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Supporting Information

A novel selenophene based non-fullerene acceptor for near-infrared organic photodetectors with ultra-low dark current

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Materials

General: Reagents and chemicals were purchased from commercial sources. Anhydrous chlorobenzene was purchased from Sigma-Aldrich. 2,7-Bis(trimethylsilyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']bis(selenophene) was synthesized according to previous literatures.

All reactions were carried out under Ar using solvents and reagents as commercially supplied, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of $CDCl_3$ are given in ppm. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh). Electrospray mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker ultrafleXtreme MALDI-TOF analyzer. Anthracene (or 2,5-dihydroxybenzoic acid) and myoglobin were used as the matrix and calibration internal standard respectively. Thermogravimetric analysis (TGA) was carried out using a PerkinElmer Pyris 1 TGA machine, with heating from 50 to 700 °C at a heating rate of 10 °C/min under N_2. Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery differential calorimeter at a scan rate of 10 °C/min from 0 °C to 300 °C under N_2. UV-vis spectra were recorded on PerkinElmer Lambda20 UV-vis spectrophotometer. Cyclic voltammetry (CV) was carried out with a standard three-electrode cell in a 0.1 M tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) solution in acetonitrile at room temperature with a scanning rate of 0.1 V s−1. A Pt rod working electrode (1.6 mm diameter), a Pt wire counter electrode, and an Ag/AgCl reference electrode were used. The oxidation potentials were calibrated with a standard ferrocene/ferrocenium (FOC) redox system as the standard (assuming the energy level of FOC is 4.8 e V below vacuum) for estimating the HOMO energy level of polymers. Compounds were named according to the ACD/IUPAC name generated using the ACD/I-Lab service via the Chemical Database Service at Daresbury. Samples were prepared by drop-casting solution on the Pt rod surface.

Crystal data for **IDSe**: $C_{74}H_{82}N_4O_2Se_2 \cdot C_6H_{14} \cdot CH_3OH$, M = 1335.56, monoclinic, $C2/c$ (no. 15), a = 29.8418(7), b = 18.0957(5), c = 13.7910(3) Å, β = 99.136(3)°, V = 7352.8(3) Å^3, Z = 4 [C_i symmetry], D_c = 1.206 g cm^{-3}, μ(Cu-Kα) = 1.629 mm^{-1}, T = 173 K,

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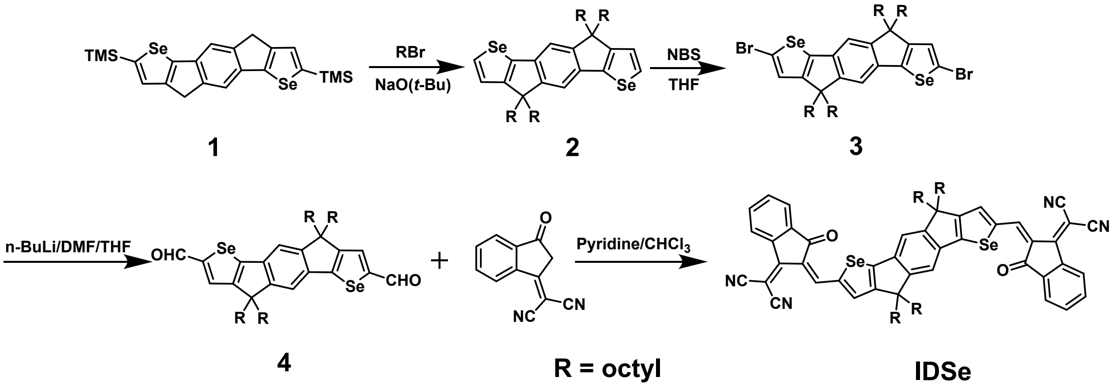
black blocky needles, Agilent Xcalibur PX Ultra A diffractometer; 7037 independent measured reflections (R_{int} = 0.0290), F^2 refinement,[1-3] R_1(obs) = 0.0553, wR_2(all) = 0.1646, 5309 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(67.7°) = 98.2%], 372 parameters. CCDC 2302807.

The structure of **IDSe** was found to sit across a centre of symmetry at the middle of the central C_6H_2 ring. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[4] This suggested a total of 287 electrons per unit cell, equivalent to 71.8 electrons per molecule. Before the use of SQUEEZE the solvent most resembled a mixture of hexane (C_6H_{14}, 50 electrons), and methanol (CH_4O, 18 electrons), and one of each corresponds to 68 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by 0.5 x [C_6H_{14} + CH_4O] = $C_{3.5}H_9O_{0.5}$ (and that for the unit cell low by $C_{28}H_{72}O_4$) compared to what is actually presumed to be present.



Scheme S1: The synthetic route to **IDSe**.

Synthesis:

4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']bis(selenophene) (2):

To a solution of 2,7-bis(trimethylsilyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']bis(selenophene) (**1**) (1.85 g, 3.67 mmol) in anhydrous DMSO (100 mL) was added sodium tert-butoxide (2.11 g, 22.03 mmol). The mixture was stirred at 70 °C for 30 min before 1-bromooctane (4.25 g, 22.03 mmol) was added dropwise. The mixture was heated to 80 °C overnight and poured into ice-water (150 mL) and extracted (3 × 100 mL hexane). The combined organics were dried by $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford a pale yellow solid (2.02 g, yield: 68 %). 7.89 (d, J = 5.3 Hz, 2H), 7.24 (s, 2H), 7.18 (d, J = 5.3 Hz, 2H), 1.98 – 1.83 (m, 8H), 1.31 – 1.08 (m, 40H), 0.89-0.78 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ (ppm): 156.8, 152.2, 144.4, 138.0, 130.6, 124.2, 113.4, 54.9, 39.1, 31.8, 30.0, 29.3, 29.2, 24.0, 22.6, 14.1. MALDI-TOF: 810.4 (M^+).

