

Extended Oligo-Cyclopentadithiophene Dyes for Liquid and Solid-state Dye-Sensitised Solar Cells

Artit Jarusarunchai,^a Xuan Liu,^b Wenjun Wu,^b and Neil Robertson*^a

^a School of Chemistry, University of Edinburgh, King's Buildings, David Brewster Road, Edinburgh, EH9 3FJ, UK. Email: Neil.Robertson@ed.ac.uk

^b Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist, Joint Research Center Shanghai Key Laboratory of Functional Materials Chemistry, School of Chemistry and Molecular Engineering, East China University of Science & Technology, 130 Meilon Road, Shanghai 200237, P. R. China. Email: wjwu@ecust.edu.cn

Material and Synthesis Procedure

Unless specified otherwise, all reagents were purchased from Sigma-Aldrich (Merck), Alfa-Aesar, Fisher Scientific and Fluorochem, and were used as received without further purification. 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) was purchased from Shanghai Qinghang Chemical Co. Ltd., China. The synthesis methods for the **T-CPDT** series are described below.

Synthesis of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (1): CPDT (3.01 g, 16.9 mmol), 1-bromohexane (8.35 g, 50.6 mmol) and KI (0.09 g, 0.55 mmol) were dissolved in 120 ml of DMSO and bubbled with N₂ for 10 min. Ground KOH (2.96 g, 52.8 mmol) was added into the mixture, and the resulting mixture was stirred at room temperature for 72 h in the dark. After adding distilled water, the mixture was extracted with hexane. The organic phase was collected, dried over anh. Na₂SO₄, filtered and evaporated to remove hexane. The residue was purified by column chromatography on SiO₂ gel column eluted with hexane to obtain light yellow oil (5.43 g, 93.0%) ¹H NMR (500 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 4.9 Hz, 2H), 6.93 (d, *J* = 4.8 Hz, 2H), 1.84 – 1.80 (m, 4H), 1.20 – 1.10 (m, 12H), 0.94 (ddd, *J* = 14.7, 6.7, 4.2 Hz, 4H), 0.81 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.15, 136.45, 124.41, 121.65, 53.26, 37.76, 31.62, 29.70, 24.49, 22.60, 14.03.

Synthesis of tributyl(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)stannane (2): Compound **1** (1.26 g, 3.64 mmol) was dissolved in 40 ml anh. THF and stirred at -78°C for 30 min under N₂ atmosphere. Then, 1.54 ml (3.85 mmol) of 2.5 M *n*-BuLi in hexane was added slowly and stirred for 1 h. After that, 1.23 ml (3.78 mmol) of Bu₃SnCl was added dropwise into the resulting mixture and stirred overnight while allowing to warm up to room temperature. Brine solution was added to the mixture before being extracted with DCM. The organic phase was collected, dried over anh. Na₂SO₄, filtered and evaporated to remove organic solvent. The obtained purple oil was used without further purification.

Synthesis of 5-(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)thiophene-2-carbaldehyde (3): Tri(*o*-tolyl)phosphine (65.2 mg, 0.214 mmol) and Tris-(dibenzylideneacetone)dipalladium (Pd₂(dba)₃) (97.4 mg, 0.106 mmol) were added to a flame-dried flask, and dried under vacuum for 30 min. A solution of Compound **2** (2.93 g,

4.62 mmol) and 5-bromothiophene-2-carbaldehyde (0.80 g, 4.21 mmol) in 30 ml of anh. toluene was transferred via cannula to the flask under N₂. The mixture was degassed by freeze-pump-thaw technique before being refluxed at 90°C overnight under N₂. After adding 1 M aqueous KF solution of 20 ml, the resulting mixture was stirred for 1 h. Then, the organic phase was extracted to DCM, dried over anh. Na₂SO₄, filtered and evaporated. The crude product was purified by column chromatography on SiO₂ gel column eluted with hexane/5% EtOAc to obtain orange oil (1.64 g, 85.2%). ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 9.83 (s, 1H), 7.68 (d, *J* = 4.1 Hz, 1H), 7.29 (d, *J* = 4.9 Hz, 1H), 7.27 (s, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 6.99 (d, *J* = 4.9 Hz, 1H), 1.88 (dd, *J* = 8.9, 7.7 Hz, 4H), 1.21 – 1.11 (m, 12H), 1.00 – 0.90 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 182.12, 159.48, 159.11, 148.14, 140.68, 138.93, 137.60, 135.77, 135.29, 126.65, 122.92, 121.81, 120.83, 37.70, 31.58, 29.61, 24.47, 22.57, 13.76. MS (ESI): [M+H]⁺ Calcd for C₂₆H₃₃OS₃: 457.1688; found: 457.1674.

Synthesis of (*E*)-2-cyano-3-(5-(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)thiophen-2-yl)acrylic acid (T-CPDT-1): In N₂ atmosphere, compound **3** (380 mg, 0.88 mmol) and 2-cyanoacetic acid (230 mg, 2.65 mmol) were dissolved with anh. CHCl₃ in an oven-dried flask. Piperidine (0.70 ml, 7.09 mmol) was added to the mixture before the mixture was refluxed for 6 h. After that, the resulting mixture was diluted with DCM and extracted with 1 M aqueous HCl. The organic phase was collected, dried over anh. Na₂SO₄, filtered and evaporated. The crude product was purified by Dry Column Vacuum Chromatography (DCVC)¹ technique eluted with gradient elution (hexane to DCM with 10% increment and DCM to 20% MeOH with 5% increment). The orange solution was diluted with DCM and extracted 1 M aqueous HCl to obtain pink solid (458 mg, 95.5%). ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 8.33 (s, 1H), 7.71 (d, *J* = 4.2 Hz, 1H), 7.37 (s, 1H), 7.32 (d, *J* = 4.9 Hz, 1H), 7.28 (d, *J* = 4.1 Hz, 1H), 7.00 (d, *J* = 4.9 Hz, 1H), 1.93 – 1.86 (m, 4H), 1.22 – 1.11 (m, 12H), 1.00 – 0.89 (m, 4H), 0.81 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 167.44, 160.49, 159.96, 150.80, 147.87, 141.51, 140.73, 136.18, 135.42, 133.46, 127.77, 123.66, 122.29, 122.14, 116.44, 95.21, 54.48, 38.22, 32.01, 30.02, 24.89, 23.01, 14.19. MS (ESI): [M]⁺ Calcd for C₂₉H₃₃NO₂S₃: 523.1668; found: 523.1661. Anal. Calcd for C₂₉H₃₃NO₂S₃: C, 66.50; H, 6.35; N, 2.67; found: C, 66.40; H, 6.31; N, 2.51.

