This article is part of the

Porphyrrins & Phthalocyanines
web themed issue

Guest editors: Jonathan Sessler, Penny Brothers and Chang-Hee Lee

All articles in this issue will be gathered together online at

www.rsc.org/porphyrins
Design and characterization of alkoxy-wrapped push–pull porphyrins for dye-sensitized solar cells† †‡

Teresa Ripolles-Sanchis,a Bo-Cheng Guo,b Hui-Ping Wu,c Tsung-Yu Pan,c Hsuan-Wei Lee,b Sonia R. Raga,a Francisco Fabregat-Santiago,a Juan Bisquert,a‰ Chen-Yu Yehab and Eric Wei-Guang Diauc

Received 15th February 2012, Accepted 9th March 2012
DOI: 10.1039/c2cc31111a

Three alkoxy-wrapped push–pull porphyrins were designed and synthesized for dye-sensitized solar cell (DSSC) applications. Spectral, electrochemical, photovoltaic and electrochemical impedance spectroscopy properties of these porphyrin sensitzers were well investigated to provide evidence for the molecular design.

Porphyrins are promising candidates as highly efficient sensitizers for dye-sensitized solar cells (DSSC) because of their superior light-harvesting ability in the visible region.1–3 Recent advances on the development of a porphyrin sensitizer (YD2-o-C8) with co-sensitization of an organic dye (Y123) using a cobalt-based electrolyte attained a power conversion efficiency of 12.3%,4 which is superior to those developed based on Ru complexes5 and becomes a new milestone in this area. The key structural feature on molecular design of a highly efficient porphyrin sensitizer is to bear with long alkoxy chains in the ortho-positions of the meso-phenyls so as to effectively envelope the porphyrin ring to reduce the degree of dye aggregation for a higher electron injection yield and to form a blocking layer for a better charge collection yield.6 In the present study, we further design three porphyrin sensitzers (YD20–YD22, Chart 1) based on the structure of YD2-o-C8 but with extended π-conjugation in order to enhance the light-harvesting ability. Basically all of them have the same ortho-substituted porphyrin core with two phenylethynyl (PE) groups acting as a π-bridge in the meso-position of the ring. YD20 and YD22 dyes have the acceptor group (ethynylbenzoic acid) the same as that of YD2-o-C8 but with different donor groups: YD20 has a triphenylamino group with two methoxyl substitutes and YD22 has a phenylamino group with two n-butyl chains. On the other hand, YD20 and YD21 dyes have the same donor group but the cyanoacrylic acid was used as an anchoring group in YD21. This approach mimics the molecular design of an organic dye7 having the acrylonitrile group with strong electron-pulling power to act as an efficient acceptor for the porphyrin dye.

The details for the syntheses, optical and electrochemical characterizations of YD20–YD22 are given in ESI.† These porphyrin dyes were fabricated into DSSC devices for photovoltaic and electrochemical impedance spectroscopy (EIS) characterizations. Fig. 1a and b show the J–V curves and the corresponding Incident Photon to Current Conversion Efficiency (IPCE) action spectra for the YD20–YD22 devices, respectively; the obtained photovoltaic parameters and the amounts of dye-loading are summarized in Table 1. The results indicate that the short-circuit current densities (JSC) exhibit a trend YD20 > YD22 > YD21 and the open-circuit voltages (VOC) display a trend YD20 > YD22 ~ YD21; the overall power conversion efficiencies (η) show the same order as JSC, which is consistent with the variations of the IPCE action spectra showing the same order. As a result, YD20 has the highest JSC (17.43 mA cm–2) and VOC (676 mV), which yields the greatest η (8.1%) among the three porphyrins under investigation. Even though the cyanoacrylic substitute makes YD21 a slight red shift in the absorption spectrum (Fig. S1, ESI†), the floppy feature of the C=C double bond might tilt the molecules adsorbed on TiO2 film to significantly decrease its IPCE values and the corresponding current density. However, YD20 and YD22 have the same anchoring group and very similar
absorption spectra (Fig. S1, ESI), therefore, the differences in IPCE and photocurrent are related to the effect of the donor groups. Note that the decrease in the IPCE occurs at a nearly constant level for all the wavelengths of the spectra for YD21 compared to YD20. Thus, the loss of electrons is independent of the energy of the absorbed photons. Transport and injection losses may be considered for the decrease in IPCE, which is discussed in the following.

Dye loading measurements yielded 161, 132, and 134 nmol cm\(^{-2}\) for YD20, YD21, and YD22, respectively. The changes in \(J_{SC}\) between the dyes with the same anchoring group, YD20 and YD22, may be understood in terms of the different amounts of loaded sensitizer. Further explanation is needed for sample YD21 as the decrease in \(J_{SC}\) is larger despite the amount of dye loading in the cell is the same as for YD22.

