Zinc(II) Tetraarylporphyrins Anchored to TiO$_2$, ZnO, and ZrO$_2$
Nanoparticle Films through Rigid-Rod Linkers

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A series of six Zn(II) tetraphenylporphyrins (ZnTPP), with a phenyl (P) or oligophenylenevinylene (OPV) rigid-rod bridge varying in length (9-30 Å) and terminated with an isophthalic acid (Ipa) anchoring unit, were prepared as model dyes for the study of sensitization processes on metal oxide semiconductor nanoparticle surfaces (MO$_n$ = TiO$_2$, ZnO, and insulating ZrO$_2$). The dyes were designed such that the electronic properties of the central porphyrin chromophore remained consistent throughout the series, with the rigid-rod anchoring unit allowing each porphyrin unit to be located at a fixed distance from the metal oxide nanoparticle surface. Electronic communication between the porphyrin and the rigid-rod unit was not desired. Rigid-rod porphyrins ZnTPP-Ipa, ZnTPP-P-Ipa, ZnTPP-PE-Ipa, ZnTPP-(PE)$_2$-Ipa, and ZnTPP-P-Ipa (with mesityl substituents on the porphyrin ring) were synthesized using combinations of mixed aldehyde condensations and Pd-catalyzed cross-coupling reactions. Their properties, in solution and bound, were compared with that of Zn(II) 5,10,15,20-tetra(carboxyphenyl)porphyrin (p-ZnTCPP) as the reference compound. Solution UV-vis and steady-state fluorescence spectra for all six rigid-rod-Ipa porphyrins were almost identical to each other and to that of p-ZnTCPP. Cyclic voltammetry and differential pulse voltammetry scans of the methyl ester derivatives of the six rigid-rod-Ipa porphyrins, recorded in dichloromethane/electrolyte, exhibited redox behavior typical of ZnTPP porphyrins, with the first oxidation in the range +0.99 to 1.09 V vs NHE. All six rigid-rod-Ipa porphyrins and p-ZnTCPP were bound to metal oxide (MO$_n$ = TiO$_2$, ZnO, and insulating ZrO$_2$) nanoparticle films. The Fourier transform infrared attenuated total reflectance spectra of all compounds bound to MO$_2$ films showed a broad band at 1553-1560 cm$^{-1}$ assigned to the ν(CO$_2$) asymmetric stretching mode. Splitting of the Soret band into two bands at 411 and 423 nm in the UV-vis spectra of the bound compounds, and broadening and convergence of both fluorescence emission bands in the fluorescence spectra of the porphyrins bound to insulating ZrO$_2$ were also observed. Such changes were less evident for ZnTPM-Ipa, which has mesityl substituents on the porphyrin ring to prevent aggregation. Steady-state fluorescence emission of rigid-rod-Ipa porphyrins bound to TiO$_2$ and ZnO through the longest bridges (>14 Å) showed residual fluorescence emission, while fluorescence quenching was observed for the shortest compounds.

1. Introduction

The study of the molecule/MO$_n$ semiconductor boundary and the characterization of heterogeneous electron transfer processes at this interface are of great importance for solar energy conversion. A,B.C For instance, many groups worldwide are developing dye-sensitized solar cells (DSSCs) that utilize photoanodes of heterogeneous photocatalytic systems and solar cell efficiencies. Although Ru polypyridine complexes and their analogues remain the most frequently used dyes due to their chemical stability and broad, tunable, metal-to-ligand charge-transfer absorption in the UV-vis region, there is increasing interest in the development of organic dyes, in particular porphyrins.D,E,F,G

Our interest in developing anchor−bridge−porphyrin model compounds started with the electron transport study of DSSCs prepared from MOCVD-grown ZnO “nanotip” films sensitized with Zn(II) 5,10,15,20-tetra(3-carboxyphenyl)porphyrin (m-ZnTCPP).H This study indicated that zinc tetrathiaporphyrin porphyrins are excellent dyes to study interfacial processes in ZnO nanotips of a semiconductor through a rigid linker.I,J

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Dyes Anchored to Nanoparticle Films

