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New ethynediyl-linked perylene diimide/2,1,3-benzothiadiazole conjugates as electron transporting materials for perovskite solar cells

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Content

General

All solvents and reagents were purified using the standard methods. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance^{TM} 400 (400 MHz) or a Avance^{TM} 500 (500 MHz) nuclear magnetic resonance (NMR) spectrometer. UV-vis absorption spectra were recorded using a Perkin Elmer Cary I optical spectrophotometer. Cyclic voltammetry measurements were performed on a potentiostat-galvanostat AUTOLAB Type III equipped with standard three-electrode scheme in an acetonitrile solution of 0.1 mol×L^{-1} tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) at a potential scan rate of 50 mV×s^{-1}. Films of the investigated compounds were deposited on a glassy carbon electrode surface and used as a working electrode. Ag/Ag$^+$ and platinum wire were used as reference and counter electrodes, respectively.

MALDI-TOF mass spectra were recorded on the Axima Confidence time-of-flight spectrometer (Shimadzu Biotech) in the reflectron high resolution mode with nitrogen laser (λ = 337 nm). Positive and negative ions were recorded. The mass range between 200 and 5000 was scanned. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as a matrix in all experiments. The target was prepared as follows. Compounds were dissolved in methylene chloride to give a concentration of 0.1 mg ml^{-1}. Twenty (20) μl of the obtained solutions were mixed with 20 μl of the 10 mg ml^{-1} matrix solution in CH_2Cl_2. The resulting mixtures were deposited on a stainless steel target and dried in air. The morphology of the perovskite/polymer double-layer stacks were investigated by an NTEGRA NT-MDT atomic force microscope in semicontacting mode on the area of 5x5 μm^2.

Perovskite solar cells based on BT-PDI and BT2-PDI2 compounds were fabricated as follows. First, a thin layer of hole-transport poly[bis(4-phenyl)(4-methylphenyl)amine] (PTA) (1.5 mg ml^{-1} chlorobenzene solution) was deposited on a thoroughly cleaned surface of a glass substrate with an electrically conductive layer of indium tin oxide (ITO) using spin-coating at 4000 rpm for 30 s. After drying the PTA layer at 110°C, a perovskite light-absorbing layer was applied to the PTA surface by a method involving the use of an anti-solvent to obtain polycrystalline films. To do this, a perovskite solution (90-100 μl, 1.3 M) in the appropriate solvent mixture (DMAA/DMSO = 4:1 for $Cs_{0.12}FA_{0.88}PbI_3$) was dropped over the PTA layer at 4000 rpm, and after 32–33 sec, chlorobenzene (100 μl) was applied to initiate the film crystallization. After thermal annealing (5 min at 110°C for $Cs_{0.12}FA_{0.88}PbI_3$), an electron transport material **BT-PDI** or **BT2-PDI2** (10 mg ml^{-1}, toluene solution) was deposited on the perovskite layer at 3000 rpm for 30 sec, following the thermal deposition of electrode material (Al, 100–120 nm) in high vacuum (8×10^{-6} mbar) at a rate of 3 Å/sec. $PC_{60}BM$ was used as a standard electronically conductive material.

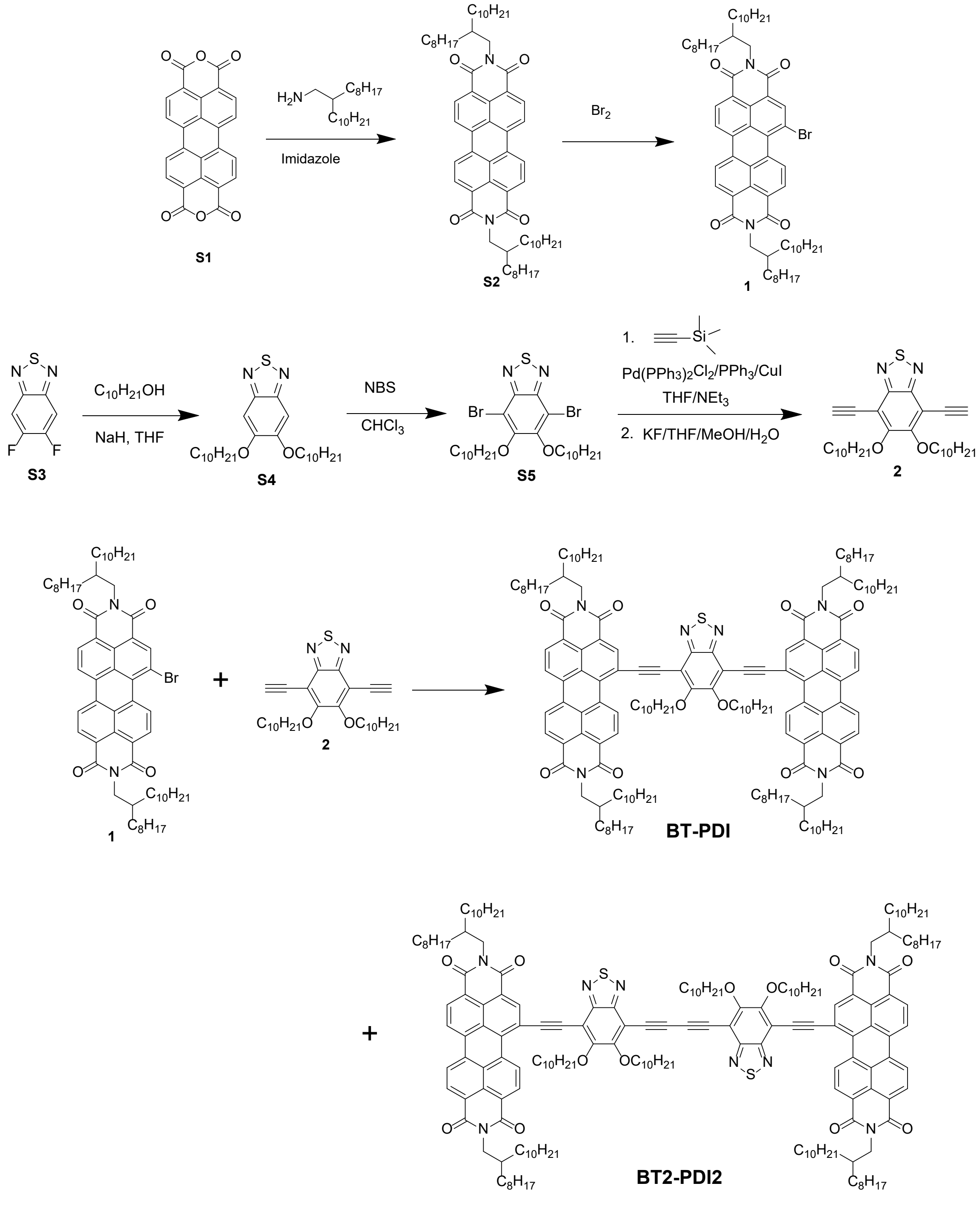
The PL spectra were recorded on a QE Pro High Performance Spectrometer Ocean Insight fiber spectrometer and a 405 nm diode laser (10 mW) as an excitation source.

The current-voltage (*J-V*) characteristics of the devices were obtained under the simulated solar illumination (100 mW cm^{-2} AM1.5) provided by a KHS Steuernagel solar simulator integrated in MBraun glove box. The intensity of the illumination was checked before every measurement using a calibrated silicon diode with a known spectral response. The *J-V* curves were recorded in an inert atmosphere using a Kethley 2400 source-measurement unit. The active areas of all devices were 0.08 cm^2. The obtained J_{SC} values were confirmed by integrating the external quantum efficiency (EQE) spectra against standard AM1.5G spectrum. The EQE spectra were measured in inert atmosphere using specially designed setup, LOMO instruments, Russia.

Compounds **1** [S1] and **S5** [S2] were prepared according to the literature methods.

