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**Quaternary Organic Solar Cells Enhanced by
Co-crystalline Squaraines with Power Conversion Efficiencies >10%**

Tenghooi Goh^{1,§}, Jing-Shun Huang^{1,5,§}, Kevin G. Yager², Matthew Y. Sfeir²,

Chang-Yong Nam², Xiao Tong², Louise M. Guard³, Patrick R. Melvin³,

Francisco Antonio¹, Benjamin G. Bartolome¹, Minjoo L. Lee⁴,

Nilay Hazari^{3★}, and André D. Taylor^{1★}

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¹Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, USA

²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

³Department of Chemistry, Yale University, New Haven, CT 06520, USA

⁴Department of Electrical Engineering, Yale University, New Haven, CT 06511, USA

⁵Currently with Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, CA 91125, USA

[§]The authors equally contributed to the work.

[★]e-mail: andre.taylor@yale.edu; nilay.hazari@yale.edu

Abstract

The incorporation of multiple donors into the bulk-heterojunction (BHJ) layer of organic polymer solar cells (PSCs) has been demonstrated as a practical and elegant strategy to improve photovoltaics performance. However, it is challenging to successfully design and blend multiple donors, while minimizing unfavorable interactions (e.g. morphological traps, recombination centers etc.). Here, we show a new Förster resonance energy transfer (FRET) based design utilizing the synergistic nature of three light active donors (two small molecules and a high-performance donor-acceptor polymer) with a fullerene acceptor to create highly efficient quaternary PSCs with power conversion efficiencies (PCEs) of up to 10.7%. Within this quaternary architecture, we reveal that the addition of small molecules in low concentrations broadens the absorption bandwidth, induces co-crystalline molecular conformations, and promotes rapid (picosecond) energy transfer processes. These results provide guidance for the design of multiple-donor systems using simple processing techniques to realize single-junction PSC designs with unprecedented PCEs.

Introduction

Polymer solar cells (PSC) are promising candidates to facilitate the use of sunlight as a renewable and sustainable energy source, due to their low cost, light weight, large area, and mechanical flexibility^[1-3]. In addition, they are often easy to process in solution, which makes them attractive for large scale production^[3]. Although PSC performance has improved steadily over the last decade, with power conversion efficiencies (PCEs) of ~8–10% reported for single-junction cells^[4-6], the performance of devices of this type is still significantly lower than those for inorganic, Si, or perovskite solar cells^[7]. As a result, further improvements in efficiency are required for PSCs to become practical.

Currently, some of the major obstacles that limit the efficiency of PSCs include: (i) the narrow photoresponse range, (ii) the high recombination rates, and (iii) a lack of control of the active layer morphology^[8-14]. Previous attempts to circumvent these problems include stacking multiple sub-cells into tandem solar cells (e.g. PSC/PSC^[15], PSC/Si^[16], PSC/perovskite^[17], PSC/inorganic^[18]) to produce higher output power. However, this approach demands extremely precise control of sub-cell thickness, film uniformity, interlayer properties, and bandgap engineering^[14, 19], which complicates processing and can lead to challenges in reliability, reproducibility, and expense. For these reasons, modern single-junction PSC designs that blend multiple active components together (e.g. dual donor, dual acceptor, incorporation of 2D or 1D

nanomaterials) have been vigorously pursued^[10, 20-24]. The major advantage of this approach is that it provides a simple and flexible method to tackle the major obstacles mentioned above^[25]. Nevertheless, careful materials design, composition, and selection are necessary to avoid problems caused by incompatible organic molecules and un-optimized loadings, which can disrupt charge transport percolation pathways or serve as recombination and trap sites^[26-31]. Recent works from Grancini et al.^[32], He et al.^[33] and Yang et al.^[31] have shown that improved PSC systems can be designed by combining low bandgap polymers^[34] with other compatible organic materials. Here, we show that strategically combining low bandgap high performance donor-acceptor (D-A) polymers with small molecules can significantly improve these PSCs.

Previously, we demonstrated the efficacy of Förster resonance energy transfer (FRET) to reduce recombination and increase exciton harvesting in a small molecule – polymer ternary system^[8], namely 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQ) in combination with poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PC₆₁BM). Overall, this ternary PSC architecture resulted in a 38% efficiency increase compared to devices containing only P3HT:PC₆₁BM. However, our best devices only generated an overall PCE of 4.51%, due to incomplete coverage of the full solar spectrum and the limitations of wide bandgap P3HT as a host donor material^[35]. Recently, we accomplished a 46% higher improvement (6.2% PCE) in FRET enhanced

small molecule-small molecule^[36] ternary devices comprised of asymmetrical 2-[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl]-4-diphenylamino] squaraine (ASSQ), 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl]squaraine (SQ), and a fullerene, C₆₀. We have also demonstrated energy transfer between P3HT and PTB7^[37]. Moreover, K. Cnops^[38] et al. and O. Reid et al.^[39] showed the feasibility of fabricating high efficiency planar heterojunction devices with FRET antenna layers. These foundational studies reveal that pairwise FRET donor and acceptor combinations in polymer-small molecule, small molecule-small molecule, and polymer-polymer designs can lead to significant PSC improvements by allowing the donors to function both independently and synergistically^[40]. Based on these findings, we hypothesized that by strategically combining multiple small molecule dyes, along with low-bandgap donor-acceptor polymers, high efficiency quaternary PSCs with several FRET pairs could be generated. To the best of our knowledge, there is almost no research into quaternary blends as a tool for further maximizing photon harvesting and establishing truly panchromatic PSCs.

In this article, we report systematic studies on ASSQ and 2,4-bis[4-(N,N-diphenylamino)-2,6-dihydroxyphenyl] squaraine (DPSQ)^[41] blended quaternary PSCs comprised primarily of a D-A copolymer with fullerene derivatives, *viz.* [6,6]-phenyl-C₆₁(or C₇₁)-butyric acid methyl ester (PC₆₁BM or PC₇₁BM). We start by examining the optoelectronic properties of the individual and blended components.

