Non-Covalent Postfunctionalization of Dye Layers on TiO$_2$ — A Tool for Enhancing Injection in Dye-Sensitized Solar Cells


Dedicated to Professor Luis Echegoyen on the occasion of his 70th anniversary

Abstract: We report on newly tailored dye layers, which were employed, on one hand, for covalent deposition and, on the other hand, for non-covalently post-functionalizing TiO$_2$ nanoparticle films. Our functionalization concept enabled intermixing a stable covalent attachment of a first layer with a highly versatile and reversible hydrogen bonding through the Hamilton receptor–cyanuric acid binding motif as a second layer. Following this concept, we integrated step-by-step a first porphyrin layer and a second porphyrin/BODIPY layer. The individual building blocks and their corresponding combinations were probed with regard to their photophysical properties, and the most promising combinations were implemented in dye-sensitized solar cells (DSSCs). Relative to the first porphyrin layer adding the second porphyrin/BODIPY layers increased the overall DSSC efficiency by up to 43%.

Introduction

The construction of hybrid architectures starting at nanosized entities and molecular building blocks is a powerful tool towards the development of advanced multifunctional materials.[1] Leading examples have made it into applications such as catalysis,[2] sensing,[3] drug delivery,[4] removal of water contaminants,[5] and dye sensitized solar cells (DSSCs). Potential pathways in terms of realizing such hybrid architectures are manifold and include among many others self-assembly via covalent or non-covalent interactions. Covalent functionalization, for example, has extensively been employed in the context of highly ordered self-assembled monolayers (SAMs).[2] This approach has enabled the realization of many functional materials like transistors[6] and DSSCs.[7] More recently, SAM post-functionalization through covalent modifications has been explored. The most prominent examples rely on nucleophilic substitutions[10] or click chemistry, especially the dipolar Huisgen 1,3-cycloaddition to couple azides and acetylenes.[11] In contrast to covalent approaches, self-assembly based on non-covalent functionalization supports a high degree of reversibility and versatility.[12] Controlled SAM formation based on covalent as well as non-covalent interactions made a series of mixed inorganic–organic nanoparticles with smoothly tunable surface properties accessible.[13] The resulting nanoparticles have, for example, been utilized in either removing contaminants from water[14] or in radiation therapy.[14] The layer-by-layer technique (LbL), which was first introduced by Decher, is one prominent example of hierarchical architectures, which are solely based on the utilization of non-covalent forces.[15] A substrate, for instance, is alternately dipped into solutions of either positively or negatively charged polymers. Hereby, the layered architectures are stabilized through electrostatic interactions. In recent years, this strategy was used for the formation of functional, nanosized architectures by layering tailored molecular building blocks and charged nanoparticles.[16] When using H-bonding, stronger binding and higher directionality evolved. Important is the fact that solvents govern the strength of H-bonding and, in turn, the precise control over the reversibility. Similar to the LbL methodology, H-bonding stands out for functionalizing nanomaterials.[17] One of the most prominent examples is the Hamilton receptor/cyanuric acid binding motif (Figure 1).[18] Its high binding constant in the range from $10^5$ to $10^6$ L mol$^{-1}$ is truly remarkable.[18a,18b] Not surprisingly, this binding motif enabled the preparation of molecular wires,[19] rotaxanes through a H-bonding template,[21] attachment to carbon allotropes,[22] perylene–fullerene–porphyrin...
hybrids with a charge-transfer character\(^{[23]}\) and even the attachment of gold nanoparticles on polymeric surfaces.\(^{[24]}\)

Our research group has taken the aforementioned as a starting point and advanced it by utilizing the Hamilton receptor/cyanuric acid binding motif to integrate tailored organic building blocks onto metal oxide nanoparticles.\(^{[25]}\) Following such a covalent/non-covalent strategy, reversible superstructures consisting of gold and TiO\(_2\) nanoparticles were held together by H-bonding.\(^{[26]}\) Through the controlled surface immobilization of a Hamilton receptor featuring carboxylic acids our group also succeeded in the non-covalent orthogonal assembly of a porphyrin–cyanurate onto TiO\(_2\) surfaces. The latter is not only redox but also photoactive and combines the benefits of the first layer functionalization based on covalent surface attachment with the control over the reversibility of the second layer functionalization based on H-bonding.\(^{[27]}\)