Figure 1. Structure of the of rigid-rod–Ipa porphyrins 1–6 and reference compound p-ZaTCP. Also shown are the anticipated binding geometries on metal oxide surfaces. The cartoons show ideal behavior of the sensitizers on the metal oxide surface, but we must assume that other binding modes are also possible.\(^5\)\(^3\)

films. More recently, we developed a series of porphyrins designed to bind “flat” and at an increasing distance from the surface of

the metal oxide semiconductor.\(^1\)\(^1\) This study suggested that the binding orientation as well as the distance from the semiconductor surface influence the photophysical properties of the bound dyes and their solar cell efficiencies.\(^1\)\(^1\) In an effort to expand and complete the study of distance and orientation effects, we report in this paper the synthesis and the photophysical and electro-chemical properties of a second series of anchor–bridge–porphyrin model compounds, named here rigid-rod–Ipa porphyrins.

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with an average diameter of approximately 10 µm thick with an average particle size of 15 nm. ZnO films were prepared by casting the colloidal paste approximately 2 µm thick with an average particle size of 15 nm. ZnO films were prepared by casting the colloidal paste onto the substrate over an area of 1 cm², followed by sintering at ~450 °C for 30 min. Lower temperatures were used for sintering the ZnO films (~300 to 350 °C). The colloidal paste was employed within 1 or 2 days and then discarded. The films were stored in the air, but reheated (see below) prior to binding. For absorption and fluorescence studies the films were cast on cover glass slides (VWR). For electrochemical studies the films were cast on transparent, conductive glass with a tin-doped indium oxide layer (8 Ω/square inch ITO, Pilkington). We refer to films cast on cover glass or ITO conductive glass as MO/G or MO/ITO, respectively, where MO is the metal oxide (TiO₂, ZnO, or ZrO₂).

**Binding.** Binding of the dye molecules to the TiO₂, ZnO, and ZrO₂ films was accomplished by immersing the films in a 0.4 mM MeOH solution of the carboxylic acid derivatives of the porphyrin dyes (Ipa derivatives) at room temperature for 1 h. Basic or acidic pretreatment of the metal oxide films was tested, but binding was found to occur best on untreated films. All films, which were stored in the air, were dried by heating to 150 °C for 30 min followed by cooling to 80 °C prior to immersion in the dye solution. The sensitized films were rinsed, immersed in MeOH to remove any physisorbed dye, and then used for the measurements.

**Spectroscopy.** The Fourier transform infrared attenuated total reflectance (FT-IR-ATR) spectra of all carboxylic acid derivatives of the neat porphyrins (as powders) were compared to the spectra of the porphyrins bound to TiO₂ or ZnO. FT-ATR-IR spectra were acquired on a Thermo Electron Corp. Nicolet 6700 FT-IR. UV–visible absorption spectra were acquired at ambient temperature in MeOH (Acros, spectroscopic grade) using a Varian Cary-500 spectrometer. The sensitized MO/G films were placed diagonally in a 1 cm² quartz cuvette in air. Steady-state fluorescence spectra were acquired on a Spex Fluorolog that had been calibrated with a standard NIST tungsten–halogen lamp. Sensitized MO/G films were placed diagonally in a 1 cm² quartz cuvette. The excitation beam was directed 45° to the film surface, and the emitted light was monitored from the front face of the sample and from a 90° angle in the case of fluid solutions. Fluorescence quantum yields for the samples (Φₛ) were calculated in MeOH solutions deaerated with a BAS potentiostat under nitrogen at room temperature with a conventional three-electrode configuration at a scan rate of 100 mV.

The subscript “s” refers to the sample, the subscript “ref” to the reference sample (in this case ZnTPP), A is the absorbance at the excitation wavelength, I is the integrated emission area, and n is the solvent refraction index.

**Electrochemistry.** Cyclic voltammetry was performed with a BAS potentiostat under nitrogen at room temperature with a conventional three-electrode configuration at a scan rate of 100 mV.

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**Figure 2.** Lengths of 1–6 and reference compound p-ZnTCPP. The length of the sensitizer–anchoring unit is here defined as the distance between the Zn(II) metal center and the midpoint between the two oxygen atoms of the C–OH bond on the isophthalic acid unit for the Ipa rods, and the distance between the Zn(II) metal center and the oxygens of the COOH group for p-ZnTCPP, as shown.¹³

These are rigid-rod porphyrins that bind through an isophthalic acid anchoring group (Ipa) and have phenyl or oligophenylene-cyclohexynylene (OPE) bridges varying in length, Figure 1.¹²,¹³ The compounds were studied in solution and bound to MOₙ films.

