Design and synthesis of organic sensitizers with enhanced anchoring stability in dye-sensitized solar cells

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Abstract: D-π-A dyes have received a special attention in the field of dye-sensitized solar cells (DSSCs). In this kind of molecules, the acceptor group (A) generally acts as an anchor, enabling the adsorption of the dye onto the metal oxide substrate (TiO₂) and providing a good electron injection. The search for new anchors represents a critical factor for the development of improved DSSCs and in recent years has been a very active research field. This mini-review focuses especially on our work on pyridine-derived anchoring groups for D-π-A dyes, with a special regard on the preparation and characterization of three different families of dyes and a critical evaluation of their stability and efficiency.

Keywords: anchoring groups; cross-coupling reactions; dye sensitized solar cells; energy conversion; ICGC-6; photovoltaics.

Introduction

According to a recent estimation [1], global energy demand reached approx. 13.7 Gtoe at the end of 2014, and, despite the below-average growth recorded in 2014 (+1.1%) and 2015 (+1.0%) [2], is presumed to further increase in the next years, up to 30% by 2040 [3]. Most of this energy is currently provided by fossil fuels, although issues connected with the limited coal, oil and natural gas supply, as well as the requirement to reduce CO₂ emissions and greenhouse effect, underlined the need for a transition towards alternative energy sources. Consequently, the development of efficient and reliable technologies to exploit renewable energy sources has become a crucial scientific goal. Among the possible options, photovoltaic conversion of solar energy into electricity is currently considered as one of the most promising approaches, given that sunlight is free, abundant and widely distributed across the globe [4]. To exploit solar energy, traditional silicon-based photovoltaic devices have been optimized and are currently dominating the market [5], however several innovative technologies have been also developed. Among new technologies, dye sensitized solar cells (DSSC) [6] offer a simple and inexpensive option. In such systems, solar light is harvested by a sensitizer adsorbed on a
nano-crystalline thin-film semiconductor, generally TiO$_2$, through a molecular bridge (this ensemble constitutes the photoanode of the cell). Upon excitation, the sensitizer transfers electrons into the conduction band (CB) of the semiconductor, from where they flow through an external circuit to reach a counter electrode. Meanwhile, on the photoanode the oxidized dye is regenerated by a suitable redox mediator contained in the electrolyte, whose oxidized form diffuses to the counter electrode to gather electrons and close the circuit [7].

To develop high-performance DSSCs, it is important to optimize all their components (sensitizer, nanocrystalline semiconductor, electrolyte, and counter electrode) in order to improve both efficiency and stability of the device. Nevertheless, a special attention needs to be dedicated to the optimization of photosensitizers, as the latter are directly involved in the light-harvesting and charge-separation processes [8], and are therefore largely responsible for cell performances.

Different classes of molecules can be employed, and among them metal-free organic dyes have been found suitable to ensure efficient light-harvesting, due to their easily tunable structures and photophysical properties, good stability and high molar extinction coefficients [9]. Indeed, a multitude of organic dyes have been already prepared and tested in DSSCs [10, 11], most of them sharing the same D-π-A architecture, characterized by electron-donating (D) and electron-accepting (A) groups linked by π-conjugated bridges. Obviously, immobilization of the adsorbed dye molecules to the surface of the semiconducting metal oxide nanoparticles represents a critical issue both to ensure an electrical current, whose generation starts with the injection of electrons from the dye into the conduction band of the metal oxide, and to achieve a stable attachment of the dye, which is essential to assure a long term stability to the final device. Such immobilization is usually achieved through the electron-accepting group, which also acts as an “anchoring group”, being able to link the dye molecule onto the surface of the metal oxide (Fig. 1).

Historically, the most frequently used anchors in DSSCs are carboxylic and cyanoacrylic acid groups, or rhodanine-3-acetic acid fragments, which are generally able to attach onto a TiO$_2$ electrode through the interaction between the carboxylate and the titanium atoms present on the TiO$_2$ surface. In particular, cyanoacrylic acids are very often used, since they are able to ensure a good electronic communication and a stable linkage between the dye and TiO$_2$ by forming a strong bidentate bridge (Fig. 2, left). However, it has been

Fig. 1: Most frequently used anchors in the D-π-A architecture of organic dyes.

