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### Highly Asymmetrical Porphyrins with Enhanced Push–Pull Character for Dye-Sensitized Solar Cells

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**Abstract:** A porphyrin  $\pi$ -system has been modulated by enhancing the push–pull character with highly asymmetrical substitution for dye-sensitized solar cells for the first time. Namely, both two diarylamino moieties as a strong electron-donating group and one carboxyphenylethynyl moiety as a strong electron-withdrawing, anchoring group were introduced into the *meso*-positions of the porphyrin core in a lower symmetrical manner. As a result of the improved light-harvesting property as well as high electron distribution in the anchoring group of LUMO, a push-pull-enhanced, porphyrin-sensitized solar cell exhibited more

**Keywords:** absorption spectroscopy • electron transfer • porphyrinoids • solar cells • titanium oxide than 10% power conversion efficiency, which exceeded that of a representative highly efficient porphyrin (i.e., YD2)sensitized solar cell under optimized conditions. The rational molecular design concept based on highly asymmetric, push-pull substitution will open the possibilities of further improving cell performance in organic solar cells.

#### Introduction

Dye-sensitized solar cells (DSSCs) based on mesoporous, nanocrystalline oxides are a promising low-cost alternative to conventional silicon-based solar cells for the conversion of solar energy to electric power.<sup>[1]</sup> Because of the critical role of sensitizers in DSSC performance, optimizing molecular design is essential to maximize power conversion efficiency ( $\eta$ ). Current high-efficiency DSSCs ( $\eta$  =10–12%) have been based on Ru complexes as sensitizers.<sup>[1-4]</sup> However, the limited supply and potential environmental impact of Ru have led to intensive search for green, organic-based dyes.<sup>[5,6]</sup> Porphyrins are a family of organic dyes that are fascinating for application in DSSCs owing to their extremely high molar extinction coefficients [i.e., intense Soret band at

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400 nm (ca.  $10^5 \,\mathrm{M\,cm^{-1}}$ ) and moderate Q bands at 500-600 nm (ca.  $10^4 \text{ M cm}^{-1}$ )] and synthetic versability.<sup>[7-11]</sup> A drawback of typical porphyrins is poor light-harvesting property at wavelengths around 450 nm and >600 nm. Nevertheless, the integrated absorption molar extinction coefficient of a typical porphyrin with respect to wavelength is several times larger than that of Ru complexes, demonstrating the potential high utility of porphyrins in DSSCs. Indeed, with elongation of  $\pi$ -conjugation as well as enhancement of push-pull character in porphyrins, the absorption can be shifted and broadened, making it possible to increase the light-harvesting property and the resultant  $\eta$ -value. Specifically, Diau and Grätzel et al. synthesized a push-pull porphyrin YD2 with a diarylamino moiety as a strong electrondonating group and a carboxyphenylethynyl moiety as a strong electron-withdrawing, anchoring group (Figure 1); YD2 exhibited a high  $\eta$ -value of 11%.<sup>[12]</sup> They further utilized a cobalt(II/III) electrolyte that can yield a higher open circuit voltage  $(V_{\rm OC})$ , with a cocktail of a YD2 derivative, YD2-o-C8 (Figure 1), and a complementary organic dye to achieve a record  $\eta$ -value of 12.3%.<sup>[13]</sup> However, there is still room to improve the  $\eta$ -value by modulating HOMO and LUMO levels as well as other critical factors affecting DSSC performance.

Herein we report the achievement of an  $\eta$ -value of 10.1 % by using an asymmetrically enhanced push-pull porphyrin, ZnPBAT (Figure 2), that is superior to YD2 ( $\eta$ =9.1 %) under our optimized conditions. We have previously examined the effects of the number and position of strongly electron-donating diarylamino groups at *meso*-positions of 5-(4-carboxyphenyl)porphyrins on DSSC performance (Figure 1).<sup>[14]</sup> With increasing the number (*n*) of diarylamino groups introduced into the *meso*-positions from n=0 to 2,

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Figure 1. Molecular structures of porphyrins in previous studies.<sup>[12-14]</sup>



the light-harvesting property of the porphyrins was im-

proved in the order ZnP-ref (n=0) < mono-ZnP (n=1) <

*cis*-ZnP  $(n=2) \approx trans$ -ZnP (n=2), but the solar cell reached

a maximum  $\eta$ -value in n=1 [trans-ZnP ( $\eta$ =3.8%) < ZnP-

Figure 2. Molecular structures of porphyrins for DSSCs.



