# Accepted Manuscript

Elucidating the impact of *N*-arylanilino substituents of squaraines on their photovoltaic performances

Daobin Yang, Yuya Hayashi, Hisahiro Sasabe, Tsukasa Igarashi, Takeshi Sano, Junji Kido

PII: S1566-1199(18)30673-6

DOI: https://doi.org/10.1016/j.orgel.2018.12.031

Reference: ORGELE 5040

To appear in: Organic Electronics

Received Date: 13 November 2018

Revised Date: 14 December 2018

Accepted Date: 18 December 2018

Please cite this article as: D. Yang, Y. Hayashi, H. Sasabe, T. Igarashi, T. Sano, J. Kido, Elucidating the impact of *N*-arylanilino substituents of squaraines on their photovoltaic performances, *Organic Electronics* (2019), doi: https://doi.org/10.1016/j.orgel.2018.12.031.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





# Elucidating the impact of *N*-arylanilino substituents of squaraines on their photovoltaic performances

Daobin Yang,<sup>a,b,‡</sup> Yuya Hayashi,<sup>c,‡</sup> Hisahiro Sasabe,<sup>a,b,c,\*</sup> Tsukasa Igarashi,<sup>c</sup> Takeshi Sano,<sup>a,b,c</sup> and Junji Kido<sup>a,b,c,\*</sup>

<sup>a</sup> Research Center for Organic Electronics, Yamagata University, Yonezawa 992-8510, Japan

<sup>b</sup> Frontier Center for Organic Materials, Yamagata University, Yonezawa 992-8510, Japan

<sup>c</sup> Department of Organic Materials Science, Yamagata University, Yonezawa 992-8510, Japan

<sup>‡</sup> The first two authors contributed equally to this work.

\*E-mail: h-sasabe@yz.yamagata-u.ac.jp (H. S.), kid@yz.yamagata-u.ac.jp (J. K.).

**Keywords:** squaraines, N-arylanilino substituent, morphology, small molecules, organic photovoltaic

**Abstract:** Squaraines have attracted increasing research attention for organic photovoltaic applications because of their facile and low-cost synthesis, and intense and broad absorption in the visible and near-infrared (Vis-NIR) regions. Herein, three new squaraines, *N*-phenylanilino substituted **SQ-EP**, *N*-2-naphthylanilino substituted **SQ-EN**, and *N*-fluorenylanilino substituted **SQ-EF**, were developed for improving the hole

mobility of aniline-based squaraines. The substitution effect of N-arylanilino groups on the optoelectronic properties of squaraines was investigated. These squaraines exhibited similar absorbance spectra, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels, and hole mobilities in their neat films. However, compared to their neat films, the hole mobility of the SQ-EP-based BHJ blend film showed the smallest decrease when blending with PC71BM ([6,6]-phenyl  $C_{71}$  butyric acid methyl ester). Besides, morphological studies have shown that a phase separation of 20-30 nm can only be observed in the SQ-EP/PC71BM blend film. Consequently, a solution-processed bulk-heterojunction (BHJ) organic photovoltaic (OPV) device fabricated with the as-cast SQ-EP/PC<sub>71</sub>BM blend film exhibited obviously higher power conversion efficiency (PCE: 5.4%) than those of the SQ-EN/PC<sub>71</sub>BM (PCE: 4.3%) or SQ-EF/PC71BM systems (PCE: 2.8%). This is one of the highest recorded PCE values in aniline-based squaraines single-junction BHJ-OPV devices. This much-enhanced PCE can be attributed to the significant increases in short-circuit current density ( $J_{sc}$ ) and fill factor (FF) of the SQ-EP/PC<sub>71</sub>BM-based device.

## 1. Introduction

Small molecules organic photovoltaic (SM-OPV) cells are considered a promising next-generation green energy technology because of their low-cost, low-weight, flexibility, color diversity, and low batch-to-batch variability.[1-4] Thus far, the highest power conversion efficiency (PCE) of a single-junction SM-OPV has reached 13.6%.[5]

However, the development of SM-OPV largely lags behind that of polymers-based OPV and perovskite solar cells.[6-9] Currently, donor materials are still one of the most important factors for obtaining high PCEs in SM-OPV devices. Therefore, chemists must focus more on the development of small molecule donor materials, to enable more predictive molecular structure/photovoltaic property relationships.

Among these small molecule donor materials, squaraines have gradually attracted great attention for use in organic photovoltaic applications, such as ternary, quaternary, tandem, and semitransparent solar cells, over the past decade.[10-21] this is for two key reasons: (1) squaraines possess intense and broad absorption in visible and near-infrared (Vis-NIR) spectral regions with very high molar extinction coefficients (typically over  $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and optical densities (typically over  $10^5$  cm<sup>-1</sup>), and (2) squaraines have a desirable facile and low-cost synthesis. A record PCE of over 7.0% has been achieved for squaraines-based a single-junction SM-OPV device.[22,23] However, this PCE still lags behind other SM-OPV devices.[24,25] Aniline-based squaraine derivative with four hydroxyl groups exhibited outstanding photovoltaic performance and has become the most classic photovoltaic materials from the squaraines family.[10] In 2009, Forrest and Thompson et al. first reported a vapor deposited planar-heterojunction (PHJ) OPV device with а PCE of 3.2%, using an aniline-based squaraine named DIB-SQ (2,4-bis[4-(*N*,*N*-diisobutylamino)-2,6-dihydroxyphenyl]squaraine).[26] Afterward, they developed a series of N,N-diarylanilino substituted squaraines to achieve a PCE of 5.7% in solution-processed PHJ-OPV devices.[27-29] However, almost all these squaraines have low solubilities, even in halogenated solvents ( $< 5 \text{ mg mL}^{-1}$ ), such as chloroform

and chlorobenzene. This greatly restricts the fabrication of solution-processed bulk-heterojunction (BHJ) OPV devices. To overcome this drawback, Collison et al. developed a series of N,N-dialkylaniline-based squaraines with extended alkyl side substituents, enabling higher solubility (> 24 mg mL<sup>-1</sup> in chloroform). This resulted in the fabrication of a solution-processed BHJ-OPV device with a PCE of 4.8%.[30-32] To further improve device efficiency, group reported a series our of *N*-alkyl-*N*-phenylaniline-based squaraines with good solubility (> 8 mg mL<sup>-1</sup> in chloroform). Nevertheless, when applied in a solution-processed BHJ-OPV, the highest PCE reached 4.9%.[33] The biggest limiting factor affecting PCE is the low hole mobility  $(\mu_{\rm h})$  in the blend film, typically  $10^{-6} \sim 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Therefore, by increasing hole mobility, the PCE of aniline-based squaraines OPV devices can be further enhanced.

