Electron Transporting Perylene Diimide-Based Random Terpolymers with Variable Co-Monomer Feed Ratio: A Route to All-Polymer based Photodiodes

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Materials and Methods

1. Materials

All solvents and reagents were purchased from Aldrich or Alfa Aesar and were used

without further purification unless otherwise stated. The polymer donor material

poly([2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene]{3-fluoro-2[(2-

ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PCE10) was purchased by Solarmer

Energy Inc. and was used as received without further purification. N,N–di(2-ethylhexyl)-

1,7/1,6-dibromo-3,4,9,10-perylene   diimide[1],   2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-

dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole (di-boronic ester-HD-carbazole)[2], 4,7-

di-(5-bromo-3,4-ethylenedioxythiophene-2-yl)-2,1,3-benzothiadiazole (diBr-EDOT-

BTZ)[3], 4,7-di-(5-bromothiophene-2-yl-2,1,3-benzothiadiazole (diBr-thien-BTZ)[4] and the

catalyst palladium (0) tetrakis triphenyl phosphine [Pd(PPh$_3$)$_4$][5] were prepared according

to literature procedures.

2. Synthetic Procedures

2.1 General synthetic procedure of polymers with di-thienyl substituted-BTZ (P1-P5)

2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole (50

mg, 0.07603 mmol) and 0.07603 mmol in variable ratio of the dibromo monomers N,N–

di(2-ethylhexyl)-1,7/1,6-dibromo-3,4,9,10-perylene   diimide   and   4,7-di-(5-

bromothiophene-2-yl-2,1,3-benzothiadiazole (di-Br-thien-BTZ) were added in a 25 mL

degassed flask with a magnetic stirrer. The flask was evacuated and filled with argon

several times and then THF (4 mL), degassed aqueous Na$_2$CO$_3$ 2M solution (547.97 mg,

5.17mmol) and the catalyst Pd(PPh$_3$)$_4$ (2.64 mg, 0.00228mmol) were added. The reaction

was degassed again and the mixture was heated to reflux for 48 h. Subsequently,

phenylboronic acid (4.64 mg, 0.038015 mmol) was added and the mixture was refluxed

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for 2 h more, after which bromobenzene (5.6 µL, 0.05322 mmol) was added and reflux continued for another 2 h. Then, the mixture was cooled to room temperature, precipitated into a methanol-water 3:1 mixture and the solid was filtered and washed with water, methanol and dried under vacuum at 40˚ C overnight. The resulting solid was stirred in acetone upon reflux for 4 h, was then filtered off and the solid was taken up in chloroform. The filtrate was concentrated by rotary evaporation, and the polymer thus obtained was dried in vacuum at 40 ˚C for 12 h. In those cases that the polymer did not dissolve completely in chloroform, it was further treated and dissolved in *ortho*-Dichlorobenzene (*o*-DCB).

Yield (80%, 0,074g). ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) = 8.90-8.75 (m, 2H PDI), 8.36-7.33 (br, aromatic protons of PDI, carbazole and TBTZ), 4.8-4.40 (br, 1H carbazole), 4.3-4.0 (br, 4H PDI),), 2.5-2.25 (m, 2H carbazole) 2.1-1.90 (br, 2H carbazole & 2H PDI), 1.51-0.83 (br, 58H).

2.2. General synthetic procedure of polymers with di-3,4-ethylenedioxythienyl substituted-BTZ (P6-P9)

2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole (50 mg, 0.07603 mmol) and 0.07603 mmol in variable ratio of the dibromo monomers N,N–di(2-ethylhexyl)-1,7/1,6-dibromo-3,4,9,10-perylene diimide and 4,7-di-(5-bromo-3,4-ethylenedioxythiophene-2-yl)-2,1,3-benzothiadiazole (diBr-EDOT-BTZ) were added in a 25 mL degassed flask with a magnetic stirrer. The flask was evacuated and filled with argon several times and then THF (4 mL), degassed aqueous Na_2CO_3 2M solution (547.97 mg, 5.17mmol) and the catalyst $Pd(PPh_3)_4$ (2.64 mg, 0.00228 mmol) were added. The reaction was degassed again and the mixture was heated to reflux for 48 h. Subsequently, phenylboronic acid (48 mg) was added and the mixture was heated to reflux for another 2 h, after which bromobenzene (0.44 mL) was added and reflux continued for 2 h. Then, the mixture was cooled to room temperature, precipitated into a methanol-water 3:1 mixture and the solid was filtered and washed with water, methanol and then dried under vacuum at 40 ˚C for 12 h. The resulting solid was stirred in acetone upon reflux for 4 h, the mixture was filtered and the solid was dissolved in chloroform.