2,7-Dibromo-4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']bisselenophene (3):

To a solution of 4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']bis(selenophene) (1.40 g, 1.73 mmol) in THF (60 mL) was added *N*-bromosuccinimide (NBS) (0.68 g, 3.81 mmol) in one portion at 0 °C and stirred at this temperature for 0.5 h. The reaction was allowed to warm to RT and stirred for 2 h. A saturated Na_2SO_3 solution (50 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organics were dried by $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford a pale yellow solid (1.36 g, yield: 91%). ^1H NMR ($CDCl_3$, 400 MHz,) δ (ppm): 7.16 (s, 2H), 7.13 (s, 2H), 1.93 – 1.79 (m, 8H), 1.24 – 1.09 (m, 40H), 0.88-0.69

(m, 20H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ (ppm): 155.3, 151.2, 145.2, 138.0, 127.6, 115.0, 113.3, 55.8, 39.0, 31.8, 29.9, 29.3, 29.2, 23.9, 22.6, 14.1. MALDI-TOF: 967.2 (M^+).

4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']bisselenophene-2,7-dicarbaldehyde (4):

A solution of *n*-BuLi (1.1 mL of a 2.5 M solution in pentane, 2.75 mmol) was added dropwise into **3** (0.91 g, 0.94 mmol) in THF (250 mL) at -100 °C. After stirred at this temperature for 10 min, anhydrous DMF (0.3 mL) was added in one portion, and the mixture was allowed to warm to RT slowly and strirred for overnight. Water (100 mL) was added, and the mixture was extracted with DCM (3 × 200 mL). The combined organics were dried by $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: DCM/hexane = 1/1, v/v) to afford an orange solid (0.69 g, yield: 85%). ^{1}H NMR ($CDCl_3$, 400 MHz,) δ (ppm): 9.80 (s, 2H), 7.86 (s, 2H), 7.42 (s, 2H), 2.07-1.89 (m, 8H), 1.22-1.10 (m, 40H), 0.87-0.75 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ (ppm): 184.1, 157.8, 154.6, 154.0, 151.0, 139.2, 133.4, 115.3, 55.5, 39.0, 31.8, 29.9, 29.2, 29.2, 24.1, 22.6, 14.1. MALDI-TOF: 867.0 (M^+).

^{1}-4,4,9,9-tetraoctyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]bisselenophene--2-yl)methylidene]-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene}propanedinitrile (IDSe):

To a mixture of 1,1-dicyanomethylene-3-indanone (202 mg, 1.04 mmol) and **4** (180 mg, 0.21 mmol) in $CHCl_3$ (20 mL) was added pyridine (0.5 mL). After addition, the mixture was heated to 80 °C and stirred for overnight, and then poured into water (30 mL) and extracted with DCM (3 × 20 mL). The combined organics were dried by MgSO4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: DCM/hexane = 2/1), followed by recrystalization from DCM/MeOH to afford a dark purple solid (220 mg, yield: 87%). ^{1}H NMR ($CDCl_3$, 400 MHz,) δ (ppm): 9.09 (s, 2H), 8.71 (d, *J* = 7.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.88 (s, 2H), 7.79-7.73 (m, 4H), 7.54 (s, 2H), 2.10-1.95 (m, 8H), 1.25-1.18 (40H), 0.81-0.78 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ (ppm): 188.9, 166.9, 160.6, 159.6, 155.9, 143.9, 141.4, 141.2, 141.0, 139.9, 136.9, 135.1, 134.4, 125.3, 123.7, 121.3, 116.4, 114.9, 110.0, 68.7, 55.4, 39.2, 34.9, 31.8, 29.9, 29.3, 29.2, 26.3, 24.2, 23.0, 22.6, 14.1. MALDI-TOF: 1219.9 (M+).

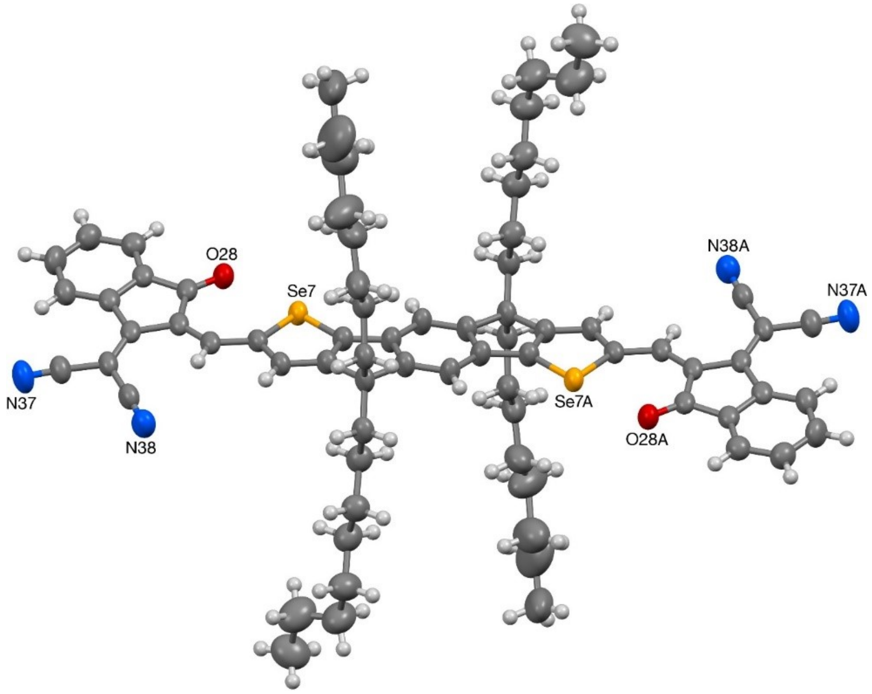


Figure S1 The crystal structure of the C_i-symmetric molecule **IDSe** (50% probability ellipsoids).