Various observations on the high degree of absorption-emission overlap and cascade energy level alignment, together with comparative results from ultrafast pump-probe spectroscopy allow us to identify the FRET pairs and show that the photophysical properties of the polymer hosts (*i.e.* (PTB7), thiophenated-PTB7 (PTB7-Th)^[42]; and poly-benzodithiophene-N-alkylthienopyrroledione (PT8)^[43]) complement the small molecules. In fact, the systems behave synergistically, for example the quaternary ASSQ:DPSQ:PTB7:PC₇₁BM system outperforms its ternary and binary counterparts. We establish correlations between the high photocurrent and fill factor observed in these quaternary films to optical, morphological, and mobility enhancement. Finally, we demonstrate that this approach can be applied to multiple D-A copolymer systems, *viz.* PTB7:PC₇₁BM, PTB7-Th:PC₇₁BM, and PT8:PC₆₁BM and report a PCE of 10.7% for our best quaternary blend.

Results and Discussions

Optical Characteristics

We show the molecular structures of the squaraine dyes, ASSQ and DPSQ, the high performance low bandgap polymers, PTB7, PTB7-Th and PT8, the acceptors PC₆₁BM and PC₇₁BM (*Figure 1a*) and the absorption spectra of the donor components (*Figure 1b*). The dyes ASSQ and DPSQ were selected for this study due to the characteristic absorption peaks at 550 nm and 720 nm, respectively. Both of these peaks

are located outside of the main absorption peaks for the D-A polymers, PTB7, PTB7-Th, and PT8. Together, ASSQ, DPSQ, and the aforementioned polymers were combined with an acceptor to design new quaternary systems with a broader absorption range. When ASSQ and DPSQ (1 wt. % each) were blended into a quaternary film we observe that the absorption increases in the expected regions at 550 nm and 720 nm (*Figure 1c*). Surprisingly, even with such low concentrations of ASSQ and DPSQ these quaternary blends exhibit significant increases in absorption presumably due to the high extinction coefficients of ASSQ ($\sim 9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 530 nm) and DPSQ ($\sim 3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 680 nm) (*Figures. 1 (c-e), SI(a-c)*). This is important as it has previously been reported that high additive loading and improper blending strategies can lead to disruptive perturbation of a film's internal structure^[44, 45] and exacerbate the extent of molecular incompatibility^[31]. As a control, we also prepared ternary films that only contain one small molecule, either ASSQ or DPSQ.

The magnitude of FRET enhancement is strongly dependent on the overlap integral of the donor emission and the absorption of the acceptor molecule^[46]. In fact, another reason for the selection of DPSQ is because of its strong absorption overlap with the photoluminescence (PL) of ASSQ, PTB7 and PT8 (*Figures SIa-c*), which we hypothesized could result in synergistic FRET combinations between ASSQ and DPSQ; ASSQ and PTB7 or PTB7-Th, as well as PT8 and DPSQ. Consistent with this proposal we measured quantum yields, Q_D , of 4.5% for ASSQ^[36], 0.97% for PTB7, and 12.6% for

PT8, respectively, in chloroform (*Table in S1d*). As the Förster radii for the different energy transfer pairs (2.9 to 6.2 nm) are comparable to the domain sizes obtained from X-ray scattering experiments (*vide infra*), the likelihood of energy transfer in quaternary films is also supported theoretically. Finally, we note that the energy levels of the multiple donors (ASSQ, polymer, DPSQ), and acceptor follows a cascading alignment and both DPSQ and ASSQ could provide additional pathways^[39] for charge dissociation in a photovoltaic device (*Figures 2a-b*).

Photophysics Study

We construct energy diagrams in *Figures 2a-b* based on the transient absorption (TA) spectroscopy experimental results, which suggest FRET occurs between ASSQ-DPSQ, ASSQ-PTB7 and PT8-DPSQ. Using a pumping wavelength of 500 nm, in the film containing only ASSQ (*Figure 2c*), the negative signal (red) between 550-600 nm at early times (<10 ps) corresponds to ASSQ absorption, and represents the ground-state bleach (GSB) of ASSQ, while the negative signal (green) at 675 nm is associated with stimulated emission of ASSQ. Combining DPSQ with ASSQ (in 1:1 weight ratio) causes a strong negative TA signal at 730 nm (*Figure 2d*), while ASSQ's GSB (550-600 nm) intensity is significantly attenuated. We assign the negative signal at 730 nm as the GSB of DPSQ. We arrive at this conclusion since DPSQ has negligible absorption at 500 nm (*Figure 1b, S2e*), which means that the observed excitation of

DPSQ is almost certainly caused by FRET from the excited ASSQ. These findings indicate that the excitation energy is successfully transferred from ASSQ to DPSQ. The GSB of DPSQ is observed almost immediately after the excitation, revealing a rapid (sub-pico second) energy transfer of excitons from ASSQ to DPSQ. Similar observations were found between PT8 and DPSQ, and the ASSQ:PT8:DPSQ films therein (*Figures 2 i-l*).

Energy transfer between ASSQ and PTB7 (or PTB7-Th) is also observed. TA spectra of control PTB7 or PTB7-Th films, (*Figures 2e, S2a*) show two negative bands (red in color) between 600-750 nm, corresponding to GSBs of the polymer's S_0-S_1 and S_0-S_2 $\pi-\pi^*$ transitions. Addition of 2% wt. ASSQ (*Figures 2f, S2b*) intensifies the bleaching signal of the polymer and further prolongs the decay time. This phenomenon is indicative of energy transfer from ASSQ to PTB7 as the negative signal increase of the S_0-S_2 band in 600-650 nm is not seen in neat ASSQ (*Figure 2c*). The increased lifetime is also consistent with the hypothesis of PTB7 sensitization by ASSQ.