Fig. 2: Binding modes of cyanoacrylate and pyridine-containing anchoring/acceptor moieties.
shown that this functional group might undergo an undesirable retroaldolic degradation reaction within the photovoltaic cell under illumination and in the presence of traces of water [12], and this can negatively affect device lifetime. For this reason, different anchoring groups have also been proposed and tested: among them there are phosphonate, sulfonate, catechol, siloxane and pyridine moieties [13].

In this microreview, we will focus in particular on pyridine-containing anchoring moieties (Fig. 2, right), which have interested various research groups. For instance, several dyes with a simple pyridine acceptor group have been prepared and showed to maintain a good charge injection efficiency in comparison with the corresponding carboxylic acids, although photovoltaic efficiencies often turned out to be only moderate at best [14–20]. Furthermore, a single example of a 2-carboxy-pyridine anchoring group was described, together with other heterocyclic, carboxylate-anchored, nitrogen-containing acceptors [21]. Moreover, to improve the electron withdrawing ability of the acceptor, a 2-cyanopyridine group has also been introduced [22], which was reported to bind TiO₂ surface via coordination of Lewis acidic titanium sites by the pyridine nitrogen. Carboxomethyl- and hydroxymethyl pyridinium salts were also described [23–26]. All these works revealed the pyridyl groups as a very promising anchoring moiety and pointed out how the binding mode on the TiO₂ surface could be affected by control of the basicity and electron density of the pyridine group.

New dyes with pyridine derivatives as anchoring groups

Design, synthesis and characterization of the dyes

Initially, we focused our interest on DSSC sensitizers with carboxypyridine-derived anchoring groups, and decided to synthesize a first series of dyes by modification of the structure of the already-known dye D5 [6]. Our first aim was that to compare the photovoltaic performances of our compounds with those of the corresponding compound bearing a classic cyanoacrylic acid acceptor, and to investigate their relative anchoring stability on TiO₂. This kind of investigation had not been reported previously.

The dyes were designed to have the same donor (a substituted triarylamine) and π spacer (vinyl thiophene moiety), but different acceptor groups, namely three different regioisomeric carboxypyridines DF13A,B,C and the classical cyanoacrylic acid anchor DF15 (Fig. 3) [27]. Furthermore, alkoxy chains on the triarylamine donor [28], were inserted on purpose, in order to minimize aggregation phenomena, often occurring with this class of molecules, as well as to red-shift and broaden the absorption spectra of the compounds.

Dyes DF13A,B,C were prepared from common advanced intermediate 1 [29–31], which was reacted with n-BuLi and ClSnBu₃ to give, after a simple aqueous work-up, stannane 3 (Scheme 1). Optimal conditions to react stannane 3 with regioisomeric bromopyridines 5a,b,c were found using Pd(PPh₃)₄ as catalyst, oxygen-free DMF as solvent, CsF and CuI as additives [32], giving rise to pyridine-containing intermediates 6a,b,c.

Fig. 3: Dyes with carboxypyridine-containing acceptor moieties.
is worth mentioning that the same compounds could also be obtained using a Suzuki-Miyaura cross-coupling between the pinacolboronic ester corresponding to stannane 3 and the appropriate heterocycle. However, when we performed such transformation it turned out to be less efficient than the Stille-Migita process described above, being affected by low yields and the formation of side products (homocoupling, protodeborylation). Finally, purification of cyanoderivatives 6a,b,c and hydrolysis with concentrated aqueous HCl afforded dyes DF13A,B,C in almost quantitative yield.

The new compounds were spectroscopically and electrochemically characterized in order to evaluate their possible application to DSSC. The UV-Vis absorption spectra of compounds DF13A,B,C and DF15, recorded both in CH₂Cl₂ and EtOH solution, as well as adsorbed on TiO₂, are shown in Fig. 4. Clearly, compounds DF13A,B,C displayed very similar UV-Vis spectra, which are blue shifted compared with that of DF15 which, in turn, showed a red-shifted absorption compared to D5 [6]. Despite that, the three new pyridine-containing compounds presented intense absorptions in the visible region (molar absorptivities in the 1.86 × 10⁴–2.69 × 10⁴ M⁻¹ cm⁻¹ range, calculated in CH₂Cl₂), as expected for dyes to be employed in photovoltaic devices. Cyclic voltammetry ensured that the four dyes all underwent reversible oxidation processes at similar potentials (+0.91 V for DF13A, +0.93 V for DF13B, +0.93 V for DF13C, and +0.94 V for DF15, all vs. NHE, respectively), indicating that the replacement of the cyanoacrylic acid with a carboxypyridine group did not affect the ground-state oxidation potentials (Eox). All potentials were much more positive than the redox potential of the iodide/triiodide couple (+0.4 V vs. NHE), suggesting that regeneration of the sensitizer during operation of a solar cell was possible.