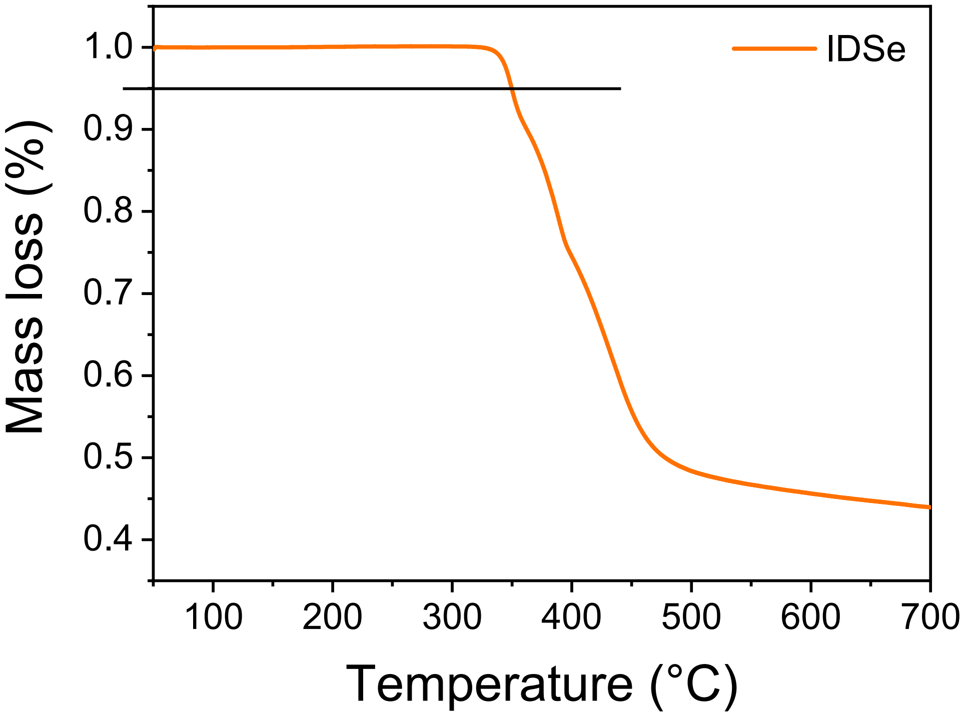


Figure S2. TGA thermogram of IDSe (heating rate of 20 °C /min) under Air.

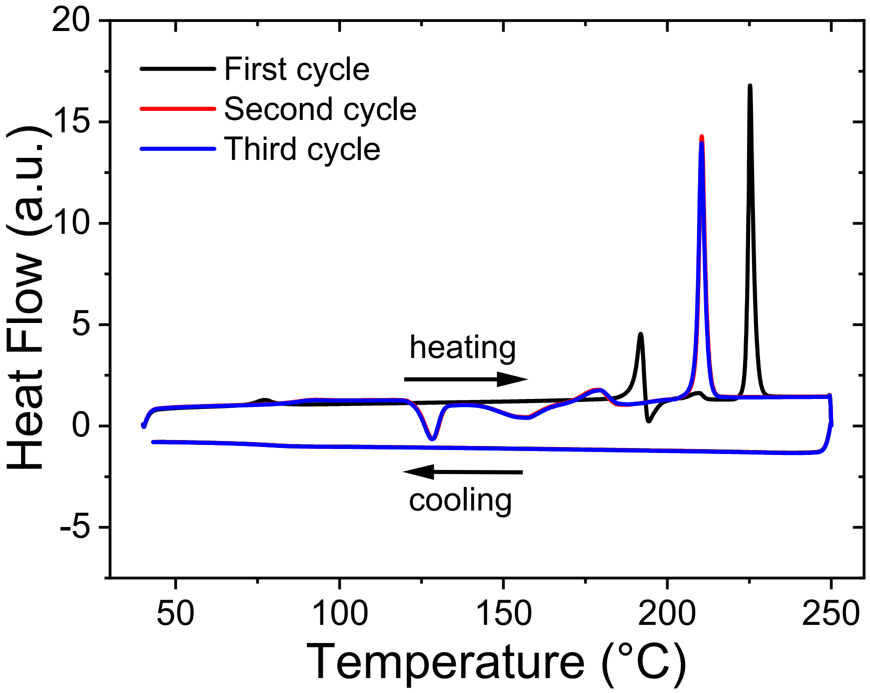


Figure S3. DSC heating and cooling traces (3 cycles) of IDS**e** at a scanning speed of 10 °C/min under N_2 (endo up).

