

Supporting Information

Enhancing the Lifetime of Inverted Perovskite Solar Cells using a new Hydrophobic Hole Transport Material

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1. Experimental

1.1 Materials

Lead Iodide (PbI₂, 99.99%) was purchased from TCI. Lead Bromide (PbBr₂, 98+%), Cesium Iodide (CsI, 99.999%) and Rubidium Iodide (RbI, 99.8%) were purchased from Alfa Aesar. Formamidinium Iodide (FAI) was purchased from GreatCell. Methylammonium Bromide (MABr) was purchased from Dyesol. Phenyl-C₆₀-Butyric acid Methyl ester (PC₆₀BM, 99.9%) was purchased from Solenne. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline-Bathocuproine (BCP), Toluene (99.8%, Anhydrous), N,N-Dimethylformamide (DMF, 99.8%, Anhydrous), Dimethyl Sulfoxide (DMSO, >99.9%, Anhydrous) and Chlorobenzene (99.8%, Anhydrous) were purchased from Sigma Aldrich. 2-Propanol (IPA, 99.5%, extra dry) and Acetonitrile (99.9+%, Extra Dry) were purchased from Acros Organics. Poly(3,4-ethylenedioxythiophene) (PEDOT:PSS, aqueous dispersion) was purchased from Clevios.

1.2 PIDTTDQ Synthesis and Characterization

1.2.1 Synthesis

All reactions are air and light sensitive and, therefore, were performed under argon and in the dark. All glassware was washed using detergent (Teepol), rinsed with excess water, acetone and methylene dichloride and dried in an oven at 120°C. All solvents and reagents were purchased from Aldrich. Toluene was distilled using calcium hydride (CaH₂) and benzophenone prior to polymerization. The thiadiazoloquinoxaline derivative was purchased from Sunatech Inc. The synthesis of the indacenodithiophene was performed according to already published procedure¹. The experimental condition for the polymerization is analytically described below: Distannyl substituted indacenodithiophene (0.5 mmol) and dibromo thiadiazoloquinoxaline derivative (0.5 mmol) were dissolved in dry toluene (0.025 M). Then, tris(dibenzylideneacetone)dipalladium(0) (Pd₂dba₃) (0.02 equiv) and tri(*o*-tolyl)phosphine (P(*o*-tol)₃) (0.04 equiv) were added and the reaction mixture was stirred at 120°C under argon atmosphere for 48 h. The polymer was purified by precipitation in methanol, filtered and washed using a Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform fraction was evaporated under reduced pressure and the polymer was precipitated in

methanol, filtered through 0.45 mm PTFE filter and finally dried under high vacuum, rendering a dark greenish solid. The yield of PIDTTDQ was 86%.

1.2.2 PIDTTDQ Characterization

Absorption spectrometry: UV-Vis absorption of the polymer solutions (concentration 10^{-5} M) and the fabricated films were recorded with a Shimadzu UV-1900 spectrometer.

Nuclear Magnetic Resonance (NMR): ^1H -NMR measurements were carried out in solutions (1% w/v) of the copolymers using CDCl_3 (Acros 99.6%) as the solvent and tetramethylsilane (TMS) as the integral standard on a Varian 600 MHz NMR spectrometer at ambient temperature.