6.5%)]. This trend can be rationalized by the lower electron density of the anchoring groups (i.e., carboxyphenyl group) in the LUMO of the zinc-porphyrin complexes (ZnP) with the two diarylamino moieties (n=2; cis-ZnP and trans-ZnP) than with the one diarylamino moiety (mono-ZnP), which would lower the electronic coupling between the excited adsorbed dye and 3d orbital of TiO<sub>2</sub>, as well as the anchoring ability onto TiO<sub>2</sub>, leading to a decrease in DSSC performance.<sup>[15]</sup> To increase the electron density of the anchoring group in the LUMO as well as the push-pull character of the porphyrin, an anchoring group with more electron-withdrawing character is desirable. More importantly, introduction of the two diarylamino moieties into the meso-positions in a low-symmetry manner, as in the case of cis-ZnP, rather than a high-symmetry manner, as in the case of trans-ZnP,<sup>[14]</sup> would further enhance the push-pull effects, as inspired by the high electronic asymmetry of photosynthetic chlorophylls that lead to broadening and redshift of the absorption and enhanced Q bands relative to Soret band.<sup>[7]</sup> In this regard, there are still challenges in synthesizing asymmetric porphyrins with different substituents at four meso-positions.<sup>[16,17]</sup> With these synthetic requirements in hand, we decided to introduce one carboxylphenylethynyl moiety as a strong electron-withdrawing, anchoring group<sup>[12,13,18,19]</sup> and two diarylamino moieties as strong electron-donating groups directly into the meso-positions in an asymmetric manner (Figure 2). One mesityl moiety was also tethered to the remaining meso-position to retain the highly asymmetrical meso-substitution. ZnPBA was utilized as a reference to address the effect of the carboxyphenylethynyl moiety (Figure 2), whereas YD2 was used to assess the asymmetric double substitution by the diarylamino moieties.



Scheme 1. Synthetic route to ZnPBAT. 1) trifluoroacetic acid, CHCl<sub>3</sub>, 96%; 2) a) NBS (0.9 equiv),  $CH_2Cl_2$ /pyridine; b)  $Zn(OAc)_2$ ,  $CH_2Cl_2$ / MeOH, 27% (2 steps); 3) triisopropylsilylacetylene, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], CuI, THF/Et<sub>3</sub>N, 87%; 4) NBS (2 equiv), CH<sub>2</sub>Cl<sub>2</sub>/pyridine, 50%; 5) bis(4-methylphenyl)amine, nBuLi, Pd(OAc)2, DPEphos, toluene, 61 %; 6) a) TBAF, THF; b) 4-iodobenzoic acid, [Pd2(dba)3], AsPh3, THF/Et3N, 79% (2 steps).

ref

 $(\eta = 4.4\%) < cis-ZnP$   $(\eta = 5.5\%) < mono-ZnP$   $(\eta =$ 

#### **Results and Discussion**

The synthesis of ZnPBAT is shown in Scheme 1. The key feature involves highly asymmetric successive introduction of three different substituents (i.e., two diarylamino, one carboxylphenylethynyl, and one trimethylphenyl moieties) into the four *meso*-positions of a porphyrin core. Monoaryl-



Scheme 2. Synthetic route to ZnPBA. 1) a)  $BF_3 \cdot OEt_2$ ,  $CHCl_3$ ; b) *p*-chloranil,  $CHCl_3$ , 2.0% (2 steps); 2)  $Zn(OAc)_2 \cdot 2H_2O$ ,  $CHCl_3/MeOH$ , 85%; 3) a) bis(4-methylphenyl)amine, iodobenzenediacetate, NaAuCl<sub>4</sub>·2H<sub>2</sub>O,  $CH_2Cl_2$ ; b) NaOH, THF; c)  $Zn(OAc)_2 \cdot 2H_2O$ ,  $CHCl_3/MeOH$ , 15% (3 steps).

