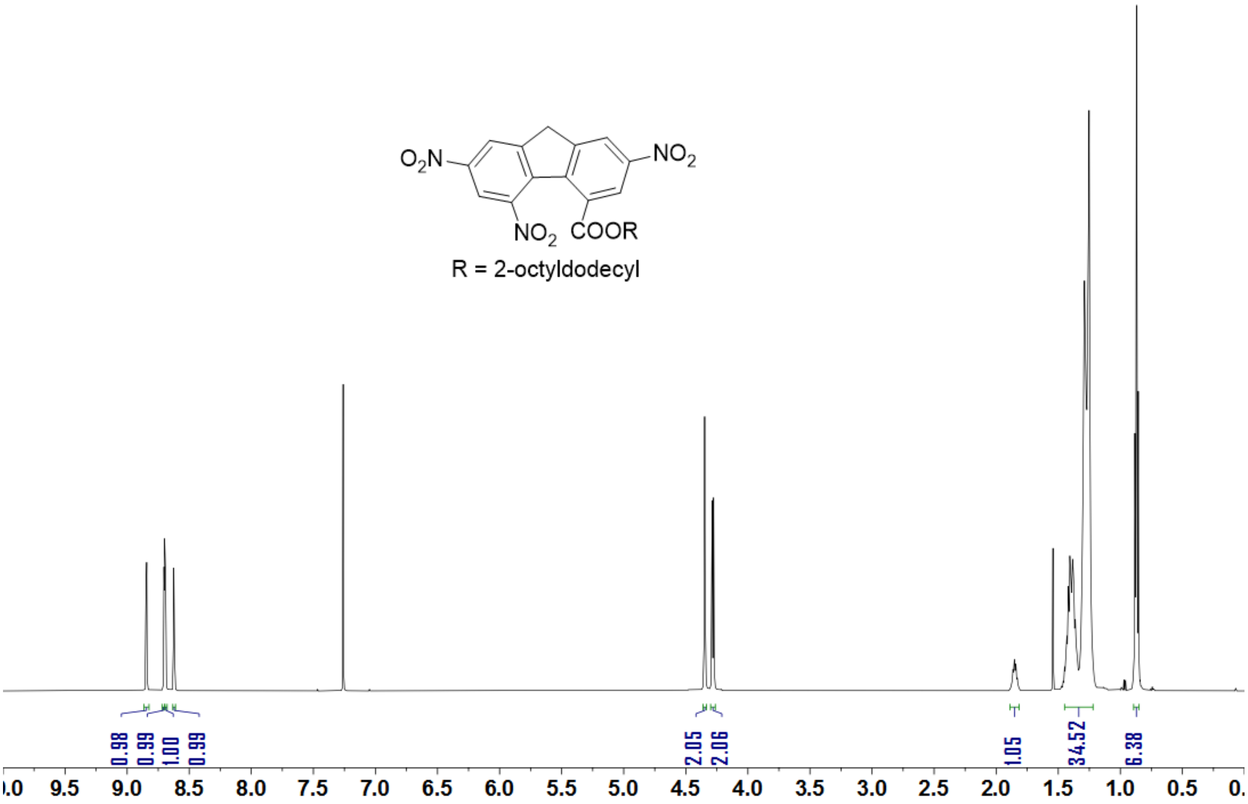
^{13}C{^{1}H} NMR (500 MHz, CDCl$_3$) spectrum of **DNFC$_4$**.



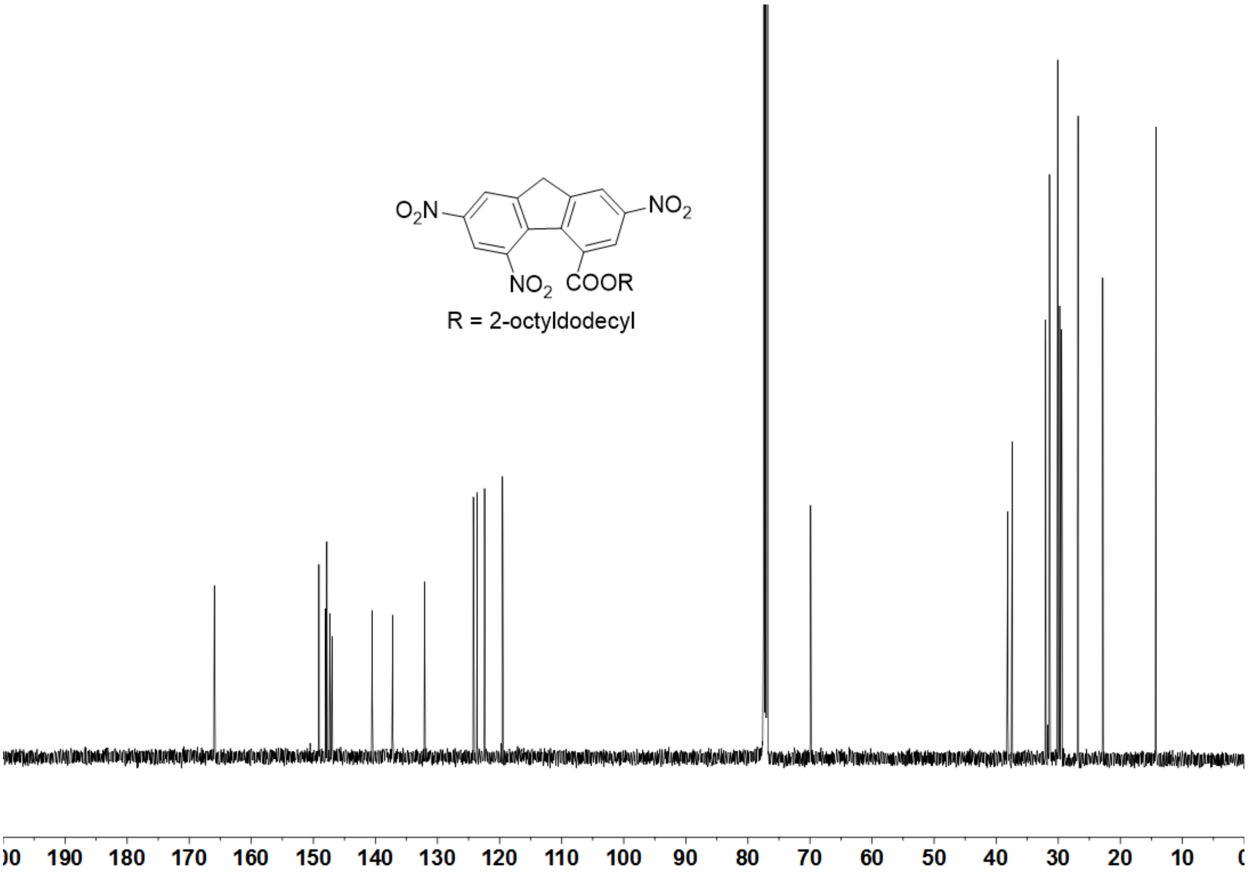
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TNFC$_4$**.



