



A comparison of carboxypyridine isomers as sensitizers for dye-sensitized solar cells: assessment of device efficiency and stability



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ABSTRACT

Three novel organic dyes (**DF13A–C**) carrying regioisomeric carboxypyridine anchoring groups were synthesized by means of a multistep synthetic sequence involving a Pd-catalyzed Stille coupling as the key step. The new compounds underwent full spectroscopic, electrochemical, and computational characterization, and their properties were compared with those of a reference compound endowed with a classic cyanoacrylic acid acceptor (**DF15**). Photovoltaic measurements showed that dye-sensitized solar cells built with dyes **DF13A–C** as photosensitizers yielded power conversion efficiencies corresponding to 54–63% of those obtained with the reference compound. Determination of desorption *pseudo*-first order rate constants indicated that isomers **DF13B–C**, having the nitrogen atom in neighboring position relative to the carboxylic moiety, were removed from TiO₂ more slowly than isomer **DF13A** or cyanoacrylic derivative **DF15**, suggesting a possible cooperative effect of the two functional groups on semiconductor binding: such hypothesis was supported by device stability tests carried out on transparent, larger area cells.

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1. Introduction

In recent years, research concerning new photovoltaic technologies has been the subject of considerable attention from the scientific community, and dye-sensitizer solar cells,¹ in particular, are currently considered one of the most promising classes of devices in the field of third-generation photovoltaics. Since their introduction in 1991,² this type of solar cells has undergone continuous improvements both in terms of power conversion efficiency (PCE) and stability. Even though for long time the best results were obtained with cells incorporating ruthenium-based sensitizers (such as bipyridine complexes **N3** and **N719**),³ and more recently with perovskite-based cells,⁴ the use of metal-free organic dyes with a D– π –A-type architecture still offers some potential advantages, such as the possibility of avoiding the use of precious metals and efficient light-harvesting due to high molar extinction coefficients.⁵ This latter feature would be particularly

advantageous in the construction of colored transparent photovoltaic modules for easy building integration.⁶

D– π –A-type dyes can be modified by introduction of various functional groups, making it possible to tune their stereoelectronic characteristics according to accurate structural design. Briefly, modification of acceptor and donor groups, as well as variation of the length of the conjugated π -bridge, can influence the photo-physical and photochemical properties of the dye, while insertion of bulky groups, such as alkyl chains and aromatic units, can minimize dye aggregation on titania (π -stacking), a phenomenon that usually leads to a decrease in the electron-injection yield of the dye due to intermolecular charge transfer. In the context of our studies on D– π –A organic dyes,⁷ we have recently focused our attention on the optimization of the anchoring/acceptor groups, since they have been less investigated compared to the other sections of the sensitizers but at the same time are essential to provide a good binding and electronic coupling between the semiconductor and the dye. Currently, the most used anchoring group is by far cyanoacrylic acid, which is able to ensure good electronic communication between the dye and TiO₂ by forming a strong bidentate bridging linkage with titanium. For these reasons, this moiety is

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present in most of the D- π -A-type dyes prepared until now. Recently, however, it has been reported that cyanoacrylic acids could undergo an undesirable retroaldolic degradation reaction within the photovoltaic cell under illumination and in the presence of traces of water,⁸ thus limiting device lifetime.

Over time, various research groups have described examples of pyridine-containing acceptor moieties in order to find a more stable anchoring group for D- π -A-type dyes. Harima et al. reported dyes with a simple pyridine acceptor group that maintained a good charge injection efficiency in comparison with carboxylic acids.^{9,10} Subsequently, Delcamp et al. reported one example of a 2-carboxypyridine anchoring group, as well as other heterocyclic, carboxylate-anchored, nitrogen-containing acceptors.¹¹ To improve the electronwithdrawing ability of the acceptor, the groups of Sun and Ooyama introduced a series of *N*-alkylpyridinium derivatives,¹² while Mao et al.¹³ described a 2-cyanopyridine group, which was reported to bind the TiO₂ surface via coordination of titanium sites by the pyridine nitrogen, according to in situ-IR studies. Soon thereafter, our group reported the synthesis of a new dye with a carboxypyridine *N*-oxide acceptor and compared its photo- and electrochemical characteristics with a simple pyridine 2-carboxylic acid analogue.¹⁴ Despite all these efforts, so far the studies on carboxypyridine anchors have only considered single isomers of the acceptor group, and have rarely compared their efficiency and/or stability with classical cyanoacrylic derivatives. For this reason, we have synthesized a first series of sensitizers characterized by the same donor (a substituted triarylamine) and π spacer (vinyl thiophene moiety), but with different regioisomeric carboxypyridines as acceptor groups (**DF13A–C**, Fig. 1), in order to determine how the structural differences would impact their molecular properties, as well as the efficiency/stability of the corresponding DSSCs. Moreover, an analogous dye with a cyanoacrylic acid anchor (**DF15**) was also synthesized to act as a reference compound for our carboxypyridine dyes. The structure of **DF15** differs from that of the

already known dye **D9** for the presence of long-chain alkoxide substituents on the triarylamine,¹⁵ whose purpose was to minimize the aggregation phenomena often occurring with this class of molecules, thus improving their solubility and photovoltaic performances.

