Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Low band gap *S*,*N*-heteroacene-based oligothiophenes as hole-transporting and light absorbing materials for efficient perovskite-based solar cell

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General remarks: NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). Chemical shift values (δ) are expressed in parts per million using residual solvent protons (^{1}H NMR, δ_H = 7.26 for $CDCl_3$ and 5.32 for CD_2Cl_2; ^{13}C NMR, δ_C = 77.0 for $CDCl_3$ and 53.84 for CD_2Cl_2;) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). Elemental analyses were performed on an Elementar Vario EL. Melting points were determined using a Mettler Toledo DSC 823. Thin layer chromatography was carried out on aluminum plates, pre-coated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel, Merck Silica 60, particle size 40−63 µm. High performance liquid chromatography was performed on a Hitachi instrument equipped with a UV-vis detector L-7420, columns (Nucleosil 100-5 NO_2 with a pore size of 100 Å) from Machery-Nagel using a dichloromethane/*n*-hexane mixture as eluent. EI mass spectra were recorded on a Varian Saturn 2000 GC-MS, MALDI-MS experiments were performed using a MS Bruker Daltonik Reflex III and Bruker solariX spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix.

UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 19 spectrometer. The absorption spectra on TiO_2 films were measured with white light from a halogen lamp (20 W) as the light source. Cyclic voltammetry experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. All potentials were internally referenced to the Fc/Fc^+ couple. *N,N*-dimethylformamide (Merck) was dried via a MB SPS-800 solvent purifying system (MBraun). All synthetic steps were carried out under argon atmosphere. *n*-Butyl lithium (1.6 mol/L in *n*-hexane) was purchased from Acros, trimethyltin chloride was purchased from Sigma-Aldrich. Tetrakis(triphenylphosphine)palladium (0) was prepared according to literature.[1]

The surface and cross-section images of the device was investigated using a high-resolution scanning electron microscope (MERLIN, Zeiss) equipped with a GEMINI II column and a Schottky field emission source. Images were acquired using an in-lens secondary electron detector.

Mobility measurement. In order to assess the potential of this new series of oligomers as electron donors for solar cell applications, hole-only devices were fabricated.[2-5] Hole mobilities were calculated using the Mott-Gurney law, by fitting Eq. 1 to experimental data in the voltage range where the obtained slope in the double log plot is equal to 2.

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{d^3} \qquad 1$$

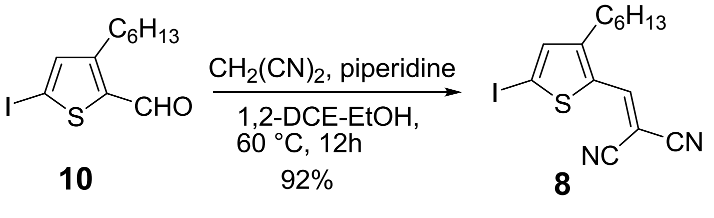
In Equation 1, J is the current density, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative permittivity of the material (approaching 3 for organic semiconductors), μ_h is the hole mobility, V is the applied voltage and d is the thickness of the active layer.

The hole-only devices were made by spin-coating PEDOT:PSS (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (15 Ω per square) (Kintec). A film of the the HTM was spin-coated on top from chloroform solution with a concentration of 8 mg/mL. The film thickness was varied by using different spin-coating speeds. As counter electrode Al was deposited on top by vacuum evaporation. The current density–voltage curves of the devices were taken with a Keithley 2400 source.

Solar Cell Fabrication. CH_3NH_3I was synthesized as reported earlier,[6] and all the other chemicals were purchased from commercial sources. The compact TiO_2 layer was deposited on the laser etched fluorine-doped tin oxide (FTO) conductive glass by spray pyrolysis at 450°C using titanium diisopropoxide bis(acetylacetonate) solution as precursor and O_2 as carrier gas. The mesoporous TiO_2 film was prepared by spin-coating the TiO_2 (Dyesol 18NRT) paste at 5000 rpm for 30 s, then sintering at 500 °C for 30 min in air. The 1.3 M PbI_2 (in DMF) solution was dropped on the TiO_2 surface and spin-coated at 6500 rpm for 30 s in the dry air box followed by annealing at 70 °C for 15 min. After cooling down, the film was dipped into CH_3NH_3I solution (10 mg/mL in 2-propanol) for 25 s, then dried at 70 °C for another 15 min. The HTM, consisting of 30 mM oligomer **1** or **2** in tetrachloroethane at 60 ^{o}C, was spin-coated on the top of the perovskite layer at a spin speed of 4000 rpm for 30 s. Finally, 60 nm of Au was deposited by thermal evaporation under a pressure of 5×10^{-6} Torr on the top. The masked active area for photovoltaic measurements was 0.285 cm^2.

Photovoltaic Characterization. A 450 W xenon lamp (Oriel) was used as the light source, equipped with a Schott K133 Tempax sunlight filter. After applying an external potential bias to the device, the generated photocurrent was recorded with a Keithley model 2400 digital source meter. The light intensity was calibrated with a silicon reference cell before each measurement. For the *I-V* measurement, the voltage step and delay time were 10 mV and 0 ms, respectively. The scan started from over the open-circuit photovoltage to 0 V with a scan rate of 0.05 V S^{-1}. IPCE spectra were measured by an array of white light emitting diodes. The excitation beam (from a 300 W xenon lamp) passed through a Genimi-180 double monochromator (Jobin Yvon Ltd) and chopped at approximately 2 Hz before it illuminated the device. The spectra were recorded using a Model SR830 DSP Lock-In Amplifier. In all the measurements, the active area of the devices was defined with a black metal aperture mask of 0.285 cm^2.

Synthesis: The building blocks 3,3',3'',4'-tetrabromo-2,2':5',2''-terthiophene[7] **5** and 2-[(3',4-dihexyl-5'-iodo-2,2'-bithien-5-yl)methylene]malononitrile[8] **9** were synthesized according to literature. 2-[(3-Hexyl-5-iodothien-2-yl)methylene]malononitrile **8** was prepared by Knoevenagel condensation of 3-hexyl-5-iodo-thiophene-2-aldehyde **10**[9,10] and malononitrile (Scheme S1). The NMR and MALDI-TOF mass spectra are shown in Fig. S7 to S15.



Scheme S1. Synthesis of building block **8**.

