Photophysics

Benzoporphyrins: Selective Co-sensitization in Dye-Sensitized Solar Cells

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Abstract: A novel class of dyes, namely benzoporphyrins, was synthesized and implemented into dye-sensitized solar cells. They feature complementary absorptions compared to **N719**, which renders them promising candidates for co-sensitization in DSSCs. Notably, metallated benzoporphyrins reveal a TiO_2 -nanoparticle attachment that is size and aggre-

Introduction

Incentives, such as low material costs and easy-to-fabricate processes, render dye-sensitized solar cells (DSSCs) a promising and competitive solar energy conversion technology.^[1] After several decades of optimization, state-of-the-art efficiencies range from 10 to $13 \,\%.^{[2-4]}$

Nevertheless, DSSCs bear several drawbacks, among which electron-hole pair recombinations stand out. Here, the electron back transfer either to the electrolyte or to the oxidized dye, reduces the open-circuit voltage (V_{oc}) .^[5] Several strategies to suppress such loss processes have been established. One of them is the use of dyes featuring bulky groups that protect the interface between the photoanode and the oxidized form of the electrolyte.^[6] Alternatively, the addition of chenodeoxy-cholic acid either to the dye solution or to the electrolyte has been shown to prevent fast back electron transfer, which, for example, dominates in ferrocene-based electrolytes.^[7]

Another aspect of significant importance in DSSCs is the absorption cross-section of the dye. The latter should match as much as possible the solar spectrum. To this end, the dye should reveal high molar extinction coefficients throughout the visible region and absorptions that extend into the near-infrared region. Considering, for example, the standard *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) complex (**N719**), maximum efficiencies of around 11% have been realized.^[8,9] Nevertheless, the use of **N719** is restricted by its lack of absorption in the far-red gation dependent. Therefore, unproductive energy-transfer events between the selectively attached dyes can be prevented. In light of the latter, an efficiency improvement of 39% has been achieved upon selective adsorption of benzo-porphyrins and **N719** onto different layers of TiO_2 photoelectrode.

region. To circumvent this limitation, the co-sensitization with another dye, whose absorption spectrum complements that of **N719**, has emerged as a powerful strategy to enhance the light-harvesting efficiency (LHE) of the photoelectrode and, in turn, the overall device efficiency.^[10]

The major asset of co-sensitization is higher short-circuit current densities (J_{sc}). The different approaches towards co-sensitization include dye cocktail,^[10,11] stepwise co-sensitization,^[12,13] selective co-sensitization,^[6,14,15] and the use of a thin top Al₂O₃ layer,^[16] which is selectively sensitized with a second dye.

The benefits that stem from co-sensitization are offset by the challenges to integrate two or more different dyes into the mesoporous photoelectrode. Hardin et al. reported that in most cases co-sensitization results in lower efficiencies.^[17] The latter relates to decreased injection efficiencies, owing to intermolecular interactions between co-adsorbed dyes.^[18] Therefore, suppression of electronic interactions between dyes adsorbed onto the photoelectrode is crucial to afford efficient DSSCs. Here, the spatial separation throughout the semiconductor network was one of the first challenges dealt with in the field of co-sensitization.

In this regard, only a few examples are known from the literature to date. In chronologically order, Lee and Park et al. demonstrated an elegant technique to place several dyes onto a single TiO₂ layer by a concept that mimics the basics of column chromatography.^[19] Although an improvement of around 28% was achieved featuring top efficiencies of 4.8%, this selective co-sensitization involved up to eight steps that render it rather time consuming. It is, nevertheless, very flexible and, indeed, it has been followed by other groups showing similar results.^[6,20]

Soon after this contribution, an impressive improvement in the overall efficiency by means of a film transfer technique was reported by Miao et al.^[21] Hence, an overall efficiency improvement of 37.6% was achieved, although this technique bears the risk of spatially intermittent layers.

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Taking all of the aforementioned into account, the grand challenge is to explore novel approaches that facilitate the selective but simple implementation of different dyes into spatially separated parts of the photoelectrode without compromising the integrity of the corresponding photoelectrodes. Towards this aim, Fan et al. have specifically designed dyes with and without bulky substituents to gain control over the adsorption kinetics and to enhance the efficiency by 18%.^[14] This approach is, indeed, very powerful, owing to the myriad of possibilities to properly modify dyes.

