ELECTRONIC SUPPLEMENTARY INFORMATION

1. Materials and methods

NMR chemical shifts (δ, in ppm) for all precursors and monomers were determined relative to the residual CHCl₃ (7.26 ppm) signal or the ¹³C resonance shift of CDCl₃ (77.16 ppm) at room temperature. Matrix-assisted laser desorption/ionization - time-of-flight (MALDI–ToF) mass spectra were recorded on a Bruker Daltonics ultrafleXtreme MALDI/TOF-TOF system. 10 μL of the matrix solution (20 mg mL⁻¹ trans-2-[3-(4-tert-butylphenyl)]-2-methyl-2-propenylidene]malononitrile (DTCB) in chloroform) was mixed with an analyte solution of approximately 1 mg mL⁻¹. 1 μL of this solution was spotted onto an MTP Anchorchip 600/384 MALDI plate. Polymer molar mass distributions were estimated by size exclusion chromatography at 160 °C on an Agilent 1260 Infinity II High-Temperature GPC system using a PL-GEL 10 μm MIXED-B column with 1,2,4-trichlorobenzene as the eluent and using polystyrene internal standards. Background corrected UV-Vis-NIR absorption spectroscopy measurements were performed on a VARIAN Cary 5000 UV-Vis-NIR spectrophotometer at a scan rate of 600 nm min⁻¹. The films for the UV-Vis-NIR absorption measurements were prepared by drop-casting a solution of the respective polymer in CHCl₃ on a quartz substrate. The solid-state UV-Vis-NIR absorption spectra were used to estimate the optical gaps (from the wavelength at the intersection of the tangent line drawn at the low energy side of the absorption spectrum with the baseline: $E_0$ (eV) = 1240/(wavelength in nm). Electrochemical measurements (cyclic voltammetry, CV) were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell with a platinum working electrode, a platinum counter electrode, and a Ag/AgNO₃ reference electrode (silver wire dipped in a solution of 0.01 M AgNO₃ and 0.1 M NBu₄PF₆ in anhydrous acetonitrile). The reference electrode was calibrated against ferrocene/ferrocenium as external standard. Sample preparation was done by dip-coating the platinum working electrode in the respective polymer solutions. The CV measurements were done on the resulting films with 0.1 M NBu₄PF₆ in anhydrous acetonitrile as electrolyte solution. The experiments were carried out under a curtain of argon to prevent air from entering the system. Cyclic voltammograms were recorded at a scan rate of 100 mV s⁻¹. For the conversion of V to eV, the onset potentials of the first oxidation/reduction peaks were used and referenced to ferrocene/ferrocenium, which has an ionization potential of ~4.98 eV vs. vacuum. This correction factor is based on a value of 0.31 eV for Fc/Fc⁺ vs. SCE¹ and a value of 4.68 eV for SCE vs. vacuum²: $E_{\text{HOMO/LUMO}}$ (eV) = $-4.98 - E_{\text{onset ox/red Ag/AgNO₃}}$ (V) + $E_{\text{onset Fc/Fc⁺ Ag/AgNO₃}}$ (V). The accuracy of measuring redox potentials by CV is about 0.01–0.02 V. Reproducibility issues can occur due to the dependence of the potentials on concentration and temperature. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q5000. Measurements were performed at a heating rate of 20 K min⁻¹ using nitrogen (25 mL min⁻¹) as the purge gas. Sample masses of approximately 1 mg were used. Rapid heat-cool calorimetry (RHC) was performed using a prototype instrument from TA Instruments. Experiments were performed at a heating and cooling rate of 500 K min⁻¹, with helium (6 mL min⁻¹) as the purge gas. Dedicated aluminum RHC crucibles were filled with around 200–250 μg of the polymer sample. A first heating was used to remove the thermal history.

2. Materials synthesis and characterization

All reagents and chemicals were obtained from commercial sources and used without further purification. The quinoxaline monomer (5,8-dibromo-2,3-bis[5-(2-ethylhexyl)thiophen-2-yl]quinoxaline) was synthesized according to a literature procedure.¹ Solvents were dried by a solvent purification system (MBraun, MB-SPS-800) equipped with alumina columns. All moisture-sensitive reactions were carried out under inert atmosphere and in flame-dried glassware. Reactions were magnetically stirred and monitored by TLC (pre-coated silica gel, 60 Å average pore diameter, 254 μm,
aluminum foil supported TLC plates). Compounds were visualized by UV S4 irradiation (254 nm). Automatic column chromatography was performed using a Buchi SepacoreTM flash apparatus, consisting of a C-660 Buchi fraction collector, C-615 Pump manager, C-630 UV Monitor, and two C-601 pump modules. Preparative (recycling) size exclusion chromatography (prep-SEC) was performed on a JAI LC-9110 NEXT system equipped with JAIGEL 1H and 2H columns (eluent CHCl$_3$, flow rate 3.5 mL min$^{-1}$). Solvents were evaporated with a rotary evaporator at a temperature of 45 °C. Yields refer to isolated compounds.

