Electronic Supplementary Information for:

**One, two and three-branched triphenylamine-oligothiophene hybrids for solution-processed solar cells**

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Experimental details

Measurements. The $^1$H and $^{13}$C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer. Mass spectra were measured on a GCT-MS micromass spectrometer using the electron impact (EI) mode or on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (dichloromethane) and thin film (on quartz substrate) UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-$n$-butylammonium hexafluorophosphate (0.1 M) in CH$_3$CN using a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudo-reference electrode. Potentials were referenced to ferrocenium/ferrocene (FeCp$_2$$^{+}$)$^{0}$) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C min$^{-1}$. Differential scanning calorimetry (DSC) measurements were performed using a METTLER differential scanning calorimeter (DSC822e) under nitrogen at a heating rate of 10 °C min$^{-1}$. The nanoscale morphology of blend film was observed by using a Veeco Nanoscopy V atomic force microscopy (AFM) in tapping mode.

Hole mobility measurements. Hole-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/TPA-2T-CA, TPA-3T-CA, L(TPA-3T-CA) or S(TPA-3T-CA)/Au. Mobilities were extracted by fitting the current density–voltage curves using the Mott–Gurney relationship (space charge limited current).
**Fig. S1** TGA curves of TPA-1T-CA, TPA-2T-CA, TPA-3T-CA, L(TPA-3T-CA) and S(TPA-3T-CA).

**Fig. S2** DSC curves of TPA-2T-CA, TPA-3T-CA, L(TPA-3T-CA) and S(TPA-3T-CA).
Fig. S3 Field dependence of the current for hole-only devices.

References