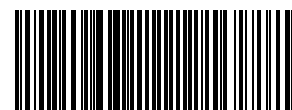# Energy & Environmental Science
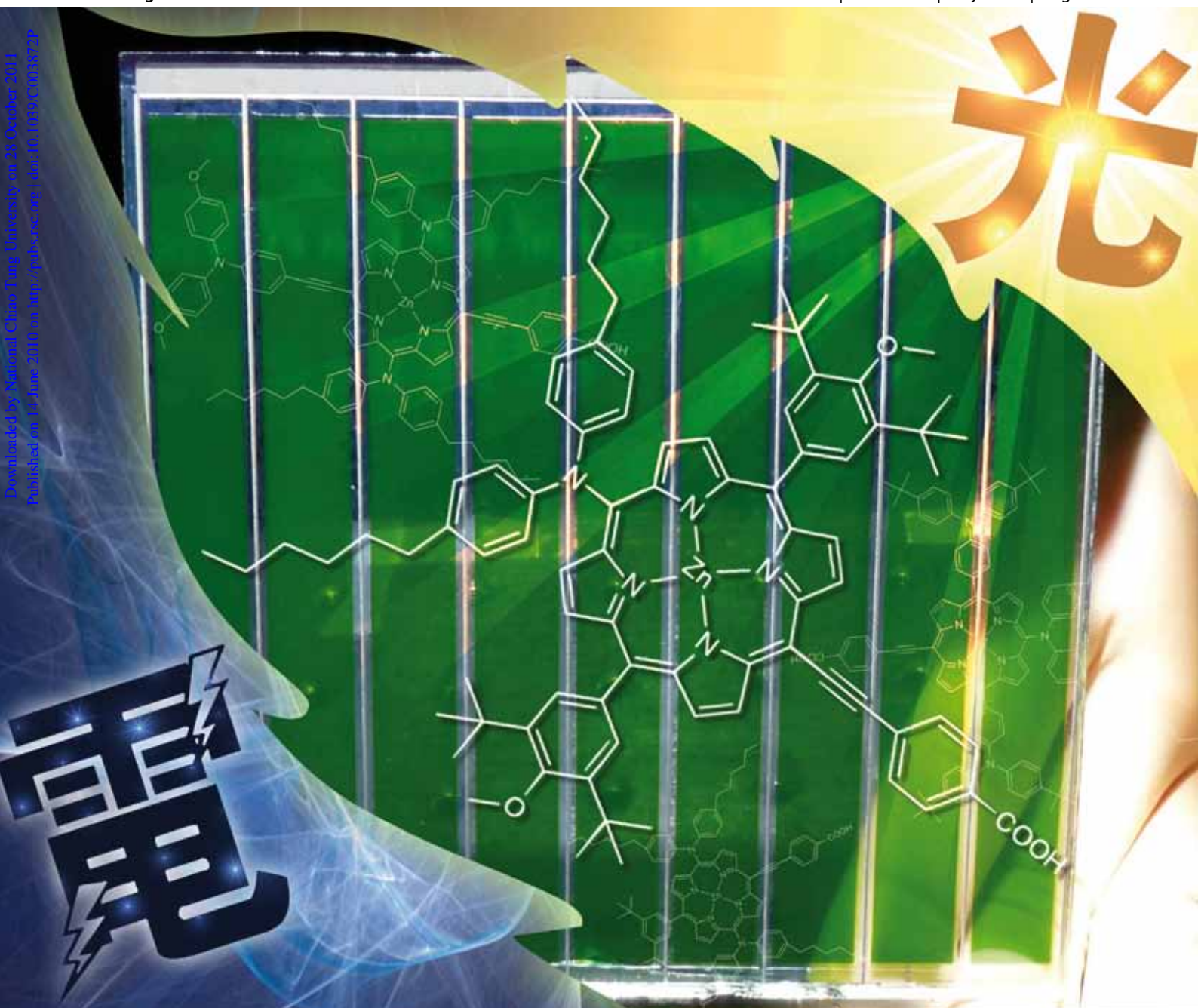
光

電

COVER ARTICLE
Diau *et al.*
Design and characterization of porphyrin sensitizers with a push-pull framework for highly efficient dye-sensitized solar cells

REVIEW
Qiao *et al.*
A review of polymer multijunction solar cells

RSCPublishing

Design and characterization of porphyrin sensitizers with a push-pull framework for highly efficient dye-sensitized solar cells†

Sung-Lin Wu,[a] Hsueh-Pei Lu,[b] Han-Ting Yu,[a] Shu-Han Chuang,[a] Chien-Lan Chiu,[a] Cheng-Wei Lee,[a] Eric Wei-Guang Diau*[b] and Chen-Yu Yeh*[a]

Novel porphyrin dyes **YD14–YD17** with a push-pull framework were synthesized for dye-sensitized solar cells (DSSC); their spectral, electrochemical and photovoltaic properties were investigated. The absorption bands of these porphyrin dyes are broadened and red-shifted upon introduction of electron-donating groups (EDG) to the *meso*-positions *via* extension of π-conjugation. Electrochemical tests show that the first oxidation for these porphyrins occurs at a potential greater than that of the I^-/I_3^- redox couple, and attachment of EDGs to the periphery of the porphyrin facilitates electron abstraction. The photovoltaic measurements show that **YD14** and **YD17** have a power conversion efficiency of ∼7%. Introduction of EDGs to various *meso*-positions is demonstrated to be achievable, and porphyrin dyes with appropriate EDGs are promising candidates for highly efficient DSSCs.

