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Fluorene functionalized porphyrins as broadband absorbers for TiO₂ nanocrystalline solar cells†

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Three 9,9-dihexyl-9H-fluorene (DHF) functionalized zinc porphyrin dyes (coded as ZZX-N3, ZZX-N4, and ZZX-N5) were designed and synthesized for dye-sensitized solar cells. Then, DHF and benzoic acid were conjugated to the porphyrin ring through triple bonds to act as a spacer to elongate the π -conjugation and as an acceptor for an efficient electron injection, respectively. A bis(9,9-dihexyl-9H-fluorene-7-yl)amine (BFA) and a bis(4-hexylphenyl)amine (BPA) were further linked to DHF to act as electron donors in ZZX-N3 and ZZX-N4, respectively. ZZX-N5 did not have any electron donor and served as a reference. Moreover, ZZX-N3- and ZZX-N4-sensitized cells exhibited broader sunlight absorption than ZZX-N5, and as a result, higher photon-to-electricity efficiency (PCE) (ZZX-N3, 3.83%; ZZX-N4, 4.2%; ZZX-N5, 3.70%) was observed. The results are consistent with well-separated HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) in ZZX-N3 and ZZX-N4 than in ZZX-N5. However, the overall conversion efficiency of ZZX-N3- and ZZX-N4-sensitized cells was low, which is due to significant dye aggregation induced by the extra long alkyl-chains on the donor groups. This was evidenced by blue and red shifts of the absorption spectra of dye-coated TiO₂ films. In addition, the extra long-chains also did not offer better shielding to prevent electron recombination of injected electrons with I_3^- in electrolyte as revealed by electrochemical impedance spectroscopy. When a cosensitizer (coded as PBS) was used, a new peak corresponding to the absorption of PBS at 560 nm was observed on the incident photon to charge carrier efficiency (IPCE) spectra; however, the overall photovoltaic performance was not improved due to the significant decrease of dye-loading density of porphyrin dyes, indicating a need to break off the trade-off between dye-loading and light-harvesting.

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Introduction

Porphyrin dyes as excellent "natural" pigments are promising for dye-sensitized solar cells (DSCs).¹⁻³ Early studies used 5,10,15,20-tetraphenylporphyrin zinc derivatives as dyes, and the resulting photoelectrodes showed a deep purple color.

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However, the energy conversion efficiency was less than 2%.⁴ In 2007, Grätzel et al. conjugated a malonic acid group to β-pyrrolic positions of the porphyrin ring.⁵ The photoelectrode exhibited a green color, and the resulting device produced an energy conversion of 7.1% under AM 1.5 G conditions. Since then, a variety of porphyrins have been synthesized and their photovoltaic performance has been evaluated. The results revealed that higher efficiency can be achieved by adding donor groups,^{1,6-16} attaching bulky substituents,¹¹ or by elongating the π -conjugation through double¹⁷ or triple bonds¹⁸ between the porphyrin ring and an anchoring carboxylic acid group. Upto now, the donor- π -acceptor structure has emerged as a premium model for constructing high performance dyes.¹⁹ In this model, a diphenylamine and a 4-ethynylbenzoic acid in the 5 and 15 positions of the porphyrin ring are usually used as an electron donor and an electron acceptor, respectively. The insertion of phenylethyne, perylene, fluorene, and anthracene units between the donor and the porphyrin ring has been found to be very effective for spectral broadening.1 Recently, the highest energy conversion efficiency of 13% was reported by Grätzel et al. using a functionalized porphyrin dye and a cobalt-based redox couple.20 This significant achievement pushes DSC



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research toward a new paradigm with commercialization not far away.

Porphyrin has a high tendency to form H-type and J-type aggregates²¹ because of its planar structural characteristics. In aggregates, the energy of excited dye molecules are more prone to transfer to neighbouring molecules, competing with the process of electron injection to the conduction band of TiO_2 nanoparticles. Long alkyl chains are often introduced into porphyrin rings to prevent the formation of aggregates. Diau *et al.* found that long alkoxyl chains ($OC_{12}H_{25}$) on the phenyl groups in the two *meso* positions of the porphyrin ring effectively enveloped the porphyrin ring with significantly lessened aggregates.¹¹ However, it is unclear if the aggregation can be further reduced when additional alkyl chains are introduced into the electron donor groups.