Herein, we report on the controlled deposition of porphyrin–dipyrromethene boron difluoride (BODIPY) and porphyrin–porphyrin bilayers onto the surface of doctor-bladed TiO\(_2\) films via the combination of covalent and non-covalent self-assembly (Scheme 1). Initially, several Hamilton receptor porphyrins and/or porphyrin cyanurates featuring one or two carboxylates as TiO\(_2\) anchors were prepared through multi-step organic syntheses. Furthermore, a series of BODIPY or porphyrin ligands equipped with a complementary supramolecular recognition motif was prepared. In a first step the supramolecular binding, electrochemistry, and photophysical properties of these building blocks were studied in solution. Finally, the binding was transferred from solution onto doctor-bladed TiO\(_2\)-films. In the resulting hierarchical architectures, a first layer, that is, a covalently attached porphyrin, was combined with a second layer, that is, a non-covalently attached porphyrin or BODIPY. Such a sequential coating enables, on one hand, optimizing the DSSC performance through complementing the absorption of a first layer dye by a second layer dye and on the other hand a high degree of versatility through the reversible H-bonding attachment.

Results and Discussion

Synthesis and complexation

We opted for a (metallo)porphyrin as first-layer dye in the DSSCs. As such, the (metallo)porphyrin should feature as suitable TiO\(_2\) anchor, on one hand, and a recognition motif for the post-functionalization by means of H-bonding, on the other hand. Therefore, the synthesis of a \(\text{trans-AB}_2\text{C}\) (metallo)por-
Phyrin carrying either a carboxylic acid ester (R1) or an iso-phthalic acid ester derivative (R2) as protected anchors, was conducted (Scheme 2). The (metallo)porphyrins synthesis was carried out in two different ways. For method A, the condensation of mesityl dipyrromethane (1), 4-[2-(trimethylsilyl)ethinyl]benzaldehyde (2) and benzaldehyde derivative (3) was initiated by addition of BF3·(OEt)2; after stirring for 2 h the reaction mixture was treated with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). In this standard wet chemical approach, the desired trans-configured porphyrin was isolated after a single-column chromatographic step in yields of 24% (4a) and 14% (4b), respectively.

Procedure B was based on utilizing microwave irradiation. In particular, iodine was added to a mixture of dipyrromethane (1) and the aldehyde building blocks (2 and 3) (Scheme 2). The mixture was heated to 40 °C for 5 min using microwave irradiation. This was followed by oxidation with p-chloranil. The desired trans-AB2C porphyrin was obtained after a single-column chromatographic step in yields of 22% (4a) and 21% (4b). Overall, the microwave-based procedure B resulted in significantly shorter reaction times and easier purification. After subsequent metalation with zinc acetate the resulting (metallo)porphyrins were subjected to desilylation using a 1 M solution of TBAF (tetrabutylammonium fluoride) in THF.

Deprotected ethinyl (metallo)porphyrins 6a and 6b were obtained in good yields. Next, an iodine-substituted Hamilton receptor (7) and an iodine-substituted cyanurate (8) were prepared according to literature procedures.28 These building blocks were then coupled to the asymmetric ethinyl (metallo)porphyrins in a Sonogashira cross-coupling reaction. In a standard approach, iodo-Hamilton receptor 7 was coupled to ethinyl (metallo)porphyrins 6a or 6b, catalyzed by Pd(PPh3)4, PPh3, and NEt3 under inert conditions. The Hamilton receptor-functionalized (metallo)porphyrins were successfully formed in up to 57% yield (9a) after stirring at 80 °C for approximately 3 days. For the preparation of the cyanuric acid-modified (metallo)porphyrin 10a, microwave syntheses were explored. Ethinyl (metallo)porphyrin 6a and 8 were treated with catalytic amounts of Pd(PPh3)4Cl2, Cul, and PPh3 (Scheme 3). After degassing the mixture, it was heated to 150 °C under microwave irradiation. A closer look at the reaction monitoring indicated that an almost complete conversion set in after 32 min. Cyanuric acid-modified (metallo)porphyrin 10a was obtained in 40% yield after column chromatography. Once again, the preparation of 10b was carried out under the previously described standard conditions in a yield of 46%. Finally, deprotection of the esters under basic conditions yielded the (metallo)porphyrin building blocks 9d and 10c for the first-layer dye. Deprotection of the monocarboxylate ester 9a to the corresponding carboxylic acid, however, was not possible. The successful de-protection of the esters was verified by means of high-resolution mass spectrometry and NMR spectroscopy. As a second layer dye, BODIPYs as well as (metallo)porphyrins were chosen. First, the asymmetrical iodo-BODIPY (11) was treated with the ethinyl Hamilton receptor 12 in a Sonogashira reaction to obtain the Hamilton receptor-functionalized BODIPY 15 after a single-column chromatographic step (Scheme 4). Cyanuric acid-functionalized BODIPY 16 was also obtained in a Sonoga...

