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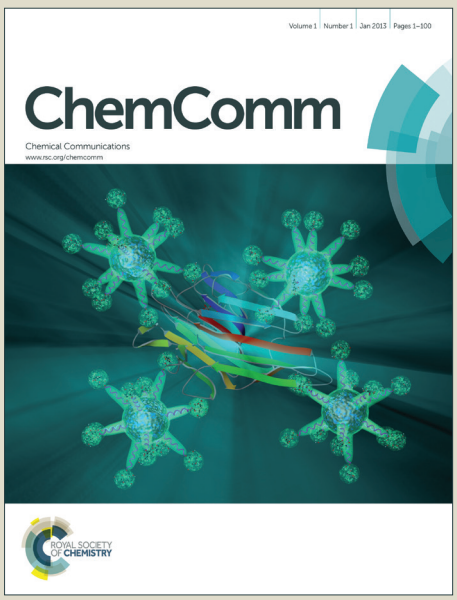

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Asymmetrical Squaraines for High-Performance Small-Molecule Organic Solar Cells with Short Circuit Current of over 12 mA cm^{-2}†

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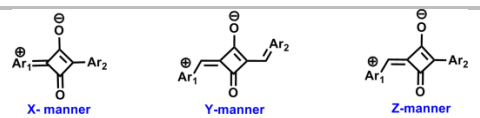
Yao Chen,‡[a] Youqin Zhu,‡[b] Daobin Yang,[a] Qian Luo,[a] Lin Yang,[a] Yan Huang,*[a] Suling Zhao*[b] and Zhiyun Lu*[a]

An asymmetrical squaraine dye (Py-3) with its two electron-donating aryls directly linked to the electron withdrawing squaric acid core possesses an ideal bandgap of 1.33 eV together with an intense and broad absorption band in 550-950 nm, hence the solution-processed solar cells display an impressive J_{sc} of 12.03 mA cm^{-2} and PCE of 4.35%.

Owing to their intense absorption in Vis-NIR regions and good photochemical/photophysical stability, squaraine dyes have drawn much attention in small-molecule organic solar cell (SMOSC) applications.[1] According to molecular framework, photovoltaic squaraine (SQ) dyes are generally classified into symmetrical (D-A-D, SSQ) and asymmetrical (D-A-D', ASQ) ones, in which squaric acid core acts as the electron acceptor (A) subunit, and electron-rich aromatic systems act as the electron donor (D or D') subunits. In addition, as illustrated in Scheme 1, for SSQ dyes, their D aryls could be linked to the A unit through either X-manner[1a, 1c] (D aryls are connected to A subunit directly) or Y-manner[2] (D aryls are linked to A subunit via methylylidene bridges); while for ASQ dyes, their D and D' aryls could be linked to A subunit not only through X- and Y-manners, but also through an extra Z-manner,[3] in which D and D' segments are connected to A subunit directly and *via* a methylylidene bridge, respectively.[4]



Scheme 1 Typical molecular frameworks of photovoltaic squaraine dyes.

Thanks to the recent enthusiastic research efforts, high-performance SSQ-based SMOSCs with record power conversion efficiency (PCE) of 5.50%[5] for X-manner and 3.14%[2a] for Y-manner have been achieved, whereas, ASQ-based SMOSCs just showed relative poor performance, with maximum PCE of 2.05% and 1.22% for Y- and Z-manner,[6] respectively. Therefore, ASQs have been considered as futureless organic photovoltaic (OPV) materials for a long time, and have received little research attention. However, in comparison with ASQs bearing a D-A-D' molecular skeleton, D-A-D-structured SSQs should possess less plenty room for molecular tailoring due to the lack of diverse combination ways of D and D' subunits as well as the Z-mannered molecular skeleton. Recently, through delicate molecular design, we have developed some high performance OPV ASQs *via* Z-manner. SMOSCs using them as electron donor materials could show maximum open circuit voltage (V_{oc}) of 1.12 V, short circuit current (J_{sc}) of 11.03 mA cm^{-2}, and PCE of 4.29%[1e, 7], indicating that ASQs are also promising OPV materials.