Introduction

The increasing demand for energy and global warming due to greenhouse gases from fossil fuels have encouraged scientists to seek environmentally benign alternative energy resources, which are vital to maintain a stable rate of growth of the global economy. Among various renewable energy resources, solar energy is the most viable to meet our energy requirement.[1] Traditional solar cells based on silicon have attained an efficiency (η) of ∼15% of power conversion,[2] but the cost of solar panels made from semiconductive silicon has limited their application. Dye-sensitized solar cells (DSSC) appear to be a promising alternative to conventional inorganic solar cells.[3] Since 1990 much effort has been devoted to the synthesis and characterization of various sensitizers for DSSCs after Grätzel *et al.*

reported the excellent performance of DSSCs based on ruthenium complexes.[4] The most efficient dyes for DSSCs are based on ruthenium polypyridyl complexes which show an efficiency of ∼11% of power conversion under standard air-mass (AM) 1.5 illumination.[5] In addition to ruthenium complexes, many organic dyes have been synthesized and their photovoltaic properties investigated.[6] Their advantages include a small cost of production, tunable electrochemical and photophysical properties, the feasible modification of their molecular structures, and a lack of pollution and resource limitation.

Porphyrins and related compounds are commonly studied heterocycles because they are ubiquitous in diverse biological systems such as hemoglobin, cytochrome P-450 and the photosynthetic reaction center.[7] Numerous model compounds have been designed and synthesized to mimic their reactivity and functions in biological processes.[8] For instance, molecules that can undergo intramolecular energy transfer and electron transfer are promising candidates for use in artificial photosynthesis.[9] Knowledge acquired from these artificial photosynthetic models not only improves our understanding of the influence of these structures on the photoinduced electron transfer but also contributes to the development of photovoltaic devices. Stimulated by the efficient energy and electron transfer in this

[a] Department of Chemistry, National Chung Hsing University, Taichung, 402, Taiwan. E-mail: cyyeh@dragon.nchu.edu.tw; Fax: (+886) 4-2286-2547

[b] Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu, 300, Taiwan. E-mail: diau@mail.nctu.edu.tw; Fax: (+886) 3-572-3764

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c003872p

Broader context

Because the sun is the most important inexhaustible and clean energy source, efficiently harvesting solar energy to generate electric power using photovoltaic technology beyond silicon systems has undergone rapid development over the past few years. The dye-sensitized solar cell (DSSC) has proved to be a highly efficient and low-cost option for conversion of solar energy. For example, ruthenium complexes such as the **N719** dye have been used as efficient photosensitizers to achieve the record for a DSSC device (η ∼12%) under one sun irradiation. Organic dyes with conversion efficiencies in a range of 5–10% have been reported. Porphyrin dyes with strong absorption in the visible region as well as tunable wavelengths are also potential candidates for DSSC applications. A previous study indicates that a push-pull zinc porphyrin (**YD2**) can be used for DSSCs to have a cell performance comparable to that of **N719**. Inspired by the molecular design of **YD2**, a new series of porphyrin sensitizers (**YD14–YD17**) are reported in the present study to show great light harvesting ability as well as promising cell performance comparable to that of **YD2**.

This journal is © The Royal Society of Chemistry 2010

Energy Environ. Sci., 2010, **3**, 949–955 | 949

photosystem, several porphyrin sensitizers[10] and related macro-cyles[11] have been designed and investigated with an aim to be applied in DSSCs. Officer and co-workers analyzed the structural dependence of diverse porphyrin dyes on their cell perfor-mance,[12] and found that conjugated links between the carboxyl anchoring group and the porphyrin ring are responsible for the superior light-harvesting ability to increase the efficiencies of power conversion of the devices; the conjugated bridges exhibit a strong interaction with the porphyrin ring, resulting in broadening and red shifting of the absorption bands. The most efficient porphyrin dye reported, which attains a conversion efficiency of 7.1%, is a zinc tetraarylporphyrin malonic acid, in which the porphyrin ring and anchoring group are linked with a butadienylene bridge *via* the β-position.[13]

In general, porphyrins show a sharp and intense Soret absorption band at about 400–450 nm and a few moderately intense Q absorption bands at about 500–650 nm. One drawback of porphyrin dyes used for DSSCs is the absorption trough between the Soret and Q bands that decreases the light-har-vesting efficiency. Imahori and co-workers reported the synthesis and photovoltaic properties of a naphthalene-fused, π-extended porphyrin;[14] elongation of the π-system caused the porphyrin dye to collect visible light efficiently, improving the cell perfor-mance by ∼50% relative to the unfused counterpart.

Organic dyes with a push-pull framework are proven to be efficient sensitizers in dye-sensitized solar cells.[15] Durrant and co-workers showed that introduction of electron-donating groups (EDG) at the *meso*-positions resulted in a decreased rate of charge recombination between injected electrons in the TiO$_2$ and the oxidized dye anchored to it.[16] We reported that porphyrin dyes substituted with a strongly electron-donating diarylamino group exhibit a cell performance of $\eta = 5$–7%.[17] As an extension of our preceding work, we have designed and synthesized porphyrin dyes, **YD14–YD17**, containing diarylamino and/or

triphenylamino moieties in various *meso*-positions (Chart 1). We report here their optical, electrochemical and photovoltaic properties.

Results and discussion

Our previous experiments on porphyrin dyes for DSSCs show that introduction of a diarylamine to the porphyrin improves the cell performance.[17] For instance, the **YD2**-based solar cell exhibits an efficiency of power conversion greater than 6.5%. As mentioned, organic dyes with EDGs can improve the perfor-mance of a DSSC. We thus designed porphyrins **YD14–YD17** to elucidate the influences of the EDG in various positions of the porphyrin ring on their optical, electrochemical and photovoltaic properties. The synthesis of **YD14–YD17** relies on amination and Suzuki coupling reactions to introduce diarylamine and benzoic acid moieties at the *meso*-positions, respectively. The detailed synthetic procedures are described in ESI.†