The energy, shape and electron density distribution of the frontier orbitals of DF13A,B,C and DF15 were also computed by means of DFT calculations at the B3LYP/6-31G* level [33], and compared with those of dye D5. All compounds presented a similar and correct electron density distribution, with the HOMOs mostly localized on the donor and π-bridge sections of the molecules and the LUMOs mainly located on the acceptor moieties (Fig. 5). Remarkably, energy differences between frontier orbitals are in good agreement with the observed spectroscopic data: DF15 displayed the smallest energy differences between frontier orbitals (2.27 eV), mostly due to a higher HOMO compared to D5, whereas the three carboxypyridine derivatives had comparably larger HOMO-LUMO gaps (2.52–2.68 eV), which could be ascribed to LUMO destabilization and reflected the weaker electron withdrawing character of the carboxypyridine groups compared with that of cyanoacrylic acid.

Scheme 1: Preparation of dyes DF13A,B,C.
To assess the photovoltaic performances of the new dyes, we prepared standard test cells (0.25 cm² active area) sensitized with DF13A,B,C, and recorded their J/V characteristics under standard AM 1.5G simulated solar irradiation (incident power 100 mW/cm²). The resulting curves are shown in Fig. 6a, together with the corresponding average photovoltaic parameters (Table 1). Although devices containing cyanoacrylic acid...
DF13 consistently yielded the best photovoltaic performance, pyridine carboxylic acid dyes DF13A,B,C still provided promising results, with power conversion efficiencies (η) in the 2.75–3.14 % range, corresponding to approx. 55–63 % of the value registered with the dye carrying the standard anchoring group. In two cases (DF13B,C) such values were improved when 1 mM chenodeoxycholic acid (CDCA) was added as a co-adsorbent in order to minimize aggregation processes [34]. IPCE analysis showed that compounds DF13A,B,C were able to convert photons to electrons in a narrower range of wavelengths compared to DF15, which resulted in lower photocurrent values. The red-shifted onset of the IPCE spectrum of DF15 was in good agreement with the profiles of the spectra recorded on TiO2 (Fig. 6b, to be compared with Fig. 4c).

To explain the lower efficiencies generated by dyes DF13A,B,C compared to DF15 we can probably claim an inferior photocurrent generation, which in turn could be due to spectral limitations in the light-absorption process (blue-shifted spectrum, slightly lower molar extinction coefficient).

In order to enhance device photovoltaic efficiency, a structural modification of the dyes was undertaken. It is known, for instance, that alkylation of the nitrogen atom of the pyridine ring might influence the dyes photophysical properties [23, 25]. Indeed, two dyes with the same structure of DF13A,B,C, but with a m-carboxyl-N-methylpyridinium (TJ101) and a N-methylcarboxylypyridinium salt (TJ102) as acceptor/anchoring groups, were reported (Fig. 7): [35] interestingly, dye TJ101, thanks to the withdrawing synergistic effect of the carboxylic group and pyridinium moiety by conjugation with the unsaturated backbone of the molecule (substitution in position 2- and 4-). Once again, the structures of DF39A,C were optimized by means of DFT calculations: energy, shape and electron density distribution of the frontier orbitals were computed for both dyes and compared with those of their non-methylated analogs.
Theoretical calculations showed an increased spatial separation between the electron density distribution of the HOMO and that of the LUMO passing from DF13 to DF39. In particular, DF39A,C were found to have very stabilized LUMOs compared to DF13A,C because of the stronger electron withdrawing character of their positively-charged pyridinium rings. As expected, the calculated absorption maxima ($\lambda_{\text{max}}$) predicted a bathochromic shift for the N-methylated compounds.