Scheme 2. Synthesis of two different trans-AB2C porphyrins featuring anchor groups for TiO2 surfaces: a) 0.9 equiv. BF3·OEt2, 2.8 equiv. DDQ, CHCl3, 2 h; b) 0.4 equiv. I2, 1.5 equiv. p-chloranil, dichloromethane (DCM), 5 min; c) 1.5 equiv. ZnOAc, THF, 2 h; and d) 3 equiv. TBAF, THF, 3 h.
shira reaction of 11 and ethinyl cyanurate (13). Several chromatographic steps including reverse-phase HPLC were, however, necessary to purify the crude reaction mixture. Finally, a new microwave-assisted procedure for preparation of the literature-known cyanuric acid (metallo)porphyrin 17 was developed. Ethinyl (metallo)porphyrin 14 and 8 were treated with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, PPh<sub>3</sub>, CuI, THF/NEt<sub>3</sub>, 80 °C, 3 days; b) Pd(PPh<sub>3</sub>)<sub>4</sub>, PPh<sub>3</sub>, CuI, THF/NEt<sub>3</sub>, 80 °C, 3 days; c) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, PPh<sub>3</sub>, CuI, THF/NEt<sub>3</sub>, 150 °C, 32 min, and d) NaOH, THF, 24 h.

Scheme 3. Synthetic pathway to different AB<sub>2</sub>C porphyrins carrying anchor groups for metal oxide surfaces and a Hamilton receptor or cyanuric acid group for further post-functionalization via hydrogen bonding: a) Pd(dba)<sub>2</sub> (dba = dibenzylidenacetone), AsPh<sub>3</sub>, CuI, THF/NEt<sub>3</sub>, 80 °C, 3 days; b) Pd(PPh<sub>3</sub>)<sub>4</sub>, PPh<sub>3</sub>, CuI, THF/NEt<sub>3</sub>, 80 °C, 3 days; c) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, PPh<sub>3</sub>, CuI, THF/NEt<sub>3</sub>, 150 °C, 32 min, and d) NaOH, THF, 24 h.

Physicochemical investigations
The absorption spectra of 9d, 16, and 9d·16 taken in chloroform are shown in Figure 3. For example, the absorption spectrum of 16 is dominated by a strong Soret-band absorption at 427 nm and weaker Q-band absorptions at 554 and 599 nm. In contrast, the absorption spectrum of 16 is dominated by a high energy π→π* transitions at 393 nm and a low energy spin-allowed π→π* transition at 550 nm. A comparison of the absorption spectra taken for 9d·16 with those of 9d and 16 revealed only minor changes. In particular, the Soret-band absorption of 9d broadens and the low-energy π→π* transition of 16 red-shifts from 543 to 549 nm. A closer look at Figure 3b reveals that all the
absorption features further broaden after adsorption on the surface of transparent TiO\(_2\) films. In solution, BODIPY-related features dominate in the 500–600 nm range of the (metallo)porphyrin-based Q-band signatures in 9d·16. In the TiO\(_2\) films, BODIPY-related transitions at 523 nm are only clearly discernable in 9d·16, but they do not dominate. 9d, 16, and 9d·16 were also studied using steady-state fluorescence spectroscopy at room temperature (Figure S29). 9d exhibits the characteristic fluorescence of (metallo)porphyrins, namely maxima at 610 and 656 nm. For 16, we note an intense fluorescence, which maximizes at 582 nm. Selective 506 nm photoexcitation of BODIPY in 9d·16 shows exclusively the fluorescence that relate to BODIPY (Figure S29a). These results suggest that BODIPY in 9d·16 has little or no effect on the fluorescence of 9d. The overlapping fluorescence of 9d and 16 render, however, an unambiguous analysis rather difficult. Analogous observations have been made with 10c·15, and 10c·15 in the steady-state absorption and fluorescence measurements (Figure S30).

