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Novel zinc porphyrins with 1–4 π-conjugated phenylethynyl (PE) units (labeled PE1–PE4) as a link of controlled length were synthesized for fundamental tests and applications as a dye-sensitized solar cell (DSSC). The UV–visible spectra of the solution samples show clear absorption patterns of the PE groups in a region 300–400 nm, consistent with results calculated with density-functional theory. Cyclic voltammograms of PE1–PE4 in tetrahydrofuran show similar electrochemical potentials for each compound. Femtosecond fluorescence up-conversion of solution samples and of porphyrin-sensitized TiO₂ films was measured with excitation at 420 or 430 nm and emission at 460, 470, 620, and 680 nm. When these porphyrins were fabricated into DSSC devices, the efficiency of power conversion of these devices decreased systematically with increasing length of the link: 2.5 ± 0.2% (PE1), 2.0 ± 0.1% (PE2), 0.78 ± 0.09% (PE3), 0.25 ± 0.02% (PE4). This great photovoltaic degradation from PE1 to PE4 is not interpretable according to the rate of electron injection independent of length; other factors, including electron transfer from the semiconductor back to the porphyrin cation or the electrolyte, must be considered to account for the observed dependence of photovoltaic performance on length.

1. Introduction

The adsorption of selected photosensitizers on nanocrystalline films, having a large surface area, of semiconductors with a wide band gap, such as titanium dioxide (TiO₂), has been an active area of research on efficient dye-sensitized solar cells (DSSC). The covalent attachment of electrochemically and photochemically active chromophores to semiconductor surfaces is an important step toward the development of such devices. Because of their efficacy in this respect, RuⅡ polypyridyl complexes adsorbed on TiO₂ nanocrystalline films have proved promising systems. Among RuⅡ polypyridyl complexes, the so-called N3 dye, Ru(dcbpyH₂)(NCS)₂, is the most efficient photosensitizer known. This N3 dye exhibits an efficiency of 85% in the region 400–800 nm and an overall efficiency (η) 11% of power conversion. Porphyrins have become prospective photosensitizers because of the vital roles of porphyrin derivatives in photosynthesis, their strong absorption in the visible region, and the ease of adjusting their chemical structures (hence their electrochemical and photochemical properties) for light harvesting. Adsorbing porphyrins with modified structures onto TiO₂ nanocrystalline films thus provides an opportunity to improve DSSC applications. The best performance of a porphyrin-sensitized SC has attained η = 7.1%. Strongly on the surface of a semiconductor, absorption of light in the visible and NIR region for efficient light harvesting, an excited-state reduction potential negative enough for efficient electron injection, a ground-state reduction potential positive enough for efficient regeneration of the dye, and a small reorganizational energy for efficient excited- and ground-state electrochemical processes. The relation between the orientation of attached porphyrins with respect to TiO₂ nanocrystalline surfaces and the cell performance has been investigated. For porphyrins, an efficient injection of electrons from the photosensitizer into a semiconductor is considered a crucial factor in developing an efficient DSSC. Apart from the effect of cosensitization, the performance of a cell can be improved through appropriate modification of a dye structure with a selected link. We reported the fundamental properties of a novel porphyrin in solution and adsorbed on TiO₂ nanocrystalline films. In our design, 10,20-biphenylolepophosphatot zinc(II) (ZnBPP) served as a light-harvesting center and a carboxylic acid as an anchoring group. To control the distance between the porphyrin and the anchoring group, we utilized a phenylethynyl (PE) unit as a bridging moiety to connect a meso position of ZnBPP and the carboxylic acid end. We chose ZnBPP because of its ease of synthesis, the stability of zinc porphyrins against irradiation, and the efficiency of zinc porphyrins that is superior to that of copper and free-base porphyrins. 4-Carboxylic acid end groups were used to ensure efficient adsorption on TiO₂ surfaces and to promote electronic coupling between the donor levels of the excited porphyrins and the acceptor levels of TiO₂. PE units were employed to control the distance because of their rigidity, their linear structure, and the possible π interactions between the porphyrin core and the anchoring end. Porphyrins with an
ethynyl motif were employed for photonic and electrochemical tests on multichromophore arrays.10

PE units as spacers have been reported for other systems.10b,11 For example, seeking to use porphyrins as molecular photonic materials, Lindsey and co-workers investigated several multi-porphyrin arrays to understand their energy-transfer phenomena;12 in their design, monomeric chromophores were linked with phenyl-ethyl-phenyl-phenyl bridging groups to create weak interactions between the chromophores and to preserve the characteristics of each chromophore.10b,c Piotrowiak et al. reported “tripod” RuII complexes with PE groups as rigid links to connect the sensitizers and TiO2;11 these sensitizers consisted of a tripod-shaped base with three COOR groups to attach to TiO2 nanocrystalline surfaces, a rigid (4-ethylphenyl)phenylethynyl spacer, and a RuII complex as a chromophoric center. The base design provides a stable and well-defined orientation of the sensitizers with respect to the nanoparticulate surfaces, whereas the rigidity of the (4-ethylphenyl)phenylethynyl spacer ensures control of the distance between the light-harvesting centers and the TiO2 surfaces.

