High performance organic photosensitizers for dye-sensitized solar cells†

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We report highly efficient organic photosensitizers containing π-conjugated alkoxy-substituted oligophenylenevinylene linkers with electron donor–acceptor units for dye-sensitized solar cells. TA-DM-CA showed an overall solar-to-energy conversion efficiency of 9.67% at AM 1.5 illumination (100 mW cm⁻²).

In recent years, dye-sensitized solar cells (DSSCs) have attracted great interest because the utilization of solar energy at low cost is one of the challenging interdisciplinary technical issues. One of the important issues in the development of high performance DSSCs is the solar-to-energy conversion efficiency, which is highly affected by the nature of the photosensitizers. The efficiency of Ru complex photosensitizers such as N3, N719 and black dyes exhibit solar-to-energy conversion efficiency of up to 11% under AM 1.5G irradiation. In addition, organic dyes for use as a photosensitizer in DSSCs have been a subject of intensive research to achieve remarkable advances in the development organic dyes with efficiencies higher than 9%. Organic dyes provide structural versatility to tune the absorption wavelength, molar extinction coefficient, and HOMO–LUMO energy levels. The characteristic structural units of efficient organic dyes include coumarin, indoline, squaraine, polyene, hemicyanine, oligothiophene, perylene, porphyrin, merocyanine and cyanine. In particular, π-conjugated molecules with electron donor-acceptor moieties for effective intramolecular charge transfer exhibited high efficiencies for DSSC applications.

In this paper, we report an organic dye, TA-DM-CA, which shows 9.67% overall solar-to-electric energy conversion efficiency. We also investigated the mask effect on the cell efficiencies of organic dyes in Fig. 1.

As shown in Fig. 1, we prepared the organic dyes TA-DM-CA, TA-TM-CA and TA-HM-CA which contain methoxy-substitued oligo-phenylenevinylene linker with the triphenylamine unit as an electron donor and cyanoacrylic acid as an acceptor moiety. We previously reported an organic dye with a phenylene vinylene linker which showed an efficiency of 9.1%. The methoxy groups were introduced at the phenylene vinylene moiety to enhance the electron donating character into the π-conjugated donor-acceptor skeleton and to increase the absorption wavelength.

As shown in Fig. 2, TA-DM-CA showed an absorption maximum at 433 nm ($\varepsilon = 46 \times 10^4$ M⁻¹ cm⁻¹) and TA-TM-CA at 432 nm ($\varepsilon = 23 \times 10^4$ M⁻¹ cm⁻¹) in ethanol. The absorption maximum of TA-HM-CA, compared with TA-DM-CA, was red-shifted to 451 nm ($\varepsilon = 39 \times 10^4$ M⁻¹ cm⁻¹) due to the extended π-conjugated spacer unit. As shown in Fig. 3, differential pulse voltammetry (DPV) was used to determine the HOMO values of the sensitizers, which were determined by the first oxidation peaks of the DPV spectra. The HOMO levels of TA-DM-CA, TA-TM-CA and

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TA-HM-CA were \(-5.51\) eV, \(-5.44\) eV, and \(-5.39\) eV. The optical bandgap estimated from the absorption onset of the absorption spectrum was \(2.49\) eV, \(2.46\) eV, and \(2.41\) eV, respectively, for TA-DM-CA, TA-TM-CA and TA-HM-CA. The calculated LUMO values were \(-3.02\) eV, \(-2.98\) eV, and \(-2.98\) eV as summarized in Table 1, which are in the range of favorable energy matching with the conduction level of the TiO\(_2\) particle for efficient electron transfer from the LUMO of the dyes to the conduction level of TiO\(_2\).\(^{18}\)

The frontier molecular orbitals of the dyes are shown in Fig. 4. At the HOMO state, the electron density is uniformly distributed along the triphenylamine unit and the \(\pi\)-conjugated linker moiety. At the LUMO level, excited electrons are shifted from the electron donor moiety to the electron accepting cyanoacrylic acid unit due to the intramolecular charge transfer along the \(\pi\)-conjugated skeleton. Therefore, the excited electrons are expected to be effectively injected into the conduction band of TiO\(_2\) through the carboxyl anchoring group adjacent to the electron accepting cyano group.