To elucidate the processes taking place upon photoexcitation, transient absorption spectroscopy (TAS) measurements were performed both in solution and on semiconducting electrodes in the presence of the electrolyte. The experiments were conducted for 9d, 16, and 9d·16 as well as for 10c, 15, and 10c·15, in a solvent mixture of THF/acetonitrile (ACN) (1:1 v/v). Time-dependent excited-state features and kinetics thereof were evaluated by means of multiwavelength analysis to corroborate the mechanism, by which charges are injected into TiO\(_2\) (vide infra).

Those experiments, which were conducted in solution, serve as reference. In the solvent mixture, 430 nm photoexcitation of either 9d or 10c commences with the formation of transient absorption spectra, which include 457, 604, and 657 nm minima and 461, 580, 635, and 1278 nm maxima, which dominate the fs-TAS dynamics (Figures S31 and S34 in the Supporting Information). The 457 nm minimum is due to ground-state bleaching of the Q-band absorption whereas the 603 and 657 nm minima are due to stimulated fluorescence. These transform into triplet-excited state features located at 450 and 840 nm within 1380 ps.

In solution, no appreciable changes are observed neither in 9d·16 nor in 10c·15 (Figures S33 and S36). Similar to the steady-state fluorescence experiments, we failed to gather evidence for any energy transfer from the (metallo)porphyrins to...
BODIPY. Instead, the differential absorption spectra look exactly like those recorded for (metallo)porphyrins 9d and 10c. Importantly, excitation of either 15 or 16 at 430 nm results in differential absorption spectra typical for BODIPYS, that is, minima at 532 and 610 nm (Figures S32 and S35). In essence, the lack of BODIPY-related features upon 430 nm photoexcitation of 9d·16 or 10c·15 is not a result of selective (metallo)porphyrin excitation.

The picture changes once 9d, 16, and 9d·16 as well as 10c, 15, and 10c·15 are deposited on 9 μm-thick TiO$_2$ films in the presence of an electrolyte: TiO$_2$·9d·16 and TiO$_2$·10c·15. Upon 430 nm excitation of 9d and 10c, they both show the instantaneous formation of the one-electron oxidized form of the (metallo)porphyrin (Figures S36 and S37). Most notable is the lack of stimulated fluorescence, on one hand, and 538 and 850 nm maxima, on the other hand. The maxima are in sound agreement with those detected upon spectro-electrochemical oxidation of, for example, 9d (Figure S44). Based on the multi-wavelength analysis, the charge injection kinetics are best described by three components.

In all cases, an ultrafast component, deconvolution of which is limited by the instrument response, is implied. The failure to detect this component, when 610 nm is used as excitation wavelength (Figures S41 and S43) rather than 430 nm, suggests that the latter is likely to be charge injection from the second singlet excited state (S$_2$). Taking into consideration that the transient absorption spectra upon 610 nm excitation features contributions from the first singlet excited state (S$_1$) and the one-electron oxidized form of the (metallo)porphyrin, it is fair to assume that upon 430 nm photoexcitation the majority of charge injection evolves from the S$_2$ state. The ultrafast charge injection stemming from S$_2$ is followed by two slower components. The faster of them, that is, the second one, takes around 5.6 and 2.47 ps in the cases of 9d and 10c, respectively. As the same lifetimes are also discernible upon 610 nm excitation it is very likely that this process is a charge injection from the S$_1$ state. The slower of them, that is, the third one
takes 227 ps for 9d and 308 ps for 10c. Based on the literature and also considering the red-shifts of the transient absorption features in the 660 to 685 nm region, the third component is assigned with confidence to charges that are injected into non-mobile surface states, which undergo thermal relaxation into the conduction band.[30]