Synthesis of 5-(6-bromo-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-2-yl)thiophene-2-carbaldehyde (4): *N*-bromosuccinimide (NBS) (0.25 g, 1.38 mmol) was added to a cold solution of compound **3** (0.63 g, 1.38 mmol) dissolved in 40 ml of THF at 0°C under N₂. After that, the mixture was stirred overnight at room temperature. Distilled water was added into the resulting mixture, followed by extraction with DCM. The organic phase was collected, dried over dried over anh. Na₂SO₄, filtered and evaporated. The pure product was obtained as orange oil (qunt.) ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 9.79 (s, 1H), 7.67 (s, 1H), 7.51 (s, 1H), 7.03 (s, 1H), 1.92 – 1.80 (m, 4H), 1.23 – 1.11 (m, 12H), 0.99 – 0.90 (m, 4H), 0.82 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 182.16, 158.29, 158.02, 147.79, 140.93, 138.15, 137.56, 136.28, 135.90, 123.16, 120.61, 112.59, 37.62, 31.57, 29.57, 24.43, 22.58, 13.75. MS (ESI): [*M*]⁺ Calcd for C₂₉H₃₁BrOS₃: 534.0715; found: 534.0706.

Synthesis of 5-(4,4,4',4'-tetrahexyl-4*H*,4'*H*-[2,2'-bi(cyclopenta[2,1-*b*:3,4-*b'*]dithiophen)]-6-yl)thiophene-2-carbaldehyde (5): Pd₂(dba)₃ (14.5 mg, 0.016 mmol) and Tri(*o*-tolyl)phosphine (10 mg, 0.033 mmol) were put in a flame-dried flask, and dried under vacuum for 30 min. A solution of Compound **2** (305 mg, 0.48 mmol) and Compound **4** (242 mg, 0.45 mmol) in 20 ml of anh. toluene was transferred via cannula to the flask under N₂. The mixture was degassed by freeze-pump-thaw technique before being refluxed at 90°C overnight under N₂. After adding 1 M aqueous KF solution of 20 ml, the resulting mixture was stirred for 1 h. Then, the organic phase was extracted to DCM, dried over anh. Na₂SO₄, filtered and evaporated. The crude product was purified by column chromatography on SiO₂ gel column eluted with hexane/10% EtOAc to obtain red oil (273 mg, 75.3%) ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 9.87 (s, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.32 (s, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 7.26 (d, *J* = 4.9 Hz, 1H), 7.15 (s, 1H), 7.12 (s, 1H), 7.02 (d, *J* = 4.9 Hz, 1H), 1.94 (ddd, *J* = 16.9, 8.4, 5.9 Hz, 8H), 1.27 – 1.17 (m, 24H), 1.09 – 0.98 (m, 8H), 0.87 (td, *J* = 7.0, 1.4 Hz, 12H). ¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 182.00, 160.24, 158.99, 158.75, 158.30, 148.09, 140.63, 140.40, 138.98, 137.63, 136.27, 135.58, 134.01, 125.31, 122.88, 121.75, 120.67, 117.85, 117.15, 37.85, 31.66, 29.72, 24.54, 22.67, 13.85. MS (ESI): [*M*]⁺ Calcd for C₄₇H₆₀NOS₅: 800.3242; found: 800.3245.

Synthesis of (E)-2-cyano-3-(5-(4,4,4',4'-tetrahexyl-4H,4'H-[2,2'-bi(cyclopenta[2,1-b:3,4-b']dithiophen)]-6-yl)thiophen-2-yl)acrylic acid (T-CPDT-2): In N₂ atmosphere, compound **5** (449 mg, 0.56 mmol) and 2-cyanoacetic acid (150 mg, 1.76 mmol) were dissolved with anh. CHCl₃ in an oven-dried flask. Piperidine (0.50 ml, 5.06 mmol) was added to the mixture before the mixture was refluxed for 6 h. After that, the resulting mixture was diluted with DCM and extracted with 1 M aqueous HCl. The organic phase was collected, dried over anh. Na₂SO₄, filtered and evaporated. The crude product was purified by DCVC¹ technique eluted with gradient elution (hexane to DCM with 10% increment and DCM to 20% MeOH with 5% increment). The red-purple solution was diluted with DCM and extracted 1 M aqueous HCl to obtain dark purple solid (372 mg, 76.3%) ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 8.33 (s, 1H), 7.70 (d, *J* = 4.2 Hz, 1H), 7.36 (s, 1H), 7.27 (d, *J* = 4.2 Hz, 1H), 7.22 (d, *J* = 4.9 Hz, 1H), 7.11 (s, 1H), 7.07 (s, 1H), 6.97 (d, *J* = 4.8 Hz, 1H), 1.97 – 1.82 (m, 8H), 1.23 – 1.13 (m, 24H), 1.03 – 0.93 (m, 8H), 0.82 (t, *J* = 6.9 Hz, 12H). ¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 161.29, 159.59, 159.44, 158.82, 147.60, 141.45, 140.71, 137.91, 136.63, 136.23, 135.64, 134.37, 133.47, 125.81, 123.58, 122.18, 121.92, 118.43, 117.55, 54.89, 38.34, 38.23, 32.05, 30.08, 24.92, 23.05, 23.03, 14.20. MS (ESI): [M+H]⁺ Calcd for C₅₀H₆₁NO₂S₅: 868.3379; found: 868.3401. Anal. Calcd for C₅₀H₆₁NO₂S₅: C, 69.16; H, 7.08; N, 1.61; found: C, 68.91; H, 7.20; N, 1.52.