Due to the relatively small spectral overlap between PTB7 (or PTB7-Th) with DPSQ (*Figure S1c*), we do not expect a strong FRET signal between these components. However, we observe charge transfer from the TA spectra (*Figures 2(g,h)* and *S2(b,d)*). The addition of a small amount of DPSQ results in a strong positive TA signal at wavelengths higher than 775 nm. We identify this positive signal as photoinduced absorption (PIA) which signifies formation of polarons, indicating the presence of

charge transfer^[47] between PTB7 (or PTB7-Th) to DPSQ. As expected, when ASSQ and DPSQ is mixed with the polymer, both energy (stronger and prolonged GSB) and charge transfer (PIA) indicators are revealed (*Figure 2h*).

Photovoltaics Performance

We show the current density–voltage (J–V) characteristics under one sun (simulated AM 1.5G irradiation at 100 mW cm⁻²) for our quaternary blend devices and the appropriate control devices (*Figure 3a*). The device performance parameters using ZnO as a buffer layer are summarized in *Table 1*. The binary PTB7:PC₇₁BM control devices exhibit a PCE of 7.17% with a short-circuit current density (J_{SC}) of 15.01 mA cm⁻², an open-circuit voltage (V_{OC}) of 0.73 V, and a fill factor (FF) of 65.5% (*Figure 3a*). The incorporation of 1% of both ASSQ and DPSQ (a total of 2% wt.) into the PTB7:PC₇₁BM blend led to significant enhancements in the J_{SC} and FF values, while the V_{OC} remains relatively constant. Films containing both ASSQ and DPSQ resulted in the highest PCE of 9.52%. The best device displayed a J_{SC} of 17.95 mA cm⁻², V_{OC} of 0.73 V and FF of 72.7% (the PCE distribution is shown in *Figure S8a*).

For comparison, ternary solar cells containing 2% of either ASSQ or DPSQ in PTB7:PC₇₁BM were prepared. Photovoltaic efficiencies of ternary cells outperform the binary control cells, although the extent of this improvement is less than in the quaternary system^[48]. The 2% ASSQ devices reach a PCE of 8.9% while 2% DPSQ cells attain 8.6% efficiency, which represent increases of 24% and 20%, respectively,

compared to the control without squaraine. There is also an enhancement in J_{sc} , FF (R_s and R_{sh}), and ideality factor for both ternary systems. The increase in J_{sc} corresponds to enhancements in the external quantum efficiency (EQE) (*Figure 3c*). We suggest that the additional increase in EQE between 300-400 nm with 2% of ASSQ in the PTB7 system could be associated to the phenomena of hole-relay enhancement reported by Yu et al.^[49]

The addition of ASSQ and DPSQ to PT8:PC₆₁BM blends also result in enhanced performance, suggesting that our approach of constructing quaternary blends can be adapted to improve polymer systems other than PTB7. In the case of the PT8 system, the J_{sc} increased from 9.33 to 10.73 mA cm⁻², the FF from 53.2% to 59.1%, and V_{oc} from 0.95 V to 0.97 V. Moreover, the R_s decreases from 5.55 to 4.40 Ω cm² and the R_{sh} increases from 540 to 591 Ω cm², while the rectification ratio also improves from 50 to 38000 (*Figure S8d*), implying less recombination loss^[50] in PT8 quaternary cells. The series resistances (R_s , defined from the J-V curves near 1 V under light illumination) and shunt resistances (R_{sh} , defined from the J-V curves near 0 V under light illumination) also improve in the presence of ASSQ and DPSQ. In the PTB7:PC₇₁BM system, the R_s decreases from 1.94 to 1.48 Ω cm² and the R_{sh} increases from 983 to 1317 Ω cm². It is known that the lower R_s implies improved charge injection/extraction and reduced charge recombination at the interface, while the high R_{sh} indicates less leakage current across the cell^[51]. Both the low R_s and high R_{sh} contribute to the

improved FF. This analysis is in agreement with the dark J–V curves (*Figures 4e-f*), where the data is plotted with one axis on a semi-log scale to extract parameters like reverse bias leakage current, rectification ratio, and ideality factor. Lower leakage currents (at -1 V) were observed for both polymers with ASSQ and DPSQ. A rectification ratio of up to ~64000 (at ± 1.5 V bias) is achieved in a PTB7:PC₇₁BM device with ASSQ and DPSQ, while it is only ~4000 for a PTB7:PC₇₁BM only device (*Figure S8b*). This trend implies that the small molecules facilitate carrier dissociation and suppress interfacial recombination^[52]. These findings suggest that FRET can prevent exciton combination in the quaternary blends, in an analogous fashion to what we demonstrated for ternary blends.^[8]

Furthermore, we compare the spectral response of quaternary, ternary, and binary blends of PTB7:PC₇₁BM systems (*Figure 3c*). The EQE^[53] spectra are consistent with the measured J_{SC} in the devices. In the range of 350–750 nm, the average EQE for PTB7:PC₇₁BM devices is 59%, and increases to 67.5%, 68.7%, and 70% with incorporation of 2% ASSQ, 2% DPSQ, and 1% of both ASSQ-DPSQ respectively. The improved photoresponse caused by ASSQ and DPSQ can be analyzed through the different EQE spectra between the quaternary devices and the binary controls. Interestingly, the Δ EQE of PTB7 system shows a relatively large peak at ~700 nm (*Figure S8b*). Since only a small amount of DPSQ is incorporated into the quaternary blends, the large increase in EQE at 700 nm could result from overlap of DPSQ

absorption and PTB7 absorption where additional excitons on PTB7 are transferred to DPSQ through FRET. Overall, the EQE spectra are consistent with the occurrence of multiple FRET based processes which result in an improvement in photocurrent.