Synthesis

General synthetic schemes



Scheme S1

5,6-Bis(decyloxy)-4,7-diethynylbenzo[*c*][1,2,5]thiadiazole (2). *Stage 1.* A solution of 4,7-dibromo-5,6-bis(decyloxy)benzo[*c*][1,2,5]thiadiazole (**S5**) (3 g, 4.95 mmol) and trimethylsilylacetylene (9.72 ml, 49.46 mmol) in a mixture of THF (80 ml) and NEt_3 (30 ml) was purged with Ar for 20 min, and catalytic amounts of $PdCl_2(PPh_3)_2$ (347 mg, 0.495 mmol), PPh_3 (324 mg, 1.24 mmol) and CuI (236 mg, 1.24 mmol) were added. The purging was continued for additional 20 min, and then the reaction mixture was refluxed for 48 h. After cooling the mixture was evaporated to dryness. The residue was dissolved in a mixture of petroleum ether/chloroform = 90:10 and flashed on short SiO_2 column (5 cm) and the product was completely eluted from the SiO_2 (TLC control in PE/$CHCl_3$ = 1:1). The solution was evaporated to dryness and used on the next stage without further purification.

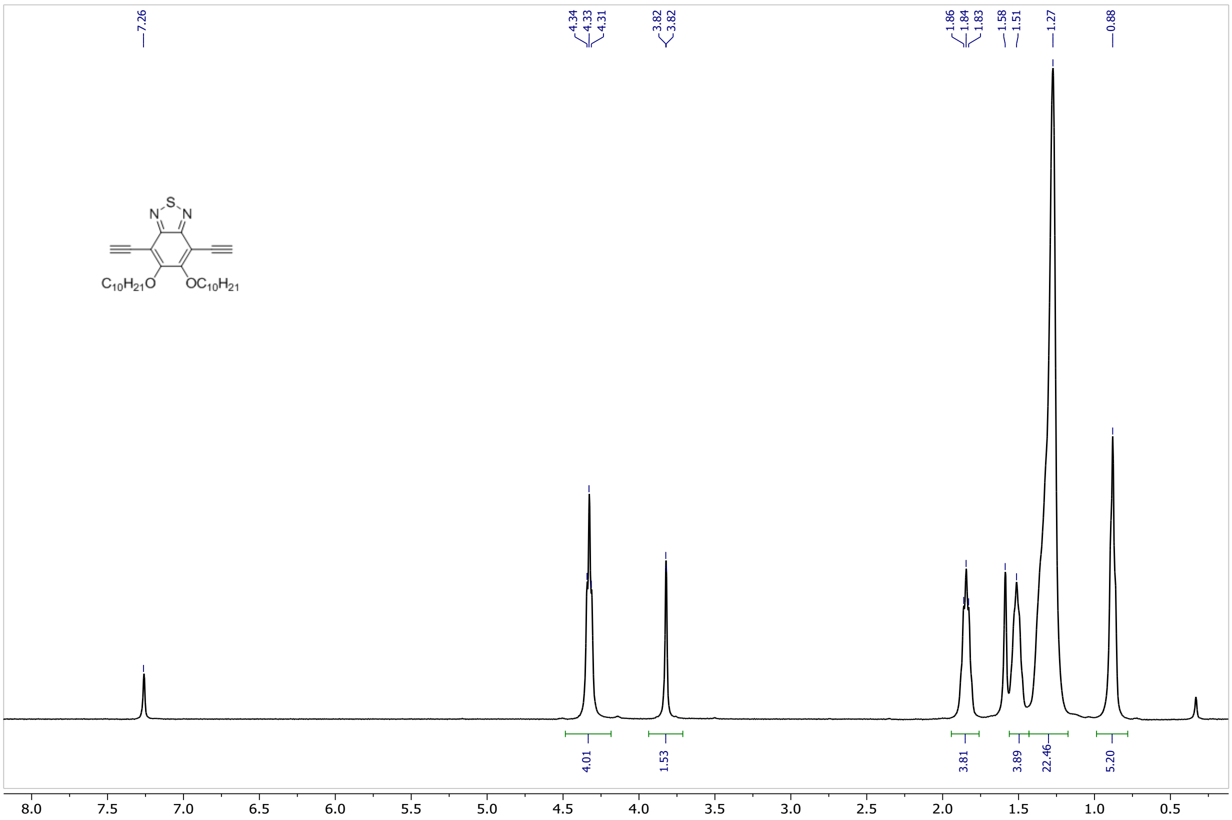
Stage 2. The product of the 1-st stage was dissolved in dry THF (200 ml) and purged with Ar for 20 min. Then a solution of KF (2.71 g, 36.13 mmol) in MeOH (25 ml) was added in one portion, and the mixture was stirred at room temperature for 3 h under argon. Then the reaction mixture was evaporated, the residue was dissolved in $CHCl_3$, washed with equal volume of water, dried over $MgSO_4$, and evaporated. The residue was purified on SiO_2 in a mixture of petroleum ether/chloroform = 3:1 as an eluent. The target compound was obtained as yellow powder with the yield of 1.680 g (53.0%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.32 (t, *J* = 5.7 Hz, 4H), 3.90–3.77 (m, 2H), 1.90–1.79 (m, 4H), 1.51 (s, 4H), 1.27 (m, 24H), 0.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.78, 151.74, 107.08, 88.53, 75.81, 75.22, 31.86, 30.24, 29.57, 29.55, 29.37, 29.29, 25.88, 22.64, 14.06. Elemental Anal. Calcd for $C_{30}H_{44}N_2O_2S$: C, 72.54; H, 8.93; N, 5.64; O, 6.44; S, 6.45. Found: C, 72.67; H, 8.19; N, 5.57; S, 6.28.

Compounds BT-PDI and BT2-PDI2. A solution of 1-bromo-*N*,*N'*-bis(2-octyldodecyl)perylene-3,4,9,10-tetracarboxybisimide (**1**) (0.6195 g, 0.60191 mmol) and 5,6-bis(decyloxy)-4,7-diethynylbenzo[*c*][1,2,5]thiadiazole (**2**) (130 mg, 0.2617 mmol) in a mixture of THF (45 ml) and NEt_3 (15 ml) was purged with argon for 20 min, then CuI (40 mg, 0.20936 mmol), PPh_3 (55 mg, 0.20936 mmol) and $PdCl_2(PPh_3)_2$ (37 mg) were added in sequence. The purging was continued for additional 20 minutes, and then the reaction mixture was refluxed for 48 h. After cooling, the solvents were evaporated and the residue was purified on SiO_2 column using a mixture of toluene/ethylacetate = 250:0.25. The first deep violet band contained **BT-PDI** product which was obtained as black powder with the yield of 292 mg (46.5%). The second brown band contained **BT2-PDI2** product which was obtained as black powder with the yield of 73 mg (19.3%).

Compound **BT-PDI**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.69 (s, 2H), 8.79 (s, 2H), 8.37 (d, *J* = 29.8 Hz, 8H), 8.10 (s, 2H), 4.85 (s, 4H), 4.22 (s, 4H), 4.07 (s, 4H), 2.21 (s, 4H), 2.07 (s, 2H), 1.93 (s, 2H), 1.76 (s, 4H), 1.64–1.01 (m, 164H), 0.82 (m, 30H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.46, 163.27, 163.07, 162.02, 158.48, 151.15, 133.77, 133.32, 132.94, 132.70, 132.09, 130.67, 129.97, 128.60, 128.43, 127.98, 126.43, 125.60, 123.50, 123.39, 122.86, 122.75, 122.35, 121.42, 119.36, 106.39, 102.54, 95.43, 76.18, 45.08, 44.88, 36.91, 36.80, 32.25, 32.10, 31.97, 31.06, 30.38, 30.07, 29.87, 29.57, 26.85, 26.76, 26.47, 22.91, 22.84, 14.26. MALDI-TOF: $C_{158}H_{220}N_6O_{10}S$, *m/z*: 2396.222 $[M+H]^+$. Calcd. 2394.665. Elemental Anal. Calcd for $C_{158}H_{220}N_6O_{10}S$: C, 79.22; H, 9.26; N, 3.51; S, 1.34. Found: C, 78.81; H, 8.94; N, 3.86; S, 1.47.

