Supporting Information for Charge Generation and Energy Transfer in Hybrid Polymer/Infrared Quantum Dot Solar Cells

Synthesis of Poly[(4,4'-bis(3-(2-hexyl-decyl)dithieno[3,2-b:2',3'-d]pyrrole)-2,6-diyl-alt-(2,5-bis(3-(2-ethyl-hexyl)thiophen-2yl)thiazolo[5,4-d]thiazole)](PPEHTT): The di(trimethyltin)-*N*-(1-hexyldecyl)dithieno[3,2-*b*:30-*d*]-pyrrole (250 mg, 0.34 mmol) and 2,5-Bis-[5-bromo-(2-ethyl-hexyl)-thiophen-2yl]-thiazolo[5,4-d]thiazole (196 mg, 0.34 mmol) and catalyst tris(dibenzylideneacetone)dipalladium (0) (6 mg, 0.07 mmol) and tri-*o*-tolylphosphine (8 mg, 0.027 mmol) in anhydrous chlorobenzene (25 mL) were heated at 125 ^{o}C for 3 days. Then the heating was reduced to 50 $^{°}$C. The reaction mixture was poured into 200 mL of methanol containing 5 mL of hydrochloric acid and stirred for 5 h. The dark brown precipitate was collected via filtration, and was further purified by Soxhlet extraction with methanol and hexane. The polymer was further purified by dissolving chloroform and then reprecipitated in methanol. The solid was filtered and dried into vacuum oven for 10 h and collected as a dark brown solid. Yield (260 mg, 81%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): 6.31-6.95 (m, 4H), 3.81 (bs, 2H), 2.75 (bs, 4H), 0.81-1.81 (m, 61H). GPC: M$_w$ = 13.46 kDa, M$_n$ = 8.41 kDa, PDI = 1.6.
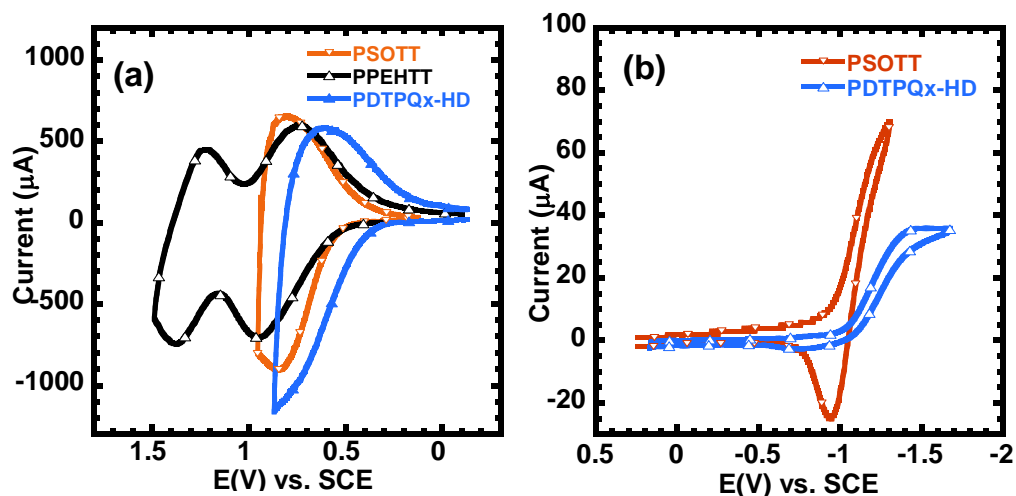

Figure SI.1 Cyclic voltammograms of PSOTT, PPEHTT and PDTPQx thin films in 0.1 M Bu$_4$NPF$_6$ solution in acetonitrile at a scan rate of 40 mV/s: (a) oxidation waves and (b) reduction waves.

