Porphyrin Dyes on TiO₂ Surfaces with Different Orientations: A Photophysical, Photovoltaic, and Theoretical Investigation

Liping Si^{†,‡} and Hongshan He^{*,†,‡}

[†]Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920, United States [‡]Center for Advanced Photovoltaics, South Dakota State University, Brookings, South Dakota 57006, United States

ABSTRACT: Porphyrin dyes with a triphenylamino group as an electron donor, *para-* or *meta-*benzoic acids as electron acceptors, and hydrogen (H) or mesityl (M) substituents on the meso position as auxiliary groups were synthesized. Their photophysical properties and photovoltaic performance in dye-sensitized solar cells were investigated. All four porphyrins exhibited similar photophysical properties in the solution and dye-loading densities on the surface of TiO₂ nanoparticles; however, the *p*-benzoic acid functionalized porphyrins, *p*-H(M)PZn, gave better photovoltaic performance than *m*-benzoic acid functionalized porphyrins, *m*-H(M)PZn. Theoretical calculations indicated that the electron density on the



frontier molecular orbital was more delocalized to *p*-benzoic acid than to *m*-benzoic acid. Absorption spectra indicated the stronger H-aggregation in *m*-H(M)PZn than that in *p*-H(M)PZn on the surface of TiO_2 nanoparticles. The mesityl groups in the meso positions reduced the dye-loading density due to steric hindrance between dyes. As a result, the *p*-MPZn exhibited the best energy conversion efficiency among the four porphyrins studied. This efficiency was further enhanced when a complementary dye BET was used.

■ INTRODUCTION

Solar energy is an environmentally friendly alternative energy source that can make a significant contribution to solving worldwide energy problems.¹⁻³ Dye-sensitized solar cells (DSCs) are lightweight devices made from inexpensive materials and can be adapted for a variety of indoor and outdoor applications with minimal environmental impact.² As such, they are a promising technology for the cost-effective conversion of solar energy to electricity. The state-of-the-art DSC is a Grätzel-type, titanium dioxide nanoparticles (TiO₂ NPs)-based electrochemical device, in which interconnected TiO₂ NPs in the anatase phase are packed randomly on a substrate, such as fluorine-tin-oxide (FTO)-coated transparent conducting glass (TCO glass).²⁻⁴ The energy conversion efficiency (η) can be calculated from open-circuit voltage (V_{oc}) , short-circuit current (J_{SC}) , fill factor (FF), and input power, whereas its photon-to-current response can be described by the incident photon to current conversion efficiency (IPCE) and is determined by the number of electrons measured as photocurrent in the external circuit divided by the monochromatic photon flux that strikes the cell. This key indicator can be calculated from eq $1^{2,5}$

$$IPCE(\lambda) = LHE(\lambda) \times \phi_{inj} \times \eta_{coll}$$
(1)

where LHE(λ) is the light-harvesting efficiency at the interested wavelength, ϕ_{inj} is the quantum yield for electron injection from the excited sensitizer to the conduction band of the semiconductor oxide, and η_{coll} is the electron collection efficiency. Therefore, maintaining a broader light absorption capability, efficient electron injection from the dye to TiO₂, and efficient electron collection are crucial to high-performance cells. To date, energy conversion efficiency of >13% has been achieved in a porphyrin-sensitized solar cell in combination with a cobalt-based electrolyte system. 6,7

The dye structure is of importance to the cell performance. Its structural characteristics will not only affect the light absorption properties but also impact the dye–dye and dye– TiO_2 communication.⁸⁻¹² The dye– TiO_2 interaction in turn will affect the electron injection, electron recombination, and dye aggregation, which could result in very different current density, open-circuit voltage, and therefore energy conversion efficiency.¹³⁻²⁴ In the state-of-the-art porphyrin dyes, a parabenzoic acid is often used as an anchoring group.^{3,6,9,14,25-41} It binds to the surface of TiO₂ nanoparticles in the bidentate mode. Porphyrin molecules align on the surface of TiO₂, and the electron injection goes from the dye molecule to the conduction band of TiO_2 . As the charge transfer from the dye molecules to the TiO₂ nanoparticles relies on the distance between them, tilting the orientation of the dye molecule on the surface of TiO₂ nanoparticles may change the distance and affect the electron injection and at the same time reduce the aggregation. Saavedra⁴² et al. found that nonvertical alignment of the phthalocyanine aggregate exhibited faster charge transfer to the semiconductor than its upright aggregate. Harima^{43,44} et al. studied a set of carbazole-based dyes and found that the orientation affected the direction of the dipole moment; therefore, it influenced the electron injection and recombination, with vertical alignment giving the best efficiency.

Received: December 24, 2013 Revised: April 11, 2014



Figure 1. Synthesis of porphyrin dyes *p*-HPZn, *p*-MPZn, *m*-HPZn, and *m*-MPZn.

Rochford^{45–47} et al. also studied several dicarboxylic benzoic acid functionalized porphyrin dyes and found that nonvertical alignment gave better IPCE. Diau²⁶ et al. studied several ethylbenzoic acid functionalized porphyrins and found that *meta*-benzoic acid derivatives did not perform better than *para*benzoic acid counterparts. In a recent study, Gou⁴⁸ et al. found that salicylic acid was better than the *para*-benzoic acid counterpart. It is unclear whether the different performance comes from different substituents, dye-loading capacity, or orientation on the surface of TiO₂ nanoparticles.

In this study, we designed four porphyrin dyes *p*-HPZn, *p*-MPZn, *m*-HPZn, and *m*-MPZn with a triphenylamine as a donor group. As shown in Figure 1, *para-* or *meta-*benzoic acid groups are used to anchor porphyrin dyes on the surface of TiO_2 nanoparticles, and mesityl groups are used to provide hindrance for aggregation. We aim to reveal how the anchoring groups (*p*-benzoic acid versus *m*-benzoic acid) and bulky substituents affect the energy conversion efficiency. We also want to reveal if the anchoring groups affect the photovoltaic performance of a complementary dye (BET) with strong absorption at around 520 nm.