In spite of what reported for the synthesis of dye TJ101 [35], direct formation of the pyridinium salt by methylation of carboxypyrindines DF13A,C was not trivial, as reaction with MeI or Me$_2$SO$_4$ gave only the undesired esterification of the carboxylic acid moiety. Using an excess of Me$_3$OBF$_4$, the desired pyridinium salts were obtained, but formation of the methyl esters was also observed, and the latter could not be saponified with bases. Consequently, we decided to protect the carboxylic acid as the corresponding allyl ester, anticipating a possible Pd-mediated deprotection under neutral conditions (Scheme 2). Allylic esters were thus prepared by activation of the corresponding acids with oxalyl chloride followed by in situ reaction with allyl alcohol. Methylation using Me$_3$OBF$_4$ occurred smoothly leading to the desired dyes, DF39C, which was recovered immediately after workup, and DF39A which was obtained after isolation by flash-chromatography and Pd-catalyzed deprotection of the corresponding ester.

Again, the two dyes were spectroscopically and electrochemically characterized, and the measured properties were in agreement with those predicted by calculations. Compared to the corresponding pyridine carboxylates DF13A,C, methylated dyes had largely red-shifted spectra both in solution (CH$_2$Cl$_2$ and EtOH, Fig. 8a and b, respectively) and adsorbed on TiO$_2$ (Fig. 8c), showing the superior electron withdrawing ability of their positively-charged pyridine rings. In addition, they also had 37–61 nm red-shifted absorptions compared to regioisomeric pyridinium salt TJ101, a clear effect of having the alkylated nitrogen atom in conjugated position relative to the sensitizers backbone. Cyclic voltammetry measurements showed that both dyes underwent reversible oxidation processes at the same potential (+0.89 V vs. NHE), which, also in this case, was more positive than the redox potential of the iodide/triiodide couple (+0.4 V vs. NHE), indicating that regeneration of the sensitizers by the latter was allowed.
Cell performances were measured under conditions similar to those applied previously for dyes DF13A–C and compared with those of reference organic dye D35 [37]. Unfortunately dye DF39C appeared to be unstable once adsorbed on TiO₂, rapidly turning to yellow and eventually detaching from the semiconductor under irradiation, thus giving cells with very low efficiencies (<0.2%). Consequently, reasonable photovoltaic parameters were obtained only for compound DF39A, which provided a power conversion efficiency of 1.69%, corresponding to approximately 42% of that obtained with reference dye D35. Such value was enhanced up to 2.61% when chenodeoxycholic acid (CDCA) was added as co-adsorbent and a thick semiconductor layer of 6 μm was used instead of the original thickness of 3 μm. Nevertheless, the recorded η values remained lower than that measured for carboxypyridine DF13A which, in the absence of CDCA, gave an efficiency of 2.79% (Fig. 9a and Table 2). IPCE analysis confirmed that the increased efficiency recorded with dye DF39A in the presence of CDCA was mostly due to photocurrent enhancement, as can be seen from the corresponding curve in Fig. 9b, giving higher conversion efficiency values along the entire absorption profile of the dye.

Clearly, no general efficiency improvement derived from alkylation of the pyridine ring. Such result is not in agreement with findings by Sun et al. [35], who reported a 22–35% increase in efficiency when dye TJ101 was used as a sensitizer instead of its neutral analog TJ101R, and can be possibly explained by the lower molar absorptivity we observed for DF39A compared to DF13A (1.73 × 10⁴ M⁻¹ cm⁻¹ vs. 2.69 × 10⁴ M⁻¹ cm⁻¹, respectively).

Sensitizers endowed with a pyridine-N-oxide anchoring moiety were also recently introduced [38]. For these compounds, photoelectrochemical data suggested a good coordination between pyridine-N-oxide and TiO₂ films, which effectively guaranteed electron injection and stable adsorption of dye molecules. As a consequence, reasonable photovoltaic performances were obtained, however such features were not compared with those of the corresponding compounds bearing the classic cyanoacrylic acid acceptor. Having been shown that both the carboxylic acid and the N-oxide function can independently act as anchoring groups, we reasoned that their contemporary presence on the terminal ring could result in very strong binding of the
sensitizer to the semiconductor surface. Furthermore, the electron withdrawing ability of the N–O bond and of the carboxylic group would make the pyridine ring a strong electron acceptor, thus improving the spectral response of the molecule in the visible region.

To evaluate the combined effect of anchoring groups, we decided to prepare three new compounds, namely compound \( \text{BC1} \), having both the N-oxide- and carboxylic moieties in the anchoring group, compound \( \text{BC2} \), where the acceptor was the simple pyridine-carboxylic acid (similar to the \( \text{DF13} \) series) and compound \( \text{BC3} \), in which the acid moiety was replaced by the electron withdrawing nitrile group, so as to affect the anchoring ability, while maintaining a similar electronic structure (Fig. 10) [39].