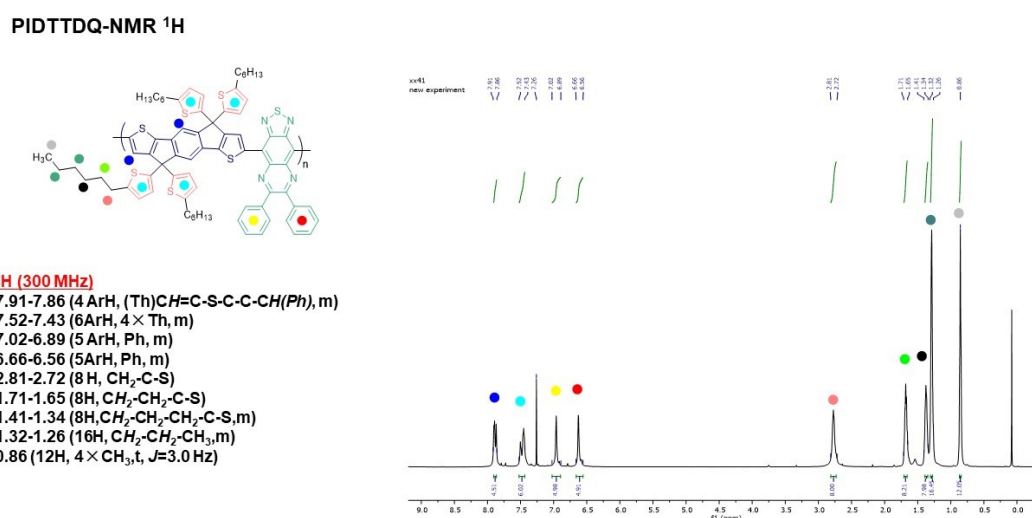


Figure S1. ^1H NMR Spectrum of PIDTTDQ.

^1H NMR (CDCl_3 , 600 MHz) δ 7.91-7.86 (m, 4H), 7.52-7.43 (m, 6H), 7.02-6.89 (m, 5H), 6.66-6.56 (m, 5H), 2.81-2.72 (m, 8H), 1.71-1.65 (m, 8H), 1.41-1.34 (m, 8H), 1.32-1.26 (m, 16H), 0.86 (t, 6H, $J = 3.0$ Hz). SEC (CDCl_3): $\bar{M}_n = 25400$ g/mol, $D = 3.9$.

1.3 Solar Cell Fabrication

Patterned glass/ITO substrates (Ossila, thickness:100nm, sheet Resistance:20 Ω sq^{-1}) were cleaned by sequential ultrasonication for 10 minutes in soapy water, deionized water, acetone, and isopropanol. The substrates were then dried in an oven for 30 minutes, following a UV-Ozone treatment for 15 minutes. For the reference device, PEDOT:PSS was filtered with a PVDF filter (0.45 μm) and was spin-coated at 7000rpm for 45s. The samples were then annealed at 120° C for 20 minutes in ambient air. After cooling to room temperature, the samples were immediately transferred to a N_2 filled glovebox for further processing. For the PIDTTDQ HTL, a stock solution with a concentration of 0.5 mg ml^{-1} in Chlorobenzene was prepared. Devices with PIDTTDQ concentrations of 0.01, 0.05, 0.1 and 0.2 mg ml^{-1} were fabricated by appropriately diluting the stock solution. For film deposition, 60 μl of each solution was spin-coated at 4000rpm for 45s without further processing. For the perovskite precursor solution, 1.24M PbI_2 (9% excess), 1.14M FAI, 0.2M PbBr_2 and 0.2M MABr were dissolved in DMF:DMSO 4:1 and then 5 vol% CsI and 4 vol% RbI from 1.5M stock solutions dissolved in DMF and DMF:DMSO 4:1 respectively were added, in order to obtain the 4-cation perovskite composition $\text{Rb}_{0.04}\text{Cs}_{0.05}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.91}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$. The solution is left stirring continuously without heating. For perovskite deposition, 45 μl of the solution was spin-coated at 6000rpm for 45s. 200 μl Chlorobenzene

was dropped 20s before the end of the spinning process. The samples were then annealed at 100°C for 45 minutes. After cooling to room temperature, the electron transport layer was deposited. For this, 45 µl of 20 mg ml⁻¹ PC₆₀BM solution in Chlorobenzene (stirring at 70°C) was spin-coated at 2000 rpm for 60s. Then, 45 µl BCP interlayer (0.5 mg ml⁻¹ in IPA, stirring at 70°C) were dynamically spin-coated at 4000 rpm for 45s. The devices were finished by thermally evaporating 100 nm thick Ag under a high vacuum (4·10⁻⁶ mbar).