Electrochemical Impedance Spectroscopy was used to complete the analysis of injection and to gain insight into the transport and charge losses characteristics of the DSSC with the different dyes.\(^8\) From the fitting of impedance spectra of the DSSC at different applied potentials under 1 sun illumination, we obtained the chemical capacitance \(C_p\), transport resistance in the TiO\(_2\) \(R_t\), recombination resistance \(R_{rec}\), and a function of the Fermi level voltage \(V_F\) shown in Fig. 2a, b, and c, respectively. Other contributions to the total resistance of the cell such as diffusion, counter electrode and FTO resistances were grouped as series resistance \(R_s\). The effect of \(R_s\) in the applied potential \(V_{app}\) was removed to obtain the \(V_F\) that may be calculated through \(V_F = V_{app} - jR_c\). From the plot of \(C_p\) vs. \(-V_F\) shown in Fig. 2a, the position of the conduction band edge of TiO\(_2\) \(E_c\) may be estimated as reported elsewhere.\(^9\) Through these calculations, we estimated that for YD20 \(E_c \approx -0.48 \text{ V vs. NHE}\), while for YD21 \(E_c\) was displaced +4 mV and YD22 −10 mV. Data from transport resistance shown in Fig. 2b also provide very small displacements in \(E_c\), corroborating that all the TiO\(_2\) conduction bands remain almost unchanged for the three dyes as obtained from the capacitance data.

To understand the origin of the small differences in the \(V_{OC}\) found for the three different dyes it is needed to analyze the behavior of the recombination resistance in Fig. 2c. In previous studies,\(^8,10\) when comparing the recombination resistance of different samples it has been found that the higher the value of \(R_{rec}\), the larger the \(V_{OC}\), while only very large changes in photocurrent produce small variations in \(V_{OC}\). The results here match very well with this analysis: as it can be seen in Fig. 2c, YD20 has the larger recombination resistance and \(V_{OC}\), whereas YD21 and YD22 have similar values of \(R_{rec}\) showing almost the same \(V_{OC}\).

Data from \(R_{rec}\) and \(R_t\) may be used to calculate the diffusion length \(L_n\) in TiO\(_2\) film shown in Fig. 2d as\(^8\)

\[
L_n = L \sqrt{\frac{R_{rec}}{R_t}}
\]

where \(L\) is the film thickness (15 μm) represented as a dashed curve in Fig. 2d. The \(L_n\) values exhibit a systematic trend with the order YD20 > YD22 > YD21 with those of YD20 and YD22 reaching values greater than their film thickness whereas those of YD21 being significantly smaller than the film thickness. This implies that the YD21 device suffers from a poorer collection efficiency of injected electrons what produces the extra decrease in \(J_{SC}\) found for this sample.

The small differences found for the position of the conduction band edge \(E_c\) may also help to fine tune the roles of the linker in these Zn-porphyrin dyes. If the Fermi level potential is shifted the amounts found for the displacement of \(E_c\), it is possible to compare the recombination resistance of the DSSC at the potential level with the same number of injected electrons. To do this we define the potential at the equivalent conduction band position\(^8\)

\[
V_{c,\text{ref}} = V_F - \frac{\Delta E_c}{e}
\]

where \(e\) is the electron charge and \(\Delta E_c = E_c - E_{c,\text{ref}}\), for which \(E_{c,\text{ref}}\) is the position of the conduction band of YD20. Based on
In conclusion, although the concept for molecular design with the cyanoacrylic acid acceptor has been widely applied in highly efficient organic dyes, \(^7\) such an approach does not work well for the porphyrin sensitizers as demonstrated herein. The greater performance in the YD20 device than the other two devices is attributed to its rigid structural feature for a larger amount of dye-loading, which combined with the higher recombination resistance and diffusion length yields to larger \(J_{SC}\) and \(V_{OC}\). Modification of the porphyrin structure with extended \(\pi\)-conjugation for better light harvesting is feasible to boost up the device performance in the near future.

This work was partially supported by National Science Council of Taiwan and Ministry of Education of Taiwan, under the ATU program. JB acknowledges support by projects from Ministerio de Ciencia e Innovación (MICINN) of Spain (Consolider HOPE CSD2007-00007, MAT2010-19827), and Generalitat Valenciana (PROMETEO/2009/058). SRR thanks financial support from Bancaixa foundation under project Innova 111272. CYY and EWGD acknowledge support by projects from National Science Council of Taiwan and Ministry of Education of Taiwan, under the ATU program.

**Notes and references**