EXPERIMENTAL SECTION

General. Chemicals were purchased from Acros and used directly without further purification except chloroform. The chloroform was dried using CaH₂ as a drying agent prior to use. BET dye was prepared as described previously.¹⁴ ¹H NMR spectra were acquired on a Bruker 400 M spectrometer. Mass spectra were obtained from a Finnigan LC QDECA spectrometer. Absorption spectra were performed on a HP Agilent 8453 UV–vis spectrophotometer. Steady-state fluorescence spectra were acquired on a FS920 spectrophotometer from Edinburgh Instrument, Inc. with a Xe900 arc lamp as the light source and a Hamamatsu R928P photomultiplier as a detector. Fluorescence decay curves were obtained on LifeSpec II from Edinburgh Instrument, Inc. with a 375 nm diode laser as the light source. The decay lifetimes were determined by deconvolution and single-exponential fitting of decay curves.

Synthesis of Porphyrin Dyes. 5-(4-Carboxyphenyl)-15-(4-diphenylaminophenyl)porphyrin Zinc (p-HPZn). A solution of 200 mL of chloroform with dipyrromethane (146.2 mg, 1.0 mmol), 4-carboxybenzaldehyde (76.1 mg, 0.5 mmol), and 4-diphenylaminobenzaldehyle (136.6 mg, 0.5 mmol) was flushed with nitrogen for 5 min and treated with BF3. OEt2 (70.0 μ L, 0.3 mmol) at room temperature for 2 h under nitrogen. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.34 g, 1.5 mmol) was added, and the mixture was stirred for another 1 h. Triethylamine (77.4 μ L, 0.3 mmol) was then added. The resulting mixture was filtered through a pad of silica gel. The pad was washed with CHCl₃ until the eluent was colorless. Solvent was then removed, and solid was redissolved in chloroform and loaded on a silica gel column for purification. $CHCl_2/CH_2OH = 100:2$ (v/v) was used as the eluent. The second band was collected as p-HPH₂ and crystallized from chloroform/hexane as a purple solid. Yield: 20 mg, 3.0%. Its purity was confirmed by TLC. The p-HPH₂ (20 mg, 0.02 mmol) was then dissolved in CHCl₃ (20 mL), and Zn(OAc)₂. 2H₂O (65.2 mg, 0.3 mmol) in methanol (2 mL) was added. The mixture was stirred overnight at room temperature. After the mixture was washed with water several times, the volume of the organic layer was reduced to 5 mL and loaded again on a silica gel column for purification using $CHCl_3/CH_3OH = 100:2$ (v/v) as the eluent. The second band was collected as final product p-HPZn. Yield: 11 mg, 50.4%. ¹H NMR (400 MHz, $CDCl_3$, ppm): 13.60–12.88 (br, 1H); 10.36 (d, J = 4.4 Hz, 2H); 9.51(m, 4H); 9.09 (d, J = 4 Hz, 2H); 8.91 (d, J = 8 Hz, 2H); 8.40 (d, J = 8 Hz, 2H); 8.33 (d, J = 8 Hz, 2H); 8.12 (d, J = 4 Hz, 2H); 7.48–7.38(m, 12H). MS (ESI, $[M - H]^{-}$, m/z): calcd. C45H29N5O2Zn, 735.2; found, 733.9.

5-(4-Carboxyphenyl)-15-(4-diphenylaminophenyl)-5,15dimesitylporphyrin Zinc (p-MPZn). This compound was prepared in a similar manner as described for p-HPZn. 5-Mesityldipyrromethane (264.6 mg, 1.0 mmol), 4-carboxybenzaldehyde (74.1 mg, 0.5 mmol), and 4-diphenylaminobenzaldehyle (136.6 mg, 0.5 mmol) were used for p-MPH₂.Yield: 81 mg, 8.8%. For the preparation of p-MPZn, free base (80 mg, 0.0879 mmol) and Zn(OAc)₂·2H₂O (192.9 mg, 0.9 mmol) were used. Yield: 60 mg, 70.3%. ¹H NMR (400 MHz, CDCl₃, ppm): 9.06 (d, J = 2 Hz, 2H); 8.76 (m, 6H); 8.65 (s, 1H); 8.42 (d, J = 2.4 Hz, 2H); 8.30 (d,J = 6 Hz, 2H); 8.03 (d, J = 7.2 Hz, 2H); 7.32 (m, 10H); 7.22 (s, 3H); 7.05 (s, 2H); 2.56 (br, 6H); 1.77 (s, 12H). MS (ESI, $[M - H]^-$, m/z): calcd. C₆₃H₄₉N₅O₂Zn, 971.32; found, 969.96. MS (ESI, $[M - H]^-$, m/z): calcd. C₆₃H₄₉N₅O₂Zn, 971.32; found, 970.00.

5-(3-Carboxyphenyl)-15-(4-diphenylaminophenyl)porphyrin Zinc (m-HPZn). This compound was prepared in a similar manner as described for *p*-HPZn. Dipyrromethane (146.2 mg, 1.0 mmol), 3-carboxybenzaldehyde (76.1 mg, 0.5 mmol), and 4-diphenylaminobenzaldehyle (136.6 mg, 0.5 mmol) were used for *m*-HPH₂. Yield: 40 mg, 5.9%. *m*-HPH₂ (40 mg, 0.06 mmol) and Zn(OAc)₂·2H₂O (129.5 mg, 0.6 mmol) were used for *m*-HPZn. Yield: 30 mg, 68.7%. ¹H NMR (400 MHz, CDCl₃, ppm): 13.52–12.99 (br, 1H); 10.37 (d,*J* = 4 Hz, 2H); 9.52(m, 4H); 9.10 (t, *J* = 5.6 Hz, 2H); 8.92 (t, *J* = 5.6 Hz, 2H); 8.45–8.30 (m, 4H); 8.12 (t, *J* = 8 Hz 2H); 7.52–7.33 (m, 10H); 7.18 (m, 2H). MS (ESI, $[M - H]^-$, *m/z*): calcd. C₄₅H₂₉N₅O₂Zn, 735.16; found, 733.95.

5-(3-Carboxyphenyl)-15-(4-diphenylaminophenyl)-5,15dimesitylporphyrin Zinc (m-MPZn). This compound was prepared in a similar manner as described for *p*-HPZn. 5-Mesityldipyrromethane (169 mg, 0.6 mmol), 3-carboxybenzaldehyde (47.4 mg, 0.3 mmol), and 4-diphenylaminobenzaldehyle (87.3 mg, 0.3 mmol) were used for *m*-MPH₂. Yield: 47 mg, 5.2%. *m*-MPH₂ (47 mg, 0.052 mmol) and Zn(OAc)₂·2H₂O (113.4 mg, 0.5 mmol) were used for *m*-MPZn. Yield: 30 mg, 59.4%. ¹H NMR (400 MHz, CDCl₃, ppm): 9.08 (d, *J* = 3.2 Hz, 2H); 8.87 (m, 6H); 8.50 (d, *J* = 8 Hz, 2H); 8.40 (d,*J* = 8 Hz, 2H); 8.13 (d, *J* = 8 Hz, 2H); 7.48 (d, *J* = 8 Hz, 4H); 7.44 (d, *J* = 4 Hz, 6H); 7.32 (s, 4H); 7.15 (s, 2H); 2.68 (br, 6H); 1.87 (s, 12H). MS (ESI, $[M - H]^-$, *m*/*z*): calcd. C₆₃H₄₉N₅O₂Zn, 971.32; found, 969.96.