A complementary dye is also used in high performance porphyrin-sensitized solar cells. This is due to the weak sunlight absorption of porphyrin dyes between 500 and 650 nm. Complementary dyes with an optimal physical footprint and photophysical properties are needed to cosensitize the devices for better efficiency.14,19,20 Several organic dyes have been successfully used in combination with porphyrin dyes. These dyes exhibited a large physical size, which reduces the dye loading density of porphyrin and limits the potential for efficiency enhancement. In a recent report,9 we found a small BODIPY sensitizer (BET) with a maximal absorption at \sim 510 nm matched the deficiency of the porphyrin absorption very well. When the BET is paired with the porphyrin dye LD12, the energy efficiency of the resulting devices increased from 6.5% to 7.2%. Given the structural flexibility of this type of dye to tune their absorption spectra, this type of complementary dye is promising for co-sensitized solar cells. It is unclear though if this type of dye can also act as an effective complementary dye in other porphyrin systems.

Thus, to this end, three new porphyrin dyes were designed and synthesized to address the aforementioned questions. Their structures are shown in Scheme 1. The design is based on a [10,20-bis(2,6-di-octoxyphenyl)porphinato]zinc(II) molecule, due to its excellent photovoltaic performance.1 A 9,9-dihexyl-9H-fluorenyl group (DHF) as a spacer was introduced between the donor and porphyrin ring to elongate the π -conjugation and thus to broaden the absorption spectra. We focus on two different electron donors: bis(9,9-dihexyl-9H-fluoren-7-yl)amine (BFA) and bis(4-hexylphenyl)amine (BPA), both having four and two *n*-hexyl chains, respectively, and are thus expected to provide better shielding to reduce electron recombination at the TiO₂/electrolyte interface. A dye without an electron donor was also designed to serve as a reference for the convenient evaluation of the other two dyes. A small organic dye (PBS) with a maximal absorption at 560 nm was prepared to complement the porphyrin dyes. We expect that the photophysical, photovoltaic, and electrochemical studies of these dyes will provide evidence to address the aforementioned questions as well as to provide fundamental information for the design of next generation of porphyrin dyes.



Scheme 1 Structure of ZZX-N3, ZZX-N4, ZZX-N5 and PBS.

Experimental section

Detailed synthetic procedures of all dyes and their characterization are described in the ESI.[†]

Theoretical calculations

Theoretical calculations were performed at the density functional theory level. The calculations were performed in a vacuum as implemented in the Gaussian 09 (ref. 22) program package. The structures were optimized at the B3LYP/6-31g(d) levels. No negative frequency was observed in the optimized structures. The molecular orbitals were visualized by GaussView 3.0 software. This method has been widely used for geometry optimization and electronic calculations of porphyrins derivatives.^{23–25} It should be pointed out that linear conformation of the alkyl chains from initial optimization was adopted for all calculations.

Fabrication of solar cells

Nanocrystalline TiO₂ paste (DSL 18NR-T, ~20 nm, Dyesol, Australia) was coated onto commercial fluorine-tin-oxide (FTO) (7 Ω cm⁻², Hartford Glass, USA) using a doctor-blade method, and 3M magic tape was used as a spacer. After the films were air dried for about 30 minutes, the samples were put into an oven for sintering using a three-stage ramp-up scheme (8 °C min⁻¹, 200 °C for 15 minutes, 350 °C for 15 minutes, and 550 °C for 30 minutes) in ambient oxygen. After the samples were cooled to room temperature slowly, they were then coated with a scattering layer (WER2-O, 150–400 nm Dyesol, Australia) and sintered again using a same three-stage ramp scheme. The samples were then cooled to room temperature and immersed in a freshly prepared TiCl₄ aqueous solution (20 mM) for one hour. The films were airdried and sintered again at 550 °C for 30 minutes. Furthermore, the films were put into the dye solution ($\sim 0.3 \text{ mM}$) at room temperature and kept for four hours. The films were then taken out, flushed with methanol, and vacuum dried for one hour. The thickness of the film was $\sim 14 \mu m$, determined from a profilometer. The counter-electrode was prepared by sputtering a 16 nm-thick film of Pt onto the FTO glass. A mask made from the Parafilm was used as a spacer for the two electrodes and sealing material. The electrolyte solution was injected from two pre-cut channels in the mask. The outside of the final cell was sealed by hot glue. The electrolyte is an acetonitrile/valeronitrile solution with 0.6 M 1-propyl-2,3dimethylimidazolium iodide, 0.05 M I₂, 0.1 M LiI, 0.1 M guanidine thiocyanate, and 0.5 M tert-butylpyridine.