The steady-state absorption spectra of porphyrins **YD14–YD17** and reference porphyrins **YD0** and **YD2** in solution are shown in Fig. 1; the absorption and emission data of these porphyrin dyes are given in Table 1. In sharp contrast to typical tetraphenylporphyrins, porphyrin **YD14** shows split Soret bands, and broadened and red-shifted Q bands, indicating a strong electronic interaction between the porphyrin and diphenylamino units. Such an absorption property has also been observed in 5,15-bis(di-*p*-anisylamino)-10,20-diphenylporphyrin by Saka-moto *et al.*[18] The absorption band of **YD14** at ∼490 nm fills the blue part of the absorption gap between the Soret and Q bands for a typical tetraphenylporphyrin. The light-harvesting effi-ciency is thus expected to improve in this region for the DSSC made with **YD14**. To further enhance the absorption in the visible region and even in the near IR region, we expanded the π-conjugation system by introducing a triphenylamine at the
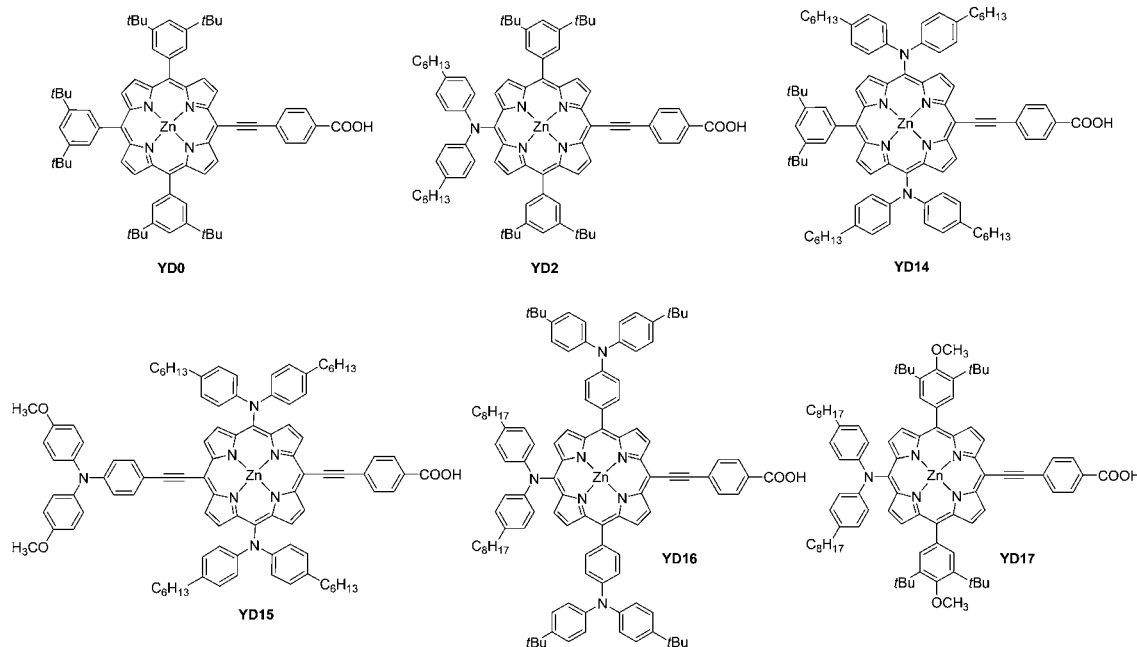

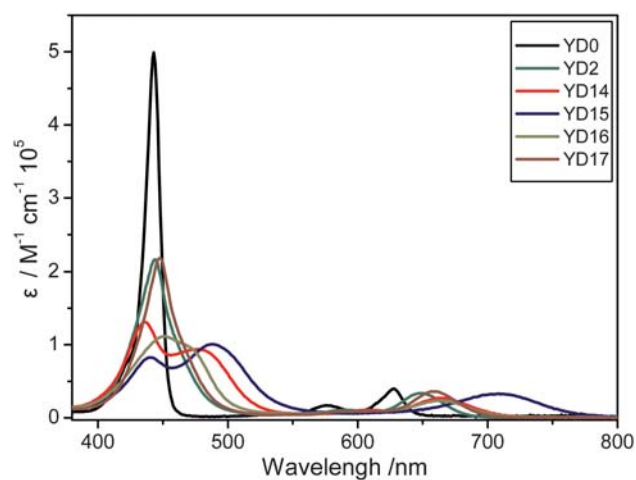**Chart 1** Molecular structures of porphyrin sensitizers.

Fig. 1 Absorption spectra of **YD0** and **YD2** in EtOH, and **YD14–YD17** in THF.

meso-position *via* an ethynylene bridge (**YD15**). This condition causes an even more pronounced red shift and broadening of both Soret and Q bands relative to **YD14**. In compound **YD16**, two strongly electron-donating triphenylamino units are directly attached at the 5,15-*meso* positions together with one diarylamino unit attached at the 10-*meso* position. The absorption spectrum of **YD16** shows that both Soret and Q bands are slightly broadened and red-shifted relative to those of **YD2**, indicating that only mild electronic communication is involved between the triphenylamino moieties and the porphyrin ring because of the steric interactions that cause the triphenylamino units to rotate from the porphyrin plane.[19] Porphyrin **YD17** has additional methoxyl groups on the phenyl ring that would increase the electron-donating ability relative to **YD2**. The spectral features of **YD17** resemble those of **YD2** except that the Soret and Q bands exhibit a slightly bathochromic shift.

The emission properties of these porphyrin dyes exhibit a trend similar to their absorption. The fluorescence data are listed in Table 1. A shift in the wavelength of maximum fluorescence toward greater wavelengths was observed as the effective conjugation in the molecules increased. Relative to **YD2**, the fluorescence of **YD14** is red-shifted from 676 to 697 nm because compound **YD14** has an additional diarylamino moiety that

enhances π-conjugation. An additional shift of emission to 750 nm was observed for **YD15** that has a greater length of conjugation. The shifts of the emission bands for **YD16** and **YD17** are only moderate as their major structural features are similar to those of **YD2**.