As all we know, the introduction of large aromatic units is a very important and effective strategy for increasing the hole mobility of electron-donor materials. Herein, three new N-(2-ethylhexyl)-N-arylanilino substituted squaraines, N-(2-ethylhexyl)-N- phenylanilino substituted **SQ-EP**, N-(2-ethylhexyl)-N-2-naphthylanilino substituted **SQ-EN**, and N-(2-ethylhexyl)-N-fluorenylanilino substituted **SQ-EF** (as shown in Scheme 1), have been designed and synthesized to improve hole mobility of aniline-based squaraines. Meanwhile, the substitution effect of N-arylanilino groups on the optoelectronic properties of squaraines was investigated. An N-2-ethylhexyl group was introduced to improve solubility. Finally, the solubility, optical, electrochemical, electronic, mobility, morphological, and photovoltaic properties were carefully investigated.





Scheme 1 Chemical structures of the three squaraines.

#### 2. Experimental section

#### 2.1 Instruments and characterization

<sup>1</sup>H NMR spectra were recorded on JEOL 400 (400 MHz) spectrometer. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under an N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>. The purity of squaraines was measured by HITACHI EZChrom Elite high-performance liquid chromatography (equipped with DAD and RI detectors). Absorption spectra of both solution and thin-film samples of squaraines were recorded using a SHIMADZU UV-3150 UV-Vis-NIR spectrophotometer. The solution samples were prepared in chloroform solution at a concentration of  $2.0 \times 10^{-6}$  mol L<sup>-1</sup>, while the thin-film samples were obtained by spin-coating from chloroform solutions (9 mg mL<sup>-1</sup>, 2000 rpm/30s) on quartz substrates in an N<sub>2</sub>-filling glovebox. The ground-state geometries and electronic structures of the three compounds were calculated with Gaussian 09 software, using density functional theory (DFT) based on B3LYP/6-31G(d,p) levels. The morphology of the blend films (substrates: ITO/ MOO<sub>3</sub> (8 nm)) was analyzed by atomic force microscopy

(AFM) in tapping mode under ambient condition using Agilent 5000.

Cyclic Voltammetry (CV) measurement was carried out in  $2.5 \times 10^{-4}$  mol L<sup>-1</sup> anhydrous dichloromethane (DCM) with 0.13 mol L<sup>-1</sup> tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>, as supporting electrolyte) under an N<sub>2</sub> atmosphere at a scan rate of 100 mV s<sup>-1</sup> using a PC controlled ALS/CHI 660B electrochemical workstation. The CV system was constructed using a glassy carbon electrode as the working electrode, Pt wire as the counter electrode, an Ag/Ag<sup>+</sup> electrode as the reference electrode, and ferrocene were used as an internal standard. The electrochemical potential is internally calibrated against the standard ferrocene/ ferrocenium redox couple (Fc/Fc<sup>+</sup>), which has a known reduction potential of –4.80 eV relative to the vacuum level. The HOMO and LUMO of squaraines were calculated according to the following equations:

$$HOMO = - [eE_{ox}^{onest} + 4.80]$$
$$LUMO = - [eE_{red}^{onest} + 4.80]$$

Where  $E_{ox}^{onset}$  and  $E_{red}^{onest}$  are the onset oxidation potential and the reduction potential onset, respectively, *vs.* Fc/Fc<sup>+</sup>.

#### 2.2 Device preparation and characterization

Electron acceptor PC<sub>71</sub>BM was purchased from Solarmer Energy, Inc. Small molecules organic photovoltaic devices were fabricated using indium-tin-oxide (ITO) coated the glass as a substrate with a sheet resistance of 10  $\Omega$  sq<sup>-1</sup>. Patterned ITO-coated glass substrates were sequentially cleaned using detergent, deionized water, acetone, and isopropanol in an ultrasonic bath for 30 min each. The cleaned substrates were dried in an

oven at 65 °C for 12 h before use. The substrates were treated by UV-ozone for 20 min, then immediately transferred into a high vacuum chamber for deposition of 8 nm MoO<sub>3</sub> at a pressure of less than  $2 \times 10^{-4}$  Pa with a rate of about 0.20 Å s<sup>-1</sup>. Subsequently, photoactive layers (thickness: around 70 nm) were fabricated by spin-coating a blend of squaraines and  $PC_{71}BM$  in chloroform with the total concentration of 20 mg mL<sup>-1</sup> in an N<sub>2</sub>-filling glovebox. Afterwards, the substrates were transferred back to the high-vacuum chamber, where BCP (bathocuproine, 10 nm) and Al (100 nm) were deposited as the top electrode at pressures of less than  $8 \times 10^{-5}$  Pa with a rate of about 0.20 Å s<sup>-1</sup> and  $2 \times 10^{-4}$  Pa with a rate of 1.5~5.0 Å s<sup>-1</sup>, respectively, resulting in a final device with the structure of ITO/MoO<sub>3</sub> (8 nm)/squaraines: PC<sub>71</sub>BM (70 nm)/BCP (10 nm)/Al (100 nm). The active area of the organic photovoltaic cell is 9 mm<sup>2</sup>. Current density-voltage (*J-V*) and external quantum efficiency (EQE) characterizations of organic photovoltaic cells were performed on a CEP-2000 integrated system manufactured by Bunkoukeiki Co. under 100 mW cm<sup>-2</sup> simulated AM 1.5G light illumination. All of the measurements were carried out in ambient air.