Characterization of devices

The applied potential and cell current were measured on an Agilent 4155C semiconductor parameter analyser with a 450 W Xenon light source. The light intensity at the surface of cell was calibrated to 100 mW cm⁻², equivalent to one sun at air mass 1.5 G condition. The efficiency (η) and fill factor (FF) were calculated by η (%) = $P_{\text{max}} \times 100/(P_{\text{in}} \times A)$ and FF = $P_{\text{max}}/(I_{\text{sc}} \times A)$ $V_{\rm oc}$), where $P_{\rm max}$ is the maximum output power of the cells (mW), $P_{\rm in}$ is the power density of the light source (mW cm⁻²), $I_{\rm sc}$ is the short-circuit current (mA), V_{oc} is the open-circuit voltage (V), and A is the active area (0.16 cm^2) of the cell. Incident photon to charge carrier efficiency (IPCE) experiments were performed on an Agilent semiconductor parameter analyzer with an Xe arc lamp and a Newport monochromator. Monochromatic light was incident on the sample through focusing lenses. The National Renewable Energy Laboratory (NREL) calibrated photodetector was used as a reference. The samples were scanned from 350-850 nm, and the voltage was recorded. IPCE was calculated using the equation IPCE = (sample voltage) \times reference voltage)/reference IPCE. The reference IPCE was supplied by the NREL-calibrated DSSC under an AM 1.5 G photon flux. Charge transport and recombination were studied by intensity-modulated photocurrent spectroscopy (IMPS) and photovoltage (IMVS) spectroscopy, respectively, as detailed previously.26-28 In brief, the cells were probed with a small sinusoidally-modulated beam of 660 nm LED light superimposed on a relatively large background (bias) illumination also at 660 nm. The probe and bias light entered the cell from the substrate side. Neutral density filters were used to vary the illumination intensity. The amplitude of the modulated photocurrent density was kept at 10% or lower compared to the steady-state photocurrent density. In addition, electrochemical impedance spectroscopy (EIS) measurements were performed with a potentiostat/frequency analyzer (PARSTAT 2273) using a two-electrode configuration, with the modulation frequencies ranging from 10^{-2} to 10^{5} Hz and a modulation amplitude of 10 mV. Z-view 2.9c (Scribner Associates) was used to fit the EIS spectra to the equivalent circuit, based on the transmission line model.29

Results and discussion

ZZX-N3, ZZX-N4, and ZZX-N5 were synthesized and purified as described in the ESI.[†] The synthesis procedure is outlined in Scheme 2. Iodofluorene derivatives 1a and 1b were prepared by the reaction of BFA (or BPA) and 2,7-diiodo-9,9-dihexyl-9H-fluorene (DIDHF) under Ullmann cross-coupling reaction conditions and the yield was \sim 40%. A slight excess of BFA and DPA to DIDHF were added to maximize the yield of target products. The intermediates 2a-2c were obtained from the reaction between 1 and (triisopropylsilyl)acetylene under Sonogashira crosscoupling conditions with excellent yields. 2a-2c were then subjected to a two-step reaction to give intermediates 4a-4c with 15-25% yield. The final products: ZZX-N3, ZZX-N4, and ZZX-N5 were obtained in 60-85% vields under the same reaction conditions by reacting 4a-4c with 4-iodobenzoic acid. All three dyes exhibited good solubility in chloroform, dichloromethane, and toluene, and were slightly soluble in acetonitrile and ethanol. PBS was prepared by three consecutive reactions as shown in Scheme 3. Further, PBH was obtained from the reaction of 4-formylbenzoic acid with 2,4-dimethylpyrrole in CH₂Cl₂, followed by oxidation with DDQ and coordination of BF₂ in the presence of TEA, giving a 23% yield. PBI was synthesized by the reaction of PBH with I₂/HIO₃ in ethanol. PBI was then treated with ethynyltrimethylsilane under Sonogashira coupling conditions to produce PBS with \sim 35% yield. PBI was purple with no fluorescence, while PBH and PBS were orange and emitted very strongly under UV and visible light illumination.