Additional PIA characterization:

We further characterize the materials by probing neat quantum dot films, polymer/fullerene films and pristine PSOTT polymer films.
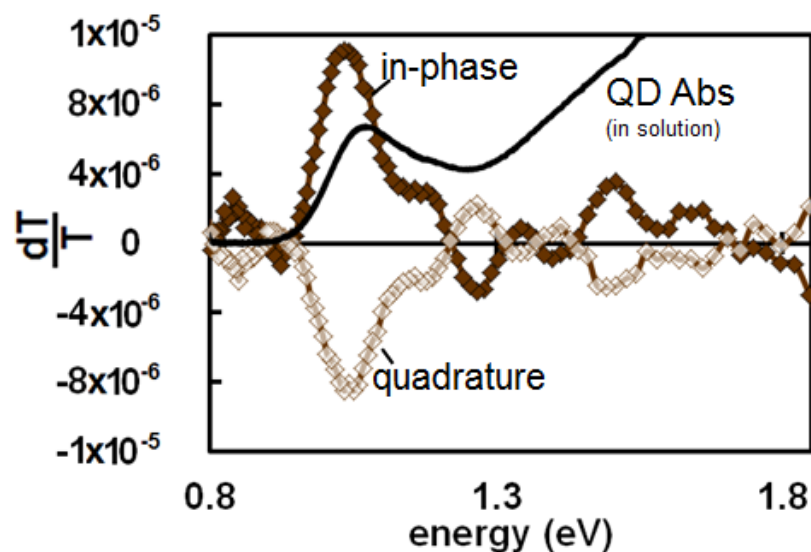
Figure SI.2 Curve with solid brown diamonds is the in-phase photoinduced absorption signal and white diamonds correspond with quadrature signal taken on a thin film of quantum dots. The quantum dot absorption spectrum is overlayed on the PIA data as a solid black line. PIA on neat PbS quantum dot film shows a bleach feature that corresponds in energy with the QD absorption peak. The bleach feature (particularly in the quadrature signal) can be significantly diminished after the films have been EDT treated.
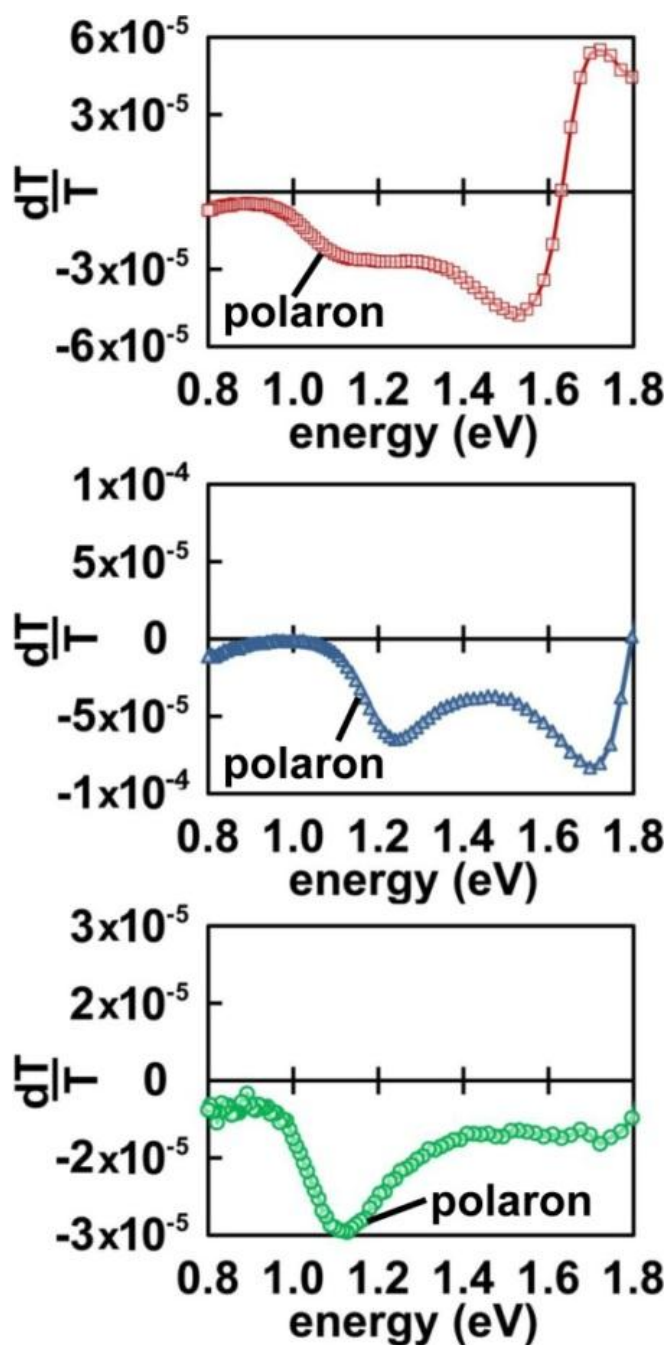
Figure SI.3 PIA signal for PDTPQx-HD, PPEHTT, and PSOTT when blended with fullerene (PC$_{60}$BM in the case of PDTPQx-HD and PPEHTT and PC$_{71}$BM in the case of PSOTT).   Of particular note, there is a clear long-lived signal for the PSOTT/fullerene blend. The polaron peaks for PDTPQx-HD and PPEHTT match the positions of the peaks in the polymer/PbS blends (main text Fig. 2). While the PSOTT/fullerene blend has a strong peak at ~1.1 eV (above) The PSOTT/PbS blend has no significant long live polaron signal at room temperature (main text Fig. 2).
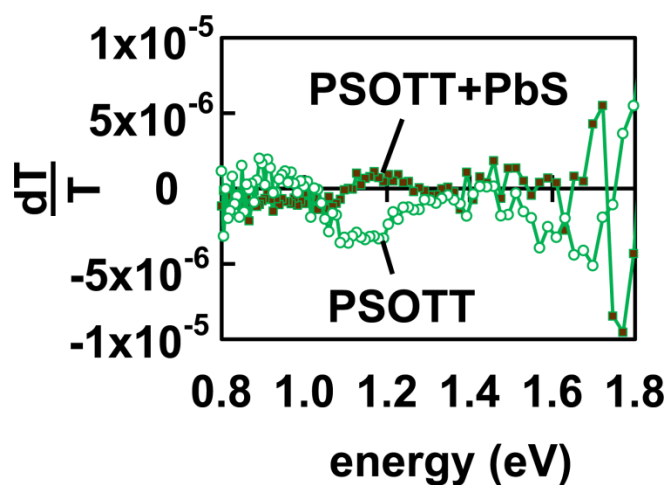
Figure SI.4 For comparison, we overlay PIA in-phase spectra of pristine PSOTT with a PSOTT/quantum blend and see comparable signal at room temperature.

