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# Molecular Engineering of Zinc Phthalocyanines with Phosphinic Acid Anchoring Groups**

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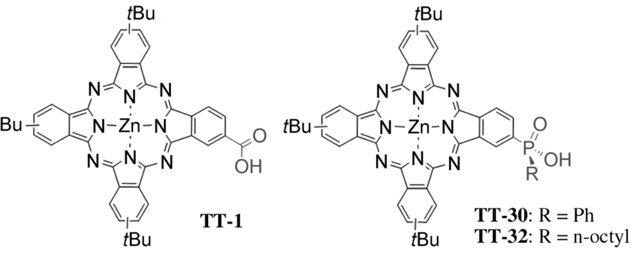
The largest scientific and technological challenge of this century is to find ways to replace the supplies of fossil fuels with renewable energy resources. Among them, solar energy is expected to play a key role in sustainable development. Dye-sensitized solar cells (DSSCs)[1] have emerged alongside conventional p-n junction solar cells as a means to efficiently converting incident solar light into electricity. One of the main components in DSSCs is a sensitizer, which absorbs light, and thereby injects electrons into the conduction band of $TiO_2$, and the holes into the electrolyte. Phthalocyanines (Pcs) are promising sensitizers for molecular photovoltaics because of their intense red absorbance and their outstanding photochemical and thermal stability.[2–4] The goal of this study was to enhance the long-term photostability of DSSCs by molecularly engineering near-IR-absorbing dyes with anchoring groups that bind to the $TiO_2$ surface more strongly than the conventional carboxylic acid groups.[5]

Herein, we report a phosphinic acid as an anchoring group for Pc-based sensitizers in DSSCs. We present results that compare two Zn(II)-Pcs with different phosphinic acid anchoring groups, **TT-30** and **TT-32** (Scheme 1), with **TT-1**,[3b] which has a carboxylic acid anchoring group. The introduction of a long alkyl chain into the phosphinic acid moiety appears to reduce dye aggregation and the rate of interfacial recombination.

The preparation of ZnPc dyes **TT-30** and **TT-32** was achieved by a convergent synthesis (Scheme 2). Iodophthalocyanine **1** was reacted with the appropriate H-phosphinate compound in the presence of a CuI–proline catalyst, which gave the corresponding ZnPc phosphinates. The phosphinates were then treated with trimethylsilyl iodide to obtain the ZnPc dye, in which the phosphinic acid group was directly attached to the Pc ring.[5]



*Scheme 1.* Molecular structures of **TT-1**, **TT-30**, and **TT-32** dyes.

In the case of **TT-32**, the introduction of the alkyl chain to the phosphinic acid moiety serves to protect the $TiO_2$ surface from water and triiodide ions. Water and triiodide ions reduce the recombination of the conduction band electrons (which are injected by the photoexcited sensitizer into the titania nanoparticles) with the $I_3^-$-oxidized form of the redox electrolyte.[6]

Figure 1a shows the photovoltaic performance of **TT-1**, **TT-30**, and **TT-32** sensitizers in DSSC devices which have standard, mesoporous, double $TiO_2$ films (7.5 μm thick transparent films plus 5 μm thick scattering layers) and a volatile, acetonitrile-based electrolyte (M1). The fabrication of the devices and composition of the electrolyte are described in the Experimental Section in the Supporting Information.

The short circuit currents ($J_{sc}$), open-circuit potentials ($V_{oc}$), fill factors (FF), and solar conversion efficiencies ($\eta$) are shown in Table 1. The photocurrent was smallest for **TT-30** and largest for **TT-1** (Figure 1a), whereas the photovoltage was smallest for **TT-1**, but larger and approximately equal for **TT-30** and **TT-32**. Based on these values, the DSSC prepared with **TT-1** performed better overall (2.57% at full sunlight AM 1.5G, 100 mW cm$^{-2}$) than those prepared with **TT-30** and **TT-32**. The enhanced $V_{oc}$ value (approximately 40 mV greater) in the **TT-32**-based device relative to the **TT-1**-

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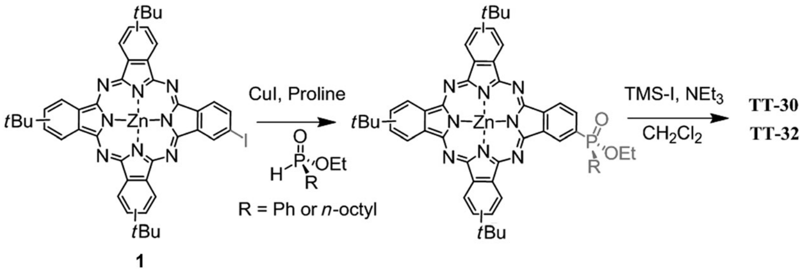

*Scheme 2.* Synthesis of **TT-30** and **TT-32** dyes. TMS = trimethylsilyl.

