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COMMUNICATION

Novel D–π–A structured Zn(II)-porphyrin dyes containing a bis(3,3-dimethylfluorenyl)amine moiety for dye-sensitised solar cells†‡

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A high solar-to-electricity conversion efficiency of 7.22% was achieved with a short circuit current (J_{sc}) of 15.30 mA cm^{-2}, an open circuit voltage (V_{oc}) of 669 mV and a fill factor (FF) of 0.71 for the 2Flu–ZnP–CN–COOH dye with a multi-functional co-adsorbent, under 100 mW cm^{-2} AM 1.5 G simulated light.

Dye-sensitised solar cells (DSSCs)[1] have been widely regarded as next-generation photovoltaics for providing electricity at lower expense and with more versatility. Although an overall light-to-electricity energy conversion efficiency above 11% has been established with ruthenium-based sensitisers,[1b] the limited resources and the environmental issues concerning ruthenium usage make it necessary to seek alternative dyes. Porphyrins are some of the most widely studied sensitisers for DSSCs because of their strongly absorbing Soret bands (400–450 nm) and moderately absorbing Q bands (550–600 nm).[2] Nevertheless, porphyrin sensitisers based on the light-harvesting properties of the basic porphyrin core typically have admittedly moderate cell performance compared with ruthenium polypyridyl complexes. Imahori and co-workers have reported that this occurs mainly because of the insufficient light-harvesting ability of the typical porphyrins used in optimised cells, especially at around 500 nm and at a wavelength beyond 600 nm,[3,4] so that broadening and red-shifting of Soret and Q bands together with an enhancement of the light-harvesting capability of the Q bands relative to the Soret band in porphyrins are straightforward approaches to increasing their efficiency as sensitisers in DSSCs.[3–5] As demonstrated for other sensitisers in DSSCs, the introduction of both an electron-donating substituent and an electron-withdrawing substituent including an anchoring group to a core with a π-system is also appealing for the modulation of the light-harvesting properties of sensitisers.[6–8] In fact, push–pull porphyrins with an electron-donating diarylamino group at the *meso*-position and an electron-withdrawing carboxyphenylethynyl anchoring group at the opposite *meso*-position have exhibited remarkably high η values of up to 12.3%.[7] The additional electron-donating group effect of the electron-donating substituent attached to the core of the π-system in sensitisers has been addressed extensively.[6] Liu and co-workers demonstrated that broad absorption bands and easy intra-molecular charge separation can be achieved by introducing a cyano-acrylic acid anchoring group linked through a phenylene bridge to the porphyrin dye, which eventually improved on the good cell performance of DSSCs.[9] In this communication, in an effort to develop a novel porphyrin sensitiser possessing both highly efficient and long-term stable properties,[8b] we report the first synthesis and the optical, electrochemical and photovoltaic properties of a push–pull porphyrin with an electron-donating bis(3,3-dimethylfluorenyl)amine group at the *meso*-position and a strongly electron-withdrawing cyano-acrylic acid anchoring group at the opposite *meso*-position linked through a phenylene π-conjugation bridge, as well as the reference porphyrin with a carboxylic acid moiety for DSSC (Fig. 1). The detailed synthetic procedure[10] and characterization are shown in the ESI.‡

The UV-visible absorption and steady-state fluorescence spectra of 2Flu–ZnP–COOH and 2Flu–ZnP–CN–COOH in THF solution and adsorption onto TiO_2 film (3 μm) were measured (see Fig. S1, ESI‡). The peak positions and molar absorption coefficients (ε) of the Soret and Q bands as well as the wavelengths for the emission maxima are listed in Table 1. The Soret and Q bands of two Zn(II)-porphyrin dyes became broader and were shifted toward longer wavelengths compared with our previously reported Zn(II)-porphyrins[2b,11] due to the

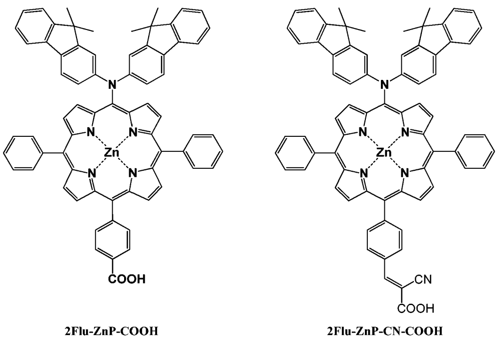

Fig. 1 Molecular structures of Zn(II)-porphyrin dyes.