2. Results and discussion

2.1. Synthesis of compounds **DF13A–C** and **DF15**

As pointed out above, all the designed structures share the same D- π moiety (Fig. 1). Therefore, known compound (*E*)-**1** (Scheme 1) was selected as a common advanced intermediate for their preparation, and synthesized by means of modified literature procedures (see Supplementary data for experimental details).^{16–18}

The preparation of sensitizer **DF15** was then completed according to the synthetic pathway reported for the well-known dye **D5**,^{19,20} although the synthetic procedures had to be adjusted in order to obtain optimal results for the new compound, for example, formylation of compound **1** under Vilsmeier–Haack conditions gave aldehyde **2** only in low yield, and therefore this step was performed via lithiation of the thiophene ring with *n*-butyllithium followed by quench with *N,N*-DMF (Scheme 1, top).

Preparation of compounds **DF13A–C** was accomplished starting from intermediate **1** as well. Attachment of the acceptor groups was carried out turning the latter compound into the corresponding boron (**3**) or tin (**4**) organometallic derivatives and performing a Pd-catalyzed cross-coupling reaction (Scheme 1, bottom). Indeed, Suzuki coupling between pinacolboronic ester **3** and the appropriate heterocycles **5A–C** was found to be affected by low yields and formation of side-products (homocoupling, protodeborylation). A similar synthetic strategy, based on the Suzuki coupling between pinacolboronic ester **3** and bromopyridine carboxylic acid methyl esters, followed by base-mediated saponification to give the corresponding carboxylates, was also complicated by various undesired side-reactions and characterized by low yield steps and difficult purification of the final products. For this reason, the corresponding tributylstannane **4** was prepared and the possibility to carry out a Stille cross-coupling was investigated. Thus, intermediate **1** was reacted with *n*-BuLi and ClSnBu₃, yielding a mixture of the desired stannane **4** and the starting material in a 3:1 ratio. Purification of the crude by flash column chromatography caused a large loss in the reaction yield due to material decomposition. Nevertheless, we observed that it was still possible to use crude stannane **4**, obtained after a simple aqueous work-up, to perform a Stille cross-coupling with the appropriate bromopyridine.

Optimal reaction conditions were found using Pd(PPh₃)₄ as the catalyst and oxygen-free *N,N*-DMF as the solvent in the presence of CsF and CuI.²¹ The desired products were obtained with excellent selectivity and in moderate to good yields. Subsequent purification of cyanoderivatives **6A–C** and hydrolysis with concentrated aqueous HCl afforded dyes **DF13A–C** in almost quantitative yield and with high selectivity, so that a further purification was often not required.

The thermal properties of the new compounds were assessed by means of TGA. All the dyes showed a good thermal stability, with $\leq 4.0\%$ weight loss up to 220 °C and decomposition temperatures above 400 °C. Only in the case of **DF13B** and **DF15**, a first slight weight loss, perhaps due to decarboxylation, was observed at approx. 240 °C (Fig. S1, Supplementary data).

2.2. Optical and electrochemical properties

The UV–vis absorption spectra of compounds **DF13A–C** and **DF15** were recorded both in CH₂Cl₂ and EtOH solution (Fig. 2, (a)

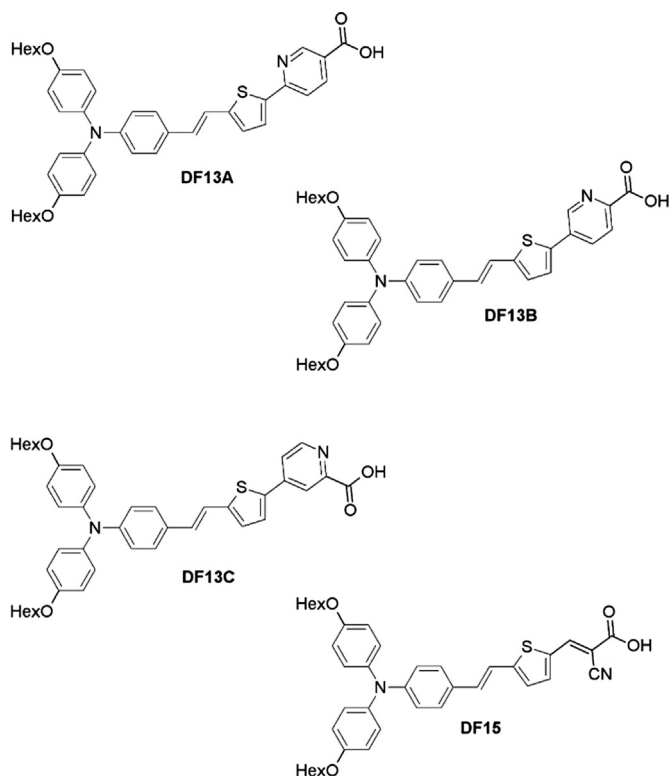


Fig. 1. Structure of the three carboxypyridine isomers **DF13A–C** and of the cyanoacrylic analogue **DF15**.

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