1.4 Material and Device Characterization

Atomic Force Microscopy (AFM) images were captured using an XE7 microscope (Park Systems) by operating in tapping mode. Water Contact angle measurements were performed on an L2004A1 goniometer from Ossila. HOMO measurements were carried out with an APS04 N2-RH system (KP Technology). Dark work function (WF) and ambient photoemission spectroscopy (APS) were conducted. More specific, contact potential difference (CPD) was measured by the vibrating gold alloy Kelvin probe (2 mm). Absolute WF of the tip estimated to be around 4.54-4.6 eV, which was calibrated by measuring a silver reference and calculating its absolute WF by APS. HOMO was determined by using a UV Light excitation source (D₂) in the range of 3.8-6 eV and by extrapolating to zero the cube root of the photoemission signal. The LUMO level was calculated in conjunction with Uv-vis measurements through the formula:

$$E_{LUMO} = E_{HOMO} + E_g \quad (5)$$

where E_g is the optical bandgap measured from the Tauc plot. Steady-state Photoluminescence measurements were performed with a commercial platform (ARKEO - Cicci Research): the substrate is illuminated with a diode-pumped solid-state (DPSS) Nd:YVO₄+KTP Laser (Peak wavelength 532 nm ± 1 nm, Optical power 1 mW on a circular spot of 2 mm of diameter: 31 mW cm⁻²) at an inclination of 45°. The fluorescence on the opposite side of the substrate is focused on a bundle of fibers (10 mm in diameter) with an aspheric lens close to the substrate to maximize the PL. The bundle sends the signal to a CCD-based spectrometer. Integration time and the number of averaging is maintained the same to better compare the results. Time-Resolved Photoluminescence (TRPL) was measured with an FS5 Spectrofluorometer from Edinburgh Instruments. A 478.4 nm laser was used as an excitation source. Transient photovoltage and Transient Photocurrent measurements were performed with a commercial apparatus (Arkeo, Cicci Research s.r.l.) based on a high-speed Waveform Generator that drives a high-speed LED (5000 Kelvin). The device is connected to a trans-impedance amplifier and a differential voltage amplifier to monitor short-circuit current or open-circuit voltage. The light intensity from the pulse is varied between 0.001-2 sun equivalent. For Transient Photovoltage, the perturbation produced by the LED is less than 10% of the background applied light bias. Transient photocurrent measurements were performed under large perturbations (Duty cycle 0.3) for a time duration of 400 µs. Devices are connected to a 50 Ω and 1 MΩ resistor for TPC and TPV measurements, respectively. J-V characteristics of devices were measured using a solar simulator (Oriel) with a 450 W Xenon Lamp. The intensity of the lamp was calibrated at 100 mW cm⁻² one sun AM1.5G illumination using a Keithley 2700 Data acquisition system equipped with a KG-5 Si diode. J-V curves of devices were measured in an N₂ filled glovebox with a multiplexor test board system (Ossila) by scanning from -0.1 V to 1.2 V, with a scan rate of 10 mV s⁻¹ and a voltage step of 10 mV. A metal mask was used to define the active area of the solar cells (0.0256 cm²). External Quantum Efficiency (EQE) was measured with a commercial system from Enlitech (QE-R2) with a chopping frequency of 65 Hz. For the ISOS stability tests, the ISOS D1 protocol was performed by storing the devices in the dark in ambient environment with humidity ranging between 50-70%, and JV curves were measured in the glovebox using the solar simulator. An ISOS testing laboratory equipment from InfinityPV was used by operating in the ISOS-L2 mode. The devices were encapsulated using a piece of glass and a UV-curable epoxy as an adhesive (Ossila E132). Then, the devices are transferred to a testing chamber where they are exposed under continuous 1 sun illumination and temperature above 65°C. Humidity was kept at 10-15%. The apparatus is equipped

with a solar simulator using a metal halide source simulating the AM1.5G spectrum in the range 300-900nm. The light intensity was calibrated at 100 mW cm⁻² using a Si reference cell. The devices were held at open circuit between each measurement.