All the molecules shared the donor and \( \pi \)-bridge units with known organic sensitizer \( \text{D5} \) (see Fig. 3), which was used as a reference.

Also in this case, DFT ground-state calculations were performed to determine the energy and shape of the new dyes frontier orbitals: thus, the computed HOMO-LUMO gaps for compounds \( \text{BC1} \) and \( \text{BC3} \) were found to be smaller than that calculated for \( \text{BC2} \) (2.52–2.53 eV vs. 2.69 eV), mostly due to a significant stabilization of their LUMOs. Such results confirm the stronger electron-accepting ability of the pyridine-N-oxide function.
compared with a simple pyridine ring. Moreover, in agreement with our expectations, the electronic structures of dyes BC1 and BC3 were found to be very similar, thus allowing a meaningful comparison of the relative binding ability to TiO2. Finally, BC1 and BC3 were predicted to have a red-shifted absorption maximum compared with dye BC2, as a consequence of their smaller HOMO–LUMO gaps. Computed energies of the LUMO levels of dyes BC1,2,3 were comprised in the −2.5 eV to −2.0 eV range vs. vacuum, and were therefore well above the generally accepted value for TiO2 conduction band (−4.0 eV), suggesting the possibility of smooth electron injection following dye photoexcitation [39].

The preparation of compounds BC1,2,3 was accomplished starting from known intermediate 7 (Scheme 3), which, in turn, was synthesized from 2-hydroxy-methylthiophene according to a reported procedure [40,41]. This was converted to the corresponding boronic ester and reacted with the suitable coupling partners (9a,b,c) which were prepared, starting from 4-bromo-2-cyanopyridine (8), in order to have the desired functional groups (N-oxide and/or carboxylic acid, protected as the methyl ester) already installed before C–C bond formation.

Normalized UV/vis absorption spectra of dyes BC1,2,3 in CH2Cl2 solution are reported in Fig. 11a. In agreement with the computational analysis mentioned above, compounds BC1 (∛max = 450 nm) and BC3 (∛max = 448 nm) displayed a clearly red-shifted absorption maxima compared to BC2 (∛max = 426 nm). Despite that, they were still hypsochromically shifted compared to reference dye D5 (∛max = 490 nm in the same solvent) [42]. Furthermore, among the three new compounds, BC1 showed the highest molar absorptivity (approx. 2.91 × 10^4 M−1 cm−1), a value more than double compared to that found for pyridine/carboxylic acid BC2 (approx. 1.07 × 10^4 M−1 cm−1), due its significantly more pronounced donor-acceptor character. Cyclic voltammetry showed that the dyes underwent quasi-reversible oxidation processes at 1.07 –1.10 V (very similar to D5), indicating that the presence of the N-oxide group did not affect the Eox of the compounds to a large extent. Potentials were much more positive than the redox potential of the most commonly used redox systems (such as the iodide/triiodide and Co(III)/Co(II) redox couples), suggesting that regeneration of the sensitizer during operation of a solar cell could indeed take place.

Unfortunately, during the course of these studies it was observed that dye BC3 was unable to be efficiently adsorbed on TiO2. This result was rather surprising, since it had been previously demonstrated by Sun et al. that pyridine N-oxide itself could function as a suitable anchoring group for organic sensitizers [38]. However, it should be pointed out that, compared to Sun's sensitizer, in BC3 the N-oxide function was positioned differently relative to the sensitizer backbone, and that an additional nitrile group was present on the terminal ring. The unfavorable steric interaction between such group and the semiconductor surface
could therefore be responsible for the poor adsorption observed for BC3. Compounds BC1 and BC2, on the other hand, were easily anchored on the semiconductor, and their corresponding UV-Vis absorption spectra are shown in Fig. 11b together with that of cyanocrylic sensitizer D5. Compared to the corresponding spectra in solution, those recorded on TiO2 were clearly blue-shifted and broader, with BC1 displaying the absorption maximum at 411 nm and BC2 at 400 nm, probably due to the deprotonation of dyes upon anchoring onto the semiconductor. Importantly, a similar phenomenon was also observed for compound D5 (446 nm vs. 490 nm for the dye dissolved in CH2Cl2), although in this case the spectrum still had a very red-shifted onset compared to those of BC1 and BC2.