Changes were noted in the transient absorption spectra of TiO$_2$·9d·16 (Figure 4). In addition to the one-electron oxidized form of the (metallo)porphyrin 9d broadening of the ground state bleaching is observed at around 565 nm. The latter is in sound agreement with the BODIPY signatures. Considering the lack of comparable observations in the solution studies, the evolving features are not a result of energy transfer processes but are rather related to a charge transfer. To gather a better understanding, we took a closer look at the energetics (Figure S46). Three scenarios are taken into consideration. First, a direct charge transfer from BODIPY to TiO$_2$; second, a charge transfer in terms of electrons from the (metallo)porphyrin to BODIPY; third a charge transfer in terms of electrons from BODIPY to the (metallo)porphyrin. Based on a previous report by our research group,[27] we rule out anchoring of the cyanurates to TiO$_2$ and direct charge injection from BODIPY to TiO$_2$. If a charge transfer from the (metallo)porphyrin to BODIPY would take place, such mechanism should be operative in solution studies as well. However, we could not gather any experimental evidence for this pathway. As such, we rule out any charge transfer from the (metallo)porphyrin to BODIPY. Upon closer inspection of the transient absorption spectra, signatures of the one-electron oxidized form of BODIPY are noted in the form of a broadened bleaching and an intensification of the 700 nm features. Both of them appear right after the conclusion of charge injection from the (metallo)porphyrin to TiO$_2$ (Figure 5).[31] Full deconvolution of the latter is, however, difficult due to the overlap with the signatures of the one-electron oxidized form of the (metallo)porphyrin. In summary, we postulate for TiO$_2$·9d·16 a charge transfer from BODIPY 16 to (metallo)porphyrin 9d following the initial charge injection from (metallo)porphyrin 9d into TiO$_2$ as the modus operandi. 15·10c shows no pronounced changes relative to 10c film.

**Figure 4.** a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of TiO$_2$·9d·16 with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 564, 665, and 837 nm.

**Application of orthogonally assembled bilayers in DSSC devices**

Following earlier work,[27] the photovoltaic characteristics were investigated using a standard sandwich-type DSSC configuration comprised of a 9 μm thick TiO$_2$ layer as photoanode (Figures S48 and S49), a I$_3$/I$_2$-based electrolyte, and a platinum counter electrode—for more information please refer to the Supporting Information. In contrast to previous studies by our group,[27] we opted for a reverse ordering of the bilayer structure and used (metallo)porphyrins with different anchors to bind to the semiconducting TiO$_2$ (Scheme 1).

First, devices featuring monolayers of 10c (TiO$_2$·10c) and bilayers of 10c·15 (TiO$_2$·10c·15) were prepared and characterized. Current–voltage (J–V) assays were performed enabling first insights into the effect of post-functionalization on the device figures-of-merit, that is, efficiency (η), fill factor (FF), short-circuit current ($I_{sc}$), and open-circuit voltage ($V_{oc}$) (Figure 5, top and Table 1). Importantly, η increased from 0.14% for TiO$_2$·10c to 0.16% for TiO$_2$·10c·15 due to higher $I_{sc}$5, namely 0.42 versus 0.46 mA cm$^{-2}$. We rationalize our J–V observation based on either a direct charge injection from BODIPY into TiO$_2$ or a charge transfer from BODIPY to the (metallo)porphyrin (vide infra). To proof or disproof these two different pathways, IPCE (incident photon-to-current efficiency) measurements were performed. By virtue of the lack of additional features in the IPCE spectra seen for TiO$_2$·10c·15, a direct charge injection from BODIPY into TiO$_2$ is very unlikely (Figure 5, bottom left). Consequently, the higher η5 are in line with the TAS measurements (vide supra) attributed to the se-
sequence of charge injection from (metallo)porphyrin 10c into TiO$_2$ followed by charge transfer from BODIPY 15 to (metallo)porphyrin 10c. Such a sequence assists in rationalizing the rather moderate increases in $h$ and $J_{SC}$. A moderate increase in $J_{SC}$ suggests one or more of the following scenarios as bottlenecks. First, the dicarboxylate anchor might potentially slow down or even hinder charge injection. Second, the positioning of the Hamilton receptor might shift the electron density away from the semiconducting surface. Third, the use of BODIPY in the post-functionalization might be inefficient in terms of charge injection.