The filtrate was concentrated by rotary evaporation, and the polymer thus obtained was dried in vacuum at 40 °C for 12 h.

Yield (70%, 0,097g). ^{1}H NMR (600 MHz, CDCl3): δ (ppm) =8.90-8.75 (m, 2H PDI), 8.60-8.45 (m, 2H EDOTBTZ), 8.30-7.30 (br, aromatic protons carbazole and PDI), 4.80-4.60 (m, 1H carbazole), 4.6-4.3 (m, 8H EDOTBTZ), 4.3-4.0 (br, 4H PDI), 2.5-2.25 (m, 2H carbazole) 2.1-1.90 (br, 2H carbazole & 2H PDI), 1.51-0.83 (br, 58H).

3. Characterization Methods

^{1}H, Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Advance (Bruker BioSpin GmbH, Magnet Division, Karlsruhe, Germany) DPX 600 spectrometer in deuterated chloroform ($CDCl_3$) containing tetramethylsilane (TMS) as internal standard.

Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer (Agilent Technologies, Santa Clara, CA, USA) equipped with two PLgel 5 µm mixed columns and a UV detector, using chloroform ($CHCl_3$) as eluent with a flow rate of 1 mL/min at 25°C calibrated versus polystyrene standards.

Single-component terpolymer solutions of all synthesized derivatives were prepared in *o*-DCB while their corresponding films were developed by drop-casting of their solutions on flat quartz substrates. Especially for the case of the P4 derivative, single component films and blend films of P4 mixed with the PCE10 donor polymer were prepared by spin-coating (E441, Ossila Ltd). A range of PCE10:P4 solutions with increasing wt% content of P4 were prepared in o-DCB with a 25 mg/ml mass concentration. The solutions were left at 100 °C for 3 h under stirring at 350 rpm and then were spun at 1000 rpm for 1 min onto pre-cleaned fused silica quartz substrates. Thermal annealing of the obtained films was performed at 100 ˚C for 20 min. For all spin-coated layers, film development and thermal annealing were performed in a N_2-filled glovebox (PureLabHE, Inert) and the thickness of the obtained films was monitored by a Dektak profilometer (Bruker, D150).

UV-Vis spectra of single component terpolymer solutions and their films on drop-casted flat quartz substrates were recorded using a Hitachi U-1800 spectrophotometer (Hitachi High-Technologies Europe GmbH, Mannheim, Germany). For these systems continuous wave photoluminescence (PL) was measured on a Perkin Elmer LS50B spectrofluorometer (Waltham, MA, USA). UV-Vis spectra of the single-component films

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of the P4 derivative of the PCE10:P4 films were recorded with UV-2700 Shimadzu spectrophotometer.

The electrochemical behavior of the terpolymers was investigated using cyclic voltammetry (CV). CV experiments were carried out in a three-electrode cell. A glassy carbon working electrode, a Pt wire secondary electrode and a saturated Ag/AgCl reference electrode were used in the cell. Thin films of the fabricated materials were drop casted on FTO coated glass slides, (Rsheet~8 Ω/square), preheated at 80°C for 20 min, from precursor solutions in o-DCB. The resulting films were further annealed at 80 °C for 15 min. An Autolab PGSTAT 302 N electrochemical analyzer connected to a personal computer running the NOVA 1.8 software was used for data collection and analysis. All experiments were carried out at a scan rate of 0.1 V/s. Tetrabutylammonium hexafluorophoshate (TBAPF$_6$) 0.1 M in anhydrous acetonitrile (CH$_3$CN) was used as supporting electrolyte. Before carrying out the measurements the cell was purged with pure argon for 20 min to remove diluted gasses. The reference electrode potential was calibrated against Ferrocene/Ferrocenium (Fc/Fc+) after each voltammetry run. The

