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Molecular engineering of potent sensitizers for very efficient light harvesting in thin film solid state dye sensitized solar cells

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Supporting Information Placeholder

ABSTRACT: Dye-sensitized solar cells (DSSCs) have shown significant potential for indoor and building integrated photovoltaic applications. Herein we present three new D-A-\pi-A organic sensitizers, XY1, XY2 and XY3, exhibiting high molar extinction coefficients and a broad absorption range. Molecular modifications of these dyes, featuring a benzothiadiazole (BTZ) auxiliary acceptor, were achieved by introducing a thiophene heterocycle, as well as by shifting the position of BTZ on the conjugated bridge. The ensuing high molar absorption coefficients enable highly efficient thin-film solid-state dye-sensitized solar cells with only 1.3 μm mesoporous TiO\textsubscript{2} layer. XY2 with a molar extinction coefficient of 6.66×10\textsuperscript{4} M\textsuperscript{-1} cm\textsuperscript{-1} at 578 nm led to the best photovoltaic performance of 7.51%.

After 25 years of thorough study and development, dye-sensitized solar cells (DSSCs) are nowadays moving towards industrial production, aided by their simple and low-cost fabrication process, large range of colors, transparency and high photovoltaic conversion efficiency (PCE), particularly under low illumination conditions.\textsuperscript{1,2} Solid-state DSSCs (ssDSSCs) employing hole-transporting materials (HTMs) instead of redox shuttles in solution, have attracted significant interest as a practical solution for the problems posed by traditional liquid electrolytes.\textsuperscript{3-5} In 1998, Spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene) was reported as the first HTM for ssDSSCs. This material has since been widely used, not only in ssDSSCs but also in perovskite solar cells.\textsuperscript{4,6-8} A challenge for ssDSSC applications, however, remains the fact that spiro-OMeTAD only insufficiently infiltrates into thick mesoporous TiO\textsubscript{2} films. These films are therefore limited to a thickness of about 2 – 5 μm.\textsuperscript{9,10} Therefore, dyes with high extinction coefficients and broad absorption range are of great importance in order to achieve high solar-to-electricity conversion efficiencies on thin TiO\textsubscript{2} layers in ssDSSCs. Highly performing ssDSSCs exhibiting thin TiO\textsubscript{2} layers and strongly absorbing dyes do also not require scattering layers for optimal light harvesting. It is for this reason that they are very promising candidates for future application in building-integrated photovoltaic windows and other areas, where aesthetics play an important role. Organic sensitizers are ideal candidates for thin film cells due to their significantly higher molar extinction coefficients and lower cost than ruthenium-based sensitizers. Furthermore, their structural flexibility allows accessing a larger parameter space for fine tuning of dye properties.\textsuperscript{11-13} This is particularly important in the case of dye regeneration and charge recombination processes at the TiO\textsubscript{2}/dye/HTM interface, where molecular-level modifications of organic sensitizers are employed as an effective approach to impede undesirable charge recombination processes.\textsuperscript{14,15} This is exemplified in the case of Y123 (Figure 1) and LEG4, featuring bulky donors and cyclopentadithiophene...
mesoporous TiO$_2$ layers (~TiO$_2$/dye/HTM, leading to highly efficient ssDSSCs with spiro-OMeTAD, leading to a PCE of 7.7% with 1,1,2,2-tetrachloroethane-doped spiro-OMeTAD. For example, Burschka et al. achieved a PCE of 7.2% with BF$_4$-doped spiro-OMeTAD.16-18 Similarly, LEG4-sensitized ssDSSCs obtained a PCE of 7.7% with 1,1,2,2-tetrachloroethane-doped spiro-OMeTAD.