The electrochemical properties of porphyrins **YD14–YD17** were investigated with cyclic voltammetry in THF containing 0.1 M TBAPF$_6$ at 25 °C. The electrochemical data (Fig. 2) are summarized in Table 1. All these porphyrin dyes exhibit reversible reduction and oxidation for the first oxidation, corresponding to the HOMO energy of the dye, at a potential greater than that of the I$^-$/I$_3^-$ redox couple, indicating effective regeneration of the oxidized state.[20] In these porphyrins, compound **YD17** exhibits an electrochemical behavior similar to that of **YD2** that reflects their structural similarity; one reversible oxidation occurs at +0.91 V and an irreversible oxidation at E_{pc} = +1.27 V. Analysis of the first oxidations of all these porphyrins shows that attachment of an EDG to the periphery of the porphyrin facilitates electron abstraction. For instance, the first oxidation occurs at +0.89 V for the reference **YD2**, which cathodically shifts to +0.86 V for **YD14**, and shifts further to +0.81 V for **YD15**. Additional EDGs help to stabilize the
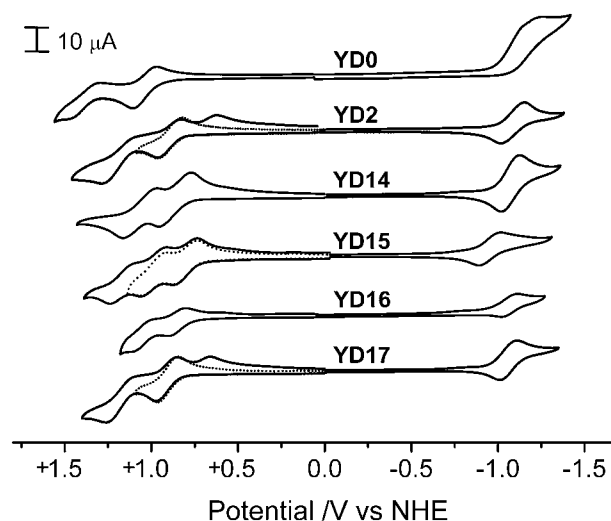

Fig. 2 Cyclic voltammograms of **YD0**, **YD2**, and **YD14–YD17** in THF containing 0.1 M TBAPF$_6$ at 25 °C.

Table 1 Absorption, fluorescence and electrochemical data for porphyrins **YD0**, **YD2**, and **YD14–YD17** [a]

Porphyrin	Absorption λ_{max}/nm (ε/10^3 M^{-1}cm^{-1})	Emission[b] λ_{max}/nm	Oxidation $E_{1/2}$/V	Reduction $E_{1/2}$/V
YD0	442 (498), 579 (16.8), 627 (39.8)	634	+1.04, +1.48[c]	−1.36[c]
YD2	444 (217), 589 (10.8), 648 (33.7)	676	+0.89, +1.29[c]	−1.09
YD14	436 (131), 476 (94.0), 615 (10.4), 660 (26.7)	697	+0.86, +1.04	−1.06
YD15	440 (82.7), 488 (101), 707 (32.5)	750	+0.81, +0.98, +1.15	−0.96
YD16	451 (112), 600 (8.8), 666 (23.6)	687	+0.85, +1.11	−1.08
YD17	448 (218), 606 (9.7), 662 (36.1)	679	+0.91, +1.27[c]	−1.08

[a] Absorption data were measured for samples in ethanol for **YD0** and **YD2**, and in THF for **YD14–17**. Emission data were measured for samples in ethanol for **YD0** and **YD2**, and in THF for **YD14–17** at 298 K. Electrochemical measurements were performed at 25 °C for samples in THF containing TBAPF$_6$ (0.1 M) as a supporting electrolyte. Potentials measured *vs.* a ferrocene/ferrocenium (Fc/Fc$^+$) couple were converted to those for the normal hydrogen electrode (NHE) by addition of +0.63 V. [b] The excitation wavelengths were 550, 600, 600, 630, 580 and 600 nm for **YD0**, **YD1**, and **YD14–YD17**, respectively. [c] Irreversible process E_{pa} or E_{pc}.
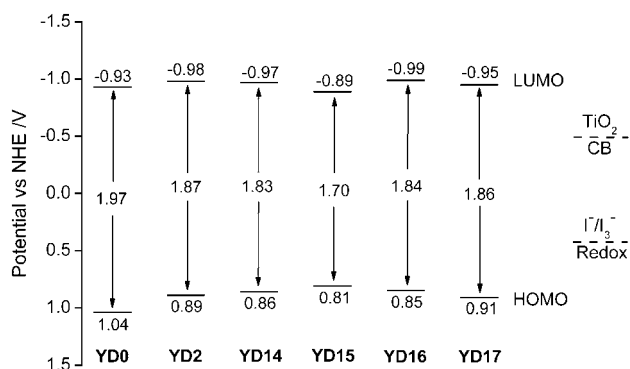
Fig. 3 Schematic energy levels of porphyrins **YD0**, **YD2** and **YD14**–**YD17**. HOMO = E_{ox1} and LUMO = $E_{0-0}*$.

oxidized species as the second oxidation for **YD14**–**YD16** is reversible whereas that for **YD2** is irreversible under similar conditions. For the reduction, **YD14**, **YD16** and **YD17** exhibit a reversible wave at $E_{1/2} = -1.10$ V whereas **YD15** shows an anodically shifted redox couple at -0.96 V because of the extension of π-conjugation that stabilizes the extra charge. Both incorporation of additional diarylamino or triphenylamino groups onto the porphyrin ring and increased length of π-conjugation decrease the electrochemical HOMO–LUMO energy gap, consistent with red shifts of both absorption and emission spectra. The potential separations between the first oxidation and reduction, $\Delta E = E_{1/2}(ox1) - E_{1/2}(red1)$, were calculated to be 1.98, 1.92, 1.77 and 1.93 V for **YD2**, **YD14**, **YD15** and **YD16**, respectively. In our previous work we showed that both porphyrin and diarylamino units were responsible for the