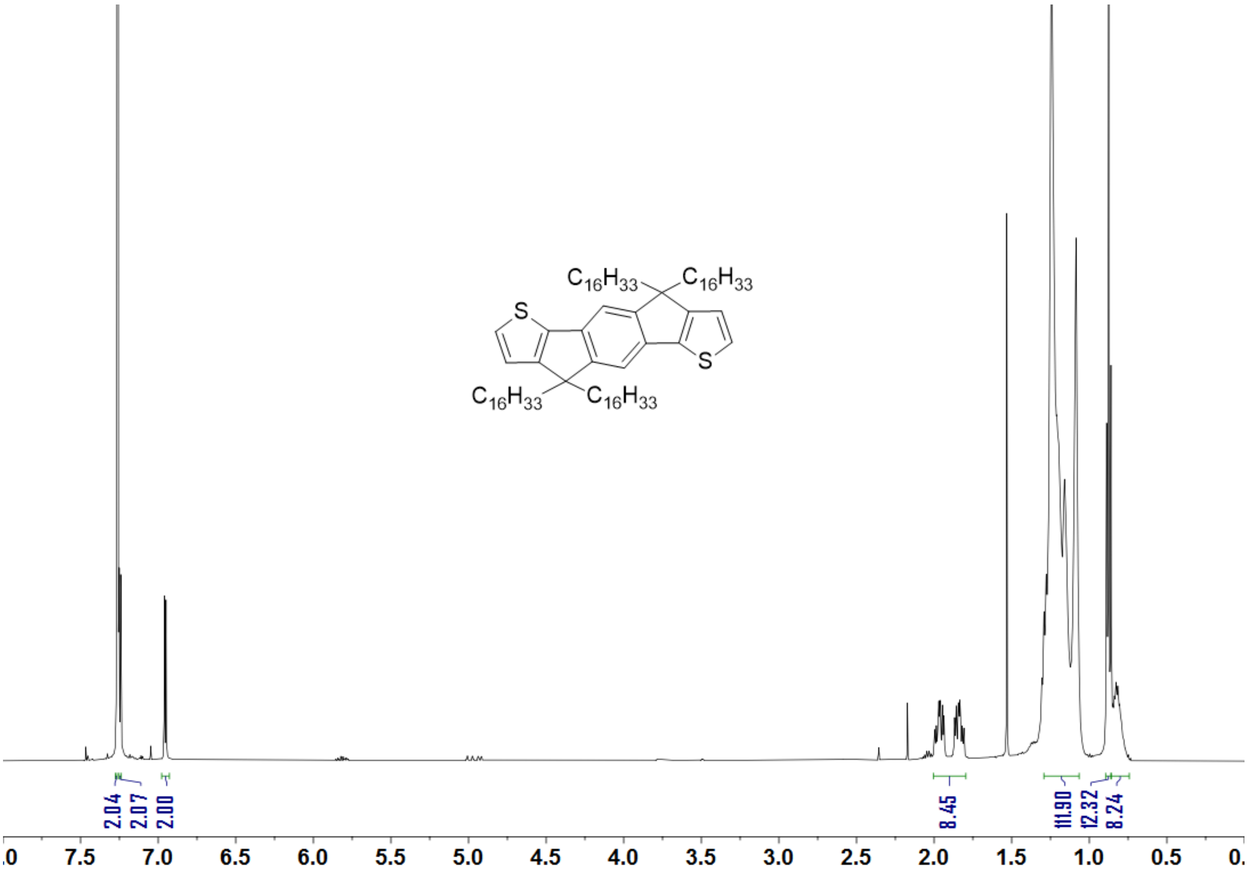
^{13}C{^{1}H} NMR (500 MHz, CDCl$_3$) spectrum of **TNFC$_4$**.