It became clear from the studies of Claudia Gude *et al.* that the photophysical properties in squaraine compounds correlate highly with their connected manners,[8] while all the hitherto developed OPV ASQs have been construction through either Y- or Z-manner, and no X-mannered examples have been exploited,[1, 2] herein, we designed and synthesized a series of novel ASQ dyes (**Py-1~3**, molecular structure shown in Scheme 2) whose D and D' segments are linked to the A subunit *via* X-manner. Through rational molecular design, one of the objective compound **Py-3** could show an ideal bandgap of 1.33 eV together with an intense and broad absorption band in 550-950 nm, and SMOSC using **Py-3** as electron donor could display an excellent J_{sc} of 12.03 mA cm^{-2} and a high PCE of 4.35%, which are the highest J_{sc} and PCE among all the reported ASQ-based SMOSCs,[1e] indicating ASQs bearing X-mannered molecular framework are quite perspective OPV materials. Since most squaraine dyes suffer from narrow absorption band, which is adverse to the light-harvesting process in solar cells,[1c, 1e] we aimed at the exploitation of ASQs showing relatively broad

[a] *Key Laboratory of Green Chemistry and Technology (Ministry of Education), College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: huangyan@scu.edu.cn, luzhiyun@scu.edu.cn*
[b] *Key Laboratory of Luminescence and Optical Information (Ministry of Education), Institute of Optoelectronics Technology, Beijing Jiaotong University, Beijing 100044, P. R. China. Email: slzhao@bjtu.edu.cn*

† Electronic supplementary information (ESI) available: Synthetic procedure, CV curves, charge carrier mobility measurement results and AFM images. For ESI and other electronic format see DOI:

‡ The first two authors contributed equally to this work.

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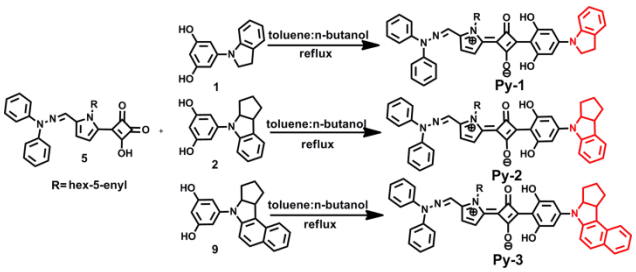

Scheme 2 Molecular structure and synthetic route of the target molecules **Py-1~3**.

absorption spectra in the Vis-NIR region. Inspired by the discovery of Marks[1a, 1b] *et al* that squaraines containing (*E*)-2-((2,2-diphenylhydrazono)-methyl)-1-(hex-5-enyl)-1*H*-pyrrole D unit own relatively broad absorption bands and good hole mobility due to the presence of double-bond end-capped alkyl side-chains, and our finding that *N*-(3,5-dihydroxyphenyl)indoline with planar geometry is an ideal D' segment for constructing high performance OPV ASQs with relatively low bandgap, initially, we designed and synthesized compound **Py-1** with (*E*)-2-((2,2-diphenylhydrazono) methyl)-1-(hex-5-enyl)-1*H*-pyrrole as the D subunit and *N*-(3,5-dihydroxyphenyl)indoline as the D' subunit, so that a broad absorption band and a low bandgap might be simultaneously acquired. Cheerfully, compared with those ASQ compounds we reported before, **Py-1** shows more widened absorption spectra in both solution and thin film states.[7, 1e] In fact, in thin film state, **Py-1** displays an intense and broad absorption band in the Vis-NIR region of 550-950 nm with full width at half maxima (FWHM) of 232 nm (vide Fig. 1 and Table 1), which has effective overlap with the solar spectrum. In addition, the bandgap of **Py-1** is 1.37 eV, which falls into the ideal bandgap range (1.2-1.6 eV) for OPVs applications,[9] and is lower than those of the OPV ASQ derivatives reported so far ($\geqslant$ 1.43 eV).[1e] However, **Py-1** shows rather poor solubility in common organic solvents (e.g., 7 mg/mL in chloroform), which might be ascribed to its rather planar molecular conformation hence severe π-π intermolecular stacking. Since the poor solubility of the opto-electronic materials should be disadvantageous to the fabrication of high-quality photoactive layers by spin-coating,[10] bulk heterojunction (BHJ) SMOSC using **Py-1** as electron-donor and $PC_{71}BM$ as electron-acceptor only exhibits a low PCE of 2.86% (device I, ITO/MoO_3 (8 nm)/**Py-1**:$PC_{71}BM$ (1:5, 80 nm)/LiF (0.8 nm)/Al (100 nm); data shown in Table 2).