Previous work on DSSCs from our own, as well as Zhu’s group demonstrated, that organic sensitizers with D-A-$\pi$-A structures outperform their D-$\pi$-A analogues because the introduction of an auxiliary acceptor between the donor and $\pi$-bridge facilitates fine-tuning of the molecular energy levels. This leads to increased absorption and to an extension of the spectral response towards the red. From these works, benzothiadiazole (BTZ) emerged as a promising acceptor functionality. Following these results, we here investigated three novel BTZ-based D-$\pi$-A sensitizers, XY1, XY2 and XY3 (Figure 1). XY1 showed a high molar extinction coefficient, which could further be increased in XY2 by introducing a heterocyclic thiophene unit onto the conjugated chain, also leading to an extension of the absorption towards the red. This effect was further enhanced upon exchanging the position of BTZ and CPDT, XY3, yielding a dye that absorbed up to the near infrared region. The high molar extinction coefficients obtained from XY1 and XY2 enabled the fabrication of devices using very thin mesoporous TiO$_2$ layers (~1.3 nm), without compromising on device performance.

The absorption spectra of XY1, XY2, XY3 as well as the reference dye Y123 in CH$_2$Cl$_2$ are shown in Figure 2 whilst the parameters of their optical and electrochemical properties are displayed in Table 1. The main absorption band can be assigned to the intramolecular charge transfer (ICT) between the bulky donor and the cyanoacetic acid acceptor moiety. From Figure 2, we can clearly see that XY1 and XY2 not only show bathochromic shifts of the low energy absorption band but also an increase in molar extinction coefficients compared to Y123. Among the investigated structures, XY2 emerges as the most suitable sensitizer for ssDSSC due to its high molar extinction coefficient of 6.66 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$ at its maximum absorption wavelength of 578 nm. Interestingly, by switching the position of BTZ and CPDT (XY3), the absorption band was largely extended to the near infrared region, red-shifting the low energy absorption peak by 40 nm compared to XY2. However, the molar extinction coefficient of XY3 drops to 2.62 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$. At the same time, the HOMO energy level of XY3 was upshifted to 0.75 V vs. NHE, whilst XY2 has its HOMO energy level at 0.91 V vs. NHE, similar to that of Y123 and XY1. Density functional theory (DFT) calculations revealed better overlap of the HOMO and LUMO orbitals in XY2, XY1 and Y123 than XY3 (Figure S1), which provides a likely explanation for the higher molar extinction coefficients of XY2, XY1 and Y123 compared to XY3. From these data, it could also be noticed that CPDT contributes to electron donation in XY3, Figure S1, thereby shifting the HOMO energy level upwards.

In order to test the performance of these dyes in an ssDSSC application, devices were prepared using spin coated thin transparent mesoporous TiO$_2$ layers. The resulting XY2-sensitized ssDSSC devices showed a reddish-purple color and substantial transparency of the light absorbing layer as shown in Figure 3 (a). The cross-sectional SEM micrograph of the same device, Figure 3 (b), shows that spiro-OMeTAD penetrates the entire mesoporous structure, while exhibiting a 100 nm capping layer on the surface, isolating the TiO$_2$ film from the Au counter electrode.

The absorption spectra of XY1, XY2, XY3 and a reference dye Y123 in CH$_2$Cl$_2$ solution are shown in Figure 2 whilst the parameters of their optical and electrochemical properties are displayed in Table 1. The main absorption band can be assigned to the intramolecular charge transfer (ICT) between the bulky donor and the cyanoacetic acid acceptor moiety. From Figure 2, we can clearly see that XY1 and XY2 not only show bathochromic shifts of the low energy absorption band but also an increase in molar extinction coefficients compared to Y123. Among the investigated structures, XY2 emerges as the most suitable sensitizer for ssDSSC due to its high molar extinction coefficient of 6.66 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$ at its maximum absorption wavelength of 578 nm. Interestingly, by switching the position of BTZ and CPDT (XY3), the absorption band was largely extended to the near infrared region, red-shifting the low energy absorption peak by 40 nm compared to XY2. However, the molar extinction coefficient of XY3 drops to 2.62 $\times$ 10$^4$ M$^{-1}$ cm$^{-1}$. At the same time, the HOMO energy level of XY3 was upshifted to 0.75 V vs. NHE, whilst XY2 has its HOMO energy level at 0.91 V vs. NHE, similar to that of Y123 and XY1. Density functional theory (DFT) calculations revealed better overlap of the HOMO and LUMO orbitals in XY2, XY1 and Y123 than XY3 (Figure S1), which provides a likely explanation for the higher molar extinction coefficients of XY2, XY1 and Y123 compared to XY3. From these data, it could also be noticed that CPDT contributes to electron donation in XY3, Figure S1, thereby shifting the HOMO energy level upwards.