1,2-bis(2,2-diethoxyethyl)disulfide (2)

Bromo-1,1-diethoxyethane (100 mL, 664.7 mmol) was added to a mixture of $S_8$ (21.23 g, 664.7 mmol), Na$_2$S.9H$_2$O (127.73 g, 531.8 mmol) and KI (5.52 g, 33.2 mmol) in ethanol (600 mL), and the mixture was heated to reflux for 12 h. After removing the majority of ethanol in vacuo, the residue was filtered and rinsed with ethyl acetate. The filtrate was washed with water (3 x 75 mL) to remove any remaining salts and the combined aqueous layers were extracted with ethyl acetate (2 x 50 mL). The combined organic phases were dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude material was then purified by vacuum distillation (80 °C at 1.10$^{-3}$ mbar) to yield the desired product as a yellow liquid with ~95% purity (59.68 g, 30%). This product was used without further purification in the next reaction. Analytical data were in accordance with data previously reported in the literature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.71$ (t, $J = 5.6$ Hz, 2H), 3.73 – 3.49 (m, 8H), 2.96 (d, $J = 5.6$ Hz, 4H), 1.22 (t, $J = 7.1$ Hz, 12H).

3-bromo-4-[(2,2-diethoxyethyl)thio]thiophene (3)

$t$-BuLi (1.9 M in pentane, 104.4 mL, 198.4 mmol) was slowly added to a stirred solution of 3,4-dibromothiophene (11 mL, 99.2 mmol) in dry diethyl ether (1 L) at –78 °C. After stirring for 1 h at –78 °C, 1,2-bis(2,2-diethoxyethyl)disulfide (2) (31.4 mL, 109.1 mmol) was added rapidly and the mixture was stirred overnight at room temperature. The reaction was then quenched by adding water (150 mL) and the organic phase was washed with a 1.0 M NaOH solution (3 x 150 mL). The water phase was extracted with dichloromethane (3 x 150 mL) and the combined organic phases were dried over MgSO$_4$, filtered, and the solvents were removed in vacuo. The product was purified by kugelrohr distillation (140 °C at 9 x 10$^{-3}$ mbar). The distillate was further purified by column chromatography (silica, petroleum ether:dichloromethane, 60:40) to yield the product as a pale yellow liquid (24.89 g, 81%). Analytical data were in accordance with data previously reported in the literature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31$ (d, $J = 3.5$ Hz, 1H), 7.24 (d, $J = 3.5$ Hz, 1H), 4.65 (t, $J = 5.6$ Hz, 1H), 3.70 – 3.48 (m, 4H), 3.05 (d, $J = 5.6$ Hz, 2H), 1.19 (t, $J = 7.1$ Hz, 6H).

3-bromothieno[3,2-b]thiophene (4)

Anhydrous amberlyst 15 (20.26 g, 95.2 mmol) was added to a solution of compound 3 (26.94 g, 86.6 mmol) in diethyl ether (500 mL) and the mixture was refluxed for 10 h. The beads were removed by filtration and refluxed in a small amount of diethyl ether. This was repeated several times to extract all products from the beads. The resulting filtrate was washed with water, dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude material was purified by column chromatography (silica, hexanes) and kugelrohr distillation (115 °C at 7.10$^{-3}$ mbar) to obtain the product as a pale-yellow liquid (13.0 g, 69%). Analytical data were in accordance with data previously reported in the literature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.43$ (dd, $J = 5.2$, 1.4 Hz, 1H), 7.29 (d, $J = 5.2$ Hz, 1H), 7.28 (d, $J = 1.5$ Hz, 1H).
3,3’-dibromo-2,2’-bithieno[3,2-b]thiophene (5)