4,5-Bis(2-ethylhexyl)-dithieno[2,3-d:2',3'-d']thieno[3,2-b:4,5-b']dipyrrole (6). In a dried Schlenk-tube a solution of 3,3',3'',4'-tetrabromo-2,2':5',2''-terthiophene **5** (929 mg, 1.65 mmol), sodium *tert*-butoxide (2.57 g, 26.7 mmol), Pd(dba)$_2$ (94.2 mg, 0.16 mmol), and dppf (367 mg, 0.66 mmol) in 30 mL of dry toluene was degassed with argon and stirred for 20 min at room temperature. After addition of freshly distilled 2-ethylhexylamine (0.65 mL, 3.96 mmol) the mixture was stirred overnight at 110 °C. After cooling down to room temperature, water was added and the product was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (SiO_2, *n*-hexane/DCM = 7:3) to give heteropentacene **6** (489 mg, 59%) as a yellow solid. Mp 82°C (DSC); ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ 7.10 (d, *J* = 5.3 Hz, 2H), 7.04 (d, *J* = 5.3 Hz, 2H), 4.37-4.24 (m, 4H), 2.03-2.01 (m, 2H), 1.27-1.15 (m, 16H), 0.83-0.78 (m, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2, ppm): δ 145.07, 145.04, 131.01, 122.13, 116.66, 116.11, 112.16, 40.88, 30.52, 30.45, 28.74, 28.63, 23.85, 23.81, 23.37, 23.34, 14.07, 14.05, 10.73, 10.66; MS (MALDI-TOF) *m/z*: $[M]^+$ calcd for $C_{28}H_{38}N_2S_3$, 498.22; found, 498.21. Anal. calcd for $C_{28}H_{38}N_2S_3$: C 67.42, H 7.68, N 5.62, S 19.28; found: C 67.28, H 7.64, N 5.58, S 19.09.

2,7-Bis(trimethylstannyl)-4,5-di(2-ethylhexyl)-dithieno[2,3-d:2',3'-d']thieno[3,2-b:4,5-b']-dipyrrole (7). To a solution of heteropentacene **6** (224 mg, 0.45 mmol) in 13 mL of dry THF was added *n*-BuLi (1.6 M in *n*-hexane, 0.73 mL, 1.17 mmol) under argon within 30 min at -78°C. After being stirred for 1 h at the same temperature, the mixture was quenched with tri-methyltin chloride (286 mg, 1.44 mmol) in 1.3 mL of THF. The mixture was first stirred at this temperature for 5 min, then overnight at room temperature. After addition of water the product was extracted with diethyl ether to provide bis-stannylated derivative **7** as an orange oil (370 mg) in quantitative yield. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 6.98 (s, 2H), 4.33-4.19 (m, 4H), 2.01-1.98 (m, 2H), 1.232-1.10 (m, 16H), 0.83-0.78 (m, 12H), 0.40 (s, 18H); MS (MALDI-TOF) m/*z*: $[M]^+$ calcd for $C_{34}H_{54}N_2S_3Sn_2$, 826.15; found, 826.49 $[M]^+$, 662.48 $[M-SnMe_3]^+$. Compound **7** was used without any further purification.

2-[(3-Hexyl-5-iodothien-2-yl)methylene]malononitrile (8). Aldehyde **10** (2 g, 6.2 mmol), malononitrile (820 mg, 12.4 mmol) and 2-3 drops of piperidine were dissolved in 30 ml of 1,2-dichloroethane-ethanol (5:1) and the mixture was heated at 60 °C for about 12 h. After completion, the solvent was concentrated under reduced pressure. The crude product was precipitated from ethanol. The solid was filtered and washed with ethanol and dried under vacuum. The product was further purified by column chromatography (SiO_2, *n*-hexane/dichloromethane = 4:1) to obtain building block **8** as yellow solid (2.1 g, 5.7 mmol) in 92% yield. Mp 154-155 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (s, 1H), 7.26 (s, 1H), 2.72 (t, *J* = 7.9 Hz, 2H), 1.59 (m, 2H), 1.31 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 156.5, 147.1, 140.1, 136.0, 114.3, 113.4, 89.6, 76.9, 31.4, 31.3, 28.9, 28.7, 22.5, 14.0. Anal. calcd for $C_{14}H_{15}IN_2S$: C 45.41, H 4.08, N 7.57, S 8.66; found: C 45.55, H 4.05, N 7.66, S 8.54.

2,2'-[(4,5-Bis(2-ethylhexyl)-dithieno[2,3-d:2',3'-d']thieno[3,2-b:4,5-b']dipyrrole-2,7-diyl)-bis(3-hexylthien-5,5'-diyl)bis(methane-1-yl-1-ylidine)]dimalononitrile (1). A solution of bis-stannylated derivative **7** (173 mg, 0.21 mmol) and 2-iodothiophene **8** (170 mg, 0.46 mmol) in 5 mL of dry DMF was carefully degassed. Then tetrakis(triphenylphosphine)-palladium(0) catalyst (14.1 mg, 12.2 µmol) was added and the reaction mixture was stirred at 70°C overnight. After cooling down to room temperature the precipitate was filtered and washed with methanol. The solid was purified by column chromatography (SiO_2, dichloromethane) to afford oligomer **1** as a green solid (165 mg, 80%). Mp 294 °C (DSC); ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.78 (s, 2H), 7.34 (s, 2H), 7.10 (s, 2H), 4.34-4.21 (m, 4H), 2.74 (t, *J* = 7.8 Hz, 4H), 2.04-1.94 (m, 2H), 1.69-1.62 (m, 4H), 1.43-1.34 (m, 12H), 1.27-1.16 (m, 16H), 0.93-0.90 (m, 6H), 0.85-0.78 (m, 12H); ^{13}C-NMR (100 MHz, CD_2Cl_2, δ): 157.51, 149.41, 146.76, 145.90, 145.87, 132.02, 131.87, 127.92, 124.75, 119.73, 118.79, 118.77, 115.50, 114.44, 111.21, 72.08, 53.44, 40.49, 31.51, 31.26, 30.05, 30.00, 29.25, 29.08, 28.20, 28.13, 23.50, 23.48, 22.96, 22.94, 22.53, 14.05, 13.89, 13.88, 10.62, 10.58; HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{56}H_{66}N_6S_5$, 982.39470; found, 982.39364 $[M]^+$, 998.38784 $[M+O]^+$, 1014.38301 $[M+2O]^+$, 1030.37792 $[M+3O]^+$. Anal. calcd for $C_{56}H_{66}N_6S_5$: C 68.39, H 6.76, N 8.55, S 16.30; found: C 68.37, H 6.79, N 8.47, S 16.44.

2,2'-[(4,5-Bis(2-ethylhexyl)-dithieno[2,3-d:2',3'-d']thieno[3,2-b:4,5-b']dipyrrole-2,7-diyl)-bis(4,3'-dihexyl-2,2'-bithien-5,5'-diyl)bis(methane-1-yl-1-ylidine)]dimalononitrile (2). A solution of bis-stannylated derivative **7** (188 mg, 0.23 mmol) and iodobithiophene **9** (271 mg, 0.50 mmol) in 5 mL of dry DMF in a Schlenk tube was carefully degassed. Then, tetrakis(triphenylphosphine)palladium(0) catalyst (16.1 mg, 13.9 µmol) was added and the reaction mixture was stirred at 70°C overnight. After cooling down to room temperature the precipitate was filtered and washed with methanol. The solid was purified by column chromatography (SiO_2, dichloromethane) to afford oligomer **2** as a brown solid (247 mg, 82%). Mp 275 °C (DSC); ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.80 (s, 2H), 7.12 (s, 2H), 7.09 (s, 2H), 7.05 (s, 2H), 4.33-4.20 (m, 4H), 2.84 (t, *J* = 7.9 Hz, 4H), 2.75 (t, *J* = 7.7 Hz, 4H), 2.06-1.96 (m, 2H), 1.76-