2. **Experimental Section**

**Metal Oxide Film Preparation.** Colloidal TiO₂ and ZrO₂ films were prepared by a sol–gel technique that produces mesoporous films approximately 10 µm thick.

Briefly, the TiO₂ films were prepared by casting the colloidal paste by the doctor blade technique onto the substrate over an area of 1 × 2 cm², followed by sintering at ~450 °C for 30 min. Lower temperatures were used for sintering the ZnO films (~300 to 350 °C). The colloidal paste was employed within 1 or 2 days and then discarded. The films were stored in the air, but reheated (see below) prior to binding. For absorption and fluorescence studies the films were cast on cover glass slides (VWR). For electrochemical studies the films were cast on transparent, conductive glass with a tin-doped indium oxide layer (8 Ω/square inch ITO, Pilkington). We refer to films cast on cover glass or ITO conductive glass as MO/G or MO/ITO, respectively, where MO is the metal oxide (TiO₂, ZnO, or ZrO₂).

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The electrochemical properties of the methyl ester derivatives of the dyes (Ipe derivatives) were studied in dichloromethane with 0.1 M Bu4NBF4 supporting electrolyte. A glassy-carbon working electrode (2 mm diameter) was used along with a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. When using a porphyrin/MO/ITO film as the working electrode, acetonitrile was used with a 0.1 M Bu4NClO4 supporting electrolyte. The potential of the Ag/AgCl electrode was calibrated externally versus the ferrocene/ferrocenium (Fc+/Fc) redox couple. The half-wave redox potentials (E1/2) were determined as (Epa + Epc)/2, where Epa and Epc are the anodic and cathodic peak potentials, respectively. It was assumed that E1/2 ≈ E° for all measurements. All potentials were referenced to the normal hydrogen electrode (NHE) to make a comparison with the conduction bands of TiO2 and ZnO. Where E1/2 could not be calculated, due to irreversible oxidation or reduction processes, Epa and Epc were reported, respectively. All redox processes were also studied by differential pulse voltammetry (DPV), using the relationship

\[ E_{1/2} = E_{\text{max}} + \Delta E/2 \]  

(2)

where Emax is the peak maxima in the DPV scan and ΔE is the pulse amplitude.57 DPV experiments were carried out at a scan rate of 20 mV s−1, pulse amplitude 50 mV, pulse width 50 μV, and pulse period 0.2 s. In some cases, namely, the third reduction process of some of the porphyrin dyes, the differential pulse voltammetry data are reported, due to poor quality cyclic voltammetry scans at such negative potentials.

The excited-state oxidation potentials E1/2(P*/P°) of all porphyrins in MeOH and bound to TiO2 and ZnO surfaces were calculated from the relationship

\[ E_{1/2}(P^*/P^0) = E_{1/2}(P^+/P) - E_{0-0} \]  

(3)

where E1/2(P*/P) is equivalent to the first oxidation potential of the ground-state porphyrin chromophore and E0-0 is the zero-zero excitation energy.18 E0-0 was calculated from the intersection of the porphyrin absorption spectrum with the fluorescence emission spectrum in MeOH at normalised absorption/emission intensity. For the solid-state measurements E0-0 was similarly calculated from the UV–vis and fluorescence measurements made on the derivatized MO/G and ZrO2/G films, respectively. E1/2(P*/P°) values were calculated from the solid-state cyclic voltammetry, UV–vis, and fluorescence data to give a closer approximation of E1/2(P*/P°) in a solid-state device as possible.

3. Results and Discussion

Synthesis. The synthesis of the rigid-rod–Ipa porphyrins is described in the Supporting Information. Briefly, the dimethylphosphonate esters (Ipe) of porphyrins ZnTMP–Ipa (1) and ZnTPP–Ipe (2) where both prepared by a mixed aldehyde condensation of dimethyl-5-formylphosphonate with mesitaldehyde and benzaldehyde, respectively, following reported methods (Scheme S3).19,20 To prepare all of the extended rigid-rod–Ipa porphyrin systems, we employed a Pd-catalyzed cross-coupling reaction21 between Zn(II) 5-(4-iodophenyl)-10,15,20-triphenylporphyrin and the rigid-rod–Ipa component, as illustrated in the general scheme below (for details see Supporting Information).