substituted free-base porphyrin 1 was synthesized from the corresponding dipyrromethanes.<sup>[20]</sup> Monobromination of 1 yielded a mixture of intermediate cis- and trans-isomers, of which the cis-intermediate was separated and subsequently treated with zinc acetate to afford the *cis*-isomer 2.<sup>[21]</sup> Sonogashira coupling of 2 and subsequent dibromination of 3 gave 4.<sup>[22]</sup> Diarylamino-substituted porphyrin 5 was obtained in 61% yield by the substitution reaction of 4 with bis(4-methylphenyl)amine.<sup>[23]</sup> Deprotection of **5** with tetrabutylammonium fluoride (TBAF) followed by Sonogashira coupling to 4-iodobenzoic acid produced ZnPBAT.<sup>[24]</sup> ZnPBA was prepared according to similar procedures,<sup>[25,26]</sup> as shown in Scheme 2. YD2 was also synthesized by following the previously reported method.<sup>[27]</sup> Synthetic procedures and optical and electrochemical properties are provided in Supporting Information (Figure S1–S3).

Figure 3 displays the UV/Vis absorption spectra of the ZnPs in EtOH. The peak positions and molar absorption coefficients ( $\varepsilon$ ) of Soret and Q bands are listed in Table S1 in the Supporting Information. The absorption bands of ZnPBAT and ZnPBA are broadened compared with those of YD2 due to the introduction of the two diarylamino moieties. Moreover, the absorption band of ZnPBAT is redshifted toward longer wavelength relative to those of ZnPBA and YD2, illustrating the improved light-harvesting property of ZnPBAT in the visible spectral region. The steady-state fluorescence spectra of the ZnPs were measured in EtOH (Figure S4 in the Supporting Information) and the emission maxima are listed in Table S1 in the Sup-



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Figure 3. UV/Vis absorption spectra of ZnPBAT (solid line), YD2 (dotted line), and ZnPBA (dashed line) in EtOH.

porting Information. In accordance with the trend of the absorption properties, the emission maximum is shifted toward longer wavelength in the order of ZnPBA, YD2, and ZnPBAT. From the intersection of the normalized absorption and fluorescence spectra, the zero-zero excitation energies ( $E_{0-0}$ ) are determined to be 1.83, 1.89, and 1.92 eV for ZnPBAT, YD2, and ZnPBA, respectively (Table S1 in the Supporting Information).

To determine the first oxidation potential  $(E_{ox})$  and the first reduction potential  $(E_{red})$  of the porphyrins in solution, differential pulse voltammetry measurements were performed in THF containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte. The  $E_{ox}$  values of ZnPBAT (0.85 V vs. NHE) and ZnPBA (0.85 V vs. NHE) are shifted in a negative direction relative to that of YD2 (0.93 V vs. NHE), whereas  $E_{\rm red}$  of ZnPBAT (-1.15 V vs. NHE) and YD2 (-1.12 V vs. NHE) are similar and shifted in a positive direction relative to ZnPBA (-1.29 V vs. NHE) (Table S1 in the Supporting Information). These results imply that the introduction of the diarylamino and carboxyphenylethynyl moieties at the meso-positions has desirable effect on the redox properties, leading to the smaller bandgap in ZnPBAT. Indeed, the electrochemical HOMO-LUMO gaps are determined to be 2.00, 2.05, and 2.14 eV for ZnPBAT, YD2, and ZnPBA, respectively, which agrees with the trend of the optical HOMO-LUMO gaps. From the spectroscopic and electrochemical measurements, driving forces for electron transfer (ET) ( $\Delta G_{ini}$ ) from the ZnP excited singlet state (<sup>1</sup>ZnP\*) to the conduction band (CB) of  $TiO_2$  (-0.5 V vs. NHE),<sup>[13]</sup> and for the regeneration of the ZnP radical cation  $(ZnP^+)$  by  $I^-/I_3^-$  redox couple (+0.4 V vs. NHE)<sup>[13]</sup> ( $\Delta G_{reg}$ ) have been evaluated (Table S1 in the Supporting Information). Both of the processes are thermodynamically feasible and the driving forces are sufficient for efficient ET.