The absorption and fluorescence spectra of ZZX-N3, ZZX-N4 and ZZX-N5 in ethanol solution are shown in Fig. 1. Three porphyrins exhibit strong absorption around 450 nm (Soret



Scheme 2 Synthesis of fluorene-based porphyrin dyes. Reaction conditions: (i) copper bronze, K_2CO_3 , 18-crown-6,1,2-dichlorobenze, reflux, (ii) ethynyltriisopropylsilane, Pd(PPh_3)_2Cl_2, Cul, THF, TEA, (iii) (a) TBAF, THF; (b) Pd(PPh_3)_2Cl_2, Cul, THF, TEA, (iv) (a) TBAF, THF; (b) Pd_2(dba)_3, AsPh_3, 4-iodobenzoic acid, THF, TEA.



Scheme 3 Synthesis of complementary dye PBS reaction conditions: (i) TFA, CH₂Cl₂, overnight, N₂, (ii) DDQ, 10 minutes, (iii) TEA, BF₃ \cdot OEt₂, (iv) I₂, HIO₃, EtOH, 60 °C, 1 h and (v) ethynyltrimethylsilane, Pd(PPh₃)₂Cl₂, Cul, THF, TEA.



Fig. 1 Absorption spectra of ZZX-N3 (A), ZZX-N4 (B) and ZZX-N5 (C) in EtOH and on TiO_2 films, and fluorescence spectra of three dyes in EtOH (D).

band). Two medium absorption peaks (Q bands) between 550 and 700 nm were also observed. The detailed spectroscopic data were listed in Table 1. The peak positions of the three porphyrins were very similar to each other except a slight red-shift of ZZX-N3 and ZZX-N4 compared to ZZX-N5. In addition, the Soret bands and Q bands of ZZX-N3 and ZZX-N4 were broader than ZZX-5, which was more pronounced on the right side of each band. The broadening, according to the Gouterman four-orbital theory,^{24,30} is due to the lower symmetry of ZZX-N3 and ZZX-N4 after adding an electron donor BFA/BPA to the DHF group. No significant difference of their emission spectra was observed. The absorption spectra of porphyrin dyes on TiO₂ nanoparticle films were also shown in Fig. 1. These spectra were obtained by dipping dye-coated films in EtOH solution. All peaks became broader and blue-shifted compared to their counterparts in

Table 1 Spectral and electrochemical data of ZZX-N3, ZZX-N4 and ZZX-N5 $\,$

	Solvent	ZZX-N3	ZZX-N4	ZZX-N5
Absorption (nm)	In EtOH On TiO ₂	459, 666 434, 465, 652	460, 666 445, 657	456, 662 445, 652
Fluorescence (nm)	In EtOH	672, 738	672, 738	668, 732

solution. The blue-shift was more pronounced in ZZX-N3. A new red-shifted shoulder was also observed for ZZX-N3, which was much weaker in ZZX-N4 and not observed in ZZX-N5. As the blue-shift is usually indicative of H-type aggregates of porphyrin dyes and a red-shift of J-type aggregates,11 the observed spectral changes indicated that H-type aggregates existed in the three dyes, which was more severe in ZZX-N3 than in the other two. J-type aggregation was also more obvious in ZZX-N3 than in ZZX-N4, whereas no sign of a J-type aggregation was observed in ZZX-5. The observations indicate that long alkyl chains on the fluorene groups induced H-type aggregation, which was consistent with a report from Diau et al.11 In that report, both the H- and J-type aggregates were observed in a porphyrin dye with two C8H17 substituents on the donor group. This suggested that additional long alkyl chains facilitated the formation of aggregates.