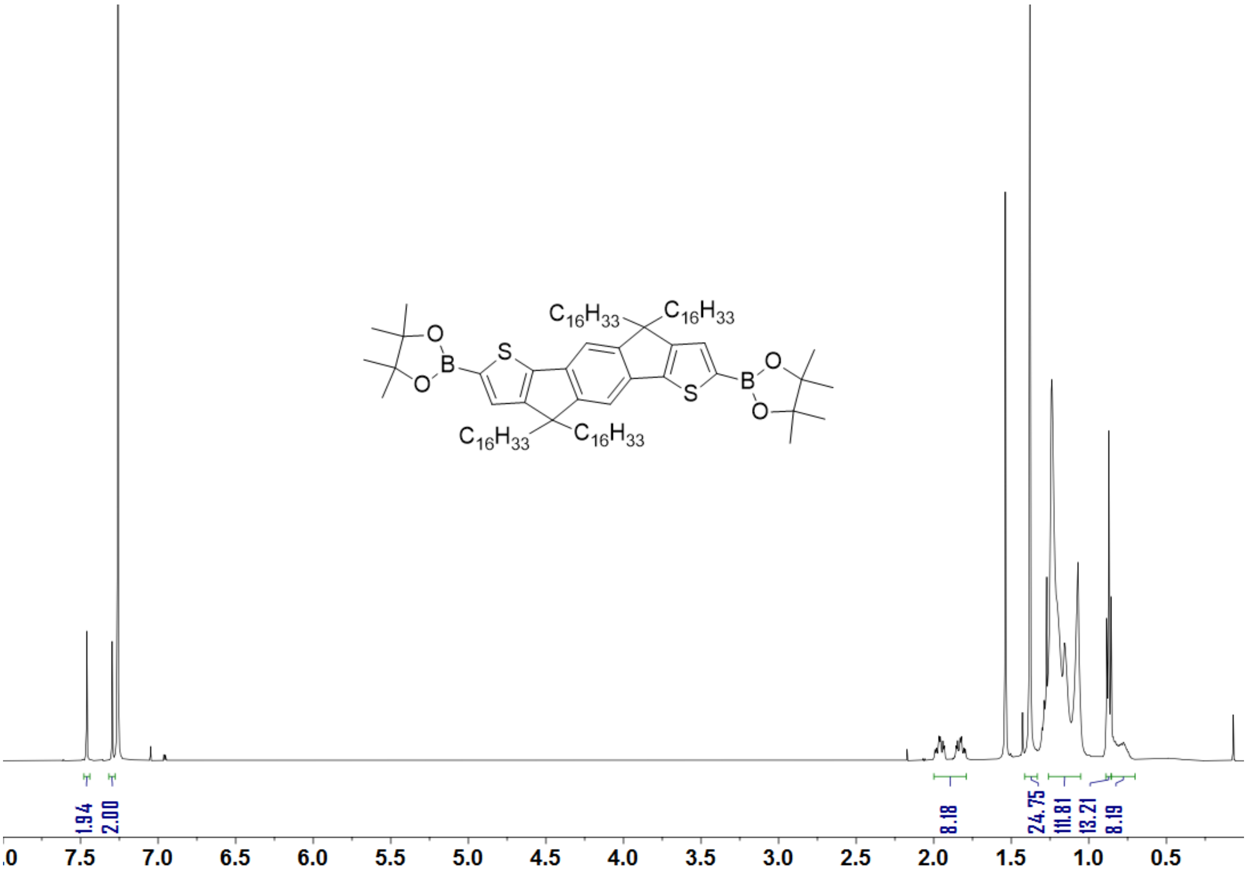
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **TNFC$_8$C$_{12}$**.



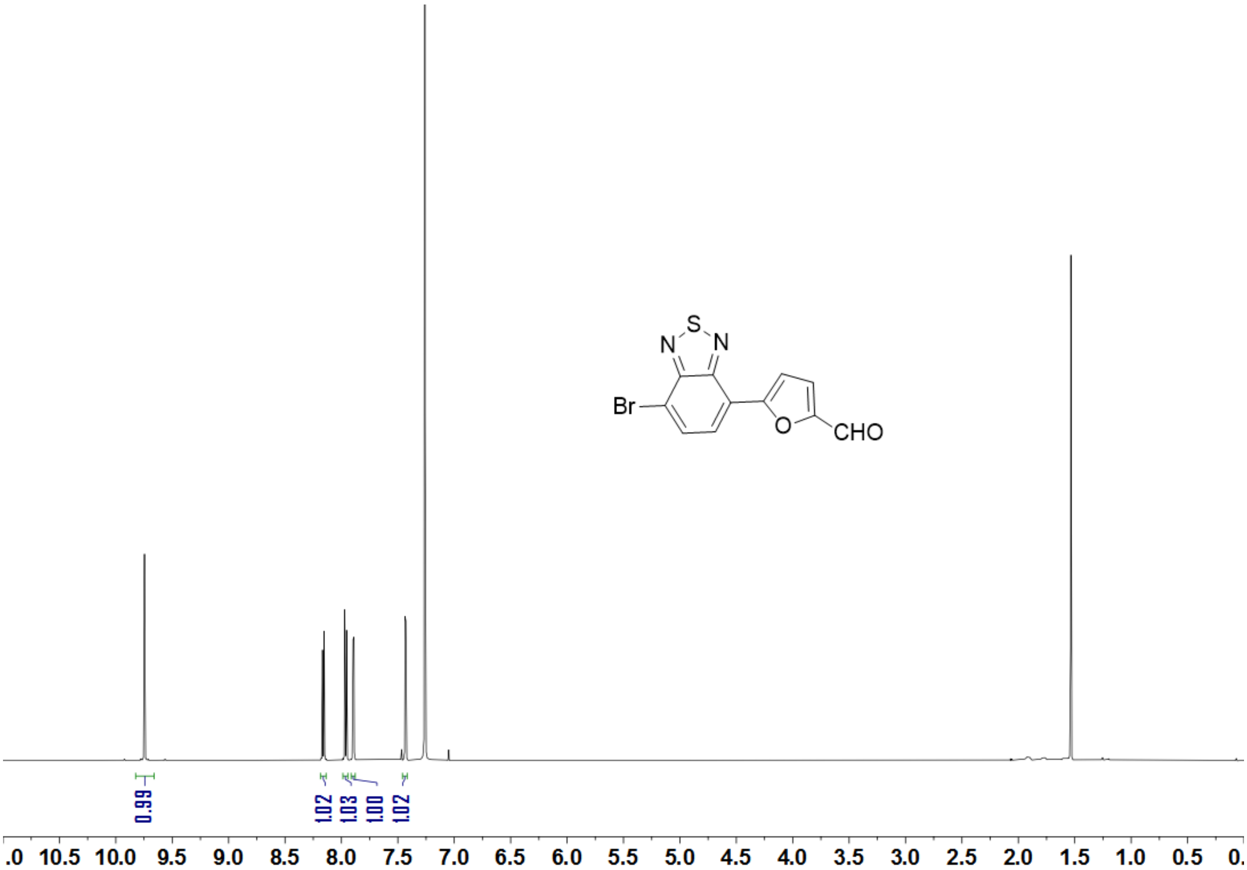
^{13}C{^{1}H} NMR (500 MHz, CDCl$_3$) spectrum of **TNFC$_8$C$_{12}$**.