Determination of Redox Potentials of Porphyrin Dyes. Cyclic voltammetry (CV) was used to determine the redox potential of porphyrin dyes. The measurements were performed on a Princeton Applied Research Versa STAT 3 voltammeter in 1.0 M tetrabutylammonium hexafluorophosphate acetonitrile solution. A Pt wire was used as a counter electrode, Ag/AgCl in 3.0 M NaCl solution was used as a reference electrode, and a Pt plate was used as a working electrode. Ferrocene was used as a reference to calculate the highest occupied molecular orbital (HOMO) of these porphyrins. The following equation was used to calculate the energy levels:²⁹ HOMO (eV) = $-[4.8 + (E_{1/2} - E_{1/2} Ferrocene)]$.

Calculations of Frontier Molecular Orbital Energy Levels. Theoretical calculations were performed at the density functional theory level. The initial structures of porphyrins were constructed based upon a single-crystal structure, as we reported previously.¹⁸ Geometry optimization and electronic structure calculations were performed using the B3LYP functional and 6-31g(d) basis set in acetonitrile solution by means of the conductor-like polarizable continuum salvation model (CPCM) as implemented in the Gaussian 09 program package.⁴⁹ The acetonitrile was used to mimic the solvents in electrolyte. Molecular orbitals were visualized by GaussView 3.0 software.⁴⁹

Determination of the Dye-Loading Density. The method reported by Imahori et al. was used to determine the dye-loading density on the film of TiO₂ nanoparticles.⁵⁰ Briefly, a small piece of glass from a microscope slide was cleaned and dried under nitrogen flow. Then, TiO₂ nanoparticle paste was coated on its surface using a doctor-bladed method. The film was sintered at 450 °C for 30 min and then cooled to room temperature. The weight difference of the glass before and after TiO₂ coating was recorded and was used to determine the total surface area of the TiO₂ nanoparticle (a surface/mass ratio of 70 m²/g was used for the calculation). The TiO₂-coated glass slide was then put into a dye solution (0.2 mM in methanol). The glass slide was taken out after 3 h, flushed with methanol, and then put into a 25 mM NaOH solution (THF/H₂O) with

known volume. After all dyes on the TiO_2 film were completely deadsorbed, the glass slide was then taken out, and the absorbance of the resulting solution at a certain wavelength (545 nm for HPZn and 557 nm for MPZn) was measured. The total amount of porphyrin dyes was calculated from a predetermined calibration curve in a 25 mM NaOH solution (THF/H₂O.) The dye-loading density (mol/cm²) was obtained by the total amount of dye divided by the total surface area of the TiO₂ paste.

Fabrication of Solar Cells. To prepare the working electrodes, a FTO-coated glass slide (TEC7, $7\Omega/cm^2$ from Hartford Glass, U.S.A.) was first cleaned in a boiling detergent aqueous solution for 10 min and then rinsed with distilled water. The slides were then sonicated in distilled water, acetone, and isopropanol for 30 min sequentially at room temperature. After drying under N₂ flow, nanocrystalline TiO₂ paste (18NTR, Dyesol, Australia) was doctor-bladed on the FTO glass using a circular mask made from 3M magic tape. After removing the mask, the sample was air-dried for about 30 min and then put in an oven for sintering (450 °C for 30 min) in oxygen ambience. The sample was cooled to room temperature, and a circular mask with the same size was applied on the film. The sample was then immersed in a TiCl₄ aqueous solution (20 mM) for 2 h. After removing the mask, the film was flushed with distilled water, air-dried, and sintered again at 450 °C for 30 min. The film was then cooled to 80 °C and put into a methanol solution of dye (~ 2.0 mM). The film was taken out after 4 h, flushed with methanol, and vacuumdried for 1 h. The counter electrode was prepared by sputtering a 16 nm thick film of Pt on the FTO glass. Two electrodes were sandwiched together using Parafilm as a spacer and sealing material. The electrolyte solution was injected from two precut channels in the Parafilm mask. Two channels were sealed by hot glue. The electrolyte is an acetonitrile/valeronitrile (v/v: 1:1) solution having 0.6 M 1-propyl-2,3-dimethylimidazolium iodide, 0.05 M I₂, 0.1 M LiI, 0.1 M guanidine thiocynate, and 0.5 M *tert*-butylpyridine. The active area was 0.16 cm^2 for all cells.

Photovoltaic Measurements of Solar Cells. Solar cells were characterized for current-voltage measurements with a standard light source (xenon arc lamp) having an intensity of 100 mW/cm² under AM 1.5G conditions using an Agilent 4155C source measure unit. The FF and overall energy conversion efficiency were calculated by η (%) = $P_{\text{max}} \times 100/$ $(P_{\text{in}} \times A)$ and FF = $P_{\text{max}}/(I_{\text{SC}} \times V_{\text{oc}})$, where P_{max} is the maximum output power of cells, P_{in} is the power density of the light source, I_{SC} is the short-circuit current, V_{oc} is the opencircuit voltage, and A is the active area of the cell. The IPCE at different wavelengths was acquired on an in-house-built system; monochromatic light was incident on the sample through focusing lenses. An NREL-calibrated photodetector was used as a reference. The samples were scanned from 350 to 850 nm, and the voltage was recorded. The IPCE spectra were calculated using the equation IPCE(λ) = (sample voltage \times reference IPCE (λ) /reference voltage. The reference IPCE was supplied by an NREL-calibrated Si solar cell under AM1.5 photon flux.

RESULTS AND DISCUSSION

Synthesis of Porphyrin Dyes. Porphyrin dyes were synthesized according to a method reported in the literature with some modifications.⁶ The synthetic routes were depicted in Figure 1. Direct coupling of dipyrromethane or 5-



Figure 2. Absorption spectra of four porphyrin dyes in CH_2Cl_2 at room temperature.



