

Electronic Supplementary Information (ESI)

Structure-Property Relationship of Anilino-Squaraines in Organic Solar Cells

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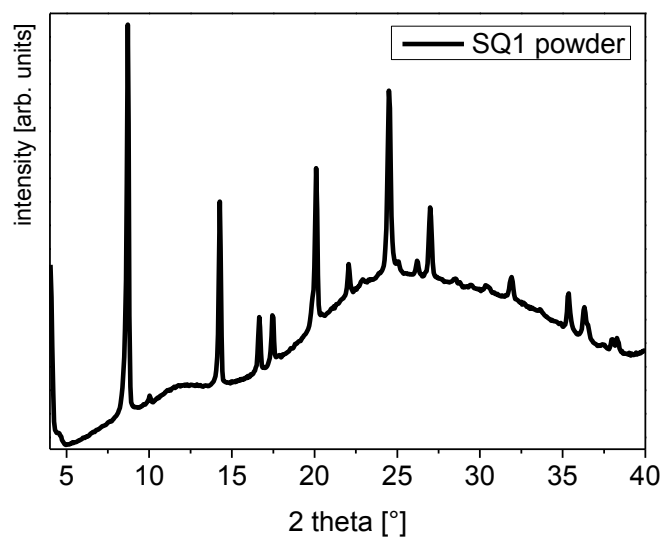


Fig. S1. XRD-pattern of SQ1 powder. Sample was prepared on glass causing the hump.

Tab. S1. Absorbance and fluorescence maxima in chloroform solution.

compound	absorbance [nm]	fluorescence [nm]
SQ1	648	671
SQ2	649	662
SQ3	650	682

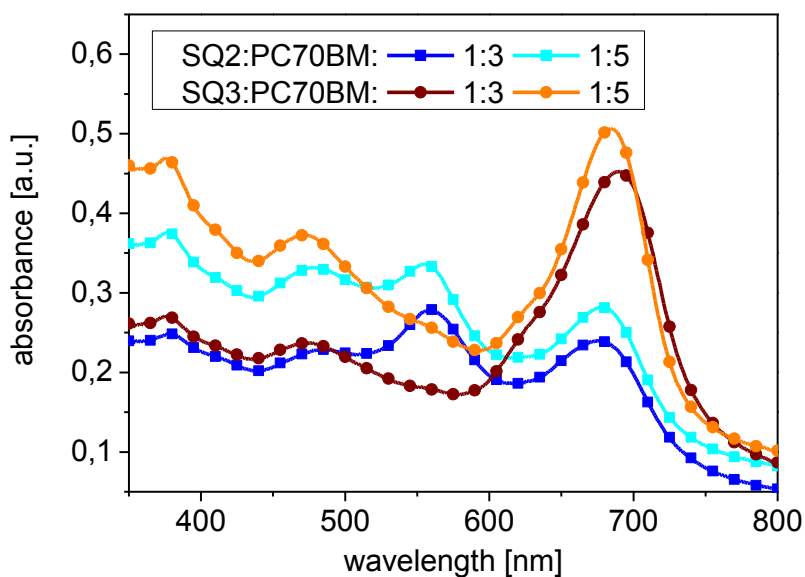


Fig. S2. UV/Vis absorbance spectra of coated SQ2:PC70BM and SQ3:PC70BM blends.