Consequently, to improve the processability of the objective compounds, we changed the 1-indolinyl D' subunit of **Py-1** into a cyclopenta[*b*]indolin-1-yl group bearing additional alkyl segments. As expected, the resulting compound **Py-2**(e.g., 20 mg/mL in chloroform) shows much enhanced solubility than **Py-1**;[7b] and its bandgap is 1.37 eV, which is identical with that of **Py-1**. Further photophysical characterization results indicated that in dilute solution, the absorption spectrum of **Py-2** resembles that of **Py-1** (Fig. 1), implying that the alteration of indolin-1-yl into cyclopenta[*b*]indolin-1-yl would have little effect on the conjugation length of the resulting ASQs. While in solid film states, the FWHM of the absorption spectrum of **Py-2** is ~10 nm narrower than that of **Py-1**, suggesting that the presence of a less-coplanar cyclopenta[*b*] indolin-1-yl in **Py-2** would trigger alleviated intermolecular interactions.[7b] Nevertheless, as intense molecular interactions in OPV materials would not only be propitious to the widening of the absorption spectra hence light-harvesting capability, but also be beneficial to the enhancement of charge-carrier mobility, to promote more effective intermolecular π-π stacking in these ASQs,[11] we designed and synthesized **Py-3**, in which an extra phenyl is fused onto the cyclopenta[*b*] indolin-1-yl segment of **Py-2**. Excitingly, **Py-3** not only shows good solubility in common organic solvents (e.g., 16 mg/mL in chloroform), but also displays ~15 nm red-shifted λ_{abs} than **Py-2** in both solution and solid-film states. In fact, in comparison with **Py-2**, **Py-3** displays an even lower bandgap of 1.33 eV and a ~5 nm larger FWHM in its absorption spectrum in solid film state. Therefore, the presence of benzo[*e*]cyclopenta[*b*]indolin-1-yl D' group in **Py-3** could endow it with not only more extended conjugation length hence lower bandgap, but also stronger intermolecular interactions hence broadened absorption band. Moreover, all the three objective compounds **Py-1~3** exhibit considerably high molar extinction coefficients of ~10^5 L mol^{-1} cm^{-1}. Taking into account that **Py-3** has strong and broad absorption in the Vis-NIR region together with low bandgap of 1.33 eV, it should be a more perspective candidate in SMOSC applications.

Table 1. Optical, electrochemical and electric properties of **Py-1~3**.

Compd	λ_{abs} [a] (nm) (log ε)	λ_{abs} [b] (nm)	FWHM (nm) Solution	FWHM (nm) film	E_g^{opt} (eV)	E_{ox} (V)	HOMO[c] (eV)	LUMO[d] (eV)
Py-1	724(5.46)	770	50	232	1.37	0.29	-5.09	-3.72
Py-2	724(5.39)	770	50	222	1.37	0.29	-5.09	-3.72
Py-3	740(5.40)	784	61	227	1.33	0.29	-5.09	-3.76

[a] Measured in dilute chloroform solution (2.00×10^{-6} M); [b] measured in thin film state; [c] derived from CV measurement results, HOMO= (-4.80- E_{ox}) eV; [d] LUMO= E_g^{opt}+HOMO.