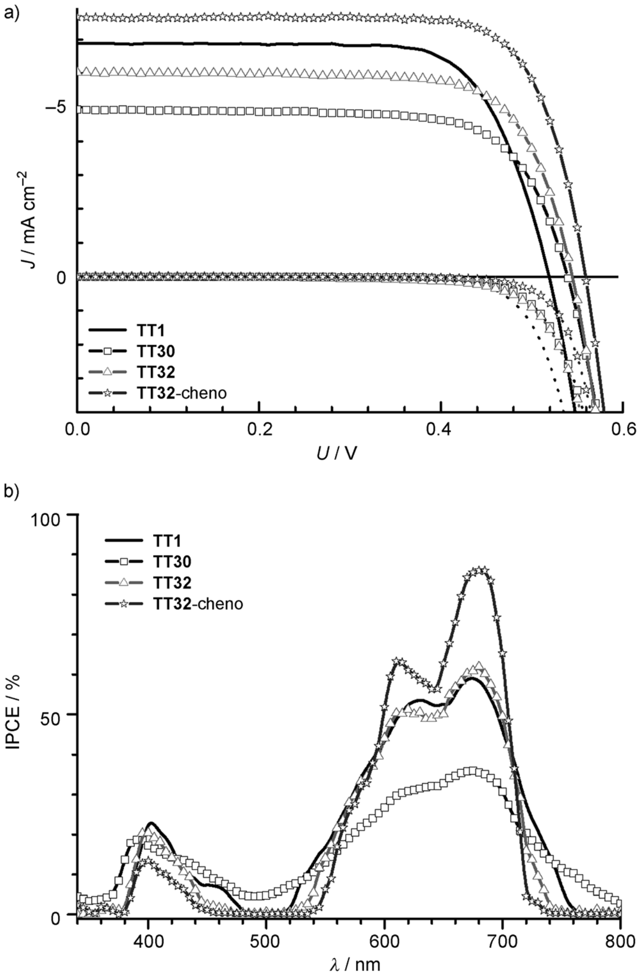

*Figure 1.* a) *J–V* characteristics of fresh devices with **TT-1**, **TT-30**, and **TT-32** sensitizers measured under illumination with AM 1.5G sunlight of 100 mW cm$^{-2}$ (solid lines) or in the dark (dashed lines). In the case of **TT-32**, the effect from the cheno coadsorbent is also presented. b) Photocurrent action spectra of fresh devices with **TT-1**, **TT-30**, and **TT-32** sensitizers. The electrolyte composition was as follows: 0.6 M methyl-*N*-butylimidiazolium iodide, 0.04 M iodine, 0.025 M lithium iodide, 0.05 M guanidinium thiocyanate, and 0.28 M *tert*-butylpyridine in a 15:85 (volume/volume) mixture of valeronitrile and acetonitrile.

based device could be due to a reduction in electron-hole recombination, or an upward shift of the conduction band edge ($E_{cb}$) position in the **TT-32**-based device. Considering the similar configuration, molecular size, and anchoring mode of these three sensitizers, this finding infers that **TT-30** has a lower surface coverage than **TT-1** and **TT-32**. Figure 1 b shows the typical photocurrent action spectra of devices with an acetonitrile-based electrolyte, combined with **TT-1**, **TT-30**, or **TT-32**. The incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The IPCE of **TT-1** and **TT-32** are similar, whereas **TT-30** has a lower and broader spectral response, especially in the Q-bands range. These findings indicate that **TT-30** aggregates, even though the concentration is the same as the other two dyes. Moreover, the lower IPCE of **TT-30** of 36 % at 680 nm could be partially correlated with the lower absorptivity of a mesoporous titania film anchored with **TT-30**, relative to the IPCE of **TT-1** or **TT-32**. As discussed below, aggregation can be substantially reduced by co-adsorption of the sensitizer with chenodeoxycholic acid (cheno), which results in an enhanced photocurrent in the case of **TT-30**.

