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

Xiaoyu Zhang\textsuperscript{a,b,‡}, Yaoyao Xu\textsuperscript{a,‡}, Fabrizio Giordano\textsuperscript{b,⁎}, Marcel R. Schreier\textsuperscript{b}, Norman Peltier\textsuperscript{b}, Yue Hu\textsuperscript{c}, Chenyi Yi\textsuperscript{b}, Neil Robertson\textsuperscript{c}, Jianli Hua\textsuperscript{a,⁎}, Shaik M. Zakeeruddin\textsuperscript{b,⁎}, He Tian\textsuperscript{a}, and Michael Grätzel\textsuperscript{b,⁎}

\textsuperscript{a} Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China
\textsuperscript{b} Laboratoire de Photoniques et Interfaces, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne, Station 6, 1015 Lausanne, Switzerland
\textsuperscript{c} School of Chemistry, University of Edinburgh, King’s Buildings, Edinburgh, EH9 3FJ, UK.

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-π-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%.

Figure 1. Molecular structures of XY1, XY2, XY3 and Y123.

After 25 years of thorough study and developement, 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'-tetakis(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{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 um.\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...
(CPDT)-based \( \pi \)-bridges, protected by alkoxy and alkyl chains, respectively. These bulky side chains shield the dye from the oxidized HTM and thereby inhibit recombination at the interface of TiO\(_2\)/dye/HTM, leading to highly efficient ssDSSCs with spiro-OMeTAD.\(^{16-18}\) For example, Burschka et al. achieved a PCE of 7.2\% from Y123-sensitized ssDSSCs using \( \text{tris}2-(1\text{H-pyrazol-1-yl})\text{pyridine} \)-cobalt(II) (FK102) as p-type HTM dopant (film thickness: 2.5 \( \mu \)m).\(^{16}\) Similarly, LEG4-sensitized ssDSSCs obtained a PCE of 7.7\% with 1,1,2,2-tetrachloroethanodoped spiro-OMeTAD (film thickness: \approx 2.5 \( \mu \)m)\(^{18}\) and 8.2\% with copper phenanthroline as hole conductor (film \approx 6 \( \mu \)m transparent + 3 \( \mu \)m scattering layer)\(^{19}\).

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.\(^{13,20,23}\) From these works, benzothiadiazole (BTZ) emerged as a promising acceptor functionality.\(^{20,22}\) Following these results, we here investigated three novel BTZ-based D-\( \pi \)-A sensitzers, 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 (\approx 1.3 \( \mu \)m), 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.\(^{13,23}\) 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 \( 6.66 \times 10^4 \text{M}^{-1} \text{cm}^{-1} \) 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 \( 2.62 \times 10^4 \text{M}^{-1} \text{cm}^{-1} \). 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.\(^{24}\) 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.

### Table 1. Optical and electrochemical properties of XY1, XY2, XY3 and Y123.

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>HOMO (vs. NHE)</th>
<th>( E_{\text{on}} ) (eV)</th>
<th>LUMO (vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y123</td>
<td>543 (4.90)</td>
<td>0.92</td>
<td>2.01</td>
<td>-1.09</td>
</tr>
<tr>
<td>XY1</td>
<td>552 (5.65)</td>
<td>0.99</td>
<td>1.97</td>
<td>-0.98</td>
</tr>
<tr>
<td>XY2</td>
<td>578 (6.66)</td>
<td>0.91</td>
<td>1.92</td>
<td>-1.01</td>
</tr>
<tr>
<td>XY3</td>
<td>618 (6.22)</td>
<td>0.75</td>
<td>1.80</td>
<td>-1.05</td>
</tr>
</tbody>
</table>

*Absorption maximum in CH\(_2\)Cl\(_2\) solution.\(^{a}\) Measured in CH\(_2\)Cl\(_2\) with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF\(_6\)) as electrolyte (working electrode; Pt; counter electrode: Pt wire; reference electrode: SCE; calibrated with ferrocene/ferrocenium (Fe/Fe\(^{\text{III}}\)) as an external reference).\(^{a}\) \( E_{\text{on}} \) was estimated from the absorption onset wavelength from UV-Vis absorption spectra of the dyes.\(^{d}\) LUMO was estimated by subtracting \( E_{\text{on}} \) from \( E_{\text{HOMO}} \).

The photovoltaic performance of ssDSSCs based on Y123, XY1, XY2 and XY3 under different light intensities are tabulated in Table 2 and their corresponding current density-voltage (\( J-V \)) curves, dark current plots and incident photon-to-electron conversion efficiency (IPCE) spectra are displayed in Figure 4. Solid-state DSSC with 1.3 \( \mu \)m TiO\(_2\) films showed good reproducibility (Figure S3). XY1 and XY2 perform significantly better than Y123 in ssDSSC devices due to their high molar extinction coefficients. The short circuit current densities (\( J_{\text{sc}} \)) of ssDSSC devices with XY1 and XY2 reached over 10 mAcm\(^{-2}\), which exceeds the 8.45 mAcm\(^{-2}\) observed from Y123. For devices based on the green dye XY3, a \( J_{\text{sc}} \) of 11.06 mAcm\(^{-2}\) was obtained but with a considerably lower \( V_{\text{oc}} \) value, losing over 100 mV compared to the other dyes. A \( V_{\text{oc}} \) of 0.798 V, 0.929 V, 0.942 V and 0.904 V was obtained with XY3, XY2, XY1 and Y123, respectively. Devices based on XY2 and XY1 led to good PCEs of 6.89\% and 6.69\%, respectively under 95\% Sun illumination, considerably higher than devices based on the reference dye Y123 (5.77\%). A PCE of 5.50\% was obtained for XY3, which is remarkable since its HOMO energy level is very
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 ($I_{sc}$).

<table>
<thead>
<tr>
<th>Dye</th>
<th>$I_{sc}$/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.

**Table 3.** Performance parameters of champion ssDSSC based on XY2 under different light intensities ($I_{sc}$).

<table>
<thead>
<tr>
<th>$I_{sc}$/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 these charge extraction measurement. The higher voltage is likely related to the more efficient photo-conversion of the dyes with higher molar extinction coefficients. Moreover, the energetics of the TiO$_2$ conduction band are affected by the dipole moment of dye and the resulting device performance, we

**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).
at spiro-OMeTAD, PCE of 5.50% was achieved in the ssDSSC using was attributed to the short electron lifetime and low driving force this dye. However, spite the small offset between the HOMO energy levels of The champion device based on 

Figure 6. Voltage (a) and electron lifetime (b) vs. extracted charge at $V_{oc}$ and electron transport time constant (c) vs. extracted charge at $J_{sc}$ in ssDSSCs based on Y123 (black) and XY1(red), XY2(blue), and XY3(green).

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 board 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 TiO$_2$ 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 of the new compounds. Methodology and results of density functional theory calculations. Details for fabrication of ssDSSCs, photovoltaic measurement and phototransient measurement. Results of re-producibility test and photovoltaic performance of ssDSSCs with different film thickness.

AUTHOR INFORMATION

Corresponding Author
fabrizio.giordano@epfl.ch
jilhua@ecust.edu.cn
shaik.zakeer@epfl.ch
michael.graetzel@epfl.ch

Author Contributions
‡These authors contributed equally.

Notes
The authors declare no competing financial interests.

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