Synthesis of 5-(6'-bromo-4,4,4',4'-tetrahexyl-4H,4'H-[2,2'-bi(cyclopenta-[2,1-b:3,4-b']dithiophen)]-6-yl)thiophene-2-carbaldehyde (6): NBS (283 mg, 1.59 mmol) was added to a cold solution of compound **5** (1.20 g, 1.50 mmol) dissolved in 40 ml of THF at 0°C under N₂. After that, the mixture was stirred overnight at room temperature. Distilled water was added into the resulting mixture, followed by extraction with DCM. The organic phase was collected, dried over dried over anh. Na₂SO₄, filtered and evaporated. The crude product was purified by column chromatography on SiO₂ gel column eluted with hexane/10% EtOAc to obtain red oil (1.26 g, 95.1%). ¹H NMR (500 MHz, Methylene Chloride-*d*₂) δ 9.87 (s, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.30 (s, 1H), 7.30 (d, *J* = 3.9 Hz, 1H), 7.11 (s, 1H), 7.11 (s, 1H), 7.04 (s, 1H), 1.96 – 1.91 (m, 4H), 1.91 – 1.85 (m, 4H), 1.27 – 1.17 (m, 24H), 1.06 – 0.96 (m, 8H), 0.86 (td, *J* = 7.0, 5.3 Hz, 12H). ¹³C NMR (126 MHz, Methylene Chloride-*d*₂) δ 182.08, 160.21, 158.85, 158.22, 156.80, 148.02, 140.66, 139.98, 138.84, 138.24, 137.63, 135.66, 124.91,

120.68, 117.62, 117.37, 111.00, 37.81, 37.73, 31.61, 29.66, 24.48, 24.44, 22.61, 13.77. MS (ESI): $[M]^+$ Calcd for $C_{47}H_{59}BrOS_5$: 878.2347; found: 878.2349.

Synthesis of 5-(4,4,4',4',4'',4''-hexahexyl-4H,4'H,4''H-[2,2':6',2''-tercyclo-penta[2,1-b:3,4-b']dithiophen]-6-yl)thiophene-2-carbaldehyde (7): Tri(*o*-tolyl)-phosphine (38.2 mg, 0.126 mmol) and $Pd_2(dba)_3$ (54.5 mg, 0.059 mmol) were put in a flame-dried flask, and dried under vacuum for 30 min. A solution of Compound **2** (1.46 g, 1.40 mmol) and Compound **6** (1.12 g, 1.27 mmol) in 30 ml of anh. toluene was transferred via cannula to the flask under N_2 . The mixture was degassed by freeze-pump-thaw technique before being refluxed at $90^\circ C$ overnight under N_2 . After adding 1 M aqueous KF solution of 20 ml, the resulting mixture was stirred for 1 h. Then, the organic phase was extracted to DCM, dried over anh. Na_2SO_4 , filtered and evaporated. The crude product was purified by column chromatography on SiO_2 gel column eluted with hexane/10% EtOAc to obtain pink-purple oil (1.05 g, 76.7%) 1H NMR (500 MHz, Methylene Chloride- d_2) δ 9.87 (s, 1H), 7.72 (d, $J = 4.0$ Hz, 1H), 7.31 (s, 1H), 7.30 (d, $J = 4.0$ Hz, 1H), 7.25 (d, $J = 4.8$ Hz, 1H), 7.13 (s, 1H), 7.12 (s, 1H), 7.11 (s, 1H), 7.10 (s, 1H), 7.01 (d, $J = 4.8$ Hz, 1H), 1.98 – 1.88 (m, 12H), 1.27 – 1.17 (m, 36H), 1.03 (ddt, $J = 21.7, 14.5, 6.9$ Hz, 12H), 0.89 – 0.83 (m, 18H). MS (ESI): $[M]^+$ Calcd for $C_{68}H_{88}OS_7$: 1144.4875; found: 1144.4860.

Synthesis of (E)-2-cyano-3-(5-(4,4,4',4',4'',4''-hexahexyl-4H,4'H,4''H-[2,2':6',2''-tercyclopenta[2,1-b:3,4-b']dithiophen]-6-yl)thiophen-2-yl)acrylic acid (T-CPDT-3): Under N_2 atmosphere, compound **7** (232 mg, 0.20 mmol) and 2-cyanoacetic acid (57.2 mg, 0.67 mmol) were dissolved with anh. $CHCl_3$ in an oven-dried flask. piperidine (0.19 ml, 1.92 mmol) was added to the mixture before the mixture was refluxed for 6 h. After that, the resulting mixture was diluted with DCM and extracted with 1 M aqueous HCl. The organic phase was collected, dried over anh. Na_2SO_4 , filtered and evaporated. The crude product was purified by DCVC¹ technique eluted with gradient elution (hexane to DCM with 10% increment and DCM to 20% MeOH with 5% increment). The purple solution was diluted with DCM and extracted 1 M aqueous HCl to obtain black solid (0.20 g, 81.2%) 1H NMR (500 MHz, Methylene Chloride- d_2) δ 8.29 (s, 1H), 7.69 (d, $J = 4.2$ Hz, 1H), 7.36 (s, 1H), 7.28 (d, $J = 4.1$ Hz, 1H), 7.21 (d, $J = 4.9$ Hz, 1H), 7.11 (s, 1H), 7.08 (s, 1H), 7.07 (s, 1H), 7.06 (s, 1H), 6.97 (d, $J = 4.8$ Hz, 1H), 1.90 (td, $J = 15.8, 9.8$ Hz, 12H), 1.22 – 1.14 (m, 36H), 1.00 (s, 12H), 0.82 (td, $J = 7.0,$

1.4 Hz, 18H). MS (ESI): $[M+H]^+$ Calcd for $C_{71}H_{89}NO_2S_7$: 1212.5011; found: 1212.4958. Anal. Calcd for $C_{71}H_{89}NO_2S_7$: C, 70.31; H, 7.40; N, 1.15; found: C, 70.72; H, 7.49; N, 1.02.

Characterisation methods

Dye structure characterisations: 1H and ^{13}C NMR spectra were recorded on Bruker Advance 500 spectrometer (500 MHz for 1H and 126 MHz for ^{13}C). All chemical shifts were reported in parts per million (ppm) and coupling constants (J) were given in hertz (Hz). The deuterated solvents used for NMR were standardized by the solvent residual signal for 1H and ^{13}C . MS were recorded on ThermoElectron MAT 900 using electrospray ionization (ESI) technique. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University using a Carlo Erba CE1108 Elemental Analyser.

Optical characterisation: UV-visible absorption spectra were recorded on Jasco V-670 UV/vis/NIR spectrophotometer controlled by the SpectraManager software. All solutions were prepared in DCM. All extinction coefficients were determined by the Beer-Lambert plot with various concentrations in a range of 5-20 μM of corresponding dye.