The methods for the cell fabrication and photovoltaic characterization are described in the Supporting Information (ESI).\(^{19}\) Fig. 5 shows the photocurrent density-photovoltage \((I-V)\) curve without mask (a) and with mask (b). An apertured black mask was introduced on the cell to reduce the effect of scattered light from the edge of the glass electrodes on the TiO\(_2\) layer.\(^{19}\) The short circuit current density \((J_{sc})\) and open circuit voltage \((V_{oc})\) of TA-DM-CA without mask were 20.85 mA/cm\(^2\) and 697 mV with a fill factor \((ff)\) of 0.666. The overall conversion efficiency \((\eta)\) for TA-DM-CA was 9.67\% in which condition the efficiency of N719 was 10.21\%. The overall conversion efficiency of TA-TM-CA and TA-HM-CA without mask was 7.09\% and 7.11\%, respectively. With an increase of the conjugation length of the linker moiety of the dyes, the absorption was shifted to longer wavelength. However, TA-DM-CA shows the highest molar absorption coefficient and highest \(J_{sc}\) to show the best cell performance among three samples. In the presence of mask, the overall efficiency of the cells with the organic dyes decreased by \(\sim 30\%\) as summarized in Table 2. In the case of N719, after mask, the efficiency decreased by 20\%.

In particular, a relatively larger decrease in \(J_{sc}\) was observed for organic dyes when a mask is used. This result is possibly due to enhanced lateral scattering of short wavelength light whose absorption is more pronounced by the organic dyes with shorter absorption maximum compared with N719.

Table 1 Electrochemical and photophysical properties of organic dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>(E_{\text{HOMO}}) (eV)(^a)</th>
<th>(E_{\text{bandgap}}) (eV)(^b)</th>
<th>(E_{\text{LUMO}}) (eV)(^c)</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\varepsilon^*) (M(^{-1}) cm(^{-1}))</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\varepsilon^*) (M(^{-1}) cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-DM-CA</td>
<td>(-5.51)</td>
<td>(2.49)</td>
<td>(-3.02)</td>
<td>304</td>
<td>27 200</td>
<td>433</td>
<td>46 100</td>
</tr>
<tr>
<td>TA-TM-CA</td>
<td>(-5.44)</td>
<td>(2.46)</td>
<td>(-2.98)</td>
<td>302</td>
<td>16 500</td>
<td>432</td>
<td>23 200</td>
</tr>
<tr>
<td>TA-HM-CA</td>
<td>(-5.39)</td>
<td>(2.41)</td>
<td>(-2.98)</td>
<td>304</td>
<td>16 000</td>
<td>451</td>
<td>39 500</td>
</tr>
<tr>
<td>N719</td>
<td>(-5.64)</td>
<td>(2.64)</td>
<td>(-3.04)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Estimated from the oxidation potential determined by DPV. \(^b\) Estimated from the edge of absorption spectra. \(^c\) Calculated from the bandgap and HOMO value. \(^d\) See ref. 18. \(^e\) Absorption spectra in ethanol.
Table 2 Photovoltaic performance of the organic dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>Without mask</th>
<th>With mask</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{SC} , (\text{mA cm}^{-2})$</td>
<td>$V_{OC} , (\text{mV})$</td>
</tr>
<tr>
<td>TA-DM-CA</td>
<td>20.85</td>
<td>697</td>
</tr>
<tr>
<td>TA-TM-CA</td>
<td>14.89</td>
<td>679</td>
</tr>
<tr>
<td>TA-HM-CA</td>
<td>16.56</td>
<td>661</td>
</tr>
<tr>
<td>N719</td>
<td>20.90</td>
<td>751</td>
</tr>
</tbody>
</table>

Fig. 6 shows the incident photon to current conversion efficiency (IPCE) data for the organic dyes and N719 as a reference. In the case of TA-DM-CA, the IPCE value reached around 80% from 440 to 510 nm, which is higher than that of N719.

We expect that further structural optimization for the absorption of longer wavelength would provide an opportunity for the organic dyes to exhibit comparable performance with Ru complexes.

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References

16 See Supplementary Information.†