FT-IR-ATR. Neat Rigid-Rod–Ipa Porphyrins. All solid rigid-rod–Ipa porphyrin samples (Figure 3 and Figures S1, S2, S3, S4 in Supporting Information) showed spectra typical of the meso-tetraphenylporphyrin macrocycle, with symmetric and asymmetric stretching bands of the pyrrole ring (ν(C−H), ν(C=C), and ν(C≡N)) in the range 700–1500 cm−1.22 All rigid-rod–Ipa porphyrins acids here studied showed a strong band in

the region of 1687–1700 cm⁻¹ due to the ν(C=O) stretch and a broad band at 1262–1286 cm⁻¹ due to the ν(C–O) stretch of the carboxylic acid groups. Weak acetylenic stretching bands were observed in the region of 2210–2213 cm⁻¹ (Figure 3), which were assigned to adsorbed moisture on the films. Also shown are the possible binding modes of the carboxylate group to TiO₂, ZnO, and ZrO samples.

**Bound to TiO₂ and ZnO.** All rigid-rod–Ipa porphyrins here studied did bind strongly to TiO₂, ZnO, and ZrO nanoparticle films. The nature of the binding interaction between the rigid-rod–Ipa porphyrins and the metal oxide surfaces was characterized by comparing changes in the region of the carboxyl group in the FT-IR-ATR spectra, Figure 3. Upon binding to TiO₂ the ν(C=O) and ν(C–O) stretching modes of the isophthalic acid group disappeared, with the appearance of a broad shoulder on the carboxylic acid groups. Weak acetylenic stretching bands were observed in the region of 2210–2213 cm⁻¹ (Figure 3), which were assigned to adsorbed moisture on the films. Also shown are the possible binding modes of the carboxylate group to TiO₂, ZnO, and ZrO samples.

**Fluorescence Spectra.** The fluorescence spectra were also typical of the p-ZnTCPP and the rigid-rod–Ipa porphyrins recorded in MeOH. Group upon binding to TiO₂ (Δν ~ 240 cm⁻¹), suggests a prevalence of chelating and/or bidentate binding modes compared to an ester-type binding for all rigid-rod–Ipa porphyrins/MO₆ (Figure 3). The possibility that only one of the COOH groups is binding to the metal oxide and the other remains unbound cannot be ruled out. Computational studies aimed to determine whether an isophthalic acid binding group can bind both acid functionalities are in progress. The weak symmetric stretch of the acetylenic units for porphyrins 4 and 5 was still evident on TiO₂ and ZnO but was not observable in the spectra of 6 on TiO₂ and ZnO.

**UV–vis Absorption and Fluorescence Emission Spectra.** Table 1 summarizes the solution absorption and emission data for the rigid-rod–Ipa porphyrins in MeOH solutions. The UV–vis ground-state absorption and fluorescence emission spectra in fluid solutions of all rigid-rod–Ipa porphyrins were almost identical to that of the reference compound p-ZnTCPP. All solution UV–vis absorption spectra exhibited features typical of the p-ZnTCPP chromophore with a Soret absorption band between 422 and 424 nm and Q bands in the 556–558 nm and 596–597 nm regions, respectively, Figure 4. Porphyrins 3, 4, 5, and 6 each showed an additional high-energy absorption in the 300–350 nm region, consistent with the π–π⁺ absorptions typical of the phenyl or OPE rigid-rod linkers. The slightly lower extinction coefficient for p-ZnTCPP compared to the Ipa-derivatized porphyrins (Table 1) had been reported before. The fluorescence spectra were also typical of the p-ZnTCPP chromophoric group, with two emission maxima observed at 602–604 nm and 654–656 nm, from the Q(0,0)* and Q(1,0)* excited states, respectively. Quantum yields ranged from 0.027 to 0.038 for the rigid-rod–Ipa porphyrins (Table 1), with p-ZnTCPP having a slightly lower quantum yield (0.026). It can be concluded from the convergence of the λ_ex max observed for all porphyrins in the UV and fluorescence spectra that the phenyl or OPE rigid-rod substituents have little or no influence on the electronic and spectroscopic properties of the porphyrin ring. Neither the number of carboxy groups (p-ZnTCPP vs rigid-rod–Ipa porphyrins) nor the length of the phenyl or OPE spacer