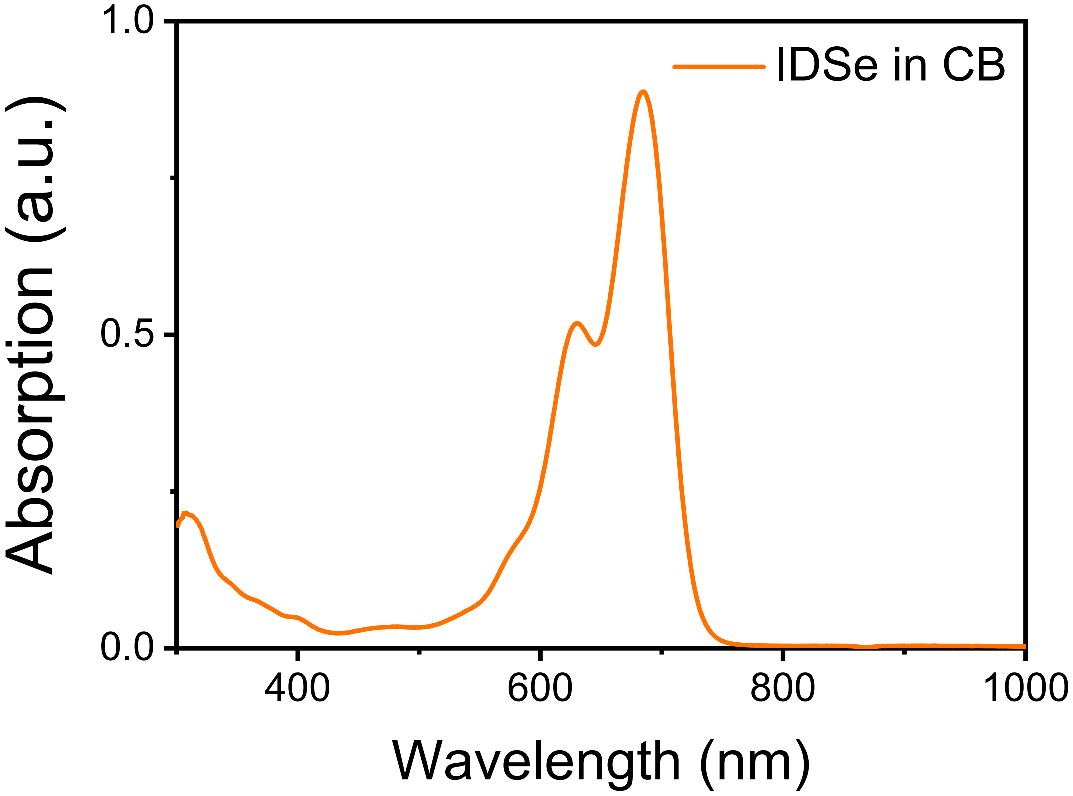


Figure S4. The UV-vis absorption spectrum of IDSe in chlorobenzene with a concentration of 5 x 10^{-6} M.

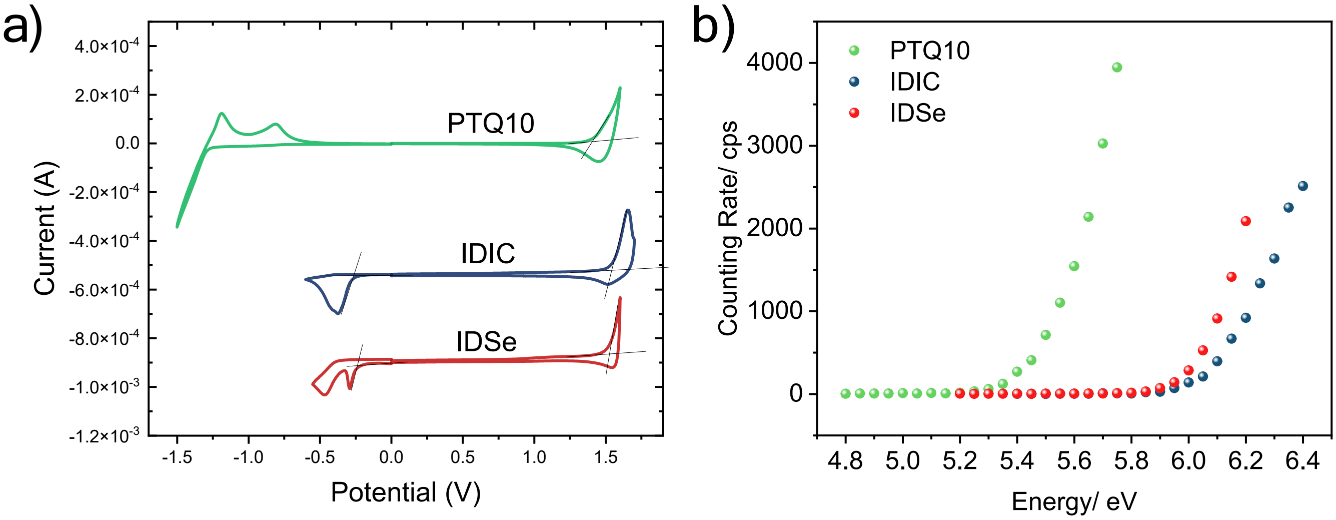


Figure S5. (a) Cyclic voltammetry (CV) on a Pt working electrode of PTQ10, IDIC and IDSe in solid state. (b) Photoelectron Spectroscopy in Air (PESA) measurement of PTQ10, IDIC and IDSe.

