

**Supporting Information for**

**Manipulating Open-Circuit Voltage in Organic  
Photovoltaic Device via Phenylalkyl Side Chain.**

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## General Information

### SQ dyes Synthesis and Characterization

#### Materials Used

All chemicals, otherwise stated, were purchased from Sigma Aldrich and used without further purifications.

#### Liquid Chromatography-Mass Spectrum (LC/MS)

Shimadzu 2020 Liquid chromatography – Mass Spectroscopy (LC/MS) was used for analyzing reaction mixture. Sonoma C18 Column, 4.6mm x 50mm, 5 $\mu$  100Å particle size columns was used. Analytical method is gradient 5% - 95% ACN over 6 minutes at a flow rate of 1mL/min. The mobile phases used for LC/MS are 0.05% FA in ACN and 0.05% FA in MilliQ-H<sub>2</sub>O.

#### Nuclear Magnetic Resonance Spectroscopy

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectroscopy were performed on 400 MHz and 300MHz NMR spectrometers. Chemical shifts are reported as  $\delta$  in units of parts per million (ppm) downfield from tetramethylsilane ( $\delta$ 0.00), using the residual solvent signal as an internal standard: chloroform-d, CDCl<sub>3</sub>, (<sup>1</sup>H NMR,  $\delta$  7.26, singlet; <sup>13</sup>C NMR,  $\delta$  77.04, triplet). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). The number of protons (n) for a given resonance is indicated by nH.

#### Cyclic Voltammetry (CV) Measurement

CV measurement was conducted in a three electrode cell consisting of reference electrode (Ag/AgCl), working electrode (Pt) and counter electrode. The working electrode was filled with electrolyte solution (non aqueous c(LiCl) 2mol/L in ethanol) from Fluka Analytical. 0.1M tetrabutylammonium hexafluorophosphate (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N(PF<sub>6</sub>) from Fluka Analytical in dichloromethane was prepared. The calibration graph for (Fc/Fc<sup>+</sup>) was measured by dissolving Ferrocene from Sigma Aldrich in the 0.1M (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N(PF<sub>6</sub>) solution. The same procedure was repeated by dissolving various squaraine dyes to obtain the CV measurement for various squaraine dyes. The E<sub>ox</sub> and E<sub>red</sub> values were determined from the CV curve and  $\lambda_{\text{ons}}$  from the UV-Abs curve. The HOMO and LUMO

energy level were then estimated from the following empirical formulae,  $E_{\text{HOMO}}^{\text{opt}} = -5.23\text{eV} - eE_{\text{ox}} + 1/2(E_{\text{cv}}^{\text{sol}} - E_{\text{g}})$ ,  $E_{\text{LUMO}}^{\text{opt}} = -5.23\text{eV} - eE_{\text{red}} - 1/2(E_{\text{cv}}^{\text{sol}} - E_{\text{g}})$ ,  $E_{\text{cv}}^{\text{sol}} = E_{\text{ox}} - E_{\text{red}}$ ,  $E_{\text{g}} = 1240/\lambda_{\text{ons}}$ .

### Device Fabrication and Characterization

Devices were fabricated according to the following structure: ITO/PEDOT:PSS(~30nm)/SQ:PC<sub>70</sub>BM(~50nm)/Ca(~25nm)/Al(~60nm). The active layer consisted of the synthesized SQ compound and PC<sub>70</sub>BM obtained from Nano-C. SQ solution was first stirred in the glove box for 12hrs at 40°C before mixing with PC<sub>70</sub>BM. The blend solution (total concentration of 16mg/ml) was then stirred for another 2hrs at 40°C. Before device fabrication, the pre-coated indium tin oxide (ITO) glass substrates were cleaned and ultrasonicated in detergent, de-ionized water, isopropyl alcohol, deionized water, and acetone, followed by UV-Ozone treatment for 20mins. PEDOT:PSS was spin-coated on the ITO glass substrate at 5000rpm and heated at 120°C for 20mins in ambient condition. SQ:PC<sub>70</sub>BM blend was spin coated on the substrate at 4000rpm and annealed at 50°C for 30mins in the glove box. Finally, Ca and Al were thermally evaporated on the substrate surface respectively.

Solar cell measurement was conducted under AM1.5 irradiation at 100mW/cm<sup>2</sup> by Newport solar simulator (93194A-1000) and Keithley 2400 source meter operated by a computer. Eko LS-100 grating spectroradiometer was used to measure the solar simulator's spectral irradiance. Thickness were measured using a Dektak 6M stylus profiler. External Quantum Efficiency of the solar cell was characterized by a home-built computerized system consisting of a monochromated halogen light source, an optical chopper, a current amplifier, a lock-in amplifier and a separate halogen lamp as light bias. The device area was defined as 0.0604m<sup>2</sup> on average.

### Thin Film Transistor Fabrication

Field effect transistors were fabricated on silicon wafer with a 300nm thick thermal oxide for all squaraines in a bottom gate, top contact configuration. The wafer was ultrasonicated in acetone and UV-Ozone treated for 20mins. HMDS (Rohm & Haas) is spin coated on the wafer at 4000rpm and baked at 100°C for 1min at ambient condition. Squaraine solution (concentration 4mg/ml) in chloroform was then spin coated at 2000rpm on top and annealed at 50°C for 30mins in the glove box. Finally, Cr (~15nm) and Au (~35nm) were thermally evaporated through a

shadow mask on the surface respectively. The channel length(L) were in various length of 0.03mm, 0.05mm, 0.06mm and 0.10mm. The channel width(W) was 4mm. Electrical characterization was carried out through a Hewlett Packard semiconductor parameter analyzer (4155A) and Interactive Characterization Software (ICS) from Metrics Technology Inc.

### **Atomic Force Spectroscopy (AFM) Characterization**

Samples for AFM were prepared by spin coating SQ:PC<sub>70</sub>BM blend (total concentration of 16mg/ml) at 4000rpm and thermal annealed at 50°C for 30mins on cleaned ITO glass coated with PEDOT:PSS. Tapping mode AFM was performed by Dimension ICON and collected in Nanoscope v8.15, courtesy of Bruker Singapore.

### **UV-VIS Measurement**

UV-Abs samples were prepared by spin-coating squaraine dyes on cleaned ITO at 4000rpm and thermally annealed at 50°C for 30mins. UV-Abs characterization was measured by UV spectrophotometer (UV-1800) from Shimadzu.

