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COMMUNICATION

A fluorene-modified porphyrin for efficient dye-sensitized solar cells†‡

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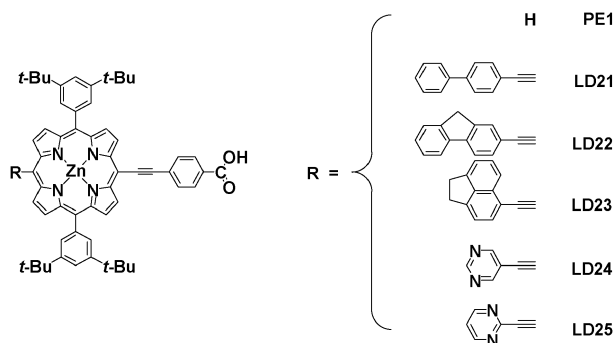
Porphyrins bearing a polyaromatic or a heterocyclic group are prepared to study their fundamental and photovoltaic properties. Solar cells sensitized with a fluorene-modified porphyrin outperform other dyes in the series, reaching ∼90% efficiency of N719 dye.

Dye-sensitized solar cells (DSSC) have drawn much attention because of the relatively high efficiencies, simple device design, and lower production cost.[1–3] Overall efficiencies (η) greater than 11% have been demonstrated with ruthenium dyes.[4–6] In recent years, other types of sensitizers have also been intensely studied for cost-effective purposes. Among the dyes under investigation, porphyrins are considered as one of the more promising sensitizers for DSSC applications[7–17] because of the vital roles of porphyrin derivatives in photosynthesis, the strong UV-visible light absorption, and the ease of modifying their chemical structures. In the development of porphyrin dyes, Officer and co-workers were the first to raise the overall efficiency of porphyrin-sensitized solar cells (PSSC) above 7% by using a side-anchoring, fully conjugated dye.[10] Using a cobalt-based electrolyte with a push–pull porphyrin co-sensitized with an organic dye, the PCE of the PSSC device attained 12.3%.[11a]

In our systematic search for an efficient porphyrin dye, we found that the photovoltaic performance of a zinc porphyrin can be improved by using a shorter anchoring group (PE1 dye),[13a] by including an anthracene to expand the light-harvesting range (LAC3),[14] or by applying an electron-donating group (Me₂N–PE1).[15] Although we recently reported that the photovoltaic performance of a PSSC can be enhanced by wrapping a porphyrin core with long alkoxyl chains (LD14 and LD16),[16] a pyrene-modified porphyrin using *tert*-butyl groups at the *meta*-positions of the phenyl rings also exhibited matching performance (LD4).[17]

In the present work, we examine the effects of a polyaromatic or a heterocyclic substituent for PSSC applications.

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Scheme 1 Molecular structures of PE1 and LD porphyrins.

As shown in Scheme 1, the common part of the LD2x dyes consists of a 4-benzoic acid as the anchoring group, an ethyne as the bridging moiety, and *tert*-butylated phenyl groups to increase solubility of the dyes in organic solvents. For LD21–LD23, a polyaromatic substituent consisting of "two phenyl rings" is attached to one of the porphyrin *meso*-positions to further modify the porphyrin. Fluorene and acenaphthene are polyaromatic hydrocarbons often used in the preparation of dyes and pharmaceuticals.[18] With fluorescence quantum yield near unity,[19] using fluorene as a substituent should improve the photovoltaic performance of the porphyrin. Because of the similarity in the chemical structure, acenaphthene and biphenyl are also studied in order to compare with fluorenyl substituents. For heterocyclic groups, pyrimidines were chosen because pyrimidines and their derivatives have been known to improve device performance of DSSC and organic photovoltaics,[20] as electrolyte additive of DSSC,[21] and of organic/polymer light-emitting devices.[22] Therefore, it would be of interest to test the impact of pyrimidines on the performance of porphyrin dyes. The LD2x dyes were readily prepared in two steps based on the Sonogashira cross-coupling method.[23]