2. Supplementary Experimental Results

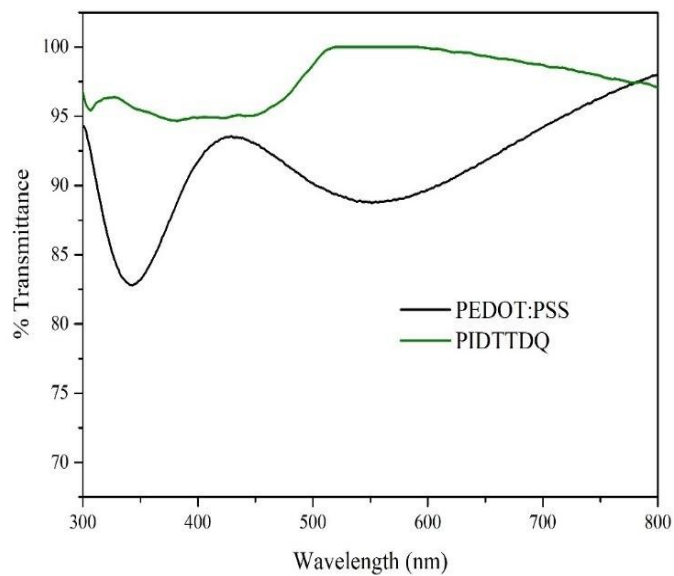


Figure S2. Transmittance spectrum of PIDTTDQ and PEDOT:PSS films with a thickness of ≈ 50 nm

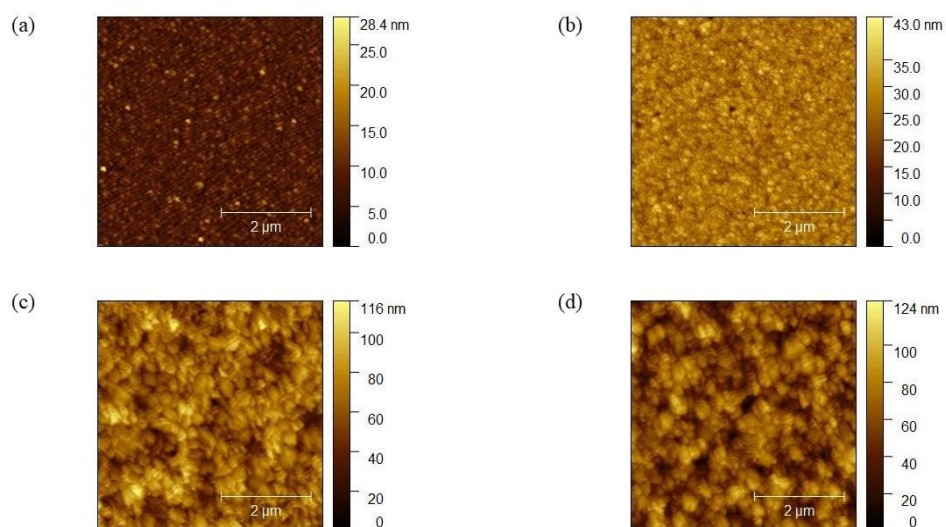


Figure S3. AFM Imaging for bare (a) PIDTTDQ ,(b) PEDOT:PSS films and for (c) PIDTTDQ /Perovskite, (d) PEDOT:PSS/ perovskite films.

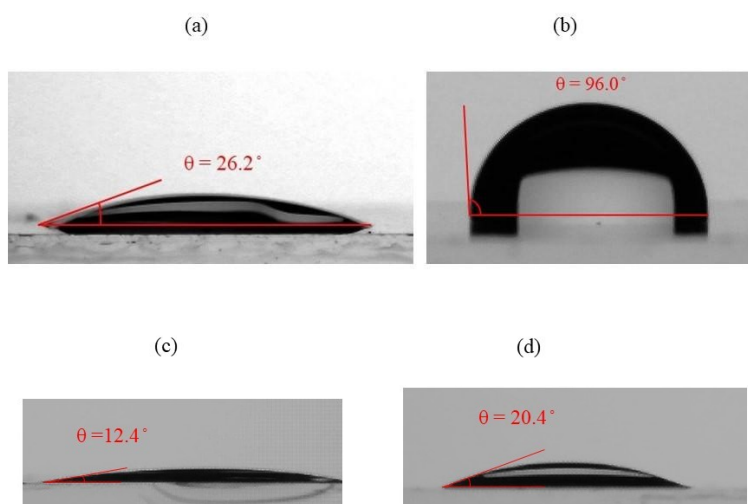


Figure S4. Water Contact angle of PEDOT:PSS (a) and PIDTTDQ (b) ,DMF Contact angle of PIDTTDQ (c) and PEDOT:PSS (d)

Table S1. Obtained energy levels for PIDTTDQ from combined APS and UV-vis results.