Electrochemical characterisation: All voltammetry measurements were performed in anhydrous DCM with 0.3 M TBAPF₆ as supporting electrolyte in a three-electrode system at room temperature. Each solution was purged with N₂ prior to measurement. The working electrode was a Pt disk while the counter electrode and reference electrode were a Pt rod and Ag/AgCl in 2 M LiCl in ethanol, respectively. All measurements were carried out by using μ AUTOLAB Type III potentiostat driven by the electrochemical software GPES. The scan rates used in Cyclic Voltammetry (CV) were 0.2, 0.4, 0.6, 0.8, and 1.0 V/s. Square-wave Voltammetry (SWV) were conducted at a step potential of 2.1 mV, amplitude of 250 mV, and frequency of 25 Hz, which gave a scan rate of 52.5 mV/s. All measurements were referenced to Ferrocene/Ferrocenium (Fc/Fc⁺) as an internal standard.

Theoretical calculations: The molecular dye structures were built in Avogadro² and adjusted the drawn molecule by using basic optimisation in Avogadro. The drawn molecules were optimised by using Gaussian 09³ at B3LYP⁴ level of theory with 6-31G(d) basis set under vacuum. After that, the optimised structures were subject to re-optimisation in DCM

(PCM solvation model)⁵. The TD-DFT calculations used the optimised structures in solvation model and were conducted by using Gaussian 09 at CAM-B3LYP⁶ level of theory with 6-31G(d) basis set and in DCM (PCM solvation model). The 50 states of singlet electronic transitions obtained from TD-DFT calculations were processed with the GaussSum software package⁷. For the dyes' dipole moment, the DFT optimised dyes in DCM solvent model were subjected to GaussView 6⁸ for visualisation.

Solar cell fabrications: There are two types of solar cells in this work. For I^-/I_3^- electrolyte-based devices (fabricated at University of Edinburgh), fluorine-doped tin oxide (FTO) coated glass (Merck, $7 \Omega \text{ sq}^{-1}$) was cleaned by using 2% Hellmanex solution with sonication in deionised water for 30 min, followed by sonication in ethanol for 30 min. The cleaned glass was treated with UV-O₃ treatment for 20 min. After that, the cleaned and treated glass was pre-treated with 40 mM aqueous solution TiCl₄ at 70°C for 30 min, which subsequently rinsed with deionised water and ethanol, respectively. The TiCl₄ treated glass was sintered at 500°C for 30 min. Upon cooling down, the sintered glass was screen printed with commercial transparent TiO₂ paste (Ti-Nanoxide T/SP, Solaronix), followed by drying at 120°C for 10 min. This process was repeated twice to obtain 2 layers of transparent TiO₂. The scattering TiO₂ paste (Ti-Nanoxide T/SP, Solaronix) was screen printed on printed glass, followed by drying at 120°C for 10 min. The films were annealed at 500°C for 15 min using programmable hotplate. The resulting TiO₂ film thickness was 12 μm with the active area of 0.28 cm². The sintered films were allowed to cool down and were treated with 40 mM aqueous solution TiCl₄ at 70°C for 30 min, rinsed with deionised water and ethanol and were sintered again at 500°C for 30 min. When the temperature dropped to about 90°C, the films were soaked in 0.5 mM dye bath (**T-CPDT** series, **CPDT-3** or **5T**) containing 5 mM CDCA in chloroform:ethanol of 3:7 v/v for 3 h. The sensitised working electrodes were removed from dye bath and washed with acetonitrile to remove unadsorbed dye molecules. The counter electrodes were pre-drilled on FTO glass, washed by sonicating in 0.1 M HCl in ethanol for 15 min, followed by sonicating in ethanol for 15 min and deionised water for 15 min, respectively. The cleaned pre-drilled glass was doctor-bladed with Platisol (Solaronix) and sintered at 450°C for 15 min. The DSSCs were assembled by using hot-melt sealing film (Solaronix). The composition of electrolyte was 0.05 M Guanidinium thiocyanate (GuSCN), 1 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.03 M I₂, 0.05 M LiI and 0.25 M 4-tert-

butyl pyridine (4-tBP) in acetonitrile:valeronitrile of 85%:15% v/v. The electrolyte was injected into the assembled cells by using Vac'n'Fill Syringe (Solaronix). The hole was covered by cover glass with hot-melt sealing film (Solaronix).

For solid-state devices, they were fabricated at East China University of Science and Technology, China. The fabrication method is as followed. FTO glass substrates (Yingkou OPV new energy technology co., LTD in China, $15 \Omega \text{ sq}^{-1}$) were cleaned respectively with a detergent solution, deionized water, acetone and ethanol in an ultrasonic bath for 30 min. Once cleaned and dried, a precursor solution of *bis*(2,4-pentanedionato) *bis*(2-propanolato) titanium was sprayed on the preheated FTO substrates to form a compact TiO_2 layer, followed by sintering at 450°C for 30 min. Subsequently, a mesoporous TiO_2 (30NR-D diluted with ethanol with the ratio of 2:3 TiO_2 :ethanol) layer was spin-coated on the FTO substrates at 4000 rpm for 30 s, followed by annealing at 500°C for 30 min in the ambient air. After cooling down to room temperature, the substrates were immersed into a 40 mM TiCl_4 solution and kept at 70°C in an oven for 30 min, rinsed with water and ethanol, and sintered. After that, the TiO_2 substrates were immersed into 0.5 mM dye solution (**T-CPDT-1**, **T-CPDT-2** and **T-CPDT-3**) and kept in the dark for 3 h, and then washed by deionized water and ethanol. Afterwards, a hole-transport material (HTM), comprised of 132 mg of Spiro-OMeTAD, 15 mg of lithium bis-(trifluoromethylsulphonyl) imide (LiTFSI) and 24 mg of 4-*tert*-butylpyridine (4-tBP) in 900 μL of chlorobenzene, was spin-coated on the above substrates at 2000 rpm for 30 s in a N_2 -protected glove box. Finally, 80 nm of gold was deposited by thermal evaporation under high vacuum (lower than 5×10^{-4} Pa).

Solar cell characterisation: For characterisation of I^-/I_3^- electrolyte-based devices, the photocurrent-voltage (J - V) measurements were carried out on an Autolab potentiostat (Metrohm), driven by electrochemical software GPES, with class AAA SLB300A solar simulator (Sciencetech) as the light source. The light intensity was calibrated to AM 1.5G by using a silicon reference cell. A black metal mask with a circular aperture of 0.0707 cm^2 was applied when measuring J - V curves. The electrochemical impedance (EIS) spectra of I^-/I_3^- electrolyte-based devices setup was similar to the J - V measurements, except for using white LED as the light source and Frequency Response Analyser (FRA) software. The EIS spectra were recorded in the frequency range between 0.1 MHz and 0.05 Hz at various forward

biases set to the corresponding voltage produced by white LED illumination. The obtained spectra were fitted with a transmission line model⁹ by using Zview (Scribner Associates) software.