1.70 (m, 4H), 1.68-1.62 (m, 4H), 1.49-1.45 (m, 4H), 1.41-1.32 (m, 20H), 1.28-1.18 (m, 16H), 0.93-0.89 (m, 12H), 0.87-0.80 (m, 12H); ^{13}C-NMR (100 MHz, CD_2Cl_2, δ): 156.48, 147.22, 147.06, 145.07, 144.91, 144.89, 140.20, 132.56, 130.82, 128.81, 127.11, 126.68, 126.36, 117.55, 117.18, 115.41, 114.11, 108.79, 99.96, 72.94, 53.23, 40.45, 31.65, 31.53, 31.29, 30.39, 30.14, 30.10, 30.08, 30.06, 29.24, 29.13, 29.06, 28.26, 28.17, 23.48, 23.45, 22.99, 22.96, 22.58, 22.54, 14.09, 14.05, 13.93, 13.92, 10.61, 10.56; HRMS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{76}H_{94}N_6S_7$, 1314.55794; found, 1314.55618 $[M]^+$, 1330.54740 $[M+O]^+$, 1346.54369 $[M+2O]^+$, 1362.539 $[M+3O]^+$. Anal. calcd for $C_{76}H_{94}N_6S_7$: C 69.36, H 7.20, N 6.39, S 17.06; found: C 69.58, H 7.48, N 6.28, S 16.96.

References

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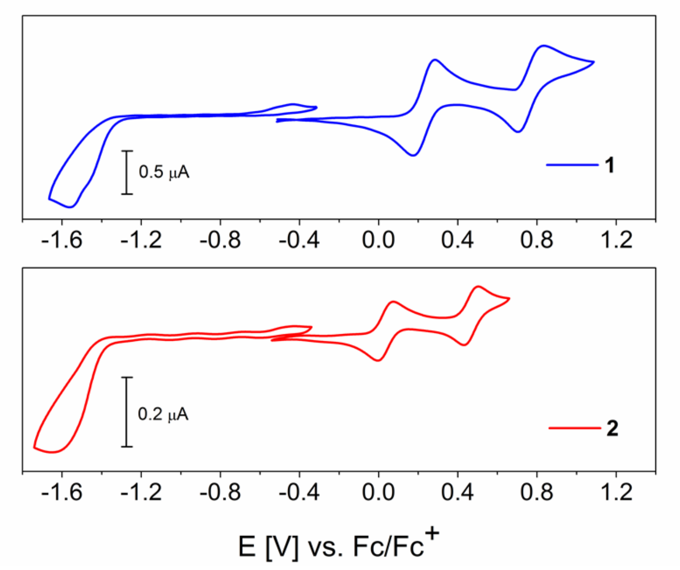

Figure S1. Electrochemical characterization of **1** and **2** in dry dichloromethane–TBAPF$_6$ (0.1 M), scan speed 100 mV/s, potentials vs. Fc/Fc$^+$.

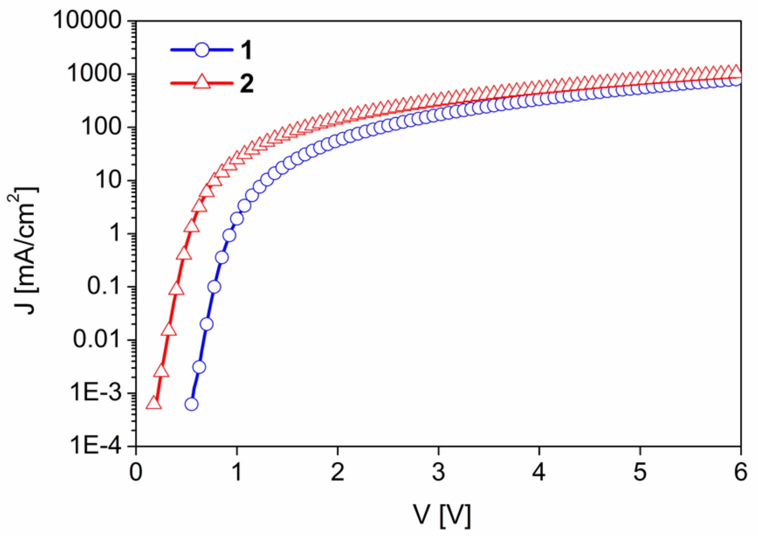

Figure S2. *J-V* plots of the hole-only devices for oligomers **1** and **2**.

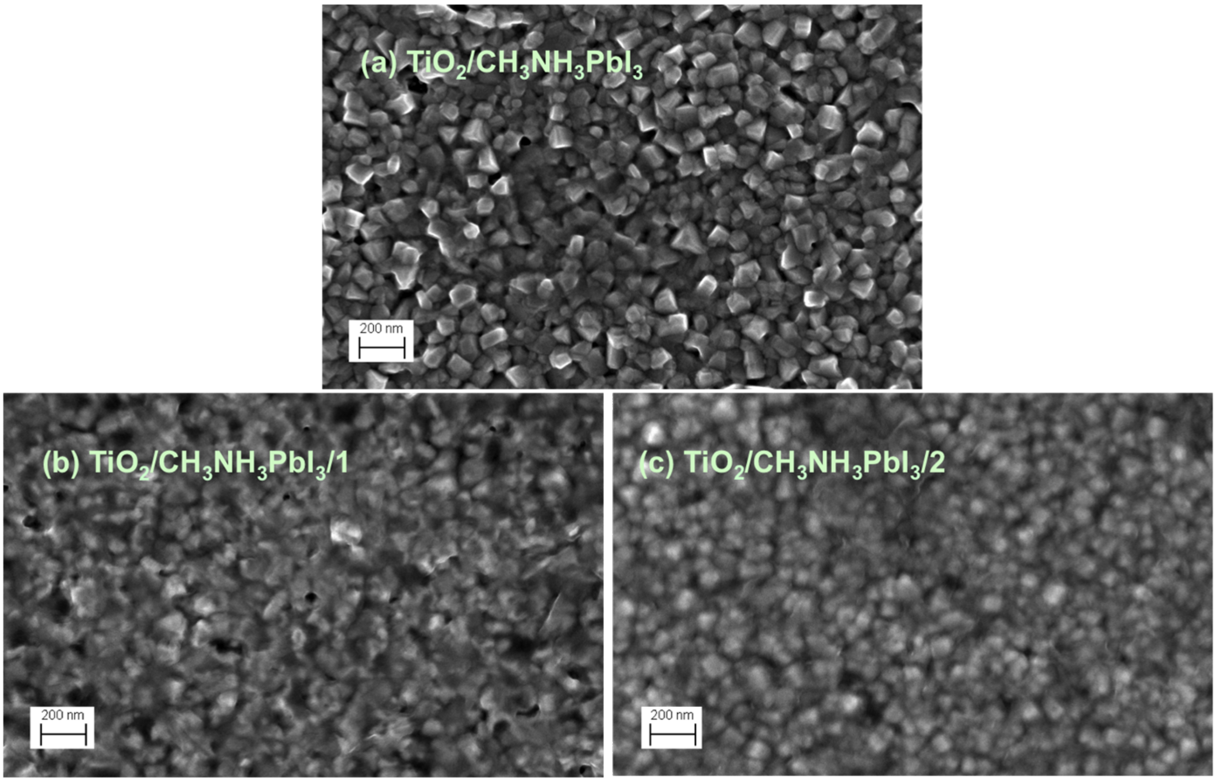

Figure S3. Top-view SEM images for the (a) $TiO_2/CH_3NH_3PbI_3$, (b) $TiO_2/CH_3NH_3PbI_3/$**1**, and (c) $TiO_2/CH_3NH_3PbI_3/$**2** films.

