Efficient Squaraine-Based Solution Processable Bulk-Heterojunction Solar Cells

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Organic photovoltaics (OPVs) offer new, renewable sources of electrical energy, capitalizing on attractions such as low fabrication cost and easy processing on flexible substrates. In the most successful embodiment, a soluble n-type fullerene, (6,6)-phenyl C_{61} butyric acid methylester (**PCBM**), is blended with conjugated *p*-type polymers to form bulk-heterojunction (BHJ) cells.[1] An attraction of these devices, which are processed from solution, is the ability to deposit active layer precursors over large areas in a single step, using techniques ranging from inkjet printing to spin-coating.[2] Small molecule donors offer the same facile processing however are easier to synthesize in many variants and purify (e.g., removal of trace metal catalysts employed in the synthesis), are intrinsically monodisperse, and are often environmentally more stable.[3]

Squaraine dyes[4] have been the subject of many recent investigations owing to their unique photochemical/photophysical properties. Applications include photoreceptors in copiers and laser printers,[5] and IR absorbers in optical disks and nonlinear optical materials.[6] Principal attractions of this dye class include facile synthetic access, a wide variety of possible structural motifs, and remarkable O_2 and moisture stability, thus enabling active layer deposition under ambient, in contrast to the inert atmosphere required for P3HT and related BHJ materials. Squaraines were studied as active components in single-layer OPVs during the 1970s−80s, affording maximum power conversion efficiencies (PCEs) of ∼0.02%, and more recently in dye sensitized-solar cells (DSSCs).[7]

In this communication, we report the use of appropriately designed squaraines as effective, long-wavelength donor components in BHJ OPVs and the effects of core modification on active layer film morphology and OPV response. The result is some of the highest PCEs reported to date for ambient solution-processed small molecule OPVs. New soluble squaraine derivatives **1** and **2** were synthesized via a modification of previously reported procedures.[8] Both linear and branched alkyl chain substituents allow manipulating the solubility, but with different effects on the solid state organization.[9] Condensation of the appropriate arylhydrazon-alkylpyrrole precursors with squaric acid in *i*-PrOH/toluene affords **1** and **2** in 45% and 48% yield, respectively (Scheme 1). All new compounds were characterized by conventional spectroscopic and analytical methods (see Supporting Information).

Figure 1A shows normalized optical spectra of **1,2**-derived films (from $CHCl_3$) and solutions (in $CHCl_3$). The absorption of the films is broad and covers the 550−900 nm region, exactly where the solar photon flux is maximum; the absorption maximum is somewhat red-shifted for squaraine **2**. The HOMO and LUMO energies of **1** and **2**, estimated by cyclic voltammetry (see Supporting Information), are −3.3 and −5.0 eV, respectively, for

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Scheme 1. Synthetic Route to Squaraine Donors[a]
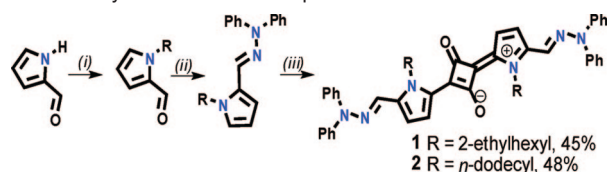
[a] (i) DMF, *t*-BuOK, RBr, 25°. (ii) *N,N*-Diphenylhydrazine hydrochloride, EtOH, 4 h reflux. (iii) Squaric acid, azeotropic mixture, reflux.
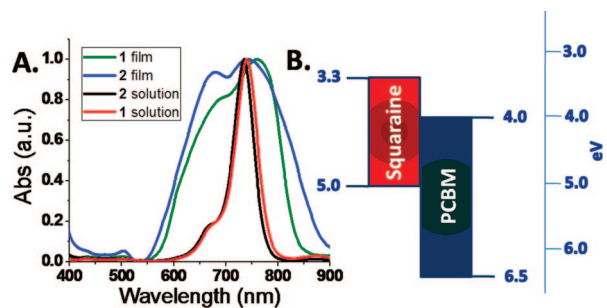

Figure 1. (A) Normalized optical absorption spectra: **1** (red line) and **2** (black line) as solutions in $CHCl_3$; **1** (green line) and **2** (blue line) as films from $CHCl_3$. (B) HOMO/LUMO levels for **1** and **2** vs **PCBM**.

both molecules, demonstrating that the alkyl chains negligibly affect the redox properties. The relevant energy level positions (Figure 1B), absorption coefficients (∼2 × 10^5 cm mol^{-1} cm^{-1}), and absorption energies suggest that these new squaraines should be effective donors in BHJ devices.