Additional device characterization

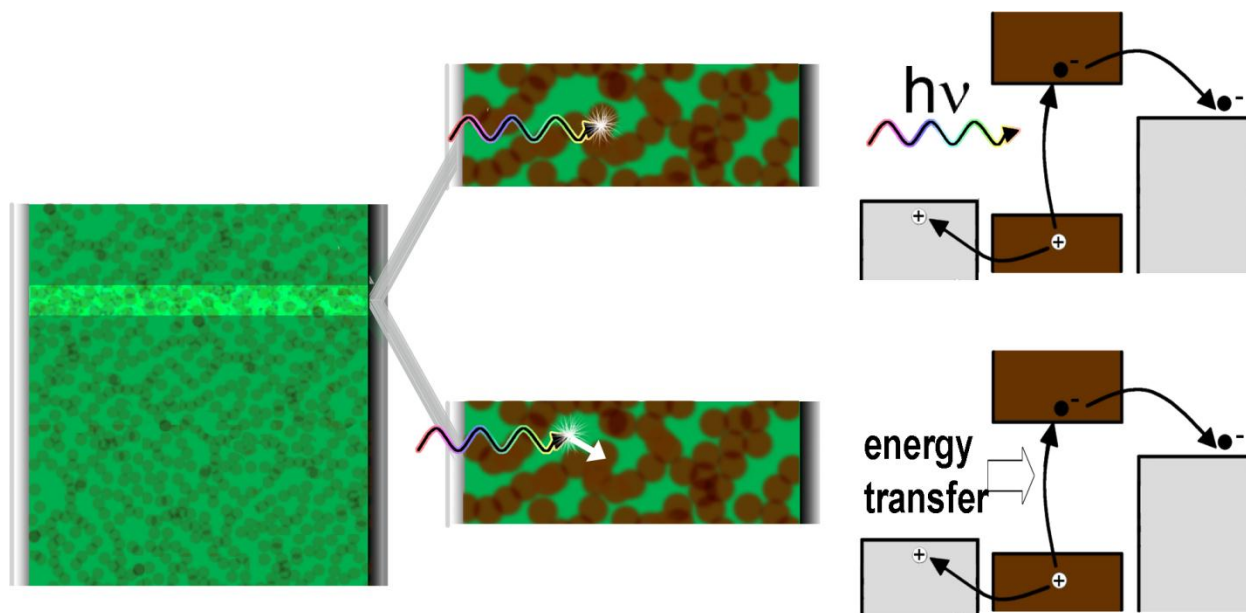*Schematic Diagram of PSOTT/PbS "Schottky-diode" device*