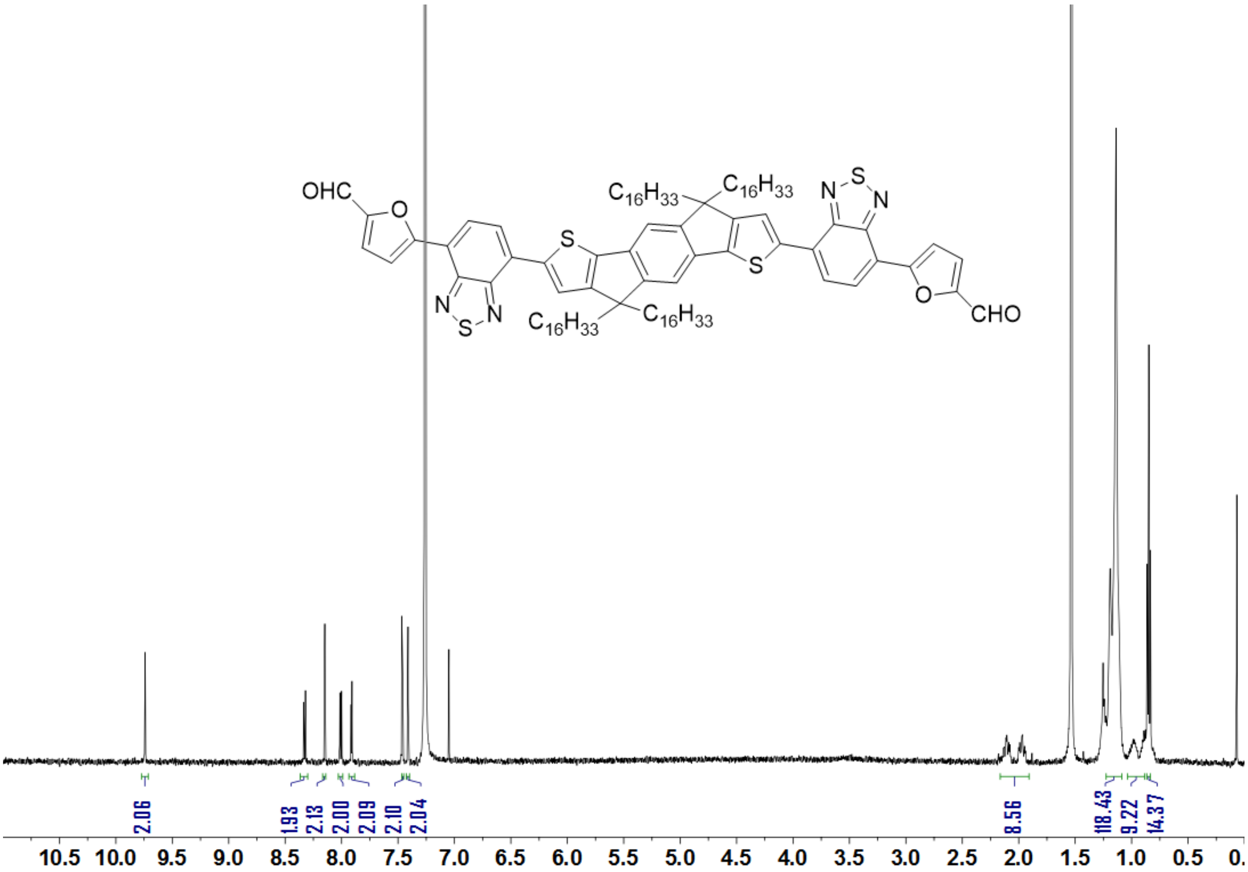
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **4**.



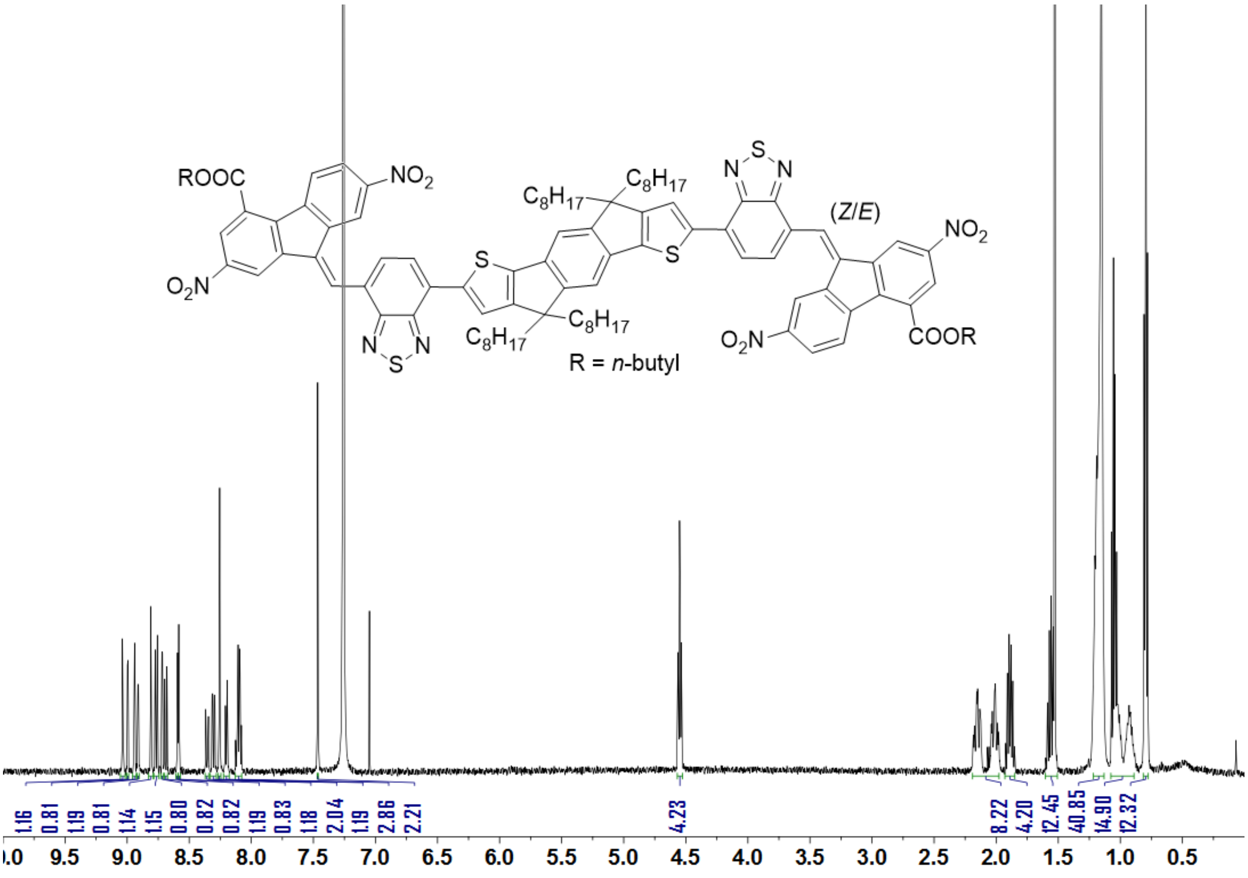
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5**.