HOMO and LUMO energy levels were calculated from the first oxidation and reduction

onset potentials, respectively, using the empirical equations[6]:

$$E_{HOMO} = e\ (E_{on}^{OXID} - E_{1/2}^{Ferrocene})\ \text{-}5.2\ [eV] \tag{1}$$

E_{on}^{OXID} = the onset determined for the oxidation peak of each molecule in cyclic

voltammetry (V) versus Ag/AgCl.

$$E_{LUMO} = e\ (E_{on}^{RED} - E_{1/2}^{Ferrocene})\ \text{-}5.2\ [eV] \tag{2}$$

E_{on}^{RED} = the onset determined for the reduction peak of each molecule in cyclic

voltammetry (V) versus Ag/AgCl.

$$E(_{1/2}^{Ferrocene}) = (E_{red} + E_{OX})/2\ \text{ vs. Ag/AgCl} \tag{3}$$

The HOMO energy levels were calculated from the E_g^{opt} using the equation:

$$E_g^{opt} = \text{HOMO-LUMO}\ [eV] \tag{4}$$

The E_g^{opt} (optical bandgap) was determined from the equation:

$$E_g^{opt} = \frac{1240}{\lambda_{onset}}\ [eV] \tag{5}$$

The value of -5.2 eV in equations (1) and (2) emerged from calibration of the Ag/AgCl

electrode versus a normal hydrogen electrode (NHE) and considering that the NHE redox

potential corresponds to -4.6 eV on the zero vacuum level scale[7,8].

Thermogravimetric analysis (TGA) was carried out on ~8 mg samples contained in alumina crucibles in a Labsys TM TG apparatus of Setaram (Caluire, France) under nitrogen and at a heating rate of 10 ˚C/min.

A Dimension Icon Bruker atomic force microscope (AFM) operated in a tapping mode was used to map topography of the spin-coated PCE10:P4 films developed for this study. Image processing and statistical analysis were conducted using the Gwyddion software. Scan rate for all the topography imaging was 1 Hz.

Photodiode devices with PCE10:P4 photoactive layers with increased wt% P4 content were fabricated by using commercially available ITO substrates (XY15S, surface polished glass/indium tin oxide substrates from Xin Yan Technology Ltd.). The ITO substrates were ultrasonically cleaned using acetone and isopropanol for 15 min. After preliminary cleaning, the substrates were washed with Hellmanex III to remove contaminants and residues from the ITO surface. The substrates were again cleaned with DI water followed by acetone and isopropanol for 15 min and soon after placed in a UV-ozone cleaner (E511, Ossila Ltd) for 10 min. For conventional device geometry samples with the glass/ITO/PEDOT:PSS/PCE10:P4/Ca/Al configuration, a PEDOT:PSS hole-

collecting layer (Clevios HTL Solar) was deposited on the glass/ITO electrodes by spin-coating and it was annealed at 140 ˚C for 50 min. Then the substrates were transferred in a N_2-filled glovebox (PureLabHE, Inert) and the PCE10:P4 photoactive layers were spun on the PEDOT:PSS layer. A thermal evaporator (Covap III, Angstrom Engineering Inc.) coupled to the N_2 glovebox was used for enabling the deposition of Ca electrodes (100 Å) capped by Al (1000 Å). The thermal evaporation of the metals was performed in vacuum (1×10^{-8} mbar), while a shadow mask was used that facilitated the formation of an effective device area of 0.0525 cm^2. For inverted device geometry samples with the glass/ITO/zinc oxide (ZnO)/PCE10:P4/Au configuration, a ZnO electron-collecting layer[9] was deposited on the glass/ITO substrate by spin-coating and it was annealed at 140 ˚C for 30 min. Then the substrates were transferred in a N_2-filled glovebox and the PCE10:P4 photoactive layers were spun on ZnO. Both conventional and inverted device geometry devices were encapsulated with degassed epoxy and glass slide of 1 mm thickness in the glovebox.