Compound **BT2-PDI2**:
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.56 (s, 2H), 8.67 (s, 2H), 8.45–8.35 (m, 6H), 8.17 (m, 4H), 4.70 (s, 4H), 4.62 (s, 4H), 4.19 (s, 4H), 4.07 (s, 4H), 2.21–1.85 (m, 14H), 1.85–1.60 (m, 14H), 1.60–1.04 (m, 184H), 0.93–0.73 (m, 36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.53, 163.25, 162.16, 159.52, 158.31, 151.47, 151.15, 137.77, 137.62, 137.54, 133.95, 133.41, 133.16, 133.01, 132.11, 130.65, 130.25, 128.51, 128.10, 126.67, 125.84, 123.32, 122.88, 122.77, 122.44, 121.64, 119.50, 106.44, 102.15, 95.21, 86.36, 78.29, , 76.02, 75.84, 44.99, 44.85, 36.87, 36.73, 32.20, 32.17, 32.08, 31.94, 30.93, 30.33, 30.11, 30.05, 29.99, 29.92, 29.89, 29.86, 29.82, 29.71, 29.68, 29.55, 26.79, 26.75, 26.53, 26.37, 22.89, 22.83, 14.29, 14.26. $C_{188}H_{262}N_8O_{12}S_2$, *m/z*: 2891.692 $[M+H]^+$. Calcd. 2889.965. Elemental Anal. Calcd for $C_{188}H_{262}N_8O_{12}S_2$: C, 78.12; H, 9.14; N, 3.88; S, 2.22. Found: C, 77.93; H, 9.20; N, 3.52; S, 2.29.

NMR characterization of the compound 2



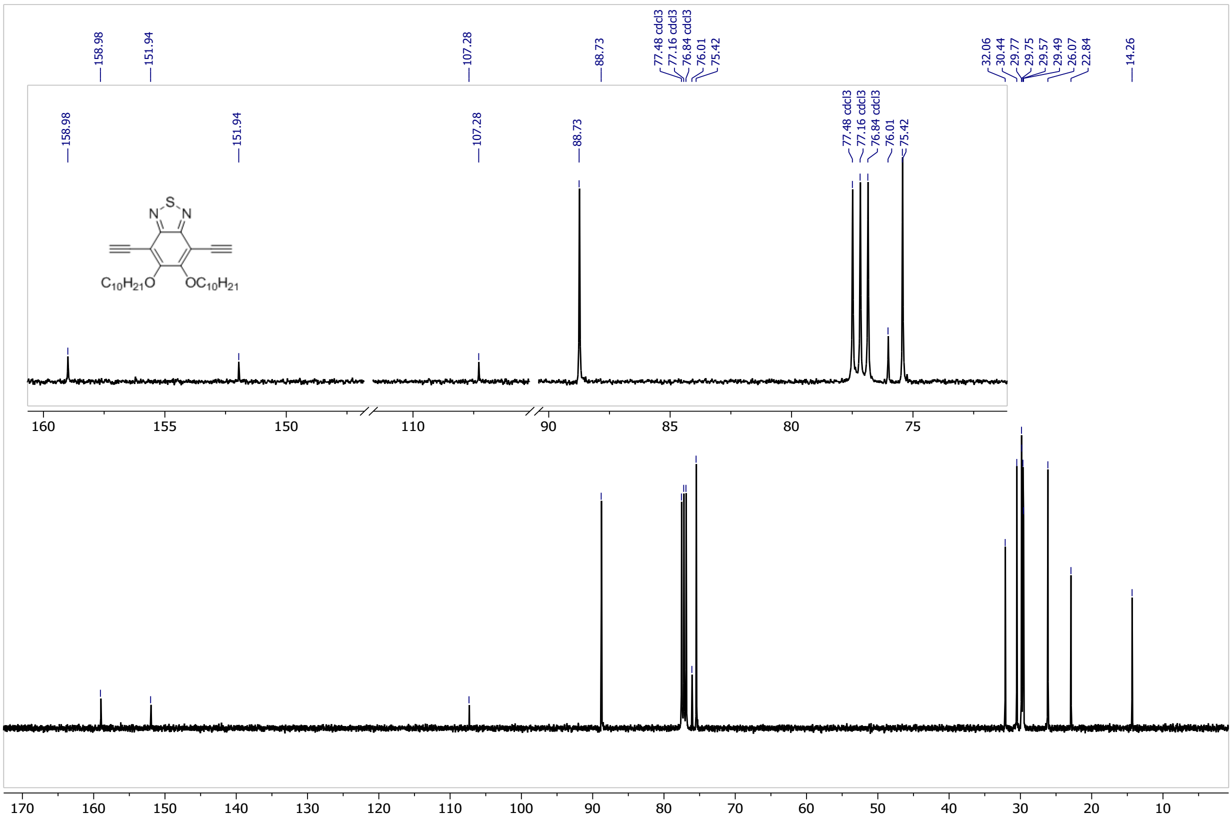
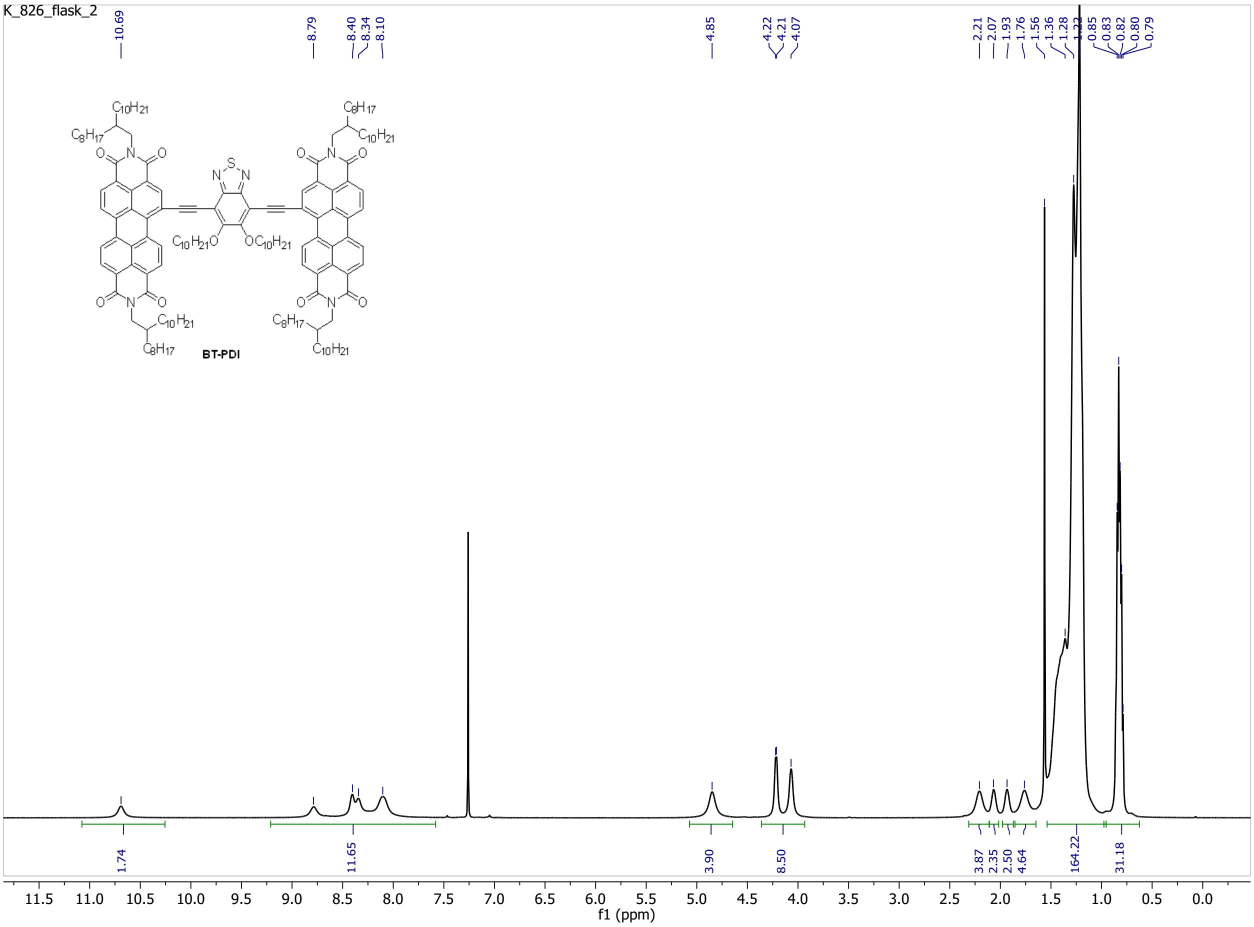
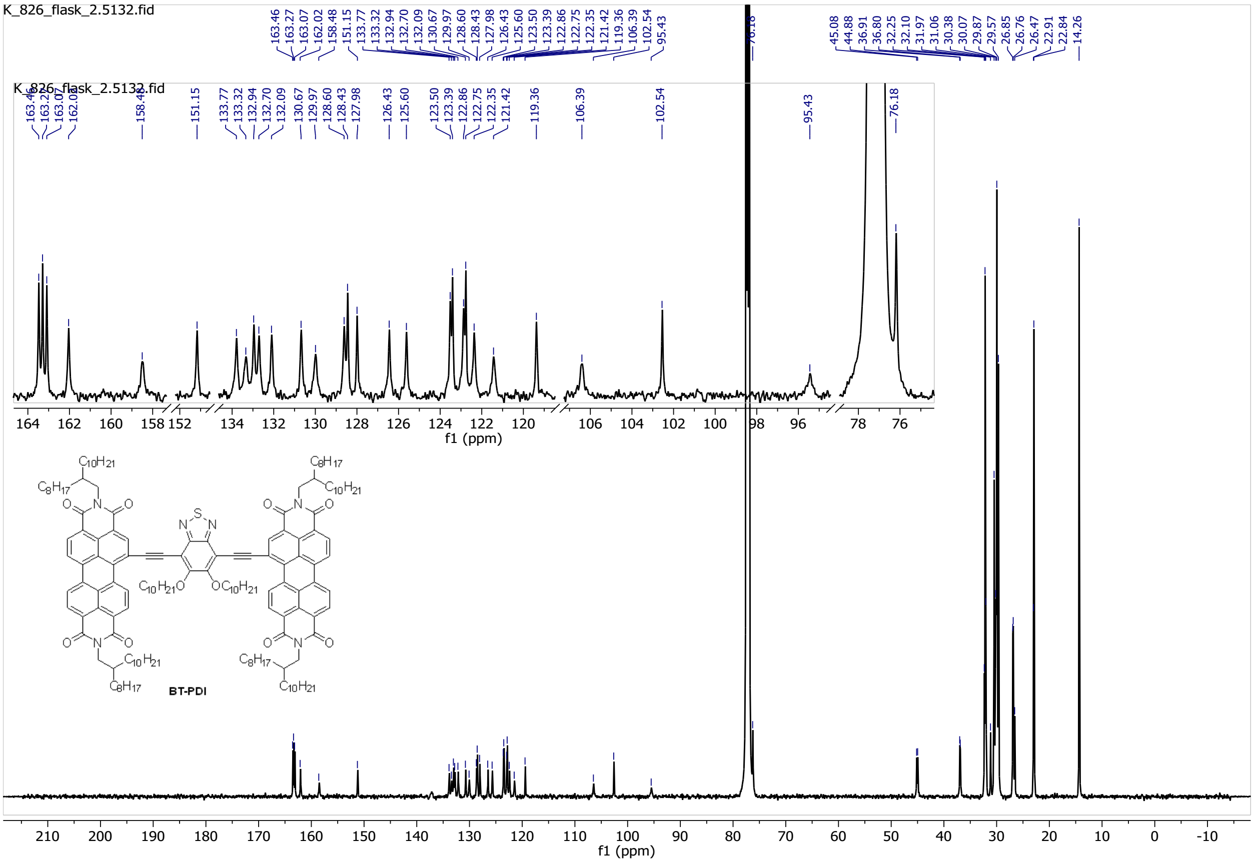