### **Transient Photovoltage Measurement**

The bimolecular recombination dynamics is characterized using transient photovoltage (TPV) measurements employed by Shuttle and co-workers<sup>1</sup>. The devices were connected to an oscilloscope (Yokogawa (DL1520L)) and illuminated with a white 'light bias' to control the open circuit voltage ( $V_{oc}$ ). Neutral density filter was added to vary the light intensity within 0.01 to 1 sun illumination. A nitrogen laser pumped-dye laser from Laser Innovation (NL110B) was used as an excitation source with wavelength of 500nm at pulse width of 4ns. The intensity of the laser pulse was altered to keep  $\Delta V_0$  lesser than 20mV. In order to measure the charge density of the device at various light bias, the device was connected to a current amplifier (Femto DHPCA-100) and to the oscilloscope. The  $V_{oc}$  at different light intensity was measured with a multimeter.

### **Grazing Incidence X-Ray Diffraction (GID) Measurement**

Samples for GID were fabricated by spin-coating active blend layer of SQ2:PC<sub>70</sub>BM and SQ-P2:PC<sub>70</sub>BM on cleaned ITO glass at 4000rpm and thermal annealed at 50°C for 30mins. The measurements were performed at 1.0 degree

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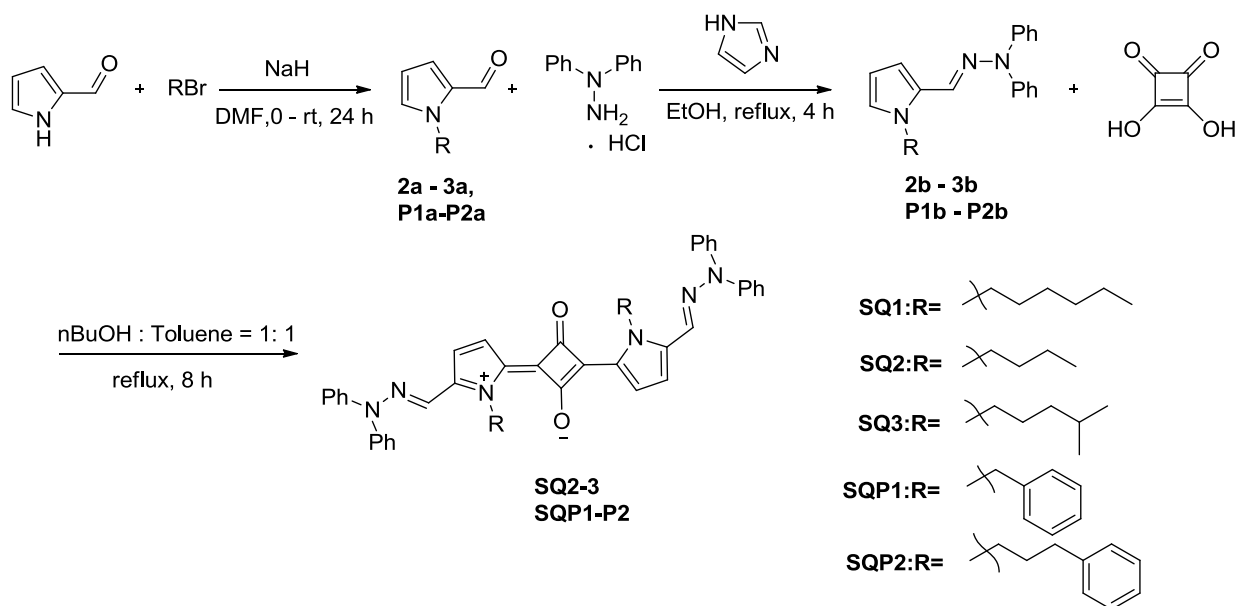
<sup>1</sup> Shuttle C. G., O'Regan B., Ballantyne A. M., Nelson J., Bradley D. D. C., de Mello J., and Durrant J. R. App.Phys.Lett. 2008,92,093311.

incident angle. GID measurements were conducted by D8 ADVANCE DaVinci diffractometer configured with the fast linear LYNXEYE detector, courtesy of Bruker Germany.

### X-Ray Crystallography

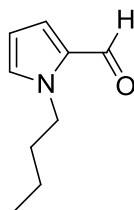
Crystals of SQ2 and SQ-P2 were obtained from DCM/EA and DCM/THF respectively. Single crystal structure X-ray analysis was conducted by X-ray Diffraction Laboratory in National University of Singapore.

### Materials Synthesis Scheme and Characterization



The squaraine dyes are synthesized according to the synthetic procedure proposed previously.<sup>2</sup> Characterization details of the dyes are summarized below.

#### 1-butyl-1H-pyrrole-2-carbaldehyde (2a)

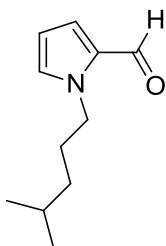


1H-pyrrole-2-carbaldehyde (570.6 mg, 6.0 mmol) in anhydrous DMF (10 ml) was added dropwise at 0 °C under nitrogen to a suspension anhydrous DMF solution of NaH (216.0 mg, 9.0 mmol). The resulting suspension was stirred at 0 °C for 10 min before adding dropwise a solution of butyl bromide (0.8 ml, 6.6 mmol) in anhydrous DMF

<sup>2</sup> Bagnis, D.; Beverina, L.; Huang, H.; Silvestri, F.; Yao, Y.; Yan, H.; Pagani, G. A.; Marks, T. J.; Facchetti, A. *J. Am. Chem. Soc.* **2010**, *132*, 4074-4075.

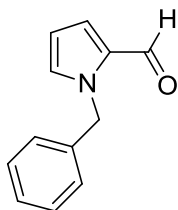
(5 ml). The suspension was then stirred for 24 h at room temperature. Upon reaction completion, the reaction mixture was poured into brine and extracted with DCM. The organic phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$  before removing the solvent under reduced pressure.

**1-(4-methylpentyl)-1H-pyrrole-2-carbaldehyde ( 3a ).**



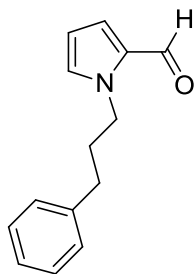
The synthetic procedure is the same as compound **2a**. The product was purified by column chromatography (silica gel, hexane/ EtOAc 100:1). Yellow oil, 58% yield. ESI-APCI MS( $m/z$ ) [ $\text{M}$ ] $^+$ : 179.26 Continue the next step reaction without freeze dried.