Figure SI.5 Schematic diagram of the PSOTT/quantum dot "Schottky-diode" device. The ITO/PEDOT hole collecting electrode is denoted by a vertical light gray bar. In the active area portion of the drawing, the green represents the PSOTT polymer and the brown circles represent PbS quantum dots.

The LiF/Al contact is drawn as a darker gray vertical strip. For clarity, the highlighted horizontal strip in the device is magnified in the two images in the center of the figure which demonstrate pictorially two routes for generating photocurrent in the Schottky-diode device. In the upper image, a photon is absorbed by a quantum dot, in the manner typical of quantum dot Schottky-diode devices. In the bottom image, the photon is absorbed by the polymer and the energy stored in the polymer excited state is then transferred to the quantum dot. The cartoons to the right of each image depict these two routes schematically.

Additional notes about device fabrication

The thicknesses of the devices reported in Fig. 3 vary between polymers. Although due to limited supply of polymer we did not undertake a systematic thickness optimization for devices, through repeated trials (with varying quantum dot batches and ligand treatments) we saw optimal thickness ranges for the respective polymer/quantum dot blends and consequently tailored further device fabrication to mirror what produced the best results for a particular blend system. We found that PPEHTT/PbS device performance was best with a ~ 60 nm active area thickness and was typically worse with 40 and 80 nm device thicknesses. PDTPQx/PbS blends had poorer performance with thinner active areas (30-40 nm) and generally improved performance with active areas anywhere between 60-100 nm. PSOTT/PbS blends conversely showed the best performance with a thinner (~40 nm) active area and device performance decreased with thicker active areas.

Although device thickness certainly impacts device performance, we found the effect minor compared to the impact of thiol treating the devices. As illustration we show EQE from a PSOTT device that was not EDT treated.
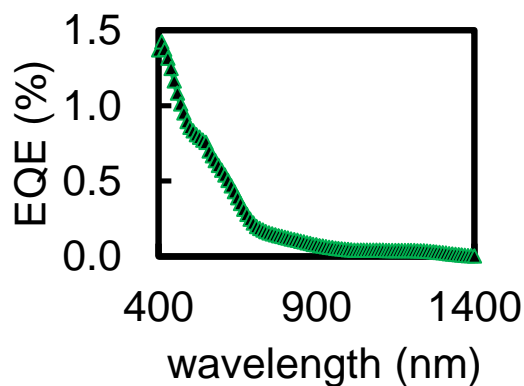

Figure SI.6 a "high performing" EQE spectrum for a PSOTT/PbS device that did not undergo EDT treatment. Photocurrent is more than an order of magnitude lower than for EDT treated devices