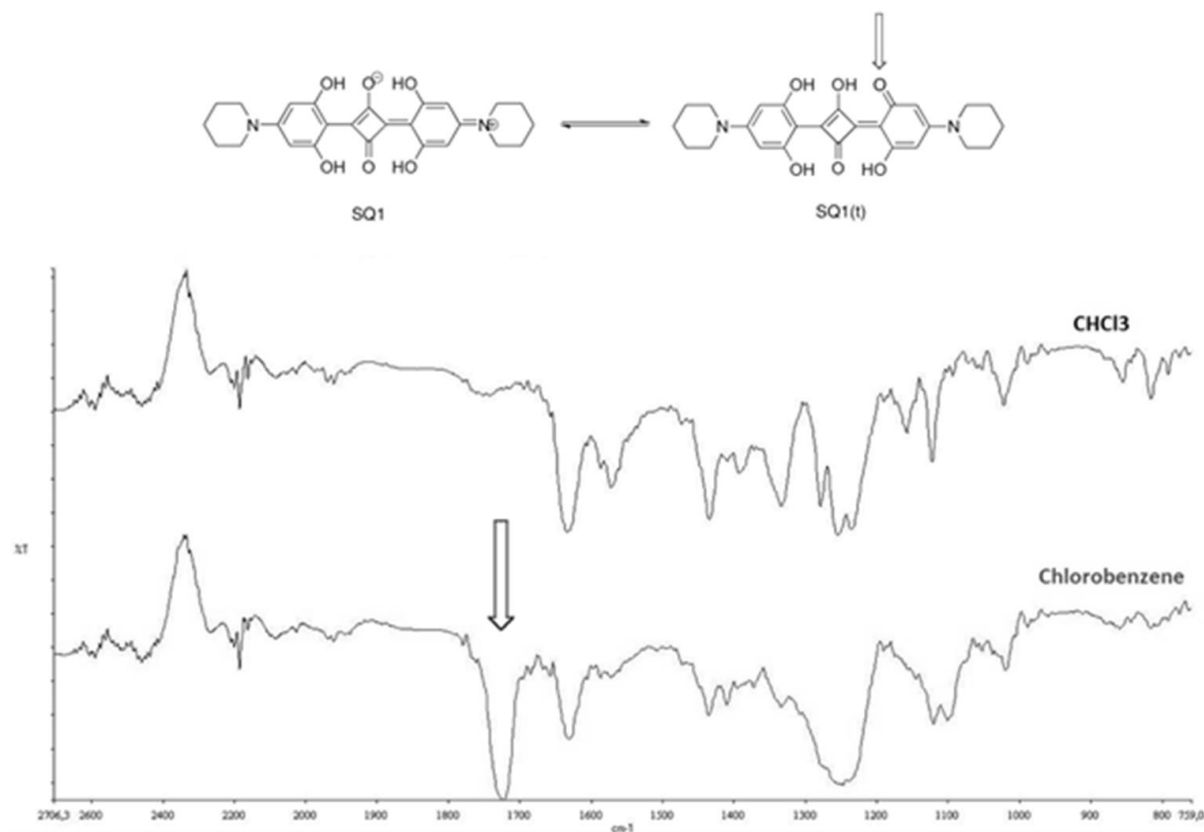


Fig. S3. The ATR-FTIR spectrum of the film casted from chlorobenzene (the solvent we used for cells fabrication) shows a peak at 1720 cm⁻¹ that does not appear in the spectrum of the chloroform casted film. Such band could correspond to the carbonyl group associated with the tautomeric form SQ1(t) (highlighted with arrows).

Tab. S2. Various annealing temperature for SQ:PC60BM 1:3 weight ratio blends, 1 sun illumination.

compound	annealing temperature [°C]	Voc [V]	Jsc [mA cm ⁻²]	FF [%]	PCE [%]
SQ2	RT	0.82	3.28	30	0.79
	30	0.81	3.37	30	0.80
	50	0.82	3.24	32	0.84
	70	0.81	3.26	31	0.82
	90	0.75	2.79	35	0.74
	110	0.63	1.74	29	0.32
	130	0.41	0.86	31	0.11
SQ3	RT	0.78	5.35	38	1.59
	30	0.77	5.50	39	1.64
	50	0.80	4.67	38	1.43
	70	0.77	4.47	37	1.29
	90	0.74	4.38	37	1.21
	110	0.65	4.12	34	0.91
	130	0.55	3.74	32	0.65

Tab. S3. Various mixing ratios by weight for SQ:PC60BM blends at optimum annealing temperature, i.e., 50°C for SQ2 and no annealing for SQ3; 1 sun illumination.

compound	mixing ratio [weight%]	Voc [V]	Jsc [mA cm ⁻²]	FF [%]	PCE [%]
SQ2	1:1	0.48	0.46	32	0.08
	1:2	0.79	2.01	36	0.57
	1:3	0.82	3.24	32	0.84
	1:5	0.83	3.74	30	0.92
	1:7	0.72	2.96	28	0.60
SQ3	1:1	0.75	1.95	40	0.58
	1:2	0.77	2.09	45	0.73
	1:3	0.78	5.35	38	1.59
	1:5	0.73	6.23	32	1.44
	1:7	0.74	4.67	31	1.07

Active layer thickness optimization

Tab. S4 The thickness of the active layer in the BHJ solar cells has been optimized by varying the spincoating conditions. The speed of the first spincoating step is given, which was maintained for 60 seconds and was followed by a drying step for 20 seconds at 3000 rpm. The SQs were blended with PC60BM in 1:5 ratio by weight.