Figure 3. The fluorescence spectra of four porphyrin dyes in $\mbox{CH}_2\mbox{Cl}_2$ at room temperature.

Table 1. Absorption and Fluorescence Data of p(m)-HPZn and p(m)-MPZn in CH₂Cl₂

| dye | absorption (nm, ε M ⁻¹ cm ⁻¹) | emission (nm, τ) |
|----------------|--|------------------------|
| p-HPZn | 414 (2.77×10^5), 545 (1.73×10^4) | 596, 643 (2.23 ns) |
| p-MPZn | 426 (3.75×10^5), 557 (1.64×10^4) | 612, 660 (1.97 ns) |
| m-HPZn | 414 (2.80×10^5), 545 (1.54×10^4) | 596, 643 (2.31 ns) |
| <i>m</i> -MPZn | 426 (3.70 × 10^5), 557 (1.72 × 10^4) | 612, 660 (2.03 ns) |

mesityldipyrromethane, 4-diphenylaminobenzaldehyle, and 3or 4-formylbenzoic acid in dry CHCl₃ in the presence of BF₃. OEt₂ and further oxidation by DDQ gave desired porphyrinfree bases, which were then transformed into their zinc complexes using zinc acetate in CHCl₃/CH₃OH at room temperature. The final products were separated and purified on a silica column using $CHCl_3/CH_3OH = 100:2$ as the eluent. Instead of using methyl-4- or 3-formylbenzoic ester as reported by Imahori⁵⁰ et al. previously, we used acid forms directly to avoid hydrolyzation in strong base. The overall yields of porphyrins were between 3 and 9%. Except p-HPZn, all porphyrin dyes were quite soluble in chloroform, dichloromethane, and methanol. Attempts to grow single crystals for structural determination were unsuccessful; however, the composition of the final products were fully characterized by ¹H NMR and mass spectra.

Photophysical Properties of Porphyrin Dyes in Solution. We first studied photophysical properties of four dyes in the solution to gain a basic understanding of these dyes. The UV–visible absorption spectra of the porphyrins in CH_2Cl_2 are shown Figure 2. All four porphyrin dyes exhibited similar spectral characteristics with strong Soret bands at 400– 450 nm and weak Q bands at 500–550 nm. Compared to the absorption spectra of *p*-HPZn and *m*-HPZn, the spectra of *p*-MPZn and *m*-MPZn red-shifted (~12 nm) with increased absorption coefficients. Therefore, introduction of two mesityl groups on the two meso positions of porphyrins lowered the band gap of porphyrin, which was consistent with theoretical calculations, as described in the following sections.

Figure 3 showed the fluorescence spectra of four dyes in CH_2Cl_2 . Again, very similar emission spectra were observed for dyes, and shifts of emission maximal peaks toward longer wavelength were observed for mesityl substituted porphyrin dyes. The decay lifetime was ~2 ns, which was much longer that the time scale of electron injection to the conduction band of TiO_2 (~several hundreds of fs). Table 1 summarizes the photophysical data of four porphyrin dyes.

Theoretical Calculations. To gain a better understanding of how the structural changes affect the photophysical properties and energy levels of frontier molecular orbitals, we performed DFT calculations for four dyes, and geometryoptimized structures and electron density distribution profiles are shown in Figure 4. No negative frequency was observed, implying that the optimized geometries are in the global energy minima. In all four porphyrin dyes, the m- or p-benzoic acid group aligned to the porphyrin planar ring with torsion angles of 65.85, 66.76, 68.69, and 68.77° for p-HPZn, p-MPZn, m-HPZn, and m-MPZn, respectively. The torsion angles of mesityl groups in *p*-MPZn and *m*-MPZn to the porphyrin ring were close to 90°. No significant structural difference between p(m)-HPZn and p(m)-MPZn porphyrins was observed. However, electron density distribution profiles of frontier molecular orbitals, especially the lowest unoccupied molecular orbital (LUMO), were different for p(m)-HPZn and p(m)-MPZn. As shown in Figure 4, the LUMO of p-HPZn and p-MPZn was more delocalized to benzoic acid groups compared to those of *m*-HPZn and *m*-MPZn. The delocalization of the LUMO to anchoring groups is known to enhance the electronic coupling between the excited dye molecules and 3d orbital of TiO₂ nanoparticles. Therefore, it is expected that the electron injection from *p*-HPZn and *p*-MPZn will be more efficient than that of *m*-HPZn and *m*-MPZn.

CV. To check whether the dyes have suitable HOMO and LUMO levels for efficient dye regeneration and electron injection, CV measurements were performed in CH₂Cl₂ containing 0.1 M Bu₄NPF₆ as a supporting electrolyte; the oxidation position are shown in Figure 5, and the data are summarized in Table 2. All porphyrins exhibited a reversible oxidation property. The oxidation potential decreased in the order of m-HPZn > p-HPZn = m-MPZn > p-MPZn. However, the difference is not significant. This indicates that the mesityl groups at the meso positions of the porphyrin ring have little effect on the HOMO energy levels. The LUMO energy levels of the porphyrins were calculated using the equation LUMO = HOMO + E_{0-0} , where E_{0-0} is the optical band gap (taken as 1240 divided by the onset of the absorption curve on the lowenergy side in nm). All of the LUMO are higher than the conduction edge (-4.1 to -4.3 eV) of TiO₂ nanoparticles, indicating that electron injection from the excited states of the

The Journal of Physical Chemistry A



Figure 4. Calculated electron density distributions of frontier molecular orbitals of four dyes.



Figure 5. CV plots of four porphyrins in CH_2Cl_2 solution.

Table 2. Electrochemical Data for Four Porphyrins

| dye | p-HPZn | <i>p</i> -MPZn | m-HPZn | <i>m</i> -MPZn |
|-----------------------|--------|----------------|--------|----------------|
| $E(S^+/S^*)/V$ | -1.07 | -1.05 | -1.11 | -1.07 |
| HOMO (eV) | -5.39 | -5.38 | -5.40 | -5.44 |
| E_{0-0}/eV | 2.03 | 1.98 | 2.03 | 1.98 |
| LUMO (eV) | -3.37 | -3.40 | -3.41 | -3.42 |

dyes to the conduction band of TiO_2 was energetically favorable, as shown in Figure 6. The HOMO levels are more positive than the oxidation potential of the I^-/I_3^- redox couple. Therefore, the oxidized dyes generated by the electron injection process could thermodynamically accept electrons from I^- ions to regenerate the dyes.