Figure S1. ^{1}H, ^{13}C NMR spectra of the compound **2**.

NMR and MALDI-TOF MS characterization of compound BT-PDI





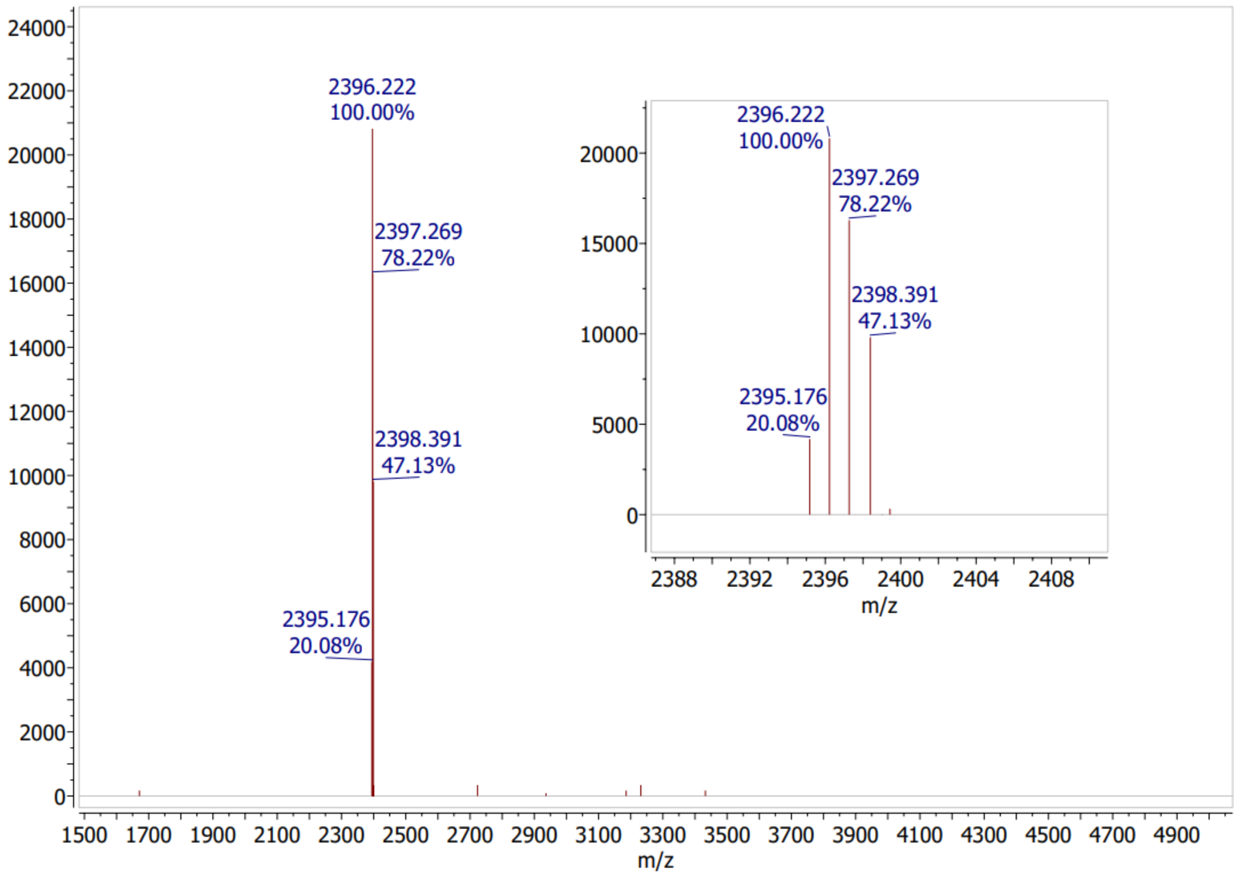
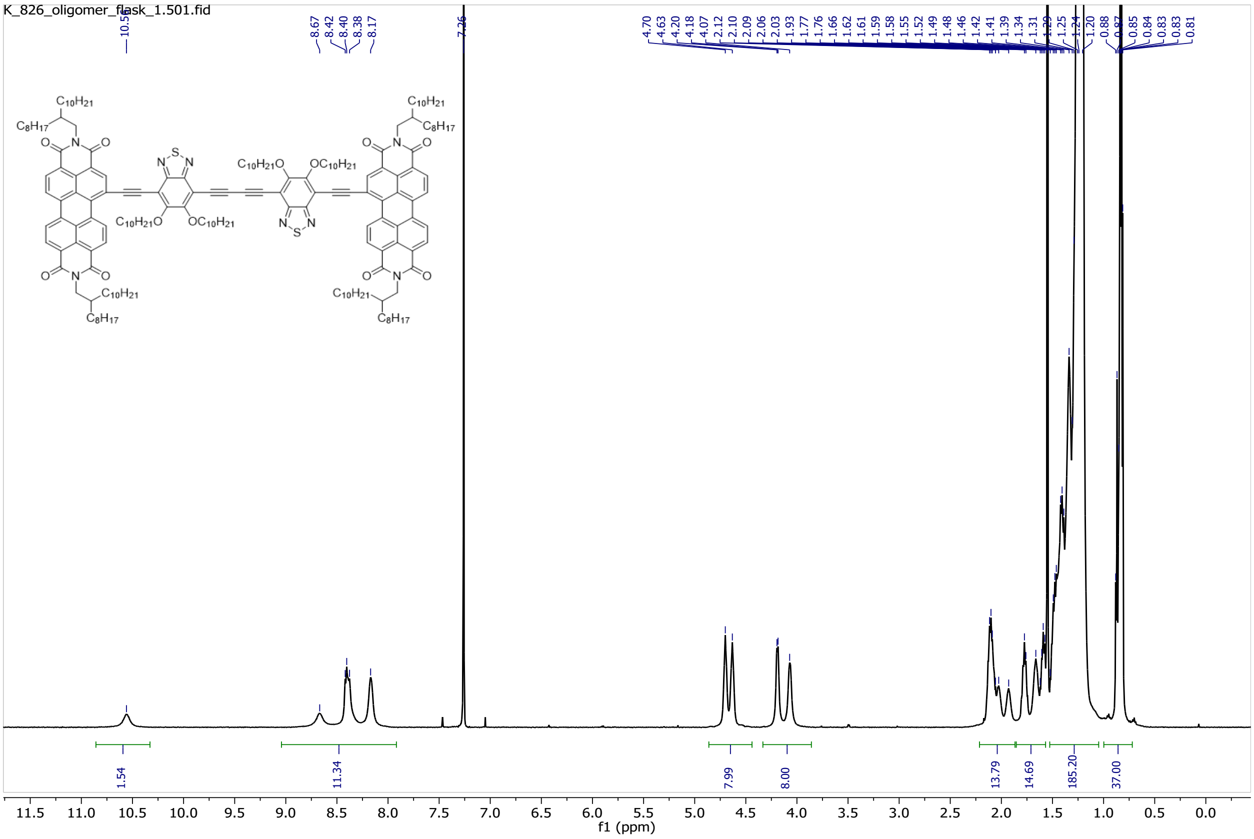
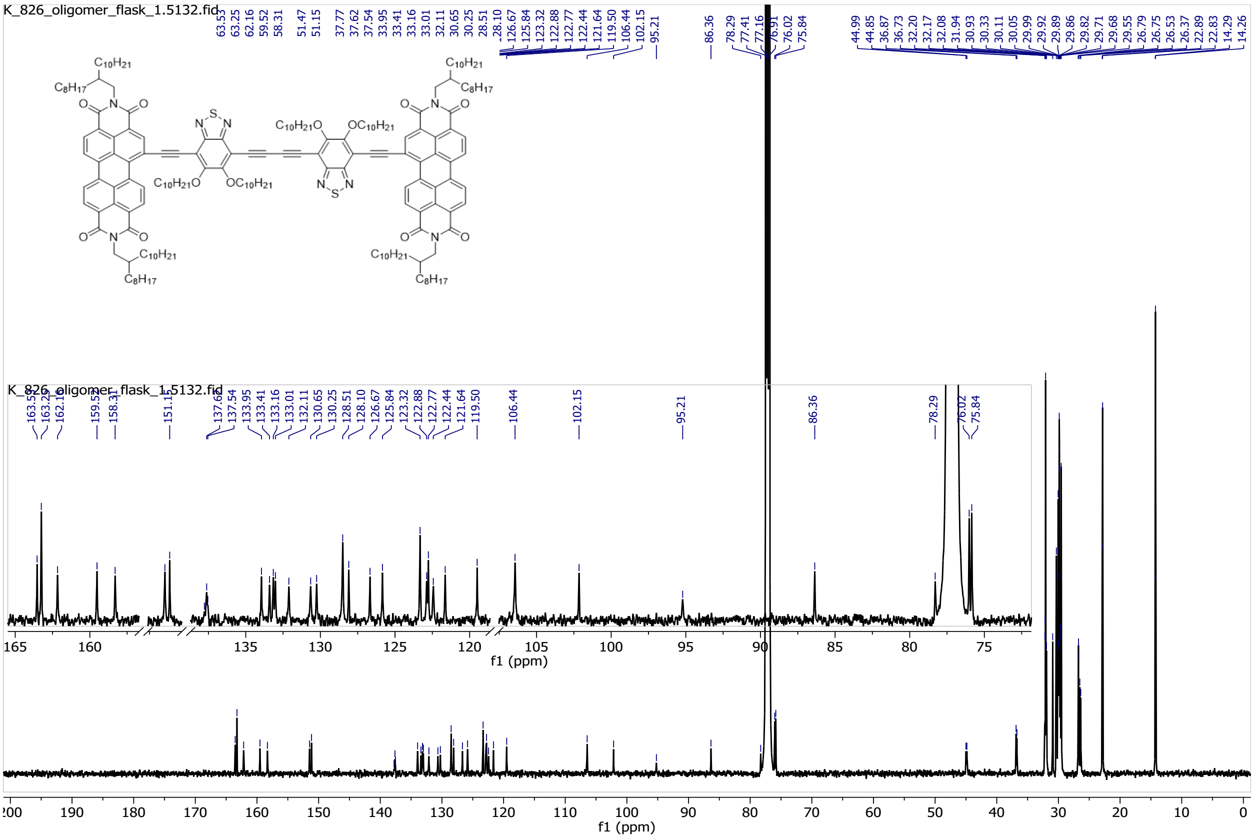


Figure S2. ^{1}H, ^{13}C NMR and MALDI-TOF spectra of compound **BT-PDI**.