**1-benzyl-1H-pyrrole-2-carbaldehyde ( P1a ).**



The synthetic procedure is the same as compound **2a**. The product was purified by column chromatography (silica gel, hexane/ EtOAc 30:1). Yellow oil, 66% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  9.51 (s, 1H), 7.30-7.21 (m, 3H), 7.12 (d,  $J = 4.0$  Hz, 2H), 6.94 (d,  $J = 4.0$  Hz, 2H), 6.25 (t,  $J = 4.0$  Hz, 1H), 5.53 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  179.6, 137.7, 131.7, 131.5, 128.8, 127.8, 127.4, 124.9, 110.2, 52.0.; ESI-APCI MS( $m/z$ ) [ $\text{M}$ ] $^+$ : 185.22

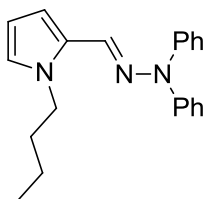
**1-(3-phenylpropyl)-1H-pyrrole-2-carbaldehyde ( P2a ).**



The synthetic procedure is the same as compound **2a**. The product was purified by column chromatography (silica gel, hexane/ EtOAc 100:1 – 50:1). Yellow oil, 83% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  9.50 (s, 1H), 7.29-7.23 (m, 2H), 7.20-7.10 (m, 3H), 6.89 (s, 1H), 6.87 (d,  $J = 11.4$  Hz, 1H), 6.18 (t,  $J = 2.8$  Hz, 1H), 4.28 (t,  $J = 7.2$  Hz,

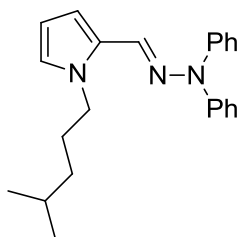
2H), 2.58 (t,  $J = 8.0$  Hz, 2H), 2.11 – 2.02 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  179.2, 141.0, 131.3, 128.4, 126.0, 124.9, 109.6, 48.6, 32.6.; ESI-APCI MS( $m/z$ ) [ $\text{M}$ ] $^+$ : 213.28

**(E)-1-butyl-2-((2,2-diphenylhydrazono)methyl)-1H-pyrrole (2b)**



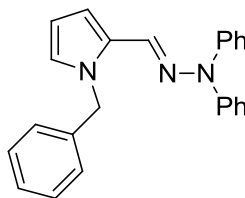
A mixture of N, N-diphenylhydrazine hydrochloride (1.43 g, 6.50 mmol), **2a** (1.09 g, 5.90 mmol) and imidazole (0.44 g, 6.50 mmol) was dissolved in anhydrous EtOH (10 mL) and refluxed for 4h. There is a gradual colour change from yellow to deep red. Solvent was then removed under vacuum, and the residue purified by column chromatography (silica gel, hexane/ EtOAc 50:1 – 30:1)

**(E)-2-((2,2-diphenylhydrazono)methyl)-1-(4-methylpentyl)-1H-pyrrole (3b)**



The synthetic procedure is the same as compound **2b**. The product was purified by column chromatography (silica gel, hexane/ EtOAc 100:1 – 50:1). Yellow oil, 91% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.41-7.36 (m, 4H), 7.17-7.10 (m, 7H) 6.70 (t,  $J = 2.2$  Hz, 1H), 6.16-6.15 (m, 1H), 6.09-6.08 (m, 1H), 4.33 (t,  $J = 7.6$  Hz, 2H), 1.91-1.83 (m, 2H), 1.63-1.56 (m, 1H), 1.31-1.25 (m, 2H), 0.89 (d,  $J = 5.3$  Hz, 6H).;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  144.1, 131.1, 130.0, 128.4, 125.5, 124.2, 122.6, 113.7, 108.1, 49.6, 36.1, 29.7, 28.2, 22.8.; ESI-APCI MS( $m/z$ ) [ $\text{M}$ ] $^+$ : 345.48

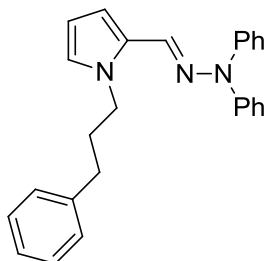
**(E)-1-benzyl-2-((2,2-diphenylhydrazono)methyl)-1H-pyrrole (P1b)**



The synthetic route is the same as **2b**. The product was purified by column chromatography (silica gel, hexane/ EtOAc 50:1 – 30:1). Yellow solid, 77% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.32-7.22 (m, 7H), 7.16 (s, 1H),

7.11-7.04 (m, 4H), 6.93 (d,  $J = 8.0$  Hz, 4H), 6.70 (s, 1H), 6.24 (s, 1H), 6.16 (s, 1H), 5.62 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  143.9, 139.2, 130.8, 129.8, 129.1, 128.8, 127.3, 126.8, 125.8, 124.2, 122.6, 113.4, 108.9, 52.3.; ESI-APCI MS( $m/z$ ) [ $\text{M}$ ] $^+$ : 351.44

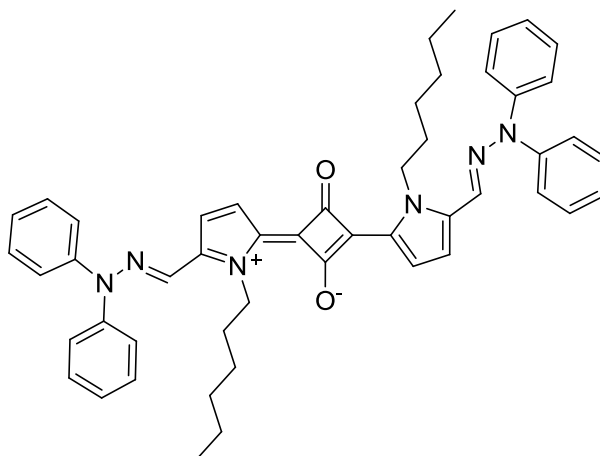
**(E)-2-((2,2-diphenylhydrazone)methyl)-1-(3-phenylpropyl)-1H-pyrrole ( P2b ).**