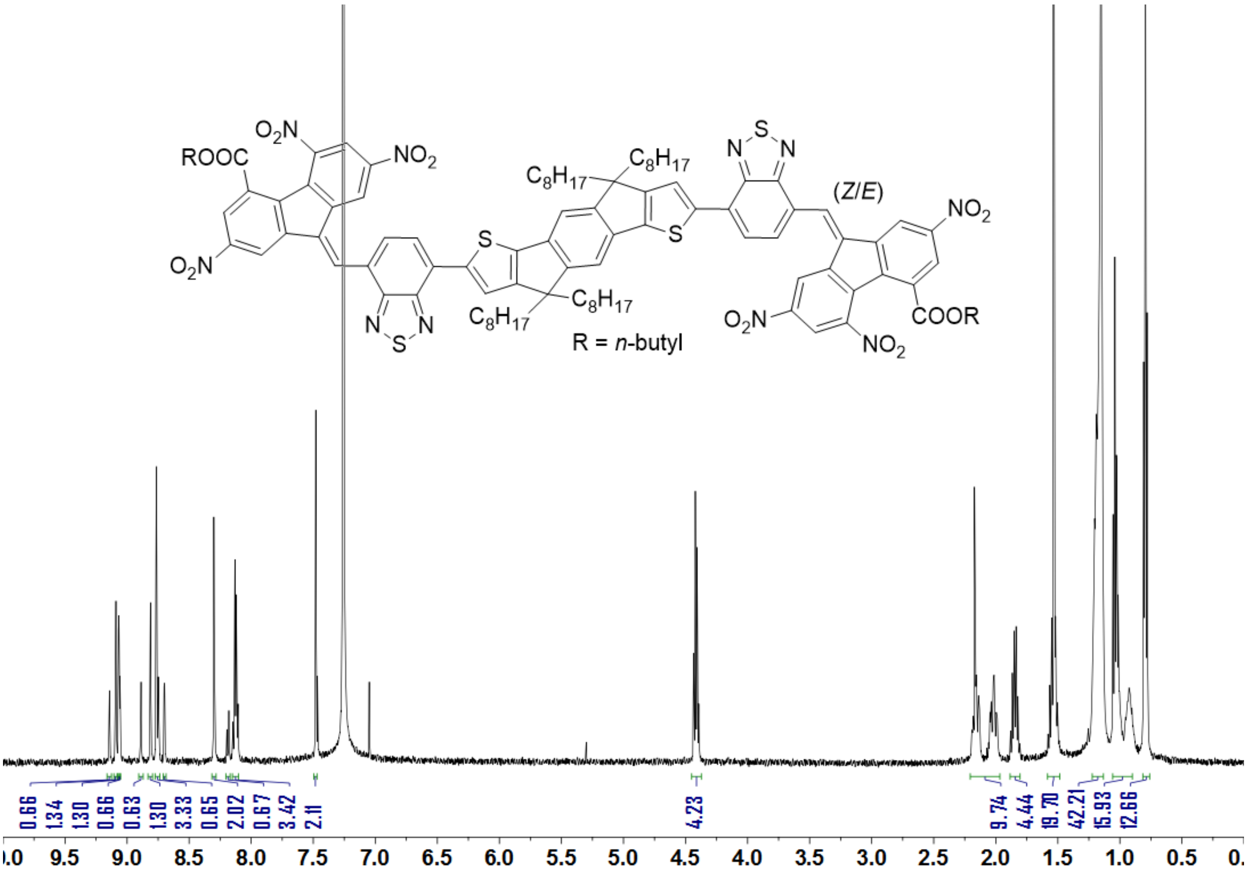
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8**.