When we inspect the EQE response of PT8:PC₆₁BM system, inclusion of dual-squaraine improves the average current generation in the visible region from 39% to 43% (*Figure 3d*). In the Δ EQE curves, a narrow peak at ~700 nm is attributed to increased absorption and charge separation by DPSQ, while the broad peak centered at 550 nm suggests that additional excitons on ASSQ are successfully transferred, dissociated into free charges, and collected. In addition, we observe a shoulder at 620 nm in the Δ EQE spectrum of the PT8 system (inset of *Figure 4d*), suggesting that additional excitons on PT8 are transferred to DPSQ presumably through FRET and then harvested. We reveal that the Δ EQE of PTB7-Th:PC₇₁BM also displays similar features (*Figure 4c*), where the broad increase in the range of 600-700 nm could be attributed to energy transfer from PTB7 to DPSQ.

Interfacial layer engineering is another viable strategy to improve PTB7 based solar cells^[4]. We reveal that by using PFN (see Method section) as the hole blocking layer, our best quaternary devices also exhibit improved efficiency from 8.7% to 10.3% (PTB7:PC₇₁BM), and from 9.6% to 10.7% (PTB7-Th:PC₇₁BM) (*Figure 3b*). The improvements for parameters J_{sc} , FF, R_s , R_{SH} , and ideality factor in the quaternary PTB7:PC₇₁BM system follow similar trends as observed in the ASSQ/DPSQ

PTB7-Th:PC₇₁BM system (*Table 1a-b*). These results unveil that PFN can serve as a more effective interlayer over conventional ZnO, suggesting that these quaternary devices can be further optimized by state-of-the-art materials used in interfacial engineering^[54-57].

Nanomorphology Enhancement

It is proposed that the dramatic enhancements in the photovoltaic performance of the quaternary devices are in part associated with changes in the morphology and molecular orientation of the blend films when the small molecules are included. We show atomic force microcopy (AFM) images of PTB7:PC₇₁BM and PT8:PC₆₁BM BHJ blends with and without ASSQ and DPSQ (*Figure 4*). The height images show that both BHJ blends become rougher after the introduction of ASSQ and DPSQ. The root-mean-square (RMS) roughness for PTB7:PC₇₁BM blends is 0.49 nm (*Figure 4a*), which increases to 0.71 nm after the incorporation of ASSQ and DPSQ (*Figure 4c*). Similarly, the RMS roughness of PT8:PC₆₁BM films increases from 1.61 nm (binary) to 2.04 nm (quaternary) in *Figure 4e* and *4g*, consistent with our previous findings studying squaraine:P3HT:PC₆₁BM blends^[8].

More importantly, we observe that the addition of squaraines induces a more homogeneously fine-dispersed surface morphology. As evident by the phase images (*Figures 4b, d, f, and h*), the addition of ASSQ and DPSQ causes reduction of the

domain sizes in quaternary PTB7:PC₇₁BM to fall below a typical range of 30-50 nm (binary)^[58, 59]; and below 20-40 nm^[43] for the PT8:PC₆₁BM. These results suggest that the squaraines encourage formation of smaller but slightly rougher domains while retaining the overall polymeric microfibrillar pattern^[11]. This perturbation was previously reported to be advantageous due to a positive correlation between an increased blend surface roughness and higher photovoltaic efficiency in BHJ solar cells^[60]. Hence, we postulate that smaller domains in devices with ASSQ and DPSQ allow for formation of higher donor/acceptor microfibril interfaces^[61] that favor charge extraction^[13], which is crucial in the case of organic semiconductors that generally suffer from short exciton diffusion length^[62]. X-ray photoelectron spectroscopy (XPS) studies further confirm that the concentration of sulfur is higher in the quaternary film, indicating that the dual squaraines promote a polymer-rich surface (*Figure S5a*). These polymer rich phases were previously shown^[11] to result in a better concentration gradient for charge extraction near the cathode interface^[11, 63] for inverted solar cells. Although nitrogen signals were not detected in the XPS measurements for the quaternary blends, energy dispersive X-ray analysis (EDAX) coupled transmission electron microscopy (TEM) images (*Figure S6b*) detect an increase of nitrogen abundance in the quaternary blends, indicating the presence of the squaraine molecules in quaternary blends.

Internal Microstructures

The binary and squaraine-added films (as-cast) were further characterized by grazing-incidence wide-angle X-ray scattering (GIWAXS). In *Figure 5*, we illustrate the 2D-GIWAXS patterns of neat ASSQ, DPSQ, ASSQ:DPSQ mix, control PTB7:PC₇₁BM, and the quaternary ASSQ:DPSQ:PTB7:PC₇₁BM, as well as the in-plane and out-of-plane linecuts. Comparing *Figures 5a-c*, the ASSQ:DPSQ mixed sample exhibits strong scattering signals in comparison to the neat ASSQ and DPSQ films. This suggests that ASSQ and DPSQ favor the formation of co-crystalline phases remarkably without any post heat treatment. Interestingly, we believe this is one of the prominent properties of ASSQ and DPSQ that eventually renders quaternary devices with efficiencies higher than the binary or ternary counterparts.

To further demonstrate the co-crystalline effect, we show the 2D-GIWAXS of the PTB7:PC₇₁BM (containing 3% v/v 1,8-diiodooctane (DIO)) with and without both dye molecules in *Figure 5f-g*. The scattering signal generally changes from featuring dispersing rings to a distinctive streaks pattern when comparing binary to quaternary blends, implying that both squaraines, together, enhance the crystallinity of the polymer:fullerene bulk. In addition, the quaternary film also displays a “staircase-slip” like conformation, as evidenced by the strong scattering streaks at multiple scattering angles. Noticeably, most of these streaks also become sharper. As the scattering peak broadness is inversely proportional to the ordered size, this suggests formation of larger

ordered domains in quaternary films. Although this effect is also observed in ternary blends the magnitude of the transformation is less prominent (*Figure S3a*).