Energy level	Value (eV)
E_{HOMO}	-4.8
E_{LUMO}	-3.6
E_{g}	1.2

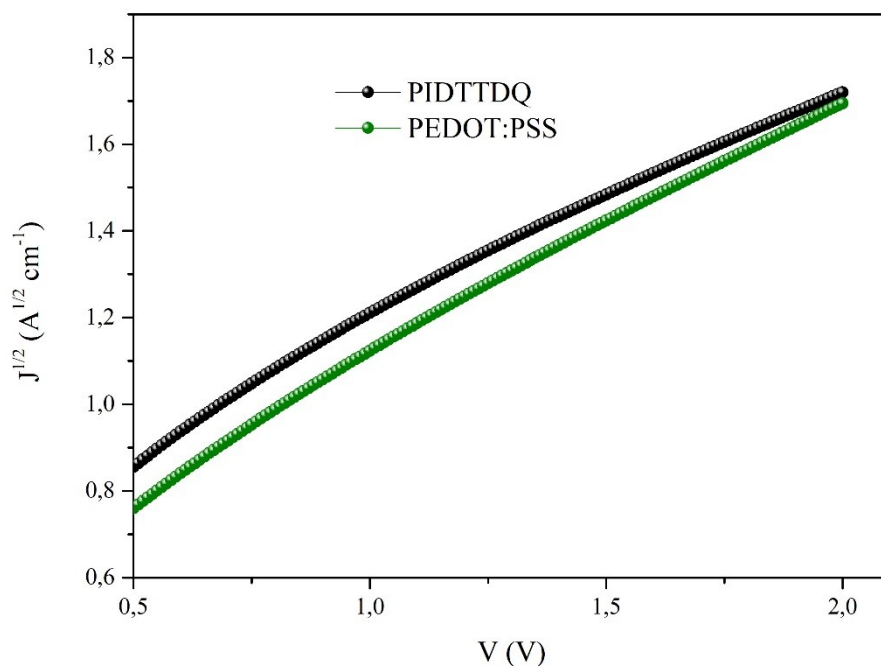


Figure S5. SCLC Measurements for hole only devices ITO/ PIDTTDQ /Au and ITO/PEDOT:PSS/Au for PIDTTDQ and PEDOT:PSS respectively.

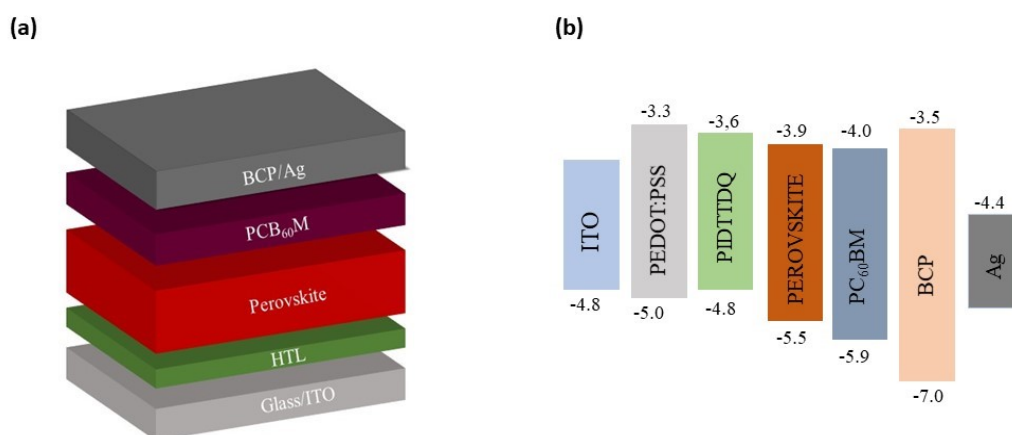


Figure S6 (a) Inverted Device architecture (b) Inverted Device Energy level scheme

Table S2. Average Photovoltaic parameters of 20 fabricated devices with various PIDTTDQ concentrations. The errors are calculated from device statistics. The brackets correspond to the champion device.