To investigate the interfacial electron transfer and for DSSC applications with a similar design, we have prepared novel porphyrins: 5-(4-carboxy-phenylethynyl)-10,20-biphenylporphinato zinc(II), 5-[4-(4-carboxy-phenylethynyl)-phenylethynyl]-10,20-biphenylporphinato zinc(II), 5-[4-[4-(4-carboxy-phenylethynyl)-phenylethynyl]-phenylethynyl]-10,20-biphenylporphinato zinc(II), and 5-{4-[4-(4-carboxy-phenylethynyl)-phenylethynyl]-phenylethynyl}-10,20-biphenylporphinato zinc(II), abbreviated PE1, PE2, PE3, and PE4, respectively. As shown in Chart 1, these porphyrins share the same light-harvesting unit (ZnBPP) with rigid, linear, edgewise, and fully conjugated substituents of varied length.

When we fabricated DSSC devices using PE1–PE4 as photosensitizers, the cell performance of the devices exhibited a systematic dependence on length according to which the DSSC with a long link (PE4) performed much less effectively than the DSSC with a short link (PE1). To understand the interfacial electron-transfer dynamics that govern the photovoltaic performance of the system dependent on length, we conducted femtosecond measurements, and we report here the spectral and electrochemical properties and the fluorescence decay of PE1–PE4 in solution and on TiO2 nanocrystalline films.

2. Results and Discussion

2.1. Synthesis. To prepare PE1–PE4, we reacted porphyrin precursors with carboxyphenylethynyl reagents according to the Sonogashira cross-coupling method.13 This synthetic strategy, which is well developed for preparing porphyrins with varied ethyne-linked functional groups,14,15 was readily adaptable to the synthesis of PE1–PE4. Among a few points worth noting, cross-coupling ZnBPPBr with a suitable substituent precursor effectively yielded PE1 and PE2, but reacting 5-(4-ethylphenyl)phenylethynyl)-ZnBPP with 4-(4-iodo-phenylethynyl)-benzoic acid seemed to be the most efficient approach to prepare PE3. Our attempts to synthesize PE3 by other routes were unsuccessful because of small yields and the difficulty of recognizing and separating the reaction products. For PE4, the strategy was simply to add a further phenyl group to the porphyrin precursor from the PE3 synthesis. Because of the carboxylic group, these porphyrins all tend to adsorb slightly on the silica gel used in chromatographic purification; the number of chromatographic separations should thus be kept to a minimum to ensure acceptable yields of the porphyrins.

2.2. Absorption and Emission Spectra of Porphyrins in Solution. Parts a and b of Figure 1 show absorption and emission spectra of ZnBPP (gray), PE1 (black), PE2 (green), PE3 (red), and PE4 (blue) in THF with λex = 430 nm.
ZnBPP; this shift is due to the extended \( \pi \)-conjugation, consistent with reports of other ethyne-linked porphyrins.\(^8\) Most importantly, the features in the absorption and emission spectra of PE1–PE4 have similar shapes and intensities, indicating that the energy gaps between the ground and the excited states of those porphyrins are similar despite the varied lengths of the PE links.

Further weak absorptions appear in the near-UV region for PE1–PE4; their wavelengths increased systematically as the conjugation length of the PE bridge increased from PE1 to PE4. From PE2 to PE4 the intensities of these near UV absorptions increased, whereas the intensities of the Soret bands decreased, indicating the existence of strong coupling between the PE bridge and the porphyrin core, so that the intensity of the former becomes “borrowed” from the intensity of the latter. As there is no such absorption in ZnBPP, we infer that these near UV absorptions arise from the PE groups of the PE1–PE4 porphyrins. Nielsen et al. reported a similar phenomenon for a zinc porphyrin linked with poly(phenylethylnyl).\(^9\) In the case of PE1–PE4, the coupling and interaction between the bridging moiety and the porphyrin core are effective because similar emission spectra, as shown in Figure 1b, were obtained when those porphyrins were excited in the near-UV region at 350 nm.

2.3. Relaxation Dynamics of Porphyrins in Solutions. Parts a–d of Figure 2 show fluorescence transients of PE1–PE4 in THF, respectively. Those transients were recorded with excitation in the Soret band at \( \lambda_{ex} = 420 \) or 430 nm and emission observed at either \( \lambda_{em} = 460 \) or 620 nm. The transients observed at \( \lambda_{em} = 460 \) nm (circles) are satisfactorily fitted with a single exponential decay convoluted with the instrument-response function (fwhm = 220 fs), which yields decay coefficients 910, 680, 610, and 600 fs for PE1–PE4, respectively. The transients observed at \( \lambda_{em} = 620 \) nm (squares) differ remarkably from the transients observed at \( \lambda_{em} = 460 \) nm (circles); the former show a rising feature with a rise coefficient comparable to the decay coefficient of the latter at short times, but the transient signals of the former increase gradually to an asymptotic level at longer times in the same range. According to femtosecond investigations reported elsewhere, the transients observed at \( \lambda_{em} = 460 \) and 620 nm reflect the dynamical behavior occurring in electronic states \( S_2 \) and \( S_1 \) of PE1, respectively. We thus conclude that internal conversion (IC) \( S_2 \rightarrow S_1 \) of PE1–PE4 in solution occurs within the observed interval \( \tau = 0.6–0.9 \) ps and that vibrationally hot \( S_1 \) species are produced on that time scale. \( \tau \) decreased significantly from PE1, \( \tau = 910 \) fs, to PE2, \( \tau = 680 \) fs, but only slightly further to \( \sim 600 \) fs for PE3 and PE4. This dynamical feature is consistent with the trend of the spectral shift of the absorption and emission spectra shown in Figure 1b in which the spectra are almost identical for PE2–PE4, but the spectrum of PE1 is somewhat blue-shifted with respect to the others. The systematic decrease of \( S_2 \) relaxation periods with increasing length of the PE bridge of PE1–PE4 implies that the electronic coupling of the extended \( \pi \)-conjugation significantly affects the IC rate for \( S_2 \rightarrow S_1 \), i.e., a longer bridge produces stronger coupling between the porphyrin core and the PE link that leads to a greater rate of internal conversion.