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close to that of Spiro-OMeTAD, suggesting that the dye regeneration takes place despite the small driving force between the HOMO levels of dye and HTM. The lower $V_{oc}$ potentially indicates increased electron recombination at the TiO$_2$/dye/HTM interface. This effect will be further investigated below. PCEs under 50% and 10% light intensity were also measured, illustrating excellent potential for Building Integrated Photovoltaic (BIPV) applications. Beyond 500 nm, devices based on XY1 and XY2 showed much higher IPCE than Y123. The peak IPCE was found to be 71% at 560 nm for XY1 and 70% at 580 nm for XY2, in contrast to 63% at 480 nm for Y123-based devices. In analogy to its absorption spectrum, devices based on XY3 showed two absorption peaks with IPCEs of 60% at 590 nm and 50% at 430 nm, respectively. The photovoltaic performance of ssDSSCs based on these dyes was assessed as a function of film thickness, ranging from 0.25 μm to 2.0 μm (see Supporting Information, section 8 and 9). Amazingly, with a TiO$_2$ film as thin as ~250 nm, ssDSSCs based on XY2 and XY1 reached PCEs of 4.34% and 4.01%, respectively.

Figure 4. (a) $I-V$ curves and dark currents of ssDSSCs with ~1.3 μm-thick TiO$_2$ layers based on Y123 (black) and XY1 (red), XY2 (blue), and XY3 (green) and (b) their corresponding IPCE plots under illumination of 10% Sun.

Table 2. Performance parameters of ssDSSCs based on XY1, XY2, XY3 and Y123 under different light intensities ($I_0$).

<table>
<thead>
<tr>
<th>Dye</th>
<th>$I_0$/Sun</th>
<th>$V_{oc}$/V</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y123</td>
<td>96.6%</td>
<td>0.904</td>
<td>8.45</td>
<td>0.729</td>
<td>5.77</td>
</tr>
<tr>
<td></td>
<td>49.9%</td>
<td>0.875</td>
<td>4.40</td>
<td>0.760</td>
<td>5.87</td>
</tr>
<tr>
<td></td>
<td>9.3%</td>
<td>0.804</td>
<td>0.80</td>
<td>0.784</td>
<td>5.44</td>
</tr>
<tr>
<td>XY1</td>
<td>95.0%</td>
<td>0.942</td>
<td>10.02</td>
<td>0.674</td>
<td>6.69</td>
</tr>
<tr>
<td></td>
<td>49.4%</td>
<td>0.907</td>
<td>5.31</td>
<td>0.717</td>
<td>6.98</td>
</tr>
<tr>
<td></td>
<td>9.2%</td>
<td>0.815</td>
<td>0.95</td>
<td>0.767</td>
<td>6.46</td>
</tr>
<tr>
<td>XY2</td>
<td>95.5%</td>
<td>0.929</td>
<td>10.14</td>
<td>0.698</td>
<td>6.89</td>
</tr>
<tr>
<td></td>
<td>50.1%</td>
<td>0.900</td>
<td>5.31</td>
<td>0.736</td>
<td>7.02</td>
</tr>
<tr>
<td></td>
<td>9.2%</td>
<td>0.823</td>
<td>1.00</td>
<td>0.774</td>
<td>6.89</td>
</tr>
<tr>
<td>XY3</td>
<td>95.6%</td>
<td>0.798</td>
<td>11.06</td>
<td>0.596</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td>49.3%</td>
<td>0.774</td>
<td>5.67</td>
<td>0.656</td>
<td>5.85</td>
</tr>
<tr>
<td></td>
<td>9.3%</td>
<td>0.703</td>
<td>0.98</td>
<td>0.683</td>
<td>5.06</td>
</tr>
</tbody>
</table>

The XY2-sensitized champion device achieved a PCE of 7.51%. This device also showed excellent PCEs under low light intensities (Table 3 and Figure 5). Under 50% Sun illumination, a high PCE of 7.64% was reached, which still amounted to 7.00% below 10% Sun. Current dynamics measurements of photocurrent vs. light intensity are shown in Figure 5(b). These measurements demonstrate a significant linearity between photocurrent and light intensity, suggesting that the photogenerated charges are efficiently evacuated in the investigated device.