Orientation analysis reveals more in-depth information about the molecular structuring of these films. We find that numerous new linecut peaks at $q_z = 0.277 \text{ \AA}^{-1}$ with the higher-order peaks at $0.55 \text{ \AA}^{-1}$ and $0.83 \text{ \AA}^{-1}$ (yellow box in *Figure 5g*) are present only in the quaternary film. Similarly, sharp peaks at $q_r = 1.21 \text{ \AA}^{-1}$ as well as $q_r = 1.35 \text{ \AA}^{-1}$ were identified, and are not observable in either the ASSQ, DPSQ, ASSQ:DPSQ, or the binary polymer:fullerene systems. We propose that these peaks are associated with the formation of dual squaraine induced crystalline phases. Polar angle analysis at ring $q = 0.277 \text{ \AA}^{-1}$ (one of the new phases in quaternary blend) reveals that 100% of the population of these phases are strongly aligned in edge-on orientation (*results tabulated in S3e*). We also notice that the q_r peaks at $1.21 \text{ \AA}^{-1}$ and $1.35 \text{ \AA}^{-1}$ exhibit a very small angular spread, again suggesting the presence of well-aligned microstructures. Moreover, similar patterns were observed in reticulated small molecule systems which were also attributed to co-crystal formation^[64, 65]

We assign $0.39 \text{ \AA}^{-1}$ to be the low- q peak corresponding to PTB7 (100) lamellar stacking of $16 \text{ \AA}$ as it appears in both binary and quaternary blends, in agreement with a previous observation by Collins et al.^[58] The intensity along this lamellar ring indicates a relatively broad orientation distribution for the polymer stacking, with a substantial (>30%) contribution of the favorable face-on orientation (*Tabulated in S3e*) in the

quaternary blend. Furthermore, the PTB7 orientation distribution across the whole film is not strongly affected by squaraine blending while the binary films show a preference of more edge-on conformation at the top surface, which could be less-favorable for charge transport in inverted solar cells^[66]. Strikingly, these findings indicate that the squaraines successfully aid in the phase separation necessary for optimized charge transport, which could be an important factor in explaining the fill factor increase in our squaraine-incorporated photovoltaic devices. We further show space charge-limited current measurements on hole-only devices (*Figure S4*). The hole mobility measured with this method quantifies how well carriers transport in the perpendicular direction to the substrates. The hole mobility for the control PTB7:PC₇₁BM film is $6.28 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \cdot \text{s}$, which is comparable to results obtained by Liang et al.^[67] This value increases to $1.12 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \cdot \text{s}$ and $1.94 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \cdot \text{s}$ in the ternary 2% ASSQ and 2% DPSQ containing films respectively. The highest mobility ($2.67 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \cdot \text{s}$) is attained in the quaternary blend, from which we ascribe this enhancement to the favorable molecular packing as shown by the GIWAXS experiments.

Conclusion

To conclude, the incorporation of small amounts of ASSQ and DPSQ in the active layer results in increases in PCE of 33%, 19%, and 30%, in PTB7:PC₇₁BM, PTB7-Th:PC₇₁BM and PT8:PC₆₁BM blends respectively, due to major improvements in

the J_{SC} and the FF. Ultrafast transient absorption spectroscopy indicates that the use of multiple FRET pairs results in rapid and efficient energy transfer, while EQE measurements show an increase in the range of photons absorbed. Quaternary PTB7:PC₇₁BM cells also show improved active layer morphology, characterized by smaller domain sizes, denser π - π stacking and preferable orientation, as well as enhanced charge transport mobility readily observed in hole-only devices. Coupling multiple small molecule D-A polymer systems with a high HOMO level acceptor such as thiophenated fullerene butyl ester, TC₇₁BM^[68] may yield devices with unprecedented results. We further show that these systems can be readily improved using interfacial improvements such as PFN hole blocking layers. The design strategies demonstrated here for multi-blend single-junction FRET systems could provide the foundation for record-breaking single-junction PSCs.

Methods

Photovoltaic Materials and Devices. ASSQ, DPSQ, and PT8 were synthesized and purified according to the procedures described in the literature^[36, 43, 69]. PTB7, PTB7-Th (1-Materials), PC₆₁BM, and PC₇₁BM (Nano-C) were used as received. Devices were fabricated on cleaned indium tin oxide-(ITO) coated glass substrates (15 Ω /sq, Zhuhai Kaivo Optoelectronics). ZnO thin films (~50 nm) were spin-coated on ITO substrates by a sol-gel process. 1.5 mg/mL of a poly

[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] or PFN solution ($1.5 \mu\text{g/mL}$ acetic acid in methanol) was coated in air at 5000 rpm for ZnO substitution experiments. Subsequently, a quaternary blend layer of PTB7:PC₇₁BM, PTB7-Th:PC₇₁BM or PT8: PC₆₁BM with or without pre-mixed squaraine(s) ($\sim 100 \text{ nm}$) was spin-coated on the ZnO thin film in a N₂-filled glove box. Finally, a MoO₃ film of 8 nm and a silver film of 120 nm were deposited on top in AMOD deposition chamber (Angstrom Engineering) under vacuum of $\leq 1 \times 10^{-6}$ torr. For preparing PTB7 (or PTB7-Th) containing quaternary blend solutions, pristine PTB7, PC₇₁BM, ASSQ, and DPSQ solutions were separately prepared in chlorobenzene (with 3 v/v% DIO) and mixed appropriately under an inert atmosphere to obtain a total concentration of 25 mg/mL with weight ratios of 1:1.5:0.01:0.01 (1:1.5:0.02 for ternary cells). Similarly, pristine PT8, PC₆₁BM, ASSQ, and DPSQ solutions were separately prepared in chloroform (with 3 v/v% DIO) and mixed appropriately in an inert atmosphere to obtain a quaternary blend solution (16 mg/mL with weight ratios of 0.8:1:0.01:0.01).