Photovoltaic Performance of Porphyrin-Sensitized Solar Cells. Photovoltaic measurements were then performed to study the impact of structural modifications on the energy conversion efficiency. A Grätzel-type sandwiched structure was adopted, in which no scattering layer was applied. The film thickness was ~6 μ m for all cells and was confirmed by crosssectional scanning electron microscope (SEM) imaging of the TiO₂ film. The active area was 0.16 cm² with a circular shape.



Figure 6. Schematic energy-level diagrams of four porphyrins relative to the TiO₂ conduction band and I^-/I_3^- redox potential.



Figure 7. The J-V curves of porphyrin-sensitized solar cells under a 4 h dye immersion time.

Table 3. Photovoltaic Parameters of Porphyrin-Sensitized Solar Cells

| dye | $J_{\rm SC}$ (mA/cm ²) | $egin{array}{c} V_{ m oc} \ ({ m mV}) \end{array}$ | FF | η (%) | $\frac{\Gamma(10^{-10}}{mol/cm^2})$ |
|---------------------|------------------------------------|--|-------|-------|-------------------------------------|
| <i>p</i> -HPZn | 2.99 | 588 | 0.62 | 1.09 | 2.20 |
| <i>p</i> -MPZn | 4.22 | 671 | 0.67 | 1.92 | 0.88 |
| <i>m</i> -HPZn | 1.41 | 528 | 0.59 | 0.44 | 1.83 |
| <i>m</i> -MPZn | 2.16 | 581 | 0.65 | 0.82 | 1.19 |
| p-HPZn/BET (1:3) | 3.56 | 612 | 0. 63 | 1.38 | |
| p-MPZn/BET (1:3) | 6.46 | 642 | 0. 63 | 2.62 | |
| BET | 0.13 | 367 | 0.12 | 0.05 | |



Figure 8. IPCE spectra of porphyrin-sensitized solar cells.



Figure 9. Normalized absorption spectra of porphyrin dyes on TiO_2 nanoparticle films.

No mask was used during the measurement. It should also be noted that the dye-loading time was fixed at 4 h, which was found optimal to achieve better efficiency in our other similar system. The J-V curves of solar cells are shown in Figure 7, and detailed photovoltaic data are listed in Table 3. The J_{SC} increased in the order of p(m)-HPZn < p(m)-MPZn. A similar order of V_{oc} was also observed. This trend was also consistent with IPCE spectra shown in Figure 8. The p(m)-MPZnsensitized solar cell exhibited better IPCE than its counterpart, the p(m)-HPZn-sensitized solar cell. In the Soret band region, p(m)-HPZn-sensitized solar cells exhibited two peaks, and spectra were much broader, whereas p(m)-MPZn-sensitized solar cells exhibited only one peak but with higher values;



Figure 10. The J-V curves of p-MPZn-sensitized solar cells with and without BET as a cosensitizer under a 4 h dye immersion time.



Figure 11. IPCE curve of p-MPZn/BET-sensitized solar cells and the absorption spectrum of the p-MPZn/BET (1:3) cosensitized TiO₂ film.

therefore, the overall contribution of the p(m)-MPZn-sensitized solar cell to their higher J_{SC} was not from this region; instead, the major contribution was from the different energy conversion capability in the Q-band region. The p(m)-MPZnsensitized solar cells exhibited broader and higher IPCE values in the Q-band region than those of p(m)-HPZn, which was more pronounced for p-MPZn -sensitized solar cells. To understand this difference, dye-loading densities (Γ) of four dyes on TiO₂ films were determined. It was found that *p*-HPZn and m-HPZn had much higher dye-loading density than p-MPZn and m-MPZn, which was due to the smaller size of p(m)-HPZn compared to p(m)-MPZn. Clearly, more dye molecules of p(m)-HPZn on TiO₂ film did not give higher energy conversion efficiency. The contribution to the better IPCE of p(m)-MPZn in the Q-band region was their energy conversion capability at longer wavelength. This is consistent with their broader absorption shown in Figure 2. Another contribution, which was more important, was from the reduced aggregation in p(m)-MPZn-sensitized solar cells. It has been widely recognized that aggregation of pophyrin dyes could be reduced dramatically by introducing bulky group. In our case, mesityl groups in p(m)-MPZn provided effective hindrance to lower the aggregation. This was supported by single Soret peaks in their absorption spectra on TiO_2 film, as shown in Figure 9. On the contrary, p(m)-HPZn exhibited a shoulder on the short



Figure 12. Decrease of the emission of BET on Al_2O_3 nanoparticles after additional *p*-HPZn (A) or *p*-MPZn (B) were adsorbed and the increase of emission of *p*-HPZn (C) and *p*-MPZn (D) after additional BET was adsorbed.

wavelength side, which was indicative of the formation of Haggregates. This is highly possible because p(m)-HPZn dyes were lacking hindrance and were much easier to stack one over another. It was also found that p-M(H)PZn exhibited better energy conversion efficiency than m-M(H)PZn. The highest energy conversion efficiency was obtained in the p-MPZnsensitized solar cell. The IPCE values for p-M(H)PZnsensitized solar cells were higher than those of m-M(H)PZnsensitized solar cells. As the dye-loading densities of m-M(H)PZn dyes were very close to those of p-M(H)PZn shown in Table 2, the major reason could come from high electron recombination.

Photovoltaic Performance of Porphyrin/BET Cosensi**tized Solar Cells.** The shortcoming of p(m)-HPZn and p(m)-MPZn porphyrin dyes is their weak absorption between 460 and 530 nm. It will be advantageous to use a secondary dye to make up this photon loss. Previously,^{14,19,51} we reported that a small and bright organic molecule, BET, could act as an excellent complementary dye for porphyrin dyes due to its strong absorption at 520 nm and exceptional fluorescence at 530 nm in most organic solvents. BET itself showed very poor photovoltaic performance.¹⁴ The structure of BET is shown in the inset of Figure 10. Therefore, we fabricated cells by immersing the TiO_2 electrodes into the porphyrin/BET (1:3) solutions for 4 h. In these studies, only p-MPZn and p-HPZn were selected for the cosensitization study. The results are also listed in Table 3. In both cases, J_{SC} increased from 2.99 to 3.56 mA/cm² for p-HPZn and 4.22 to 6.46 mA/cm² for p-MPZn,

which corresponded to a 26.6 and 36.5% efficiency increase, respectively. The J-V curves of *p*-MPZn-sensitized solar cells with and without BET are shown in Figure 10.