Because of the rising character of the transients shown in Figure 2, the transients observed at \( \lambda_{em} = 620 \) nm are described satisfactorily according to a consecutive kinetic model, \( A \rightarrow B \rightarrow C \), with the signals convoluted with the laser pulse. For PE1, the first component (B) rises with \( \tau_1 = 910 \) fs and decays with \( \tau_2 = 8.5 \) ps, whereas the second component (C) appears following the decay of the first component but persists on a scale with \( \tau_3 \approx 2 \) ns (Table 2); for PE2–PE4, \( \tau_1 = 680, 610, \) and 600 fs and \( \tau_2 = 8.4, 8.2, \) and 8.4 ps, respectively. As the fluorescence transients observed at \( \lambda_{em} = 620 \) nm reflect the relaxation dynamics of PE1–PE4 in the \( S_1 \) state, the observed two consecutive components (B and C) might be assigned to hot and cold \( S_1 \) species, respectively; component A represents the \( S_2 \) species not observed at \( \lambda_{em} = 620 \) nm. Accordingly, the hot \( S_1 \) species were produced from the \( S_2 \) state in 910–600 fs. The excess vibrational energies in the hot \( S_1 \) species become released to the solvent molecules via vibrational relaxation, and this process yields the cold \( S_1 \) species produced in \( \sim 8.5 \) ps.

**Table 1: Absorption Maxima and Absorption Coefficients\(^a\) of Zinc Porphyrins in THF**

<table>
<thead>
<tr>
<th>dye</th>
<th>near-UV bands</th>
<th>( \lambda_{S2} ) (log ( \epsilon ))/nm</th>
<th>( \lambda_{S1} ) (log ( \epsilon ))/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBPP</td>
<td>not observed</td>
<td>412 (5.71)</td>
<td>543 (4.27), 579 (3.34)</td>
</tr>
<tr>
<td>PE1</td>
<td>not observed</td>
<td>439 (5.64)</td>
<td>567 (4.21), 616 (4.41)</td>
</tr>
<tr>
<td>PE2</td>
<td>304, 353</td>
<td>443 (5.57)</td>
<td>569 (4.27), 618 (4.60)</td>
</tr>
<tr>
<td>PE3</td>
<td>322, 359</td>
<td>443 (5.58)</td>
<td>569 (4.21), 619 (4.56)</td>
</tr>
<tr>
<td>PE4</td>
<td>338, 363</td>
<td>444 (5.56)</td>
<td>569 (4.17), 619 (4.53)</td>
</tr>
</tbody>
</table>

\(^a\) The absorption coefficient (\( \epsilon \)) has a unit of cm\(^{-1}\) M\(^{-1}\).

**Table 2: Fluorescence Maxima and Lifetimes\(^a\) of the Excited State of Zinc Porphyrins in THF**

<table>
<thead>
<tr>
<th>dye</th>
<th>emission /nm</th>
<th>( \tau_{S2}/)ps</th>
<th>( \tau_{S1}/)ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBPP</td>
<td>636, 699</td>
<td>0.91</td>
<td>1.90</td>
</tr>
<tr>
<td>PE1</td>
<td>621, 674</td>
<td>0.68</td>
<td>2.10</td>
</tr>
<tr>
<td>PE2</td>
<td>624, 678</td>
<td>0.61</td>
<td>2.10</td>
</tr>
<tr>
<td>PE3</td>
<td>624, 677</td>
<td>0.60</td>
<td>2.10</td>
</tr>
<tr>
<td>PE4</td>
<td>624, 677</td>
<td>0.60</td>
<td>2.10</td>
</tr>
</tbody>
</table>

\(^a\) \( S_2 \) and \( S_1 \) lifetimes were monitored at 460 and 620 nm, respectively.
of the eg orbitals. The HOMO and LUMO of PE1, respectively, whereas LUMO and LUMO

ZnTPP system, for which the lifetime of the S2 state of ZnTPP

picosecond measurements. Our direct observation on the

of PE1

predicted by Gouterman’s four-orbital model,16 i.e., HOMO-1

These MO patterns of PE1

Levels.

Figure 3 displays cyclic voltammograms (CV) for

PE1

electrochemical potentials. The first reduction of ZnBPP gave

from the nonrelaxed vibronic state of the hot S1 species occurs

-0.49 V vs SCE. Peak-to-peak separations (mV) are shown in

parentheses for quasireversible reactions. For irreversible reactions,

only the anodic peak potentials, denoted $E_{pa}$, are shown.