Fig. 1a and b show the absorption and emission spectra of LD2x in THF, respectively. The wavelength maxima as well as the first porphyrin-ring reduction potentials are listed in Table 1. As shown in Fig. 1, the absorption and emission bands of LD2x are all red-shifted relative to those of PE1. This can be attributed to the extended π-conjugation provided by the additional substituents.[13–17] For the UV-visible spectra, LD2x dyes exhibit typical porphyrin absorption characteristics:[24] strong B (or Soret) bands were found near 450 nm, whereas weaker Q bands were observed near 670 nm. Small differences in the intensities and wavelengths were also observed. For example, the absorption
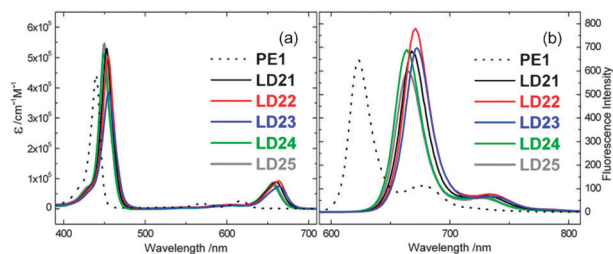
Fig. 1 (a) Absorption spectra of the LD porphyrins in THF. (b) B band-excited fluorescent emission spectra ([LD] = 2×10^{-6} M in THF).

Table 1 Absorption wavelength, B band-excited fluorescence maxima and first porphyrin-ring reduction potentials of the porphyrins in THF

Dye	Absorption/nm (log ε/M^{-1} cm^{-1})	Emission/ nm	$E_{1/2}$/V vs. SCE
PE1[a]	439 (5.64), 567 (4.21), 616 (4.41)	621, 674	−1.23
LD21	453 (5.72), 660 (4.95)	668, 731	−1.07
LD22	455 (5.70), 663 (4.97)	671, 732	−1.01
LD23	455 (5.59), 664 (4.89)	672, 734	−1.07
LD24	449 (5.71), 656 (4.91)	664, 725	−0.96
LD25	450 (5.74), 656 (5.02)	665, 728	−0.97

[a] Taken from ref. 13a.

bands of LD22 and LD23 are more red-shifted than those of LD21 owing to the more extended π-conjugation.

For the fluorescence spectra, the emission bands of LD2x show mirror images of the Q bands. The trend of the wavelengths is similar to those of the Q bands, suggesting that the additional substituents affect porphyrin similarly in both light absorption and emission. The stronger fluorescence intensity of LD22 than that of LD21 is consistent with the fact that a fluorene group features more rigid structure and very high fluorescence quantum yield (~1.0). In sharp contrast, the structure of a biphenyl group is loose and may undergo non-radiative relaxation via rotation, thus the fluorescence quantum yield is merely ~0.2.[19] For LD21 dye, effective non-radiative relaxation at the biphenyl site would compete with electron injection processes to TiO$_2$ upon excitation, hampering photovoltaic performance of the DSSC.

For the electrochemistry of the LD2x porphyrins, the first porphyrin-ring reductions were observed as quasi-reversible reactions near −1.0 V vs. SCE (Table 1; ESI‡, Fig. S1). These potentials are consistent with the formation of porphyrin anion radicals,[13–17,25] and they are positively shifted from that of PE1. The anodic shifts are consistent with the extended π-conjugation. Among the LD2x dyes, LD24 and LD25 are the easiest to reduce, indicating the electron-withdrawing nature of pyrimidinyl groups. The oxidations of LD2x were observed as irreversible reactions.

Fig. 2 compares the HOMO/LUMO potentials of LD2x with those of the electrolyte and the conduction band of TiO$_2$. This diagram is based on the literature reports[1] and the experimental results. The first porphyrin-ring reductions were used to establish the LUMOs of the dyes. Normalized Q absorption bands and fluorescence emissions are used to estimate the gaps between the LUMOs and the HOMOs because the first oxidations are irreversible reactions. The estimated HOMO potentials are consistent with the peak potentials of LD2x's oxidation waves. As shown in Fig. 2,
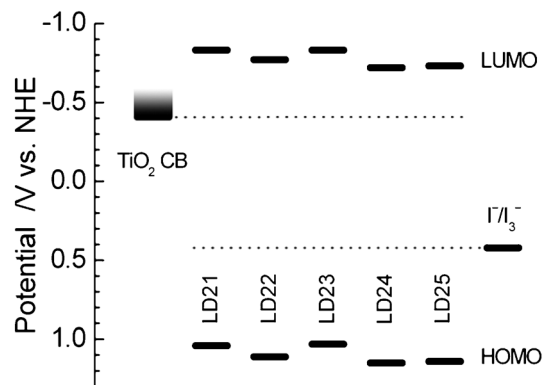

Fig. 2 Comparison of LD2x, I$^-$/I$_3^-$ and TiO$_2$ potentials.

the LUMOs of LD2x are noticeably higher than the CB of TiO$_2$ and the HOMOs are much lower than the redox potentials of I$^-$/I$_3^-$. This indicates that all LD2x dyes should be capable of injecting electrons into TiO$_2$ upon excitation and can be efficiently regenerated by the electrolyte. Note that the LUMOs of LD24 and LD25 are lower than those of LD21–LD23 due to the more electron-withdrawing pyrimidinyl groups. Consequently, the electron injection processes could be less favourable.