BET-sensitized solar cells exhibited negligible energy conversion efficiency (<0.1%). This deficiency could come from either inefficient electron injection from BET to the TiO₂ conduction band or significant electron recombination with oxidized BET. BET alone was not a functional dye for DSCs. The significant enhancement of the energy conversion efficiency came from complementary absorption of BET, as shown clearly in Figure 11. Photons in the 500-550 nm region were picked up by complementary dye BET, which matched the absorption features of this porphyrin/BET adsorbed on the TiO₂ film. This enhancement, as we described previously, stemmed from the Förster resonance energy transfer (FRET) process. In our previously work,¹⁴ we studied this FRET process in solution; here, we present more relevant experiments using Al₂O₃ nanoparticles to replace TiO₂ nanoparticles and studied the fluorescence of BET in the presence of p-MPZn (vice versa). The results are presented in Figure 12. We found that the fluorescence of a BET-coated film decreased when a different amount of p-MPZn (a, b, c) was adsorbed on the Al₂O₃ film. The fluorescence of BET was almost completely quenched after enough p-MPZn was adsorbed. As the florescence quantum yield of p-MPZn was generally low, no obvious increase of fluorescence of p-MPZn was observed. In a different experiment, the p-MPZn-coated Al₂O₃ film was immersed in BET solution for a short period of time, and fluorescence spectra were recorded. A new peak centered at 590 nm was observed, which was shifted to a longer wavelength when more BET molecules were adsorbed.

CONCLUSIONS

Four porphyrin dyes with triarylamino groups as a donor group and p(m)-benzoic acid as an acceptor group were synthesized. The effects of locations of the carboxylic acid group and the substituents at meso positions of porphyrins on the physical and photovoltaic performance were investigated. Our study confirmed that the *p*-benzoic acid is a better acceptor than *m*benzoic acid. The frontier molecular orbital is more delocalized to *p*-benzoic acid than to *m*-benzoic acid and is more effective for electronic coupling with the conducting band of TiO₂. It was also found that the mesityl groups on the porphyrin ring led to a ~12 nm red shift of absorption, resulting in better energy conversion efficiency. In addition, a 26–32% increase of energy conversion efficiency was obtained when a complementary dye BET was used.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hhe@eiu.edu. Phone: 217-580-6631 (Office).

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

L.S. would like to thank Dr. Yinghong Li and Dr. Xiangming Guan, Department of Pharmaceutical Science, SDSU, for ESI-MS data collection and Dr. Qiliang Chen and Dr. Qiquan Qiao, Center for Advanced Photovoltaic, SDSU, for CV measurements. The National Science Foundation (#1229577) and the Council on Faculty Research Grant are acknowledged.

REFERENCES

(1) O'Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films. *Nature* **1991**, 353, 737–740.

(2) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* 2010, *110*, 6595–6663.

(3) Li, L. L.; Diau, E. W. Porphyrin-Sensitized Solar Cells. *Chem. Soc. Rev.* 2013, *42*, 291–304.

(4) Grätzel, M. Recent Advances in Sensitized Mesoscopic Solar Cells. *Acc. Chem. Res.* 2009, *42*, 1788–1798.

(5) Halme, J.; Vahermaa, P.; Miettunen, K.; Lund, P. Device Physics of Dye Solar Cells. *Adv. Mater.* **2010**, *22*, E210–E234.

(6) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12% Efficiency. *Science* **2011**, *334*, 629–634.

(7) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; CurchodBasile, F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; NazeeruddinMd, K.; Grätzel, M. Dye-Sensitized Solar Cells with 13% Efficiency Achieved through the Molecular Engineering of Porphyrin Sensitizers. *Nat. Chem.* **2014**, *6*, 242–247.

(8) He, J.; Wu, W.; Hua, J.; Jiang, Y.; Qu, S.; Li, J.; Long, Y.; Tian, H. Bithiazole-Bridged Dyes for Dye-Sensitized Solar Cells with High Open Circuit Voltage Performance. *J. Mater. Chem.* **2011**, *21*, 6054–6062.

(9) Brewster, T. P.; Konezny, S. J.; Sheehan, S. W.; Martini, L. A.; Schmuttenmaer, C. A.; Batista, V. S.; Crabtree, R. H. Hydroxamate Anchors for Improved Photoconversion in Dye-Sensitized Solar Cells. *Inorg. Chem.* **2013**, *52*, 6752–6764.

(10) Qin, C.; Peng, W.; Zhang, K.; Islam, A.; Han, L. A Novel Organic Sensitizer Combined with a Cobalt Complex Redox Shuttle for Dye-Sensitized Solar Cells. *Org. Lett.* **2012**, *14*, 2532–2535.

(11) Cho, C.-P.; Chu, C.-C.; Chen, W.-T.; Huang, T.-C.; Tao, Y.-T. Molecular Modification on Dye-Sensitized Solar Cells by Phosphonate Self-Assembled Monolayers. J. Mater. Chem. **2012**, 22, 2915–2921.

(12) Ji, Z.; Natu, G.; Huang, Z.; Kokhan, O.; Zhang, X.; Wu, Y. Synthesis, Photophysics, and Photovoltaic Studies of Ruthenium Cyclometalated Complexes as Sensitizers for p-Type Nio Dye-Sensitized Solar Cells. J. Phys. Chem. C 2012, 116, 16854–16863.

(13) Chang, C.-W.; Bhongale, C. J.; Lee, C.-S.; Huang, W.-K.; Hsu, C.-S.; Diau, E. W.-G. Relaxation Dynamics and Structural Characterization of Organic Nanobelts with Aggregation-Induced Emission. *J. Phys. Chem.* C **2013**, *116*, 15146–15154.

(14) Shrestha, M.; Si, L.; Chang, C.-W.; He, H.; Sykes, A.; Lin, C.-Y.; Diau, E. W.-G. Dual Functionality of Bodipy Chromophore in Porphyrin-Sensitized Nanocrystalline Solar Cells. *J. Phys. Chem. C* **2012**, *116*, 10451–10460.

(15) Mulhern, K. R.; Detty, M. R.; Watson, D. F. Aggregation-Induced Increase of the Quantum Yield of Electron Injection from Chalcogenorhodamine Dyes to TiO_2 . J. Phys. Chem. C **2011**, 115, 6010–6018.

(16) Pastore, M.; Angelis, F. D. Aggregation of Organic Dyes on TiO_2 in Dye-Sensitized Solar Cells Models: An Ab Initio Investigation. ACS Nano 2009, 4, 556–562.