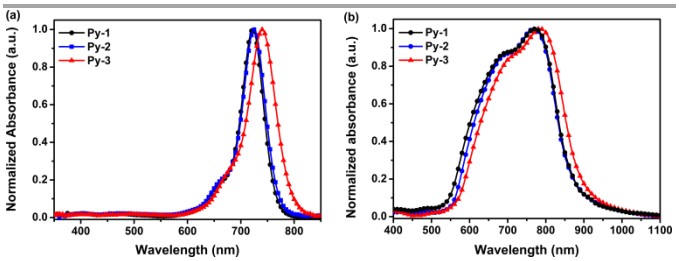

Fig.1 Absorption spectra of molecules in solution (a) and thin films (b).

Additional cyclic voltammetry (CV) measurements indicated that all these three compounds show two-electron reversible oxidation wave at 0.29 V and 0.69 V during the anodic scan, hence the highest occupied molecular orbital (HOMO) energy levels of **Py-1~3** were all calculated to be -5.09 eV. While the lowest unoccupied molecular orbital (LUMO) energy levels of **Py-1**, **Py-2** and **Py-3** were estimated to be -3.72 eV, -3.72 eV and -3.76 eV in sequence according to the HOMO energy level and optical bandgap data (Table 1 and Fig. S1 in the ESI†).

To gain deeper insight into the relationship between molecular structure and photovoltaic properties of these objective ASQ compounds, two solution-processed BHJ SMOSCs with similar device structure of **Py-1**-based device I were fabricated using **Py-2** (device II) and **Py-3** (device III) as the electron donor, respectively. The representative photovoltaic data of these devices are summarized in Table 2, and the current density-voltage (*J-V*) and external quantum efficiency-wavelength (EQE) curves are shown in Fig. 2. In comparison with device II, device III shows analogous V_{oc} but higher J_{sc} (11.22 mA cm^{-2} *vs* 10.32 mA cm^{-2}) and higher FF (0.46 *vs* 0.42), hence higher PCE (3.98% *vs* 3.30%). In principle, J_{sc} should correlates highly not only with the light-harvesting capability and the hole-mobility of the electron-donor materials, but also with the morphology of the donor-acceptor blending films,[12] hence we firstly investigated the EQE curves of devices II and III. As shown in Fig. 2b, consistent with the absorption spectral properties of **Py-2** and **Py-3** in thin film state, more broadened spectral response toward EQE could be observed in device III than device II. The integration areas of the EQE curves in 300-900 nm were calculated to be 159.5 for device II and 175.4 for device III, implying that the more

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Table 2 Photovoltaic performance of BHJ-OPVs based on **Py-1~3**.

Device	Active layer (w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
I	Py-1:$PC_{71}BM$=1:5	0.75±0.01	9.40±0.17	0.39±0.02	2.81±0.05
II	Py-2:$PC_{71}BM$=1:5	0.78±0.01	10.08±0.24	0.40±0.02	3.16±0.14
III	Py-3:$PC_{71}BM$=1:5	0.78±0.01	10.98±0.24	0.44±0.02	3.75±0.23
IV	Py-2:$PC_{71}BM$=1:5[a]	0.79±0.01	10.82±0.22	0.42±0.02	3.58±0.14
V	Py-3:$PC_{71}BM$=1:5[a]	0.78±0.01	11.80±0.23	0.45±0.02	4.12±0.23

[a] Device annealed at 70 ℃ for 10 min.

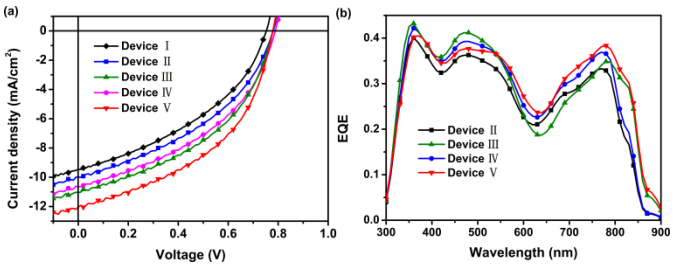

Fig. 2 *J-V* characteristics (a) and EQE characteristics (b) of the OPV devices.