The cold S1 species endure because $S_1 \rightarrow T_1$ intersystem crossing of PE1–PE4 in solution occurs in $\sim 2$ ns, as confirmed by our picosecond measurements. Our direct observation on the PE1–PE4 system is consistent with femtosecond results for the ZnTPP system, for which the lifetime of the $S_1$ state of ZnTPP was reported in a range 1.45–2.35 ps, and vibrational cooling from the nonrelaxed vibronic state of the hot $S_1$ species occurs on a time scale $\sim 10$ ps.18–20

2.4. Electrochemistry, DFT Calculations, and Energy Levels. Figure 3 displays cyclic voltammograms (CV) for PE1–PE4 reductions in THF, and Table 3 presents their electrochemical potentials. The first reduction of ZnBPP gave a quasireversible couple at $-1.40$ V vs SCE, consistent with the formation of the tetraphenylporphinato zinc(II) anion radical at $-1.31$ V.23 For PE1–PE4, reduction of the first porphyrin ring occurs at about $-1.20$ V.22 The positive shift of the reduction potentials is attributed to the extended $\pi$-conjugation. In contrast, the first oxidations of PE1–PE4 are all irreversible reactions (not shown), likely due to THF being capable of attacking the oxidized products. Nevertheless, the oxidation potentials of all these complexes are similar: $E_{pa} = +1.07$ V vs SCE, Table 3.

To assist our qualitative understanding of the reduction behaviors of these complexes, we performed calculations with DFT on ZnBPP and PE1–PE4 at the B3LYP/LanL2DZ level. Figure 4 depicts their MO patterns from HOMO-1 to LUMO+2. These MO patterns of PE1–PE4 are consistent with those predicted by Gouterman’s four-orbital model,16 i.e., HOMO-1 and HOMO resemble those of the $a_{1g}$ and $a_{2g}$ orbitals, respectively, whereas LUMO and LUMO+1 are similar to those of the $e_g$ orbitals. The HOMO and LUMO of PE1–PE4 are, however, partially delocalized from the porphyrin core to the

substituents; this minor deviation from Gouterman’s four-orbital model is rationalized through the decreased symmetry of the complexes and the extended $\pi$-conjugation of the substituents. LUMO+2 was found to be concentrated at the $\pi$-conjugated substituents, consistent with the result of Wang et al. based on a time-dependent DFT approach for a series of $\beta$-substituted zinc porphyrins.4c

Figure 5 compares the energy levels of PE1–PE4 and TiO2. This illustration was prepared on the basis of the electrochemical results and the absorption spectra according to literature methods.23,24 Figure 5 shows that the conducting band (CB) of TiO2 is located between the LUMO and the HOMO of PE1–PE4, and the MO energy levels between PE1–PE4 are similar, consistent with the DFT results. These results indicate that electron injection from LUMO of the porphyrin to the CB of TiO2 is feasible and that the rate of electron injection for such a process might be similar for PE1–PE4/TiO2 films because of their similar energy levels.

2.5. Absorption Spectra of Porphyrins on TiO2 Nanocrystalline Films. Figure 6 displays UV–visible absorption spectra of PE1–PE4/TiO2 nanocrystalline films in air (black curves) and PE1–PE4 in THF (gray curves). Comparison of the film spectra with the solution spectra reveals that the $Q$ bands of the PE1–PE4/TiO2 films are only slightly shifted and broadened from those of the solution spectra, whereas the B bands became blue-shifted with a red shoulder. These shoulders of the Soret bands in the film spectra represent a small proportion of monomeric porphyrins adsorbed on TiO2 films; their wavelengths are the same as those of the B bands in solution.25 In spectra of PE1–PE4 films the blue-shifted B bands occur at 413, 415, 420, and 426 nm, respectively. These bands are not caused by effects of reflection26 because the quality of TiO2 films (e.g., thickness) seems to have only a slight effect on the intensities. We suggested previously an attribution of these blue-shifted B bands to the H-aggregation of the porphyrin assembly on the surfaces of TiO2 nanocrystalline films.27 The stacked, face-to-face porphyrin $\pi$-aggregation (H-type) is well documented to produce a blue shift of the absorption, whereas the side-by-side porphyrin $\pi$-aggregation (I-type) results in a red shift.27 This phenomenon has been observed for not only porphyrins28 but also other planar dyes.29 Measurements30 with atomic-force microscopy show little variation of morphology between bare TiO2 nanocrystalline film surfaces and those modified with porphyrin, indicating that the film surfaces are covered with a porphyrin monolayer (thickness only 1–3 nm), supporting the possibility of porphyrins being H-aggregated on the surfaces.

2.6. Relaxation Dynamics of Porphyrins on TiO2 Nanocrystalline Films. To investigate the dependence of the relaxation dynamics of porphyrin/TiO2 films on the length of the PE link, we sensitized the four porphyrins on identical TiO2 nanocrystalline films. Figure 7 shows a scanning electron microscopy image of a typical TiO2 film (thickness $\sim 5$ μm) with nanoparticle size $\sim 20$ nm. Figure 8 shows the absorption spectra of the four porphyrin-sensitized films with the absorbance of the $Q(0,0)$ band adjusted to be equal for PE1–PE4. Parts a–d of Figure 9 show the fluorescence transients of PE1–PE4 on TiO2 nanocrystalline films, respectively, obtained with excitation at $\lambda_{ex} = 420$ nm and emission observed at $\lambda_{em} = 470$ nm. The transients observed at $\lambda_{em} = 470$ nm (circles) are satisfactorily fitted with a single exponential decay convoluted with the instrument response function (fwhm = 220 fs), which yields decay coefficients smaller than 100 fs for all porphyrins. According to our previous work,8a the $S_2$ dynamics of the PE1/
TiO$_2$ films reflect not only the aggregate-induced energy transfer among porphyrins but also an interfacial electron transfer from porphyrin to TiO$_2$. Because the fluorescence transients were observed also at the S$_1$ state (see below), we conclude that the S$_2$ $\rightarrow$ S$_1$ IC is ultrarapid, $<$100 fs. In the present work we extended the investigation of the S$_2$ dynamics to porphyrins with an extended PE bridge. The length of the PE group did not affect the observed S$_2$ dynamics, which are due mainly to the ultrarapid aggregate-induced IC relaxation for all our porphyrin/TiO$_2$ films. The hot S$_1$ species were thus produced in $<$100 fs, and the relaxation dynamics occurring at the porphyrin/TiO$_2$ interface were probed as described in the following.