DFT calculations were employed to gain insight into the equilibrium geometry and electronic structures of the frontier orbitals of the ZnPs.<sup>[14]</sup> They are found to possess planar porphyrin rings, to which the diarylamino and trimethylphenyl moieties are almost perpendicular, avoiding the steric congestion around the *meso*-positions (Figure S5). Porphyrins with  $D_{4h}$  symmetry generally reveal two energetically degenerate LUMOs (LUMO+1, LUMO) and two nearly degenerate HOMOs (HOMO, HOMO-1).<sup>[14]</sup> All the studied porphyrins largely retain these characteristics (Table S2 in the Supporting Information). The HOMO–LUMO gaps of the ZnPs are as follows: ZnPBAT (2.15 eV) < YD2 (2.25 eV) < ZnPBA (2.41 eV). This trend agrees well with those of the optical and electrochemical HOMO–LUMO gaps. The electron density distributions of the ZnPs in their respective HOMOs and LUMOs are visualized in Figure S6 in the Supporting Information. As expected, the electron densities of the anchoring group in the LUMOs of ZnPBAT and YD2 are comparable and significantly larger than that of ZnPBA. Accordingly, we can anticipate a high electron injection efficiency ( $\phi_{inj}$ ) of ZnPBAT from the <sup>1</sup>ZnP\* to the CB of TiO<sub>2</sub>, similar to YD2 (vide infra).<sup>[12,13]</sup>

A TiO<sub>2</sub> electrode was immersed into a solution of the porphyrin in EtOH to give a porphyrin-stained TiO<sub>2</sub> electrode. The porphyrin surface coverage ( $\Gamma$ ) adsorbed on the TiO<sub>2</sub> film was determined by measuring the absorbance of the porphyrin that was dissolved from the porphyrin-stained TiO<sub>2</sub> film into an alkaline aqueous solution containing THF. During the immersion, all the porphyrins reach saturated surface coverage on the TiO<sub>2</sub> films in 3 h (Figure 4). The



Figure 4. Plots of porphyrin surface coverage ( $\Gamma$ ) as a function of immersion time for ZnPBAT (solid line with circles), YD2 (dotted line with triangles), and ZnPBA (dashed line with squares) that adsorb on the TiO<sub>2</sub> films without the scattering layer.

saturated  $\Gamma$  values of the three porphyrins are comparable:  $\Gamma = 9.2 \times 10^{-11}$ ,  $8.9 \times 10^{-11}$ , and  $8.7 \times 10^{-11} \text{ mol cm}^{-2}$  for ZnPBAT, YD2, and ZnPBA, respectively. Given a projected area of one porphyrin molecule on a flat TiO<sub>2</sub> surface with a perpendicular orientation, the saturated  $\Gamma$  values are calculated to be  $9.6 \times 10^{-11} \text{ mol cm}^{-2}$  for ZnPBAT and ZnPBA and  $1.0 \times 10^{-10} \text{ mol cm}^{-2}$  for YD2. Taking into account the comparable calculated and experimental  $\Gamma$  values together with the saturated adsorption behavior on the TiO<sub>2</sub> surface, all the porphyrins are concluded to form well-packed porphyrin monolayers on TiO<sub>2</sub>. The FTIR spectra of ZnPBAT, YD2, and ZnPBA that were obtained from solid samples reveal the characteristic band of  $\nu$ (C=O) of the carboxylic acid group at around 1700 cm<sup>-1</sup> (Figure S7 in the Supporting Information).<sup>[14]</sup> This diagnostic peak for  $\nu$ (C=O) disappears for the FTIR spectra of TiO2/ZnPBAT, TiO2/YD2, and TiO<sub>2</sub>/ZnPBA. The FTIR spectra exhibit a significant increase in the symmetric carboxylate band,  $\nu(\text{COO}_{s}^{-})$ , at around 1400 cm<sup>-1</sup>.<sup>[14]</sup> The disappearance of  $\nu(\text{C=O})$  and the increased intensity of  $\nu(\text{COO}_{s}^{-})$  corroborate that a proton is detached from the carboxylic acid group during the porphyrin adsorption on the TiO<sub>2</sub> surface, leading to the bidentate binding of the carboxylate group to TiO<sub>2</sub>. This is consistent with the previous assignment that a carboxylic acid of analogous porphyrins is bound to a TiO<sub>2</sub> surface by means of a bridging bidentate mode.<sup>[14]</sup>