broadened absorption band of **Py-3** relative to **Py-2** indeed contributes to the light-harvesting hence the enhancement of J_{sc} in device III than device II. Subsequently, we measured the hole-mobility of the neat ASQ films and ASQ/$PC_{71}BM$ blended ones by a space charge limited current (SCLC) method. According to the experimental and calculation results, the hole-mobility of the **Py-2** and **Py-3** films is 5.21 × 10^{-5} cm^2 V s^{-1} and 5.56 × 10^{-5} cm^2 V s^{-1}, respectively; and that of the **Py-2**/$PC_{71}BM$ and **Py-3**/$PC_{71}BM$ composite film is 3.27 × 10^{-6} cm^2 V s^{-1} and 4.95 × 10^{-6} cm^2 V s^{-1}, respectively (Fig. S2, ESI†). Obviously, **Py-3** shows higher hole-mobility than **Py-2** in both neat and ASQ/$PC_{71}BM$ composite films, which may be attributed to the more effective intermolecular packing triggered by its benzo[*e*]cyclopenta[*b*]indolin-1-yl D' segment with more extended π-system.[11] Further AFM characterization results revealed that both the **Py-2**/$PC_{71}BM$ and **Py-3**/$PC_{71}BM$ composite films show quite smooth surfaces with analogous root-mean-square (RMS) of 0.25 nm and 0.23 nm, respectively (Fig. S3, ESI†). Consequently, the higher J_{sc} of device III relative to device II should originate from the broadened absorption band and higher hole-mobility of **Py-3** relative to **Py-2**. In addition, the FF of device III is higher than that of device II (0.46 *vs.* 0.42), which might also arise from the higher hole-mobility of **Py-2**.[13]

Because thermal annealing is a well-adopted process for enhancing the performance of OPV devices,[14] device IV (**Py-2**-based) and device V (**Py-3**-based) with their photoactive layers annealed at 70 ℃ for 10 min were fabricated. As shown in Fig. 2 and Table 2, upon thermal treating, the PCEs of both devices IV (3.72%) and V (4.35%) were increased relative to device II and III, respectively. It is noteworthy that, to the best of our knowledge, the J_{sc} of 12.03 mA cm^{-2} and the PCE of 4.35% in device V are both the record ones in ASQ-based OPV devices.[1e, 2a] In fact, the OPV devices reported here have not been further optimized, and more improved device performance could be expected if additional optimizations on blending ratio of the electron-donor/electron-acceptor, solvent-annealing and additives have been carried out.

In summary, a series of novel ASQ derivatives **Py-1~3** were designed and synthesized. Different from those known high performance OPV ASQs whose D aryls are generally directly connected to the A subunit but D' aryls are linked to the A subunit *via* a methylylidene bridge, **Py-1~3** have both their D and D' aryls linked directly to the A subunit. Through rational molecular design, **Py-3** showing good solubility, relative low bandgap, broad and intense absorption band in Vis-NIR region, and effective intermolecular packing property has been achieved. BHJ-SMOSCs using **Py-3** as electron-donor material show high photovoltaic performance with PCE of 4.35% and J_{sc} of 12.03 mA cm^{-2}, both are the highest values among BHJ-SMOPVs with ASQs as electron-donor materials. All these preliminary results indicated that ASQ derivatives with their D and D' aryls linked to the A subunit directly should be quite promising OPV electron-donor materials.

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Notes and references

1 (a) D. Bagnis, L. Beverina, H. Huang, F. Silvestri, Y. Yao, H. Yan, G. A. Pagani, T. J. Marks and A. Facchetti, *J. Am. Chem. Soc*., 2010, **132**, 407; (b) F. Silvestri, M. D. Irwin, L. Beverina, A. Facchetti, G. A. Pagani and T. J. Marks, *J. Am. Chem. Soc*., 2008, **130**, 17640; (c) G. Chen, H. Sasabe, Y. Sasaki, H. Katagiri, X. Wang, T. Sano, Z. Hong, Y. Yang, and J. Kido, *Chem. Mater*., 2014, **26**, 1356; (d) L. Beverina, and P. Salice, *Eur. J. Org. Chem*., 2010, 1207; (e) D. Yang, Q. Yang, L. Yang, Q. Luo, Y. Chen, Y. Zhu, Y. Huang, Z. Lu and S. Zhao, *Chem. Commun*., 2014, **50**, 9346; (f) S. L. Lam, X. Liu, F. Zhao, C. L. Lee and W. L. Kwan, *Chem. Commun*., 2013, **49**, 4543.