Concentration (mg ml ⁻¹)	PCE %	FF %	J _{sc} (mA cm ⁻²)	V _{oc} (V)
0.01	10.81±2.12 (13.77)	68.12± 7.40 (75.32)	15.01± 1.71 (17.12)	1.01± 0.04 (1.03)
0.05	13.07±0.68 (14.70)	74.96±1.83 (77.51)	15.88± 0.85 (16.97)	1.04± 0.04 (1.06)
0.1	12.15± 0.80 (13.97)	71.59± 2.86 (77.01)	16.86± 0.91 (16.48)	0.97± 0.04 (1.05)
0.2	11.22±1.42 (12.60)	68.93± 5.90 (73.25)	16.68± 0.88 (17.52)	0.95± 0.02 (0.96)

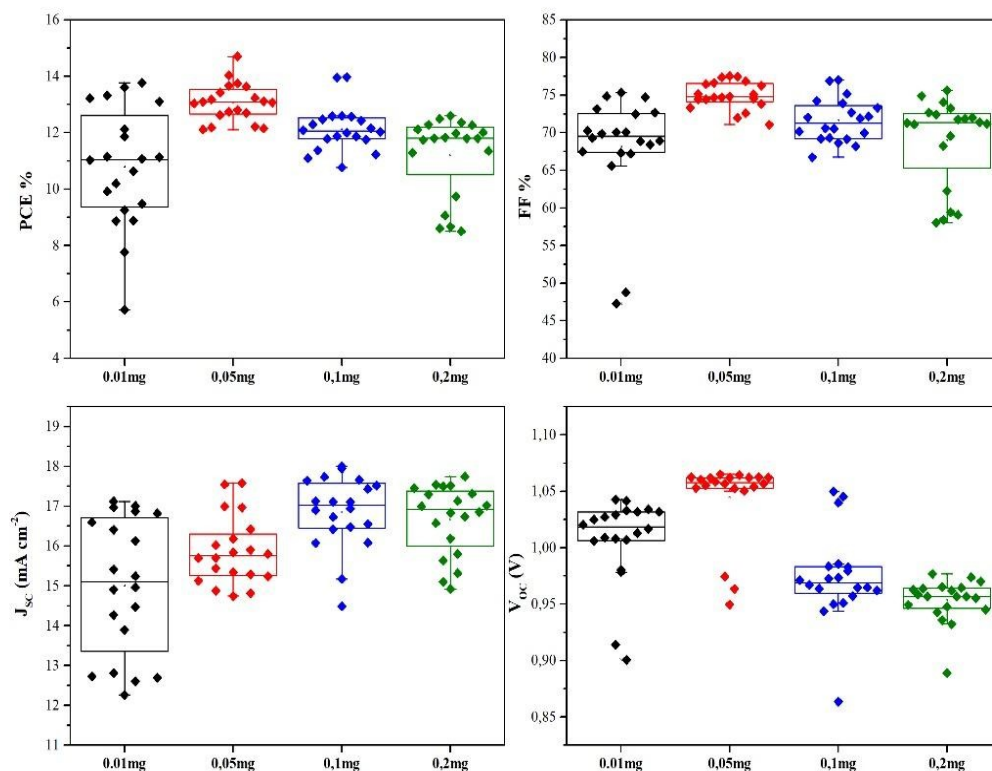


Figure S7. Box plots with photovoltaic parameters for 20 devices for various PIDTTDQ concentrations.

