

# Synthesis and characterization of diporphyrin sensitizers for dye-sensitized solar cells†

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Received (in Cambridge, UK) 21st August 2009, Accepted 4th November 2009

First published as an Advance Article on the web 24th November 2009

DOI: 10.1039/b917316a

**Novel porphyrin dimers with broad and strong absorption in the visible and/or near IR regions have been synthesized; the *meso-meso*-linked porphyrin dimer (YDD1) exhibited the best photovoltaic performance with power conversion efficiency 5.2% under AM 1.5G one solar illumination.**

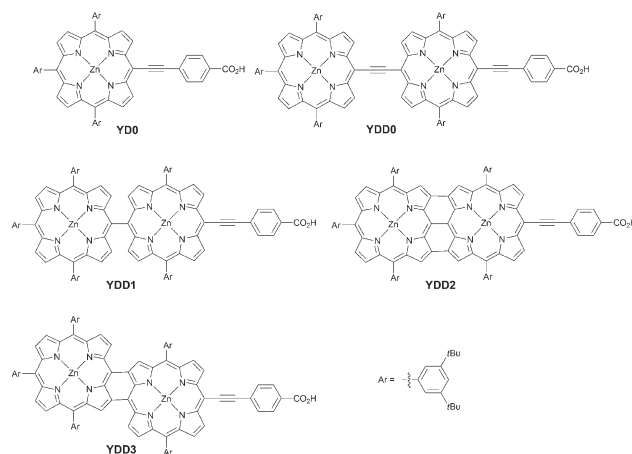
The development of clean and renewable energy sources reflects the limited fossil resources and severe environmental problems caused by their combustion. Infinite and inexhaustible solar energy is a key resource to meet a rapidly increasing global demand for energy. Dye-sensitized solar cells (DSSC) are promising devices to generate clean energy as an alternative to the traditional solar cells based on silicon. A typical DSSC comprises dye-sensitized nanocrystalline films of TiO<sub>2</sub> and an iodide/triiodide mediator.<sup>1</sup> The greatest efficiency ( $\eta$ ) for the conversion of solar to electric energy for a DSSC is >10% based on ruthenium polypyridine complexes.<sup>1b</sup> In view of the cost and environmental concerns about ruthenium dyes, organic dyes have attracted attention because of their diversity, the facile modification of their molecular structures, their intense absorption and cheap production.<sup>2–11</sup>

To generate a large photocurrent response, organic dyes in an efficient DSSC must have broad and intense absorption in the visible and near IR regions.<sup>12</sup> Porphyrin sensitizers are dominant candidates for this purpose because of their intense absorption in Soret and Q bands to harvest solar energy efficiently in a broad spectral region,<sup>13</sup> but the existence of a gap between the Soret and Q bands in monomeric porphyrins limits their cell performances. Porphyrin arrays linked with conjugated acetylene bridges exhibit strong electronic coupling between porphyrin rings, resulting in splitting of the Soret band and broadening of the Q bands.<sup>14</sup> Electronic absorption spectra of *meso-meso*-linked porphyrin arrays and their corresponding doubly and triply fused porphyrin arrays also show wide absorption covering the visible and near IR region.<sup>15</sup> By dint of such spectral features, these porphyrin arrays are prospectively efficient sensitizers for application in DSSC. Here we report the synthesis and the spectral,

electrochemical and photovoltaic properties of four porphyrin dimers; their molecular structures show diverse connectivity between the two porphyrin macrocycles, as displayed in Scheme 1. Details of their synthetic procedures appear in the ESI†.<sup>16–19</sup>

Absorption spectra of these porphyrin dyes are shown in Fig. 1; the corresponding spectral properties are listed in Table S1 (ESI†). All porphyrin dimers exhibit a much broader absorption than that of reference compound **YD0**. Compound **YDD0** shows split Soret bands in the range 400–500 nm, and red shifts and broadening of the Q bands due to interporphyrin electronic coupling. Dimer **YDD1** also exhibits a split Soret band ascribed to excitonic coupling. The absorption spectra of **YDD2** and **YDD3** exhibit a typical feature for fused porphyrin dimers with three major bands. Bands I and II of **YDD2** and **YDD3** feature a range across almost the entire visible region. Bands III appears at 756 and 845 nm for **YDD3**, whereas those for **YDD2** are much wider and range from 900 to 1300 nm. The molar absorption coefficients at the maximum absorption wavelengths for these dimers are all large and fall in the range  $0.3\text{--}2.9 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Fluorescence spectra of **YDD2** and **YDD3** were unobtainable because of the sensitivity limit of our detector for this region, but they are expected to fall in the near IR region.<sup>20</sup>

The reduction and oxidation potentials of these porphyrin dyes are summarized in Table S1 (ESI†). The cyclic voltammogram of **YDD0** shows two 1-e<sup>-</sup> reversible oxidations at  $E_{1/2} = +0.89$  and  $+1.08$  V (Fig. S1, ESI†). The first and second oxidations are cathodically shifted by 0.15 and 0.40 V relative to those of **YD0**, reflecting elevated energy levels due

