Electronic Supplementary Information. Organic Photodiodes from Homochiral Squaraine Compounds with Strong Circular Dichroism

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Figure S1: (a) Photograph of $444 \,\mu\text{M}$ **ProSQC-16** dissolved in chloroform and in ACN:CHCl₃ mixtures with varying ACN percentage as indicated. Final **ProSQ-C16** concentration was $14.8 \,\mu\text{M}$. The change in color due to aggregate formation is clearly visible by eye. (b) Photograph of spin-casted neat and PCBM-blended **ProSQ-C16** thin films from chloroform solutions subsequently annealed at the indicated temperature for 20 min. (c) Photograph of spin-casted neat and PCBM-blended **ProSQ-C6** thin films from chloroform solutions subsequently annealed at the indicated temperature for 20 min.



Figure S2: As-measured CD spectra in mdeg of 444 µM **ProSQC-16** in solutions with varying ACN percentages as indicated.

Table S1: Comparison of layer thicknesses determined by SE and by AFM, as well as RMS surface roughness parameter spot tests obtained by AFM. Note that SE measures over a macroscopic sample area while AFM measures highly localized. The AFM overestimated the layer thickness by approximately 20%. Note that AFM is destructive to the sample since scanning of sharp scratches in the layer is required. The quality of the scratches in the organic layer are suspected to be the limiting factor here. However, AFM confirmed that all films were smooth and continuous and thus well-suited for SE analysis. Fitting of the SE data was still very difficult in case of the thinnest layer, i.e. neat **ProSQ-C16** leading to a large standard deviation.

Active layer	SE thickness	AFM thickness	RMS roughness
	/ nm	/ nm	/ nm
neat $ProSQ-C16 4 mg/mL$	30 ± 10	—	_
ProSQ-C16:PCBM 1:2 12 mg/mL	71 ± 2	—	_
neat $ProSQ-C6.6 mg/mL$	46 ± 2	—	_
ProSQ-C6:PCBM 2:3 15 mg/mL	106 ± 2	125 ± 8	4 ± 1
ProSQ-C6:PCBM 2:3 10 mg/mL	68 ± 2	80 ± 5	8 ± 2
ProSQ-C6:PCBM 3:7 $10\mathrm{mg/mL}$	57 ± 4	65 ± 5	12 ± 3



Figure S3: As-measured CD spectra of (a) neat **ProSQ-C16** and (b) PCBM-blended **ProSQ-C16**, and (c) neat **ProSQ-C6** and (d) PCBM-blended **ProSQ-C6** thin films for varying annealing temperatures as indicated.



Figure S4: Sketch of the conventional bulk-heterojunction (BHJ) architecture of the organic photodiode devices. The layer sequence reads as following: ITO / MoOx (8 nm)/ **ProSQ**:PCBM / LiF (1 nm)/ Al (150 nm) / LiF (250 nm). The active layer thickness and composition is altered for the device studies.



Figure S5: **ProSQ-C16**:PCBM 1:2 12 mg/mL annealed at 90 °C (a) J-V curves with varying illumination intensity showed a strong S-shape that diminishes with reducing the illumination intensity. (b) Jsc versus illumination intensity could not be fitted with a single curve. The slope for higher illumination intensities approaches a three-quarter dependence of Jsc on intensity hinting to a space-charge limitation of the short circuit current. For lower illumination intensities Jsc approaches a linear scaling with intensity. (c) EQE increased with increasing reverse bias voltage, but always stayed well below the absorption of the device indicating strong losses. The increase in EQE was slightly more pronounced within the PCBM absorption regime and does not saturate. For bias voltages exceeding -3 V no EQE spectra could be recorded. The **ProSQ-C16** was not only defeated by **ProSQ-C6** due to the CD properties, but also the repeatability of the device preparation was poor: only 1 out of 4 attempts resulted in functioning devices.

Table S2: Photovoltaic performance key parameters of **ProSQ-C16**:PCBM photodiodes with 1:2 blend ratio and 12 mg/mL concentration annealed at 90 °C, N = 3, and illumination intensity dependence parameter α for Jsc according to $Jsc \propto I^{\alpha}$.

Voc	Jsc	\mathbf{FF}	PCE	α	α
/ V	$/ \text{ mAcm}^{-2}$	/ %	/ %	$(20 - 100 \mathrm{mW/cm^2})$	$(< 20\mathrm{mW/cm^2})$
0.67 ± 0.01	1.9 ± 0.2	20 ± 2	0.26 ± 0.05	0.78 ± 0.04	0.98 ± 0.01



Figure S6: Representative differential J-V-characteristics dJ/dV versus voltage with varying illumination intensity as indicated for different **ProSQ-C6**:PCBM active layer blends (a) 2:3 15 mg/mL (b) 2:3 10 mg/mL (c) 3:7 10 mg/mL showing the conductivity per area of the devices. The conductivity is a function of voltage for all cases approaching a constant level for increasing reverse bias voltages. The conductivity at 0V and in reverse bias is proportional to the reciprocal of the shunt resistance. The shunt resistance is increasing with decreasing illumination intensity. The conductivity at Voc and for higher forward bias is proportional to the reciprocal of the series resistance. The series resistance is strongly increasing with voltage and increasing with decreasing illumination intensity. The hump in the differential curves (b) and (c) for voltages within the fourth quadrant of the normal J-V curve indicate their S-shape. The hump, i.e. the S-shape is gradually diminishing with reducing illumination intensity.



Figure S7: Representative J-V-characteristics with varying illumination intensity as indicated normalized at -1.0 V for different **ProSQ-C6**:PCBM active layer blends (a) 2:3 15 mg/mL (b) 2:3 10 mg/mL (c) 3:7 10 mg/mL. All devices had the same interfacial layers and electrodes, and were subjected to the same processing conditions, but only the curves in (b) and (c) show S-kinks. It becomes obvious that the S-kink is more pronounced for higher light intensities and is gradually decreasing until it vanishes, because this behavior leads to a point of intersection since Voc increases with light intensity. This point of intersection is characteristic for the presence of an extraction barrier. The spread of the curves around Voc of the non-S-shaped devices (a) indicates that bimolecular recombination was present as loss mechanism at this operation regime for the complete intensity range.