2 (a) B. A. Rao, K. Yesudas, G. S. Kumar, K. Bhanuprakash, V. J. Rao, G. D. Sharama and S. P. Singh, *Photochem. Photobiol. Sci*., 2013, **12**, 1688. (b) U. Mayerhoffer, K. Deing, K. Gruss, H. Braunschweig, K. Meerholz and F. Würthner, *Angew. Chem. Int. Ed*., 2010, **132**, 4074; (b) I. A. Karpenko, A. S. Klymchenko, S. Gioria, R. Kreder, I. Shulov, P. Villa, Y. Mély, M. Hibert and D. Bonnet, *Chem. Commun*., 2015, **51**, 2960.

3 S. Sreejith, P. Carol, P. Chithras and A. Ajayaghosh, *J. Mater. Chem*., 2008, **18**, 264.

4 L. Beverina, R. Ruffo, G. Patriarca, F. De Angelis,; D. Roberto, S. Righetto, R. Ugo and G. A. Pagani, *J. Mater. Chem*., 2009, **19**, 8190.

5 G. Wei, S. Wang, K. Sun, M. E. Thompson and S. R. Forrest, *Adv. Energy Mater*., 2011, **1**, 184.

6 (a) S. So, H. Choi, H. M. Ko, C. Kim, S. Paek, N. Cho, K. Song, J. K. Lee and J. Ko, *Sol. Energy Mater. Sol. Cells*, 2012, **98**, 224; (b) K. C. Deing, U. Mayerhoffer, F. Würthner and K. Meerholz, *Phys. Chem. Chem. Phys*., 2012, **14**, 8328.

7 (a) D. Yang, Q. Yang, L. Yang, Q. Luo, Y. Huang, Z. Lu and S. Zhao, *Chem. Commun*., 2013, **49**, 10465; (b) L. Yang, Q. Yang, D. Yang, Q. Luo, Y. Zhu, Y. Huang, S. Zhao and Z. Lu, *J. Mater. Chem. A*, 2014, **2**, 18313.

8 C. Gude and W. Retting, *J. Phys. Chem. A*, 2000, **104**, 8050.

9 X. Liu, Y. Sun, B. B. Y. Hsu, A. Lorbach, L. Qi, A. J. Heeger and G. C. Bazan, *J. Am. Chem. Soc*., 2014, **136**, 5697.

10 (a) B. Walker, C. Kim and T.-Q. Nguyen, *Chem. Mater*., 2011. **23**, 470; (b) S. Wang, L. Hall, V. V. Diev, R. Haiges, G. Wei, X. Xiao, P. I. Djurovich, S. R. Forrest and M. E. Thompson, *Chem. Mater*., 2011, **23**, 4789.

11 (a) S. Paek, N. Cho, S. Cho, J. K. Lee and J. Ko, *Org. Lett*., 2012, **14**, 6326; (b) O. P. Lee, A. T. Yiu, P. M. Beaujuge, C. H. Woo, T. W. Holcombe, J. E. Millstone, J. D. Douglas, M. S. Chen and J. M. J. Fréchet, *Adv. Mater*., 2011, **23**, 5359.

12 B. Kan, Q. Zhang, M. Li, X. Wan, W. Ni, G. Long, Y. Wang, X. Yang, H. Feng and Y. Chen, *J. Am. Chem. Soc*., 2014, **136**, 15529;

13 J. Zhou, Y, Zou, X, Wan, G. Long, Q. Zhang, W. Ni, Y, Liu, Z. Li, G, He, C. Li, B. Kan, M. Li and Y. Chen, *J. Am. Chem. Soc*., 2013, **135**, 8484.

14 Y. Huang, E. J. Kramer, A. J. Heeger and G. C. Bazan, *Chem. Rev*., 2014, **114**, 7006.

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