Lithium diisopropylamide (LDA) was prepared by adding n-BuLi (2.5 M in hexane, 10 mL, 25.1 mmol) dropwise to a solution of diisopropylamine (3.4 mL, 25.1 mmol) in THF (10 mL) at 0 °C. The fresh LDA solution was added dropwise to a solution of 3-bromothieno[3,2-b]thiophene (4) (5.0 g, 22.81 mmol) in THF (50 mL) at −78 °C and the mixture was stirred for 1 h at this temperature. After adding CuCl₂ (3.37 g, 25.10 mmol) at −78 °C, the mixture was allowed to gently reach room temperature and the reaction was continued for 12 h at room temperature. THF was removed in vacuo, diethyl ether (200 mL) was added, and the mixture was washed with water (3 x 50 mL). The aqueous phase was extracted with dichloromethane (3 x 50 mL) and the combined organic phases were dried over MgSO₄, filtered, and concentrated in vacuo. The crude product was then redissolved in chloroform and purified by recrystallization in ethanol and column chromatography (silica, hexanes) to yield a fluffy yellow powder (2.43 g, 48%). Analytical data were in accordance with data previously reported in the literature.⁵

¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, J = 5.2 Hz, 2H), 7.33 (d, J = 5.2 Hz, 2H).


A solution of compound 5 (600 mg, 1.38 mmol), t-BuONa (317 mg, 3.30 mmol), Pd₂dba₃ (63 mg, 0.069 mmol), BINAP (171 mg, 0.28 mmol), and dodecylamine (255 mg, 1.38 mmol) in dry toluene (15 mL) was refluxed overnight under inert atmosphere. Equal amounts of Pd₂dba₃ and BINAP were added and the mixture was again refluxed overnight under inert atmosphere. Diethyl ether (50 mL) was added and the solution was washed with water (3 x 75 mL). The aqueous phase was extracted with dichloromethane (75 mL) and the combined organic phases were dried over MgSO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (silica, hexanes:dichloromethane, 80:20) to yield the pure product as a yellow solid (411 mg, 65%).

¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, J = 5.2 Hz, 2H), 7.25 (d, J = 5.2 Hz, 2H), 4.34 (t, J = 7.1 Hz, 2H), 1.96 (p, J = 7.2 Hz, 2H), 1.47 – 1.37 (m, 2H), 1.36 – 1.18 (m, 16H), 0.89 (t, J = 6.9 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 138.5, 134.8, 123.7, 123.6, 121.3, 117.9, 48.4, 32.0, 31.7, 29.7, 29.6, 29.49, 29.45, 29.35, 26.9, 22.8, 14.3.

MALDI-ToF-MS: calcd. for C₉₂H₇₀NS₄ [M⁺]: m/z = 459.12, measured: m/z = 459.15.


n-BuLi (2.5 M in hexane, 1.3 mL, 3.33 mmol) was added dropwise to a solution of TTP 6 (383 mg, 0.83 mmol) in THF (15 mL) at −78 °C. After the reaction was stirred for 1 h at −78 °C, trimethyltin chloride (3.8 mL, 3.75 mmol) was added rapidly and the reaction was allowed to stir overnight. The crude material was purified via prep-SEC and the stannylated product was obtained as a yellow solid (400 mg, 61%).

¹H NMR (400 MHz, CDCl₃): δ = 7.31 (s, 2H), 4.41 (t, J = 7.1 Hz, 2H), 2.07 – 1.91 (m, 2H), 1.47 – 1.18 (m, 18H), 0.87 (t, J = 9.2, 3H), 0.37 (s, 18H).

MALDI-ToF-MS: calcd. for C₉₀H₄₅NS₄Sn₂ [M⁺]: m/z = 785.05, measured: m/z = 785.08.

PTTPQx

(76.9 mg, 0.11 mmol), tris(dibenzyldieneacetone)dipalladium(0) (3.1 mg, 3 µmol) and tri(ortho-tolyl)phosphine (4.1 mg, 12 µmol) were dissolved in dry, degassed chlorobenzene (1.6 mL). The resulting mixture was stirred at 130 °C for 24 h, after which the crude polymer was diluted in chlorobenzene (5 mL). Diethylammonium diethyldithiocarbamate (50 mg) was added and the mixture was stirred at 100 °C for 1 h. The resulting mixture was poured out in methanol. The obtained precipitate was filtered in a thimble and purified by repetitive Soxhlet extractions using methanol, acetone, n-hexane, dichloromethane, and chloroform. The chloroform fraction obtained from Soxhlet extraction was added to methanol and the resulting precipitate was filtered and dried, yielding a dark green solid (54 mg, 50%). GPC (1,2,4-trichlorobenzene, 160 °C, PS standards): $M_n = 12.8$ kg/mol, $D = 2.3$. UV-Vis-NIR: $\lambda_{\text{max, film}} = 732$ nm.
Figure S1: $^1$H (top) and $^{13}$C (bottom) NMR spectra of TTP monomer 6.
Figure S2: $^1$H NMR spectrum of stannylated TTP monomer 7.