The synthesis procedure is the same as compound **2b**. The product was purified by column chromatography (silica gel, hexane/ EtOAc 100:1 – 50:1). Yellow oil, 69% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.47 (t,  $J = 3.3$  Hz, 4H), 7.44-7.37 (m, 2H), 7.34-7.18 (m, 10H) 6.75 (t,  $J = 3.1$  Hz, 1H), 6.23-6.21 (m, 1H), 6.17-6.14 (m, 1H), 4.50 (t,  $J = 9.6$  Hz, 2H), 2.80-2.74 (m, 2H), 2.32-2.27 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  143.8, 141.4, 130.9, 129.7, 128.4, 128.1, 126.0, 125.5, 124.0, 122.4, 113.8, 108.0, 48.6, 32.8, 29.6.; ESI-APCI MS( $m/z$ ) [ $\text{M}$ ] $^+$ : 379.50

The synthetic route for **SQ1, SQ2, SQ3, SQ-P1 and SQ-P2** was based on a previously published work.<sup>1</sup>

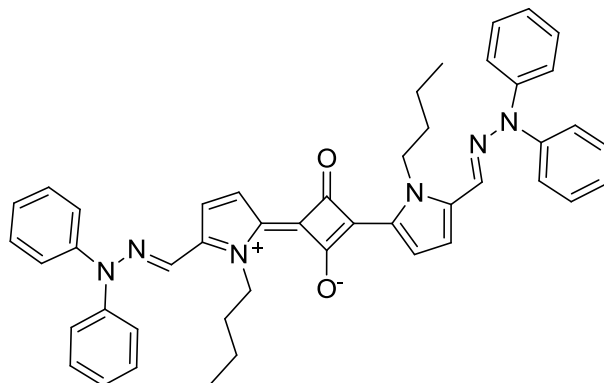
**SQ1.**



Green golden solid, 46% yield, m.p. 231-233°C.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.79 (d,  $J = 4.5$  Hz, 2H), 7.48-7.44 (m, 8H), 7.27 (t,  $J = 7.4$  Hz, 4H), 7.21-7.19 (m, 8H), 7.08 (s, 2H), 6.84 (d,  $J = 4.2$  Hz, 2H), 4.75 (t,  $J = 6.8$  Hz, 4H), 1.69-1.62 (m, 4H), 1.31-1.15 (m, 12H), 0.84 (t,  $J = 7.1$  Hz, 6H).;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  168.8, 143.3, 142.7, 130.2, 125.9, 125.4, 123.9, 122.7, 116.8, 47.7, 32.1, 31.8, 26.4, 22.8, 14.2.;  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) = 727 nm.

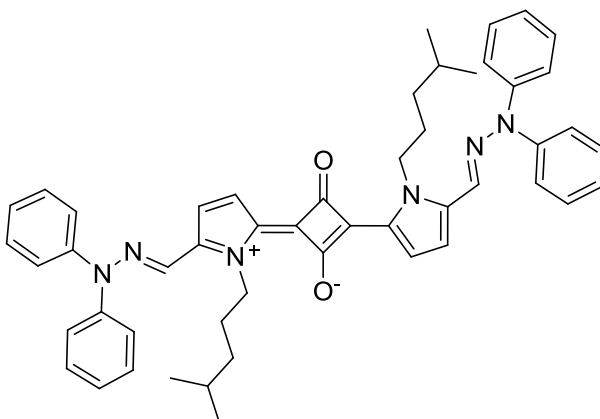


**SQ2.**



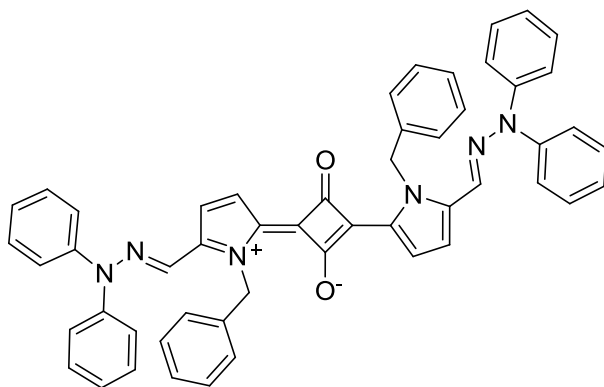
Green golden solid, 42% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.51-7.49 (d,  $J = 8.0$  Hz, 8H), 7.30-7.25 (m, 12H), 7.12 (s, 2H), 4.80 (s, 4H), 1.71-1.67 (m, 8H), 1.37-1.30 (m, 4H), 0.88-0.85 (t,  $J = 8.0$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  142.49, 130.08, 128.98, 125.75, 125.46, 123.67, 122.51, 116.61, 76.74, 47.34, 34.00, 19.73, 13.91.  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) = 727 nm.

**SQ3.**



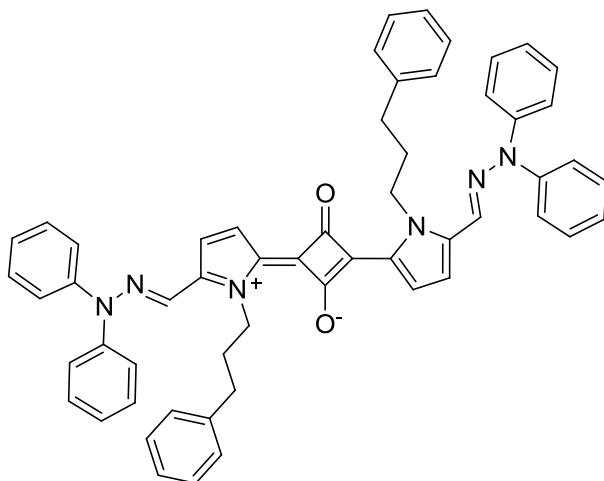
Green golden solid, 24% yield, m.p. 264-268°C.;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.80 (d,  $J = 4.6$  Hz, 2H), 7.48-7.44 (m, 8H), 7.29-7.25 (m, 4H), 7.21-7.19 (m, 8H), 7.08 (s, 2H), 6.84 (d,  $J = 4.4$  Hz, 2H), 4.73 (t,  $J = 7.0$  Hz, 4H), 1.69-1.62 (m, 4H), 1.49-1.43 (m, 2H), 1.19-1.13 (m, 4H), 0.80 (d,  $J = 6.6$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  168.6, 143.3, 142.7, 131.3, 130.3, 129.2, 125.9, 125.3, 123.9, 122.7, 116.7, 47.9, 35.6, 30.1, 28.1, 22.8.;  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) = 730 nm.