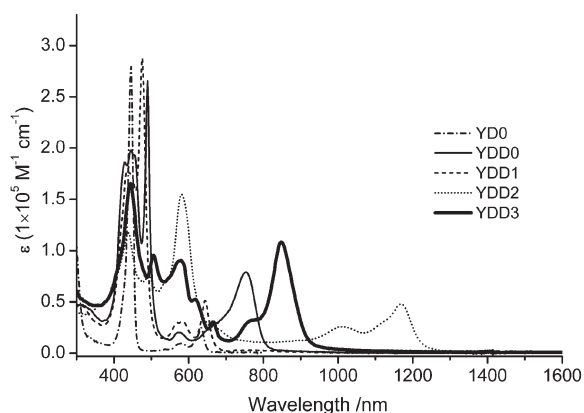


**Scheme 1** Molecular structures of porphyrin dyes.

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† Electronic supplementary information (ESI) available: Syntheses, characterizations, devices, measurements, supplementary Table S1 and Fig. S1–S4. See DOI: 10.1039/b917316a

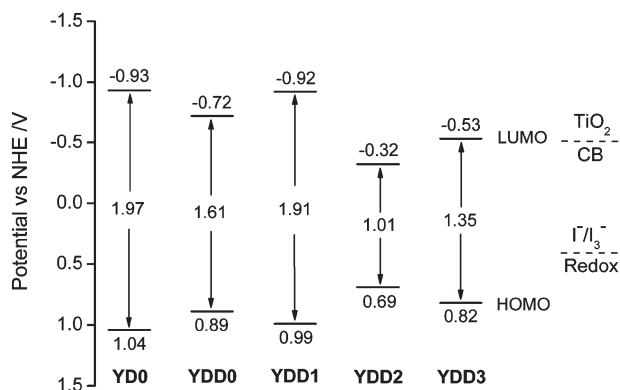


**Fig. 1** Calibrated absorption spectra of **YD0** and **YDD0–YDD3** in  $\text{CH}_2\text{Cl}_2/\text{pyridine}$  (100/1).

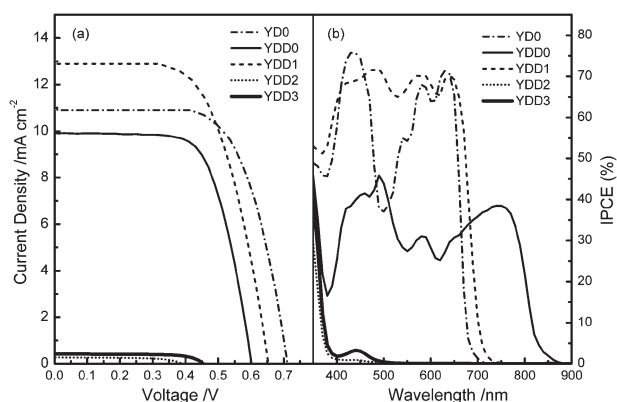
to strong interporphyrin interaction in **YDD0**. Compound **YDD1** exhibits two overlapping oxidation waves at  $E_{1/2} = +0.99$  and  $+1.17$  V, corresponding to  $1\text{-e}^-$  abstraction from each porphyrin ring. The cyclic voltammogram of **YDD2** displays two oxidations at  $E_{1/2} = +0.69$  and  $+1.03$  V, which are cathodically shifted by  $0.30$  and  $0.14$  V, respectively, relative to those of *meso-meso*-linked dimer **YDD1**. Similar electrochemical behavior was observed for fused porphyrin **YDD3**. The CV results of fused porphyrins show elevated HOMO and decreased LUMO energy levels, caused by extended  $\pi$ -conjugation over the two porphyrin macrocycles, consistent with results obtained from DFT calculations (Fig. S2, ESI†).

Fig. 2 shows energy levels of **YDD0–YDD3**, with **YD0** for comparison. The HOMO levels were derived from the first oxidation potentials of the porphyrins and the LUMO levels from the difference of the HOMO level and the absorption threshold of each porphyrin. The HOMO levels of these porphyrin dimers are all more positive than the oxidation potential for  $\text{I}^-/\text{I}_3^-$ , indicating that dye regeneration might be feasible for all sensitizers; the LUMO energy levels of only **YDD0** and **YDD1** are more negative than the conduction-band (CB) edge of  $\text{TiO}_2$ , whereas those of **YDD2** and **YDD3** are not negative enough for effective injection of the excited-state electrons into the CB of  $\text{TiO}_2$ .

Fig. 3a and b show the current–voltage characteristics and efficiencies of conversion of incident photons to current



**Fig. 2** Schematic energy levels of porphyrins **YD0** and **YDD0–YDD3** based on absorption and electrochemical data in ESI†.



**Fig. 3** (a) Current–voltage characteristics of DSSC devices with sensitizers **YD0–YDD3** under illumination of simulated AM1.5 full sunlight ( $100 \text{ mW cm}^{-2}$ ) with active area  $0.16 \text{ cm}^2$ ; (b) Corresponding action spectra for the efficiency of incident photon-to-current conversion.