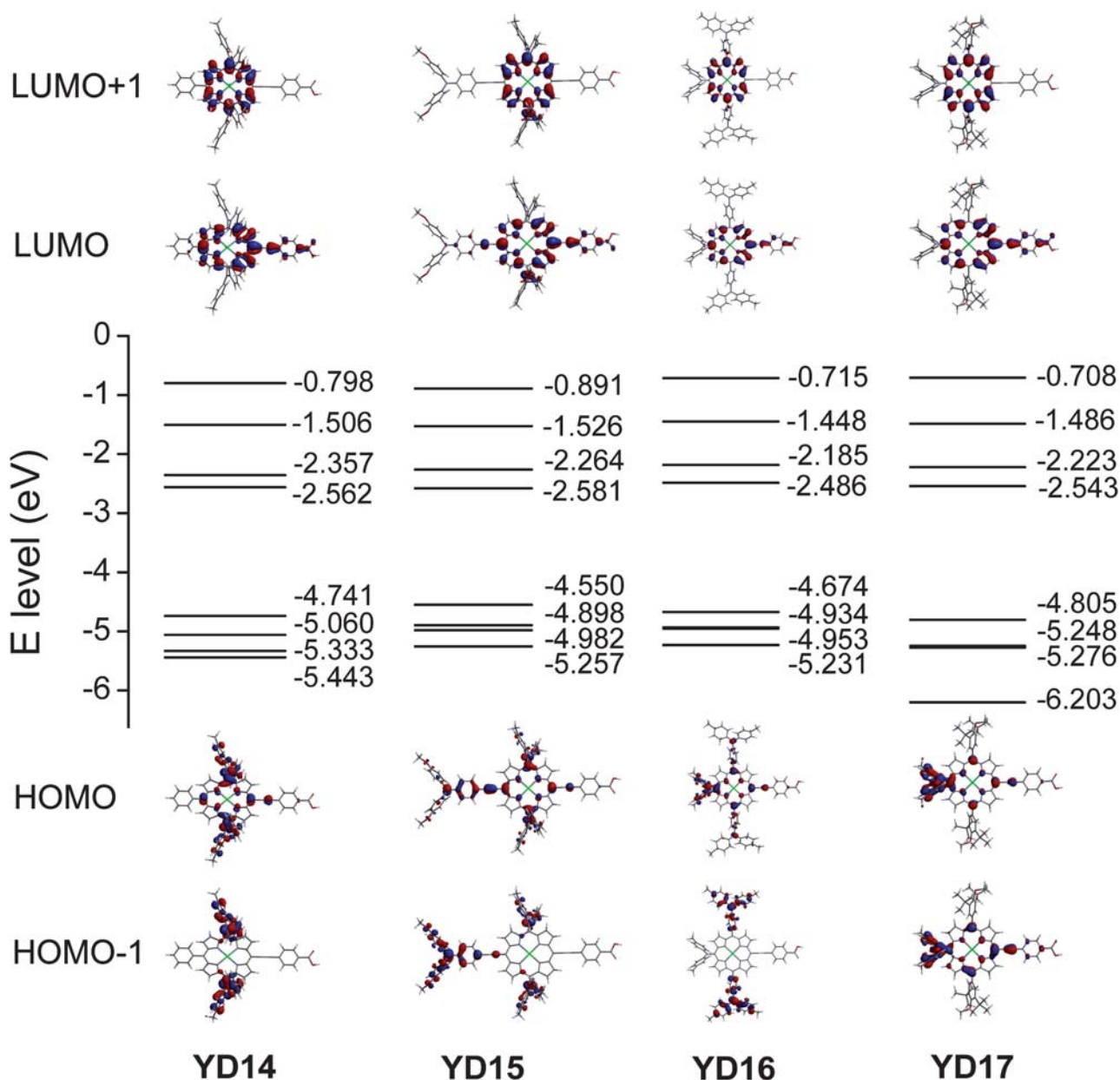**Fig. 4** Energy levels and the corresponding molecular orbitals of porphyrins **YD14**–**YD17** calculated at the B3LYP/6-31G(d) level of theory.

952 | *Energy Environ. Sci.*, 2010, **3**, 949–955

This journal is © The Royal Society of Chemistry 2010

first and second oxidations of **YD2** because the electron densities of HOMO and HOMO-1 were distributed onto these two units.[17d] Similarly, the first and second oxidations of **YD14**, **YD16** and **YD17** involve charge delocalization through the porphyrin and diarylamino moieties. In the case of **YD15**, the charge density was delocalized over the porphyrin ring, diarylamino and triphenylamino groups upon oxidation. These results agree with those predicted from quantum-chemical calculations discussed in the following paragraph.

With the absorption data and oxidation potentials we evaluated the relative potentials of HOMO and LUMO energy levels. The excited-state oxidation potentials ($E_{0-0}*$) were obtained from the relation $E_{0-0}* = E_{ox1} - E_{0-0}$, in which E_{ox1} is the first oxidation potential of a porphyrin dye and E_{0-0} is the zero-zero excitation energy obtained from the onset of absorption.[20,21] As shown in Fig. 3, the derived $E_{0-0}*$ values are all more negative than the conduction edge (–0.50 V *vs.* NHE) of TiO_2, indicating that the driving force is appropriate for electron injection from the excited state of the dye to the conduction band (CB) of TiO_2. As the HOMO levels are more positive than the oxidation potential for the I^-/I_3^- redox couple (+0.40 V *vs.* NHE), the energy levels of **YD14–YD17** are all thermodynamically favorable for effective regeneration of the dye in a DSSC system.