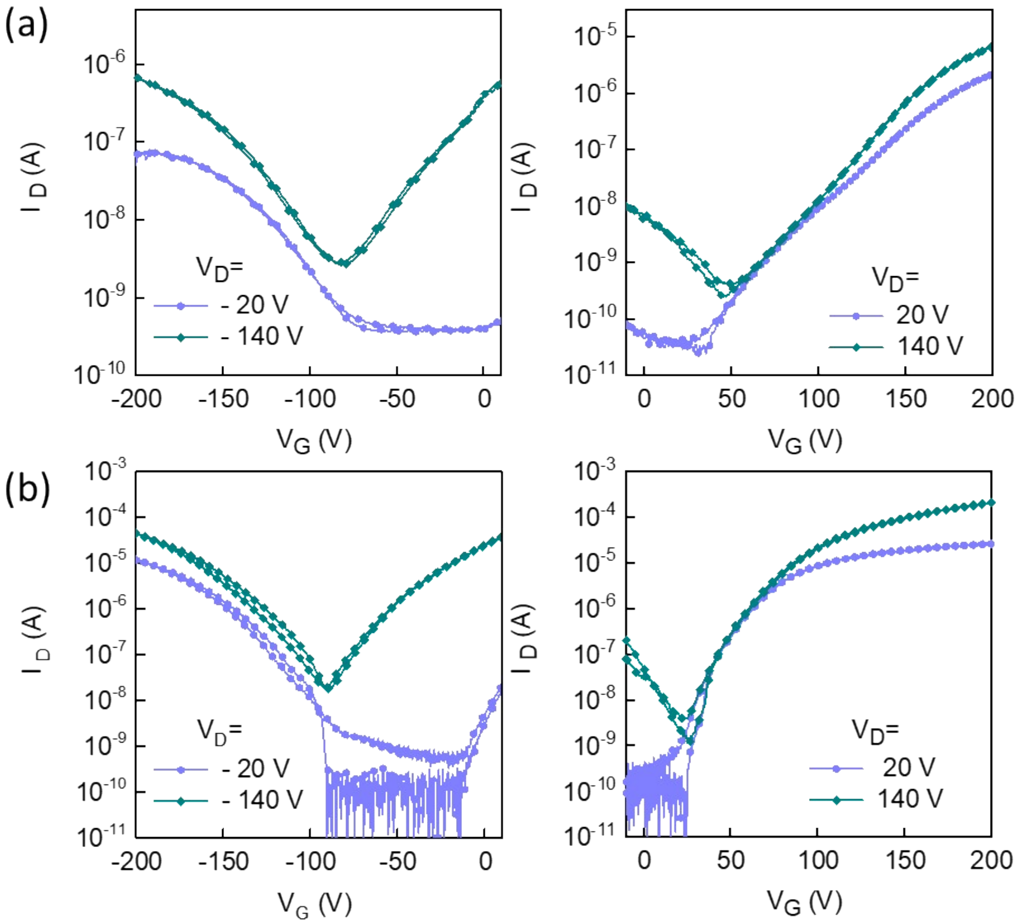


Figure S6. Representative transfer characteristics of BG-TC (a) IDIC and (b) IDSe OTFTs, with channel length 30 μm and width 1000 μm.

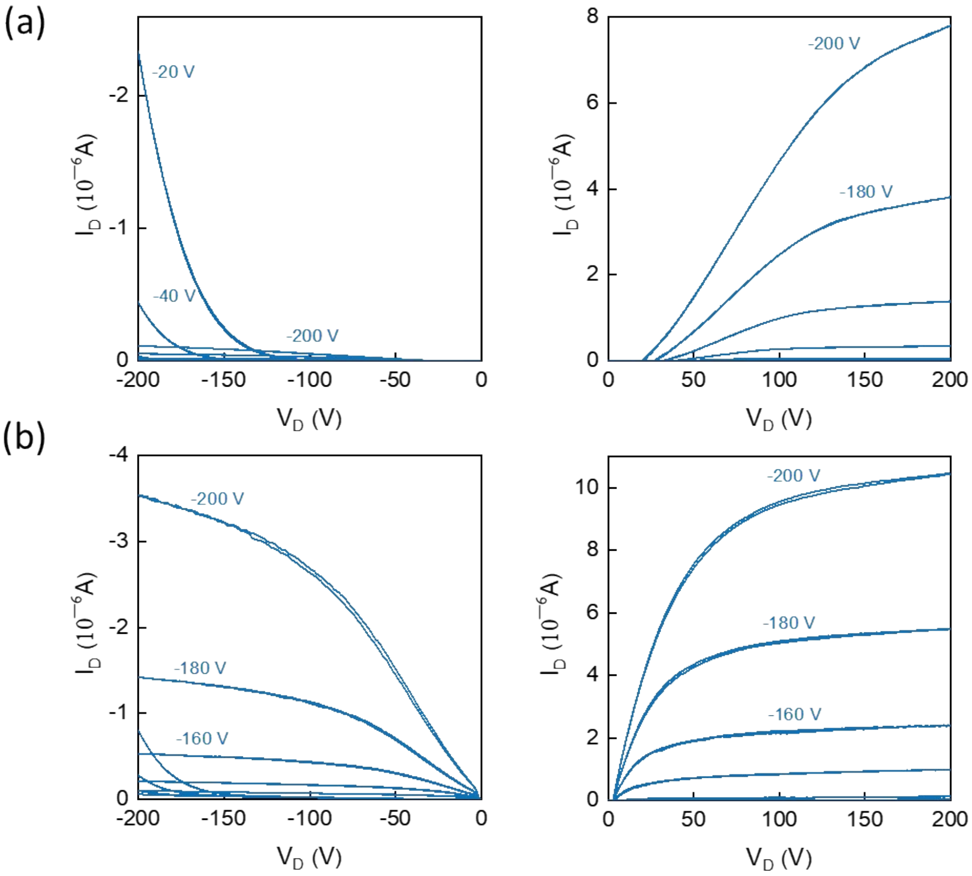


Figure S7. Representative output characteristics of BG-TC (a) IDIC and (b) IDSe OTFTs with channel length 30 µm and width 1000 µm.

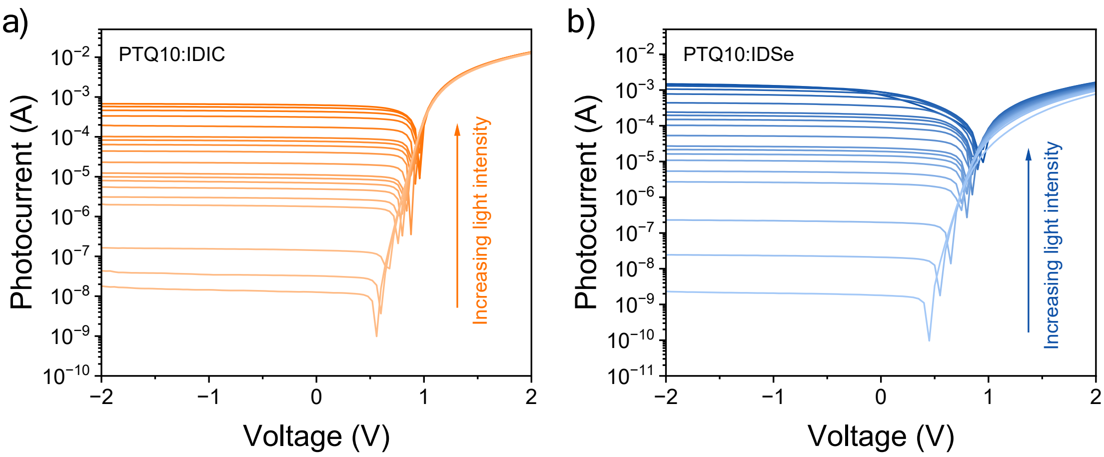


Figure S8. Current density-voltage characteristics of (a) PTQ10:IDIC and (b) PTQ10:IDSe under while LED at different light intensities.