(17) Katoh, R.; Furube, A.; Barzykin, A. V.; Arakawa, H.; Tachiya, M. Kinetics and Mechanism of Electron Injection and Charge Recombination in Dye-Sensitized Nanocrystalline Semiconductors. *Coord. Chem. Rev.* **2004**, *248*, 1195–1213.

(18) He, H.; Dubey, M.; Zhong, Y.; Shrestha, M.; Sykes, A. G. 2-(1-Acetyl-2-oxopropyl)-5,10,15,20-tetraphenylporphyrin and Its Transition-Metal Complexes. *Eur. J. Inorg. Chem.* **2011**, 2011, 3731–3738.

(19) He, H.; Gurung, A.; Si, L.; Sykes, A. G. A Simple Acrylic Acid Functionalized Zinc Porphyrin for Cost-Effective Dye-Sensitized Solar Cells. *Chem.Comm.* **2012**, *48*, 7619–7621.

(20) Zervaki, G. E.; Roy, M. S.; Panda, M. K.; Angaridis, P. A.; Chrissos, E.; Sharma, G. D.; Coutsolelos, A. G. Efficient Sensitization of Dye-Sensitized Solar Cells by Novel Triazine-Bridged Porphyrin– Porphyrin Dyads. *Inorg. Chem.* **2013**, *52*, 9813–9825.

(21) Zegkinoglou, I.; Ragoussi, M.-E.; Pemmaraju, C. D.; Johnson, P. S.; Pickup, D. F.; Ortega, J. E.; Prendergast, D.; de la Torre, G.; Himpsel, F. J. Spectroscopy of Donor– π –Acceptor Porphyrins for Dye-Sensitized Solar Cells. J. Phys. Chem. C 2013, 117, 13357–13364.

(22) Sharma, D.; Steen, G.; Korterik, J. P.; García-Iglesias, M.; Vázquez, P.; Torres, T.; Herek, J. L.; Huijser, A. Impact of the Anchoring Ligand on Electron Injection and Recombination Dynamics at the Interface of Novel Asymmetric Push–Pull Zinc Phthalocyanines and TiPO₂. J. Phys. Chem. C 2013, 117, 25397–25404.

(23) Negre, C. F. A.; Milot, R. L.; Martini, L. A.; Ding, W.; Crabtree, R. H.; Schmuttenmaer, C. A.; Batista, V. S. Efficiency of Interfacial Electron Transfer from Zn-Porphyrin Dyes into TiO₂ Correlated to the Linker Single Molecule Conductance. *J. Phys. Chem. C* 2013, *117*, 24462–24470.

(24) Milot, R. L.; Moore, G. F.; Crabtree, R. H.; Brudvig, G. W.; Schmuttenmaer, C. A. Electron Injection Dynamics from Photoexcited Porphyrin Dyes into SnO_2 and TiO_2 Nanoparticles. *J. Phys. Chem. C* **2013**, *117*, 21662–21670.

(25) Ambrosio, F.; Martsinovich, N.; Troisi, A. What Is the Best Anchoring Group for a Dye in a Dye-Sensitized Solar Cell? J. Phys. Chem. Lett. 2012, 3, 1531–1535.

(26) Luo, J.; Xu, M.; Li, R.; Huang, K.-W.; Jiang, C.; Qi, Q.; Zeng, W.; Zhang, J.; Chi, C.; Wang, P.; et al. N-Annulated Perylene as an Efficient Electron Donor for Porphyrin-Based Dyes: Enhanced Light-Harvesting Ability and High-Efficiency Co(II/III)-Based Dye-Sensitized Solar Cells. J. Am. Chem. Soc. 2013, 136, 265–272.

The Journal of Physical Chemistry A

(27) Hsu, H.-Y.; Chiang, H.-C.; Hu, J.-Y.; Awasthi, K.; Mai, C.-L.; Yeh, C.-Y.; Ohta, N.; Diau, E. W.-G. Field-Induced Fluorescence Quenching and Enhancement of Porphyrin Sensitizers on TiO_2 Films and in Pmma Films. *J. Phys. Chem. C* **2013**, *117*, 24761–24766.

(28) Ambre, R.; Chen, K.-B.; Yao, C.-F.; Luo, L.; Diau, E. W.-G.; Hung, C.-H. Effects of Porphyrinic *meso*-Substituents on the Photovoltaic Performance of Dye-Sensitized Solar Cells: Number and Position of *p*-Carboxyphenyl and Thienyl Groups on Zinc Porphyrins. J. Phys. Chem. C 2012, 116, 11907–11916.

(29) Wang, C.-L.; Lan, C.-M.; Hong, S.-H.; Wang, Y.-F.; Pan, T.-Y.; Chang, C.-W.; Kuo, H.-H.; Kuo, M.-Y.; Diau, E. W.-G.; Lin, C.-Y. Enveloping Porphyrins for Efficient Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2012**, *5*, 6933–6940.

(30) Wu, C.-H.; Pan, T.-Y.; Hong, S.-H.; Wang, C.-L.; Kuo, H.-H.; Chu, Y.-Y.; Diau, E. W.-G.; Lin, C.-Y. A Fluorene-Modified Porphyrin for Efficient Dye-Sensitized Solar Cells. *Chem. Commun.* **2012**, *48*, 4329–4331.

(31) Ripolles-Sanchis, T.; Guo, B.-C.; Wu, H.-P.; Pan, T.-Y.; Lee, H.-W.; Raga, S. R.; Fabregat-Santiago, F.; Bisquert, J.; Yeh, C.-Y.; Diau, E. W.-G. Design and Characterization of Alkoxy-Wrapped Push–Pull Porphyrins for Dye-Sensitized Solar Cells. *Chem. Commun.* **2012**, *48*, 4368–4370.

(32) Shiu, J.-W.; Lan, C.-M.; Chang, Y.-C.; Wu, H.-P.; Huang, W.-K.; Diau, E. W.-G. Size-Controlled Anatase Titania Single Crystals with Octahedron-Like Morphology for Dye-Sensitized Solar Cells. *ACS Nano* **2012**, *6*, 10862–10873.

(33) Barea, E. M.; Gónzalez-Pedro, V.; Ripollés-Sanchis, T.; Wu, H.-P.; Li, L.-L.; Yeh, C.-Y.; Diau, E. W.-G.; Bisquert, J. Porphyrin Dyes with High Injection and Low Recombination for Highly Efficient Mesoscopic Dye-Sensitized Solar Cells. *J. Phys. Chem. C* 2011, *115*, 10898–10902.