After fabrication, devices were illuminated at 100 mW cm^{-2} from a 150 W solar simulator with AM 1.5G filters (PV Measurements). The illumination intensity was determined by a NREL calibrated Si solar cell with KG-5 color filter. All electrical measurements were carried out in air at room temperature. The active area of the device irradiated by the light was defined as 6 mm^2 using a photomask, so no extra current outside of the defined area was collected. Current density–voltage (J–V) curves were

measured with a Keithley 2400 source measurement unit. The ideality factor was obtained by linear fitting at the diffusion current region. Devices with PFN as interlayer were light-soaked for 15 minutes before J-V measurement. The absorption spectra of dried films and solutions were obtained using a Varian Cary 3E UV-vis spectrophotometer. The EQE measurements were performed in air using a PV Measurements QEX7 system. Hole only devices were made by sandwiching the active layer between two interlayers of MoO₃ where the cathode is ITO and Au is the anode. Mobility measurements were performed in the dark with the same device area and chassis grounded anode connector.

Ultrafast Transient Spectroscopy. Broadband TA spectra were obtained using an amplified Ti:Sapphire laser system (Tsunami, Spectra Physics) and optical parametric amplifier (OPA)^[70]. Briefly, spin-casted films were resonantly excited with ~100 fs laser pulses generated by the OPA at a repetition rate of 1 kHz. Time-resolved absorption spectra were obtained using a broadband supercontinuum probe pulse that is overlapped in time and space with the femtosecond pump pulse. The supercontinuum is produced by focusing a small portion of the amplified laser fundamental into a sapphire plate. Multi-wavelength transient spectra were recorded using dual spectrometers (signal and reference) equipped with fast Si array detectors. Films were pumped at 500 nm to selectively excite ASSQ, PTB7, PTB7-Th, or PT8. The laser fluence was set to 8 $\mu\text{J cm}^{-2}$, to ensure linear response of the TA signals from ASSQ, PTB7 and PT8 and rule

out effects from exciton-exciton elimination arises from high power excitation. Chirping due to dispersion in the white probe beam was corrected before the data analysis. Samples prepared for this study were spin-coated at 750 rpm for PTB7, PTB7-Th films and 1500 rpm for PT8 films to produce thicker films to induce stronger changes in optical density for better signal-to-noise ratio.

Grazing-incidence X-ray Scattering (GIXS). X-ray scattering experiments were performed at the X9 undulator-based beamline at the National Synchrotron Light Source. An incident X-ray beam of energy 13.5 keV (wavelength = 0.0918 nm) was collimated using a two-slit system, and focused to a beam 100 μm wide by 60 μm tall at the sample position using a Kirkpatrick-Biaz mirror system. Samples were spin-coated on pre-cleaned silicon wafers and mounted on a translation stack under vacuum (~ 40 Pa). Grazing-incidence experiments were performed over a range of incidence angles (7 to 15 θ), both below and above the film-vacuum critical angle. Two-dimensional scattering images were measured in ~~both the small angle (GISAXS) and wide-angle~~ (GIWAXS) using two charged-coupled device (CCD) detectors. The WAXS detector (Photonic Sciences CCD area detector) has a readout background of ~ 1000 counts/pixel" and placed at 270 mm from the sample. Data conversion to q-space was accomplished using Silver Behenate powder as a standard. Details on the quantification and analysis are provided in the supplementary materials, section S3f.

X-ray Photoelectron Spectroscopy (XPS). The XPS experiments were carried out in a

ultra-high vacuum chamber equipped with an X-ray photoelectron spectrometer—SPECS Phoibos 100 MCD analyzer, Ar ion sputtering gun and non-monochromatized Al-Ka X-ray source ($h\nu = 1,486.6$ eV). Organic samples were spin-coated on cleaned silicon wafers and loaded into chamber which typically has a base pressure of $\sim 2 \times 10^{-10}$ Torr. XPS spectra were referenced to adventitious carbon peak at 284.5 eV.

References

- [1] L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street, Y. Yang, *Adv. Mater.* **2013**, 25, 6642.
- [2] F. C. Krebs, N. Espinosa, M. Hösel, R. R. Søndergaard, M. Jørgensen, *Adv. Mater.* **2014**, 26, 29.
- [3] A. J. Heeger, *Adv. Mater.* **2014**, 26, 10.
- [4] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nature Photon.* **2012**, 6, 593.
- [5] X. Guo, N. Zhou, S. J. Lou, J. Smith, D. B. Tice, J. W. Hennek, R. P. Ortiz, J. T. L. Navarrete, S. Li, J. Strzalka, L. X. Chen, R. P. H. Chang, A. Facchetti, T. J. Marks, *Nature Photon.* **2013**, 7, 825.
- [6] L. Dou, W.-H. Chang, J. Gao, C.-C. Chen, J. You, Y. Yang, *Adv. Mater.* **2013**, 25, 825.
- [7] Y. Liang, L. Yu, *Acc. Chem. Res.* **2010**, 43, 1227.
- [8] J.-S. Huang, T. Goh, X. Li, M. Y. Sfeir, E. A. Bielinski, S. Tomasulo, M. L. Lee, N. Hazari, A. D. Taylor, *Nature Photon.* **2013**, 7, 479.
- [9] L. Yang, H. Zhou, S. C. Price, W. You, *J. Am. Chem. Soc.* **2012**, 134, 5432.
- [10] Y.-C. Chen, C.-Y. Hsu, R. Lin, K.-C. Ho, J. Lin, *ChemSusChem* **2013**, 6, 20.
- [11] G. J. Hedley, A. J. Ward, A. Alekseev, C. T. Howells, E. R. Martins, L. A. Serrano, G. Cooke, A. Ruseckas, I. D. W. Samuel, *Nat. Commun.* **2013**, 4, 2867.
- [12] W. Chen, T. Xu, F. He, W. Wang, C. Wang, J. Strzalka, Y. Liu, J. Wen, D. J. Miller, J. Chen, K. Hong, L. Yu, S. B. Darling, *Nano Lett.* **2011**, 11, 3707.
- [13] Y. Gu, C. Wang, T. P. Russell, *Adv. Energy Mater.* **2012**, 2, 683.
- [14] J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Commun.* **2013**, 4, 1446.
- [15] L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G.