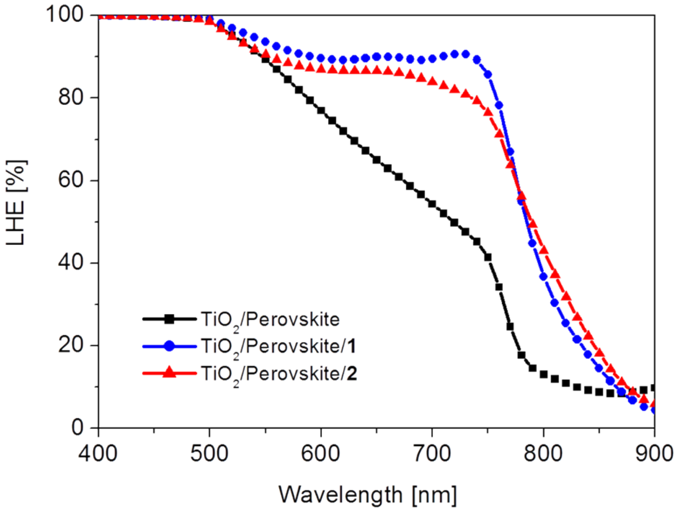

Figure S4. The light harvesting efficiency (LHE) spectra of the heterojunction solar cells based on HTMs **1** and **2**, and a reference cell without HTM.

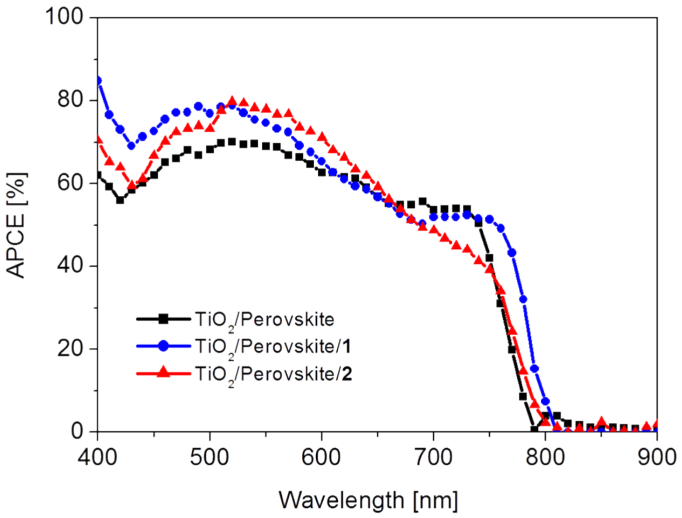

Figure S5. The absorbed photo-to-current conversion efficiency (APCE) spectra of the heterojunction solar cells based on HTMs **1** and **2**, and a reference cell without HTM.

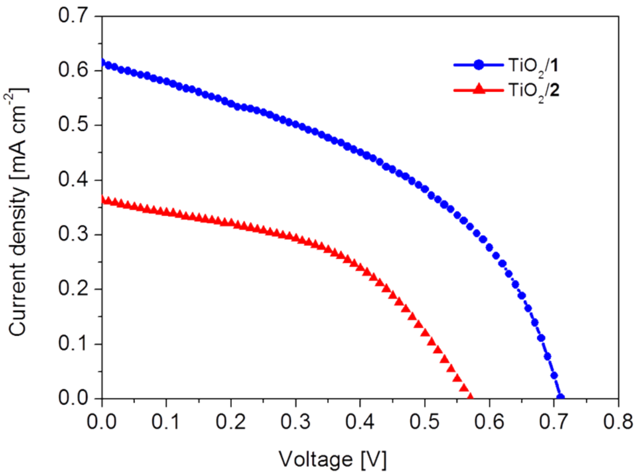

Figure S6. The *J-V* characteristics of the heterojunction solar cells based on the device configuration of TiO_2/HTM **1** or **2**/Au.

Table S1. Photovoltaic parameters of batch of five devices without HTM measured under simulated AM 1.5G irradiation.

Device	P_{in} [mW cm^{-2}]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF	PCE [%]
1	99.9	14.0	790	0.69	7.6
2	99.9	13.9	740	0.65	6.7
3	99.1	12.5	762	0.71	6.8
4	98.0	13.0	780	0.69	7.1
5	97.8	12.4	733	0.68	6.3
Aver. ± std dev [%]		13.2 ± 0.76	761 ± 25	0.68 ± 0.02	6.9 ± 0.5

Table S2. Photovoltaic parameters of a batch of ten devices with oligomer **1** measured under simulated AM 1.5G irradiation.

Device	P_{in} [mW cm^{-2}]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF	PCE [%]
1	100.8	16.4	992	0.65	10.5
2	98.0	16.5	962	0.64	10.4
3	99.0	16.1	981	0.65	10.4
4	98.7	15.8	957	0.62	9.5
5	96.9	15.7	969	0.65	10.2
6	99.4	16.7	910	0.63	9.6
7	98.2	16.7	918	0.61	9.5
8	99.8	16.4	983	0.64	10.3
9	98.6	15.3	982	0.65	9.9
10	99.1	16.2	942	0.61	9.4
Aver. ± std dev [%]		16.2 ± 0.46	960 ± 28	0.64 ± 0.02	10.0 ± 0.4

Table S3. Photovoltaic parameters of a batch of ten devices with oligomer **2** measured under simulated AM 1.5G irradiation.

Device	P_{in} [mW cm^{-2}]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF	PCE [%]
1	98.0	15.2	900	0.68	9.5
2	100.4	15.8	831	0.66	8.6
3	100.8	15.3	848	0.68	8.8
4	101.2	15.4	853	0.69	9.0
5	98.1	15.2	886	0.68	9.3
6	99.6	15.1	897	0.67	9.1
7	100.4	15.7	833	0.64	8.3
8	100.3	13.9	873	0.67	8.1
9	99.2	15.0	907	0.66	9.1
10	99.1	15.8	897	0.65	9.3
Aver. ± std dev [%]		15.2 ± 0.55	873 ± 29	0.67 ± 0.01	8.9 ± 0.5

Table S4 . Photovoltaic parameters of the hybrid solar cell devices TiO_2/**1**/Au and TiO_2/**2**/Au without the perovskite layer.