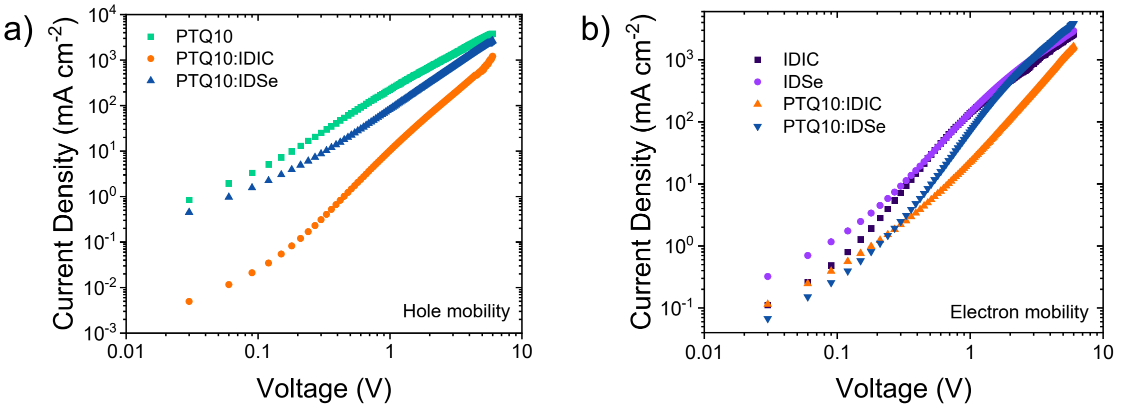


Figure S9. SCLC measurements for both pristine and blend materials.

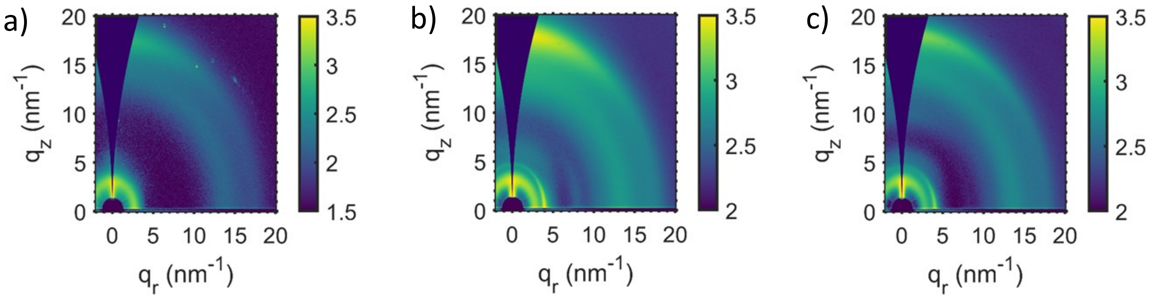


Figure S10. 2D GIWAXS plots for PTQ10 (a), PTQ10:IDIC (b) and PTQ10:IDSe (c).