The photovoltaic performance of ZZX-N3, ZZX-N4, and ZZX-N5 were examined in solar cells using a conventional "sandwiched" configuration. The Pt-coated FTO glass was used as a counter electrode. The thickness of the film (compact laver + nanocrystalline layer + scattering layer) was 14 µm. The measurements were performed under AM 1.5 G conditions. Their J-V curves and IPCE spectra are shown in Fig. 2 and Fig. 3 with the detailed photovoltaic parameters in Table 2. The overall energy conversion efficiency changed in the order of ZZX-N3 (3.83%) < ZZX-N4 (4.20%) > ZZX-N5 (3.70%). The ZZX-N3- and ZZX-N4-sensitized cells exhibited slightly higher V_{oc} than ZZX-N5-sensitized cells, but this was only $\sim 2\%$ larger. A much bigger difference was observed in Jsc. ZZX-N3- and ZZX-N4 sensitized cells exhibited \sim 13% larger J_{sc} than that of ZZX-N5 sensitized solar cells. The trend in J_{sc} was consistent with their IPCE, as shown in Fig. 3. The three dyes exhibited photon-toelectron responses from 350 nm to 725 nm. Strong IPCE values at 472 and 670 nm corresponded to Soret and Q bands in their absorption spectra. The IPCE maximums of ZZX-N3 and ZZX-N4 were similar to that of ZZX-N5, but the two bands were broader than the latter, which was consistent with their absorption behaviour on the films. The measured amounts of dye molecules on TiO_2 films were nearly the same for all three dyes (10.37 \times 10 $^{-9}$, 10.45 \times 10 $^{-9}$, and 10.14 \times 10 $^{-9}$ mol for ZZX-N3, ZZX-N4, and ZZX-N5, respectively), indicating that the better



Fig. 2 *J*–*V* curves of ZZX-N3-, ZZX-N4- and ZZX-N5-sensitized solar cells.



Fig. 3 IPCE spectra of ZZX-N3-, ZZX-N4- and ZZX-N5-sensitized solar cells.

 Table 2
 Photovoltaic parameters of ZZX-N3-, ZZX-N4- and ZZX-N5sensitized solar cells

	$J_{ m sc}~({ m mA~cm^{-2}})$	$V_{\rm oc}$ (mV)	FF	η^{a} (%)		
ZZX-N3	9.93 ± 0.06	659 ± 3	0.586 ± 0.02	3.83 ± 0.02		
ZZX-N4	9.97 ± 0.05	662 ± 2	0.637 ± 0.02	4.20 ± 0.01		
ZZX-N5	8.79 ± 0.09	649 ± 1	0.649 ± 0.05	3.70 ± 0.01		
ZZX-N3/PBS	7.73 ± 0.05	632 ± 1	0.662 ± 0.03	3.24 ± 0.03		
ZZX-N4/PBS	8.88 ± 0.06	643 ± 3	0.658 ± 0.03	3.75 ± 0.05		
ZZX-N5/PBS	$\textbf{6.32} \pm \textbf{0.04}$	653 ± 2	$\textbf{0.669} \pm \textbf{0.03}$	2.76 ± 0.02		
^{<i>a</i>} Raw data, see Table S1 in the ESI.						

photovoltaic performance of ZZX-N3 and ZZX-N4 was caused by the existence of donor groups. These results confirmed that the addition of an electron donor to the fluorenyl group enhances the cell's light-harvesting capacity, leading to a higher $J_{\rm sc}$.

To shield some light on the different photovoltaic performance of the three dyes, we performed density functional theory (DFT) calculations for the three molecules at the B3LYP/ 6-31g(d) level. This method has previously been successfully used for the geometry optimization and frontier molecular orbital calculations in zinc porphyrin compounds.10,24,31 In our calculations, linear configurations of long alkyl or alkoxyl chains were adopted in the initial structures to simplify the calculations. The geometry-optimized structures are shown in Fig. 4. The fluorene core of the spacer DHF group was aligned in the plane of the porphyrin ring with a torsion angle less than 1°. Two n-hexyl chains were aligned on the two sides of fluorenyl unit and stretched away from each other. Furthermore, when the donor BFA was attached to DHF, the four n-hexyl chains on BFA aligned in a cross-over configuration with an angle $\sim 86^{\circ}$; whereas, when BPA was used, two n-hexyl chains stretched out with an angle $\sim 148^{\circ}$. Two 2,4-bis(*n*-octoxyl)phenyl groups on the meso positions of the porphyrin ring were tilted in two different directions. As a result, the four alkoxyl groups also formed a cross-over shape with angles of $\sim 13^{\circ}$, 21° , and 28° , for ZZX-N3, ZZX-N4, and ZZX-N5, respectively. The four alkoxyl chains became more parallel after the BFA and BPA groups were introduced into the system. It should be pointed out that the actual configurations of these alkyl chains may be different