Figures 10 and 11 show the S$_1$ relaxation dynamics of porphyrin/TiO$_2$ films probed at $\lambda_{em}$ = 620 and 680 nm, respectively, with PE1–PE4 for parts a–d in each figure ($\lambda_{ex}$ = 430 nm). All fluorescence transients were fitted with two decay components and a tiny offset. At $\lambda_{em}$ = 620 nm, the rapid-decay coefficient $\tau_1$ was observed to be 180 fs for PE1, remaining almost constant from PE2 ($\tau_1$ = 200 fs), PE3 ($\tau_1$ = 190 fs), and PE4 ($\tau_1$ = 170 fs); the slow-decay coefficient $\tau_2$ increased slightly from 1.2 ps for PE1 to 1.6 ps for PE4, but the variation was within experimental error. At $\lambda_{em}$ = 680 nm, $\tau_1$ was in a range 390–540 fs for PE1–PE4 and $\tau_2$ in a range 2.7–3.7 ps for PE1–PE4. The relaxation dynamics observed at 620 nm are much more rapid than those observed at 680 nm because the detection window at the former wavelength probed more “hot” species than that at the latter wavelength.

Two contributions are responsible for the observed S$_1$ dynamics: interfacial electron transfer from dye to TiO$_2$ (electron injection) and aggregate-induced energy transfer among dye molecules. Because the TiO$_2$ films were prepared identically and the absorbances of the dye were similar for PE1–PE4 (Figure 8), we expect that the amounts of dye loading on TiO$_2$ films were also similar for PE1–PE4. By assumption that the extents of aggregation inside the nanoporous environment of the TiO$_2$ films were similar for PE1–PE4, our observations thus indicate that electron injection occurring in the S$_1$ state might be independent of the length of the link between porphyrin and
TiO₂. DFT calculations (Figure 4) indicate, however, that the electron densities of the HOMO and LUMO are localized in the porphyrin ring and extend only to the first unit of the PE link. The detection window of the time-resolved emission occurring from the S₁ state was therefore limited mainly to the porphyrin core. When the electron transfer occurred from the porphyrin moiety to the anchoring group through the PE link, the emission decay might reflect only the initial propagation of electrons in the excited state and thus lack sensitivity for the detection of electron transfer toward longer links. From the measurement of transient absorption, Galoppini and co-workers found that the biexponential decays of a Ru-bpy/TiO₂ system occur on a scale of 10⁻¹⁰⁰ ps, and the time coefficients decreased with increasing length of the rigid π-conjugated PE links. The discrepancy between our results (porphyrin/PE/TiO₂) and their results (Ru-bpy/PE/TiO₂) might be due to the detection window, which is much broader using a transient absorption method than using an emission decay method. As a result, the length-dependent trend of electron transfer through PE links of varied length was observed from the former method reported by Galoppini. Alternatively, if the electron transfer though the PE link is not a kinetic bottleneck, the discrepancy might reflect the varied number of anchoring groups in the dyes and the structure of the links on the TiO₂ surface, which might affect also the electron injection kinetics. For perylene/TiO₂ films Gundlach et al. found that the rate of electron injection of a rigid-rod system is much greater than that of a tripod system, providing evidence for the variation of electron injection kinetics with structure of the anchoring groups. The dependence of the performance of the porphyrin-sensitized solar cells on the length of the link is discussed in the following section.

2.7. Photovoltaic Performance of Porphyrin-Sensitized Solar Cells. By use of PE₁–PE₄ as sensitizers, we fabricated DSSC devices according to a standard procedure described in the experimental section. To demonstrate the reproducibility of the data, three independent measurements were performed for each dye using TiO₂ films fabricated with an identical procedure. The measured photovoltaic performances of the DSSC devices with PE₁–PE₄ are shown in parts a–d of Figure 12; the corresponding parameters are summarized in Table 4. As a reference, the average value of η of the Zn-3-sensitized DSSC was 4.0 ± 0.2%, which is smaller than the literature value (η = 5.2%) because of thinner TiO₂ films without addition of the scattering layer in our case. The efficiencies of power conversion of the devices decreased greatly, from 2.5 ± 0.2 (PE₁), 2.0 ± 0.1 (PE₂), 0.78 ± 0.09 (PE₃), to 0.25 ± 0.02% (PE₄). This systematic variation of the cell performance reflects the photocurrent density, which decreased from 6.6 ± 0.6 (PE₁), 5.5 ± 0.1 (PE₂), 2.0 ± 0.3 (PE₃), to 0.70 ± 0.03 mA cm⁻² (PE₄) as the length of the PE link increased from d/Å = 1.2 (PE₁), 1.9 (PE₂), 2.6 (PE₃), to 3.3 (PE₄). Our results unambiguously demonstrate that the cell performance depends directly.
on the length of a rigid \(\pi\)-conjugated link: the longer the link, the poorer the cell performance becomes. The observed length-dependent photovoltaic performance of the porphyrin-based DSSC is similar to the trend reported for a rigid planar meta-substituted porphyrin/TiO\(_2\) system,\(^{11f}\) for which a short link with enhanced photovoltaic efficiency was attributed to increased efficiency of electron injection from porphyrin to TiO\(_2\).