(IPCE) of porphyrin-based DSSC; the corresponding photo-voltaic parameters are summarized in Table S1 (ESI†). Both porphyrin dimers **YDD0** and **YDD1** perform similarly to the reference compound (**YD0**), but the fused porphyrins (**YDD2** and **YDD3**) exhibit poor cell performance. In particular, the photocurrents of **YDD2** and **YDD3** are small, consistent with the potential feature shown in Fig. 2. For **YDD2**, essentially no injected electrons were observed (Fig. 3b), because the energy level of LUMO is substantially lower than the CB edge of  $\text{TiO}_2$ . For **YDD3**, a small response in the IPCE action spectrum corresponds to the contribution of broad Bands I and II of the fused porphyrin, but no injected electrons were observed for the broad Band III in region  $700\text{--}900 \text{ nm}$ . We infer that electron injection from the excited states of **YDD3** to  $\text{TiO}_2$  competed with energy relaxation from higher excited states (Bands I/II) to the lowest excited state (Band III), and there was insufficient kinetic energy for the electrons to inject from Band III of **YDD3** to the CB of  $\text{TiO}_2$ .

Integrating the IPCE over the AM 1.5G solar spectrum yields a calculated  $J_{\text{SC}}$  similar to the collected value for devices of **YD0**, **YDD0** and **YDD1** (Fig. S3, ESI†), confirming the accuracy of the current–voltage results shown in Fig. 3a. As shown there, the short-circuit photocurrent density ( $J_{\text{SC}}$ ) of **YDD1** is greater than that of **YD0**, whereas the open-circuit voltage ( $V_{\text{OC}}$ ) of the former is smaller than the latter; the net effect produces a slightly greater power-conversion efficiency of the former than that of the latter ( $\eta = 5.23$  vs.  $5.14\%$ ). The fact that the  $J_{\text{SC}}$  value of **YDD1** was significantly greater than that of **YD0** is understood to be due to the effective excitonic coupling of the two porphyrin macrocycles in the dimer, whereas such a character was absent in the monomer. As a result, the IPCE spectrum of **YDD1** exhibits a flat response over the entire visible region whereas that of **YD0** shows a large gap between the Soret and Q bands (Fig. 3b). In contrast, the overall efficiency of **YDD0** was significantly smaller than that of **YDD1** ( $4.07$  vs.  $5.23\%$ ) because of the smaller  $J_{\text{SC}}$  and  $V_{\text{OC}}$  values of the former. Even though the IPCE spectrum of **YDD0** shown in Fig. 3b displays a broad feature covering spectral range  $400\text{--}800 \text{ nm}$ , the IPCE values of **YDD0** were much smaller than those of **YDD1** in the region of spectral response.

We notice that the absorption coefficients of **YDD0** are, in general, greater than those of **YD0** and **YDD1** (Fig. 1), but the values of IPCE of the former are substantially lower than those of the latter (Fig. 3b). As the results of dye-loading experiments (Fig. S4, ESI†) show similar amounts of dye molecules ( $\sim 75 \text{ nmol cm}^{-2}$ ) being sensitized on  $\text{TiO}_2$  films for **YD0-YDD1**, the smaller external quantum efficiencies of **YDD0** relative to those of **YD0** or **YDD1** are thus inferred to arise from the efficiency of electron injection into  $\text{TiO}_2$ , which was smaller for the former than for the latter. There are two reasons that explain these effects; one is that the LUMO energy level of **YDD0** is much lower than that of **YD0** or **YDD1**, which might impede electron injection for the former. The other is that the nearly planar structure of **YDD0** facilitates  $\pi$ -conjugation between two porphyrin macrocycles and provides a decreased driving force to push electrons toward  $\text{TiO}_2$ ; this explanation is consistent with the frontier orbital pictures shown in the supplementary Fig. S2 (ESI†). The planar geometry of **YDD0** might also facilitate the formation of dye aggregates that significantly decrease the efficiency of electron injection.

In conclusion, we have synthesized porphyrin dimers with varied connectivity (**YDD0-YDD3**) between the two porphyrin moieties; their nature significantly influences their spectral, electrochemical and photovoltaic properties. Among these porphyrin dimers, **YDD1** exhibited the greatest photocurrent density because of its flat IPCE spectrum with external quantum efficiencies  $\sim 70\%$  covering the entire visible spectral region. Although **YDD0** displayed a further broad IPCE spectrum extending to the near-IR region, the cell performance was not improved because of the smaller quantum efficiencies (producing a smaller short-circuit current density) and open-circuit voltage. The best photovoltaic performance of **YDD1** attained 5.2%, which is slightly greater than, but comparable with, that of the reference monoporphyrim **YD0**. Introduction of an electron-donating group such as diarylamine into the *meso*-position opposite the anchoring group significantly increases the efficiency of conversion of solar energy to electricity.<sup>21</sup> Preparation of diporphyrin dyes incorporating electron-donating groups to improve the cell performance for DSSC applications is in progress.

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

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