Figure 5. (a) $I-V$ curves of champion XY2-sensitized ssDSSC device under different light intensities (solid: 1 Sun; dash: 0.5 Sun; dash dot: 0.1 Sun; dot: dark) and (b) the current dynamics (solid: measured data; dot, integrated results under 1 Sun).

Table 3. Performance parameters of champion ssDSSC based on XY2 under different light intensities ($I_0$).

<table>
<thead>
<tr>
<th>$I_0$/Sun</th>
<th>$V_{oc}$/V</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.5%</td>
<td>0.902</td>
<td>10.96</td>
<td>0.764</td>
<td>7.51</td>
</tr>
<tr>
<td>51.7%</td>
<td>0.870</td>
<td>5.80</td>
<td>0.785</td>
<td>7.64</td>
</tr>
<tr>
<td>9.6%</td>
<td>0.799</td>
<td>1.05</td>
<td>0.803</td>
<td>7.00</td>
</tr>
</tbody>
</table>

In order to better understand the relationship between the molecular structure of the dye and the resulting device performance, we performed charge extraction and transient optoelectronic analyses. Two devices were measured for each dye. The voltage vs. charge plot (Figure 6a) showed a weak upward shift of the electron quasi fermi level in TiO$_2$ for XY1 and XY2 when compared to Y123. No shift was found for XY3. The higher open circuit voltage of the devices employing XY1 and XY2 compared to Y123 is in good agreement with the data on electron lifetime shown in Figure 6c. For XY1 and XY2 the electron lifetime is 3 to 2 times lower compared to Y123, depending on the illumination condition.

The lower open circuit voltage of the devices employing XY3 is directly related to the electron lifetime. From Figure 6b it becomes clear that the recombination is ten times faster for XY3 compared to Y123. The higher recombination rate is thus responsible for the 100 mV difference in $V_{oc}$ between these dyes. We suggest that the presence of an auxiliary acceptor close to the TiO$_2$ surface could play a role in accelerating the recombination rate in comonitance with its lower driving force for regeneration. Interestingly, we observed slightly longer electron transport time constants for XY1 and XY2 compared to Y123 and XY3, as shown in Figure 6c.
Atmospherically high PCEs of 6.69% and 6.89%, much higher than for spiro-OMeTAD, PCE of 5.50% was achieved in the ssDSSC using XY3 because of the short electron lifetime and low driving force for dye regeneration, thus resulting in a low device efficiency. The champion device based on XY3 shows a board absorptance of $\pi J V oc$. In conclusion, through rational molecular structure modifications, we designed and investigated three novel organic sensitizers XY1, XY2, and XY3, among which XY1 and XY2 exhibit very high molar extinction coefficients and XY3 shows a broad absorption range reaching the near infrared region. By these modifications, we were able to achieve the best efficiency reported to date for D-A-n-A sensitizers in a ssDSSC application. With a TiO2 film thickness of ~1.3 µm, ssDSSCs based on XY1 and XY2 reached impressively high PCEs of 6.69% and 6.89%, much higher than for Y123. The champion device based on XY2 achieved a PCE of 7.51%. Despite the small offset between the HOMO energy levels of XY3 and spiro-OMeTAD, PCE of 5.50% was achieved in the ssDSSC using this dye. However, XY3 led to more charge recombination, which was attributed to the short electron lifetime and low driving force for dye regeneration, thus resulting in a low device $V oc$.

ASSOCIATED CONTENT

Supporting Information

Details for regents, materials, instruments and characterization. Synthetic routes, procedures and characterization data of all the new compounds. Methodology and results of density functional theory calculations. Details for fabrication of ssDSSCs, photovoltaic measurement and phototransient measurement. Results of reproducibility test and photovoltaic performance of ssDSSCs with different film thickness.

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Notes
The authors declare no competing financial interests.

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REFERENCES