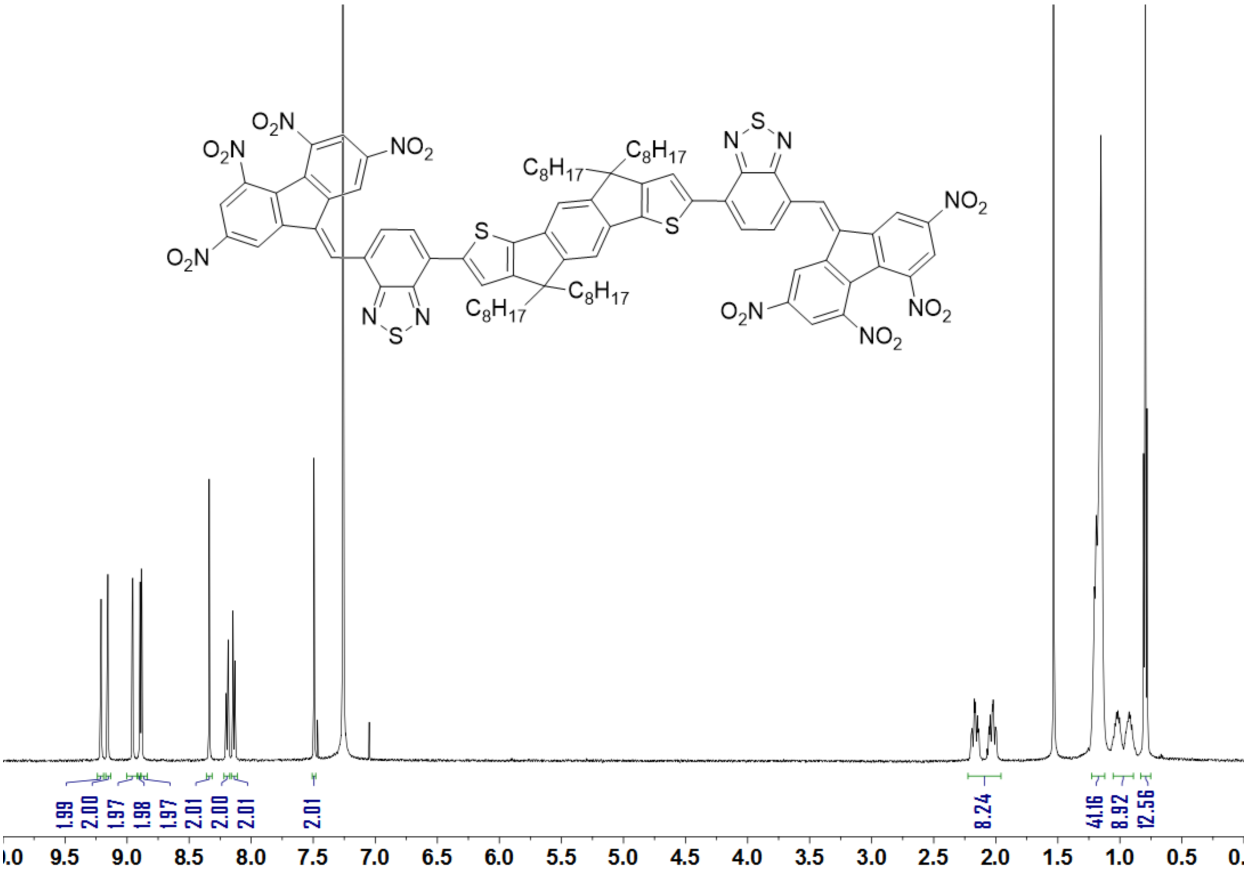
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **IDTBF-2CHO**.



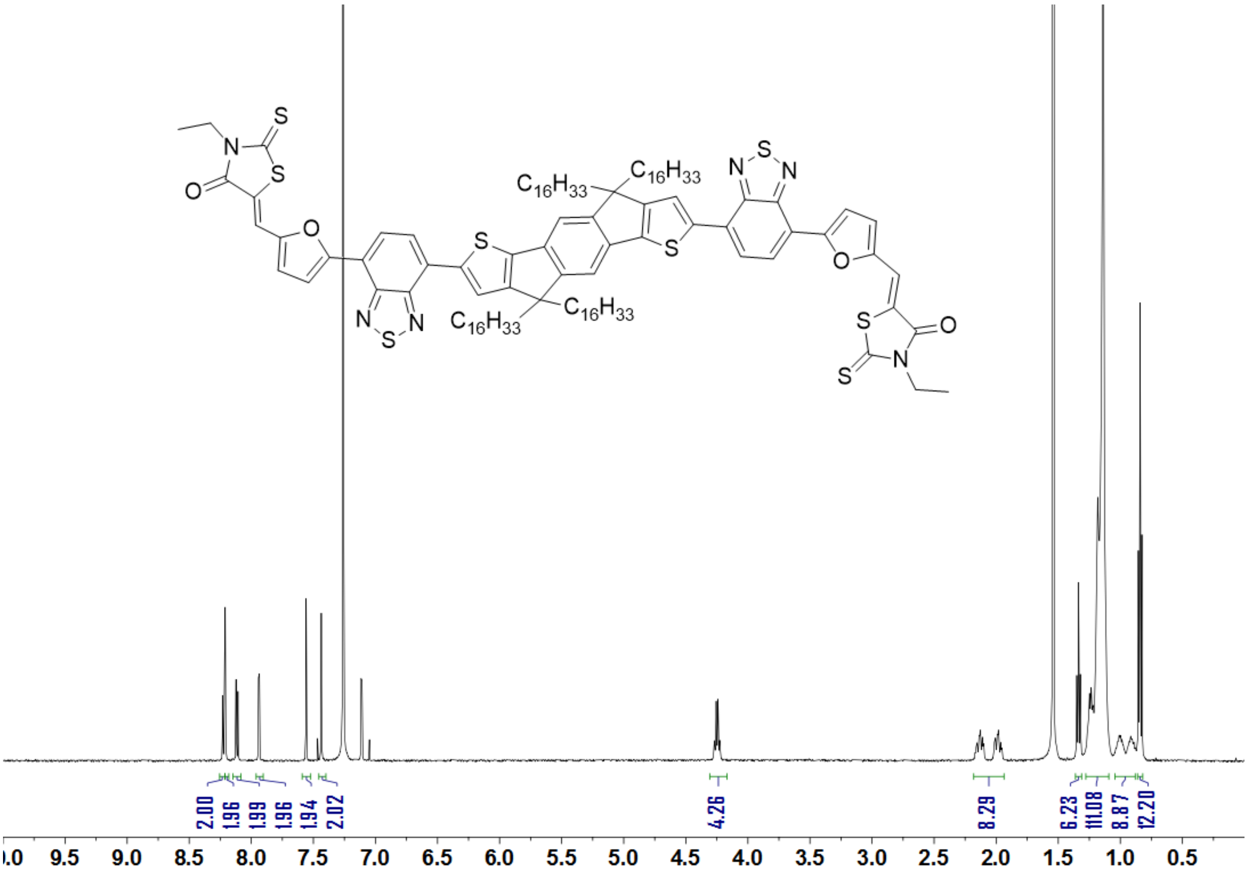
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **IDTB-DNFC4**.