We measured the conversion efficiency of incident photons to current (IPCE) for the devices with PE1 and PE4 in the wavelength range 400–800 nm; the results appear in Figure 13. The photocurrent action spectra of the PE1 and PE4 devices mimic their corresponding absorption spectra, but the IPCE values of PE1 are ten times those of PE4, consistent with the difference in \(J_{SC}\) and \(\eta\) for these two devices. The IPCE is expressible in terms of the light-harvesting efficiency (LHE), the quantum yield of electron injection (\(\phi_{inj}\)), and the efficiency of charge collection at the counter electrode (\(\eta_c\)) according to

\[
\text{IPCE}(\lambda) = \text{LHE}(\lambda) \phi_{inj} \eta_c
\] (1)

As the absorbances of all sensitized films are similar, the values of LHE of all porphyrin-sensitized films are likewise similar. The factor affecting the IPCE values and other photovoltaic parameters (\(J_{SC}\) and \(\eta\)) between PE1 and PE4 might be due to \(\eta_c\), which is dependent upon both the rate of charge recombination from the reduced TiO\(_2\) nanoparticles to the oxidized porphyrin and the rate of dye regeneration by the oxidation of electrolyte.\(^{11f}\) For the dependence on distance of the open-circuit voltage in a triopodal sensitizer system, Clark et al. found that \(V_{OC}\) was much greater for a device with a longer PE link.\(^{32}\) In general, \(V_{OC}\) is larger if the dye regeneration (dye\(^+\) + e\(^-\) \rightarrow \text{dye}) due to oxidation (3I\(^-\) \rightarrow I_3\(^-\) + 2e\(^-\)) occurs over a greater distance from the TiO\(_2\) surface. The charge recombination between TiO\(_2\)(e\(^-\)) and I\(^-\) would hence be much slower over a greater distance so as to increase the efficiency of dye regeneration for the sensitizer with a longer link. We found, however, that \(V_{OC}\) in porphyrin-sensitized SC was even smaller in the porphyrin with the longest link (PE4), in contrast with the results reported for the Ru-bpy/TiO\(_2\) system.\(^{32}\) The smaller \(J_{SC}\) observed for the device with a longer PE link might reflect much more
TABLE 4: Photovoltaic Parameters of Porphyrin-Based DSSCs under AM1.5 Illumination (Power 100 mW cm\(^{-2}\)) and Active Area 0.25 cm\(^2\)

<table>
<thead>
<tr>
<th>dye</th>
<th>films</th>
<th>(J_{sc}/\text{mA cm}^{-2})</th>
<th>(V_{oc}/\text{V})</th>
<th>FF</th>
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<tr>
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<td>0.51 ± 0.02</td>
<td>0.69 ± 0.04</td>
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Rapid electron transfer from TiO\(_2\) back to the dye cation. The kinetics of charge recombination for the system reported here are thus of great interest; this work is in progress.

3. Conclusion

Novel porphyrins (PE1–PE4) were designed and synthesized for the purposes of investigating the interfacial electron-transfer and DSSC applications. The porphyrins involve a ZnBPP moiety as a light-harvesting center and a carboxylic acid as an anchoring group with the \(\pi\)-conjugated PE units serving as a link to control the distance between the porphyrin core and the TiO\(_2\) surface. When these porphyrins were fabricated into DSSC devices, the efficiencies of power conversion of these devices decreased systematically from 2.5 \(\pm\) 0.2% for PE1 to 0.25 \(\pm\) 0.02% for PE4. Measurements of femtosecond fluorescence of the porphyrin-sensitized TiO\(_2\) films showed that the emission decays of the system are similar for PE1–PE4, indicating that electron injection from the porphyrin core to the surface of TiO\(_2\) might be equally rapid for PE1–PE4. DFT calculations indicate that electron densities are localized on the porphyrin core and the first PE link, which might indicate that our observations reflect a narrow detection window that lacks sensitivity to probe electron transfer through links of varied length. Although a slow electron injection in a long link might occur at the dye/TiO\(_2\) interface, as Galoppini and co-workers\(^{11e}\) and Gundlach et al.\(^{31}\) reported, other factors must be considered to account for the great degradation of performance in the devices with a long PE link.

4. Experiments

4.1. Materials. Solvents CH\(_2\)Cl\(_2\), CHCl\(_3\), and ethyl acetate (ACS grade, Mallinkrodt Baker, Kentucky, USA), hexanes (Haltermann, Hamburg, Germany), and THF (Merck, Darmstadt, Germany) in the syntheses were used as received unless otherwise stated. THF and tetrabutylammonium perchlorate (TBAP) were purified according to literature methods.\(^{33}\) Pd\((\text{PPh}_3)_4\) catalyst (Strem Chemical Inc., MA, USA), silica gel 60 for chromatographic purification (230–400 mesh, Merck), and other chemicals (Acros Organics, NJ, USA) were obtained from the indicated suppliers.