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‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc31384g

Table 1 Photophysical, electrochemical and photovoltaic performance data of Zn(II)-porphyrin dyes

Dye	Absorption $\lambda_{max}{}^a$/nm (ε/M^{-1} cm^{-1})	Emission $\lambda_{max}{}^a$	Potentials and energy level: $E_{ox}{}^b$/V (*vs.* NHE)	$E_{0-0}{}^c$/V (*vs.* NHE)	$E_{ox} - E_{0-0}{}^d$/V	Photovoltaic performance data^d	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η (%)
2Flu–ZnP–CN–COOH	420(201508), 570(8065), 625(10271)	671	0.89	1.93	−1.04	without CDCA	10.037	579	0.75	4.37
						with CDCA	14.588	628	0.72	6.64
						with HC-A	15.303	669	0.71	7.22
2Flu–ZnP–COOH	419(253788), 569(9169), 623(10273)	667	0.89	1.94	−1.05	without CDCA	7.371	558	0.77	3.16
						with CDCA	11.104	580	0.73	4.7
N719							16.738	708	0.73	8.64

[a] Absorption and emission spectra were measured in THF solution. [b] The oxidation potentials of dyes were measured in THF with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) with a scan rate of 50 mV s^{-1} (*vs.* NHE). [c] E_{0-0} was determined from the intersection of normalized absorption and emission spectra. [d] The concentration was maintained at 2×10^{-4} M in ethanol solution, with 0.4 mM chenodeoxycholic acid (CDCA) or in ethanol/THF (2 : 1) solution with 0.1 mM HC-A as a coadsorbent, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.1 M LiI, 0.05 M I$_2$, 0.5 M 4-*tert*-butylpyridine (TBP) in dry acetonitrile as electrolyte. Performances of DSSCs were measured within a 0.16 cm^2 working area using a metal mask.

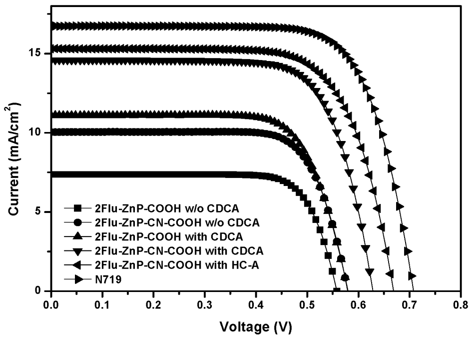

Fig. 2 Photocurrent density *vs.* voltage curves for DSSCs based on Zn(II)-porphyrin dyes and N719 under AM 1.5 G simulated solar light (100 mW cm^{-2}) and TiO$_2$ film thickness and active area of 20 (12 + 8) μm and 0.16 cm^2, respectively.

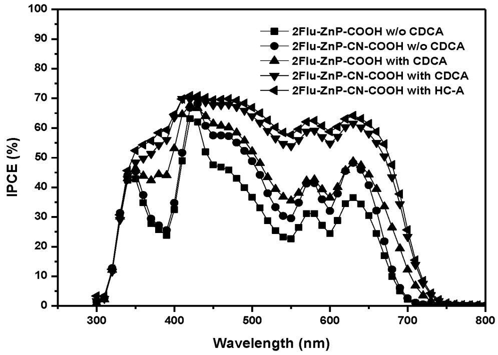

Fig. 3 The incident photon-to-current conversion efficiency (IPCE) spectra for DSSCs based on Zn(II)-porphyrin dyes.