Oligomer	P_{in} [mW cm^{-2}]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF	PCE [%]
1	99.9	0.62	710	0.44	0.2
2	99.9	0.36	571	0.47	0.1

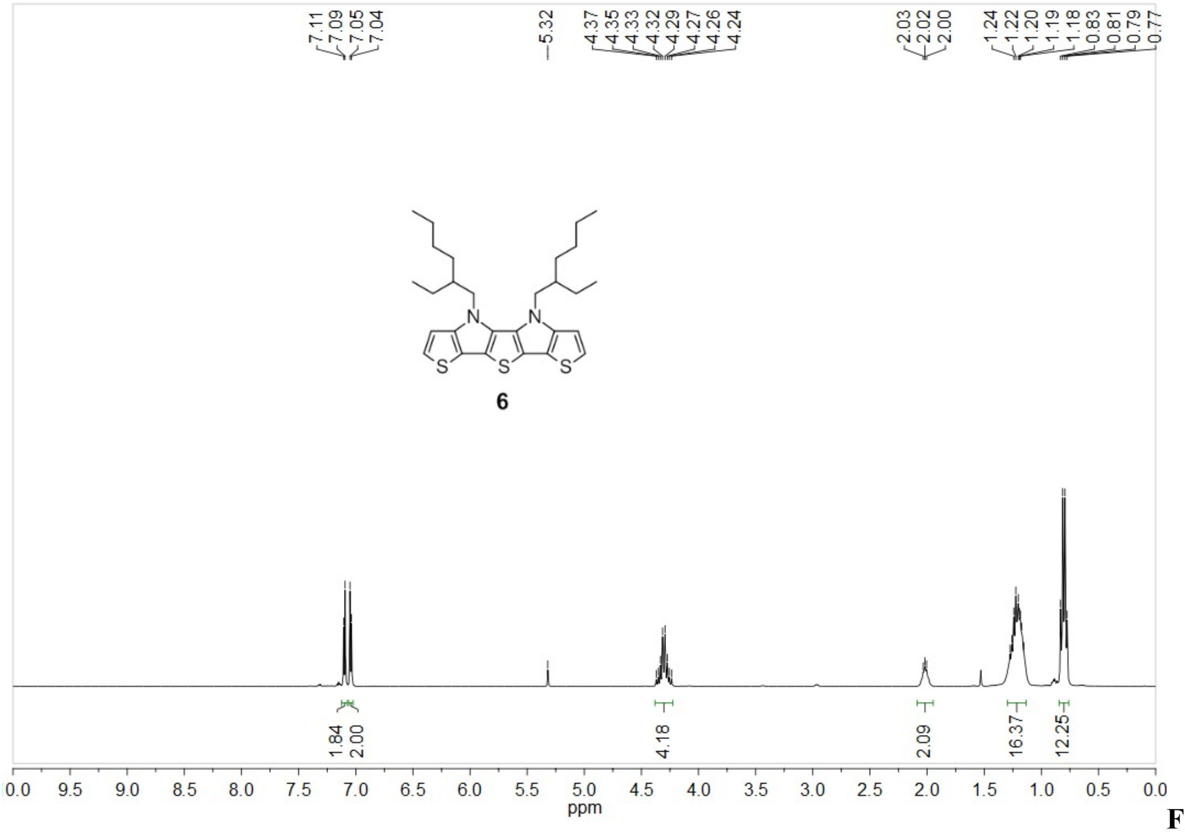

Figure S7. ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of compound **6**.

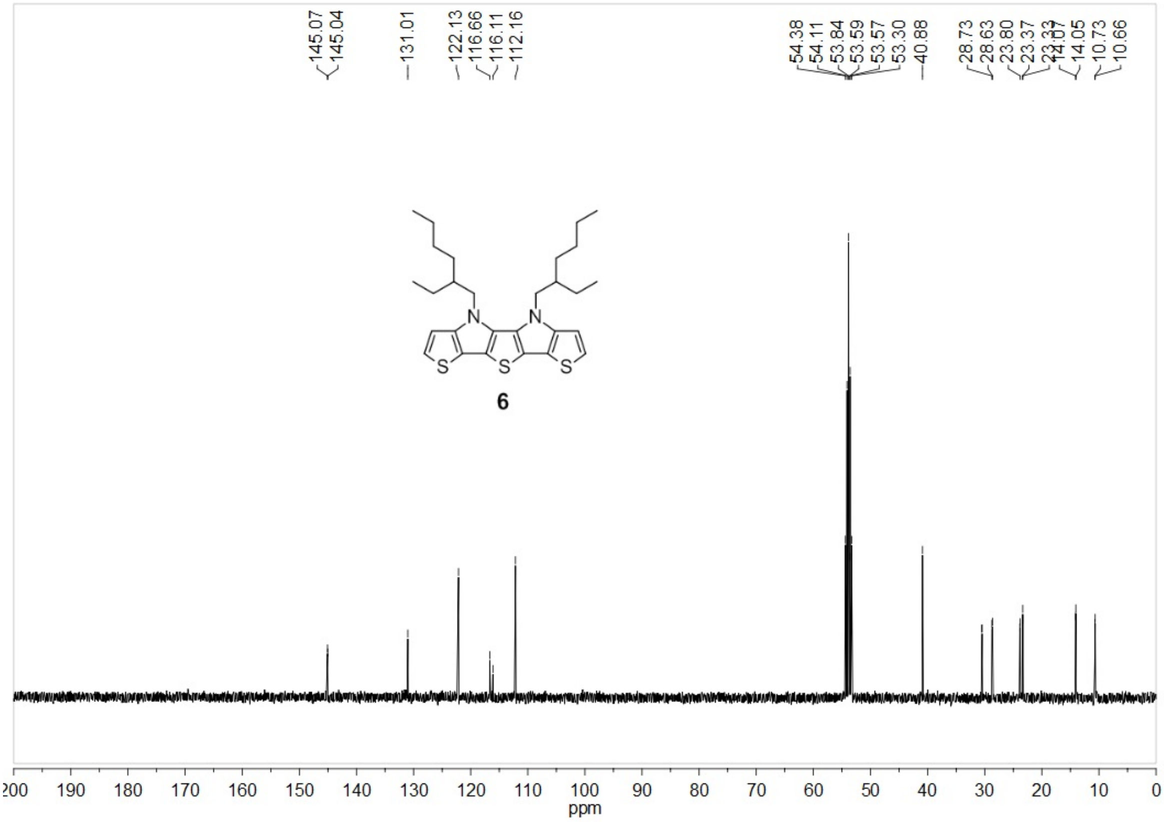

Figure S8. ^{13}C-NMR spectrum (100 MHz, CD_2Cl_2) of compound **6**.