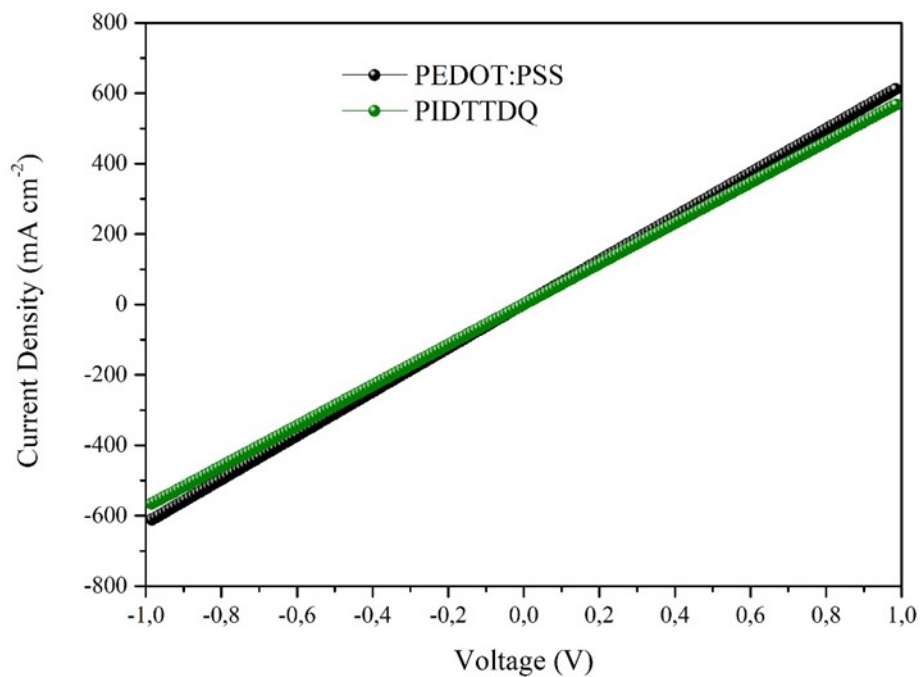


Figure S8 Measured Conductivity J-V Curves of PIDTTDQ and PEDOT:PSS using the diode configuration ITO/PIDTTDQ or PEDOT:PSS/Au

Table S3. Photovoltaic parameters of 20 fabricated Reference devices with PEDOT:PSS.

#	PCE %	FF %	J _{sc} (mA cm ⁻²)	V _{oc} (V)
1	12.16	75.32	16.08	0.95
2	12.14	77.49	15.95	0.93
3	12.11	76.40	16.14	0.93
4	12.08	77.62	15.73	0.94
5	12.08	75.76	15.83	0.96
6	12.04	77.83	15.70	0.94
7	11.96	77.79	15.54	0.94
8	11.93	76.37	15.59	0.95
9	11.91	77.33	15.65	0.93
10	11.86	75.82	15.69	0.95
11	11.85	76.86	15.60	0.94
12	11.80	77.29	15.65	0.93
13	11.74	78.29	15.32	0.93
14	11.63	72.75	16.41	0.93
15	11.61	75.79	16.73	0.90
16	11.60	75.96	16.44	0.91
17	11.57	77.31	15.60	0.91
18	11.50	74.91	15.38	0.95
19	11.45	77.26	15.34	0.92
20	11.45	77.03	15.96	0.91
AVERAGE	11.82± 0.24	76.56± 1.29	15.82± 0.38	0.93± 0.02

Table S4. Photovoltaic parameters of 20 fabricated devices with PIDTTDQ.

#	PCE %	FF %	J _{sc} (mA cm ⁻²)	V _{oc} (V)
1	14.70	77.51	16.97	1.06
2	14.04	77.36	16.18	1.07
3	13.75	77.48	16.02	1.05
4	13.67	76.64	17.58	0.96
5	13.64	76.84	15.84	1.06
6	13.42	76.46	15.71	1.06
7	13.24	74.82	15.91	1.06
8	13.18	75.11	17.55	0.95
9	13.11	74.71	15.70	1.06
10	13.10	75.15	17.00	0.97
11	13.07	71.97	16.43	1.05
12	13.04	76.26	15.34	1.06
13	12.80	74.69	15.44	1.05
14	12.74	72.60	15.80	1.06
15	12.70	74.41	15.29	1.06
16	12.62	74.56	15.13	1.06
17	12.21	74.45	14.75	1.06
18	12.18	73.84	14.88	1.05
19	12.15	73.32	14.82	1.06
20	12.11	71.08	15.24	1.06
AVERAGE	13.07±0.68	74.96±1.83	15.88± 0.85	1.04± 0.04

Table S5 Series Resistance Values for 20 fabricated devices with PEDOT:PSS and PIDTTDQ

#	R _s (Ω cm ²)	
	PEDOT:PSS	PIDTTDQ
1	5.64	5.34
2	5.34	5.83
3	5.24	5.79
4	5.24	3.71
5	5.23	5.66

6	5.21	6.22
7	5.43	5.54
8	5.25	3.95
9	5.73	5.60
10	5.11	3.92
11	5.41	5.89
12	5.41	5.97
13	5.11	6.20
14	5.63	5.91
15	4.74	6.56
16	4.89	6.06
17	5.19	6.42
18	5.51	6.91
19	5.43	6.58
20	4.82	8.14
AVERAGE	5.28± 0.26	5.81± 1.0