speed [rpm]	layer thickness [nm]	PCE SQ2 [%]	PCE SQ3 [%]
500	110-140	0,39	0,81
1000	90-100	0,68	0,99
1500	80-90	0,92	1,44
2000	70-80	0,71	1,38

Charge carrier mobility (hole-only devices):

The hole-only devices for investigation of the charge carrier mobility of the squaraines had the layer sequence ITO / PEDOT:PSS / SQ / Au. The SQ layers were spincoated from chlorobenzene solutions and dried without annealing. Unfortunately, it was again not possible to obtain a homogeneous film by spincoating from a neat SQ1 solution. The film was highly discontinuous showing large aggregates very similar to the layers deposited from SQ1:PC60BM blends. Consequently, the SQ1 devices did not show any useful performance. The film thicknesses of SQ2 and SQ3 were measured to be 20-30 nm.

The effective hole mobility μ_h was derived by the SCLC model^{S1} from J - V characteristics of the hole-only devices. In this model, the current density J is given by the Mott-Gurney law:

$$J = \frac{9}{8} \cdot \epsilon_r \cdot \epsilon_0 \cdot \mu \cdot \frac{V^2}{d^3}$$

where ϵ_r is the relative permittivity of the organic semiconductors, here estimated to be 3,^{S1} ϵ_0 the vacuum permittivity, V the applied voltage, and d the film thickness. The electrical contacts of the electrodes to the organic semiconductor are considered to be ohmic, so that no injection limitation is present. At low voltages, typically up to 2 V for organic semiconductors, there is an ohmic regime with $J \sim V$ followed by the SCLC regime with $J \sim V^2$ for higher voltages. Usually, this transition is not sharp in amorphous organic layers, but characterized by a trap-filling regime which distorts the shape of the J - V curves to a higher power dependence law on voltage.

For our data, the current density J was plotted versus voltage squared V^2 , and the graph was fitted with a straight line in the linear regime, as shown exemplarily for selected graphs from **SQ2** and **SQ3** in Fig. S4. The hole mobilities were calculated from the linear fits of multiple devices and averaged.

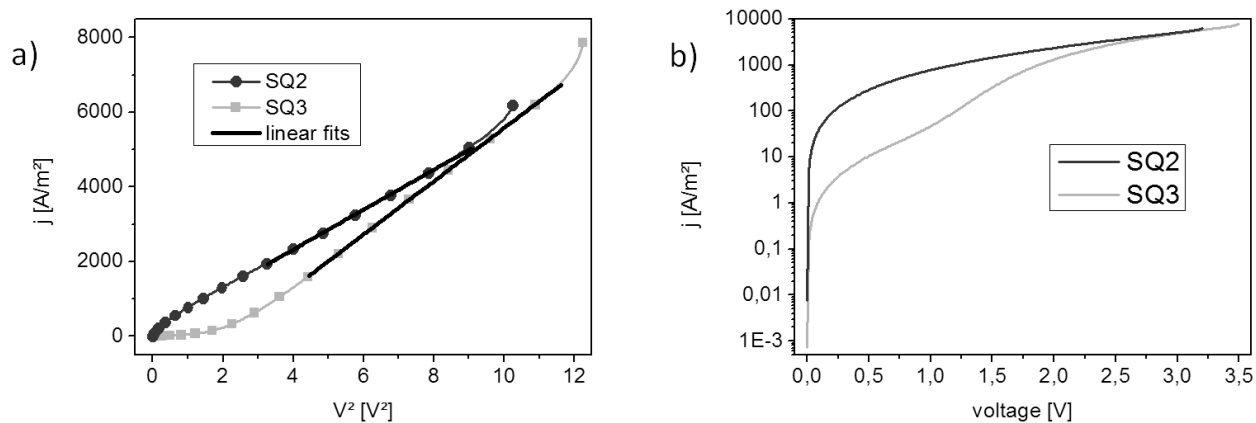


Fig. S4. a) Current density j plotted versus voltage squared V^2 with a straight line fit in the linear regime. The ranges of the curves before the SCLC regime look substantially different for **SQ2** and **SQ3** hinting to a different spatial and energetic distribution of trap states. b) Semi-logarithmic plot of current density versus voltage.

[S1] a) M. Schwoerer, H. C. Wolf, *Organic Molecular Solids*, Wiley-VCH, Weinheim, Germany 2007; b) A. Rose, *Phys. Rev.* 1955, **97**, 1538; c) A. Carbone, B. K. Kotowska, D. Kotowski, *Phys. Rev. Lett.* 2005, **95**, 236601.