**SQ-P1.**

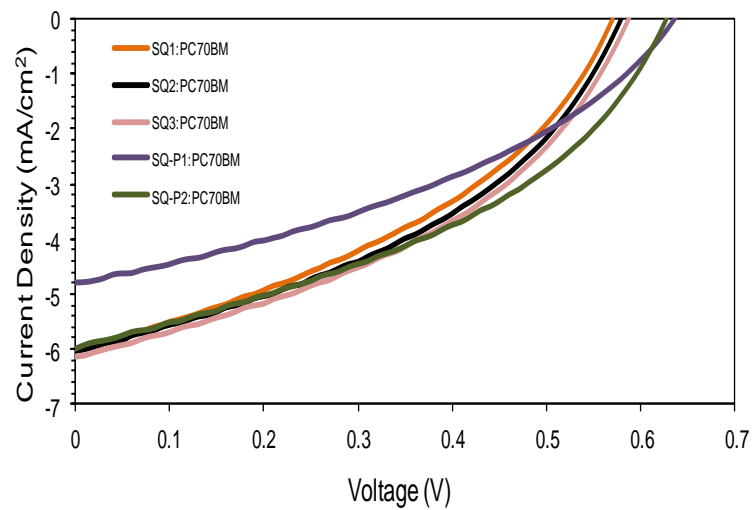


The synthesis route is the same as SQ2. Green golden solid, 52% yield, m.p. 289-291°C.;  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) = 733 nm. (solubility: 0.13mg/ml, 25 °C), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.82-7.81 (d,  $J$  = 4.5 Hz, 1H), 6.40-6.36 (t,  $J$  = 7.7 Hz, 5H), 7.23-7.21 (t,  $J$  = 7.2 Hz, 2H), 7.17 (s, 3H), 7.01-6.80 (m, 6H), 6.79 (s, 2H), 6.03 (s, 2H); ESI-APCI MS( $m/z$ ) [M]<sup>+</sup>: 780.55

**SQ-P2.**



Golden solid, 42% yield, m.p. 273-275°C.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.82 (d,  $J$  = 4.5 Hz, 2H), 7.47-7.43 (m, 8H), 7.29-7.27 (m, 6H), 7.20-7.18 (m, 10H), 7.14-7.10 (m, 6H) 7.08 (s, 2H), 6.80 (d,  $J$  = 4.3 Hz, 2H), 4.94 (t,  $J$  = 6.9 Hz, 4H), 2.67 (t,  $J$  = 8.3 Hz, 4H), 2.05-2.01 (m, 4H).; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  168.4, 143.2, 142.7, 141.7, 131.7, 130.3, 128.5, 126.0, 125.4, 124.0, 122.7, 117.4, 47.8, 33.8, 32.9.;  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) = 731 nm.



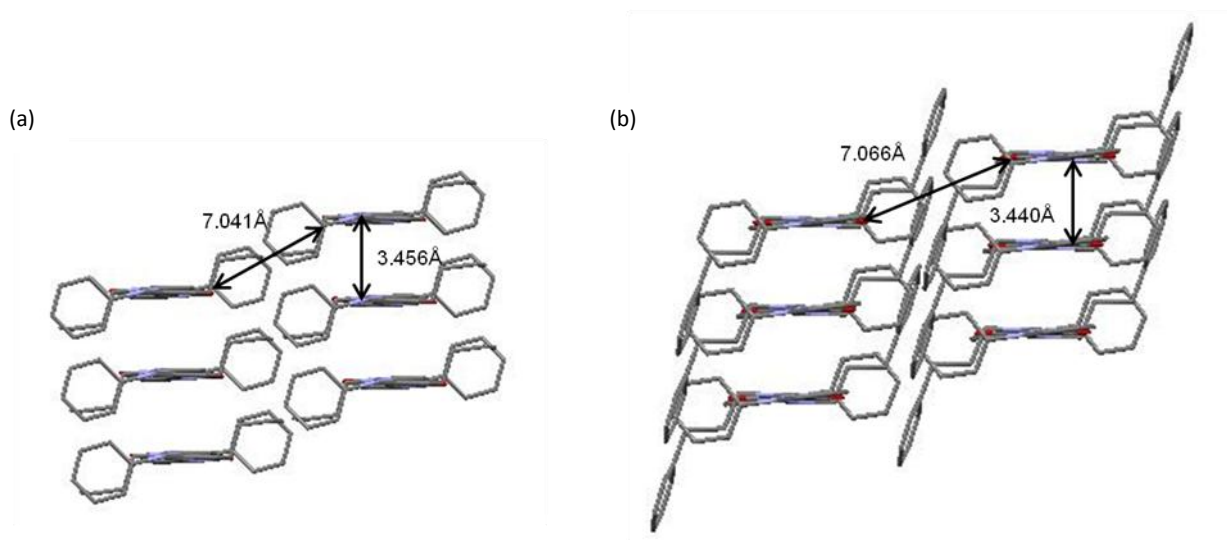
**Figure S1:** *J-V* curves of solution processed solar cell fabricated from SQ under illumination of AM1.5G