4.2. General Syntheses. The Sonogashira cross-coupling method was used to perform most reactions: 13 5-bromo-10,20-biphenylporphinoxidizinc(II) (ZnBPPBr, 100 mg) under dinitrogen was typically mixed with ethynyl substituents (2–4 equiv), Pd\((\text{PPh}_3)_4\) (20 mol%), CuI (10 mol%), and Et\(_2\)NH (5 mL) in freshly distilled THF (75–85 mL). The degassed reaction mixtures were stirred under dinitrogen at 40 °C and monitored with thin-layer chromatography and UV–visible spectra. Upon completion, the reactions were quenched with NH\(_4\)Cl\(_{aq}\) washes followed by chromatographic separation on silica gel with CH\(_3\)OH/CH\(_2\)Cl\(_2\) eluents and crystallization from THF/hexanes.

PE1 was synthesized on cross-coupling ZnBPPBr and 4-ethynylbenzoic acid in 80% yield. 4-Ethynylbenzoic acid was obtained from cross-coupling trimethylsilylacetylene with 4-iodobenzoic acid (78%) with deprotection from tetrabutylammonium fluoride (TBAF/THF) in 82% yield.\(^1\) H NMR (\(\delta_\text{ppm}\) 10.36 (s, 1H), 9.84 (d, J 5 Hz, 2H), 9.46 (d, J 5 Hz, 2H), 8.92 (d, J 5 Hz, 2H), 8.25 (m, 8H), 7.86 (m, 6H). Anal. C\(_{34}\)H\(_{24}\)N\(_4\)O\(_2\)Zn: calcd. C 72.83%, H 4.35%, N 7.55%; found C 72.35%, H 4.60%, N 6.65%. Visible absorption/nm: 443 (log \(\epsilon\)/cm\(^{-1}\) M\(^{-1}\) = 5.64), 567 (4.21), 616 (4.41).

PE2 was prepared from ZnBPPBr and 4-(4-ethynyl-phenylethynyl)benzoic acid in 32% yield. 4-(4-Ethynyl-phenylethynyl)benzoic acid was generated on cross-coupling 4-propargylbenzoic acid with 4-iodobenzaldehyde (72%) after chromatographic separation.\(^1\) H NMR (\(\delta_\text{ppm}\) 10.34 (s, 1H), 9.38 (d, J 5 Hz, 2H), 9.45 (d, J 5 Hz, 2H), 9.89 (d, J 5 Hz, 2H), 8.90 (d, J 5 Hz, 2H), 8.25 (m, 8H), 7.86 (m, 6H). Anal. C\(_{34}\)H\(_{24}\)N\(_4\)O\(_2\)Zn: calcd. C 72.83%, H 4.35%, N 7.55%; found C 72.35%, H 4.60%, N 7.27%. Visible absorption/nm: 439 (log \(\epsilon\)/cm\(^{-1}\) M\(^{-1}\) = 5.64), 567 (4.21), 616 (4.41).

PE3 was obtained on reacting 5-(4-ethynyl-phenylethynyl)-ZnBPP with 4-(4-iodo-phenylethynyl)benzoic acid in 81% yield after chromatographic separation.\(^1\) H NMR (\(\delta_\text{ppm}\) 10.33 (s, 1H), 9.83 (d, J 5 Hz, 2H), 8.20 (t, J 4 Hz, 6H), 8.01 (d, J 8 Hz, 2H), 7.74 (m, 2H), 7.14 (d, J 8 Hz, 2H). Anal. C\(_{49}\)H\(_{28}\)N\(_4\)O\(_2\)Zn: calcd. C 75.05%, H 4.27%, N 6.68%. Visible absorption/nm: 443 (log \(\epsilon\)/cm\(^{-1}\) M\(^{-1}\) = 5.64), 567 (4.21), 616 (4.40).
Ethynyl-phenylethynyl)benzoic acid was generated on cross-ethynyl)-ZnBPP with 1,4-diiodobenzene (yield 39%). 4-(4-ethynyl-phenylethynyl)benzoic acid was synthesized on cross-coupling 5-(4-ethynyl-phenyl-ethynyl)-ZnBPP and 4-(4-ethynyl-phenylethynyl)benzoic acid (yield 72.59%, H 4.46%, N 5.26%). Visible absorption/nm: 443 (log ϵ = 5.58), 569 (4.21), 619 (4.56).

PE4 was prepared from 5-[4-(4-iodo-phenylethynyl)-phenylethynyl]-ZnBPP and 4-(4-ethynyl-phenylethynyl)benzoic acid in 38% yield. 5-[4-(4-Iodo-phenylethynyl)-phenylethynyl]-ZnBPP was synthesized on cross-coupling 5-(4-ethynyl-phenylethynyl)-ZnBPP with 1,4-diiodobenzene (yield 39%). 4-(4-Ethynyl-phenylethynyl)benzoic acid was generated on cross-coupling 1,4-diethynylbenzene with 4-iodobenzoic acid (yield 65%). 1H NMR δ(DMSO) at 2.50 ppm δ (1H), 9.83 (d, J 4 Hz, 2H), 9.45 (d, J 4 Hz, 2H), 8.90 (d, J 4 Hz, 2H), 8.82 (d, J 4 Hz, 2H), 8.20 (t, J 4 Hz, 6H), 7.95 (d, J 8 Hz, 2H), 7.86 (overlapped, 8H), 7.66 (overlapped, 10H). Anal. C_{67}H_{32}N_{4}O_{2}Zn·H_{2}O: calcd. C 72.82%, H 4.43%, N 5.86%; found C 77.61%, H 4.00%, N 5.36%. Visible absorption/nm: 444 (log ϵ = 5.56), 569 (4.17), 619 (4.53).