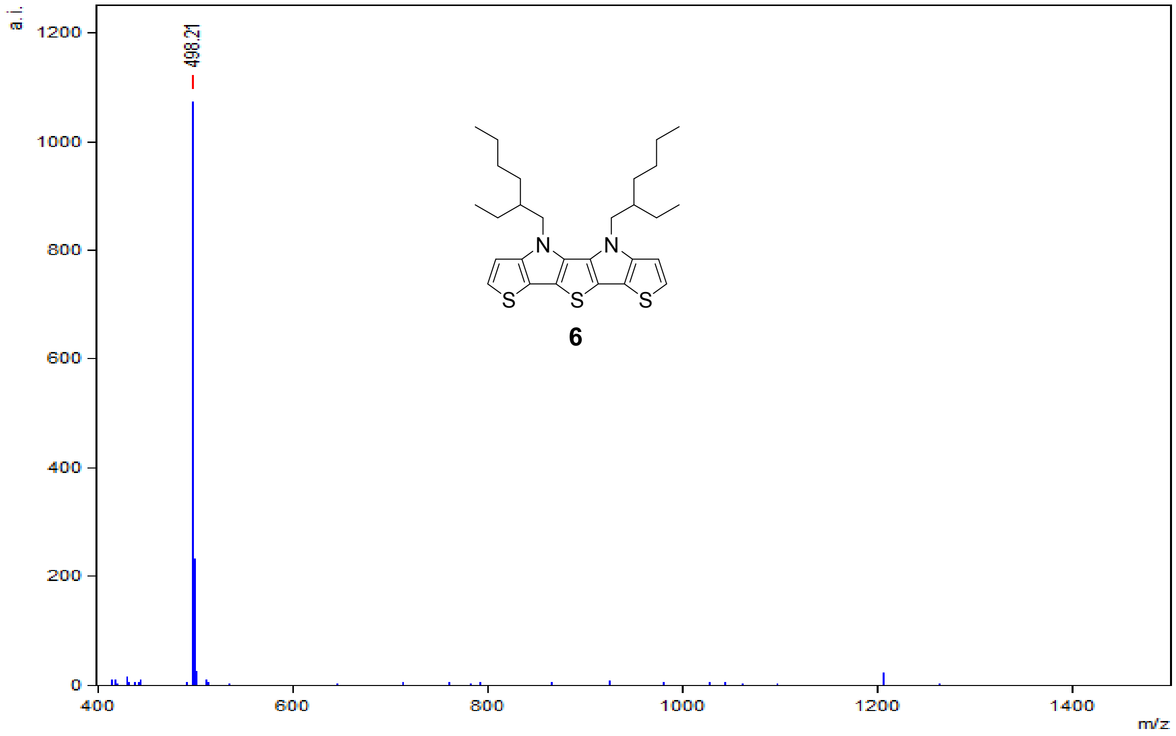

Figure S9. MALDI-TOF-MS spectrum of compound **6**.

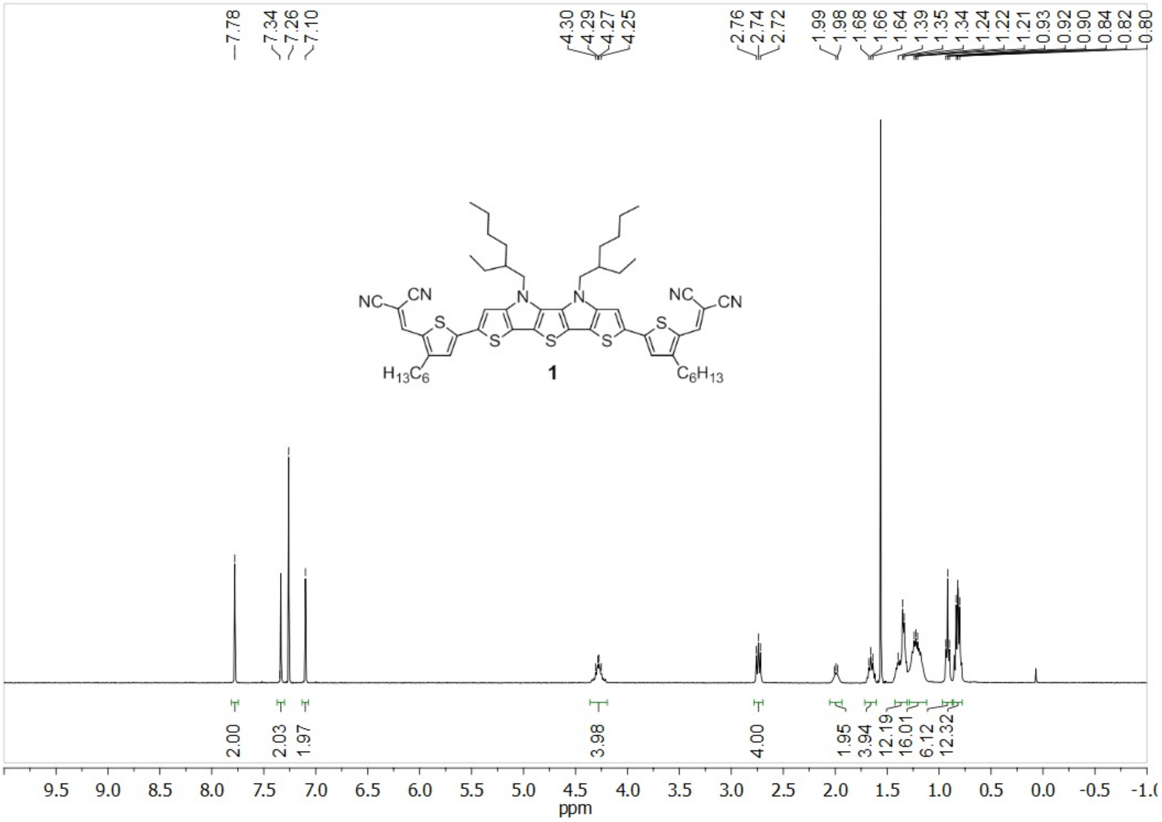

Figure S10. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **1**.