To gain insight into the electron distribution at the frontier and nearby molecular orbitals, we performed quantum-chemical calculations on porphyrins **YD14–YD17** using density-functional theory (DFT) at the B3LYP/6-31G(d) level (Spartan 08 package). To simplify the computations, some alkyl groups on phenyl rings were replaced with hydrogen atoms or methyl groups. Fig. 4 shows the energy levels and the corresponding molecular orbitals for these porphyrin dyes. A discrepancy for the HOMO–LUMO gaps shown occurs between Fig. 3 and 4 because the electron correlation and the solvent effect were not taken into account. A comparison of **YD14–YD17** with **YD2** shows that the HOMO–LUMO gap is decreased upon incorporation of additional electron-donating groups on the porphyrin ring because there is considerable electronic coupling between the electron-donating groups and the porphyrin core. This phenomenon is more pronounced for **YD15** because of the extended π-system. These results are consistent with the red shift and broadening in the absorption bands, the electrochemical data and the tendency for variation of the HOMO–LUMO gap shown in Fig. 3.

In our previous work we showed that the electronic density of **YD2** is mainly located on the π-system of the porphyrin and the diarylamine at the HOMO and HOMO-1.[17d] The electronic distribution of the frontier orbitals for compound **YD17** resembles that for **YD2** because of the structural similarity. The electron densities of the HOMOs of **YD14** and **YD16** are also greatly delocalized over the porphyrin and diphenylamine moieties despite the structural diversity of these two porphyrins. For **YD15** the electron density of the HOMO is delocalized across not only the porphyrin and diphenylamine units, but also the triphenylamine *via* the conjugated ethynylene link. Similar to the LUMO of **YD2**, the π-conjugation is extended to only the porphyrin, ethynylphenylene link and carboxyl anchoring group at the LUMO of **YD14–YD17**.

Porphyrins **YD0**, **YD2** and **YD14–YD17** were sensitized onto TiO_2 films (with an active layer of thickness 10 μm and scattering

layer of 4 μm) to serve as working electrodes of a DSSC; the details of device fabrication of porphyrin-based DSSC appear elsewhere.[17] With the TiO_2 films soaked in dye solutions (concentration of ~2 × 10⁻⁴ M) for 6 h for each dye, the amounts of dye loading on TiO_2 films (Table 2), in the order **YD2 > YD17 > YD0 > YD14 > YD15 > YD16**, are sufficient for photovoltaic measurements. Fig. 5a and b show the current–voltage characteristic curves and the corresponding IPCE action spectra of the devices, respectively; the derived photovoltaic parameters are summarized in Table 2. The device performance shows an order of **YD2 > YD17 > YD14 > YD16 > YD0 > YD15**. The top three dyes perform similarly with η ~7%, whereas the performances of **YD15** and **YD16** are comparable to only that of **YD0** (η ~5%). For **YD16**, the poor cell performance is consistent with the smaller amount of dye loading, which gives a J_{SC} value

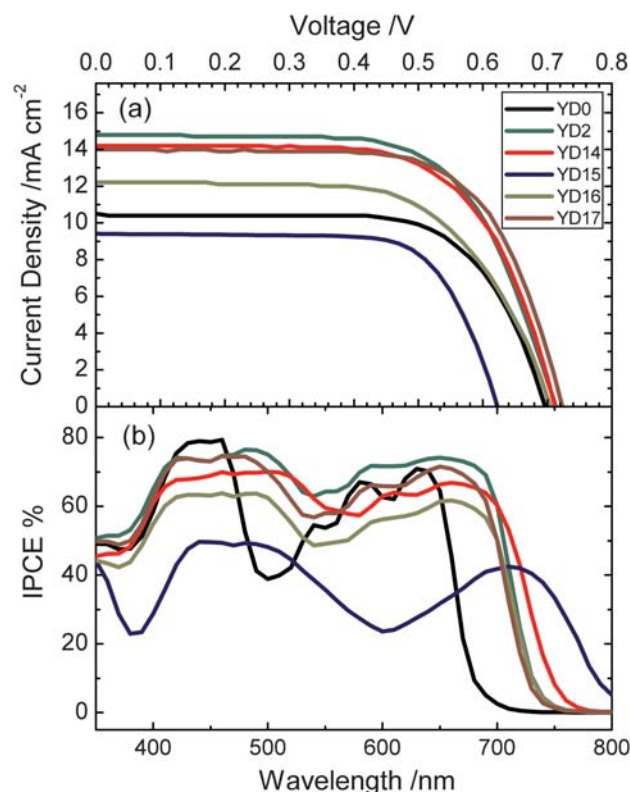**Fig. 5** (a) Current–voltage characteristics of **YD0**, **YD2** and **YD14–YD17**; (b) the corresponding IPCE action spectra.

Table 2 Photovoltaic parameters and dye loading of DSSC with TiO_2 films sensitized with **YD0**, **YD2** and **YD14–YD17** under simulated AM-1.5 illumination (power 100 mW cm⁻²) and an active area of 0.16 cm²

Dye	Dye-loading/ nmol cm⁻²	J_{SC}/mA cm⁻²	V_{OC}/mV	FF	η (%)
YD0	140	10.42	697	0.69	5.0
YD2	148	14.80	714	0.67	7.1
YD14	131	14.27	712	0.67	6.8
YD15	128	9.42	623	0.71	4.2
YD16	111	12.21	704	0.64	5.5
YD17	142	13.99	722	0.69	7.0

substantially lower than for the top three dyes. However, the absorption spectra of all porphyrins adsorbed on TiO$_2$ films (Figure S1, ESI†) indicate that the light-harvesting efficiencies of all porphyrins are close to one for both major absorption bands. Therefore, electron injection and/or charge collection efficiencies might play a role in the observed cell performance. Apparently the two bulky triphenylamino units on the 5,15-*meso*-position hinder the dye adsorption on the TiO$_2$ surface. The poor performance of **YD15** reflects its smaller J_{SC} and V_{OC} values, which are understood to be due to the effect of aggregation described elsewhere.[17c,22] We encountered difficulty in dissolving **YD15** in ethanol; the cell performance reported for **YD15** was obtained from immersion of the TiO$_2$ films in a CH$_2$Cl$_2$ solution.