*Table 1:* Photovoltaic parameters of devices with sensitizers **TT-1**, **TT-30**, and **TT-32** with and without coadsorbent in liquid (M1, fresh devices) and ionic liquid DSSC (Z952, after light-soaking under 1 sun for 72 h at 60 °C) at full sunlight (AM 1.5G, 100 mW cm$^{-2}$).

| | Electrolyte | $V_{oc}$ [mV] | $J_{sc}$ [mA cm$^{-2}$] | FF | $\eta$ [%] |
|---|---|---|---|---|---|
| **TT-1** | M1 | 519 | 6.89 | 0.72 | 2.57 |
| | Z952 | 540 | 5.33 | 0.72 | 2.09 |
| **TT-1** + cheno | M1 | 557 | 6.43 | 0.75 | 2.75 |
| | Z952 | 594 | 4.28 | 0.80 | 2.10 |
| **TT-30** | M1 | 539 | 4.94 | 0.72 | 1.90 |
| | Z952 | 525 | 2.16 | 0.74 | 0.83 |
| **TT-30** + cheno | M1 | 563 | 7.07 | 0.75 | 2.97 |
| | Z952 | 544 | 3.95 | 0.77 | 1.63 |
| **TT-32** | M1 | 544 | 6.03 | 0.73 | 2.39 |
| | Z952 | 582 | 4.67 | 0.77 | 2.10 |
| **TT-32** + cheno | M1 | 559 | 7.67 | 0.76 | 3.24 |
| | Z952 | 635 | 4.02 | 0.80 | 2.06 |

Our earlier study on **TT-1** showed that adding cheno to $TiO_2$ nanoparticles not only reduces the adsorption of Pc sensitizers, but also prevents aggregation of the sensitizer, which leads to an enhanced photovoltaic performance.[3b,4b] Table 1 also shows the photovoltaic performance of the ZnPc-sensitized solar cells in the presence or absence of cheno. For the **TT-1**-sensitized cell with the same size $TiO_2$ nanocrystalline film and with cheno as coadsorbent, the $J_{sc}$ value decreased from 6.89 mA cm$^{-2}$ to 6.43 mA cm$^{-2}$, whereas the photovoltage increased from 519 mV to 557 mV. Thus, a small net enhancement to efficiency of 2.75 % was obtained. Relative to **TT-1**, the efficiency of **TT-30**- and **TT-32**-sensitized cells in the presence of coadsorbent cheno increased significantly from 1.90 % to 2.97 % for **TT-30**, and from 2.39 % to 3.24 % for **TT-32**. The increase in efficiency is largely a result of an increase in photovoltage, as well as an increase in photocurrent, which is in agreement with the measured IPCEs (Table 1 and Figure 1 b). The $V_{oc}$, $J_{sc}$, and

FF values of devices derivatized with **TT-32** and cheno (Figure 1) were 7.67 mA cm$^{-2}$, 559 mV, and 0.76, respectively. These values resulted in an impressive efficiency of 3.24 %. Figure 1b clearly shows that adding cheno into the dye solution (dye to coadsorbent molar ratio = 10:1) can enhance the IPCE spectra response in the Q-band range, which mainly contributes to a higher photocurrent in this case. Interestingly, cheno has the most apparent influence on the photocurrent of the DSSC devices sensitized with **TT-30** (43 % enhancement, see Table 1).

The stability of DSSC devices sensitized with each of the three ZnPc sensitizers under moderate thermal stress and visible-light soaking was compared. As a result of a sealing issue with volatile solvents such as acetonitrile, solvent-free experiments were conducted with a binary ionic liquid based electrolyte. Figure 2 shows the current density/voltage characteristics of devices sensitized with **TT-1**, **TT-30**, and **TT-32**, with and without coadsorbent cheno, in combination with a solvent-free, binary ionic liquid electrolyte at an irradiance of AM 1.5G full sunlight, or in the dark. The parameters were the stabilized values after 72 h of light-soaking, which allowed for optimal reorganization of the dye molecules on the TiO$_2$ surface. The corresponding photovoltaic parameters are given in Table 1. After three days of light-soaking, the photocurrent for the three sensitizers tested was smallest for **TT-30** and largest **TT-1**, whereas the photovoltage was smallest for **TT-30** and largest for **TT-32** (Figure 2). Based on these values, the DSSC prepared with **TT-1** has an overall efficiency of 2.09 % under full sunlight conditions. For a device based on **TT-32**, the corresponding device parameters ($J_{sc}$, $V_{oc}$, FF, and $\eta$) shown in Figure 2 are 4.67 mA cm$^{-2}$, 582 mV, 0.77, and 2.10 %, respectively, and for the device sensitized with **TT-30** these values are 2.16 mA cm$^{-2}$, 525 mV, 0.74, and 0.83 %, respectively. The addition of coadsorbed cheno resulted in a net increase in the performance of devices sensitized with **TT-1** and **TT-32**, principally because of the high $V_{oc}$ values. It is interesting to note that co-adsorption of cheno with **TT-30** increased the $V_{oc}$ value by 19 mV and the $J_{sc}$ value by approximately 1.8 mA cm$^{-2}$. These increases enhance the overall efficiency by almost 100 %, to 1.6 %.