![Figure 3. FT-IR-ATR spectra of ZnTPP-(PE)₂-Ipa (6) as the neat solid (bottom) and adsorbed on TiO₂ and ZnO (middle and top, respectively). The broad bands observed at ~3000 cm⁻¹ for the TiO₂ and ZnO samples are assigned to adsorbed moisture on the films. Also shown are the possible binding modes of the carboxylate group to TiO₂ and ZnO.](Image 59x430 to 268x739)

![Figure 4. Solution UV–vis absorption spectra of p-ZnTCPP and the rigid-rod–Ipa porphyrins recorded in MeOH.](Image 340x601 to 515x740)
Figure 5. UV–vis absorption spectra of reference compound p–ZnTCPP (solid red line) and the rigid-rod–Ipa porphyrins bound to ZnO films.

between the porphyrin ring and the Ipa groups caused any significant shift in their absorption or emission maxima. These similarities may be attributed to the lack of electronic communication between the aryl substituents and the central porphyrin ring itself and are consistent with what we had observed in our previous studies of tetrachelate p–ZnTPP systems.13

In this respect, the rigid-rod porphyrins here studied represent ideal models to determine the effect of the sensitizer distance to the porphyrin ring itself and are consistent with what we had observed in our previous studies of tetrachelate p–ZnTPP systems.13

Figure 4 to ZnO are shown in Figure 5 (for TiO2 and ZnO semiconductors). Figure 4 shows an overlay of the UV–vis spectra of all rigid-rod–Ipa porphyrins in MeOH. An overlay of the fluorescence spectra, also recorded in MeOH, is shown in Figure S-6.

Bound to TiO2, ZnO, and ZrO2 Films. The UV–vis absorption spectra of p–ZnTCPP and the rigid-rod–Ipa porphyrins bound to ZnO are shown in Figure 5 (for TiO2 see Figure S-7). One notable feature in the spectrum of p–ZnTCPP is the splitting of the Soret band into two bands at 411 and 423 nm. This phenomenon is due to exciton coupling between adjacent porphyrin chromophores at the ZnO surface as a result of H-aggregate formation (face-to-face stacking). Such behavior has been observed previously and was described in our recent study of p–ZnTCPP in comparison to a number of tetrachelate systems.27

All Soret maxima of the rigid-rod–Ipa porphyrins were not observable on the 10 µm thick TiO2 film due to a high optical density of sensitizer (Figure S-7). H-aggregate formation was evident, however, for all sensitizers (p–ZnTPP and rigid-rod–Ipa porphyrins) on the thinner ~2 µm thick ZnO films (Figure 5). As expected, aggregation was largely decreased for the mesityl-substituted porphyrin ZnTMP-Ipa, which only showed a slight shoulder on the high energy side of its Soret absorption.

Almost identical UV–vis spectra were observed for all porphyrins on ZrO2 and TiO2 (Figure S-7 and S-8 in Supporting Information). Because of the wider bandgap, ZrO2 behaves as an insulator precluding electron injection from the lowest excited state of all porphyrins studied here (E vg ~ 5 eV for ZrO2 compared to ~3 eV for TiO2 and ZnO).28 Since the fluorescence emission is not quenched, ZrO2 films are an excellent substrate to study the fluorescence emission of dyes bound to a surface that closely resembles the morphology of TiO2 films. The fluorescence spectra of p–ZnTCPP and the rigid-rod–Ipa porphyrins bound to ZrO2, all showed broadening and convergence of both their fluorescence bands (Figure 6).