Fig. 3 displays the current–voltage (I–V) and incident photon-to-current conversion efficiency (IPCE) curves of the LD2x-sensitized solar cells. The photovoltaic parameters are collected in Table 2. The overall efficiencies of the LD2x solar cells follow the trend of LD22 > LD23 > LD21 > LD24 > LD25. This trend can be understood according to the I–V and IPCE results. The V_{OC} values of the LD2x dyes are divided into two tiers: the LD21–LD23 cells show higher open-circuit voltages (>0.68 V), whereas the LD24 and LD25 cells show lower voltages (~0.63 V). This is consistent with the LUMO levels (Fig. 2). As for J_{SC}, the values follow the trend of LD22 > LD23 ≫ LD21 > LD24 > LD25. This trend may be explained by the HOMO/LUMO patterns of the LD2x dyes (ESI‡, Fig. S2). Although not deliberately designed to be dyes with a strong push–pull effect as some of the reported porphyrin dyes,[11,15,16] LD22 and LD23 show slight localization of electron distributions at the polyaromatic sites and the anchoring group for the HOMO and LUMO levels, respectively. This may translate to a push–pull effect upon dye excitation, leading to a more favourable electron injection from the dye to TiO$_2$. Combining the push–pull tendency, the higher LUMO, and the higher fluorescence emission, these features render LD22 a better electron donor, thus a superior dye. In contrast, the push–pull phenomenon is less apparent for LD21, LD24
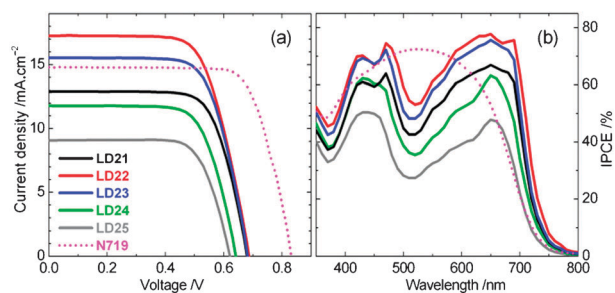

Fig. 3 (a) Current–voltage characteristics of LD-sensitized solar cells and N719 cells; (b) corresponding IPCE action spectra.

Table 2 Photovoltaic parameters of LD2x-sensitized solar cells[a]

Dye	J_{SC}/mA cm^{-2}	V_{OC}/V	FF	η (%)
LD21	12.92	0.682	0.717	6.3
LD22	17.26	0.689	0.681	8.1
LD23	15.51	0.685	0.700	7.4
LD24	11.78	0.644	0.708	5.4
LD25	9.07	0.624	0.727	4.1
N719[b]	14.79	0.836	0.746	9.2

[a] Under AM1.5 illumination (power 100 mW cm^{-2}) with an active area of 0.16 cm^2. [b] As a reference, the overall efficiency of N719 sensitized solar cells was determined.

and LD25. In fact, the LUMO patterns of LD24 and LD25 show quite electron distribution at the pyrimidinyl sites. This suggests that pyrimidine groups would attract electron density away from TiO$_2$ upon dye excitation. As a result, the pull–pull effect should cause LD24 and LD25 to be poor electron donors, thus inferior dyes.[15] For the IPCE spectra (Fig. 3b), the LD2x cells show stronger responses in the 400–500 and 550–750 nm region. These two groups of responses correspond to porphyrin B and Q bands. Again, the IPCE curves follow the trend of LD22 > LD23 > LD21 > LD24 > LD25, consistent with the trends observed in the J_{SC} and the overall performance values.

In summary, we successfully prepared a series of zinc porphyrins modified with a polyaromatic or a heterocyclic substituent. Photovoltaic measurements show that the fluorene-modified porphyrin, LD22, outperforms other dyes in this work with an overall efficiency of 8.1%. This value is about 90% that of the N719 cells under similar conditions. The superior performance of LD22 results from stronger J_{SC}, higher V_{OC}, and stronger and broader photovoltaic responses from 350 to near 750 nm. These qualities should be attributed to LD22 having a more rigid substituent with a very high fluorescence quantum yield, a higher LUMO level and more red-shifted absorption bands. Therefore, our results suggest that rigid molecular structure and high fluorescence quantum yield of a substituent can be important factors when designing an efficient photo-sensitizer.

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