To investigate the aforementioned series of devices, featuring monolayers of 9a (TiO$_2$·9a) or bilayers of 9a·16 and 9a·17 (TiO$_2$·9a·16 and TiO$_2$·9a·17), were prepared and characterized by means of $J$–$V$ and IPCE assays. To this end, 9a was synthesized with only a monocarboxylic ester anchor rather than a dicarboxylate anchor like in 10c and a Hamilton receptor instead of a cyanurate. Additionally, the post-functionalization includes BODIPY (16) as well as (metallo)porphyrin 17. When comparing the figures-of-merit for TiO$_2$·9a with TiO$_2$·10c, a higher efficiency of 0.2% for TiO$_2$·9a rather than 0.14% for TiO$_2$·10c stem from different $J_{SC}$: 0.62 versus 0.42 mA cm$^{-2}$. The post-functionalization with 16 and 17 resulted, however, in lower $V_{OC}$ of 0.1% and 0.19% for 9a·16 and 9a·17, respectively. Lower $V_{OC}$ is linked to lesser FFs, $V_{OC}$, and $J_{SC}$. The latter goes hand-in-hand with weaker contributions in the Soret-band region at around 430 nm in the IPCE measurements upon post-functionalization. A closer inspection of the devices following the measurements showed that the red-colored electrolyte turned bright green as a consequence of post-functionalization. This is taken as clear evidence for desorption from the semiconducting TiO$_2$. From the aforementioned we conclude that changing to a Hamilton receptor rather than a cyanurate affects $h$, but a monocarboxylic ester anchor leads to quick and quantitative desorption when post-functionalized.

To remedy this shortcoming, TiO$_2$·9d was prepared and tested in combination with TiO$_2$·16 and TiO$_2$·17. 9d is still a Hamilton receptor, but features unlike 9a a dicarboxylate anchor. The figures-of-merit for TiO$_2$·9d taken from the $J$–$V$ measurements show a $V_{OC}$ of 0.62 V compared to 0.52 V determined for 9b. This is attributed to a better surface coverage. Of even greater importance is, however, a $J_{SC}$ of 1.25 mA cm$^{-2}$ for 9d, which is with 0.62 mA cm$^{-2}$ double than that seen for TiO$_2$·9a. Accordingly, $h$ for TiO$_2$·9d is 0.54%; please compare that to a $h$ of 0.2% for TiO$_2$·9a. The main reason behind the $J_{SC}$ changes is explained by the IPCE assays. Here, a broadening and an increase regarding contributions in the Soret- and Q-

![Figure 5. J-V assays (top) and IPCE measurements (bottom) of TiO$_2$ devices: TiO$_2$·10c and TiO$_2$·10c·15 (left), TiO$_2$·9a, TiO$_2$·9a·16, and TiO$_2$·9a·17 (middle), and TiO$_2$·9d, TiO$_2$·9d·16, and TiO$_2$·9d·17 (right).](image-url)

Table 1. Summary of the devices' figures of merits.

<table>
<thead>
<tr>
<th>Dye combination</th>
<th>Efficiency [%]</th>
<th>FF [%]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$V_{OC}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10c</td>
<td>0.14</td>
<td>65</td>
<td>0.42</td>
<td>0.51</td>
</tr>
<tr>
<td>15·10c</td>
<td>0.16</td>
<td>68</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>9a</td>
<td>0.20</td>
<td>62</td>
<td>0.62</td>
<td>0.52</td>
</tr>
<tr>
<td>9a·16</td>
<td>0.10</td>
<td>60</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>9a·17</td>
<td>0.19</td>
<td>60</td>
<td>0.60</td>
<td>0.51</td>
</tr>
<tr>
<td>9d·16</td>
<td>0.54</td>
<td>75</td>
<td>1.25</td>
<td>0.62</td>
</tr>
<tr>
<td>9d·17</td>
<td>0.61</td>
<td>74</td>
<td>1.43</td>
<td>0.57</td>
</tr>
<tr>
<td>9d·17</td>
<td>0.77</td>
<td>76</td>
<td>1.50</td>
<td>0.61</td>
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</table>

band regions are noted for TiO\textsubscript{2}9d relative to the observations made for TiO\textsubscript{2}9a (Figure 5 middle and right).