The IPCE action spectra (Fig. 5b) reflect the efficiency of photoelectric conversion at each wavelength. Although there is a large gap between the Soret and the Q bands of the absorption spectra of porphyrins (Fig. 1), this feature is not evident in the IPCE spectra because the effect of light scattering by TiO$_2$ nanoparticles increases the photocurrents for the weak absorption in that region. There still exists a small gap near 500 nm for **YD0**, but such a feature becomes obscure for other push-pull porphyrins. The reported push-pull porphyrins all exhibit a flat IPCE spectral feature covering the entire visible region. For **YD16** and **YD17**, the IPCE spectral features are similar to that of **YD2** but the corresponding efficiencies are **YD2** > **YD17** > **YD16**, consistent with the variation of J_{SC}, which shows the same order (J_{SC}/mA cm^{-2} = 14.80, 13.99 and 12.21 for **YD2**, **YD17** and **YD16**, respectively) because integrating the IPCE over the AM 1.5G solar spectrum would give a calculated J_{SC} similar to the collected value. In contrast **YD14** and **YD15** exhibit a broader IPCE spectral feature than that of **YD2**. For **YD14**, even though the IPCE values are smaller than those of **YD2** by 5–10%, the extended IPCE spectrum makes its J_{SC} value less than that of **YD2** by only 3.6%. For **YD15**, the IPCE spectrum extends beyond 800 nm. The problem of aggregation for this porphyrin makes the average IPCE value significantly lower than those of the other porphyrins under investigation, which results in a much smaller J_{SC} (9.42 mA cm^{-2}).

Conclusion

For four new porphyrin sensitizers, **YD14–YD17**, for use in DSSC, the influences of the nature and positions of substitution of various EDGs on the spectral, electrochemical, and photo-voltaic properties of the porphyrin sensitizers were examined. In general, increasing the number of diarylamino and/or triarylamino groups at the *meso*-positions increases the light-harvesting efficiency of the porphyrin through the extension of π-conjugation. The electrochemical measurements show that the involvement of an EDG increases the stability of the oxidized porphyrin, which is an essential requirement for their application in a DSSC. The DSSC devices based on the **YD14** and **YD17** sensitizers have achieved efficiencies of 6.8% (J_{SC} = 14.27 mA cm^{-2}, V_{OC} = 0.712 V, FF = 0.67) and 7.0% (J_{SC} = 13.99 mA cm^{-2}, V_{OC} = 0.722 V, FF = 0.69) of power conversion, respectively, under AM 1.5 illumination (100 mW cm^{-2}). In view of the prospective light-harvesting ability of **YD15**, from the approach of molecular design it is desirable to eliminate the effect of dye aggregation on the TiO$_2$ surface so as to enhance its cell performance significantly. Work along this line is in progress.

Notes and references

1 P. V. Kamat, *J. Phys. Chem. C*, 2007, **111**, 2834.
2 M. Grätzel, *Nature*, 2001, **414**, 338.
3 (*a*) Y. Ooyama and Y. Harima, *Eur. J. Org. Chem.*, 2009, 2903; (*b*) M. Grätzel, *Acc. Chem. Res.*, 2009, **42**, 1788; (*c*) T. W. Hamann, R. A. Jensen, A. B. F. Martinson, H. V. Ryswyk and J. T. Hupp, *Energy Environ. Sci.*, 2008, **1**, 66; (*d*) N. Robertson, *Angew. Chem., Int. Ed.*, 2006, **45**, 2338.
4 (*a*) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; (*b*) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382; (*c*) M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, 2001, **123**, 1613.
5 (*a*) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2008, **130**, 10720; (*b*) Y. Cao, Y. Bai, Q. Yu, Y. Cheng, S. Liu, D. Shi, F. Cao and P. Wang, *J. Phys. Chem. C*, 2009, **113**, 6290.
6 (*a*) P. Xie and F. Guo, *Curr. Org. Chem.*, 2007, **11**, 1272; (*b*) A. Mishra, M. K. R. Fischer and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 2474; (*c*) Z. Ning and H. Tian, *Chem. Commun.*, 2009, 5483; (*d*) Y. Ooyama and Y. Harima, *Eur. J. Org. Chem.*, 2009, 2903; (*e*) H. Imahori, T. Umeyama and S. Ito, *Acc. Chem. Res.*, 2009, **42**, 1809.
7 (*a*) J. Deisenhofer and J. R. Norris, *The Photosynthetic Reaction*, Academic Press, New York, 1993; (*b*) W. Nam, *Acc. Chem. Res.*, 2007, **40**, 522; (*c*) S. H. Kim, R. Perera, L. P. Hager, J. H. Dawson and B. M. Hoffman, *J. Am. Chem. Soc.*, 2006, **128**, 5598; (*d*) R. Perera, M. Sono, J. A. Sigman, T. D. Pfister, Y. Lu and J. H. Dawson, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 3641.
8 (*a*) N. Hessenauer-Ilicheva, A. Franke, M. Wolak, T. Higuchi and R. ven Eldik, *Chem.–Eur. J.*, 2009, **15**, 12447; (*b*) G. Kodis, P. A. Liddell, L. de la Garza, P. C. Clausen, J. S. Lindsey, A. L. Moore, T. A. Moore and Gust, *J. Phys. Chem. A*, 2002, **106**, 2036; (*c*) A. K. Burrell, D. L. Officer, P. G. Plieger and D. C. W. Reid, *Chem. Rev.*, 2001, **101**, 2751; (*d*) D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22; (*e*) S. Balieu, I. Hijazi, N. Motreff, F. Lachaud, P. Even-Hernandez and B. Boitrel, *Org. Lett.*, 2010, **12**, 8.
9 (*a*) T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163; (*b*) N. P. Redmore, I. V. Rubtsov and M. J. Therien, *J. Am. Chem. Soc.*, 2003, **125**, 8769; (*c*) M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435; (*d*) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2009, **42**, 1890.
10 (*a*) T. Hasobe, H. Imahori, P. V. Kamat, T. K. Ahn, S. K. Kim, D. Kim, A. Fujimoto, T. Hirakawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2005, **127**, 1216; (*b*) A. Huijser, T. J. Savenije, A. Kotlewski, S. J. Picken and L. D. A. Siebbeles, *Adv. Mater.*, 2006, **18**, 2234; (*c*) G. M. Hasselman, D. F. Watson, J. R. Stromberg, D. F. Bocian, D. Holten, J. S. Lindsey and G. J. Meyer, *J. Phys. Chem. B*, 2006, **110**, 25430; (*d*) S. Eu, S. Hayashi, T. Umeyama, A. Oguro, M. Kawasaki, N. Kadota, Y. Matano and H. Imahori, *J. Phys. Chem. C*, 2007, **111**, 3528; (*e*) H. Imahori, S. Hayashi, H. Hayashi, A. Oguro, S. Eu, T. Umeyama and YoMatano, *J. Phys. Chem. C*, 2009, **113**, 18406; (*f*) J. K. Park, J. Chen, H. R. Lee, S. W. Park, H. Shinokubo, A. Osuka and D. Kim, *J. Phys. Chem. C*, 2009, **113**, 21956.
11 (*a*) B. C. O'Regan, I. López-Duarte, M. V. Martínez-Díaz, A. Forneli, J. Albero, A. Morandeira, E. Palomares, T. Torres and J. R. Durrant, *J. Am. Chem. Soc.*, 2008, **130**, 2906; (*b*) J.-J. Cid, J.-H. Yum,