- Li, Y. Yang, *Nature Photon.* **2012**, 6, 180.
- [16] J. Kim, Z. Hong, G. Li, T.-b. Song, J. Chey, Y. S. Lee, J. You, C.-C. Chen, D. K. Sadana, Y. Yang, *Nat. Commun.* **2015**, 6, 6391.
- [17] C.-C. Chen, S.-H. Bae, W.-H. Chang, Z. Hong, G. Li, Q. Chen, H. Zhou, Y. Yang, *Mater. Horiz.* **2015**, 2, 203.
- [18] M. Reinhard, P. Sonntag, R. Eckstein, L. Bürkert, A. Bauer, B. Dimmler, U. Lemmer, A. Colmann, *Appl. Phys. Lett.* **2013**, 103, 143904.
- [19] G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, C. J. Brabec, *Adv. Mater.* **2008**, 20, 579.
- [20] T. Ameri, P. Khoram, J. Min, C. J. Brabec, *Adv. Mater.* **2013**, 25, 4245.
- [21] L. Yang, L. Yan, W. You, *J. Phys. Chem. Lett.* **2013**, 4, 1802.
- [22] N. Balis, D. Konios, E. Stratakis, E. Kymakis, *ChemNanoMat* **2015**, 1, 346.
- [23] S. Liu, P. You, J. Li, J. Li, C.-S. Lee, B. S. Ong, C. Surya, F. Yan, *Energy Environ. Sci.* **2015**, 8, 1463.
- [24] H. Benten, T. Nishida, D. Mori, H. Xu, H. Ohkita, S. Ito, *Energy Environ. Sci.* **2016**, 9, 135.
- [25] L. Lu, M. A. Kelly, W. You, L. Yu, *Nature Photon.* **2015**, 9, 491.
- [26] H. D. Kim, H. Ohkita, H. Benten, S. Ito, *ACS Appl. Mater. Interfaces* **2014**, 6, 17551.
- [27] F. Machui, S. Rathgeber, N. Li, T. Ameri, C. J. Brabec, *J. Mater. Chem.* **2012**, 22, 15570.
- [28] N. Cooling, K. B. Burke, X. Zhou, S. J. Lind, K. C. Gordon, T. W. Jones, P. C. Dastoor, W. J. Belcher, *Sol. Energy Mater. Sol. Cells* **2011**, 95, 1767.
- [29] M. Lv, M. Lei, J. Zhu, T. Hirai, X. Chen, *ACS Appl. Mater. Interfaces* **2014**, 6, 5844.
- [30] H. Kang, K.-H. Kim, T. E. Kang, C.-H. Cho, S. Park, S. C. Yoon, B. J. Kim, *ACS Appl. Mater. Interfaces* **2013**, 5, 4401.
- [31] Y. Yang, W. Chen, L. Dou, W.-H. Chang, H.-S. Duan, B. Bob, G. Li, Y. Yang, *Nature Photon.* **2015**, 9, 190.
- [32] G. Grancini, R. S. S. Kumar, M. Maiuri, J. Fang, W. T. S. Huck, M. J. P. Alcocer, G. Lanzani, G. Cerullo, A. Petrozza, H. J. Snaith, *J. Phys. Chem. Lett.* **2013**, 4, 442.
- [33] Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell, Y. Cao, *Nature Photon.* **2015**, 9, 174.
- [34] T. Liu, L. Huo, X. Sun, B. Fan, Y. Cai, T. Kim, J. Y. Kim, H. Choi, Y. Sun, *Adv. Energy Mater.* **2016**, 6, 201502109.
- [35] M. Koppe, H.-J. Egelhaaf, G. Dennler, M. C. Scharber, C. J. Brabec, P. Schilinsky, C. N. Hoth, *Adv. Funct. Mater.* **2010**, 20, 338.
- [36] T. Goh, J.-S. Huang, E. A. Bielinski, B. A. Thompson, S. Tomasulo, M. L. Lee, M. Y. Sfeir, N. Hazari, A. D. Taylor, *ACS Photonics* **2015**, 2, 86.
- [37] T. Goh, J.-S. Huang, B. Bartolome, M. Y. Sfeir, M. Vaisman, M. L. Lee, A. D.

Taylor, J. Mater. Chem. A **2015**, 3, 18611.

[38] K. Cnops, B. P. Rand, D. Cheyns, B. Verreert, M. A. Empl, P. Heremans, Nat. Commun. **2014**, 5, 4406.

[39] O. G. Reid, G. Rumbles, J. Phys. Chem. C **2016**, 120, 87.

[40] K. Feron, W. J. Belcher, C. J. Fell, P. C. Dastoor, Int. J. Mol. Sci. **2012**, 13, 17019.

[41] G. Wei, X. Xiao, S. Wang, K. Sun, K. J. Bergemann, M. E. Thompson, S. R. Forrest, ACS Nano **2012**, 6, 972.