Following the above observations, a series of photovoltaic cells was then built using dyes BC1,2 as well as cyanocrylic acid-based sensitizer D5. Representative J/V curves are shown in Fig. 11c, together with the corresponding average photovoltaic parameters (Table 3). Clearly the efficiency of devices built with dye BC1 was consistently superior to that provided by dye BC2, corresponding to approx. 66 % of that obtained with reference dye D5. The main reason for such behavior can be found in the much higher photocurrent density, which is in agreement with the superior light harvesting efficiency observed for dye BC1 relative to BC2.

Thus, the stronger electron withdrawing character of the pyridine N-oxide/carboxylic acid anchoring group compared to the simple pyridine/carboxylic acid acceptor can be responsible for an improvement in

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<th>Dye</th>
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<td>BC1</td>
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<td>0.68</td>
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<td>BC2</td>
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<td>D5</td>
<td>9.12</td>
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the optical properties of the corresponding sensitizer, which ultimately resulted in an enhanced photovoltaic performance.

**Stability tests of the dyes**

As can be concluded from the previous discussion, the new photosensitizers endowed with pyridine-containing anchoring groups, although in some cases presented promising photovoltaic parameters, were never able to match the efficiencies recorded with their cyanoacrylic acid-containing analogs. Nevertheless, power conversion efficiency is not the only important parameter to assess the performance of a DSSC: cell stability (in turn heavily influenced by the robustness of the dye/semiconductor interface) is also fundamental to evaluate the potential for practical application of the device. In order to understand if the new anchoring groups we introduced could indeed affect the stability of the dye/semiconductor assembly, and thus the stability and durability of the final devices, we studied the kinetics of base-promoted desorption of the dyes from TiO$_2$.

This studies were performed for dyes **BC1-2** and **DF13A,B,C**, which were compared to the corresponding reference dyes **D5** and **DF15**, respectively. Dyed semiconductor films were immersed in a 0.1 M KOH solution in an EtOH/THF 9:1 mixture, and the absorbance of the desorption solution was measured at fixed time intervals. A simple mathematical treatment allowed definition of a “desorption fraction” parameter (namely the amount of desorbed dye in solution relative to the initial amount of adsorbed dye), according to which pseudo-first-order rate constants could be calculated [39].

The experimental plots are reported in Fig. 12a,b and evidently show how desorption of compounds **DF13B** and **DF13C** proceeded more slowly than that of both **DF13A** and reference sensitizer **DF15** (a), while desorption of pyridine-N-oxide **BC1** was slower than that of pyridine carboxylic acid **BC2** and reference dye **D5** (b). Concerning carboxypyridine dyes, the slower desorption of **DF13B** and **DF13C** supports the hypothesis of a possible combined effect of the nitrogen atom and the adjacent carboxylic acid moiety to enhance the stability of the dye/semiconductor assembly (see Fig. 2), which would be impossible in the case of isomer **DF13A**. This observation is not surprising, considering that even the simple pyridine ring has been reported to serve as anchoring group [14]. Based on these observations, device stability tests were also conducted on larger area, transparent cells, which indeed showed that devices built using compounds **DF13B** and **DF13C** retained their efficiency after 930 h of continuous simulated solar irradiation at 50 °C [27]. A similar observation was also made by Grätzel and co-workers, who synthesized a series of very efficient porphyrin sensitizers carrying pyridine-containing anchoring groups (Fig. 13), and found out that dye **MH1** (having the same acceptor as **DF13C**) gave the most stable attachment to TiO$_2$, resulting in more than 90% efficiency retention of the corresponding DSSC after 1000 h of light soaking at 60 °C [43].

The results obtained for compounds **BC1-2** confirm, as we expected, that the simultaneous use of the N-oxide and the carboxylic acid on the pyridine ring provided a very robust attachment of the former dye on
TiO$_2$ surface, although at present it is not clear if the two anchoring groups act by chelating the same titanium atom or rather bind to two different titanium atoms on the semiconductor surface [39]. On the other hand, the difference observed between compounds D5 and BC2 was again consistent with the hypothesis that the pyridine nitrogen could also participate to semiconductor binding.

The results summarized above indicate that the preparation and use of organic sensitizers endowed with pyridine-containing anchoring moieties are usually associated with improved anchoring stability to TiO$_2$ and, in some cases, satisfactory photovoltaic performances, and can thus represent a promising strategy to enhance DSSC lifetime and durability.

References