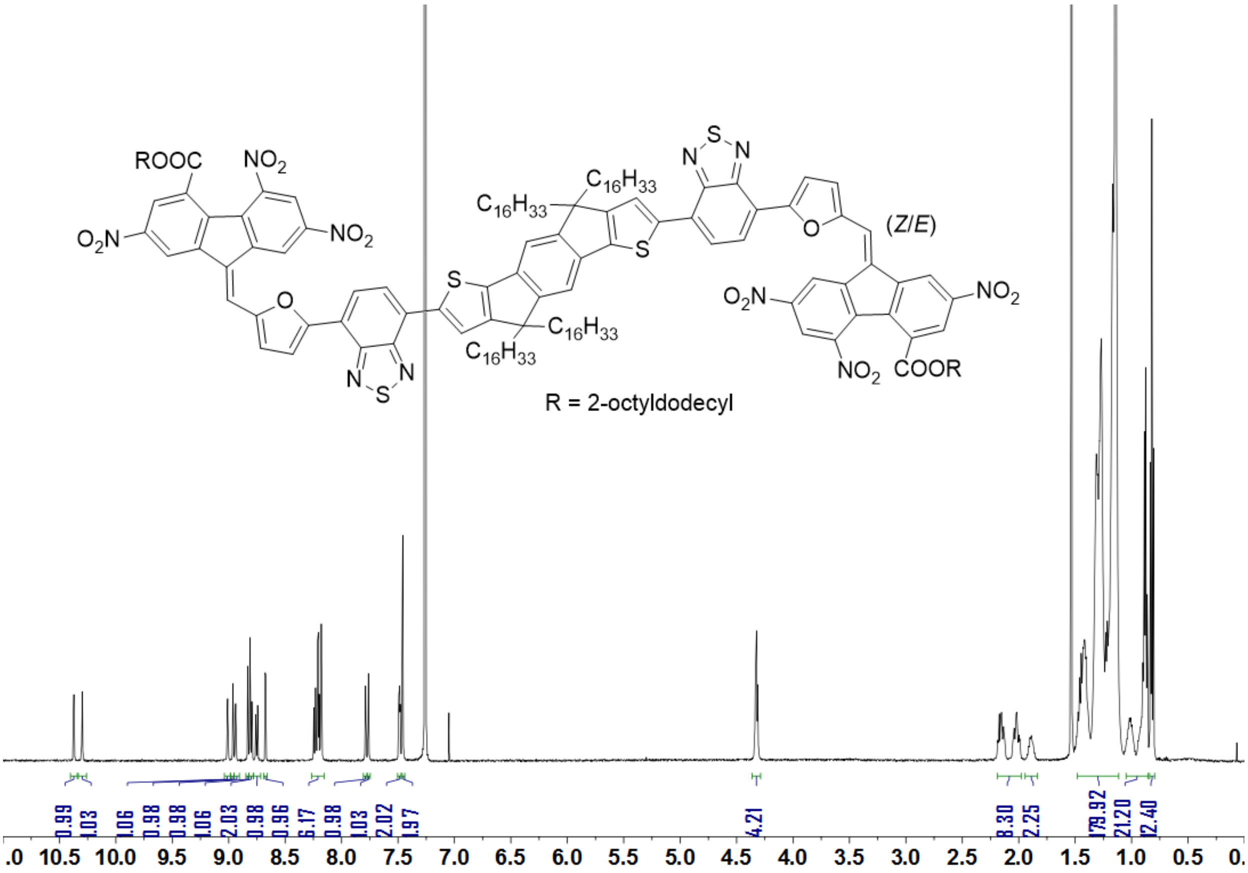
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **IDTB-TNFC4**.