To optimize the DSSC performance, we first examined the effects of immersion time of the TiO<sub>2</sub>/ZnPBAT, TiO<sub>2</sub>/ YD2, and TiO<sub>2</sub>/ZnPBA electrodes (Figure S8 in the Supporting Information).<sup>[28]</sup> The  $\eta$ -value is derived from the equation:  $\eta = J_{SC} \times V_{OC} \times ff$ , in which  $J_{SC}$  is the short circuit current and ff is the fill factor. The change in the  $\eta$ -value of the TiO<sub>2</sub>/YD2 and TiO<sub>2</sub>/ZnPBA cells as a function of immersion time matches the adsorption behavior of YD2 and ZnPBA on TiO<sub>2</sub>. On the other hand, the  $\eta$ -value of the TiO<sub>2</sub>/ZnPBAT cell is increased rapidly with increasing the immersion time to reach a maximum in 1 h and then decreased to level off in 2 h. This suggests a stronger aggregation tendency of ZnPBAT than YD2 and ZnPBA, as seen in the adsorption behavior of analogous porphyrins on TiO2.<sup>[14]</sup> Note that the maximum  $\eta$  values are 7.1% after 1 h sensitization for ZnPBAT, 6.7% after 3 h for YD2, and 4.3% after 3 h for ZnPBA. To further optimize the cell performances, each porphyrin was sensitized onto the TiO<sub>2</sub> surface under the best immersion time conditions in which coadsorbant chenodeoxycholic acid (CDCA) was added to the porphyrin solution to reduce the porphyrin aggregation on the TiO<sub>2</sub> (Figure S9 in the Supporting Information). Maximum  $\eta$ values are obtained at different CDCA concentrations for the various ZnPs (ZnPBAT: 8.6% with 10 equiv CDCA; YD2: 8.1% with 2 equiv CDCA; ZnPBA: 6.2% with 5 equiv CDCA), reflecting the difference in aggregation behavior of the porphyrins. Finally, TiO<sub>2</sub>/ZnPBAT, TiO<sub>2</sub>/YD2, and TiO<sub>2</sub>/ZnPBA cells were kept under dark conditions to evaluate the aging effect under dark conditions on the DSSC performance (Figure 5).<sup>[29]</sup> All the cells reach the highest  $\eta$ -value after several days aging. Figure 6 depicts the photocurrent-voltage characteristics of the TiO<sub>2</sub>/ZnPBAT, TiO<sub>2</sub>/YD2, and TiO<sub>2</sub>/ZnPBA cells under the respective maximal  $\eta$ -conditions (Table 1).

Table 1. Photovoltaic performance under the optimized conditions.<sup>[a]</sup>

	Aging	$J_{\rm SC}$	V <sub>oc</sub>	ff	η
	[days]	$[mA cm^{-2}]$	[V]		[%]
ZnPBAT	1.5	19.33	0.719	0.724	10.1
		$(18.61\pm0.7)$	$(0.712 \pm 0.007)$	$(0.734 \pm 0.01)$	$(9.7 \pm 0.4)$
YD2	2	17.05	0.742	0.718	9.1
		$(16.75 \pm 0.3)$	$(0.742 \pm 0.006)$	$(0.715 \pm 0.02)$	(8.9±0.2)
ZnPBA	8	16.26	0.713	0.719	8.3
		$(15.69 \pm 0.6)$	$(0.713 \pm 0.002)$	$(0.731 \pm 0.01)$	$(8.2\pm0.1)$

[a] Values correspond to photovoltaic parameters exhibiting the highest  $\eta$  value. Values in parenthesis also denote average values from five independent experiments.