NMR and MALDI-TOF MS characterization of compound BT2-PDI2





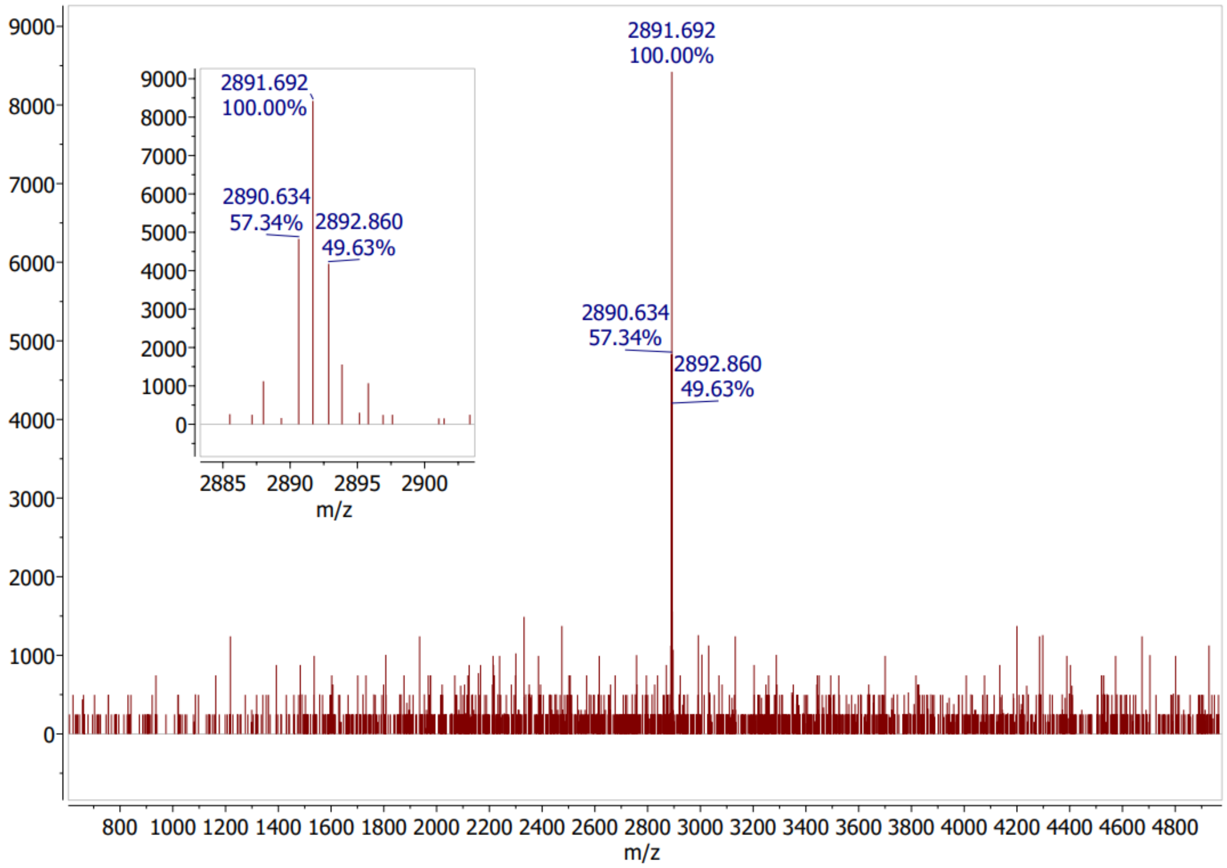
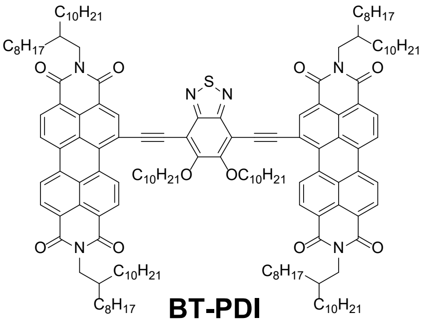
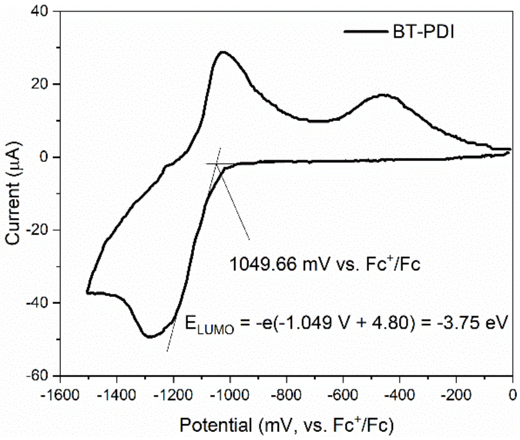


Figure S3. ^{1}H, ^{13}C NMR and MALDI-TOF spectra of compound **BT2-PDI2**.

Optical and electrochemical studies



E_{red} *vs*. Fc /V	E_{HOMO} /eV	E_g^{opt} /eV	E_{LUMO} /eV
-1.050	-5.66	1.91	-3.75



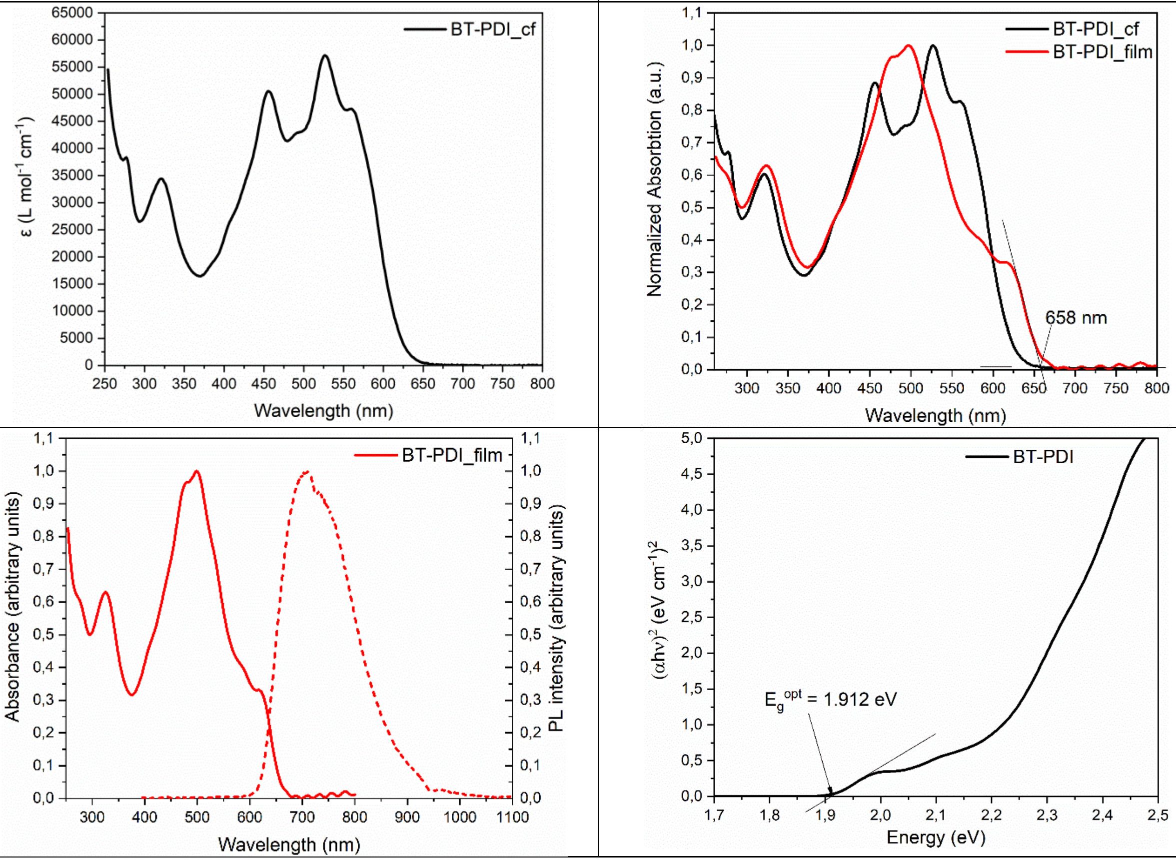
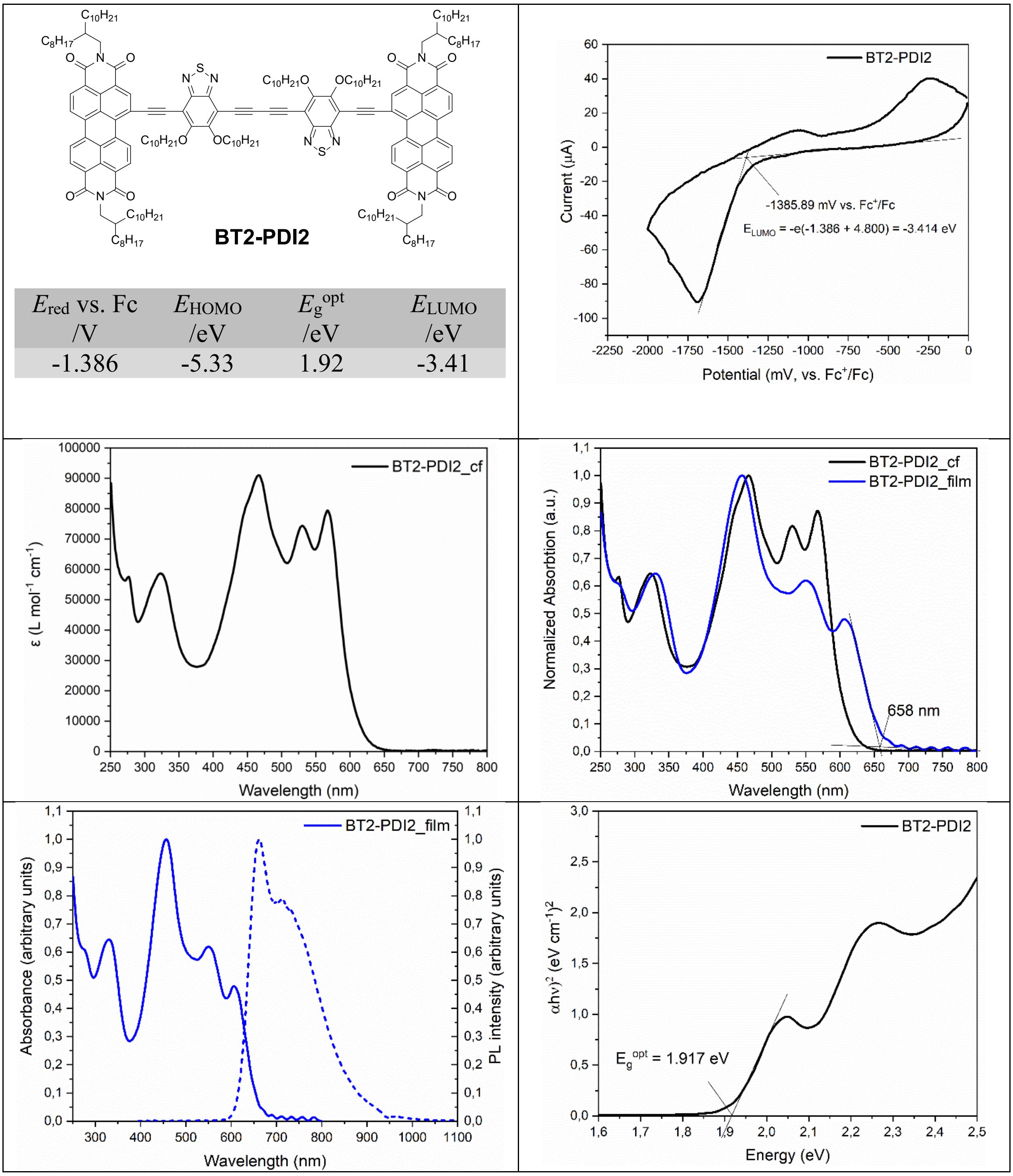