directly connected chemical structure between the electron-rich N atom and the porphyrin unit, as expected.[12] The absorptions at 800 nm for the dyes adsorbed onto a TiO$_2$ film are not consistent with the IPCE spectrum. These absorptions can be attributed to absorption of light by the dye cation due to the introduction of the diarylamino groups on the porphyrin.[5b] The zero–zero excitation energies (E_{0-0}) were determined to be 1.93 eV for 2Flu–ZnP–CN–COOH and 1.94 eV for 2Flu–ZnP–COOH, respectively, through the intersection of the normalised absorption and emission spectra (Fig. S2, ESI‡). The oxidation potentials of porphyrins were measured by cyclic voltammetry (see Fig. S5, ESI‡) and are also summarised in Table 1. The injection potential ($E_{S+/S*}$) was calculated by subtracting the excitation energy (E_{0-0}) from the first oxidation potential ($E_{S+/S}$) of the sensitiser. Both porphyrin dyes showed the same $E_{S+/S}$ values of +0.89 V *vs.* NHE, which are low enough to be below the redox potential of I$^-$/I$_3{}^-$ to ensure efficient regeneration. The injection potential (−1.04 V *vs.* NHE for 2Flu–ZnP–CN–COOH and −1.05 V *vs.* NHE for 2Flu–ZnP–COOH) is also energetically favourable because of the more negative LUMO values above the conduction band edge of TiO$_2$ (commonly recognised as −0.5 V *vs.* NHE[13]). The current density–voltage (*J–V*) curves and the incident photon to current conversion efficiency (IPCE) spectra of DSSCs incorporated with porphyrins are shown in Fig. 2 and 3, respectively. The relevant parameters are also listed in Table 1. The detailed cell fabrication procedure is presented in the ESI.‡ As illustrated in Fig. 3, the IPCE spectrum of 2Flu–ZnP–CN–COOH-based cells with co-adsorbents such as CDCA or HC-A (see Fig. S8, ESI‡) showed an onset as long as 740 nm and steeply reached nearly a plateau value close to 70% from around 650 nm up to 400 nm, demonstrating efficient light harvesting in the visible region. Interestingly, the IPCE response of the 2Flu–ZnP–CN–COOH-based device with the multi-functional co-adsorbent HC-A[14] was enhanced compared to that with CDCA. We previously reported that both J_{sc} and V_{oc} of organic dye-based DSSCs could be dramatically enhanced by introducing a multi-functional co-adsorbent due to the light-harvesting effect at shorter wavelength regions and efficient retardation of charge recombination.[14,15] However, in the case of 2Flu–ZnP–COOH-based cells, the spectrum onset is shifted toward shorter wavelength regions around 700 nm with a reduced IPCE value. The 2Flu–ZnP–CN–COOH based-cell without CDCA showed similar behaviour to 2Flu–ZnP–COOH. This indicates that the introduction of a cyano-acrylic acid electron accepting group promoted efficient intra-molecular charge separation. As we know, the aggregation of dye could decrease both J_{sc} and V_{oc} and the use of CDCA could effectively suppress dye aggregation.[14–16] When CDCA is not introduced into the device, rapid charge recombination between neighbouring dye molecules occurs so that intra-molecular charge separation may be interfered with due to rapid migration of excited state electrons.[15] Such an enhanced spectral response induced by the efficient intra-molecular charge separation and use of the multi-functional co-adsorbent HC-A resulted in an overall photovoltaic performance of

J_{sc} = 15.30 mA cm^{-2}, V_{oc} = 669 mV, FF = 0.71 and η = 7.22%.

We carried out density-functional theory (DFT) calculations to investigate the structures and charge transfer properties employing Becke's three parameterised Lee–Yang–Parr (B3LYP) exchange correlation functional and 6-31G* basis sets using a suite of Gaussian 09 programmes.[17] The molecular orbital shapes of 2Flu–ZnP–COOH and 2Flu–ZnP–CN–COOH show a remarkable difference of charge transfer (see Fig. S6, ESI‡). The highest occupied molecular orbital (HOMO) shapes of both porphyrins were very similar. However, the lowest unoccupied molecular orbital (LUMO) shapes of the two porphyrins are very different. The electrons in the LUMO of 2Flu–ZnP–COOH were mainly distributed over the porphyrin moiety. On the other hand, the electrons in the LUMO of 2Flu–ZnP–CN–COOH were mainly distributed over the cyano-acryl substituted phenyl moiety, which is responsible for the charge transfer.

To further clarify the effect of the chemical structure of porphyrin dyes on the *J–V* characteristics, electrochemical impedance spectroscopy (see Fig. S7 and Table S1, ESI‡) was performed under dark conditions at a forward bias of −0.6 V.[14,15] The larger semicircle at intermediate frequencies represents the interfacial charge transfer resistance (R_{ct}) at the dyed TiO_2/electrolyte interface. The fitted R_{ct} values of 2Flu–ZnP–CN–COOH-based devices (155.6 Ω for 2Flu–ZnP–CN–COOH/HC-A, 40.94 Ω for 2Flu–ZnP–CN–COOH/CDCA) are much higher than those of a 2Flu–ZnP–COOH-based device (22 Ω for 2Flu–ZnP–COOH/CDCA), which was consistent with the sequence of open circuit voltage values in the devices. In particular, the dramatically increased V_{oc} value of the DSSC based on 2Flu–ZnP–CN–COOH/HC-A compared to that of 2Flu–ZnP–CN–COOH/CDCA can be explained from this experiment. The smaller R_{ct} value means that the electron recombination from the conduction band to the electrolyte occurs more easily, thus resulting in lowering of both J_{sc} and V_{oc}.[14–16] The adsorbed amount of porphyrin dyes on the TiO_2 film was calculated according to a literature procedure[16] and the results are summarised in Table S2 (ESI‡). Previously, we reported that the Y-shaped structure of HC-A is allowed to be more efficient than CDCA in decreasing dye adsorption.[14,15] However, in this case, the dye coverage of the cell based on 2Flu–ZnP–CN–COOH with HC-A was greater than with CDCA, which is not consistent with our previous results. We assume that this may have resulted from variations in the immersion conditions. Nevertheless, despite the high dye coverage of the device based on 2Flu–ZnP–CN–COOH/HC-A, it showed a higher R_{ct} value than that with CDCA, indicating more efficient retardation of charge recombination which is caused by the effective breakup of dye aggregation.