Hole-only and electron-only devices were fabricated with the structure of ITO/MoO<sub>3</sub> (8 nm)/squaraines (65 nm) or squaraines: PC<sub>71</sub>BM (70 nm)/MoO<sub>3</sub> (8 nm)/Al (100 nm) and ITO/ZnO (20 nm)/squaraines: PC<sub>71</sub>BM (70 nm)/BCP (10 nm)/Al (100 nm), respectively. Mobility is extracted by fitting the current density-voltage curves using space charge limited current (SCLC),[34] the *J-V* curves of the devices are plotted as  $J^{0.5}$  versus V using the following equation:

$$J = \frac{9}{8} \frac{\varepsilon_r \times \varepsilon_o \times \mu \times V^2}{L^3} \exp\left(0.89\beta \sqrt{\frac{V}{L}}\right)$$

where *J* is current density, *L* is film thickness of active layer,  $\mu_h$  is hole mobility,  $\mu_e$  is electron mobility,  $\varepsilon_r$  is relative dielectric constant of the transport medium,  $\varepsilon_0$  is permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $V (= V_{appl} - V_{bi})$  is the internal voltage in the device, where  $V_{appl}$  is the applied voltage to the device and  $V_{bi}$  is the built-in voltage due to the relative work function difference of the two electrodes.

#### 2.3 Synthesis

The synthetic details of intermediates **1a-1c**, **2a-2c**, and **3a-3c** are shown in the Supporting Information. All the chemicals were obtained from commercial sources and used as received without further purification.



Scheme 2 Synthetic routes to the three squaraines.

#### Compound SQ-EP

Compound **3a** (925 mg, 2.95 mmol) and squaric acid (167 mg, 1.46 mmol) were dissolved in 15 mL of *n*-butanol and 45 mL of toluene, and the reaction mixture was degassed with nitrogen for 30 min. Then, the reaction mixture was refluxed for 24 h. The reaction mixture was concentrated to about 10 mL. 20 mL of cyclohexane was added to the reaction mixture, which precipitated a green solid. The green solid was filtered, and recrystallized from cyclohexane/ ethanol (V/ V=3/ 1) to afford compound **SQ-EP** as a green solid (860 mg, yield: 83%). M.p 163-164 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 10.94 (s, 4H, OH), 7.89 (t, 4H, *J*=7.2 Hz, ArH), 7.45 (t, 2H, *J*=7.2 Hz, ArH), 7.18 (d, 4H, *J*=7.2 Hz, ArH), 5.74 (s, 4H, ArH), 3.66 (d, 4H, *J*=7.2 Hz, NCH<sub>2</sub>), 1.73-1.67 (m, 2H, CH), 1.43-1.16 (m, 16H, CH<sub>2</sub>), 0.87-0.80 (m, 12H, CH<sub>3</sub>); purity: 100% (HPLC, eluent: tetrahydrofuran/methanol=1/4); MS (ESI): m/z [M+H]<sup>+</sup> 706; elemental anal. Calcd for C<sub>44</sub>H<sub>52</sub>N<sub>2</sub>O<sub>6</sub>: C 74.97, H 7.44, N 3.97; found, C 74.95, H 7.35, N 3.91.

#### Compound SQ-EN

Compound **SQ-EN** was obtained as a yellow liquid (1000 mg, yield: 85%) from the reaction of compound **3b** (1072 mg, 2.95 mmol) and squaric acid (167 mg, 1.46 mmol) according to the same procedures described for the synthesis of compound **SE-EP**. M.p 252-253 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 10.96 (s, 4H, OH), 7.92 (d, 2H, *J*=8.0 Hz, ArH), 7.89-7.87 (m, 2H, ArH), 7.83-7.80 (m, 2H, ArH), 7.66(d, 2H, *J*=1.2 Hz, ArH),

7.56-7.52 (m, 4H, ArH), 7.28 (d, 2H, J=8.0 Hz, ArH), 5.79 (s, 4H, ArH), 3.78 (d, 4H, J=7.2 Hz, NCH<sub>2</sub>), 1.78-1.70 (m, 2H, CH), 1.50-1.18 (m, 16H, CH<sub>2</sub>), 0.85-0.81 (m, 12H, CH<sub>3</sub>); purity: 100% (HPLC, eluent: tetrahydrofuran/methanol=1/4); MS (ESI): m/z [M+H]<sup>+</sup> 806; elemental anal. Calcd for C<sub>52</sub>H<sub>56</sub>N<sub>2</sub>O<sub>6</sub>: C 77.58, H 7.01, N 3.48; found, C 77.48, H 6.85, N 3.46.

#### Compound SQ-EF

Compound **SQ-EF** was obtained as a green solid (1080 mg, yield: 79%) from the reaction of compound **3c** (1267 mg, 2.95 mmol) and squaric acid (167 mg, 1.46 mmol) according to the same procedures described for the synthesis of compound **SQ-EP**. M.p 241-242 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 10.95 (s, 4H, OH), 7.76 (d, 2H, *J*=8.0 Hz, ArH), 7.73 (d, 2H, *J*=6.0 Hz, ArH), 7.45 (d, 2H, *J*=6.0 Hz, ArH), 7.39-7.33 (m, 4H, ArH), 7.24 (d, 2H, *J*=2.0 Hz, ArH), 7.14 (d, 2H, *J*=8.0 Hz, ArH), 5.82 (s, 4H, ArH), 3.70 (d, 4H, *J*=7.6 Hz, NCH<sub>2</sub>), 1.75-1.68 (m, 2H, CH), 1.49 (m, 12H, CH<sub>3</sub>), 1.45-1.15 (m, 16H, CH<sub>2</sub>); 0.85-0.80 (m, 12H, CH<sub>3</sub>); purity: 100% (HPLC, eluent: tetrahydrofuran/ methanol=1/4); MS (ESI): *m*/*z* [M+H]<sup>+</sup>938; elemental anal. Calcd for C<sub>62</sub>H<sub>68</sub>N<sub>2</sub>O<sub>6</sub>: C 79.46, H 7.31, N 2.99; found, C 79.39, H 7.35, N 2.97.