(34) Wang, C.-L.; Chang, Y.-C.; Lan, C.-M.; Lo, C.-F.; Wei-Guang Diau, E.; Lin, C.-Y. Enhanced Light Harvesting with π -Conjugated Cyclic Aromatic Hydrocarbons for Porphyrin-Sensitized Solar Cells. *Energy Environ. Sci.* **2011**, *4*, 1788–1795.

(35) Chang, Y.-C.; Wang, C.-L.; Pan, T.-Y.; Hong, S.-H.; Lan, C.-M.; Kuo, H.-H.; Lo, C.-F.; Hsu, H.-Y.; Lin, C.-Y.; Diau, E. W.-G. A Strategy to Design Highly Efficient Porphyrin Sensitizers for Dye-Sensitized Solar Cells. *Chem. Commun.* **2011**, *47*, 8910–8912.

(36) Lo, C.-F.; Hsu, S.-J.; Wang, C.-L.; Cheng, Y.-H.; Lu, H.-P.; Diau, E. W.-G.; Lin, C.-Y. Tuning Spectral and Electrochemical Properties of Porphyrin-Sensitized Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 12018–12023.

(37) Bessho, T.; Zakeeruddin, S.; Yeh, C. Y.; Diau, E. G.; Grätzel, M. Highly Efficient Mesoscopic Dye-Sensitized Solar Cells Based on Donor–Acceptor-Substituted Porphyrins. *Angew. Chem., Int. Ed.* **2010**, *49*, 6646–6649.

(38) Hsieh, C.-P.; Lu, H.-P.; Chiu, C.-L.; Lee, C.-W.; Chuang, S.-H.; Mai, C.-L.; Yen, W.-N.; Hsu, S.-J.; Diau, E. W.-G.; Yeh, C.-Y. Synthesis and Characterization of Porphyrin Sensitizers with Various Electron-Donating Substituents for Highly Efficient Dye-Sensitized Solar Cells. *J. Mater. Chem.* **2010**, *20*, 1127–1134.

(39) Wu, S.-L.; Lu, H.-P.; Yu, H.-T.; Chuang, S.-H.; Chiu, C.-L.; Lee, C.-W.; Diau, E. W.-G.; Yeh, C.-Y. Design and Characterization of Porphyrin Sensitizers with a Push–Pull Framework for Highly Efficient Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2010**, *3*, 949–955.

(40) Luo, L.; Lin, C.-J.; Tsai, C.-Y.; Wu, H.-P.; Li, L.-L.; Lo, C.-F.; Lin, C.-Y.; Diau, E. W.-G. Effects of Aggregation and Electron Injection on Photovoltaic Performance of Porphyrin-Based Solar Cells with Oligo(Phenylethynyl) Links inside TiO_2 and Al_2O_3 Nanotube Arrays. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1064–1071.

(41) Lee, C.-W.; Lu, H.-P.; Lan, C.-M.; Huang, Y.-L.; Liang, Y.-R.; Yen, W.-N.; Liu, Y.-C.; Lin, Y.-S.; Diau, E. W.-G.; Yeh, C.-Y. Novel Zinc Porphyrin Sensitizers for Dye-Sensitized Solar Cells: Synthesis and Spectral, Electrochemical, and Photovoltaic Properties. *Chem.*— *Eur. J.* **2009**, *15*, 1403–1412.

(42) Lin, H.-C.; Polaske, N. W.; Oquendo, L. E.; Gliboff, M.; Knesting, K. M.; Nordlund, D.; Ginger, D. S.; Ratcliff, E. L.; Beam, B. M.; Armstrong, N. R.; et al. Electron-Transfer Processes in Zinc Phthalocyanine–Phosphonic Acid Monolayers on ITO: Characterization of Orientation and Charge-Transfer Kinetics by Waveguide Spectroelectrochemistry. J. Phys. Chem. Lett. **2012**, *3*, 1154–1158.

(43) Harima, Y.; Fujita, T.; Kano, Y.; Imae, I.; Komaguchi, K.; Ooyama, Y.; Ohshita, J. Lewis-Acid Sites of TiO₂ Surface for Adsorption of Organic Dye Having Pyridyl Group as Anchoring Unit. J. Phys. Chem. C 2013, 117, 16364–16370.

(44) Ooyama, Y.; Shimada, Y.; Inoue, S.; Nagano, T.; Fujikawa, Y.; Komaguchi, K.; Imae, I.; Harima, Y. New Molecular Design of Donor–Acceptor Dyes for Dye-Sensitized Solar Cells: Control of Molecular Orientation and Arrangement on TiO_2 Surface. *New J. Chem.* **2011**, 35, 111–118.

(45) Rochford, J.; Galoppini, E. Zinc(II) Tetraarylporphyrins Anchored to TiO_2 , Zno, and ZrO_2 Nanoparticle Films through Rigid-Rod Linkers. *Langmuir* **2008**, *24*, 5366–5374.

(46) Rochford, J.; Chu, D.; Hagfeldt, A.; Galoppini, E. Tetrachelate Porphyrin Chromophores for Metal Oxide Semiconductor Sensitization: Effect of the Spacer Length and Anchoring Group Position. J. Am. Chem. Soc. 2007, 129, 4655–4665.

(47) Galoppini, E.; Rochford, J.; Chen, H.; Saraf, G.; Lu, Y.; Hagfeldt, A.; Boschloo, G. Fast Electron Transport in Metal Organic Vapor Deposition Grown Dye-Sensitized ZnO Nanorod Solar Cells. *J. Phys. Chem. B* **2006**, *110*, 16159–16161.

(48) Gou, F.; Jiang, X.; Li, B.; Jing, H.; Zhu, Z. Salicylic Acid as a Tridentate Anchoring Group for Azo-Bridged Zinc Porphyrin in Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12631–12637.

(49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(50) Imahori, H.; Hayashi, S.; Hayashi, H.; Oguro, A.; Eu, S.; Umeyama, T.; Matano, Y. Effects of Porphyrin Substituents and Adsorption Conditions on Photovoltaic Properties of Porphyrin-Sensitized TiO₂ Cells. J. Phys. Chem. C **2009**, 113, 18406–18413.

(51) He, H.; Gurung, A.; Si, L. 8-Hydroxylquinoline as a Strong Alternative Anchoring Group for Porphyrin-Sensitized Solar Cells. *Chem. Commun.* **2012**, *48*, 5910–5912.