**Table S1:** Electrochemical Properties and Hole Mobility of Squaraines

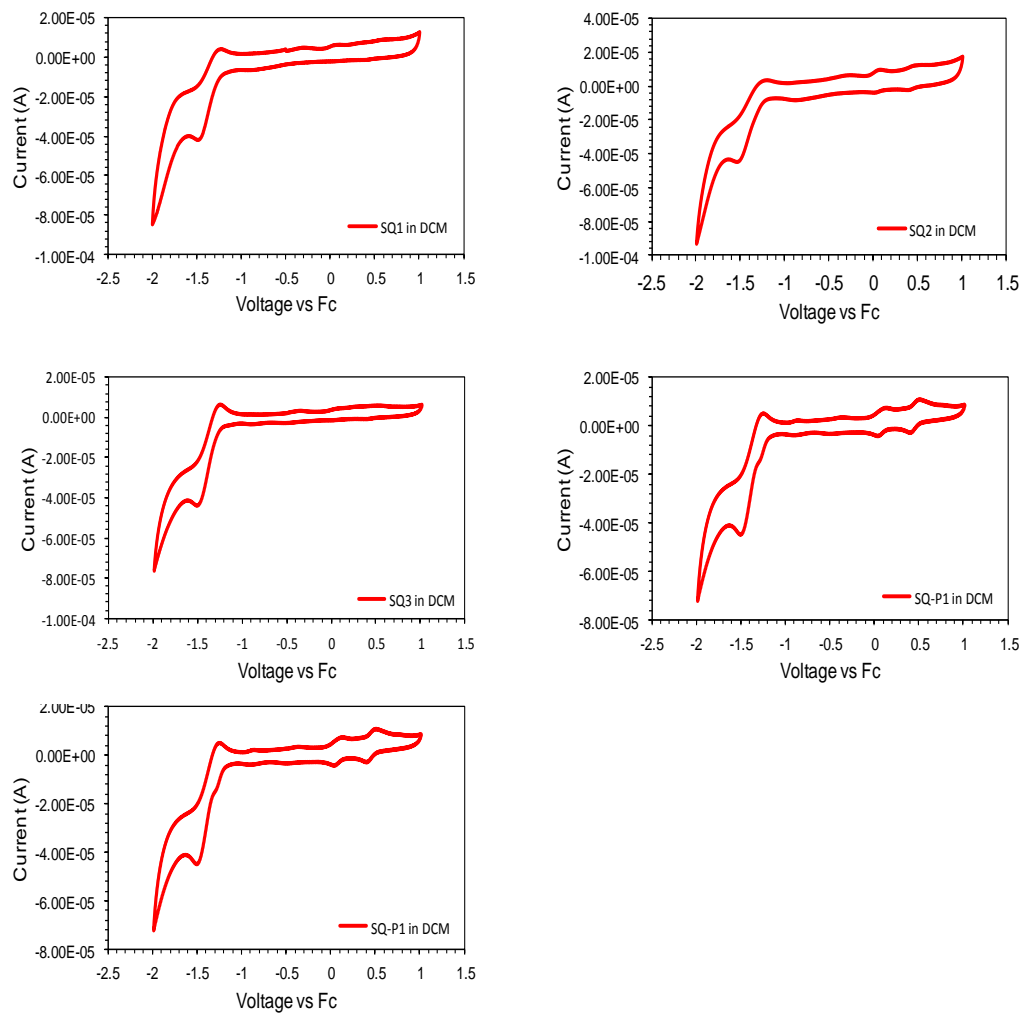
Squaraine	HOMO (eV)	LUMO (eV)	Hole Mobility (cm <sup>2</sup> /(v.s))
SQ1	-5.37	-3.79	5 x 10 <sup>-5</sup>
SQ2	-5.37	-3.78	6 x 10 <sup>-5</sup>
SQ3	-5.36	-3.77	2 x 10 <sup>-5</sup>
SQ-P1	-5.36	-3.78	2 x 10 <sup>-5</sup>
SQ-P2	-5.37	-3.78	3 x 10 <sup>-5</sup>

**Table S2:** Measured Performance Characteristics for All Squaraines at different ratio

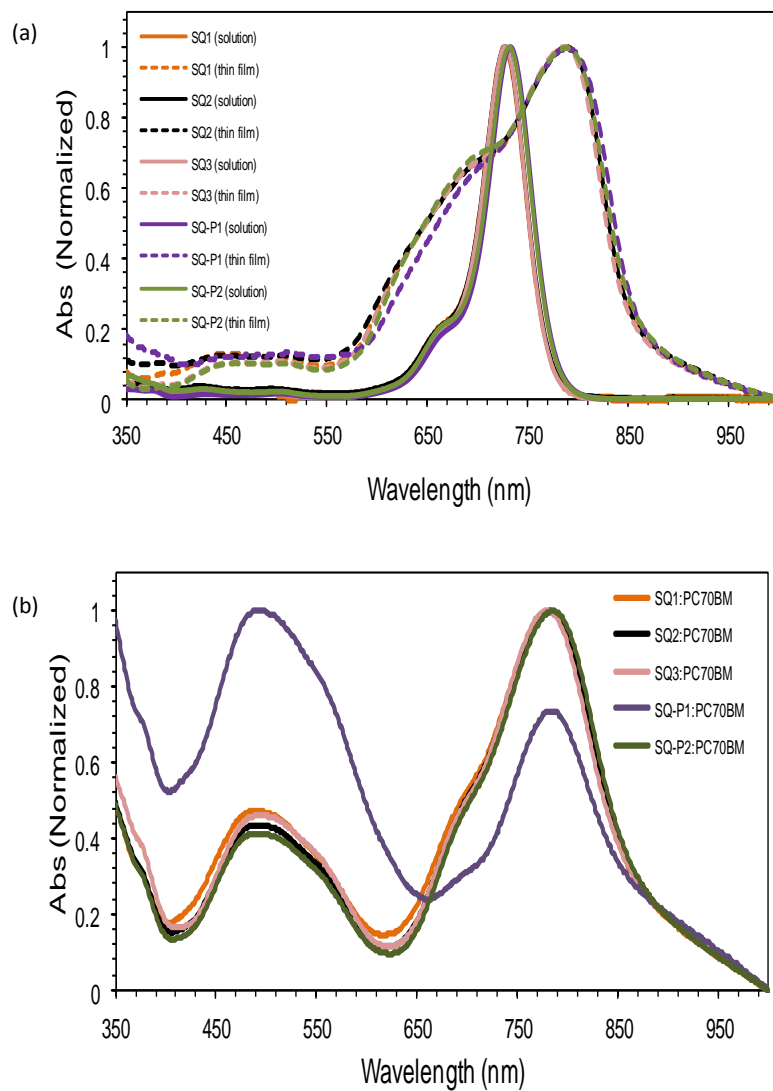
Squaraine	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE(%)
SQ1:PC <sub>70</sub> BM (1:3)	0.57	-6.04	39	1.37
SQ2:PC <sub>70</sub> BM (1:2)	0.57	-5.08	40	1.22
SQ2:PC <sub>70</sub> BM (1:3)	0.57	-6.19	37	1.34
SQ2:PC <sub>70</sub> BM (1:6)	0.57	-5.56	37	1.21
SQ3:PC <sub>70</sub> BM (1:2)	0.58	-6.23	36	1.31
SQ3:PC <sub>70</sub> BM (1:3)	0.58	-6.12	40	1.49
SQ3:PC <sub>70</sub> BM (1:6)	0.56	-7.11	34	1.39
SQ-P1:PC <sub>70</sub> BM (1:3)	0.63	-5.48	33	1.20
SQ-P1:PC <sub>70</sub> BM (1:6)	0.63	-5.01	34	1.08
SQ-P2:PC <sub>70</sub> BM (1:2)	0.64	-6.07	39	1.57
SQ-P2:PC <sub>70</sub> BM (1:3)	0.63	-6.68	36	1.52
SQ-P2:PC <sub>70</sub> BM (1:6)	0.64	-6.70	35	1.53