BHJ OPV cells were fabricated by spin-coating under ambient atmosphere squaraine:**PCBM** (x:y wt:wt ratio, x = 1,2; y = 1,3) blends, first in *o*-dichlorobenzene (ODCB), then in $CHCl_3$ onto cleaned tin-doped indium oxide (ITO)-coated glass anodes, modified by first spin-coating on PEDOT:PSS [poly(3,4-ethylenedioxythio-phene):polystyrenesulfonate] as a hole extraction/electron-blocking layer (∼30 nm), affording an active layer thickness of 30−140 nm. After drying, the cells were then completed by sequential thermal vacuum deposition of LiF and Al as the cathode. All devices were characterized under the standard AM1.5G 1 Sun test conditions using instrumentation and analysis procedures described previously,[10] and PCEs were derived from eq 1

$$\eta_p = (J_{sc}V_{oc}FF)/P_o \qquad (1)$$

where J_{sc} is the short circuit current, V_{oc} the open circuit voltage, FF the fill factor, and P_o the incident light intensity, in W/area. Before OPV testing, the squaraine−PCBM blend morphologies were characterized by tapping mode AFM; the images of blends spin-coated from several solvents reveal smooth morphologies with rms rough-

Table 1. Comparison of Solution-Processed Squaraine:PCBM BHJ Photovoltaic Cells[a]

active layer [wt:wt]	solvent/ T_a	d [nm]	J_{sc} [mA/cm^2]	V_{oc} [V]	FF [%]	η [%]
1/PCBM (1:1)	ODCB/na	140	1.85	0.58	31	0.33
1/PCBM (1:1)	ODCB/70	140	2.35	0.60	32	0.45
1/PCBM (1:1)	ODCB/70	100	2.65	0.60	34	0.54
1/PCBM (1:1)	ODCB/70	50	2.93	0.59	35	0.61
1/PCBM (1:1)	ODCB/na	30	3.10	0.64	39	0.77
1/PCBM (1:1)	ODCB/70	30	3.01	0.61	36	0.66
1/PCBM (1:3)	ODCB/na	30	3.89	0.60	32	0.75
1/PCBM (2:1)	ODCB/na	140	0.88	0.56	27	0.13
1/PCBM (1:1)	CHCl$_3$/na	30	3.24	0.62	32	0.64
1/PCBM (1:3)	CHCl$_3$/na	30	5.70	0.62	35	1.24
2/PCBM (1:1)	ODCB/na	140	1.31	0.58	30	0.23
2/PCBM (1:1)	ODCB/70	140	1.56	0.59	31	0.29
2/PCBM (1:3)	CHCl$_3$/na	30	4.72	0.59	32	0.89

[a] The general structure of devices is ITO/PEDOT:PSS/Sq:**PCBM**blend/ LiF/Al, with ∼6 mm^2 illuminated areas. T_a = annealing temperature (°C); na: not annealed. Otherwise annealing is for 1 h.
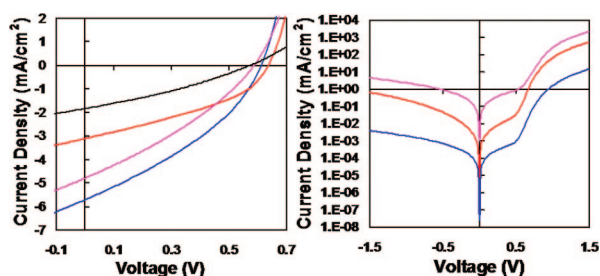