#### 3. Results and discussion

#### 3.1 Synthesis and characterization

The synthetic routes to the three objective squaraines are illustrated in Scheme 2. All the

squaraines were synthesized via a four-step facile procedure consisting of an Ullmann, Buchwald-Hartwig, demethylation, and dehydration condensation reactions in series. The molecular structures of the three squaraines were carefully characterized using <sup>1</sup>H NMR spectroscopy, mass spectrometry, and elemental analysis analyses. Furthermore, the purities of the three squaraines were confirmed to be > 99.9% by HPLC analyses. Additionally, good solubility is essential to prepare smooth, uniform films in solution-processed OPV devices. As shown in Table 1, among these squaraines, SQ-EP and SQ-EF have good solubilities (> 25 mg mL<sup>-1</sup>) in halogenated solvents such as chloroform (CHCl<sub>3</sub>) and dichlorobenzene (CB), whereas **SQ-EN** is only moderately soluble (around 9 mg mL<sup>-1</sup> in CHCl<sub>3</sub> and CB). Interestingly, **SO-EP** is even soluble in non-halogenated or green solvents such as toluene, tetrahydrofuran (THF), N-methyl pyrrolidone (NMP), indicating great potential for the fabrication of solution-processed OPV devices, without the use of halogenated solvents.[35] As shown in Fig. S1 and Table 2, all the squaraines show a high decomposition temperature  $(T_d)$  of over 300 °C, demonstrating that they have good thermal stability.

squaraines	CHCl <sub>3</sub>	CB	toluene	THF	NMP
SQ-EP	> 30	> 30	> 15	>15	> 15
SQ-EN	$\approx 9^{a}$	$\approx 9^{a}$	< 1	< 1	< 1
SQ-EF	> 25	> 25	$\approx 5$	> 10	pprox 8

**Table 1** The solubility of the three squaraines (unit: mg mL<sup>-1</sup>).

<sup>*a*</sup> Heated at 70 °C for 5 min, then returned to room temperature.

#### **3.2 Optical properties**

The UV-Vis-NIR absorption spectra of the three squaraines in dilute chloroform solutions and in thin films are shown in Fig. 1, with the corresponding data summarized in Table 2. In dilute solution, all the squaraines display a strong absorption band with  $\lambda_{max}$  of 652-661 nm, and a very high molar extinction coefficient of over  $1.0 \times 10^5 \text{ M}^{-1}$ cm<sup>-1</sup>. Relative to SQ-EP ( $\lambda_{max}$  = 652 nm), the absorption maxima of SQ-EN is red-shifted by only 5 nm, while that of SQ-EF is slightly red-shifted by 9 nm. The red-shift can be attributed to its slightly larger  $\pi$ -conjugation. In comparison to their dilute solution samples, all the squaraines show a red-shifted and broadened absorbance spectra over the 550 to 750 nm range in thin films with a maximum optical density of over  $1.0 \times 10^5$  cm<sup>-1</sup>. However, in absorbance spectra, SQ-EP shows a red-shifted peak maxima of 36 nm, between the solution and thin film sample, whereas SQ-EN displays a red-shifted peak maxima of 34 nm and SQ-EF has only 29 nm red-shifted. The optical band gaps of the squaraines are determined by their absorption edges. SQ-EN, and SQ-EF are calculated to have a band gap of 1.58 and 1.57 eV, respectively, which are slightly lower than that of SQ-EP (1.61 eV). Additionally, the absorption spectra of squaraines/PC<sub>71</sub>BM-blend films were measured. As shown in Fig. 2, the squaraines absorbance band of the blend films are consistent with the corresponding neat squaraines films absorbance spectra, indicating that the PC71BM does not influence the  $\pi$ -conjugation of these squaraines molecules.



Fig. 1 UV-Vis-NIR absorbance spectra of the three squaraines in solutions (a), and thin films (b).

Squaraines	Absorption 2	λ <sub>abs max</sub> (nm)	$E_g^{opt}$	T <sub>d</sub>	НОМО	LUMO
	Solution ( $M^{-1} cm^{-1}$ )	Film (cm <sup>-1</sup> )	(eV)	(°C)	(eV)	(eV)
SQ-EP	$652 (3.28 \times 10^5)$	$688 (1.25 \times 10^5)$	1.61	305	-5.32	-3.65
SQ-EN	$657 (3.05 \times 10^5)$	$691 (1.19 \times 10^5)$	1.58	313	-5.32	-3.67
SQ-EF	661 (2.91×10 <sup>5</sup> )	$690 (1.10 \times 10^5)$	1.57	305	-5.30	-3.66

 Table 2 Optical and electrochemical properties of the three squaraines.



Fig. 2 UV-Vis-NIR absorbance spectra of the squaraines/PC<sub>71</sub>BM (1:2, weight ratio)-blend films.

#### **3.3 Electrochemical properties**

To estimate the energy levels of the molecules, the electrochemical properties were

investigated by cyclic voltammetry. As shown in Fig. 3, all the three squaraines exhibit similar oxidation and reduction potentials. Thus, they have similar HOMO (~ -5.30 eV) and LUMO (~ -3.66 eV) energy levels (see Table 2). These deep HOMO energy levels are beneficial for obtaining a high  $V_{oc}$  in OPV devices.[36] Moreover, the LUMO energy differences between the three squaraines and PC<sub>71</sub>BM (-4.0 eV) is 0.34 eV, which is very close to the ideal value (0.30 eV). It is indicated that efficient exciton dissociation and charge separation can be achieved in these OPV devices.[37]



Fig. 3 Cyclic voltammogram of the three squaraines.