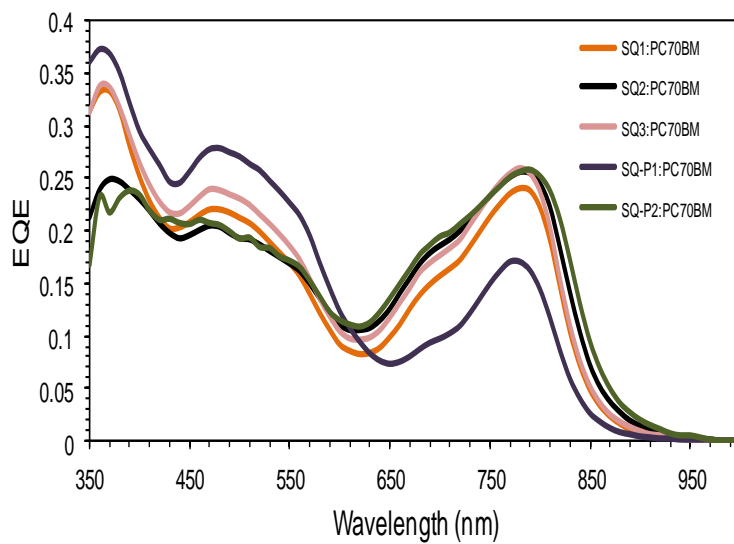
**Figure S2:** Molecular Packing Diagram of (a) SQ2 (b) SQ-P2.  
Hydrogen atoms are removed for clarity.



**Figure S3:** Cyclic voltammograms of SQ1-3,P1,P2 in 0.1 M TBAHF DCM solutions at a scan rate of 100 mV/s. Ferrocene is used as the internal standard.

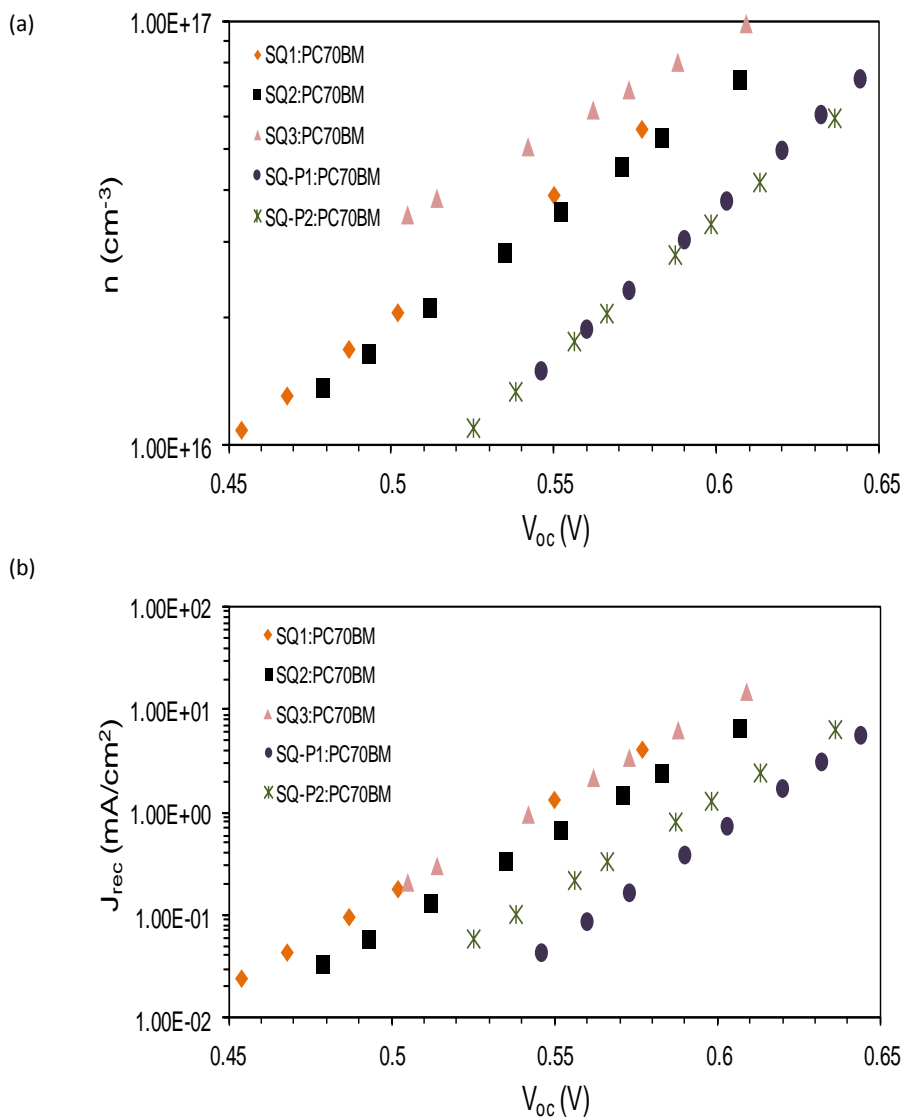


**Figure S4:** (a) Normalized optical absorption spectra in solution (solid line) and thin film (dashed line).  
(b) Normalized UV-Abs Spectra for all SQ:PC<sub>70</sub>BM Device  
SQ1:PC<sub>70</sub>BM (1:3), SQ2:PC<sub>70</sub>BM (1:3), SQ3:PC<sub>70</sub>BM (1:3), SQ-P1:PC<sub>70</sub>BM (1:3), SQ-P2:PC<sub>70</sub>BM (1:2)



**Figure S5:** External Quantum Efficiency for all SQ:PC<sub>70</sub>BM Device  
SQ1:PC<sub>70</sub>BM (1:3), SQ2:PC<sub>70</sub>BM (1:3), SQ3:PC<sub>70</sub>BM (1:3), SQ-P1:PC<sub>70</sub>BM (1:3), SQ-P2:PC<sub>70</sub>BM (1:2)