Figure SI.7 shows the photovoltaic behavior of each blend device measured as a function of applied voltage under broadband illumination from a filtered Xenon arc source.
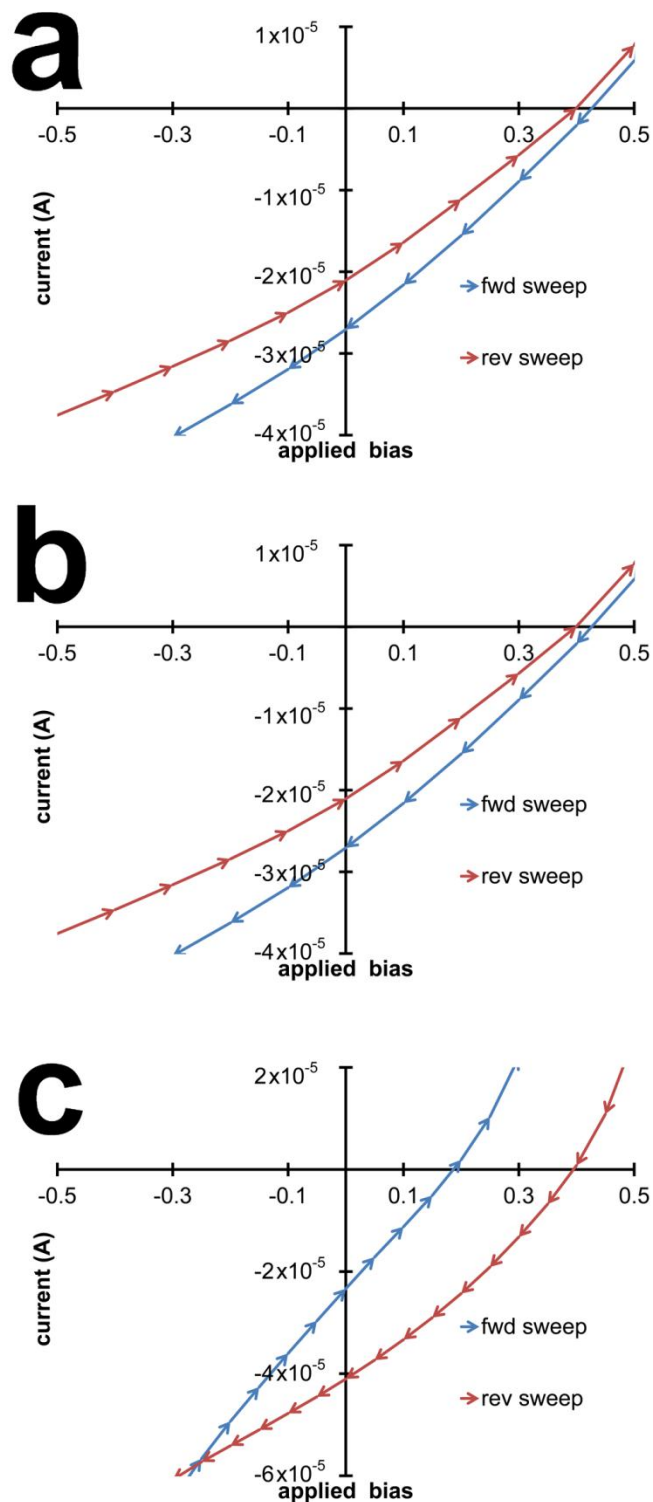
a

b

c

Figure SI.7 IV curves for the three devices in figure 3 of the main text. Following the labeling of figure 3, (a) is PDTPQx/PbS (b) is PPEHTT/PbS and (c) is PSOTT/PbS. All devices were masked so that the illuminated area was 0.018 cm^2. They were swept first from -2 to 2 V (forward sweep, blue data) and then 2 V to -2 V (reverse sweep, red data). Data from both sweeps are included (rather than averaged)

to show the varying degrees of hysteresis. These data were taken using a solar simulator, but the solar simulator intensity and spectral mismatch factors were not properly calibrated. As such the general Voc and FF trends are likely to be correct, but the exact values and short circuit current are not reflective of the true AM1.5 performance and we therefore refrain from quoting efficiency (though these data along with the EQE data in the main text could be used to estimate upper limits for these unoptimized devices.)