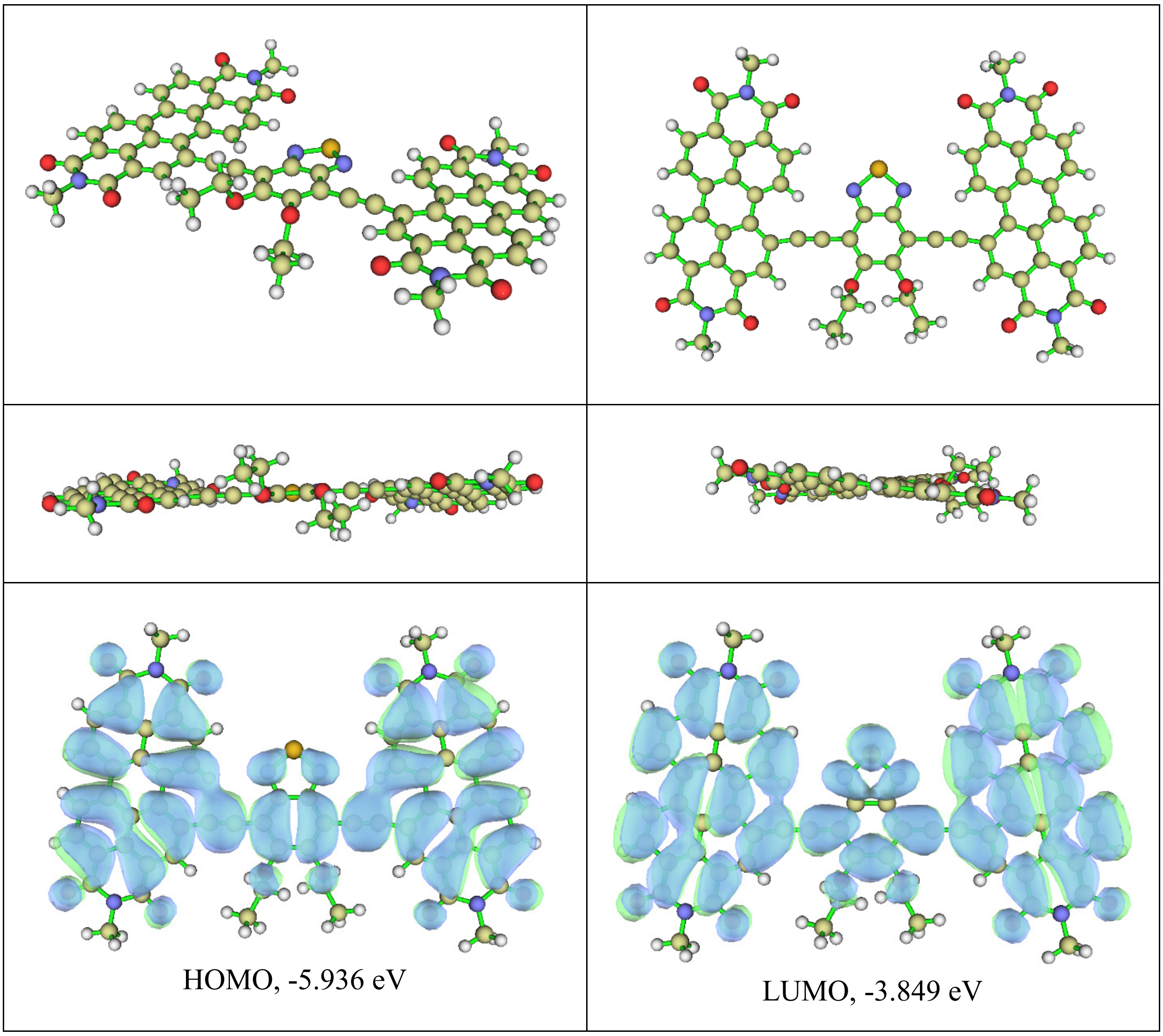
Figure S4. UV, PL, and CVA characterization and Tauc plot for **BT-PDI** compound.



E_{red} vs. Fc /V	E_{HOMO} /eV	E_g^{opt} /eV	E_{LUMO} /eV
-1.386	-5.33	1.92	-3.41

Figure S5. UV, PL, and CVA characterization and Tauc plot for **BT2-PDI2** compound.