The external quantum efficiency (EQE) response of the fabricated PCE10:P4 photodiodes was determined with monochromatic illumination provided by a 250 W power Quartz

Tungsten Halogen (QTH) lamp enclosed in an F/1-aperture lamp housing and coupled to

a Cornerstone 1/8 m monochromator (CS-130-USB-3-MC) capable of covering the 300-

2200 nm spectral range. The optical power output of the lamp was determined based on a

calibrating photodiode (818-UV/DB UV Detector, Newport DB15 Calibration Module)

with known responsivity, and the EQE spectra of the devices were determined based on

the device light current as acquired by a source meter unit (SMU, Keithley 2401).

A diode pumped solid-state continuous-wave (DPSS CW) laser (MGL-III-532, CNI

Optoelectronics Tech.CO. Ltd) was used for photoexciting the encapsulated PCE10:PC-

TBTZ25-PDI75 photodiodes at 532 nm. A set of light current J-V curves was recorded

for each device in a range of laser excitation intensities. The corresponding dark current

density of the photodiodes was monitored with the acquisition of dark J-V curves

recorded in the voltage range between -2 – 3 V. The dark current, the laser-induced short-

circuit photocurrent and the open-circuit voltage of the devices were monitored with the

SMU Keithley 2401. The laser output of the cw-laser source was progressively attenuated

with the use of combined neutral density filters of known transmittance values at the

photoexcitation wavelength. All measurements of the encapsulated photodiodes were

performed in ambient conditions, and excellent reproducibility of the device

photoresponse was found.

Unipolar devices with PCE10:P4 layers of increased wt% P4 content were fabricated for

studying the composition dependent charge transport properties of the PCE10:P4

composite system. The device configuration of the hole-only and electron-only devices

was glass/ITO/PEDOT:PSS/PCE10:P4/Au and glass/ITO/ZnO/PCE10:P4/Ca/Al,

respectively. For the latter, a built-in voltage V_{bi}= 1.5 V was considered due to the

different work function (Φ) values of the ZnO (Φ_{ZnO}= 4.4 eV) and Ca (Φ_{Ca}= 2.9 eV)

device electrodes. For each blend composition, the thickness of the obtained PCE10:P4

films was accurately determined by a Tencor P16 Stylus profiler. The dark current

density of all photodiodes was monitored based on the dark J-V curves recorded in the

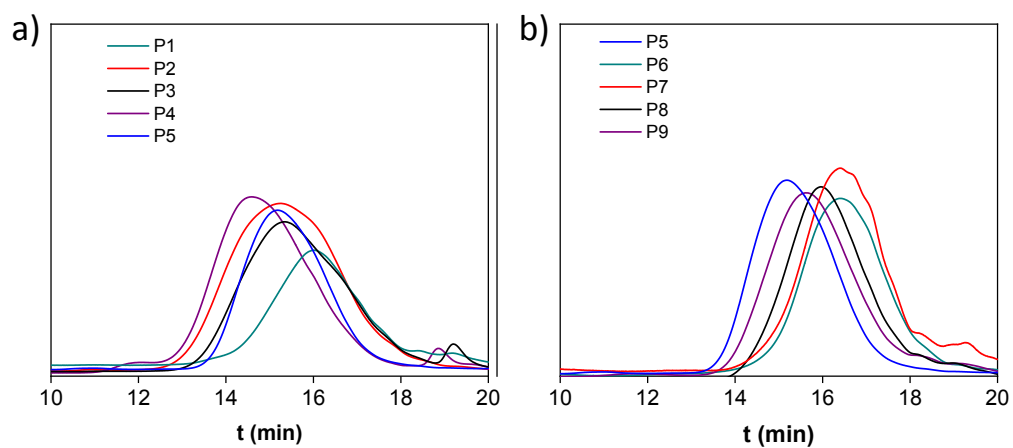voltage range between -1 – 19 V with the SMU 2401.