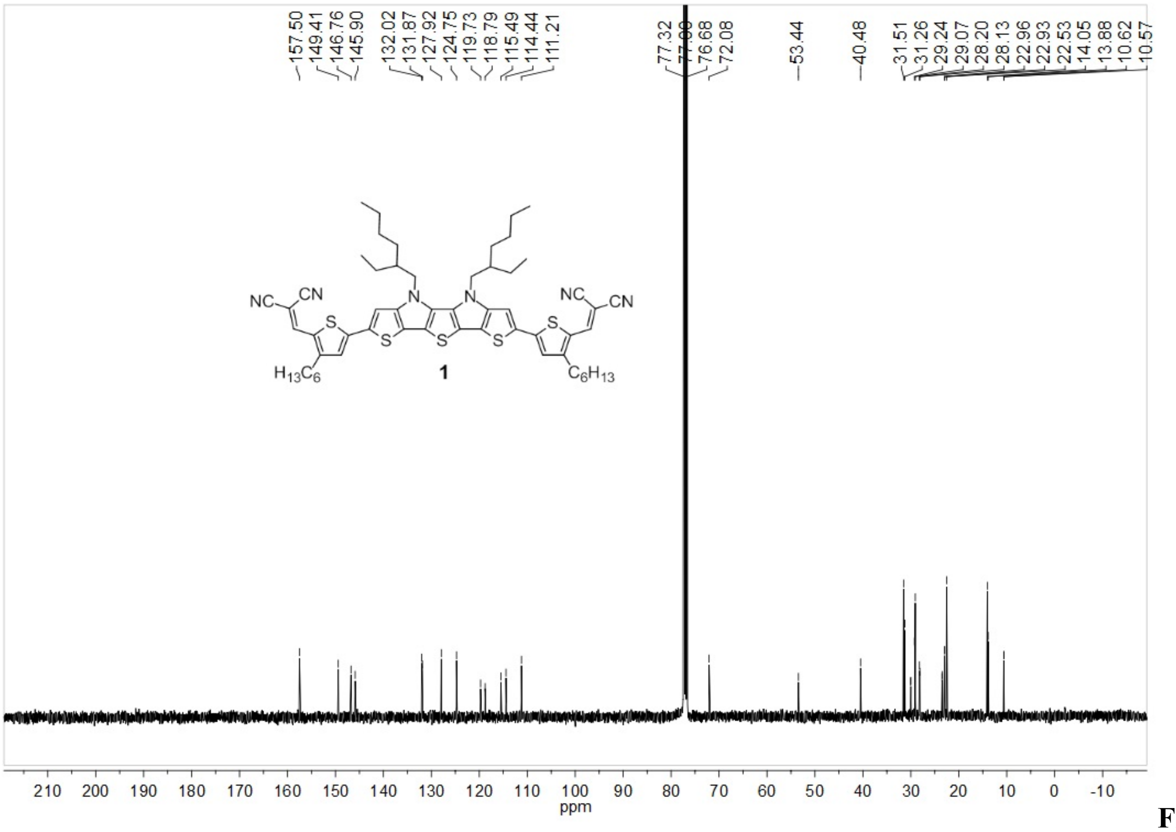

Figure S11. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **1**.

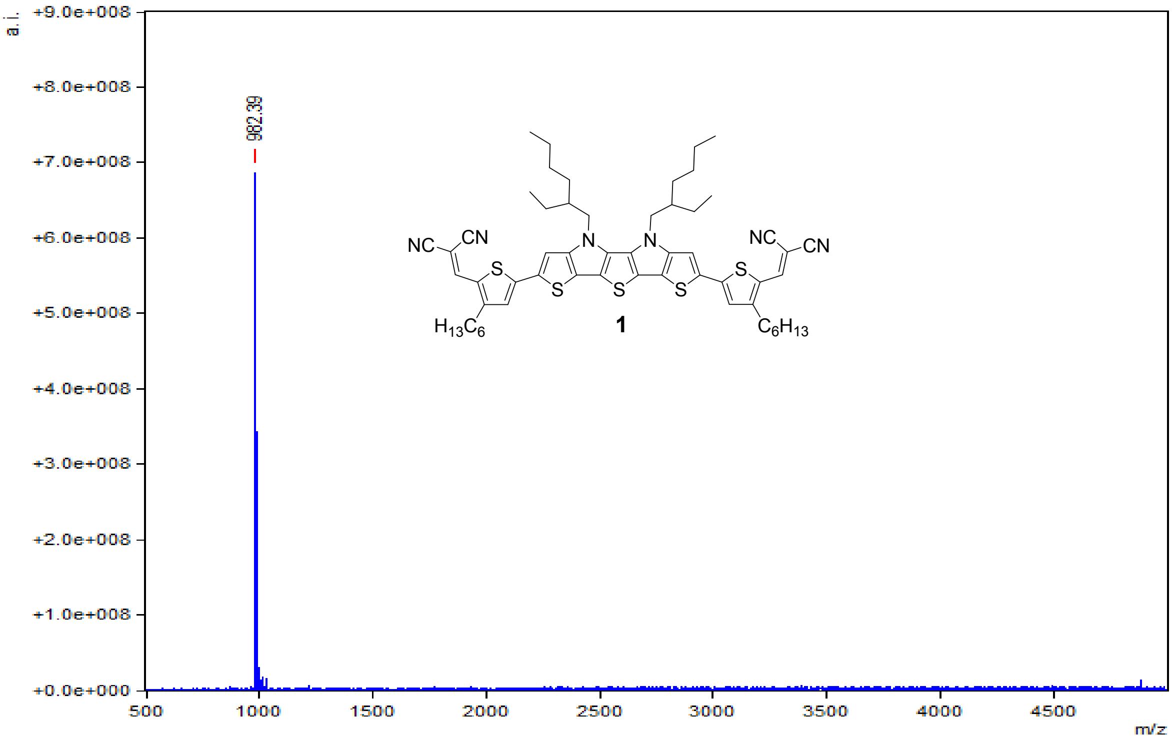

Figure S12. HRMS (MALDI-TOF) spectrum of compound **1**.

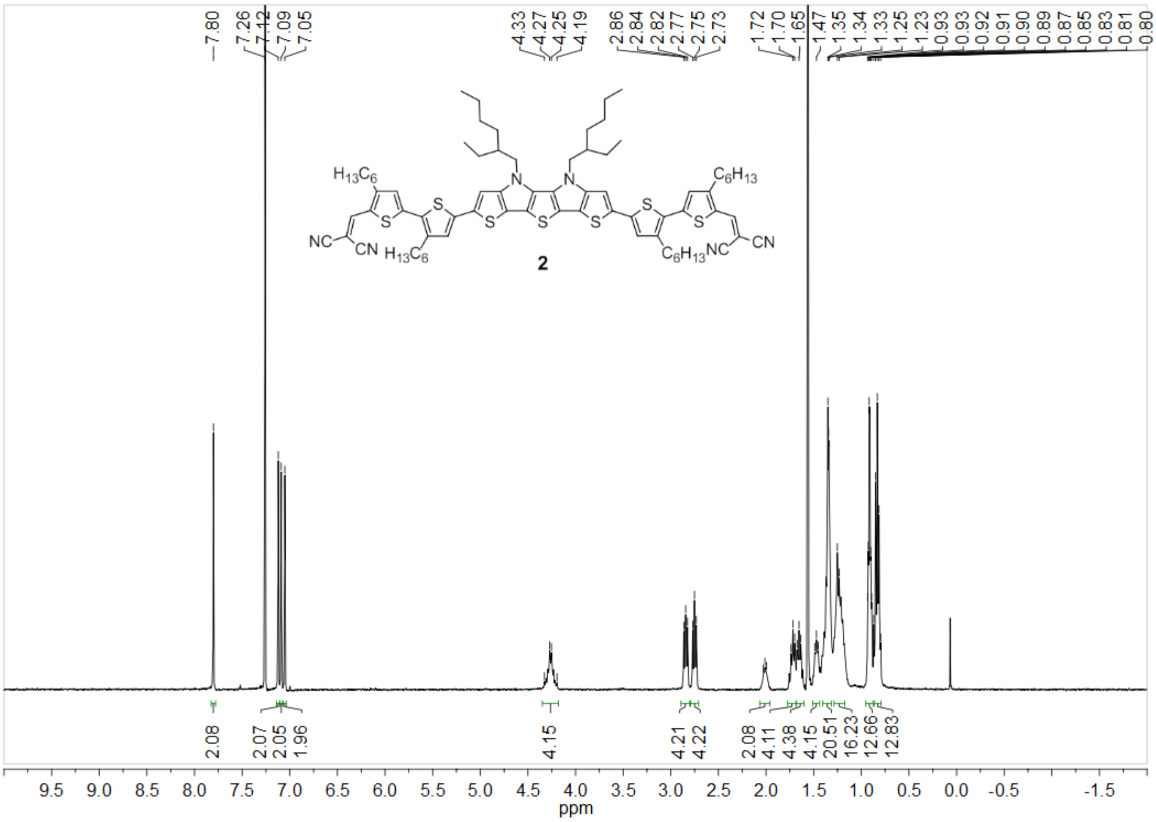

Figure S13. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **2**.