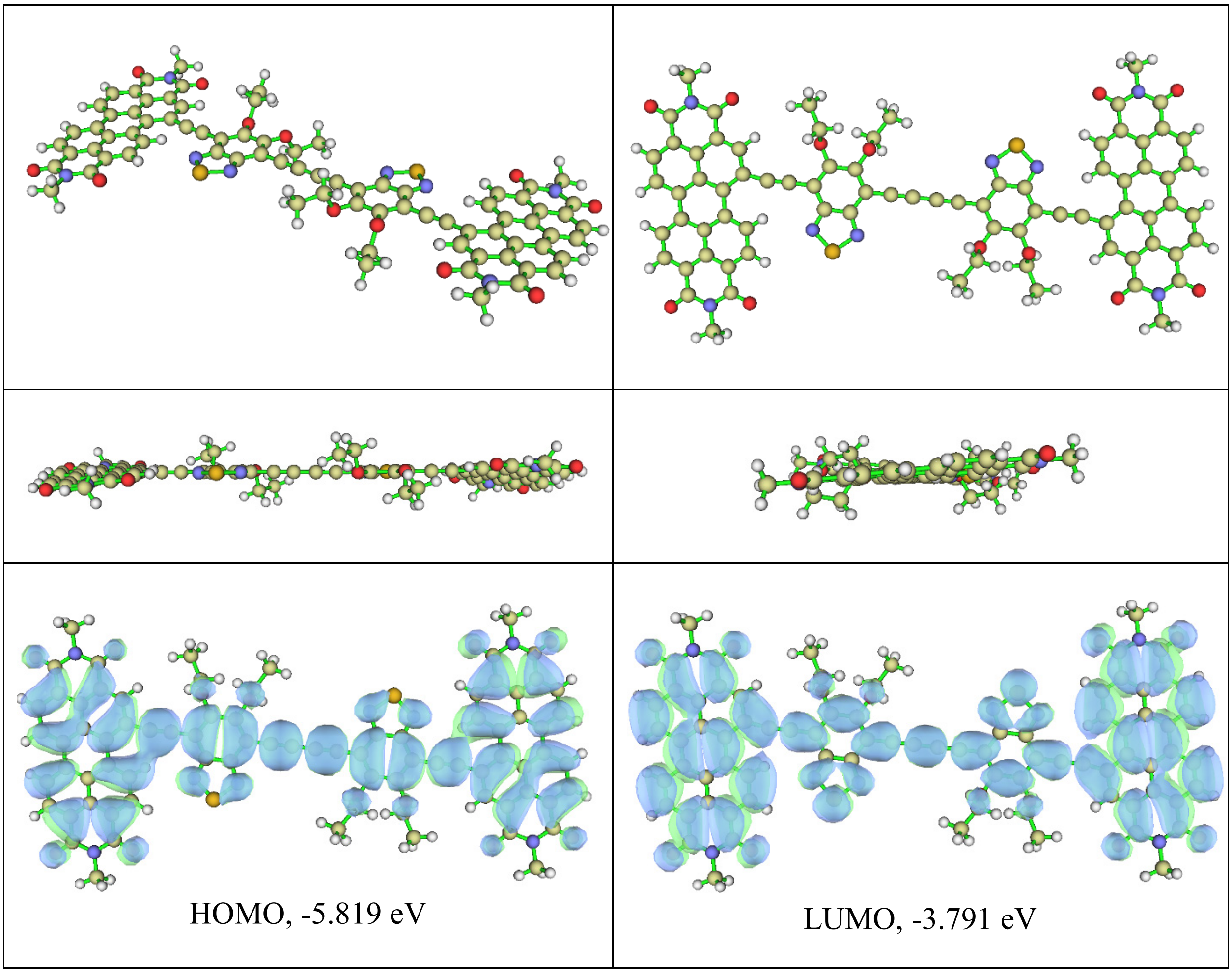
Calculations



HOMO, -5.936 eV

LUMO, -3.849 eV

Figure S6. Perspective, top, front, and side views, and HOMO/LUMO distribution, for **BT-PDI** molecule

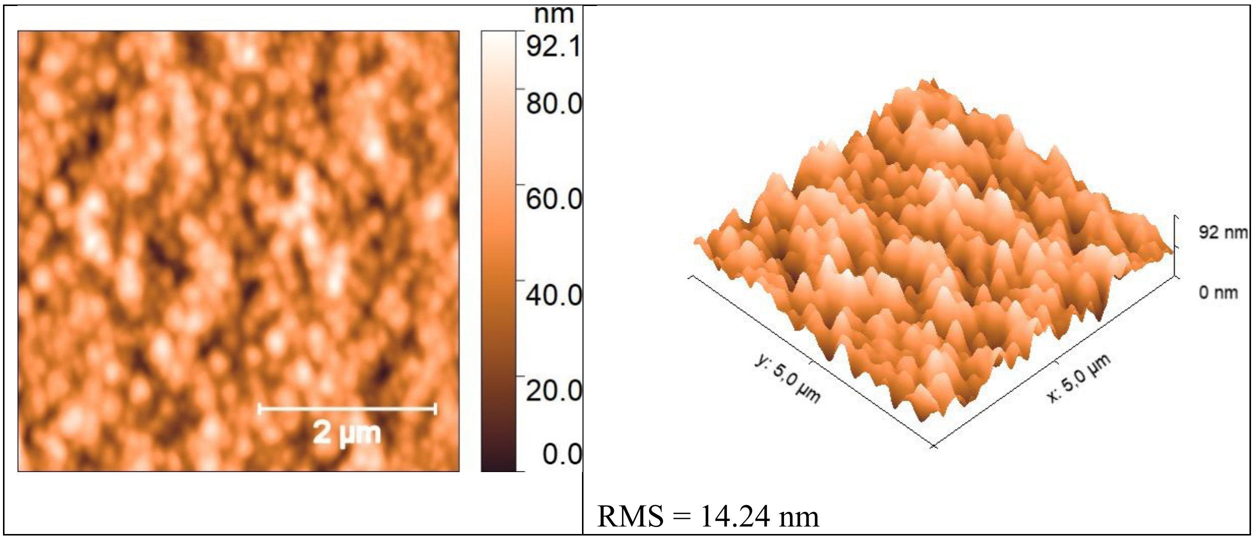


HOMO, -5.819 eV

LUMO, -3.791 eV

Figure S7. Perspective, top, front, and side views, and HOMO/LUMO distribution, for **BT2-PDI2** molecule.

AFM study



RMS = 14.24 nm

Figure S8. AFM images of $Cs_{0.12}FA_{0.88}PbI_3$ perovskite film without coating.

Electron mobility measurements

The electron mobility of **BT-PDI** and **BT2-PDI2** was determined using photo-CELIV method. For this experiments, OPV-like devices with architecture ITO/PEDOT:PSS/active layer/PFN/Field's alloy were fabricated. To do this, solutions of **BT-PDI** or **BT2-PDI2** in chlorobenzene with concentration 10 mg ml^{-1} were prepared firstly. Then regiorandom P3HT (Ossila Ltd.) was added to these solutions with concentration 2 mg/ml.

The substrates/ITO (Ω = 20 Ω/sq (S101), purchased from Ossila Ltd.) were mechanically cleaned in a surfactant solution, then ultrasonicated sequentially in a surfactant solution, distilled water, acetone and ethanol. The substrates were then dried with a stream of clean air and exposed to UV ozone for 60 minutes. Spin Coatier T100 was used to apply films from solutions. A solution of PEDOT:PSS (Al 4083, purchased from Ossila Ltd.) was filtered through a hydrophilic filter with a pore size of 0.45 μm and spin-coated onto the surface of pre-cleaned ITO substrates at 5000 rpm for 30 s. Immediately after application, the PEDOT:PSS layer was annealed at 140 °C for 10 minutes in air. The active layer was spin-coated from pre-prepared solutions by centrifugation at 1000 rpm for 1 minute. The active layer consisted of the regiorandom P3HT:NFA 1:10 w:w composite. PFN was used as an electron-conducting layer. It was spin-coated at 3500 rpm for 30 seconds. The cathode material was Field's alloy (Bi/In/Sn = 32.5% / 51% / 16.5%). It was deposited onto the electron-conducting layer by dripping at 100 ºC.

Photo-CELIV experiment was performed as described in ref. [S3]. Since hole mobility in regiorandom P3HT is very low, and its fraction in the composite is small, the effective mobility measured by photo-CELIV is determined by the electron mobility of the acceptor.

The effective mobility μ was estimated using the relation [S4]:

$$\mu = 2L^2/3At_m^2,$$

where t_m is the position of the maximum of the current transient, A is the voltage ramp rate. The thickness of the active layer was determined by AFM profilometry.

References:

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