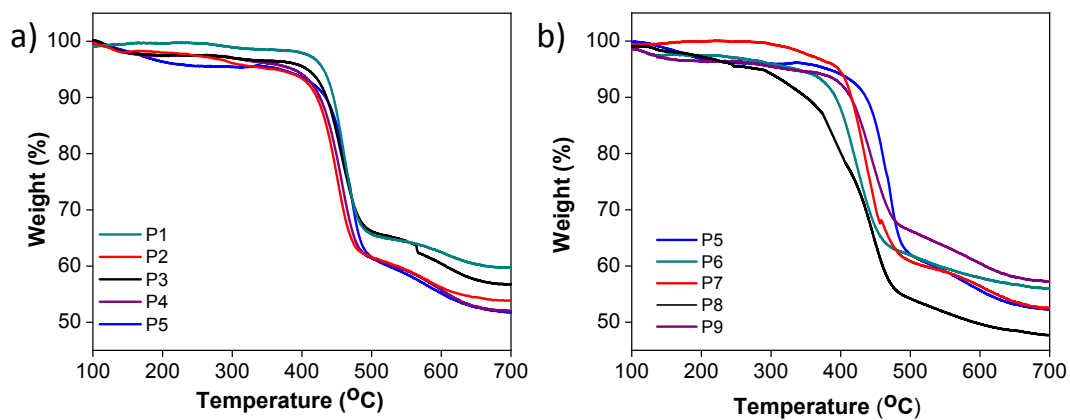**Figure S1.** GPC traces of random terpolymers a) P1-P5 and b) P5-P9.