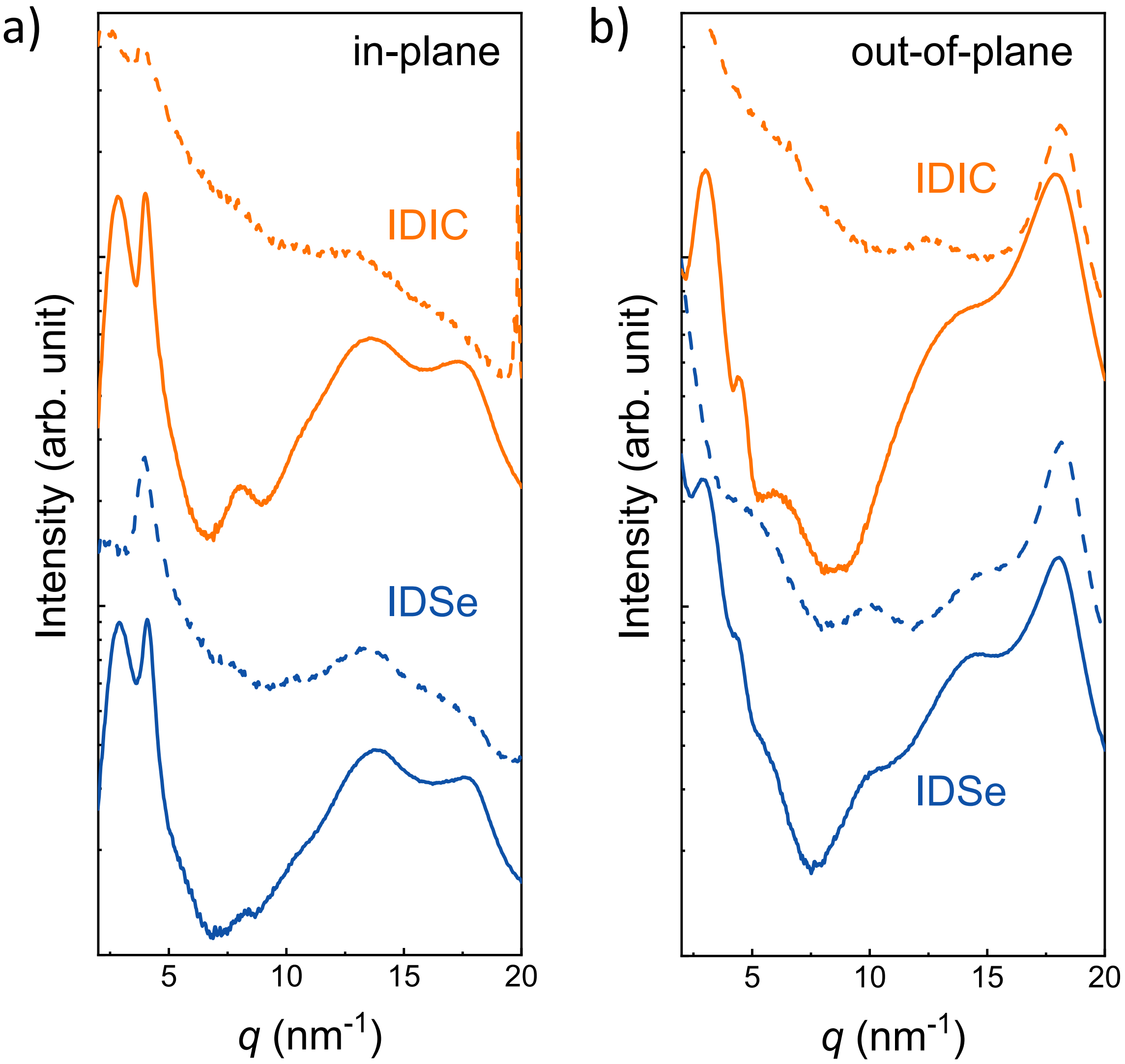


Figure S11. In-plane (a) and out-of-plane (b) scattering profiles integrated from the 2D-GIWAXS patterns for IDIC and IDSe fims. Neat NFAs are shown in dashed line and blends are shown in solid line.

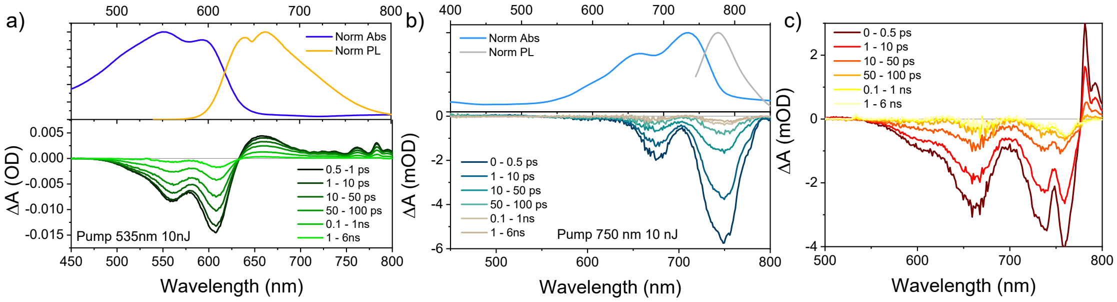


Figure S12. TA, normalised absorbance and photolyminescence spectra of pristine thin films of a) PTQ10 under 535 nm excitation 2 µJ cm^{-2} ; b) IDSe under 700 nm excitation 2 µJ cm^{-2} ; c) IDIC under 700 nm excitation 2 µJ cm^{-2}.

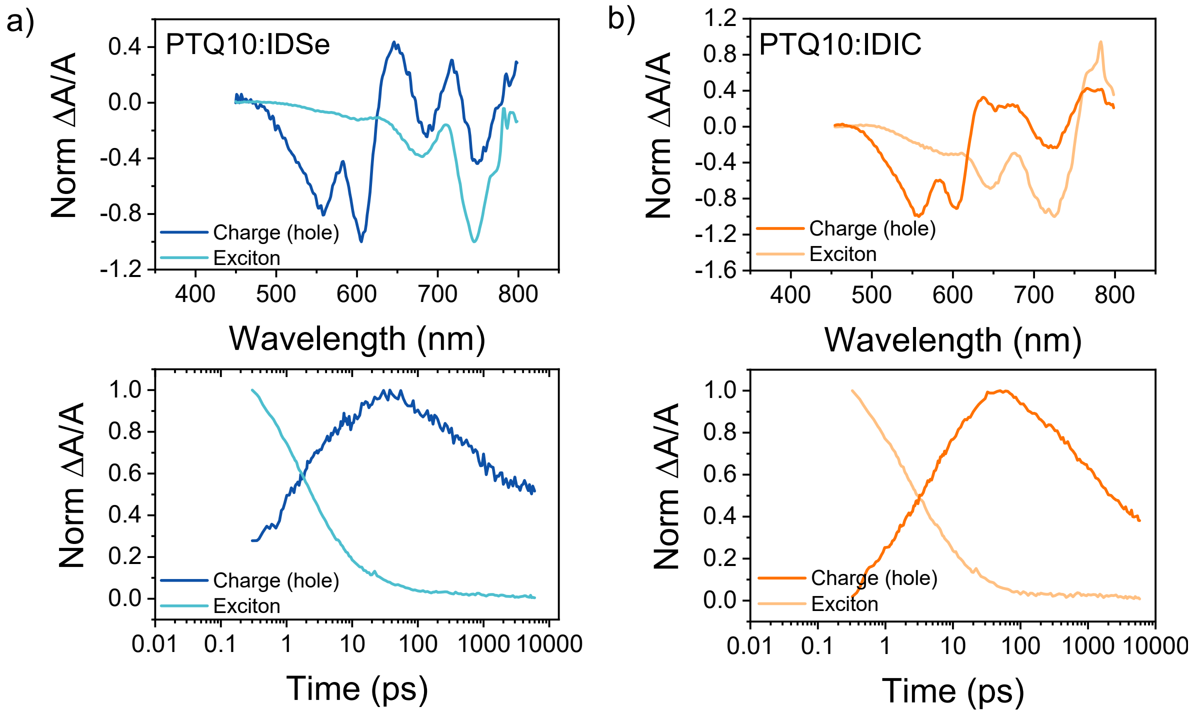


Figure S13. Global analysis results of the visible blend TA data. 2-spectral components with the associated kinetics for (a) PTQ10:IDSe and (b) PTQ10:IDIC blend. GA was performed with early time neat acceptor spectra as references.