#### **3.4 Electronic properties**

To gain further insights into the effect of an *N*-arylanilino substituent on the electronic properties of squaraines, quantum chemical density functional theory (DFT) calculations were performed. As shown in Fig. 4, all these squaraines show very large dihedral angles between the *N*-aryl and anilino units: 74° for **SQ-EP**, 68° for **SQ-EN**, and 75° for **SQ-EF**. Hence, it can be concluded that the contribution of the *N*-aryl groups to the  $\pi$ -conjugation of the whole molecular skeleton is limited. This can be verified from the electronic

density distribution of these squaraines. As shown in Fig. 5, most of their HOMO electronic density distributions are delocalized on the molecular skeleton, not on *N*-aryl groups.



Fig. 5 The electron density distributions of the three squaraines.

#### 3.5 Photovoltaic performance

To gain insight to the chemical structure-photovoltaic property relationship, BHJ-OPV devices with a conventional structure of ITO/ MoO<sub>3</sub> (8 nm)/ squaraine:  $PC_{71}BM$  (70 nm)/ BCP (10 nm)/ Al (100 nm) were fabricated, in which the squaraine and  $PC_{71}BM$  acted as the donor (D) and acceptor (A), respectively. First the blend ratios of squaraines:  $PC_{71}BM$  were tuned from 1:1 to 1:2, and 1:3 to optimize the photovoltaic performance of the

BHJ-OPV devices (see Fig. S2, S3, S4, and Table S1, S2, S3). The squaraine: PC<sub>71</sub>BM blend ratio of 1:2 was selected for in-depth research. The current density-voltage (J-V) curves and the external quantum efficiency (EQE) spectra are shown in Fig. 6, and the corresponding data are listed in Table 3. Among these BHJ-OPV devices, the **SQ-EP**/PC<sub>71</sub>BM-based device exhibits the highest PCE of 5.42% with a  $V_{\infty}$  of 1.00 V,  $J_{sc}$ of 10.85 mA cm<sup>-2</sup>, and FF of 0.50 without any treatment. This is one of the highest PCEs recorded for squaraines-based solution-processed BHJ-OPV devices. Whereas the PCE of SQ-EN/PC71BM- and SQ-EF/PC71BM-based devices are 4.33% and 2.84%, respectively. This drop in PCE can be attributed to their much lower  $J_{sc}$  and FF, as compared to the SQ-EP/PC<sub>71</sub>BM-based device. All the devices show an extremely high  $V_{oc}$  of 1.00 V, which is consistent with their deep HOMO energy levels (~-5.30 eV). To elucidate the origin of the decreased  $J_{sc}$ , the external quantum efficiency (EQE) spectra of the devices were measured. As listed in Table 3, the integrated current densities  $(J_{sc}^{EQE})$  of EQE spectra of the SQ-EP/PC71BM-, SQ-EN/PC71BM-, and SQ-EF/PC71BM-based devices are 10.60, 9.68, and 7.69 mA cm<sup>-2</sup>, respectively. These values are in agreement with the  $J_{\rm sc}$  values obtained from the J-V curves, with less than 5% mismatch. As shown in Fig. 6 (b), the broad and efficient EQE spectra from 600 to 750 nm indicates that these squaraines make strong contributions to the photo-current. Among these EQE spectral, the SQ-EN/PC<sub>71</sub>BM- and SQ-EF/PC<sub>71</sub>BM- based devices exhibit slightly broader EQE spectral responses from 735 to 800 nm. However, between 300 to 730 nm, the SQ-EN/PC71BM- and SQ-EF/PC71BM-based devices show much lower EQE values than that of the SQ-EP/PC<sub>71</sub>BM-based devices, thereby resulting in obviously a lowered  $J_{sc}$ .

The FF of the **SQ-EN**/PC<sub>71</sub>BM- and **SQ-EF**/PC<sub>71</sub>BM-based devices is also remarkably lower than that of the **SQ-EP**/PC<sub>71</sub>BM-based device. The lowed FF can be attributed to the decreased hole mobility and poorly balanced hole/electron mobility.



**Fig. 6** a) *J-V* curve and b) EQE spectra of OPV cells fabricated with the **SQ-EP**/PC<sub>71</sub>BM, **SQ-EN**/PC<sub>71</sub>BM, and **SQ-EF**/PC<sub>71</sub>BM blend films.

Active layers	$V_{ m oc}{}^a$	$J_{\rm sc}^{a}$	$J_{sc}^{EQE}$	FF <sup><i>a</i></sup>	PCE <sup><i>a</i></sup>
(D : A = 1 : 2)	(V)	$(mA cm^{-2})$	$(mA cm^{-2})$		(%)
$SQ-EP : PC_{71}BM$	1.00 (1.00)	10.85 (10.60)	10.33	0.50 (0.50)	5.42 (5.30)
<b>SQ-EN</b> : $PC_{71}BM$	1.00 (1.00)	10.08 (9.68)	9.67	0.43 (0.43)	4.33 (4.16)
<b>SQ-EF</b> : PC <sub>71</sub> BM	1.00 (1.00)	7.90 (7.69)	7.66	0.36 (0.36)	2.84 (2.77)

Table 3 Photovoltaic performance of organic solar cells.

<sup>*a*</sup> Average values of eight individual cells are given in parentheses.