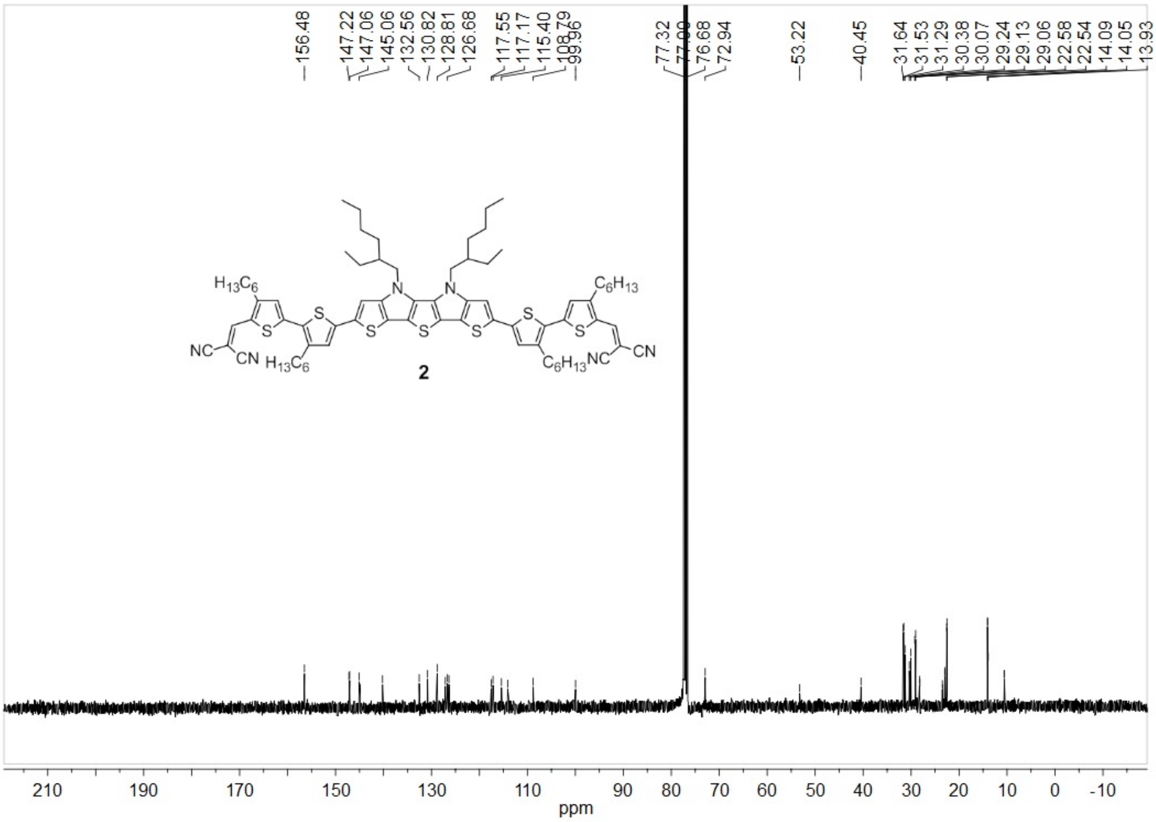

Figure S14. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of compound **2**.

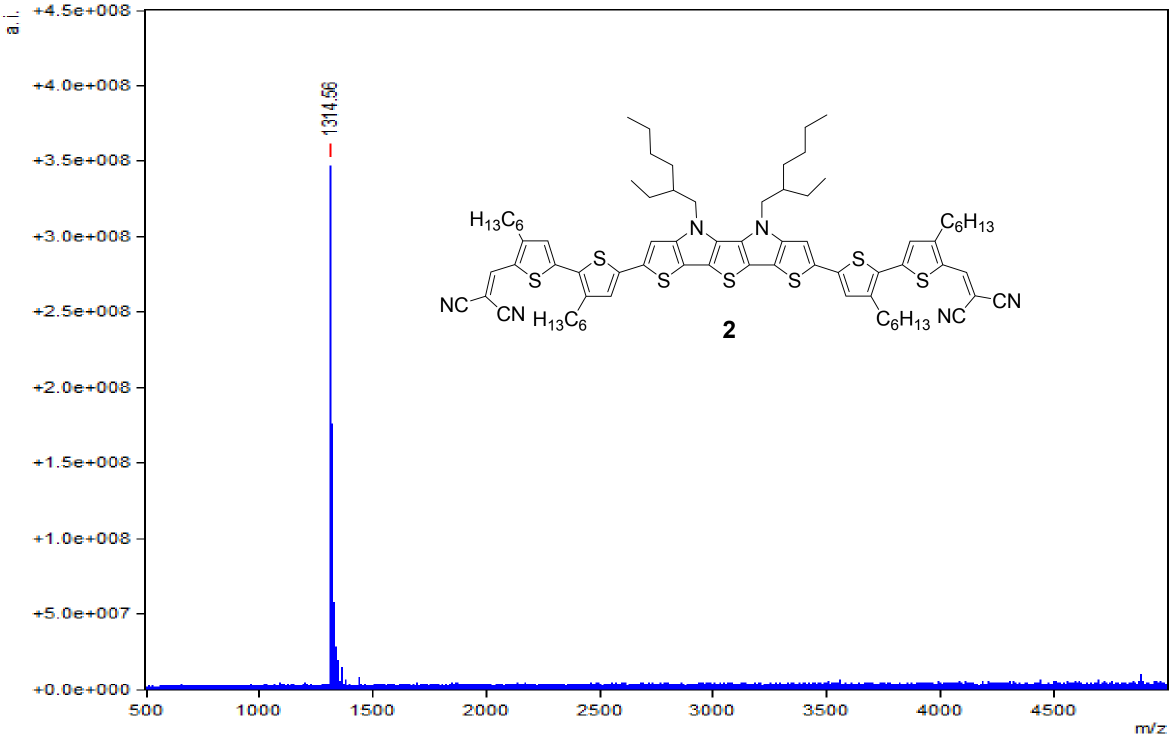

Figure S15. HRMS (MALDI-TOF) spectrum of compound **2**.