S.-R. Jang, M. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, Michael Grätzel and T. Torres, *Angew. Chem., Int. Ed.*, 2007, **46**, 8358; (*c*) P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikantam, J.-H. Yum, K. Kalyanasundaram, M. Grätzel and M. K. Nazeer, *Angew. Chem., Int. Ed.*, 2007, **46**, 373.

12 (*a*) W. M. Campbell, A. K. Burrell, D. L. Officer and K. W. Jolley, *Coord. Chem. Rev.*, 2004, **248**, 1363; (*b*) Q. Wang, W. M. Campbell, E. E. Bonfantani, K. W. Jolley, D. L. Officer, P. J. Walsh, K. Gordon, R. Humphry-Baker, M. K. Nazeeruddin and M. Grätzel, *J. Phys. Chem. B*, 2005, **109**, 15397.

13 W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. Schmidt-Mende, M. K. Nazeeruddin, Q. Wang, M. Graetzel and D. L. Officer, *J.Phys. Chem. C*, 2007, **111**, 11760.

14 (*a*) M. Tanaka, S. Hayashi, S. Eu, T. Umeyama, Y. Matano and H. Imahori, *Chem. Commun.*, 2007, 2069; (*b*) S. Hayashi, M. Tanaka, H. Hayashi, S. Eu, T. Umeyama, Y. Matano, Y. Araki and H. Imahori, *J. Phys. Chem. C*, 2008, **112**, 15576.

15 (*a*) Z. S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo and K. Hara, *J. Phys. Chem. C*, 2007, **111**, 7224; (*b*) N. Koumura, Z. S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, *J. Am. Chem. Soc.*, 2006, **128**, 14256; (*c*) H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin and M. Grätzel, *Angew. Chem., Int. Ed.*, 2008, **47**, 327; (*d*) S. Hwang, J. H. Lee, C. Park, H. Lee, C. Kim, C. Park, M.-H. Lee, W. Lee, J. Park, K. Kim, N.-G. Park and C. Kim, *Chem. Commun.*, 2007, 4887.

16 J. N. Clifford, G. Yahioglu, L. R. Milgrom and J. R. Durrant, *Chem. Commun.*, 2002, 1260.

17 (*a*) C.-W. Lee, H.-P. Lu, C.-M. Lan, Y.-L. Huang, Y.-R. Liang, W.-N. Yen, Y.-C. Liu, Y.-S. Lin, E. W.-G. Diau and C.-Y. Yeh, *Chem.–Eur. J.*, 2009, **15**, 1403; (*b*) H.-P. Lu, C.-L. Mai, C.-Y. Tsia, S.-J. Hsu, C.-P. Hsieh, C.-L. Chiu, C.-Y. Yeh and W.-G. Eric Diau, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10270; (*c*) H.-P. Lu, C.-Y. Tsai, W.-N. Yen, C.-P. Hsieh, C.-W. Lee, C.-Y. Yeh and E. W.-G. Diau, *J. Phys. Chem. C*, 2009, **113**, 20990; (*d*) C.-P. Hsieh, H.-P. Lu, C.-L. Chiu, C.-W. Lee, S.-H. Chuang, C.-L. Mai, W.-N. Yen, S.-J. Hsu, E. W.-G. Diau and C.-Y. Yeh, *J. Mater. Chem.*, 2010, **20**, 1127.

18 R. Sakamoto, T. Sasaki, N. Honda and T. Yamamura, *Chem. Commun.*, 2009, 5156.

19 C.-W. Huang, K. Y. Chiu and S.-H. Cheng, *Dalton Trans.*, 2005, 2417.

20 D. P. Hagberg, J.-H. Yum, H. Lee, F. D. Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2008, **130**, 6259.

21 J. K. Park, H. R. Lee, J. Chen, H. Shinokubo, A. Osuka and D. Kim, *J. Phys. Chem. C*, 2008, **112**, 16691.

22 L. Luo, C.-J. Lin, C.-Y. Tsai, H.-P. Wu, L.-L. Li, C.-F. Lo, C.-Y. Lin and E. W.-G. Diau, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1064.