#### 3.6 Mobility

The hole  $(\mu_h)$  and electron  $(\mu_e)$  mobility of the three squaraines neat films and squaraine/PC<sub>71</sub>BM (1:2, wt%) blend films were evaluated by the space charge limited

current (SCLC) method, these results are listed in Table 4. All neat films of the three squaraines show a very similar  $\mu_h$  around  $1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , indicating that larger *N*-arylanilino units do not necessarily improve overall hole mobility. However, we observe quite different  $\mu_h$  from the squaraine/PC<sub>71</sub>BM blend films; the  $\mu_h$  of the **SQ-EP**/PC<sub>71</sub>BM blend film is  $3.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , whereas the  $\mu_h$  of the **SQ-EN**/PC<sub>71</sub>BM and **SQ-EF**/PC<sub>71</sub>BM blend films are  $2.3 \times 10^{-5}$  and  $1.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. Hence, for squaraines with smaller *N*-arylanilino units, the blend film has a greater  $\mu_h$ . Moreover, the **SQ-EP**/PC<sub>71</sub>BM blend film  $(\mu_e/\mu_h; 3.1)$  has a more balanced hole and electron mobility than the **SQ-EN**/PC<sub>71</sub>BM ( $\mu_e/\mu_h$ : 4.2) and **SQ-EF**/PC<sub>71</sub>BM systems ( $\mu_e/\mu_h$ : 5.7). This results in a higher FF for the **SQ-EP**/PC<sub>71</sub>BM-based device. Therefore, a higher  $\mu_h$  together with a better-balance of  $\mu_e/\mu_h$  in the blend films leads to more effective charge carrier transport and extraction, which contributes to an increased  $J_{sc}$  and FE.[38]

	A			
Squaraines	$\mu_h^a$ $\mu_h^b$		$\mu_e{}^b$	$\mu_e/~\mu_h$
SQ-EP	$1.1 \times 10^{-4}$	$3.0 \times 10^{-5}$	$9.4\times10^{-5}$	3.1
SQ-EN	$1.3 \times 10^{-4}$	$2.3\times10^{-5}$	$9.7\times10^{-5}$	4.2
SQ-EF	$1.1 \times 10^{-4}$	$1.6  imes 10^{-5}$	$9.2  imes 10^{-5}$	5.7

Table 4 The mobility of the three squaraines. (unit:  $cm^2 V^{-1} s^{-1}$ )

<sup>*a*</sup> neat films; <sup>*b*</sup> blend films of squaraines/PC<sub>71</sub>BM (1/2, wt%).

#### **3.7 Morphology**

The morphologies of the squaraines/PC71BM blend films were evaluated by atomic

force microscopy (AFM). The phase and height images are shown in Fig. 7. As shown in Fig. 7d, 7e, and 7f, all the blend films have a similar root mean square (RMS), 1.3 nm for the **SQ-EP**/PC<sub>71</sub>BM blend film, 1.2 nm for the **SQ-EN**/PC<sub>71</sub>BM blend film, and 1.1 nm for the **SQ-EF**/PC<sub>71</sub>BM blend film. This indicates that they have all very smooth surfaces. However, their phase separations are much different. As shown in Fig. 7a, 7b, and 7c, the **SQ-EP**/PC<sub>71</sub>BM blend film exhibits an excellent nanoscale phase separation of 20-30 nm, whereas this phase separation cannot be observed in the **SQ-EN**/PC<sub>71</sub>BM and **SQ-EF**/PC<sub>71</sub>BM blend films. These other two films are amorphous, in particular, the **SQ-EF**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation for the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film of the separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film of the separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film. The nanoscale phase separation of the **SQ-EP**/PC<sub>71</sub>BM blend film of the separation of the **SQ-EP**/PC<sub>71</sub>BM blend film of the separation of the **SQ-EP**/PC<sub>71</sub>BM blend film of the separation of the separati



**Fig. 7** AFM phase (up) and height (down) images of the **SQ-EP**/PC<sub>71</sub>BM (a, d), **SQ-EN**/PC<sub>71</sub>BM (b, e), and **SQ-EF**/PC<sub>71</sub>BM (c, f) blend films.

### 4. Conclusion

In conclusion, we elucidated the impact of N-arylanilino (N-phenylanilino, N-2-naphthylanilino, and N-fluorenylanilino) substituents of squaraines on solubility, absorption, energy level, hole mobility, phase separation, and subsequently, photovoltaic performance of the squaraines/PC71BM-based BHJ-OPV devices. Despite their molecular structural differences, the absorbance spectra, HOMO and LUMO energy levels, and hole mobility of the neat films are very similar for each squaraine, since they share a very similar  $\pi$ -conjugated backbone. However, the differences in properties affecting the photovoltaic performances become apparent when these squaraines are blended with PC<sub>71</sub>BM. For smaller, planar N-arylanilino substituted squaraines, the hole mobility of the squaraines/PC<sub>71</sub>BM blend films show a smaller drop as compared to their neat films. In addition, the phase separation of the squaraines/PC<sub>71</sub>BM blend films happens gradually, leading to a large increase in the  $J_{sc}$  and FF of their OPV devices. As a result, the SQ-EP/PC71BM-based solution-processed BHJ-OPV device exhibits a PCE of 5.4%, which is higher than the PCE values of the **SQ-EN**/PC<sub>71</sub>BM and **SQ-EF**/PC<sub>71</sub>BM-based device. This is, to the best of our knowledge, one of the highest PCE values in aniline-based squaraines single-junction BHJ-OPV devices. This interesting result demonstrates that the photovoltaic performance of smaller planar N-arylanilino substituted squaraines can still be improved. Moreover, SQ-EP is a promising candidate for solution-processed OPV devices, using halogenated and green solvents.

#### **Supporting Information**

The synthesis of intermediates, TGA curves, the photovoltaic performances and *J*-*V* curve characteristics of OPV devices fabricated with squaraines/PC<sub>71</sub>BM of different blend ratios.

#### Acknowledgments

We thank the Japan Science and Technology Agency (JST) for financial support via the Center of Innovation (COI) program and the Adaptable and Seamless Technology Transfer Program (A-STEP, AS251Z00216M).