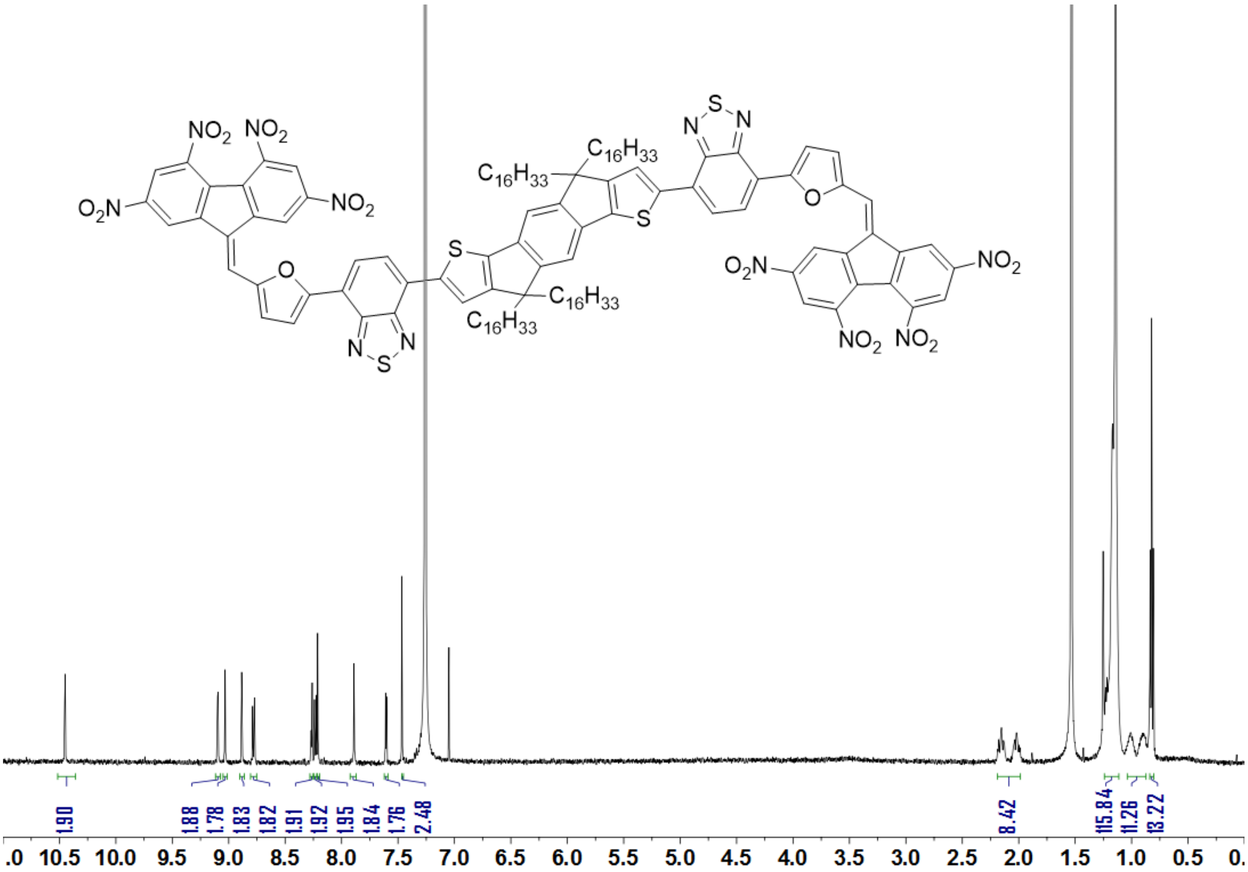
^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **IDTB-TeNF**.



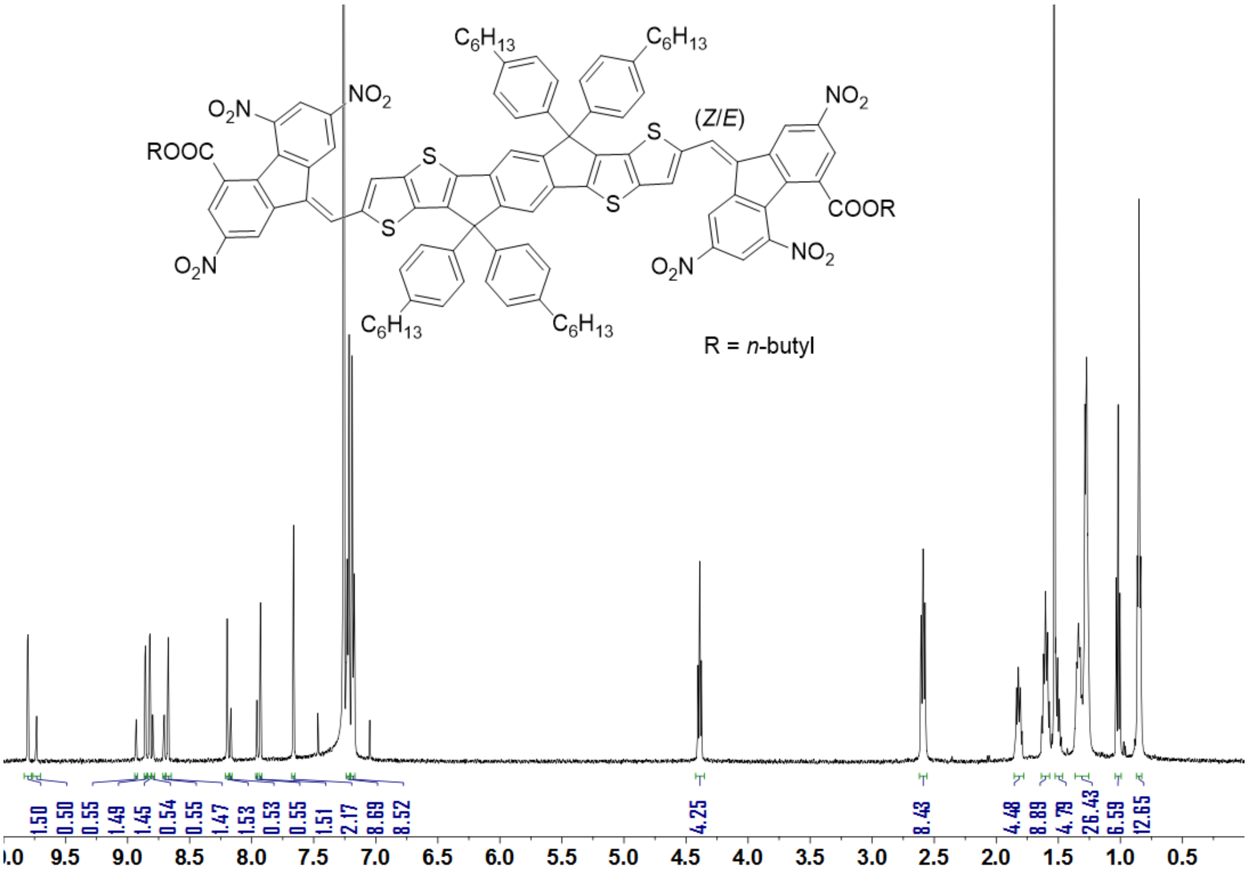
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **IDTBF-R**.



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **IDTBF-TNFC$_8$C$_{12}$**.



^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **IDTBF-TeNF**.



^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **IT-TNFC$_4$**.

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