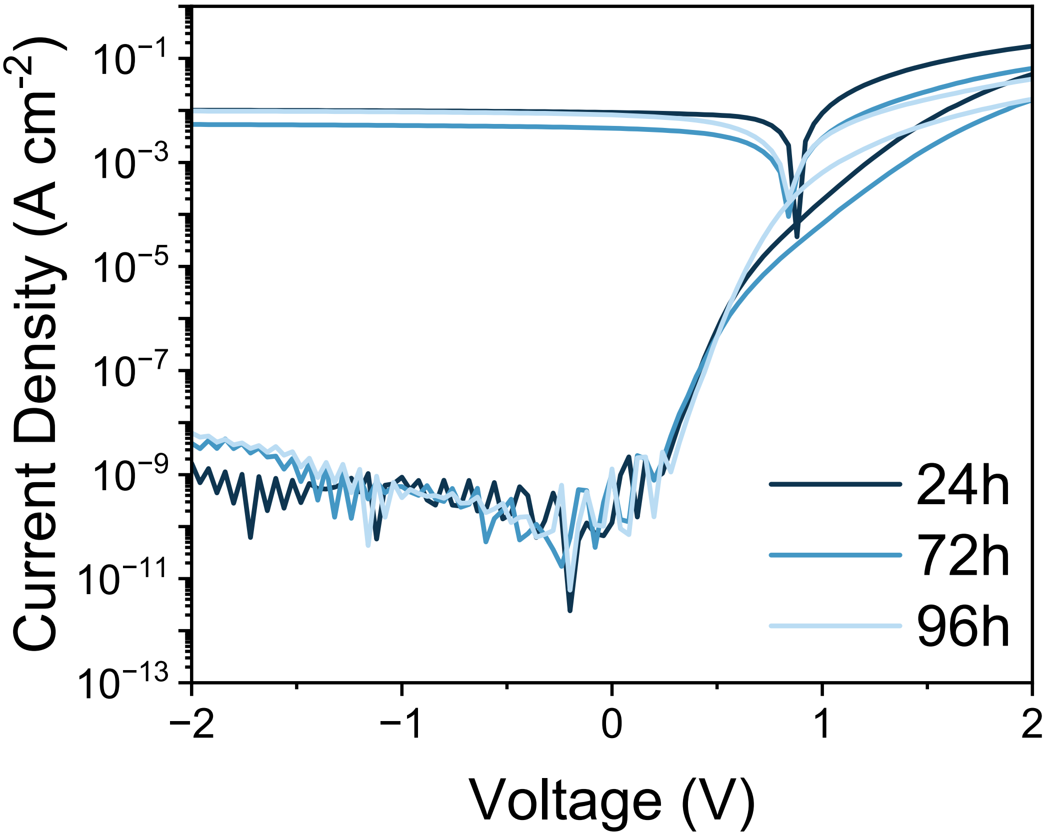


Figure S14. Device stability in terms of light current and dark current over 96 hours for PTQ10:IDSe devices.

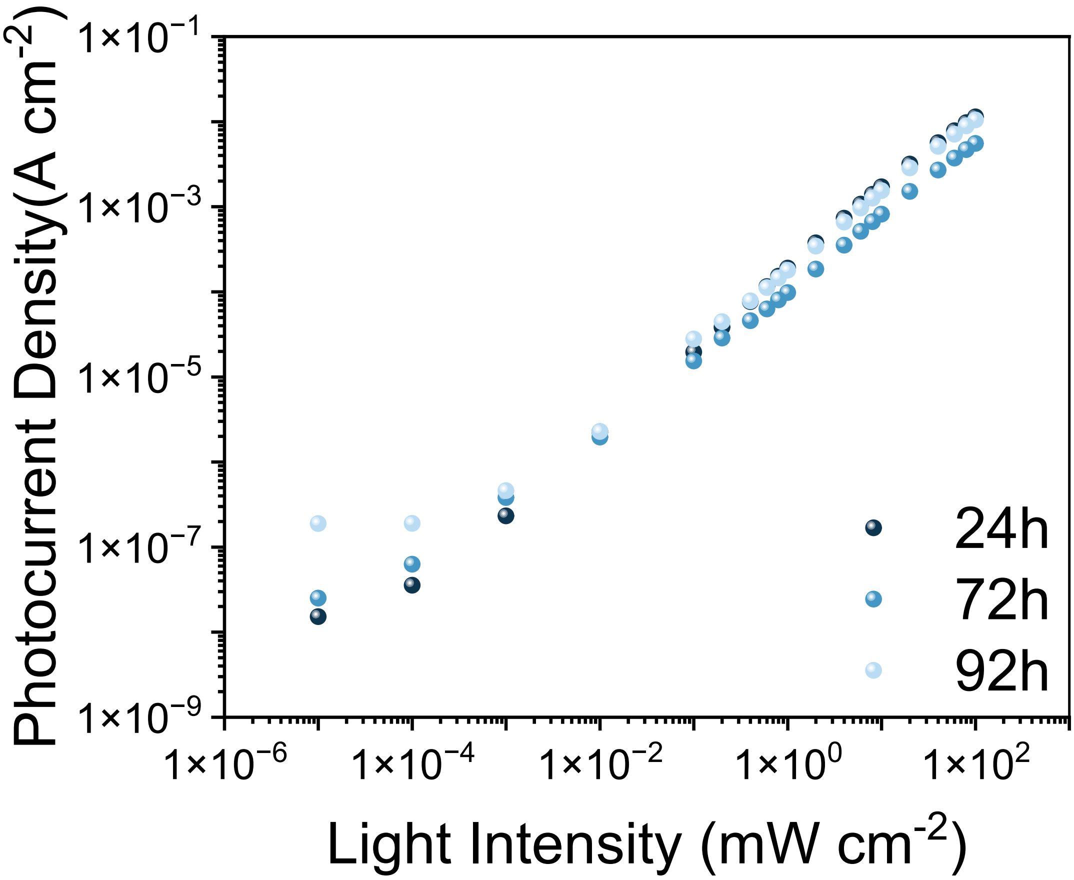


Figure S15. LDR measured after 24h, 72h and 96h bias stress for PTQ10:IDSe devices.

References

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