Figure S2. Thermogravimetric analysis of a) P1-P5 and b) P5-P9 terpolymers with a heating rate of 10 °C/min under an inert nitrogen atmosphere.
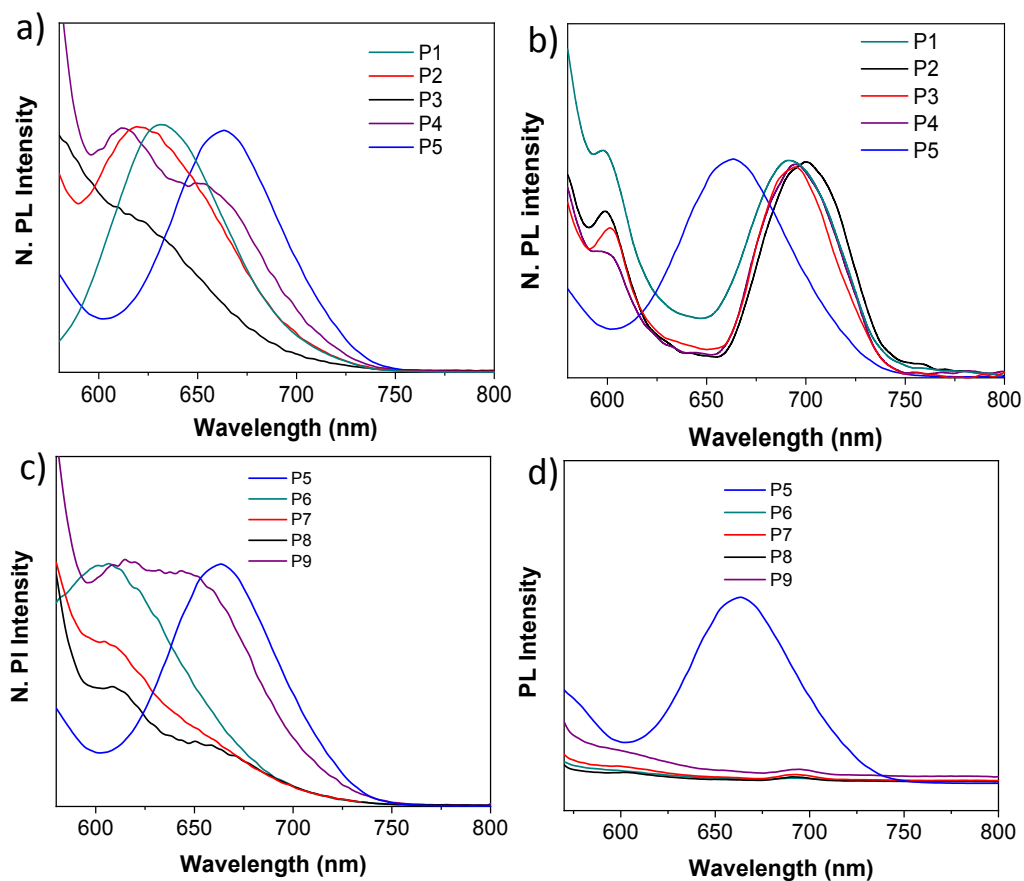
Figure S3. PL spectra of a) P1-P5 terpolymer solutions in *o*-DCB b) P1-P5 drop-casted films, c) P5-P9 terpolymer solutions in *o*-DCB, and d) P5-P9 drop-casted. All films were developed on quartz substrates. PL spectra were registered after photoexcitation at 550 nm. In all cases except d), the PL spectra are normalized to the maximum of the PL intensity.
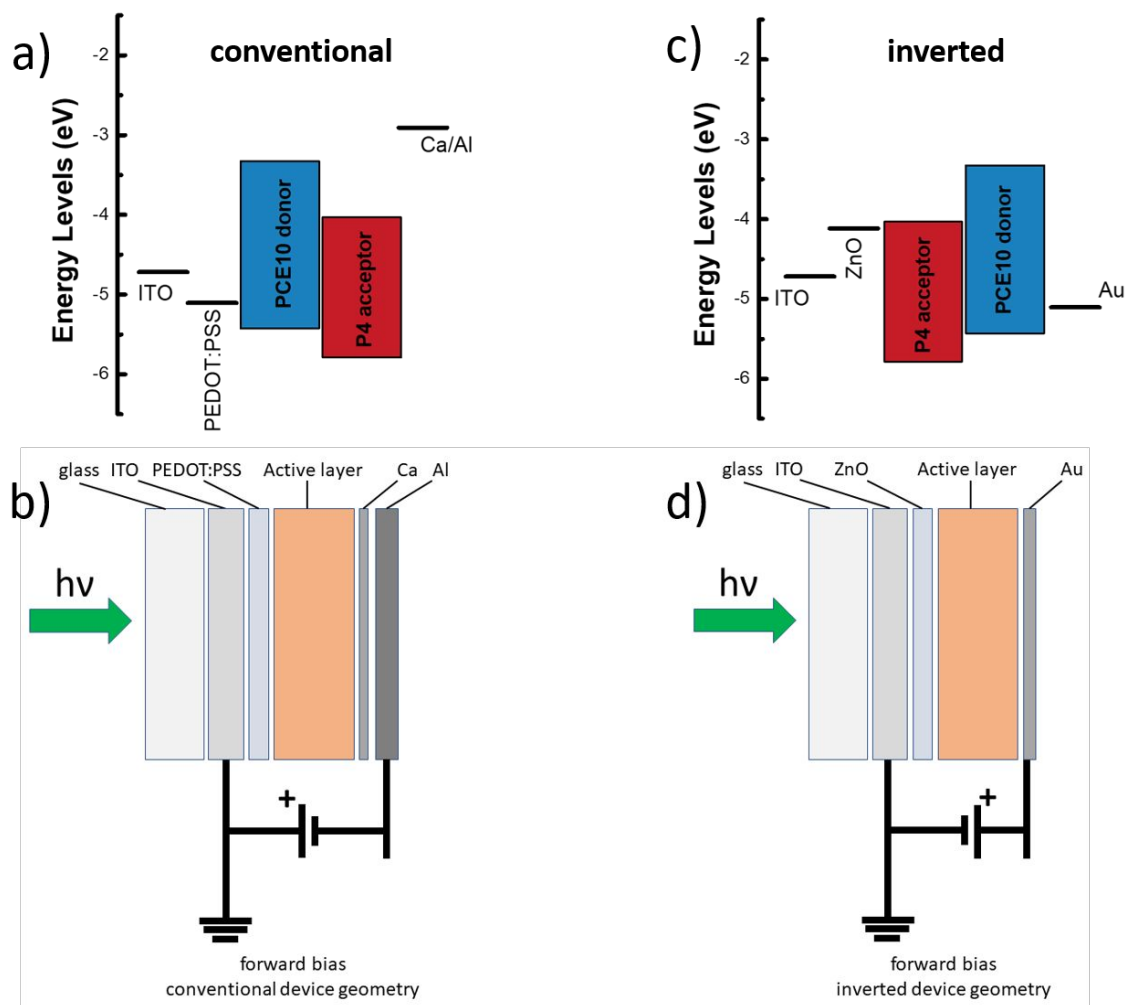
Figure S4. Conventional device geometry with PCE10:P4 active layer: a) energetics of frontier orbitals in respect to the work function