In the current work, the major thrust is to combine the complementary absorption features of two carboxy-substituted tetraphenylbenzoporphyrins (H₂cTPBP and ZncTPBP) relative to N719 and their selective adsorption behavior towards a novel co-sensitization concept in DSSCs. Two key aspects should be highlighted. Firstly, to the best of our knowledge, TPBP have not yet been explored as sensitizers in DSSCs, although they complementary absorb relative to N719 (Figure 1). Secondly, zinc-containing TPBP (ZncTPBP) shows an unforeseen adsorption behavior, which depends on the size of the TiO₂ nanoparticles and the nature of the solvent. Notably, the last feature is a breakthrough towards straightforward selective co-sensitization in a simple device architecture, in which ZncTPBP covers only the transparent part of the photoelectrode, while the light-scattering part is only covered by N719. As a matter of fact, the success of our co-sensitization approach is documented by a 39% enhancement of the overall device efficiency when compared to a non-co-sensitized device with N719.



Figure 1. Steady-state absorption spectra of H_2cTPBP (red spectrum) and **ZncTPBP** (black spectrum) in ethanol as well as **N719** (grey spectrum) in ethanol/acetonitrile (1:1 v/v). Inset: molecular structure of H_2cTPBP for $M=H_2$ and **ZncTPBP** for M=Zn.

Results and Discussion

Details regarding the synthesis of asymmetrical carboxy-substituted **cTPBP** are provided in the Supporting Information. In brief, applying literature-known protocols, a tetrahydroisoindole precursor was prepared,^[22] which was reacted in a mixedaldehyde approach^[23] to yield the desired benzoporphyrin H_2 cTPBP after a dehydrogenation procedure (Schemes S1 and S2 in the Supporting Information). The zinc complex **ZncTPBP** was obtained by a simple metalation reaction.

Figure 1 shows the absorption spectra of H₂cTPBP and **ZncTPBP** in ethanol. Here, the benefit of the π -extended framework is clearly documented in terms of their absorption features in comparison to standard porphyrins such as 5,10,15,20-tetraphenylporphyrin (TPP) or zinc(II)-5,10,15,20-tetraphenylporphyrin (ZnTPP; Figure 1 and Figure S1 in the Supporting Information). In particular, a 40 nm bathochromic shift is noted for the Soret band of H₂cTPBP and ZncTPBP, which appear at 460 and 462 nm, respectively. Likewise, the Q bands are red-shifted and evolve between 600 and 750 nm. As a matter of fact, both exhibit complementary absorption spectra to that of N719 (Figure 1). Next, the singlet excited state features of H₂cTPBP and ZncTPBP were investigated by means of steady-state fluorescence spectroscopy. As shown in Figure S2 in the Supporting Information, upon exciting H₂cTPBP at 460 nm (i.e., the Soret band), 699 and 780 nm fluorescence bands evolved. As expected, the fluorescence of ZncTPBP is blue shifted with respect to that of H₂cTPBP, showing fluorescence maxima at 660 and 721 nm (Figure S2). For H₂cTPBP and ZncTPBP, the fluorescence quantum yields are around 0.029. Additionally, their singlet excited-state lifetimes were determined by means of time-correlated single photon counting (TCSPC; Figure S3 in the Supporting Information). In dilute ethanol solutions of H_2 cTPBP and ZncTPBP (2×10⁻⁶ M), which were utilized to avoid aggregation and/or inner filter effects, lifetimes of 2.98 and 0.37 ns were determined, respectively. The short ZncTPBP lifetime relates to heavy atom effect, which enhances intersystem crossing from the singlet to the triplet excited states.^[24]

To implement both TPBPs into TiO₂-based DSSCs, we utilized a standard double-layer architecture that consists of a transparent layer (TL TiO₂) at the bottom and a light-scattering layer (LS TiO₂) on the top. The latter was stepwise firstly sensitized with both TPBPs using different soaking times and secondly with N719 for 18 h. Remarkably, ZncTPBP attached only to TL TiO₂ leaving LS TiO₂ for adsorption of N719 (Figure 2), while H₂cTPBP attached equally to TL TiO₂ and LS TiO₂. Hence, the selective adsorption behavior of ZncTPBP enables straightforward co-sensitization by sequential dipping of photoelectrodes into different dye solutions. The integrity of the TiO_2 layer is not compromised, which circumvents drawbacks related to spatially intermittent electrical contacts between different layers of the electrode. As a matter of fact, our finding might contribute to tackle the challenge in co-sensitization, if the device performance gives rise to improvement.

To corroborate our hypothesis, we firstly focused on documenting a complete TL TiO₂ coverage with **ZncTPBP** by means of adsorption kinetic assays (Figure S4 in the Supporting Information). Saturation of the photoelectrode was noted after 12 h. From the latter we conclude that TL TiO₂ will not at all or only negligibly be covered with **N719** after more than 12 h adsorption times. Hence, it is safe to compare the stepwise cosensitized TL TiO₂/LS TiO₂ photoanodes with a LS TiO₂ **N719** photoanode as reference.

