A strategy to design highly efficient porphyrin sensitzers for dye-sensitized solar cells†

Yu-Cheng Chang, a Shin-Li Wang, b Tsung-Yu Pan, a Shang-Hao Hong, b Chi-Ming Lan, a
Hsin-Hui Kuo, c Chen-Fu Lo, b Hung-Yu Hsu, a Ching-Yao Lin* b and Eric Wei-Guang Diau* a

Received 11th May 2011, Accepted 6th June 2011
DOI: 10.1039/c1cc12764k

We designed highly efficient porphyrin sensitzers with two phenyl groups at meso-positions of the macrocycle bearing two ortho-substituted long alkoxy chains for dye-sensitized solar cells; the ortho-substituted devices exhibit significantly enhanced photovoltaic performances with the best porphyrin, LD14, showing $J_{SC} = 19.167 \text{mA cm}^{-2}$, $V_{OC} = 0.736 \text{V}$, $FF = 0.711$, and overall power conversion efficiency $\eta = 10.17\%$.

Because of their excellent light-harvesting property with intense absorption throughout the visible to the near-IR region, various porphyrins have been designed and applied for dye-sensitized solar cells (DSSC).1 Optimization of the device performance for a push–pull zinc porphyrin (YD2) has attained power conversion efficiency $\eta = 11.0\%$,2 which is a new milestone for a porphyrin-based DSSC to compete with the highly efficient ruthenium-based DSSC developed almost two decades ago. This great performance of YD2 is due to its superior light-harvesting ability through introduction of a diarylamino group at the meso-position of the porphyrin ring.3 A similar approach was applied in introducing a pyrene moiety through a $\pi$-conjugated link coupled to a porphyrin core (LD4) to enhance greatly the light-harvesting ability beyond 800 nm.4 The open-circuit voltages ($V_{OC}$) of those highly efficient porphyrin dyes were reported,3,4 however, to be significantly less than that of the commonly used ruthenium dye N719. Mozer et al.5 stated that the significantly diminished electron lifetime is the main reason accounting for the smaller $V_{OC}$ of porphyrins; they proposed that $I_{3}^{-}$ in the electrolyte might be attached to the positively charged Zn-center of the porphyrin core for an efficient electron injection from the TiO$_2$ surface to occur. Tian and co-workers,6 who reviewed the photovoltaic results for many organic and ruthenium sensitizers, concluded that $V_{OC}$ can be improved upon decreasing the charge recombination and increasing the efficiency of electron injection with an appropriate design for an organic dye. To tackle this problem, we introduce in this communication a new concept to design a zinc porphyrin sensitizer with long alkoxy chains to protect the porphyrin core for a retarded charge recombination and also to decrease effectively the dye aggregation for an efficient electron injection.

Chart 1 shows the molecular structures of the proposed porphyrins based on this design. The core structures are based on PE1 reported elsewhere,7 with two phenyl substituents bearing two dodecoxyl (–OC$_{12}$H$_{25}$) chains at the ortho-position of each phenyl group (labeled LD12); the reference porphyrin (LD11) has three dodecoxyl groups at the meta- and para-positions of each phenyl group. We designed similarly a push–pull porphyrin (LD14) based on the structure of LD13 reported elsewhere.8 The syntheses of these porphyrins are similar to those reported elsewhere;7,9 details of the procedures are given in ESI.† Fig. S1† shows UV/vis absorption spectra of the four porphyrins in THF solution; the related spectral data are summarized in Table S1.† We investigated the electrochemical properties of these porphyrins using cyclic voltammetry (CV); the cyclic voltamograms are shown in Fig. S2† with the resulting oxidation and reduction potentials summarized in Table S1.† Based on the CV results, a potential-level diagram showing the HOMO and the LUMO of each porphyrin is presented in Fig. 1. These CV results indicate that the porphyrins with long alkoxy chains attached at the ortho-positions of the phenyl rings have more negative reduction and oxidation potentials than those with long

† Electronic supplementary information (ESI) available: Fig. S1–S10, Tables S1–S5, and experimental details. See DOI: 10.1039/c1cc12764k
alkoxyl chains attached at meta- and para-positions of the phenyl rings. As a result, the LUMO levels of LD12 and LD14 are above those of LD11 and LD13, respectively. Such information further implies that the ortho-substituted porphyrins might have larger $V_{OC}$ and more rapid electron injection than their meta-substituted counterparts, to enhance the photovoltaic performance of the corresponding devices, as discussed below.

The LD11–LD14 porphyrins were fabricated into DSSC devices according to procedures reported elsewhere. Fig. 2a and b show current–voltage characteristics and IPCE action spectra of the corresponding devices, respectively; the resulting photovoltaic parameters are summarized in Table 1. Both $V_{OC}$ and $J_{SC}$ of LD12 are significantly greater than those of LD11, leading to 55% enhancement of the overall power conversion efficiency for the two devices (7.43 vs. 4.78%). The amounts of dye loading were determined to be 96 and 153 nmol cm$^{-2}$ for LD12 and LD11, respectively, which show a trend opposite to their $J_{SC}$ values (13.235 vs. 9.735 mA cm$^{-2}$). As expected, $J_{SC}$ becomes significantly improved on incorporating the π-conjugated phenylethynyl dimethylamino group for both LD14 and LD13 (19.167 and 18.438 mA cm$^{-2}$), and $V_{OC}$ of the former is also greater than that of the latter (0.736 vs. 0.697 V). Both the enhanced $V_{OC}$ and $J_{SC}$ of the LD14 device yield a remarkable power conversion efficiency, $\eta = 10.17\%$.