Figure 5. Plots of the power conversion efficiency ( $\eta$ ) as a function of aging time for TiO<sub>2</sub>/ZnPBAT cell (solid line with circles), TiO<sub>2</sub>/YD2 cell (dotted line with triangles), and TiO<sub>2</sub>/ZnPBA cell (dashed line with squares). The solar cells were kept under dark condition except the period of the photovoltaic measurements.<sup>[29]</sup> The porphyrin-stained TiO<sub>2</sub> electrodes were prepared under the optimized conditions (immersion time: 1 h for ZnPBAT and 3 h for YD2 and ZnPBA; CDCA concentration: 10 equiv CDCA for ZnPBAT, 2 equiv CDCA for YD2, and 5 equiv CDCA for ZnPBA).



Figure 6. Photocurrent–voltage characteristics of the  $TiO_2/ZnPBAT$  cell (solid line), the  $TiO_2/YD2$  cell (dotted line), and the  $TiO_2/ZnPBA$  cell (dashed line).

The highest DSSC performance increases in the order TiO<sub>2</sub>/ZnPBA ( $J_{\rm SC}$ =16.26 mA cm<sup>-2</sup>,  $V_{\rm OC}$ =0.713 V, ff=0.719,  $\eta$ =8.3%) < TiO<sub>2</sub>/YD2 ( $J_{\rm SC}$ =17.05 mA cm<sup>-2</sup>,  $V_{\rm OC}$ =0.742 V, ff=0.718,  $\eta$ =9.1%) < TiO<sub>2</sub>/ZnPBAT ( $J_{\rm SC}$ =19.33 mA cm<sup>-2</sup>,  $V_{\rm OC}$ =0.719 V, ff=0.724,  $\eta$ =10.1%). Large improvement of the TiO<sub>2</sub>/ZnPBA cell over the TiO<sub>2</sub>/*trans*-ZnP and *cis*-ZnP cells<sup>[14]</sup> derives from the difference in the device fabrication (i.e., immersion solvent, electrolyte solution, and TiO<sub>2</sub> film) and the aging effect under dark conditions.

It should be emphasized here that the  $\eta$ -value under our experimental conditions of the TiO<sub>2</sub>/ZnPBAT cell is higher than that of the TiO<sub>2</sub>/YD2 cell that has been reported to exhibit one of the highest  $\eta$  values (11%) of DSSCs.<sup>[12,13]</sup> Diau and Yeh et al. reported that YD14 ( $\eta$  = 6.8%) with two diarylamino groups at the *meso*-positions with *trans*-configuration (Figure 1) is comparable to YD2 ( $\eta$  = 7.1%) in terms of photovoltaic performances under their optimized conditions,<sup>[30]</sup> supporting the advantage of the highly asymmetrical



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Figure 7. Photocurrent action spectra of the  $TiO_2/ZnPBAT$  cell (solid line), the  $TiO_2/YD2$  cell (dotted line), and the  $TiO_2/ZnPBA$  cell (dashed line).



Figure 8. UV/Vis/NIR absorption spectra of the TiO<sub>2</sub>/ZnPBAT electrode (solid line), the TiO<sub>2</sub>/YD2 electrode (dotted line), and the TiO<sub>2</sub>/ZnPBA electrode (dashed line). The scattering TiO<sub>2</sub> layers were not applied to the TiO<sub>2</sub> electrodes to measure absorbance accurately. The weak absorption at 800 nm can be attributed to the formation of ZnP<sup>+</sup> on the TiO<sub>2</sub>.<sup>[27]</sup>

substitution in ZnPBAT in which the two diarylamino groups are introduced at the *meso*-positions with a *cis*-configuration.