This behavior is consistent with H-aggregate formation of the porphyrin chromophores on the ZrO2 surface (as observed in the TiO2 and ZnO UV–vis spectra) and once more correlate well with our previous study comparing p–ZnTCPP to a number of tetrachelate systems.13 Aggregation effects were again less pronounced for the mesityl-substituted porphyrin ZnTMP-Ipa which showed the highest resolution between its Q(0,0)* and Q(1,0)* emission bands. Interestingly, residual fluorescence was observed for some of the rigid-rod–Ipa porphyrins on the TiO2 and ZnO semiconductors (Figure S-9 and Figure 7, respectively). It should be emphasized here that although strong quenching of

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the static fluorescence of these porphyrin systems bound to TiO$_2$ and ZnO is indicative of electron injection into the conduction band of the semiconductors, it is not direct evidence. Ultrafast time-resolved fluorescence and IPCE measurements are currently in progress. It is assumed from this point on, however, in accordance with previous results from this laboratory$^{10,11}$ and other literature$^{3b,8}$ that the observed quenching of the porphyrin static fluorescence on TiO$_2$ and ZnO is due to electron injection into the conduction band of the semiconductors. The fact that quenching was only observed on TiO$_2$ and ZnO semiconductors and not on the ZrO$_2$ insulator substantiates this assumption.

It appears that, as the porphyrin chromophore becomes more distant from the semiconductor surface, due to the increasing length of the rigid-rod linker,$^{12}$ charge injection from its photoexcited state to the metal oxide conductance band becomes less efficient. Such behavior was not observed previously for the planar tetrachelate systems,$^{13}$ which showed no residual fluorescence emission when bound to either TiO$_2$ or ZnO nanoparticle films. In fact, the planar orientation of these tetrachelate systems showed highly improved charge-injection characteristics in comparison to the vertically assembled p-ZnTCPP, even for the most distant sensitizer (ca. 9 Å).$^{11}$ Residual fluorescence emission on the semiconductor TiO$_2$ and ZnO surfaces was here observed only from the rigid-rod–Ipa porphyrins with the longer bridges, i.e., ZnTPP–P–Ipa, ZnTPP–PE–Ipa, ZnTPP–(PE)$_2$–Ipa, and ZnTPP–(PE)$_3$–Ipa, having estimated distances of 14, 16, 23, and 30 Å, respectively (Figure 2).$^{12}$

Also, the growth of the Q(0,0)$^*$ emission band with the linker’s length (and, therefore, distance from the surface) was less efficient than that for the Q(1,0)$^*$ emission band of these rigid-rod–Ipa porphyrins. A possible explanation for this observation is that a more efficient charge injection occurs from the Q(0,0)$^*$ excited state than for the Q(1,0)$^*$ excited state for the Zn(II) porphyrin chromophores 10–30 Å long. This is more evident in Figures 8–10 and Supplementary Figure S-10, where is given a plot of the ‘emission quantum efficiency’ of both the Q(0,0)$^*$ and Q(1,0)$^*$ emission bands vs the length of porphyrins ZnTPP–P–Ipa, ZnTPP–PE–Ipa, ZnTPP–(PE)$_2$–Ipa, and ZnTPP–(PE)$_3$–Ipa bound to ZnO (TiO$_2$ in Supplementary Figure S-10).$^{28}$ These results provide evidence the complexity of heterogeneous electron transfer at the dye–semiconductor interface, i.e., varying charge-injection efficiency from the same electronic excited state of the porphyrin chromophore was observed depending on (i) the vibrational states involved, i.e., Q(0,0) or Q(1,0), and (ii) the porphyrin rigid-rod’s length.

Interestingly, the “shorter” (<10 Å) porphyrins p-ZnTPP, ZnTMP–Ipa, and ZnTPP–Ipa showed no residual emission both on TiO$_2$ and on ZnO films, indicating efficient charge injection from their excited states into the conduction bands of TiO$_2$ or ZnO over these distances.$^{12}$ Although we cannot be certain whether the linkers bind perpendicularly or at an angle(s) with respect to the semiconductor surface, prior injection kinetics studies of Ru–polypyrpyridyl–Ipa rods bound to TiO$_2$ suggest that the longer the bridge, the longer the distance from the metal oxide surface.$^{7c}$

**Electrochemical Properties.** Solution. Redox potentials vs NHE of the methylester derivatives (Ipe) of the rigid-rod porphyrins recorded in CH$_2$Cl$_2$ are listed in Table 2. The methyl ester derivatives were employed for all compounds, since a common organic solvent in which all the isophthalic acid derivatives were soluble, and which was suitable for electrochemical measurements, could not be found.