Such a broadening is associated with stronger interactions with TiO\textsubscript{2}. In turn, charge injection is facilitated and \( J_{\text{sc}} \) is increased. Next, we turned to devices based on bilayers of 9d·16 and 9d·17 and their characterization. Most important is the fact that \( \eta \) further increased from 0.54% for TiO\textsubscript{2}9d to 0.61% and 0.77% for TiO\textsubscript{2}9d·16 and TiO\textsubscript{2}9d·17, respectively. The (metallo)porphyrin post-functionalization, that is, TiO\textsubscript{2}9d·17, outperforms the BODIPY post-functionalization, that is, TiO\textsubscript{2}9d·16, by 26%. The main cause is again an enhanced \( J_{\text{sc}} \), most likely due to a charge transfer from 16 and 17 to 9d. To summarize, all factors, that is, the use of a Hamilton receptor and its positioning, the post-functionalization as well as the respective anchor are critical in terms of maximizing the overall efficiencies. This highlights the necessity of a stable and robust anchor as well as a tailored self-assembly to generate high-performing devices. Building on the knowledge gathered through this work, higher overall efficiencies could be targeted through careful synthetic modifications of the first- and second layer dyes. In particular, a direct attachment of the supramolecular recognition motif and the carboxylate anchoring groups to the porphyrin moiety, as well as addition of strong electron donor groups, could lead to significantly higher efficiencies.

Conclusions

In this work, we prepared a library of AB\textsubscript{2}C (metallo)porphyrins featuring a stable anchoring group, on one hand, as well as a versatile supramolecular recognition motif, on the other hand. Additionally, we complemented the supramolecular recognition motif by designing corresponding porphyrins and BODIPYs. In a step-by-step fashion, we succeeded in binding the anchor to TiO\textsubscript{2} nanoparticles and in employing a second dye layer via hydrogen bonding. In short, our coating strategy synergizes the benefits of a strong covalent anchoring of the first dye layer, that is, a (metallo)porphyrin, with the versatility of a non-covalently attaching a second dye layer, that is, either a (metallo)porphyrin or a BODIPY. Our investigations were, however, not only limited to solution studies but were matched with corresponding DSSC-based assays. Our studies demonstrated the importance of integrating the Hamilton receptor within the first dye layer and using a dicarboxylic acid anchor to prevent desorption from the TiO\textsubscript{2} nanoparticles. To this end, highest DSSC efficiencies were noted when employing Hamilton receptor porphyrin 9d and TiO\textsubscript{2} to afford TiO\textsubscript{2}9d. A non-covalent post-functionalization with either cyanuric acid BODIPY 16 or cyanuric acid (metallo)porphyrin 17 led to an increase in DSSC efficiency. TiO\textsubscript{2}9d·17, which turned out to be more effective bilayer, improved the DSSC efficiency by 43%. A comprehensive understanding of the underlying mechanisms came from transient absorption spectroscopy (TAS) measurements with the (metallo)porphyrin-BODIPY couples 10c·15 and 9d·16. It is only in TiO\textsubscript{2}9d·16 that the spectroscopic features of the one-electron oxidized form of the (metallo)porphyrin 9d and those of the one-electron oxidized BODIPY 16 were observed. This suggests for TiO\textsubscript{2}9d·16 an intramolecular charge-transfer process from 16 to 9d following the initial interfacial charge injection from 9d into TiO\textsubscript{2}.

Experimental Section

Full experimental details regarding the synthesis and characterization of all organic building blocks, electrochemical characterization, optical spectroscopy, and the preparation of DSSC devices are given in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

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