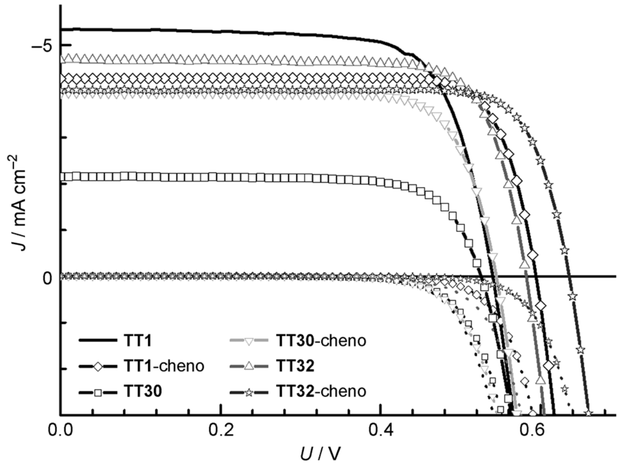

***Figure 2.*** *J–V* characteristics of fresh devices with **TT-1**, **TT-30**, and **TT-32** sensitizers, with and without cheno coadsorbent, measured under illumination with AM 1.5G sunlight of 100 mW cm$^{-2}$ (lines beginning at −2 mA cm$^{-2}$ or lower) or in the dark (lines beginning at the origin). The electrolyte composition was as follows: 1,3-dimethylimidazolium iodide/1-ethyl-3-methylimidazolium-iodide/1-ethyl-3-methylimidazolium tetracyanoborate/iodine/N-butylbenzoimidazole/guanidinium thiocyanate (molar ratio 12:12:16:1.67:3.33:0.67).

As shown in Figure S6 in the Supporting Information, the devices that were sensitized with **TT-1**, **TT-30**, and **TT-32** demonstrated very good stability under light-soaking at 60 °C. After 1000 h of illumination, the efficiency of the devices changed from 2.10 % to 1.96 % for **TT-1** (93 % retention), from 0.83 % to 0.96 % for **TT-30** (116 % retention), and from 2.11 % to 2.05 % for **TT-32** (97 % retention). In most cases, a small drop in the $V_{oc}$ value was offset by an increase in the $J_{sc}$ values. The photovoltage drop is attributed to the downward shift of the $E_{cb}$ value of TiO$_2$ (see the discussion below). The enhanced stability of the new anchoring group when a cheno coadsorbent was used in the devices is clearly demonstrated in Figure S7 in the Supporting Information. The performance of the cell containing **TT-1** degraded more rapidly. This cell retained only 18 % of its initial efficiency after 1000 h of illumination. We attribute this degradation to desorption of dye molecules and the coadsorbent, which induces a reduction in the $J_{sc}$ and the associated $V_{oc}$. In contrast, under similar conditions the cells containing **TT-30** and **TT-32** had better photochemical and thermal stability. After 1000 h of illumination, these cells retained 75 % and 62 % of their initial efficiency, respectively. The higher stability of devices sensitized with **TT-30** and **TT-32** can be ascribed to the structure of the anchoring group of the dye, which protects the TiO$_2$ surface and hinders desorption.