All rigid-rod–Ipa porphyrins exhibited redox behavior typical of Zn$^{II}$TPP porphyrins. Formation of the porphyrin radical cation was observed over the range +0.99 to 1.10 V vs NHE. The dication was observed over the range +1.38 to +1.47 V vs NHE. In the negative potential region three reversible/quasi-reversible reduction

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**Figure 8.** Plot of “emission quantum efficiency” vs porphyrin rod lengths for both the Q(0,0)$^*$ and Q(1,0)$^*$ emission bands in the fluorescence spectra of ZnTPP–P–Ipa, ZnTPP–PE–Ipa, ZnTPP–(PE)$_2$–Ipa, and ZnTPP–(PE)$_3$–Ipa bound to ZnO. Higher emission quantum efficiencies correspond to less effective fluorescence quenching of the porphyrin excited state by the semiconductor.

**Figure 9.** Solution cyclic voltammogram (top, 0.1 M Bu$_4$NBF$_4$, CH$_2$Cl$_2$, scan rate 100 mV s$^{-1}$) and differential pulse voltammogram (bottom, 0.1 M Bu$_4$NBF$_4$, CH$_2$Cl$_2$, scan rate 20 mV s$^{-1}$; pulse amplitude, 50 mV; pulse width, 50 mV; pulse period, 0.2 s) scans of ZnTPP–(PE)$_3$–Ipa.

**Figure 10.** Cyclic voltammogram scans of ZnTPP–(PE)$_3$–Ipa bound to TiO$_2$/ITO (top) and ZnO/ITO electrodes (bottom) (0.1 M Bu$_4$NClO$_4$, CH$_2$CN, scan rate 100 mV s$^{-1}$).
voltammetry experiments. Cyclic voltammetry and differential pulse voltammetry scans for ZnTPP of the dication species was observed in the range of the formation of the porphyrin radical cation species. Formation and ZnO/ITO mesoporous thin films is shown in Table 3.

The excited-state oxidation potentials, discoloration of the electrolyte solution was observed during of the radical cation may also be involved, in fact slight transport through the already oxidized layer of porphyrin on the could possibly be explained by a reduced efficiency of charge adsorbed layer of dye lateral to the surface of the nanocrystalline electronic properties of this series of rigid-rod sensitizers again suggests that the rigid-rod—Ipa porphyrins could be useful models for studying the effect of the linker length (and therefore the chromophore’s distance) on charge transfer at the dye-semiconductor interface.

4. Conclusions

A series of rigid-rod—Ipa porphyrins, made of Zn(II) tetraphenylporphyrin (ZnTPP) chromophores, with a phenyl or oligophenylethenylene rigid-rods bridge varying in length, and terminated with an Ipa anchoring unit, were studied in solution and bound to metal oxide (TiO₂, ZnO, and ZrO₂) nanoparticle films. Zn(II) porphyrin p-ZnTCP ester was used as the reference compound. The series was designed to determine the effect of the linkers’ length (9–30 Å) on their photoelectrochemical and photophysical properties and to make comparisons with a series of previously studied porphyrins that bind flat on the surface of the semiconductor. Solution UV–vis and fluorescence spectra, and redox properties for all model compounds suggested that the electronic structure of the porphyrin chromophoric unit is mostly unchanged by the linkers’ structure and length. In this respect, the rigid-rod porphyrins here studied are good models to determine the effect of the sensitizer distance on excited-state electron transfer processes. Electrochemical studies were performed in solution and bound to MO₂/ITO films. The methyl ester (Ipe) derivatives, which were soluble in dichloromethane/ electrolyte, were employed for solution electrochemical studies. The excited-state oxidation potentials, E₁/₂(P⁺/P°), of the rigid-rod—Ipa porphyrins bound to TiO₂ and ZnO lie in the range −0.93 to −0.96 V vs NHE. This value is quite negative with respect to the conduction bands positions of both the TiO₂ and ZnO⁻²⁻ semiconductors, therefore facilitating a thermodynamically favored electron transfer to the lower-lying conduction band of the semiconductors. Such consistency in the electronic properties of this series of rigid-rod sensitizers again

Table 2. Solution Redox Potentials of Porphyrin Methyl Esters in Dichloromethane Reported vs NHE (V)¹