Fig. 4 Geometry-optimized structure of ZZX-N3, ZZX-N4 and ZZX-N5. The red sphere at the bottom of each image represents O atoms of benzoic acid. The images were produced from a view with the porphyrin ring perpendicular to the paper. The donor is on the top and the acceptor is at the bottom. The phenyl groups on two *meso* positions fall into the lines of the long alkyl chains.

from the geometry-optimized structures due to their high flexibility; however, these results provide a snapshot of the possible relaxation states on the surface of the TiO₂ nanoparticles.

The electron density distribution profiles of the frontier orbitals of the three dyes are shown in Fig. 5, and the calculated energy levels are summarized in Table 3. The LUMO energy levels of all three dyes were higher than the conduction band of $TiO_2 NP (-4.67 \text{ eV})$, indicating that these dyes were energetically favourable for DSC operation. A distinct separation of HOMO and LUMO was observed in ZZX-N3 and ZZX-N4. This will be beneficial to the charge separation during the cell operation. ZZX-N5 did not show such a separation because of the lack of a donor group in its structure.

Electrochemical impedance spectroscopy (EIS) was carried out to determine the electron recombination resistance at the interface between the $TiO_2/dye/electrolyte$ medium. Fig. 6 shows the typical Nyquist plots of the impedance responses for a ZZX-N3-sensitized solar cell measured at three different bias voltages under open circuit under illumination. The model used for the impedance analysis has been discussed in detail previously.^{32–34} From these plots, two features of the impedance response can be identified: (1) a large semicircle at low frequencies, which corresponds to the back charge-transfer process at the $TiO_2/redox$ electrolyte interface with a recombination resistance; and (2) a small semicircle at high frequencies, which is associated with the charge-transfer process at the



Fig. 5 Electron density distribution profiles of LUMO (top) and HOMO (bottom) of ZZX-N3, ZZX-N4 and ZZX-N5.

spectroscopy

600

10

8

4

2

0

Jsc (mA/cm²) 6 η = 3.75%

η = 3.24%

n = 2.74%

0.1 0.2 0.3 0.4 0.5 0.6 0.7

 Table 3
 Calculated frontier molecular orbital energy levels^a

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	ZZX-N3	ZZX-N4	ZZX-N5
HOMO (eV)	-4.5772	-4.5590	-4.6817
LUMO (eV)	-2.4373	-2.3851	-2.4169
LUMO-HOMO(eV)	2.1399	2.1739	2.2648

^a In vacuum.



Fig. 6 Typical Nyquist plots of the electrochemical impedance responses of a solar cell using the ZZX-N3 dye with three different bias voltages

counter electrode/electrolyte interface with a charge-transfer resistance. Normally, there is a linear region with 45° slope at medium frequencies, which is characteristic for the transmission line model and can be used to derive the transport resistance of the TiO₂ electrode. However, this feature is not clear in the current study. However, this does not affect our understanding on the charge recombination resistance at the TiO₂/redox electrolyte interface.

Fig. 7 shows the electron recombination resistance and electron lifetime measured at different biases. It was expected that long alkyl groups on the donor could provide extra shielding to minimize the charge recombination on the interface between TiO₂ and the electrolyte. However, it was found that the charge recombination resistance of ZZX-N3 and ZZX-N4

Recombination lifetime (s)

Fig. 7 Electron recombination and recombination lifetimes of ZZX-

N3, ZZX-N4, and ZZX-N5 obtained from electrochemical impedance

10

ZZX-N3

ZZX-N4

77X-N5

0.45 0.50 0.55 0.60 0.65 0.70 0.75

Voltage (V)

are very similar to ZZX-N5 under open circuit voltage, which is consistent with their recombination lifetimes of electrons on the TiO₂ surface. These results indicate that the long alkyl groups on the electron donor of ZZX-N3 and ZZX-N4 did not offer an extra shielding effect to reduce the charge recombination than ZZX-N5 at the TiO₂/redox electrolyte interface. The four alkoxyl chains (OC_8H_{17}) are sufficient enough to reduce the charge recombination.