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Figure 2. Upper part: schematic representation of different device architectures (left: $TL + LS TiO_2$, middle: $LS + TL TiO_2$, right: $MS + LS TiO_2$). Lower part: the corresponding photographs of the different TiO_2 electrode configurations after having been immersed into a **ZnTPBP** solution for 12 h are shown.

Figure 3 depicts the corresponding J–V curves and the incident photon-to-electron conversion (IPCE) spectra of the cosensitized and the non-co-sensitized N719 reference DSSCs. The latter features V_{oc} of 645 mV, J_{sc} of 7.20 mA cm⁻², and FF of 0.72, which result in an overall efficiency of 3.46% (Table 1). Co-sensitized DSSCs exhibit very different trends. For instance, although H₂cTPBP/N719 DSSCs reveal a significant contribution of the Soret and Q band absorptions in the IPCE spectrum, J_{sc} values are lower than in the non-co-sensitized N719 reference DSSCs (Figure 3). This is further corroborated in the IPCE spectrum by a maximum value of only 31.7% at the Soret band maximum at 470 nm. In addition, time-dependent adsorption assays show that the efficiencies decrease upon longer adsorption times with H₂cTPBP (Figure 3). This trend is caused by diminished V_{ocr} FF, and, especially, J_{scr} which is ascribed to unproductive energy transfer events, due to the nonselective adsorption of $H_2 cTPBP$ and $N719,\ vide$ supra. As a consequence, the most efficient solar cells are found upon the shortest H₂cTPBP adsorption time of 1 h, which resulted in a $V_{\rm oc}$ of 567 mV, $J_{\rm sc}$ of 1.92 mA cm⁻², FF of 0.72, and, in turn, an efficiency of 0.78%. In stark contrast, the results from the cosensitized devices with ZncTPBP/N719 show a significant enhancement compared to non-co-sensitized reference devices. As a matter of fact, the efficiencies increase upon longer adsorption times peaking at 12 h (Figure 3). Here, the device features (V_{oc} of 732 mV, J_{sc} of 9.56 mA cm⁻², FF of 0.69, and efficiencies of 4.83%) outperform the non-co-sensitized N719 reference devices. Under optimized ZncTPBP adsorption times, that is, 12 h, the overall efficiency increased by 39% when compared to the reference DSSCs. A better light-harvesting, especially around 470 and 650 nm, which stems from the Soret and Q band absorptions, respectively, is noted in the IPCE spectrum (Figure 3). In fact, after 12 h adsorption time the TL TiO₂ layer is fully covered with **ZncTPBP**, avoiding any unproductive energy transfers, vide supra. Longer ZncTPBP adsorption times fail to result in higher currents and, in turn, in higher efficiencies (Figure 3). This is likely to relate to ZncTPBP aggregation at the surface, hampering the dye regeneration. It is interesting to note that after 12 h adsorption of ZncTPBP, the non-co-sensitized N719 reference and the ZncTPBP/N719 co-sensitized devices exhibit identical contributions in the parts of the IPCE spectra, where N719 absorbs. In a stark con-



Figure 3. Upper part: *J–V* curves of best performing reference N719 (grey), H₂cTPBP/N719 (red), and ZncTPBP/N719 (black) DSSCs. Middle part: corresponding IPCE spectra of the best performing N719 (grey), H₂cTPBP/N719 (red), and ZncTPBP/N719 (black) DSSCs. Lower part: efficiency of H₂cTPBP/ N719 (red) and ZncTPBP/N719 (black) DSSCs versus adsorption time of TPBP. The efficiency of N719 reference DSSCs is given by the dashed line.

trast, co-sensitized DSSCs built with H_2 cTPBP/N719 give rise to decreased contributions of N719 due to the competitive adsorption of H_2 cTPBP and N719.

A reasonable rationale for the distinct adsorption behavior could imply the different aggregation behaviors of both benzoporphyrins when dissolved in ethanol. In particular, H_2cTPBP does not exhibit any aggregation in solution even at high concentrations of 1×10^{-4} m, since the full width at half maximum (FWHM) of the Soret band exhibits a constant value of around 13.5 nm (Figure S5 in the Supporting Information). In stark contrast, pronounced aggregation of **ZncTPBP** in ethanol at con-