<table>
<thead>
<tr>
<th>porphyrin</th>
<th>oxidation (V)</th>
<th>reduction (V)</th>
<th>E₀,₁/₂ (V)</th>
<th>E₁/₂(P⁺/P°) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>p-ZnTCP ester</td>
<td>1.10</td>
<td>1.47</td>
<td>−1.13</td>
<td>−1.46</td>
</tr>
<tr>
<td>ZnTMP—Ipe (1 ester)</td>
<td>0.99</td>
<td>1.41</td>
<td>−1.44</td>
<td>−1.65</td>
</tr>
<tr>
<td>ZnTPP—Ipe (2 ester)</td>
<td>1.08</td>
<td>1.39</td>
<td>−1.10</td>
<td>−1.47</td>
</tr>
<tr>
<td>ZnTPP-P—Ipe (3 ester)</td>
<td>0.98</td>
<td>1.40</td>
<td>−1.10</td>
<td>−1.42</td>
</tr>
<tr>
<td>ZnTPP-(PE)−Ipe (4 ester)</td>
<td>1.08</td>
<td>1.39</td>
<td>−1.12</td>
<td>−1.36</td>
</tr>
<tr>
<td>ZnTPP-(PE)−Ipe (5 ester)</td>
<td>1.09</td>
<td>1.38</td>
<td>−1.10</td>
<td>−1.30</td>
</tr>
<tr>
<td>ZnTPP-(PE)−Ipe (6 ester)</td>
<td>1.09</td>
<td>1.38</td>
<td>−1.10</td>
<td>−1.30</td>
</tr>
</tbody>
</table>

¹ All cyclic voltammograms were measured at a scan rate of 100 mV s⁻¹ using a glassy carbon working electrode. Determined from differential pulse voltammetry experiments.

Table 3. Redox Potentials of p-ZnTCP and Rigid-Rod—Ipa Porphyrins Bound to TiO₂/ITO and ZnO/ITO Films vs NHE (V)²

<table>
<thead>
<tr>
<th>porphyrin</th>
<th>TiO₂/ITO (V)</th>
<th>ZnO/ITO (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>p-ZnTCP ester</td>
<td>1.09</td>
<td>1.38⁶</td>
</tr>
<tr>
<td>ZnTMP—Ipe (1)</td>
<td>1.04</td>
<td>1.36</td>
</tr>
<tr>
<td>ZnTPP—Ipe (2)</td>
<td>1.07</td>
<td>1.37</td>
</tr>
<tr>
<td>ZnTPP-P—Ipe (3)</td>
<td>1.05</td>
<td>1.36</td>
</tr>
<tr>
<td>ZnTPP-(PE)−Ipe (4)</td>
<td>1.04</td>
<td>1.38</td>
</tr>
<tr>
<td>ZnTPP-(PE)−Ipe (5)</td>
<td>1.07</td>
<td>1.38</td>
</tr>
<tr>
<td>ZnTPP-(PE)−Ipe (6)</td>
<td>1.06</td>
<td>1.37</td>
</tr>
</tbody>
</table>

² All samples were run at a scan rate of 100 mV s⁻¹ using the sensitized MO₂/ITO films as the working electrode. Determined from differential pulse voltammetry experiments.

observed for the longest model compounds (10–30 Å) on TiO₂ and ZnO films, suggesting a reduced charge injection efficiency with increasing distance from the semiconductor surface. Time-resolved injection and recombination studies for the rigid-rod–Ipa porphyrins studied here as well as of the previously reported porphyrins that bind “flat” to the surface are in progress.

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**Supporting Information Available:** Synthesis of all porphyrins here studied, FT-IR-ATR spectra of 1, 2, 3, 4, and 5, neat, bound to TiO₂, and bound to ZnO, UV–vis absorption spectra on TiO₂ and ZrO₂, fluorescence emission spectra in solution and bound to TiO₂, plot of “emission quantum efficiency” vs porphyrin rods length of 3, 4, 5, and 6 bound to TiO₂, cyclic voltammetry of 1, 2, 3, 4, and 5 bound to TiO₂ and bound to ZnO, and complete ref. This information is available free of charge via the Internet at http://pubs.acs.org.

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