For solid-state device characterisation, the J - V curves were measured by a Keithley 2400 sourcemeter under AM1.5G illumination using an Oriel 91106 solar simulator (Newport, USA). The black metal mask with an area of 0.124 cm² was used for J - V curve measurements.

The incident-photon-to-current conversion efficiency (IPCE) spectra for both types of devices were recorded in East China University of Science and Technology, China by using Newport-74125 system (Newport Instruments).

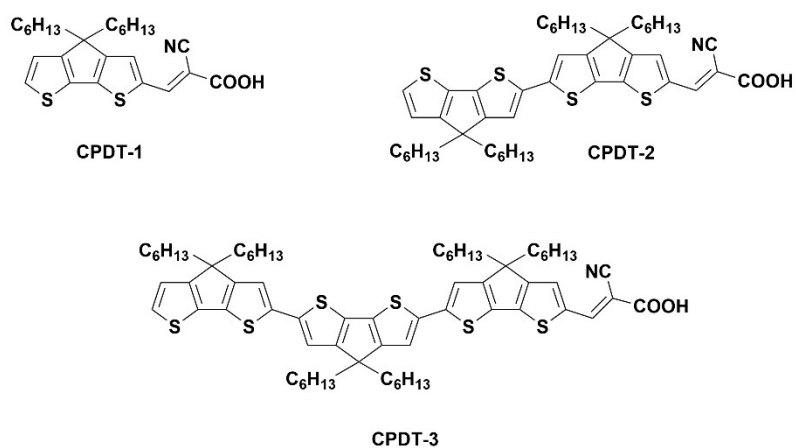


Figure S1 Molecular structures of CPDT series

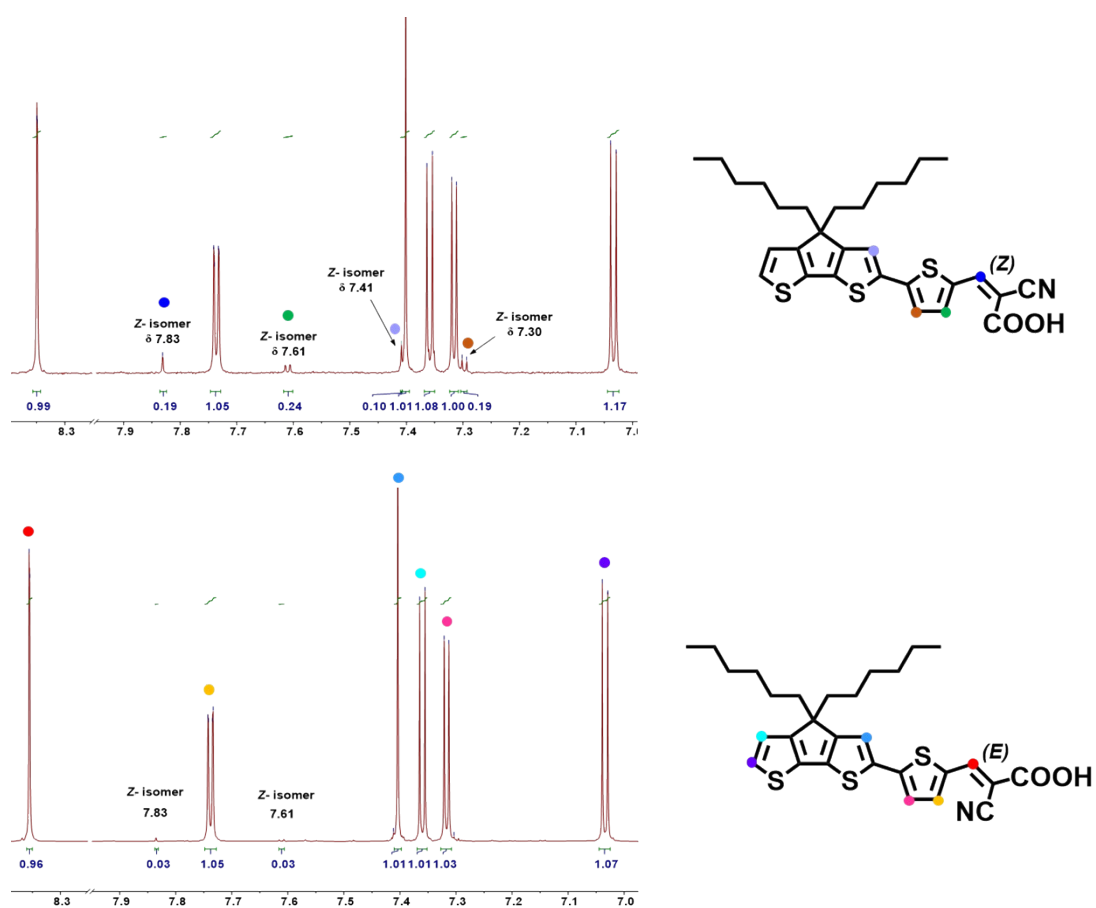


Figure S2 ^1H NMR of T-CPDT-1 (top) showing the mixture of (*E*)- and (*Z*)-isomer with the ratio of 84:16, and (bottom) showing around 97% purity of (*E*)-isomer signals in aromatic region