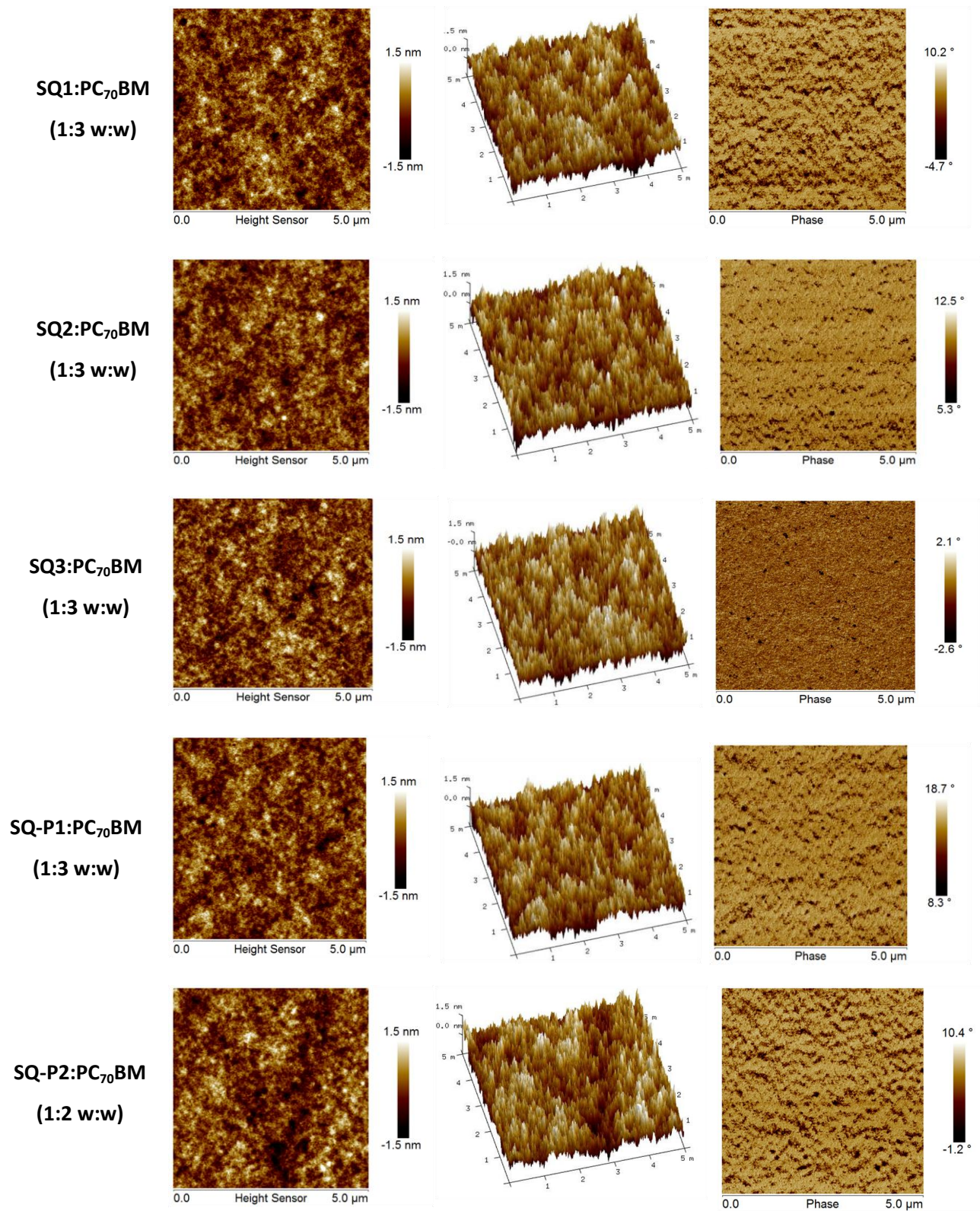




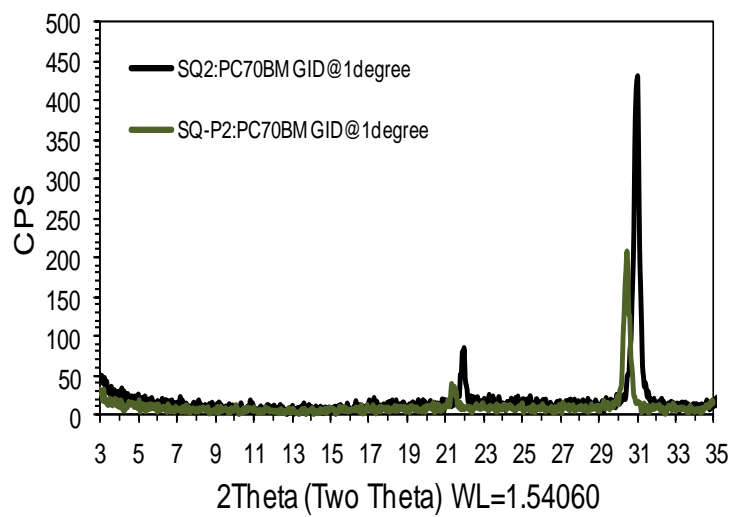
**Figure S6:** (a) Plot of average carrier density,  $n$  ( $\text{cm}^{-3}$ ) against  $V_{oc}$  (V)  
 (b) Plot of bimolecular recombination current density,  $J_{rec0}$  ( $\text{mA}/\text{cm}^2$ ) against  $V_{oc}$  (V)

**Table S3:**  $n(\text{cm}^{-3})$  and  $K_{rec}$  ( $\text{cm}^3/\text{s}$ ) at 1 sun intensity for all Squaraines

Squaraine	$n$ ( $\text{cm}^{-3}$ ) at 1 sun intensity	$K_{rec}$ ( $\text{cm}^3/\text{s}$ ) at 1 sun intensity
SQ1:PC <sub>70</sub> BM	$6 \times 10^{16}$	$1.49 \times 10^{-12}$
SQ2:PC <sub>70</sub> BM	$7 \times 10^{16}$	$1.40 \times 10^{-12}$
SQ3:PC <sub>70</sub> BM	$10 \times 10^{16}$	$1.73 \times 10^{-12}$
SQ-P1:PC <sub>70</sub> BM	$7 \times 10^{16}$	$1.19 \times 10^{-12}$
SQ-P2:PC <sub>70</sub> BM	$6 \times 10^{16}$	$2.10 \times 10^{-12}$



**Figure S7:** AFM topographic image (left), 3D surface image (middle) and phase image (right) of the individual SQ:PC<sub>70</sub>BM blend on ITO glass/Pedot:PSS substrates



**Figure S8:** GID Spectra of SQ2:PC<sub>70</sub>BM and SQ-P2:PC<sub>70</sub>BM measured at 1.0 degree