Taking into account the rather similar  $V_{\rm OC}$  and ff values, the difference in the  $\eta$  values primarily results from differences in the  $J_{\rm SC}$  values. Each of the photocurrent action spectra (Figure 7) follows the absorption feature of the corresponding porphyrins on TiO<sub>2</sub> (Figure 8). In fact, the order of the improvement in the incident photon-to-current efficiency (IPCE) values at 650–800 nm matches that in the light-harvesting ability of the porphyrins (Figure 2), rationalizing the higher  $J_{\rm SC}$  and  $\eta$  values of the TiO<sub>2</sub>/ZnPBAT cell than the TiO<sub>2</sub>/YD2 cell. As a result of the enhanced pushpull character achieved with the highly asymmetric substitution, the TiO<sub>2</sub>/ZnPBAT cell exhibits efficient photocurrent generation extending to 800 nm.

The IPCE is divided into three components in the following equation: IPCE = LHE ×  $\phi_{inj} \times \eta_{col}$ , in which LHE (lightharvesting efficiency) is the number of absorbed photons per the number of incident photons and  $\eta_{col}$  is the charge collection efficiency. The relative integrated IPCE value in-

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creases in the order TiO<sub>2</sub>/ZnPBA (1) < TiO<sub>2</sub>/YD2 (1.11) < TiO<sub>2</sub>/ZnPBAT (1.28), which parallels the trend of the  $J_{\rm SC}$  values (Table 1). The maximum adsorbed photon-to-current efficiency (APCE) value at 400–500 nm is close to a unity and increases slightly in the order TiO<sub>2</sub>/YD2 (88%) < TiO<sub>2</sub>/ZnPBA (92%) < TiO<sub>2</sub>/ZnPBAT (95%). This implies that the  $\phi_{\rm inj}$  and/or  $\eta_{\rm col}$  are somewhat different for the three ZnPs, resulting in a switched order between TiO<sub>2</sub>/YD2 and TiO<sub>2</sub>/ZnPBA for the APCE values.

Electron injection and charge recombination (CR) of the ZnP-sensitized TiO<sub>2</sub> films were examined by time-resolved transient absorption (TA) spectroscopy, similarly to what was performed previously for other ZnPs on  $TiO_2$  (Figure S10 in the Supporting Information).<sup>[31-33]</sup> TA spectra were measured in the wavelength range 475 to 750 nm for the dyes in ethanol (Figure S10A-S10C in the Supporting Information), as well as attached on the nanostructured TiO<sub>2</sub> electrodes (Figure S10D–S10F in the Supporting Information). From these spectra, kinetics can be obtained at key wavelengths to illustrate the dynamics of excited state decay, electron injection and CR. Thus, kinetics at about 700 nm probes both decay of <sup>1</sup>ZnP\* stimulated emission and ZnP<sup>++</sup> formation and decay, and can therefore be used to monitor both electron injection and CR (Figure S10E and S10F in the Supporting Information). As discussed in more detail in Supporting Information, electron injection is very fast, occurring on the few ps timescale and competing with relaxation from higher excited states and solvation dynamics. CR, on the other hand, is very slow,  $\geq 100$  ns for all the sensitizers (Figure S10G in the Supporting Information). Compared to previously studied ZnPs on TiO2, [31-33] electron injection is faster and CR much slower, conditions ideal for high IPCE values. The similar electron injection and CR for all three ZnPs in addition rationalizes the small difference in APCEs.

To understand the slight difference in the  $V_{\rm OC}$  values, we also applied electrical impedance spectroscopy (EIS) to compare the electron flow in the solar cells. The EIS Nyquist plots for DSSCs based on ZnPBAT, YD2, and ZnPBA were obtained under standard AM 1.5 illumination at opencircuit conditions (Figure S11 in the Supporting Information).<sup>[34,35]</sup> The small semicircle at the left-hand side, large semicircle in the middle, and the small semicircle at the right-hand side of Figure S11 correspond to the ET processes at the Pt electrode, at the TiO2-dye-electrolyte interface  $(R_{\rm p})$ , and in the electrolyte, respectively. A small  $R_{\rm p}$  should reflect faster ET between the TiO<sub>2</sub> and the electrolyte, contributing to a decrease in the  $V_{\rm OC}$  values. In fact, the trend in the  $V_{\rm OC}$  values is largely consistent with that in the  $R_{\rm p}$ values [ZnPBAT (15.28  $\Omega$ ) < ZnPBA (18.41  $\Omega$ ) < YD2  $(20.06 \Omega)$ ]. We also measured the current-voltage characteristics under dark conditions (Figure S12 in the Supporting Information). As a more positive voltage is applied, the onset appears in the order ZnPBAT < ZnPBA < YD2, which is in good agreement with the trend of the  $R_p$  values. Overall, the difference in the  $J_{\rm SC}$  and  $V_{\rm OC}$  values of the three  $TiO_2$  cells matches that in the  $\eta$  values.