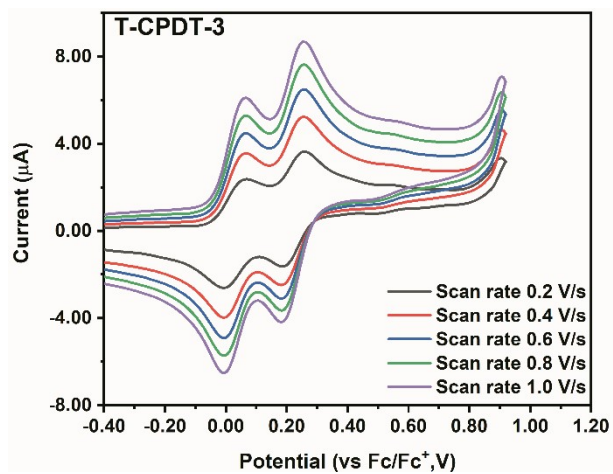
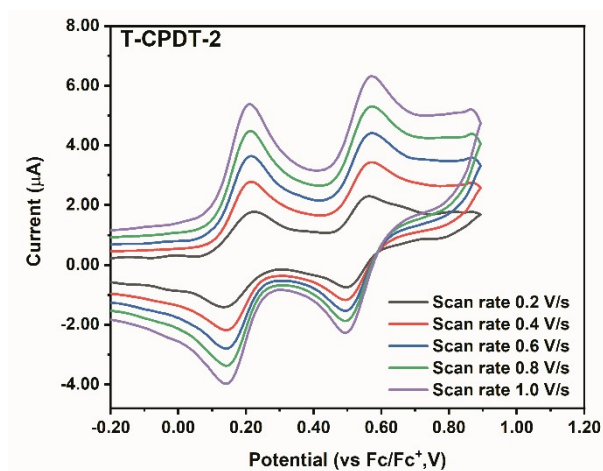
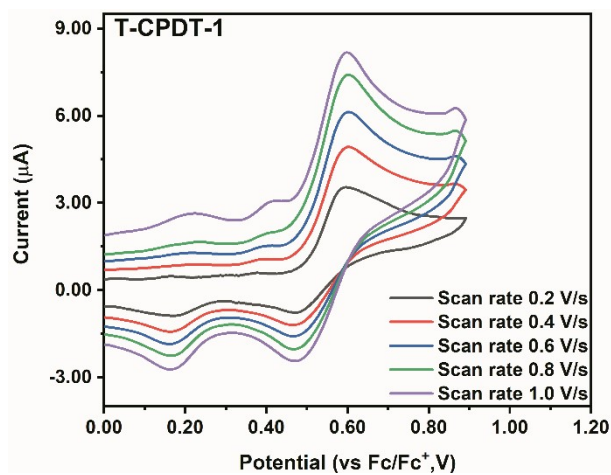


Figure S3 Cyclic voltammograms of T-CPDT series: (top) T-CPDT-1, (middle) T-CPDT-2 and (bottom) T-CPDT-3

Table S1 Photovoltaic parameters and TiO₂ thickness of ssDSSCs with Spiro-OMeTAD as HTM for **T-CPDT-3** in comparison to some other ssDSSCs with the same additives

Dye	TiO ₂ thickness (μm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	ff	PCE (%)	Ref.
T-CPDT-3	0.96	11.27	0.68	0.58	4.38	This work
C220	2.0	9.74	0.88	0.71	6.08	10
D35	2.7	7.21	0.86	0.73	4.50	11
M14	2.7	8.08	0.82	0.67	4.37	11
5T	1.5	7.69	0.92	0.62	4.40	12

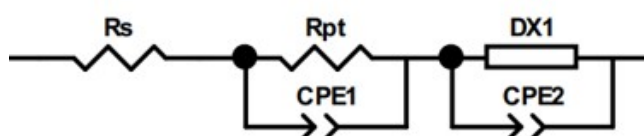
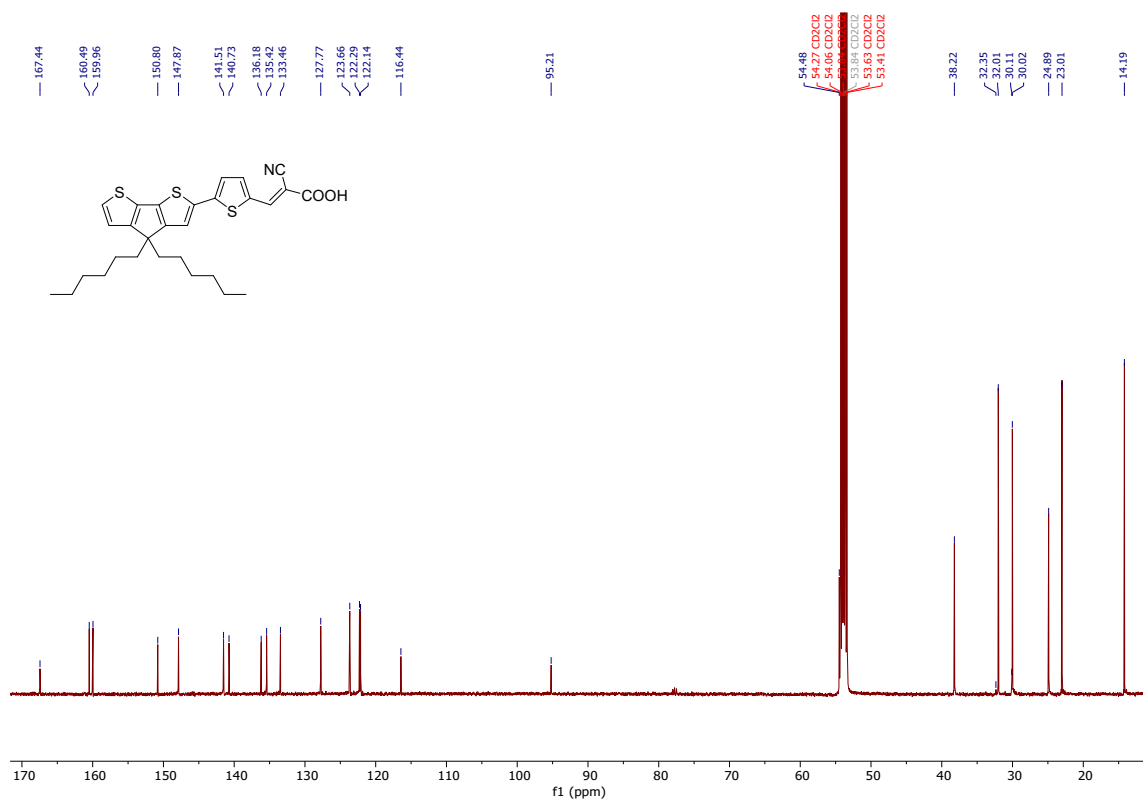
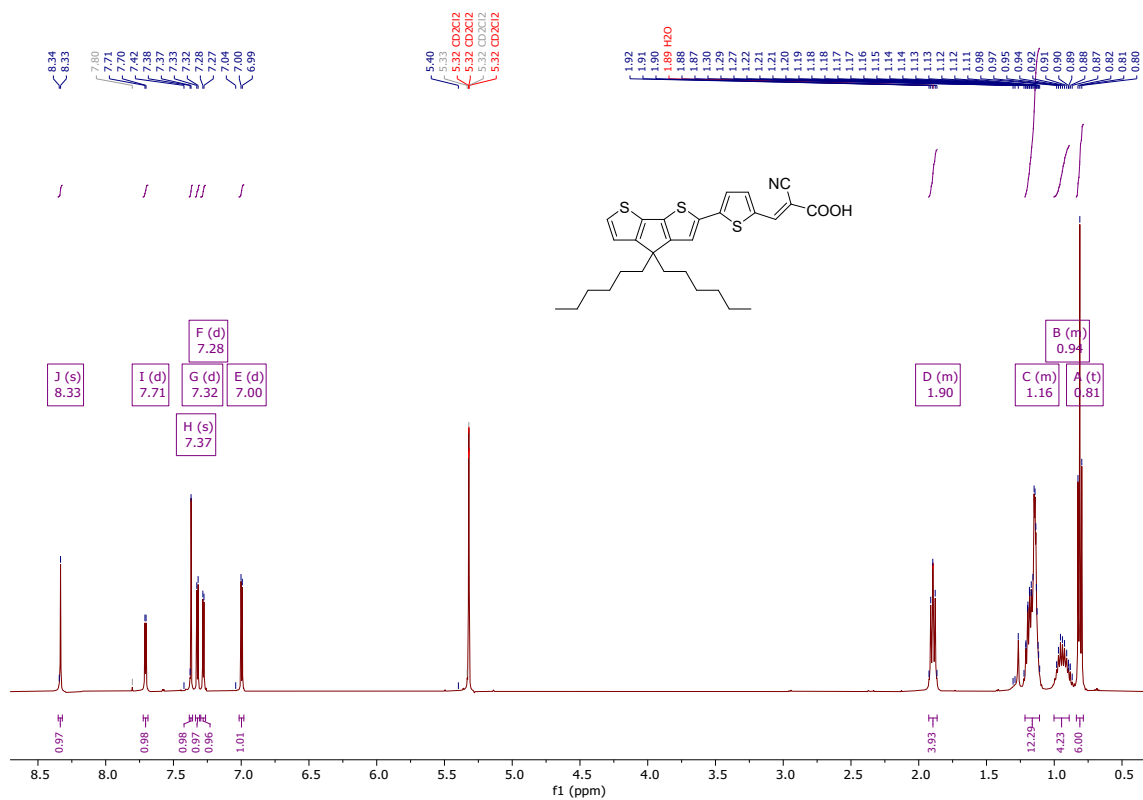