#### References

[1] J. Roncali, P. Leriche, P. Blanchard, Molecular materials for organic photovoltaics: small is beautiful, Adv. Mater. 26 (2014) 3821-3838.

[2] L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, Low-bandgap near-IR conjugated polymers/ molecules for organic electronics, Chem. Rev. 115 (2015) 12633-12665.

[3] S.D. Collins, N.A. Ran, M.C. Heiber, T.-Q. Nguyen, Small is powerful: recent progress in solution-processed small molecule solar cells, Adv. Energy Mater. 7 (2017) 1602242.

[4] O. Inganäs, Organic photovoltaics over three decades, Adv. Mater. 30 (2018) 1800388.

[5] Z. Zhou, S. Xu, J. Song, Y. Jin, Q. Yue, Y. Qian, F. Liu, F. Zhang, X. Zhu, High-efficiency small-molecule ternary solar cells with a hierarchical morphology enabled by synergizing fullerene and non-fullerene acceptors, Nat. Energy 3 (2018) 952-959.

[6] Z. Xiao, X. Jia, L. Ding, Ternary organic solar cells offer 14% power conversion efficiency, Sci. Bull. 62 (2017) 1562-1564.

Li, H. Yan, Use of two structurally similar small molecular acceptors enabling ternary organic solar cells with high efficiencies and fill factors, Energy Environ. Sci. 11 (2018) 3275-3282.

[7] T. Liu, Z. Luo, Q. Fan, G. Zhang, L. Zhang, W. Gao, X. Guo, W. Ma, M. Zhang, C. Yang, Y.

[8] N.J. Jeon, H. Na, E.H. Jung, T.-Y. Yang, Y.G. Lee, G. Kim, H.-W. Shin, S. Il Seok, J. Lee, J. Seo, A fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells, Nat. Energy 3 (2018) 682-689.

[9] D. Luo, W. Yang, Z. Wang, A. Sadhanala, Q. Hu, R. Su, R. Shivanna, G.F. Trindade, J.F. Watts, Z. Xu, T. Liu, K. Chen, F. Ye, P. Wu, L. Zhao, J. Wu, Y. Tu, Y. Zhang, X. Yang, W. Zhang, R.H. Friend, Q. Gong, H.J. Snaith, R. Zhu, Enhanced photovoltage for inverted planar heterojunction perovskite solar cells, Science 360 (2018) 1442-1446.

[10] G. Chen, H. Sasabe, T. Igarashi, Z. Hong, J. Kido, Squaraine dyes for organic photovoltaic cells, J. Mater. Chem. A 3 (2015) 14517-14534.

[11] F. Silvestri, M.D. Irwin, L. Beverina, A. Facchetti, G.A. Pagani, T.J. Marks, Efficient squaraine-based solution processable bulk-heterojunction solar cells, J. Am. Chem. Soc. 130 (2008) 17640-17641.

[12] G. Chen, H. Sasabe, Z. Wang, X.-F. Wang, Z. Hong, Y. Yang, J. Kido, Co-evaporated bulk heterojunction solar cells with > 6.0% efficiency, Adv. Mater. 24 (2012) 2768-2773.

[13] J.-S. Huang, T. Goh, X. Li, M.Y. Sfeir, E.A. Bielinski, S. Tomasulo, M.L. Lee, N. Hazari,A.D. Taylor, Polymer bulk heterojunction solar cells employing Forster resonance energy transfer,Nat. Photon. 7 (2013) 479-485.

[14] T. Goh, J.-S. Huang, K.G. Yager, M.Y. Sfeir, C.-Y. Nam, X. Tong, L.M. Guard, P.R. Melvin,

F. Antonio, B.G. Bartolome, M.L. Lee, N. Hazari, A.D. Taylor, Quaternary organic solar cells enhanced by cocrystalline squaraines with power conversion efficiencies >10%, Adv. Energy Mater. 6 (2016) 1600660.

[15] D. Yang, Y. Jiao, Y. Huang, T. Zhuang, L. Yang, Z. Lu, X. Pu, H. Sasabe, J. Kido, Two different donor subunits substituted unsymmetrical squaraines for solution-processed small molecule organic solar cells, Org. Electron. 32 (2016) 179-186.

[16] J. Liu, S. Zhao, Y. Huang, Z. Xu, B. Qiao, L. Yang, Y. Zhu, Z. Li, B. Yuan, X. Xu, Improving charge transport and suppressing charge recombination in small molecule ternary solar cells via incorporating Bis-PC<sub>71</sub>BM as a cascade material, Org. Electron. 46 (2017) 126-132.

[17] D. Yang, T. Sano, H. Sasabe, L. Yang, S. Ohisa, Y. Chen, Y. Huang, J. Kido, Colorful squaraines dyes for efficient solution-processed all small-molecule semitransparent organic solar cells, ACS Appl. Mater. Interfaces 10 (2018) 26465-26472.

[18] J.D. Zimmerman, B.E. Lassiter, X. Xiao, K. Sun, A. Dolocan, R. Gearba, D.A. Vanden Bout,
K.J. Stevenson, P. Wickramasinghe, M.E. Thompson, S.R. Forrest, Control of interface order by
inverse quasi-epitaxial growth of squaraine/fullerene thin film photovoltaics, ACS Nano 7 (2013)
9268-9275.

[19] D. Yang, H. Sasabe, Y. Jiao, T. Zhuang, Y. Huang, X. Pu, T. Sano, Z. Lu, J. Kido, An effective  $\pi$ -extended squaraine for solution-processed organic solar cells with high efficiency, J. Mater. Chem. A 4 (2016) 18931-18941.

[20] Q. Xiao, Y. Li, M. Han, F. Wu, M. Xie, Z. Li, L. Zhu, Z. Li, Butterfly-shaped asymmetric squaraine dimers for organic photovoltaics, J. Mater. Chem. C 6 (2018) 10547-10556.