Figure S3: $^1$H NMR spectrum of PTTPQx in chlorobenzene-$d_5$ at 80 °C.
Figure S4: MALDI-ToF mass spectrum of PTTPQx.

Figure S5: Overlay of the reduction (a) and oxidation (b) curves of PTTPQx (pink) and PDTPQx (blue) obtained via cyclic voltammetry.
Figure S6: RHC measurement (2nd heating) (a), showing the absence of a melting peak and glass transition up to 250 °C, and TGA (b), showing mass loss starting at ~300 °C, for PTTPQx.

Figure S7: Absolute (a) and normalized (b) UV-Vis-NIR absorption spectra for a solution of PTTPQx in chlorobenzene left open to the air for one week (inset: photographs of the polymer solution at the start and the end of the week).

3. Device manufacturing and characterization

Bulk heterojunction organic photodetectors (OPDs) for both donor polymers were prepared using the inverted architecture glass/ITO/ZnO/active layer/MoO₃/Ag. Devices made from PDTPQx were prepared according to literature. For PTTPQx, the OPDs were prepared as reported below. The ITO (indium-tin-oxide) coated substrates (100 nm, Kintec, sheet resistivity 20 Ω sq⁻¹) were thoroughly cleaned via sonication in acetone, followed by a UV/O₃ treatment for 30 min. ZnO was deposited by spin-coating with a layer thickness of ~20 nm. The ZnO layer was annealed at 200 °C for 20 min. Further processing was performed under nitrogen atmosphere in a glove box (< 1 ppm O₂ and H₂O). The photoactive layer solution, consisting of the active polymer and PC₆₁BM (Solenne), was then spin-coated from chloroform, chlorobenzene, or ortho-dichlorobenzene. The best performing devices were obtained with a blend solution of 1:3 (wt/wt) PTTPQx:PC₆₁BM, with a total concentration of 32 mg mL⁻¹ in chlorobenzene. The solution was stirred overnight at 40 °C to ensure complete dissolution. Finally, the MoO₃ (10 nm) hole transporting layer and Ag (100 nm) top electrode were sequentially deposited on top of the active layer through a shadow mask by thermal evaporation (< 5 × 10⁻⁶ mbar) to afford photodetector devices with an active area of 0.8 mm². The cavity OPDs were fabricated using the inverted device structure Eagle XG glass/Au (1.5 nm)/Ag (28 nm)/PEIE/active layer/MoO₃/Ag. The semi-transparent thin Ag films were fabricated by thermal evaporation (< 5 × 10⁻⁶ mbar) with an extremely thin Au seed layer beneath. The deposition rate for Au and Ag was 0.5 and 4 Å s⁻¹,
respectively. All other parameters for the cavity OPDs were equal to the regular OPDs. The film thickness of the active layer was controlled by varying the spin speed. The freshly fabricated devices were measured in an inert atmosphere and light and dark \( J-V \) curves (forward scan with a step of 25 mV) were recorded using a Keithley 2400 Source Meter under AM1.5 1-sun illumination, provided by a solar simulator (Newport 91195A) with a silicon calibrated intensity equivalent to 100 mW cm\(^{-2}\), and under dark, respectively. The EQE\(_{PV}\) spectrum for each cell was measured under chopped (123 Hz) monochromatic illumination from a Xe lamp (100 W, Newport) modulated by a Newport Cornerstone™ 130° Monochromator and an optical wheel chopper. The generated photocurrent from the solar cells was amplified with a Stanford Research System Model SR830 lock-in amplifier, and a calibrated silicon FDS100-CAL photodiode was employed as a reference cell. For the sensitive EQE measurements, an INVENIO R (Bruker Optics) with an external detector was employed. A low-noise current amplifier was used to amplify the photocurrent generated under illumination of the devices, with the illumination light modulated by the Fourier-transform infrared (FTIR) setup. The blend thickness was monitored by a Bruker Veeco Dektak XT profilometer. Atomic force microscopy (AFM) experiments were performed (on the devices used for the \( J-V \) measurements) with a JPK NanoWizard 3 AFM (JPK Instruments AG, Berlin, Germany) using AC mode in air. Silicon ACTA-50 tips from AppNano with cantilever length of ~125 mm, spring constant of ~40 N m\(^{-1}\) and resonance frequency of ~300 kHz were used. The scan angle, set point height, gain values, and scan rate were adjusted according to the calibration of the AFM tip. Grazing incidence wide angle X-ray scattering was performed at the Stanford Synchrotron Radiation Lightsource on beamline 11-3, with an X-ray energy of 12.7 keV and an incidence angle of 0.1°. The sample to detector distance was 307.5 mm and was calibrated to a polycrystalline LaB\(_6\) standard. Measurements were performed in a helium chamber to minimize air scattering. All data were corrected for the geometric distortion of the flat detector used, normalized by exposure time, sample thickness, and monitor counts, and analyzed using Nika 1D SAXS and WAXstools software in Igor Pro.\(^8\) Mobility measurements were done using a Space Charge Limited Current (SCLC) diode, and calculated from the equation \( J = (9\varepsilon\varepsilon_0\muV^2/(8L^3)) \).\(^9\) The hole mobilities were determined using a hole only diode with the device architecture ITO/PEDOT:PSS/active layer/MoO\(_3\)/Ag. Contact angles with water were measured with a Dataphysics contact angle system OCA 15 plus. The films were prepared by spin-coating solutions of the active layer materials on glass substrates. The materials were dissolved in chloroform (10 mg/mL) and the solutions were stirred at 50 °C before spin-coating.