Figure S4 Equivalent circuit of full transmission line model for EIS fitting where R_s is a series resistance due to FTO and wires; R_{pt} and CPE1 are a charge transfer resistance and a constant phase element at Pt/electrolyte interface, respectively; DX1 is an extended element (model 11: Bisquet #2 in Zview) representing the transmission line model of the diffusion-recombination processes at TiO₂/electrolyte interface; and CPE2 is a constant phase element at FTO/TiO₂/electrolyte.



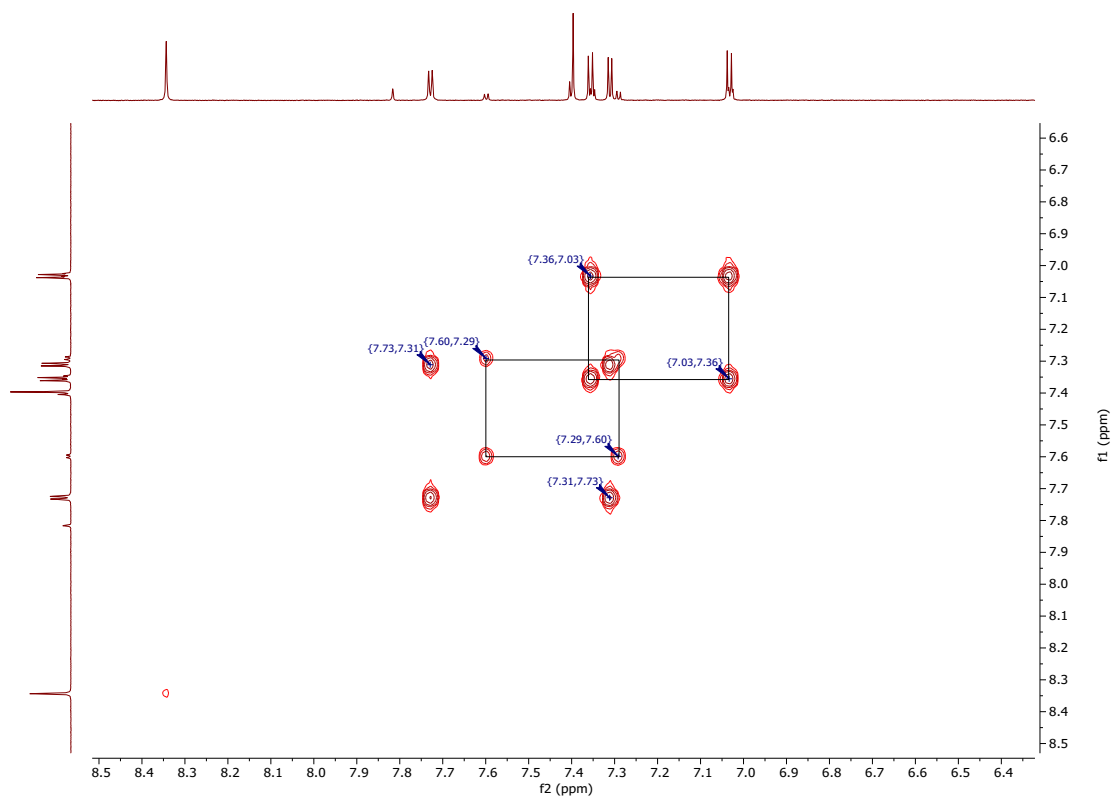


Figure S6 COSY spectrum of an isomeric mixture of **T-CPDT-1**; the rectangles showing the minor isomer