Figure 2. (A) $J-V$ response of **1**:PCBM BHJ OPV devices as a function of D:A ratio; 1:1 ratio from ODCB (140 nm, black line), 1:1 ratio from ODCB (30 nm, red line), 1:3 ratio from CHCl$_3$ (140 nm, pink line), and 1:3 ratio from CHCl$_3$ (30 nm, blue line). (B) Dark current measurements for 1:1 ratio films from ODCB (30 nm, red line), 1:3 ratio from CHCl$_3$ (140 nm, pink line), and 1:3 ratio from CHCl$_3$ (30 nm, blue line).

nesses ∼0.35 nm (see Supporting Information). Initial OPV studies employed squaraine **1**, spin-coating the blend from ODCB in air. With 140 nm thick films, J_{sc} is low, probably reflecting limited charge mobility, in accord with TFT-derived mobilities, $\mu_h \approx 10^{-4}-10^{-5}$ cm^2 V^{-1} s^{-1}.[11] By reducing the solution concentration and therefore the film thickness, OPV performance can be enhanced, with ∼30 nm films increasing J_{sc} from 1.85 to 3.10 mA/cm^2 and PCE from 0.33% to 0.77% (Table 1, Figure 2A).

The literature suggests that BHJ active layer thermal annealing can optimize film phase separation/microstructural order and thereby OPV performance.[12] For the present materials, optimum annealing conditions are 70 °C/1 h as evidenced by the increased phase separation (AFM Figures S1−S4). As in MDMO-PPV/**PCBM** solar cells,[13] enhancing carrier mobility by adjusting the donor:acceptor ratio also contributes to enhanced PCEs. In the present study, devices fabricated with 1:3 **1:PCBM** ratios exhibit significant increases in J_{sc} (to 3.89 mA/cm^2), with PCE = 0.75%. In contrast, devices with a 2:1 ratio exhibit decreases in both short circuit current and PCE (Table 1). Spin-casting the 1:3 **1:PCBM** blend from CHCl$_3$ rather than ODCB solutions yields a maximum PCE of 1.24%, with a short circuit current of 5.70 mA/cm^2, 1.5 times higher than the ODCB result, tentatively ascribed to the microstructure evolution effects of more rapid film growth and drying.

That PCE values increase with decreasing thickness is consistent with the higher observed short circuit currents for thinner films. The same effect is observed on changing the **1:PCBM** ratio. The EQE (external quantum efficiency) for the most efficient devices peaks at ∼20% @ 750 nm, averaging ∼10% in the 400−800 nm region. The dark data in Figure 2B indicate smaller rectification in

diodes with 1:1 blend ratios spin-coated from ODCB than from CHCl$_3$, and with lower leakage currents, presumably reflecting the superior film quality. We also fabricated and evaluated OPV cells using **2** and **PCBM**; efficiencies are somewhat lower (∼0.9%) than devices prepared with **1** (Table 1), however trends are similar.

In summary, we report the fabrication and initial characterization of BHJ solar cells based, for the first time, on squaraine derivatives as molecular donors and **PCBM** as the acceptor. These devices, solution-processed in air, exhibit some of the highest PCEs reported for small molecule OPVs (cf., anthradithiophene/fullerene = 1.0%,[14a] phenyl-core thiophene dendrimers = 1.3%,[14b] star-shaped derivatives = 1.3%[14c]). Studies are currently underway to better define and optimize processing/microstructure/photovoltaic response relationships.

Supporting Information Available: Synthetic procedures for **1** and **2**, device fabrication and characterization details, optical spectra of blends, and film AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Thompson, B. C.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58. (b) Yip, H.-L.; Hau, S. K.; Baek, N. S.; Ma, H.; Jen, A. K.-Y. *Adv. Mater.* **2008**, *20*, 2376. (c) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533.

(2) (a) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222. (b) Hoth, C. N.; Choulis, S. A.; Schilinsky, P.; Brabec, C. J. *Adv. Mater.* **2007**, *19*, 3973. (c) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.