In conclusion, two kinds of push–pull Zn(II)-porphyrin dyes with an electron-donating bis(3,3-dimethylfluorenyl)amine group at the *meso*-position were successfully designed and synthesised. The results of calculations and experiments clearly demonstrate that efficient intra-molecular charge separation of D–π–A Zn(II)-porphyrin can be induced by inserting a strongly electron accepting cyano-acrylic acid substituent, resulting in relatively high overall energy conversion efficiency. The IPCE response and *J–V* characteristics were further enhanced by co-adsorption of HC-A instead of CDCA, making it a promising candidate for highly efficient DSSCs. EIS measurements also showed that charge recombination at the TiO_2/dye/electrolyte interface can be efficiently suppressed by intra-molecular charge separation as well as co-adsorption of HC-A, thus resulting in higher V_{oc}.

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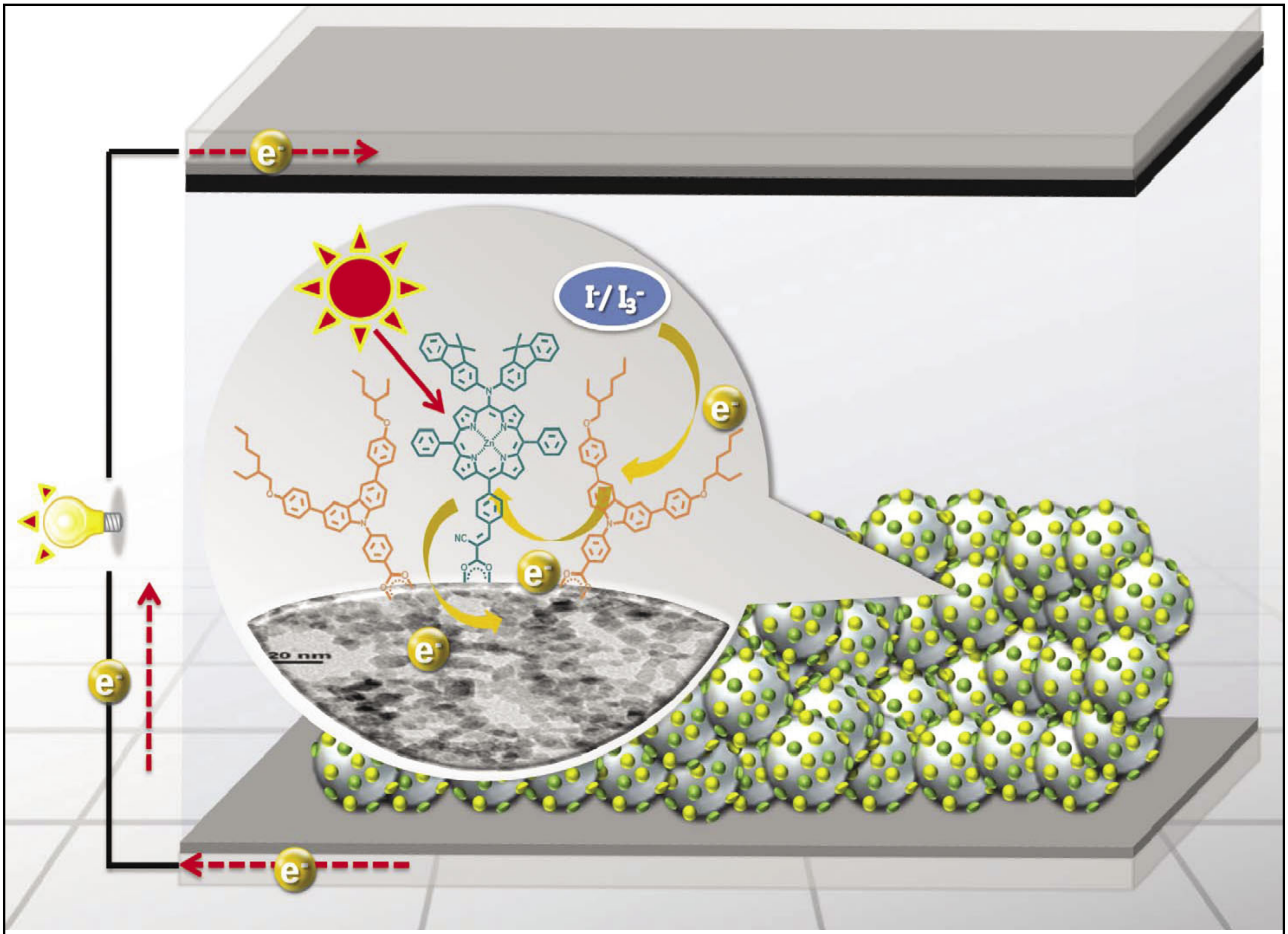

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