Finally, the long-term stability of the TiO<sub>2</sub>/ZnPBAT cell was assessed under the standard AM 1.5 condition (Figure S13 in the Supporting Information). Continued exposure of the TiO<sub>2</sub>/ZnPBAT cell for 300 h to the full sunlight at 25 °C showed only a 10% decrease of the overall efficiency over this extended light-soaking period. Note that the initial increase in the  $\eta$  value is related to the aging effect on the photovoltaic performance, as shown in Figure 5. Overall, the cell is robust and that the small decline is probably caused by losses of the volatile acetonitrile solvent and desorption of ZnPBAT from the TiO<sub>2</sub> electrode.

#### Conclusion

We have successfully designed and synthesized highly asymmetric porphyrin ZnPBAT with enhanced push-pull character for DSSCs for the first time. ZnPBAT improved the light-harvesting property compared with references in visible region. More importantly, the ZnPBAT-sensitized solar cell exhibited more than  $\eta = 10\%$ , which exceeds that of the widely known YD2-sensitized solar cell under our optimized conditions. The molecular design concept based on the push-pull enhancement by the asymmetric substitution will be useful for further improving cell performance in DSSCs.

#### **Experimental Section**

Photovoltaic measurements: Preparation of TiO2 electrodes and the fabrication of sealed cells for photovoltaic measurements were performed following the previously reported method.<sup>[28]</sup> Nanocrystalline TiO<sub>2</sub> parti-(d=20 nm, CCIC:PST18NR, JGC-CCIC, and d=30 nm,cles CCIC:PST30NRD, JGC-CCIC) were used as the transparent layer of the photoanode, whereas submicrocrystalline  $TiO_2$  particles (d = 400 nm, CCIC:PST400C, JGC-CCIC) were used as the light-scattering layers of the photoanode. A TiO<sub>2</sub> film with a three-layer structure composed of PST18NR (8 µm thickness), PST30NRD (4 µm thickness), and PST400C (4 µm thickness) was fabricated on a FTO glass (Solar 4 mm thickness, 10  $\Omega \square^{-1}$ , Nippon Sheet Glass). These thickness conditions were initially optimized by using YD2. The TiO2 electrode was immersed into a solution of the porphyrin in ethanol (0.20mm; 10mL) containing CDCA (0~ 7.85 mg). The sandwich cell was prepared by using the dye-anchored TiO<sub>2</sub> film as a working electrode and a counter Pt electrode. An electrolyte solution consisting of 1,3-dimethylimidazolium iodide (1.0 M), I<sub>2</sub> (0.03 M), LiI (0.05 M), guanidinium thiocyanate (0.1 M), and 4-tert-butylpyridine (0.50 M) in an 85:15 acetonitrile/valeronitrile mixture was used for the cell.<sup>[12]</sup> Incident photon-to-current efficiency (IPCE) and photocurrent-voltage (J-V) performance were measured on an action spectrum measurement setup (CEP-2000RR, BUNKOUKEIKI) and a solar simulator (PEC-L10, Peccell Technologies) with a simulated sunlight of AM 1.5 (100 mW cm<sup>-2</sup>), respectively: IPCE (%) =  $100 \times 1240 \times i/(W_{in} \times \lambda)$ , in which *i* is the photocurrent density (A cm<sup>-2</sup>),  $W_{in}$  is the incident light intensity (W cm<sup>-2</sup>), and  $\lambda$  is the excitation wavelength (nm). During the photovoltaic measurements, a black plastic mask was attached on the back of the TiO<sub>2</sub> electrode except for the TiO<sub>2</sub> film region to reduce scattering light.

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