[42] S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng, S.-A. Chen, Adv. Mater. **2013**, 25, 4766.

[43] J. Yuan, Z. Zhai, H. Dong, J. Li, Z. Jiang, Y. Li, W. Ma, Adv. Funct. Mater. **2012**, 23, 885.

[44] R. A. Street, P. P. Khlyabich, A. E. Rudenko, B. C. Thompson, J. Phys. Chem. C **2014**, 118, 26569.

[45] Y. Zheng, T. Goh, P. Fan, W. Shi, J. Yu, A. D. Taylor, ACS Appl. Mater. Interfaces **2016**, DOI: 10.1021/acsami.6b03453.

[46] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York **2006**.

[47] R. Miranti, Y. Firdaus, E. Fron, M. Van der Auweraer, J. Parisi, H. Borchert, J. Phys. Chem. C **2015**, 119, 22669.

[48] *To clarify, we fixed the total squaraine loadings to 2% for fair comparison. Without a full combinatorial studies, it is not possible to conclude that quaternary cells are always better than their ternary or binary counterparts at all dye loadings.*

[49] L. Lu, W. Chen, T. Xu, L. Yu, Nat. Commun. **2015**, 6, 7327.

[50] V. Gupta, A. K. K. Kyaw, D. H. Wang, S. Chand, G. C. Bazan, A. J. Heeger, Sci. Rep. **2013**, 3, 1965.

[51] B. Qi, J. Wang, Phys. Chem. Chem. Phys. **2013**, 15, 8972.

[52] K. Lu, J. Fang, X. Zhu, H. Yan, D. Li, C. a. Di, Y. Yang, Z. Wei, New J. Chem. **2013**, 37, 1728.

[53] *To clarify, EQE experiments in figure 3 were measured using ZnO based devices.*

[54] S.-H. Liao, H.-J. Jhuo, P.-N. Yeh, Y.-S. Cheng, Y.-L. Li, Y.-H. Lee, S. Sharma, S.-A. Chen, Sci. Rep. **2014**, 4, 6813.

[55] H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, Science **2014**, 345, 542.

[56] Z. a. Tan, S. Li, F. Wang, D. Qian, J. Lin, J. Hou, Y. Li, Sci. Rep. **2014**, 4, 4691.

[57] S. Nam, J. Seo, S. Woo, W. H. Kim, H. Kim, D. D. C. Bradley, Y. Kim, Nat. Commun. **2015**, 6, 8929.

[58] B. A. Collins, Z. Li, J. R. Tumbleston, E. Gann, C. R. McNeill, H. Ade, Adv. Energy Mater. **2013**, 3, 65.

[59] M. R. Hammond, R. J. Kline, A. A. Herzing, L. J. Richter, D. S. Germack, H.-W. Ro, C. L. Soles, D. A. Fischer, T. Xu, L. Yu, M. F. Toney, D. M. DeLongchamp, ACS Nano **2011**, 5, 8248.

- [60] Y. Yao, J. H. Hou, Z. Xu, G. Li, Y. Yang, *Adv. Funct. Mater.* **2008**, 18, 1783.
- [61] B. Kan, M. Li, Q. Zhang, F. Liu, X. Wan, Y. Wang, W. Ni, G. Long, X. Yang, H. Feng, Y. Zuo, M. Zhang, F. Huang, Y. Cao, T. P. Russell, Y. Chen, *J. Am. Chem. Soc.* **2015**, 137, 3886.
- [62] K. J. Bergemann, S. R. Forrest, *Appl. Phys. Lett.* **2011**, 99, 243303.
- [63] L. Zhang, X. Xing, L. Zheng, Z. Chen, L. Xiao, B. Qu, Q. Gong, *Sci. Rep.* **2014**, 4, 5071.
- [64] S. J. Kang, J. B. Kim, C.-Y. Chiu, S. Ahn, T. Schiros, S. S. Lee, K. G. Yager, M. F. Toney, Y.-L. Loo, C. Nuckolls, *Angew. Chem. Int. Ed.* **2012**, 51, 8594.
- [65] T. Schiros, S. Mannsfeld, C.-y. Chiu, K. G. Yager, J. Ciston, A. A. Gorodetsky, M. Palma, Z. Bullard, T. Kramer, D. Delongchamp, D. Fischer, I. Kymissis, M. F. Toney, C. Nuckolls, *Adv. Funct. Mater.* **2012**, 22, 1167.
- [66] V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, *Nature Photon.* **2015**, 9, 403.
- [67] Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* **2010**, 22, E135.
- [68] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.* **2014**, 5, 5293.
- [69] S. Wang, L. Hall, V. V. Diev, R. Haiges, G. Wei, X. Xiao, P. I. Djurovich, S. R. Forrest, M. E. Thompson, *Chem. Mater.* **2011**, 23, 4789.
- [70] F. Gesuele, M. Y. Sfeir, W. K. Koh, C. B. Murray, T. F. Heinz, C. W. Wong, *Nano Lett.* **2012**, 12, 2658.

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Contributions

A.D.T and J.-S.H. initially conceptualized the project. J.-S.H. performed the preliminary device experiments and T.G. designed and performed the rest of experiments necessary for publication, while B.B. assisted in film preparation. J.-S.H., T.G. and M.Y.S. performed the ultrafast experiments and resulting data analysis. J.-S.H., T.G. performed the AFM and EQE experiments. C.N. and T.G. examined device performance in BNL.

T.G., F.A. and K.G.Y. conducted GIXS experiments. T.G. and X.T. ran XPS studies. J.-S.H., T.G. recorded the TEM images and F. A. performed cross-section SEM. L.M.G., P.R.M. and N.H. contributed to the synthesis of the squaraine dyes, PT8 polymer, and guided in data analysis.

Competing financial interests

The authors declare no competing financial interests.