4.3. Steady-State Spectral Measurements. Absorption spectra (Agilent 8453 UV–visible spectrophotometer), fluorescence spectra (Cary Eclipse fluorescence spectrophotometer), NMR spectra (Varian Unity Inova 300WB NMR spectrometer), and elemental analyses (Elementar Vario EL III) were measured with the indicated instruments. Cyclic voltammograms (CH Instruments Electrochemical Workstation 660/A) were recorded with a standard three-electrode cell: a Pt working electrode, a Pt auxiliary electrode isolated from the main compartment by a layer of fine glass frit, and a reference electrode (SCE) isolated from the main compartment by a junction tipped with a platinum wire. A glovebox (M. Braun Unilab), a vacuum line, and an auxiliary electrode isolated from the main compartment by a Pt wire. A glovebox (M. Braun Unilab), a vacuum line, and an auxiliary electrode isolated from the main compartment by a Pt wire. A glovebox (M. Braun Unilab), a vacuum line, and an auxiliary electrode isolated from the main compartment by a Pt wire. A glovebox (M. Braun Unilab), a vacuum line, and an auxiliary electrode isolated from the main compartment by a Pt wire.

4.4. Time-Resolved Fluorescence Measurements. Fluorescence decays were recorded with an optically gated (up-conversion) system (FOG100, CDP), described elsewhere. Briefly, the femtosecond laser system (Mira 900D, Coherent) generated output pulses at 860 nm (or 840 nm) of duration ~120 fs at a repetition rate 76 MHz. The frequency of the laser pulse was doubled for excitation (λex = 430 or 420 nm). The residual fundamental pulse served as an optical gate; a dichroic beam splitter separated excitation and gate beams. The intensity of the excitation beam was appropriately attenuated and focused onto a rotating cell (optical path of length 1 mm) containing either the solution or the solid thin-film samples. The emission was collected with two parabolic mirrors and focused onto a crystal (BBO type-I); the gate pulse was also focused on that BBO crystal for sum-frequency generation. The latter signal was collected with a lens, separated from interference light with an iris, a band-pass filter, and a double monochromator (DH10, Jobin Yvon) in combination, and then detected with a photomultiplier (R1527P, Hamamatsu) connected to a computer-controlled photon-counting system. Variation of the temporal delay between gate and excitation pulses via a stepping-motor translational stage, we obtained a temporal profile (transient). The polarization between pump and probe pulses was fixed at the magic-angle condition, 54.7°.

4.5. Cell Fabrication and Performance Characterization. Three key components are essential in the construction of a sandwich-type DSSC device: a light-harvesting layer (dye/TiO2) is deposited on a transparent conducting oxide (TCO) surface to serve as a working electrode (anode); a Pt-coated layer is deposited on a TCO surface to serve as a counter electrode (cathode), and an diiodine-based electrolyte fills the space between the anode and the cathode to serve as a redox couple of the cell. For a working electrode, a TiO2 nanoparticulate film was produced on a fluoride-doped tin oxide (FTO, 30 Ω/□, Sinonar, Taiwan) glass via screen printing. Crystallization of TiO2 films (thickness ~6 μm and active area 0.25 cm2) was performed on annealing in two stages: heating at 450 °C for 5 min followed by heating at 500 °C for 30 min. The TiO2 film was then immersed in a aqueous solution of TiCl4 (40 mM, 70 °C, 30 min) followed by the same two-stage thermal treatment for final annealing of the electrode. The electrode was then immersed in the dye/THF solution for dye loading onto the TiO2 film. The Pt counter electrodes were prepared on spin-coating drops of H3PtCl6 solution onto FTO glass and heating at 400 °C for 15 min. To prevent a short circuit, the two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, Solaronix, thickness 25 μm). The electrolyte solution containing LiI (0.1 M), I2 (0.05 M), BMII (0.6 M), and 4-tert-butylpyridine (0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 1:1) was introduced into the space between the two electrodes, so completing the fabrication of these DSSC devices.

The performance of a DSSC device was assessed on measurement of an IV curve with an AM-1.5 solar simulator (Newport-Oriel 91160). The solar simulator employs filters and other optical components to mimic solar radiation with an air mass 1.5 spectrum; the output intensity is evenly distributed over a large area. When the device is irradiated with the solar simulator, the source meter (Keithley 2400, computer-controlled) sends a voltage (V) to the device, and the photocurrent (I) is read at each step controlled by a computer via a GPIB interface. The solar simulator was calibrated with a Si-based reference cell (S1133, Hamamatsu) and an IR-cut filter (KG5) to correct the spectral mismatch of the lamp. The actively illuminated area was 0.25 cm2 for all measurements.


References and Notes

porphyrins are expected to adsorb on TiO₂ surfaces in monomeric form with a less extent of aggregation.