of the PEDOT:PSS and Ca/Al electrodes, b) directionality of incoming light and forward bias electrode polarization conditions. Inverted device geometry with PCE10:P4 active layer: c) energetics of frontier orbitals in respect to the work function of the ZnO and Au electrodes, d) directionality of incoming light and forward bias electrode polarization conditions.
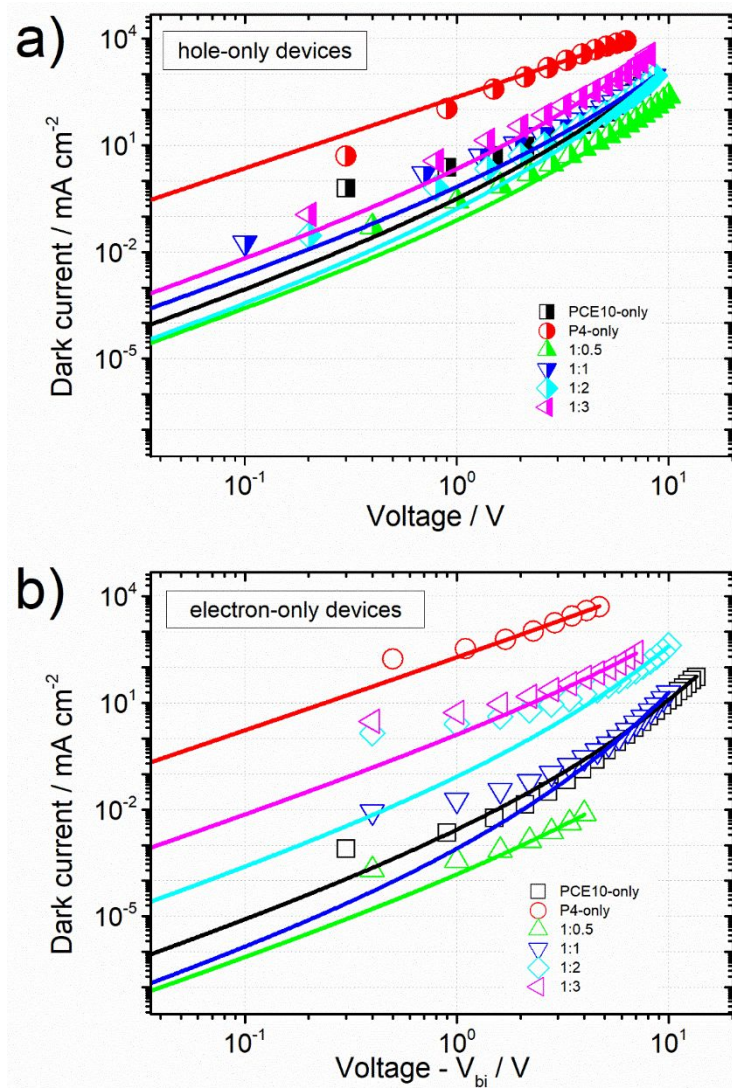
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Figure S5. Dark J-V curves of a) hole-only ITO/PEDOT:PSS/active layer/Au devices and b) electron-only ITO/ZnO/active layer/Ca/Al devices. The solid lines are fits on the data and V_{bi}= 1.5 V (see main text).

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