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| Table 1. Device parameters obtained under AM 1.5 conditions and 1 sun | | | | | | |
|---|--|--|--|--|--|--|
| illumination for the best performing devices. | | | | | | |

| Compound | Adsorption time of TPBP+N719 [h] | V _{oc} [mV] | J _{sc} [mA cm ⁻²] | FF | η [%] | | |
|---|---|--------------------------|---|------------------------------|------------------------------|--|--|
| $\begin{array}{l} H_{2}cTPBP + N719^{[a]} \\ ZncTPBP + N719^{[a]} \\ N719 + ZncTPBP^{[b]} \\ N719^{[c]} \end{array}$ | 1+18 12+18 18+12 18 | 567 732 737 645 | 1.92 9.56 10.17 7.20 | 0.72 0.69 0.63 0.72 | 0.78 4.83 4.74 3.46 | | |
| [a] Regular electrodes: a 7 μ m TL TiO ₂ layer and 7 μ m LS TiO ₂ layer. [b] Inverted electrodes: a 7 μ m LS TiO ₂ layer and 7 μ m TL TiO ₂ layer. [c] Refer- | | | | | | | |

verted electrodes: a 7 μm LS TiO_ layer and 7 μm TL TiO_ layer. [c] Reference DSSCs with 7 μm LS TiO_ electrodes.

centrations higher than 5×10^{-7} M is observed. Here, the FWHM decreases from 9.5 to 7 nm, which implies a reduced broadness of the Soret band and, as a consequence, decreased aggregation. Based on these results, we deduce that adsorption from an aggregated solution onto LS TiO₂ layers is effectively hampered. Strikingly, LS TiO₂ photoanodes remain even after 72 h of adsorption from ethanol solutions of ZncTPBP uncolored. In stark contrast, ZncTPBP lacks aggregation in THF as the FWHMs taken at the high and low wavelength side of the Soret band is more or less with 10.5 nm (Figure S5). The lower tendency towards aggregation is explained by the coordinating character of THF as it binds to the metal center of the benzoporphyrins. As a consequence, the different aggregation behavior of **ZncTPBP** in THF compared to ethanol is likely to suppress the dye adsorption onto TiO₂ films even after 72 h or more of adsorption times (Figure S6 in the Supporting Information). As such it is safe to conclude that selective adsorption onto TiO₂ films is limited to aggregates as they are present in solutions.

To further provide a mature study of the unique adsorption behavior of ZncTPBP, two additional experiments were performed. On one hand, another light-scattering layer containing medium-size TiO₂ (MS TiO₂) was utilized. This was meant to elucidate the adsorption selectivity of ZncTPBP in dependence on the TiO₂ size. The average crystallite sizes of TiO₂ in the films were investigated by XRD measurements using the Scherrer equation (Figure S7 in the Supporting Information). The particle sizes of TL, MS, and LS TiO₂ were 12.49, 20.81, and 34.25 nm, respectively. Diffuse reflectance measurements further corroborate the increased particle size, since the lightscattering features follow the later trend (Figure S5).^[25] Owing to the fact that **ZncTPBP** also immobilizes onto MS TiO₂ (Figure 2), the adsorption selectivity is only seen for LS TiO₂. In other words, the size of the TiO₂ nanoparticles matters in terms of ZncTPBP adsorption. H₂cTPBP attaches to all of the aforementioned TiO₂ layers, a finding that further corroborates our assumption.

On the other hand, an inverted device, in which the LS layer is at the bottom of the FTO and the TL layer is placed on top (FTO/(LS + TL TiO₂)), was assembled. This assisted in ruling out that the layer distribution is decisive for the adsorption phenomenon. With the LS layer at the bottom of the FTO, it is exposed to the same conditions as the TL layer in the former experiments, vide supra. Again, **ZncTPBP** attaches only to TL TiO₂ (top layer) but not to LS TiO_2 (bottom layer) as shown in Figure 2. We exclude, at this point, a device architecture dependent selective adsorption behavior. Notably, the device performances of inverted layer DSSCs are comparable to those of standard layer architecture DSSCs (Table 1).

Conclusions

In summary, we have successfully implemented for the first time a novel class of dyes, namely TPBPs, into TiO2-based DSSCs. Our work underpins, firstly, the complementary absorption features of TPBPs with respect to N719 and, secondly, the selective adsorption of ZncTPBP into specific layers of the photoelectrodes in ethanol solutions. This phenomenon depends, on one hand, on the TiO₂ nanoparticle size but not on the layer architecture, and, on the other hand, on the different aggregation behavior in solution. In fact, we took this finding further and fabricated co-sensitized DSSCs by integrating ZncTPBP and N719 into spatially separated regions of the photoanodes in a two-step procedure. By means of eliminating energy wastage and unproductive energy-transfer processes between the two dyes we realized 39% more efficient DSSCs relative to a non-co-sensitized N719 reference device. It is important to point out that the rationale design of **ZncTPBPs** in terms of linkers, bulky groups, etc., is a valuable strategy to reach new heights in overall DSSC efficiencies.

Experimental Section

Experimental details are provided in the Supporting Information.

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