We measured the photovoltage decay transients of devices with the volatile electrolyte at various white-light bias intensities, to study the charge recombination rates ($k_{re}$) between photoinjected electrons and triiodide ions in the electrolyte. Figure S8 in the Supporting Information shows a comparison of the charge recombination lifetime of DSSCs sensitized with **TT-1**, **TT-30**, or **TT-32** with various electrolytes, as a function of charge density ($n_t$). The $n_t$ value was determined by charge extraction, and the recombination lifetime was derived from small perturbation photovoltage decays. Note that we use the terms recombination lifetime and recombination rate constant. The term "recombination rate constant" denotes the pseudo-first-order rate constant (which was estimated by fitting the small perturbation photovoltage decays), which is the inverse of the lifetime. After the increase in the extracted charge density from the TiO$_2$ films, the recombination lifetimes ($\tau_e$, $\tau_e = 1/k_{re}$) became shorter as a result of the higher electron density at the TiO$_2$ and the larger driving forces for the interfacial recombination. The $V_{oc}$ value in the device is given by the difference between the redox level of the electrolyte and the quasi Fermi level in the TiO$_2$, which is determined by the concentration of free charge carriers. Therefore, this plot allows us to compare the interfacial recombination rate constants at equal charge density concentrations in the TiO$_2$ film. The extracted charge under the same irradiation (for example, 150 %

sunlight intensity for the first point of each curve) was $1.46 \times 10^{17}\,cm^{-3}$ for **TT-1**, $2.20 \times 10^{17}\,cm^{-3}$ for **TT-30**, and $4.40 \times 10^{17}\,cm^{-3}$ for **TT-32**. The estimated charge recombination lifetime ($\tau_e$) under the same incident irradiation intensity ($150\,mW\,cm^{-2}$) was 2.7 times longer for the DSSC sensitized with **TT-32** than for the device sensitized with **TT-1**. The $\tau_e$ value was 1 ms for **TT-1**, 1.7 ms for **TT-32**, and 2.7 ms for **TT-32**. These values clearly demonstrate the advantage of the dyes with the phosphinic acid anchoring groups. Our previous reports showed that co-adsorption of sensitizers with cheno onto $TiO_2$ nanoparticles not only reduces the adsorption of Pc sensitizers, but also prevents sensitizer aggregation, which leads to different photovoltaic performance.

Electrochemical impedance spectroscopy (EIS) was also utilized to scrutinize the effect of different dyes (**TT-1** or **TT-32**), electrolytes (M1 or Z952), and the co-absorption of cheno on the dark current. The dark current is generated under forward bias at the nanocrystalline $TiO_2$/electrolyte junction through the reduction of triiodide ions by conduction band electrons. Figure S9 in the Supporting Information shows the effect of the applied voltage on the electron transport resistance ($R_t$) under dark conditions for the device sensitized with **TT-32** combined with electrolytes M1 or Z952, and in the presence or absence of coadsorbed cheno. For comparison, the resistance in the $TiO_2$ film of devices with **TT-1** and M1 electrolyte is also provided. The logarithm of $R_t$, which depends on the number of free electrons in the conduction band ($[e_{cb}^-]$), shows parallel behavior for the various devices. Note that there is no big difference in the equilibrium potential of the electrolytes M1 and Z952, even though the concentration of the redox couple in the electrolyte is not the same. Thus, this behavior implies that the shift in the resistances of the steady-state electron transport in those devices is caused by a change in the position of the $E_{cb}$. Figure S9 illustrates that there is a small downward shift of about 30 mV in the $E_{cb}$ for the device with **TT-32** and cheno coadsorbed onto the $TiO_2$ film, relative to that of the device which contains **TT-32** alone. This effect arises from protonation of the titania surface by the carboxylic acid anchoring group. As a result of this shift, the concentration $[e_{cb}^-]$ at a given forward bias voltage $U$ is higher for the film derivatized with **TT-32**/cheno than it is for the film derivatized with **TT-32** only. This should increase the rate of electron transfer to the triiodide ions. However, the electronically insulating action of the alkyl chain which is close to the anchoring group on the sensitizer clearly overcompensates for this increase of the interfacial electron-transfer rate. This overcompensation results in a net retardation of the dark current (or interfacial recombination procedure) and suggests that the interfacial recombination of the electrons in the conduction band of the $TiO_2$ with the triiodide ions in the electrolyte is retarded by the alkyl group on the sensitizer, as illustrated in Figure S9.

In conclusion, two new zinc phthalocyanine dyes which have different anchoring groups have been used to sensitize $TiO_2$ for DSSC applications. The effects of the anchoring groups on solar conversion efficiencies have been explored in detail. The results show that a carboxylic acid function as an anchoring group leads to higher levels of dye adsorption than does a phosphinic acid anchoring group, and thus gives a slightly higher solar conversion efficiency. However, the phosphinic acid was shown to have stronger binding properties than the carboxylate anchoring group, which improves the durability of the DSSCs.

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