The EIS results combined with the absorption spectra of the dye-coated TiO₂ films also indicated that the different photovoltaic performances of ZZX-N3 and ZZX-N4 was mainly caused by the dye aggregation. The long alkyl chains on the donor led to increased dye aggregates.11 In ZZX-N3, the two phenyl groups in the two meso positions are almost vertical to the porphyrin ring (torsion angle 86.52°). The two phenyl groups from the neighbouring molecules are more parallel, making them much easier to stack over each other than those from ZZX-N4 and ZZX-N5 (torsion angles are 84.57° and 79.91°, respectively).

In an effort to enhance the light-harvesting capacity in the region between the Soret band and O bands, a co-sensitizer PBS was synthesized. PBS is a BODIPY-based dye with strong absorption at 560 nm, which is complementary to the absorption of ZZX-N3, ZZX-N4 and ZZX-N5. The solutions containing PBS and porphyrin dyes were used for the cell preparation. The *I-V* curves of the co-sensitized solar cells are shown in Fig. 8. The molar ratio of PBS to porphyrin dye was fixed at 1:1, and the dye-loading time was 4.5 h. The overall energy conversion efficiency of these cells changed in the order of ZZX-N3/PBS (3.24%) < ZZX-N4/PBS (3.75%) > ZZX-N5/PBS (2.74%), which is lower than their counterparts without co-sensitization, owing to the reduced J_{sc} . The results are consistent with the decreased IPCE as shown in Fig. 3 and 9.

The decreased IPCE of co-sensitized solar cells is due to the decreased dye-loading density of the porphyrin dyes on the TiO₂ surface. When PBS was co-sensitized with porphyrin, the cell indeed picked up the photons in the region around 560 nm, as shown in Fig. 9; however, the IPCE of the co-sensitized cells was generally lower than those of the cells without co-sensitization and a typical comparison was shown in Fig. 10. As we previously reported in similar systems,15 this reduction in IPCE magnitude is ascribed to the decreased loading density of porphyrin, as



Recombination resistance (Ω)

10

10

10

300

ZZX-N3

77X-N4

77X-N5

400 500

Voltage (mV)

ZZX-N3/PBS 77X-N4/PBS ZZX-N5/PBS



Fig. 9 IPCE spectra of ZZX-N3/PBS, ZZX-N4/PBS, and ZZX-N5/PBS sensitized solar cells.



Fig. 10 Absorption spectrum of ZZX-N3/PBS in ethanol (solid line) and the IPCE of ZZX-N3- and ZZX-N3/PBS-sensitized solar cells (dotted lines).

porphyrin and PBS compete for binding to TiO_2 NP with a fixed surface area. This trade-off could be maximized by choosing the appropriate: molar ratio of PBS and porphyrin dyes, dye loading time, and thickness of the film, because these factors will affect the thermal dynamics and kinetics of the dye adsorption process.³⁵⁻³⁸

Conclusions

In an effort to broaden the photo-to-current response of dyesensitized solar cells, new porphyrin dyes, ZZX-N3, ZZX-N4, ZZX-N5, and a complementary dye, PBS, were developed. It was found that further linkage of bis(9,9-dihexyl-9*H*-fluoren-7-yl)amine (BFA) or bis(4-hexylphenyl)amine (BPA) to DHF as a donor led to broader Soret and Q bands, because of the loss of symmetry, resulting in a higher energy conversion efficiency of BFA and BPA-functionalized porphyrin dyes than the porphyrin dye without a donor. Comparison of the dye absorption on TiO₂ nanoparticle films revealed that extra long-alkyl-chains on the donor promoted the formation of aggregates. The application of complementary dye PBS indicated the photon-to-electron response around 560 nm; however, the overall light-harvesting efficiency decreased due to the trade-off between decreased dyeloading density and broadened absorption spectra.

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