(3) (a) Brumbach, M.; Placencia, D.; Armstrong, N. R. *J. Phys. Chem. C* **2008**, *112*, 3142. (b) Rand, P. B.; Genoe, J.; Heremans, P.; Poortmans, J. *Prog. Photovolt: Res. Appl.* **2007**, *15*, 659. (c) Yoo, S.; Potscavage, W. J., Jr.; Domercq, B.; Han, S.-H.; Li, T.-D.; Jones, S. C.; Szoszkiewicz, R.; Levi, D.; Riedo, E.; Marder, S. R.; Kippelen, B. *Solid-State Electron.* **2007**, *51*, 1367.

(4) Squaraine synthesis reviews: (a) Schmidt, A. H. *Synthesis* **1980**, 961. (b) Sprenger, G. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530.

(5) (a) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449. (b) Law, K. Y.; Bailey, F. C. *J. Org. Chem.* **1992**, *57*, 3278. (c) Law, K. Y. *J. Phys. Chem.* **1987**, *91*, 5184.

(6) (a) Chen, C.; Marder, S. R.; Cheng, L. T. *J. Am. Chem. Soc.* **1994**, *116*, 3117. (b) Chen, C.-T.; Marder, S. R.; Cheng, L. T. *J. Chem. Soc., Chem. Commun.* **1994**, 259. (c) Beverina, L.; Crippa, M.; Salice, P.; Ruffo, R.; Ferrante, C.; Fortunati, I.; Signorini, R.; Mari, C.; Bozio, R.; Facchetti, A.; Pagani, G. *Chem. Mater.* **2008**, *20*, 3242, and references therein.

(7) (a) Yum, J.; Walter, P.; Huber, S.; Rentsch, D.; Geiger, T.; Nüesch, F.; De Angelis, F.; Grätzel, M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.* **2008**, *129*, 10320. (b) Liang, K. N.; Law, K. Y.; Whitten, D. G. *J. Phys. Chem.* **1995**, *99*, 16704. (c) Piechowski, A. P.; Bird, G. R.; Morel, D. L.; Stogryn, E. L. *J. Phys. Chem.* **1984**, *88*, 934. (d) Merrit, V. Y.; Hovel, H. J. *Appl. Phys. Lett.* **1976**, *29*, 414.

(8) (a) Beverina, L.; Crippa, M.; Landenna, M.; Ruffo, R.; Salice, P.; Silvestri, F.; Versari, S.; Villa, A.; Ciaffoni, L.; Collini, E.; Ferrante, C.; Bradamante, S.; Mari, C. M.; Bozio, R.; Pagani, G. A. *J. Am. Chem. Soc.* **2008**, *130*, 1894. (b) Beverina, L.; Abbotto, A.; Landenna, M.; Cerminara, M.; Tubino, R.; Meinardi, F.; Bradamante, S.; Pagani, G. A. *Org. Lett.* **2005**, *7*, 4257.

(9) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 7390.

(10) (a) Irwin, M. D.; Buchholz, B.; Hains, A. W.; Chang, R. P. H.; Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 2783. (b) Hains, A. W.; Marks, T. J. *Appl. Phys. Lett.* **2008**, *92*, 023504.

(11) (a) TFT measurement performed in our laboratory on Si-SiO$_2$ substrates with top Au source/drain contacts. (b) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953.

(12) (a) Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. *Adv. Funct. Mater.* **2003**, *13*, 85. (b) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S. *Appl. Phys. Lett.* **2001**, *78*, 841–843.

(13) Sheenan, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *14*, 865.

(14) (a) Lloyd, M. T.; Mayer, A. C.; Subramanian, S.; Mourey, D. A.; Herman, D. J.; Bapat, A. V.; Anthony, J. E.; Malliaras, G. G. *J. Am. Chem. Soc.* **2007**, *129*, 9144. (b) Kopidakis, N.; Mitchell, W. J.; Lagemaat, J. V. d.; Ginley, D. S.; Rumbles, G.; Shaheen, S. E. *Appl. Phys. Lett.* **2006**, *89*, 103524. (c) Chang, H.; Qingguo, H.; Yuanping, Y.; Guanglong, W.; Fenglian, B.; Zhigang, S.; Yongfang, L. *J. Mater. Chem.* **2008**, *18*, 4085.

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