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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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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\(^{1,1a}\) (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.\(^4\)

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%\(^6\) 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,\(^7\) 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%\(^8\)\(^9\), indicating that ASQs are also promising OPV materials.

It became clear from the studies of Claudia Gude \etal\ that the photophysical properties in squaraine compounds correlate highly with their connected manners\(^1\), 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\(^a\) 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\(^a\),\(^e\) we aimed at the exploitation of ASQs showing relatively broad...
absorption spectra in the Vis-NIR region. Inspired by the discovery of Marks et al. that squaraines containing \((E)-2-(2,2-
olink{di}phenylhydrazono)\)-methyl]-1-(hex-5-enyl)-1H-pyrrrole 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 \((E)-2-(2,2-
olink{di}phenylhydrazono)\)-methyl]-1-(hex-5-enyl)-1H-pyrrrole 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.\(^7\)\(^{1a}\) 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 (\(\geq 1.43\) eV).\(^{1b}\) 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 \(\pi-\pi\) 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\(_{70}\)BM as electron-acceptor only exhibits a low PCE of 2.86% (device I, ITO/MoO\(_3\) (8 nm)/Py-1:PC\(_{70}\)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 \(\sim 10\) 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 beneficial to the enhancement of charge-carrier mobility, to promote more effective intermolecular \(\pi-\pi\) 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 \(\sim 15\) nm red-shifted \(\lambda_{\text{abs}}\) 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 \(\sim 5\) nm larger FWHM in its absorption spectrum in solid film state. Therefore, the presence of benzene[\(e\)]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 \(\sim 10^4\) 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.

Additional cyclic voltammetry (CV) measurements indicated that all these three compounds show two-electrode 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
Table 2 Photovoltaic performance of BHJ-OPVs based on Py-1-3.

<table>
<thead>
<tr>
<th>Device</th>
<th>Active layer (w/w)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Py-1:PC_{71}BM:1-3</td>
<td>0.75±0.01</td>
<td>9.46±0.17</td>
<td>0.39±0.02</td>
<td>2.81±0.05</td>
</tr>
<tr>
<td>II</td>
<td>Py-2:PC_{71}BM:1-3</td>
<td>0.78±0.01</td>
<td>10.86±0.24</td>
<td>0.40±0.02</td>
<td>3.16±0.14</td>
</tr>
<tr>
<td>III</td>
<td>Py-3:PC_{71}BM:1-3</td>
<td>0.78±0.01</td>
<td>10.98±0.24</td>
<td>0.44±0.02</td>
<td>3.75±0.23</td>
</tr>
<tr>
<td>IV</td>
<td>Py-2:PC_{71}BM:1-3</td>
<td>0.79±0.01</td>
<td>10.82±0.22</td>
<td>0.42±0.02</td>
<td>3.58±0.14</td>
</tr>
<tr>
<td>V</td>
<td>Py-3:PC_{71}BM:1-3</td>
<td>0.78±0.01</td>
<td>11.80±0.23</td>
<td>0.45±0.02</td>
<td>4.12±0.23</td>
</tr>
</tbody>
</table>

* Device annealed at 70 °C for 10 min.

Because thermal annealing is a well-adopted process for enhancing the performance of OPV devices, device IV (Py-2-based) and device V (Py-3-based) with their photoactive layers annealed at 70 °C 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. 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-annueling 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 methylenedioxy 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.

We acknowledge the financial support for this work from the National Natural Science Foundation of China (project No.21432005, 21190031 and 21372168) and the Research Fund for the Doctoral Program of Higher Education (No.20120009130005). We also thank the Analytical & Testing Center, SCU, and Comprehensive Training Platform of Specialized Laboratory, College of Chemistry, SCU for providing NMR and HRMS data for the intermediates and objective molecules.