[21] J. Wu, D. Yang, Q. Wang, L. Yang, H. Sasabe, T. Sano, J. Kido, Z. Lu, Y. Huang, Central dicyanomethylene-substituted unsymmetrical squaraines and their application in organic solar cells, J. Mater. Chem. A 6 (2018) 5797-5806.

[22] D. Yang, H. Sasabe, T. Sano, J. Kido, Low-band-gap small molecule for efficient organic solar cells with a low energy loss below 0.6 eV and a high open-circuit voltage of over 0.9 V, ACS Energy Lett. 2 (2017) 2021-2025.

[23] Y. Chen, L. Yang, J. Wu, G. Wang, W. Huang, F.S. Melkonyan, Z. Lu, Y. Huang, T.J. Marks,A. Facchetti, Performance, morphology, and charge recombination correlations in ternary squaraine solar cells, Chem. Mater. 30 (2018) 6810-6820.

[24] D. Deng, Y. Zhang, J. Zhang, Z. Wang, L. Zhu, J. Fang, B. Xia, Z. Wang, K. Lu, W. Ma, Z.Wei, Fluorination-enabled optimal morphology leads to over 11% efficiency for inverted small-molecule organic solar cells, Nat. Commun.7 (2016) 13740.

[25] L. Xiao, T. Lai, X. Liu, F. Liu, T.P. Russell, Y. Liu, F. Huang, X. Peng, Y. Cao, A low-bandgap dimeric porphyrin molecule for 10% efficiency solar cells with small photon energy loss, J. Mater. Chem. A 6 (2018) 18469-18478.

[26] S. Wang, E.I. Mayo, M.D. Perez, L. Griffe, G. Wei, P.I. Djurovich, S.R. Forrest, M.E. Thompson, High efficiency organic photovoltaic cells based on a vapor deposited squaraine donor, Appl. Phys. Lette. 94 (2009) 233304.

[27] S. Wang, L. Hall, V.V. Diev, R. Haiges, G. Wei, X. Xiao, P.I. Djurovich, S.R. Forrest, M.E. Thompson, N,N-Diarylanilinosquaraines and their application to organic photovoltaics, Chem. Mater. 23 (2011) 4789-4798.

[28] G. Wei, X. Xiao, S. Wang, J.D. Zimmerman, K. Sun, V.V. Diev, M.E. Thompson, S.R.

Forrest, Arylamine-based squaraine donors for use in organic solar cells, Nano Lett. 11 (2011) 4261-4264.

[29] G. Wei, X. Xiao, S. Wang, K. Sun, K.J. Bergemann, M.E. Thompson, S.R. Forrest,Functionalized squaraine donors for nanocrystalline organic photovoltaics, ACS Nano 6 (2012)972-978.

[30] C. Zheng, D. Bleier, I. Jalan, S. Pristash, A.R. Penmetcha, N.J. Hestand, F.C. Spano, M.S.Pierce, J.A. Cody, C.J. Collison, Phase separation, crystallinity and monomer-aggregatepopulation control in solution processed small molecule solar cells, Sol. Energy Mater. Sol. Cells157 (2016) 366-376.

[31] C. Zheng, I. Jalan, P. Cost, K. Oliver, A. Gupta, S.T. Misture, J.A. Cody, C.J. Collison, Impact of alkyl chain length on small molecule crystallization and nanomorphology in squaraine-based solution processed solar cells, J. Phys. Chem. C 121 (2017) 7750-7760.

[32] T. Coffey, A. Seredinski, J.N. Poler, C. Patteson, W.H. Watts, K. Baptiste, C. Zheng, J. Cody,C.J. Collison, Nanoscale characterization of squaraine-fullerene-based photovoltaic active layersby atomic force microscopy mechanical and electrical property mapping, Thin Solid Films 669(2019) 120-132.

[33] H. Sasabe, T. Igrashi, Y. Sasaki, G. Chen, Z. Hong, J. Kido, Soluble squaraine derivatives for4.9% efficient organic photovoltaic cells, RSC Adv. 4 (2014) 42804-42807.

[34] J. Dacuña, A. Salleo, Modeling space-charge-limited currents in organic semiconductors: extracting trap density and mobility, Phys. Rev. B 84 (2011) 195209.

[35] S. Zhang, L. Ye, H. Zhang, J. Hou, Green-solvent-processable organic solar cells, Mater. Today 19 (2016) 533-543.

[36] D. Yang, Q. Yang, L. Yang, Q. Luo, Y. Huang, Z. Lu, S. Zhao, Novel high performance asymmetrical squaraines for small molecule organic solar cells with a high open circuit voltage of 1.12 V, Chem. Commun. 49 (2013) 10465-10467.

[37] M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells-towards 10% energy-conversion efficiency, Adv. Mater. 18 (2006) 789-794.

[38] D. Yang, Y. Wang, T. Sano, F. Gao, H. Sasabe, J. Kido, A minimal non-radiative recombination loss for efficient non-fullerene all-small-molecule organic solar cells with a low energy loss of 0.54 eV and high open-circuit voltage of 1.15 V, J. Mater. Chem. A 6 (2018) 13918-13924.

[39] B. Walker, A.B. Tamayo, X.-D. Dang, P. Zalar, J.H. Seo, A. Garcia, M. Tantiwiwat, T.-Q. Nguyen, Nanoscale phase separation and high photovoltaic efficiency in solution-processed, small-molecule bulk heterojunction solar cells, Adv. Funct. Mater. 19 (2009) 3063-3069.

# Highlights

- Three *N*-arylanilino substituted squaraines are developed for organic photovoltaic.
- The hole mobility of the larger planar *N*-arylanilino substituted squaraines/PC<sub>71</sub>BM blend films show a larger drop.
- One of the highest PCE in aniline-based squaraines bulk-heterojunction organic photovoltaic.
- The photovoltaic performance of smaller planar *N*-arylanilino substituted squaraines can still be improved.