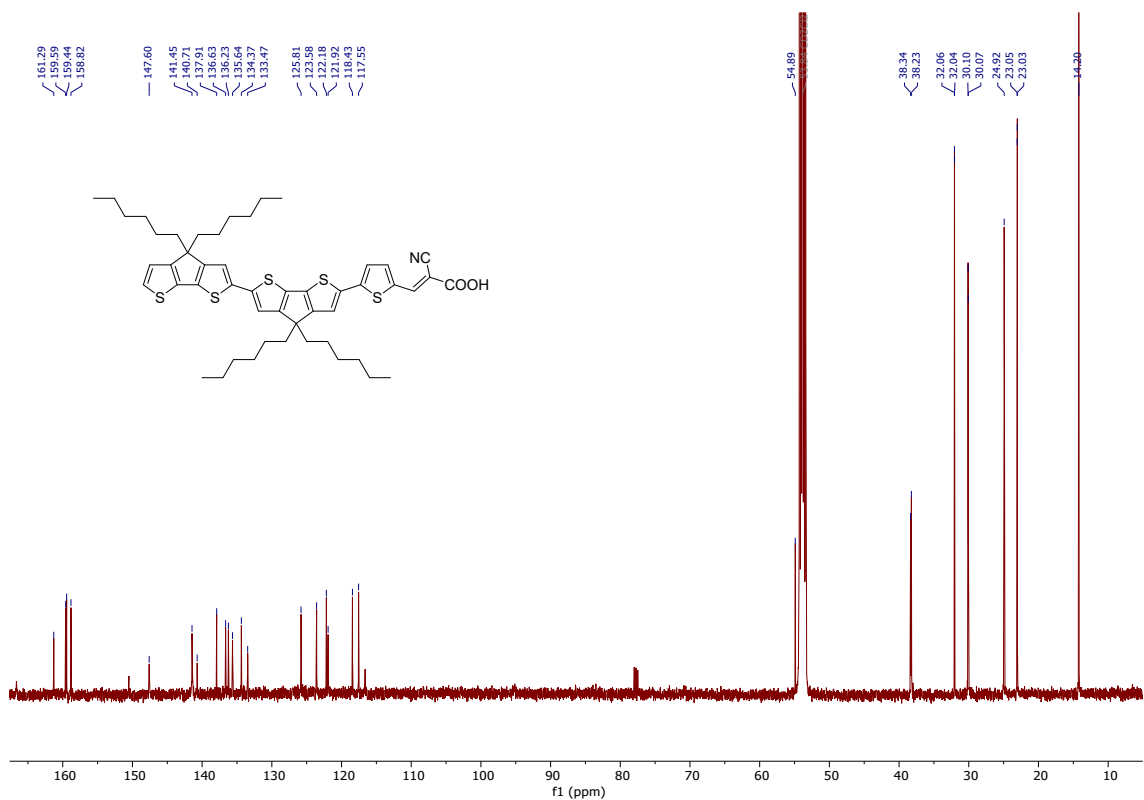
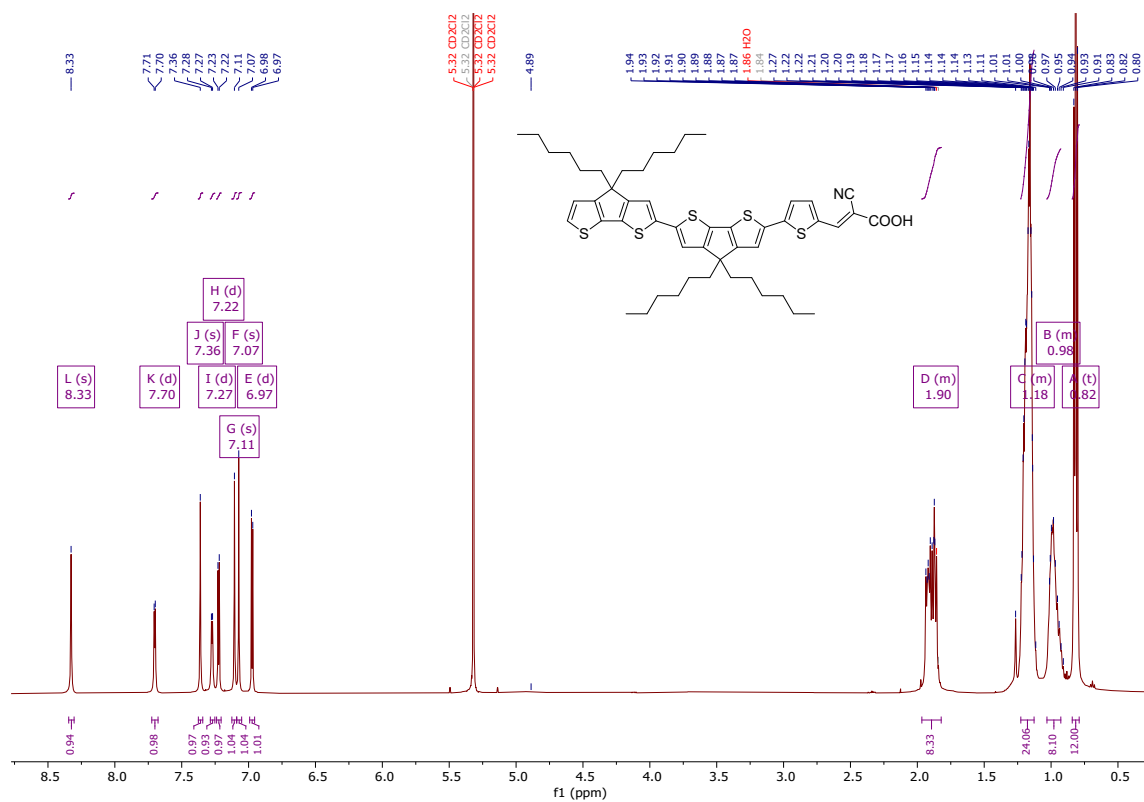


Figure S7 ¹H and ¹³C NMR spectra of T-CPDT-2

References

- 1 D. S. Pedersen and C. Rosenbohm, *Synthesis (Stuttg.)*, 2001, **2001**, 2431–2434.
- 2 M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *J. Cheminform.*, 2012, **4**, 17.
- 3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox and I. Gaussian, 2013.
- 4 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.
- 5 M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.
- 6 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51–57.
- 7 N. M. O'boyle, A. L. Tenderholt and K. M. Langner, *J. Comput. Chem.*, 2008, **29**, 839–845.
- 8 R. Dennington, T. A. Keith, J. M. Millam and S. Inc., 2016.
- 9 F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo and A. Hagfeldt, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 117–131.
- 10 N. Cai, S.-J. Moon, L. Cevey-Ha, T. Moehl, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *Nano Lett.*, 2011, **11**, 1452–1456.
- 11 X. Jiang, K. M. Karlsson, E. Gabrielsson, E. M. J. Johansson, M. Quintana, M. Karlsson, L. Sun, G. Boschloo and A. Hagfeldt, *Adv. Funct. Mater.*, 2011, **21**, 2944–2952.
- 12 A. Abate, M. Planells, D. J. Hollman, S. D. Stranks, A. Petrozza, A. R. S. Kandada, Y. Vaynzof, S. K. Pathak, N. Robertson and H. J. Snaith, *Adv. Energy Mater.*, 2014, **4**, 1400166.