The electron-transport kinetics were measured with seven white-light intensities as bias irradiation (powers in a range 10–70 mW cm$^{-2}$). The intensities of the probe pulse at 655 nm were appropriately attenuated so that the perturbation characteristic of the probe was maintained. For each measurement the probe pulse was focused on the device with the bias irradiation; a quick shutter in the probe path was triggered to block the probe beam so as to determine the zero of reaction duration. The resulting transients are shown in Fig. S3–S10 (ESI†); the corresponding kinetic parameters, determined from fitting the transients according to a procedure introduced previously, are summarized in Tables S2–S5. Fig. 3a and b show plots of chemical capacitance ($C_{ip}$) vs. $V_{OC}$ for the LD11/LD12 and the LD13/LD14 systems, respectively; a characteristic exponential rise feature of $C_{ip}$ as a function of $V_{OC}$ was obtained for each plot. As $C_{ip}$ is proportional to the density of states of TiO$_2$ at each $V_{OC}$, the plots shown in Fig. 3 provide direct information about the shift of the conduction band edge of TiO$_2$ ($E_{CB}$) upon dye uptake.

The results indicate that there exists an apparent potential shift of $E_{CB}$ for each system: $E_{CB}$ of LD12 and LD14 were increased by 34 and 24 mV compared to that of LD11 and LD13, respectively, explaining the enhancement of $V_{OC}$ of the corresponding devices shown in Fig. 2. The observed increased $E_{CB}$ of the ortho-substituted devices is consistent with the raised $E_{LUMO}$ of the corresponding porphyrins shown in Fig. 1.

To compare the charge recombination kinetics at the electrolyte/TiO$_2$ interface for the LD11/LD12 system and the LD13/LD14 system, respectively, Fig. 4a and b show semilogarithmic plots of electron lifetime ($\tau_R$) vs. $V_{OC}$. Because of the shifts of $E_{CB}$ for the LD12 and LD14 devices, a fair comparison of the degree of charge recombination should be made at the same reference potential level. As a result, the potential scales of $\tau_R$ were decreased by 34 and 24 mV for LD12 and LD14, respectively, so that the electron lifetimes could be compared at the same ‘equivalent common conduction band’ level.

![Fig. 2](image-url)  
Fig. 2 (a) Current–voltage curves and (b) IPCE action spectra of devices made of LD11–LD14 porphyrins.

![Fig. 1](image-url)  
Fig. 1 Potential-level diagram of the LD11–LD14 porphyrins, the TiO$_2$ conduction band, and the redox mediator.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{SC}$/mA cm$^{-2}$</th>
<th>$V_{OC}$/mV</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD11</td>
<td>9.735</td>
<td>674</td>
<td>0.728</td>
<td>4.78</td>
</tr>
<tr>
<td>LD12</td>
<td>13.235</td>
<td>741</td>
<td>0.758</td>
<td>7.43</td>
</tr>
<tr>
<td>LD13</td>
<td>18.438</td>
<td>697</td>
<td>0.727</td>
<td>9.34</td>
</tr>
<tr>
<td>LD14</td>
<td>19.167</td>
<td>736</td>
<td>0.721</td>
<td>10.17</td>
</tr>
</tbody>
</table>

Table 1 Photovoltaic parameters of TiO$_2$ films sensitized with porphyrins LD11–LD14 under simulated AM-1.5G illumination (100 mW cm$^{-2}$) and an active area of 0.16 cm$^2$.
factor accounting for the enhanced $V_{OC}$, as we observed for the LD12 and LD14 devices.

A strategy to improve $V_{OC}$ for organic dyes has always been an issue attracting many profound investigations. For example, Tian and co-workers, who studied cone-shaped organic dyes, observed an enhanced $V_{OC}$ for the dye with a methoxyl group; they speculated that the increased $E_{LUMO}$ might produce deep electron injection for retarded charge recombination. Mori and co-workers found only a little influence on the shift of electron injection for retarded charge recombination. Mori and co-workers, who studied cone-shaped organic dyes, observed significant decreases of $V_{OC}$ for organic sensitizers relative to those of Ru complexes is due mainly to their smaller electron lifetimes. Hagfeldt and co-workers investigated triphenylamino organic dye-based solar cells and made a similar conclusion: varied $V_{OC}$ reflect varied electron lifetimes rather than varied positions of $E_C$. For zinc porphyrin sensitizers, we observed significant decreases of $E_C$ for porphyrins with a long phenylethynyl link. In the present work, not only the contribution of charge recombination but also the increased $E_C$ through dye uptake should be considered for the observed $V_{OC}$ enhancement.

Porphyrins bearing bulky ortho-substituted alkoxyphenyl groups at meso-positions of the ring are reported for other applications because of their great steric hindrance preventing molecular aggregation. For porphyrin-sensitized solar cells, Hupp and co-workers reported that ortho-substituted porphyrins with two anchoring groups showed a device performance slightly less than that of an N719 dye. In the present work, such a molecular design was applied for a push–pull porphyrin (LD14) to attain an exceptional cell performance, $\eta = 10.2\%$. According to the crystal structure of an ortho-substituted porphyrin reported by Nikiforov et al., we expect that the four dodecyl chains in the devices play a key role in wrapping the porphyrin core in a shape that prevents dye aggregation effectively and forms a blocking layer on the TiO$_2$ surface. The net effect is to increase $E_{LUMO}$ of the molecule, to up-shift $E_C$ of TiO$_2$ upon dye uptake, and to retard charge recombination in the electrolyte/TiO$_2$ interface for an enhanced device performance. Work is in progress to incorporate this concept of molecular design for other porphyrins to attain even better device performance.

National Science Council of Taiwan and Ministry of Education of Taiwan, under the ATU program, provided support for this project.

**Notes and references**