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**Figure S8:** EQE spectra for inverted photodiode devices with the PTTPQx:PC\(_{61}\)BM (1:3) active layer spin-coated from chloroform (CF), chlorobenzene (CB), and ortho-dichlorobenzene (o-DCB).
Figure S9: AFM images of PTTPQx:PC61BM (1:3) blends spin-coated from CF (left) and CB (right), with an Rq of 0.68 and 0.45 nm, respectively.

Figure S10: Optical microscopy images of the ITO-active layer interface for PTTPQx:PC61BM (1:3) blends spin-coated from CF (left) and CB (right).

Figure S11: Current density versus applied voltage curves for the hole-only diode devices prepared from (a) blends of PTTPQx:PC61BM (1:3) (pink) and PDTPQx:PC61BM (1:4) (blue), and (b) the pristine polymers PTTPQx (pink) and PDTPQx (blue).
Figure S12: 2D-GIWAXS patterns for the neat PDTPQx (top left) and PTTPQx (top right) polymers with lineouts in $Q_z$ (bottom left) and $Q_{xy}$ (bottom right).

Figure S13: 2D-GIWAXS patterns for the PDTPQx (top left) and PTTPQx (top right) polymers blended with PC$_{61}$BM (in a 1:4 and 1:3 ratio, respectively), with lineouts in $Q_z$ (bottom left) and $Q_{xy}$ (bottom right).
**Table S1**: Fitting values calculated for both polymer blends based on Ref 10.

<table>
<thead>
<tr>
<th>Blends</th>
<th>$E_{CT}$ (eV)</th>
<th>$\lambda$ (eV)</th>
<th>$f$ (eV²)</th>
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<tr>
<td>PDTPQx:PC$_{61}$BM (1:4)</td>
<td>1.06</td>
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<td>PTTPQx:PC$_{61}$BM (1:3)</td>
<td>1.01</td>
<td>0.15</td>
<td>0.135</td>
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To determine $E_{CT}$, a fitting procedure was applied on the low energy tail of the sensitively measured EQE(E) spectrum, using the following equation:

$$EQE(E) \sim \exp \left( -\frac{(E - \lambda - E_{CT})^2}{4\lambda k_B T} \right)$$

with $\lambda$ the reorganization energy, $k_B$ the Boltzmann constant, and $T$ the temperature (in this case room temperature, making $k_B T$ equal to 0.025). To reliably consider the low energy part of the spectrum, the fitting was done on the natural logarithm of the EQE(E) spectrum.

**Figure S14**: Water contact angles for films of the neat active layer materials: (a) PC$_{61}$BM, (b) PDTPQx, and (c) PTTPQx.

**Figure S15**: Refractive index ($n$) and absorption coefficient ($k$) for PTTPQx on a normal (a) and logarithmic (b) scale.
Figure S16: Simulated EQEs for the cavity device with device stack glass/Au (2 nm)/Ag (28 nm)/ZnO (40 nm)/active layer (130–270 nm)/MoO₃ (12 nm)/Ag (100 nm), assuming an internal quantum efficiency of 0.79.

Table S2: Performance parameters for the PTTPQx-based optical cavity devices.

<table>
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<th>Detector wavelength (nm)</th>
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<th>R_{shunt} (Ω cm²)</th>
<th>f_{noise} (A cm⁻¹ Hz⁻¹/²)</th>
<th>Spectral response (A W⁻¹)</th>
<th>D' (Jones)</th>
<th>FWHM (nm)</th>
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4. References