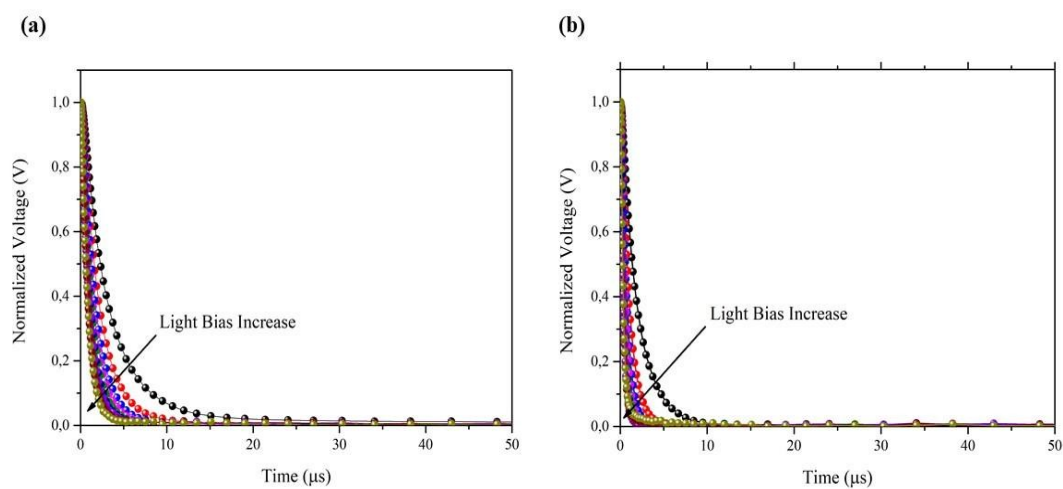


Figure S9. Transient Photovoltage decays for various light intensities for (a) PIDTTDQ and (b) Reference Device.

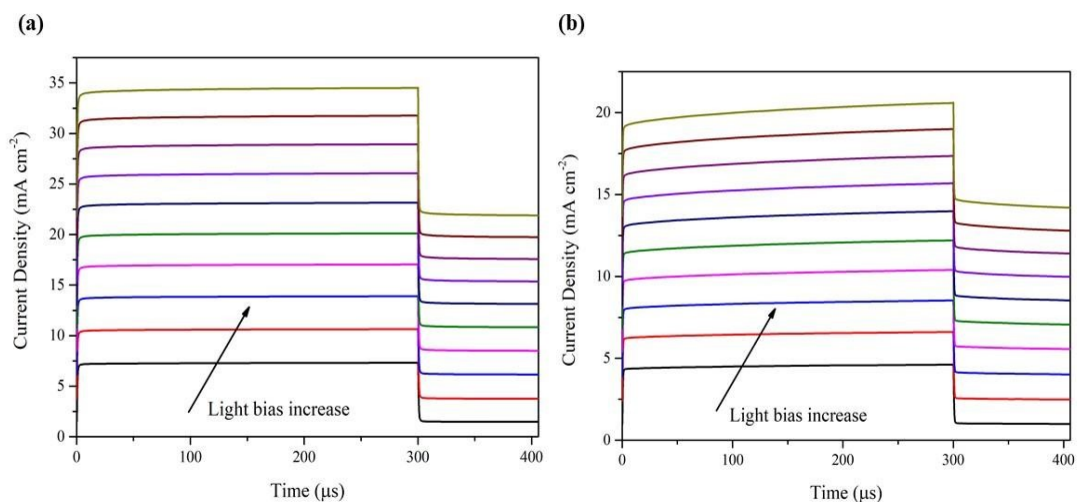


Figure S10. Transient Photocurrent transients for various light intensities for (a) PIDTTDQ and (b) Reference Device.

Table S6. Obtained time constants from TRPL decays using the TCSPC method

Configuration	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
Perovskite	10.54	162	158.1
Perovskite/PEDOT:PSS	2.67	49.2	46.1
Perovskite/ PIDTTDQ	5.02	132.5	128.7

References

- 1 C. CL, K. A, G. N, K. C, A. T, B. CJ and A. A, *Macromol. Rapid Commun.*, , DOI:10.1002/MARC.201600614.
- 2 B. Huang, Q. Fu, Q. Ai, L. Tan, L. Chen and Y. Chen, *Mater. Chem. Front.*, , DOI:10.1039/c6qm00210b.