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DSSCs based on aniline derivatives functionalized with a *tert*-butyldimethylsilyl group and the effect of the π-spacer

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ABSTRACT

We have developed four new dyes for DSSCs with a *tert*-butyldimethylsilylether in order to test their physical and photovoltaic properties. These dyes consist of a novel donor based on a functionalized *N,N*-dialkylaniline, a heteroaromatic π-conjugated spacer, such as thiophene or benzothiadiazole ring, and cyanoacetic acid as acceptor group. DFT theoretical studies predict, on the one hand, higher molar extinction coefficient for dyes with thiophene spacers than for those with benzothiadiazole groups while, on the other hand, the use of benzothiadiazole ring would give rise to the reduction of the back electron transfer (BET). The experimental studies have confirmed the predicted higher absorption of thiophene dyes and the better photovoltaic performance of the DSSCs prepared with these dyes. Finally, the stability of the response would support further studies of dyes with anilines functionalized with a *tert*butyldimethylsilyl group to perform long-term devices.

1. Introduction

Solar energy is one of the most competitive alternatives to replace fossil fuels in order to satisfy the growing energy demand. Therefore it is necessary to develop new photovoltaic devices which could compete with traditional schemes. In order to expand the market with new materials with better features as flexibility and the possibility to work using artificial light, alternatives, such as DSSCs (Dye-sensitized solar cells) [1,2], have been developed. These cells are composed by a photoanode consisting of a crystalline semiconductor with adsorbed dye molecules, a redox mediator and a counter electrode. Among them, the sensitizer dye is probably the key element since it governs the light harvesting as well as the free charge generation by the injection of electrons into the nanostructured semiconductor oxide. The organic dyes used as sensitizers are usually based on a D-π-A structure and are both easy to synthesize and environmentally friendly.

Among the variety of donor groups, the aniline moieties offer a simple structure and a good electron-donating ability [3]. Several studies comparing the performance of DSSCs sensitized with *N,N*-dialkylaniline dyes and triphenylamine dyes have been carried out [4]. Clearly, the dyes based on *N,N*-dimethylaniline are superior to those based on TPA in terms of light harvesting, showing batochromic shifted absorption bands. However, this light harvesting advantage does not always result in a higher efficiency because the steric hindrance of the *N,N*-dimethylaniline is not enough to suppress the charge recombination processes [4]. One important factor to take into account to obtain good photovoltaic properties is related to the minimization of π - π stacking which causes aggregation. This may be performed by using additives, such as deoxycholic acid (DCA) [5,6] or by the introduction of bulky groups either in the donor or in the π - bridge [7,8]. The modification of the chromophore shape with bulky substituents makes them more spherical, limiting intermolecular interactions. Although it is relatively difficult to synthesize dyes with bulky chains in the conjugated spacer [9–11] because it requires tedious and multiple reaction steps, organic dyes for DSSCs featuring a trialkylsilyl ether ($R_1R_2R_3SiO$) on the π-spacer were prepared [12]. Studies of nonlinear D-π-A chomophores with a *tert*-butyldimethylsilylether group on the donor part were carried out in our research group

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[13]. This functionalization contributes to increase the solubility of this kind of compounds, a key factor for macroscopic studies and the improvement of the stability of the systems has been reported [13]. Besides this *tert*-butyldimethylsilylether group is readily prepared from alcohols in presence of a weak base [14].

As concerns the π-bridge, it has been demonstrated its relevance in tuning the main photochemical properties [15–19] of the sensitizer and it is commonly designed to expand the solar cell absorption to the red region of the sun spectrum. Among others, various heteroaromatic derivatives, such as oligothiophene, phenyl, pyridine, fluorene, thienothiophene, and benzothiadiazole (BTZ) [20–22] have been explored as π-spacers due to its significant role in regulating the HOMO-LUMO energy levels. In particular, the BTZ unit is used as a building block of low-band gap [23,24]. The incorporation of a BTZ unit in the conjugated π-spacer of metal-free sensitizers results in a red shift of the absorption spectra of the dyes and it has been reported that BTZ based devices have good performance [23,24]. On the other hand, the use of thiophene-based π-bridge provides chemical stability [25] to the final dye.

Finally, most of the D-π-A organic dyes utilize the cyanoacrylic acid as anchoring moiety because the presence of an electron withdrawing cyano group near the anchoring carboxylic acid group enhances the spectral response through intramolecular charge transfer (ICT) as well as its electron injection ability.

The goal of this paper is to study the ability of the novel *N,N*-dialkylaniline functionalized with the *tert*-butyldimethylsilyl group as donor as well as the effect of different heteroaromatic ring based π-spacers on the photovoltaic properties of new D-π-A sensitizers. The four synthesized dyes bear a cyanoacetic acid group as acceptor. In particular, one dye has a thiophene unit in the spacer and another is its higher vinilogue. Moreover, two benzothiadiazole-containing sensitizers are also prepared: one with the benzothiadiazole directly connected to the anchoring group and another with the benzothiadiazole linked to a phenyl. These studies pursue to provide a deeper insight into the structure-properties relationship.

2. Results and discussion

2.1. Synthesis and characterization

Chart 1 shows the D-π-A structure of the four new dyes (**AT-SIL**), (**AT-L-SIL**), (**ABTZ-SIL**) and (**ABTZ-Ph-SIL**). (**TPA**) compound is a well-known dye [3] used for DSSC as a reference in order to compare with the photovoltaic properties and the stability of the new dyes.

Scheme 1 shows the synthesis of these dyes. The aldehydes (**4**), (**5**) and (**6**) were prepared as explained as follows. The donor moiety (**2**) was synthesized according to a procedure described in the literature [26]. In particular, compound (**1**) was prepared by bromination of *N*-methyl-*N*-(2-hydroxyethyl)aniline, and then, the hydroxyl group was protected with *tert*-butyldimethylsilyl chloride to give the compound (**2**). The reactions of the donor moiety (**2**) with the corresponding π-spacers (thiophene, benzothiadiazole and phenylbenzothiadiazole [27]) to give aldehydes (**4**), (**5**) and (**6**) were carried out by the Stille cross coupling reaction which is a versatile carbon-carbon bond formation reaction [28]. The intermediate stannanes are not stable and therefore, compound (**3**) was used in the next step without previous purification.

Aldehyde (**8**) was prepared with two consecutive reactions (Scheme S1, Supporting Information). Firstly, compound (**7**) was synthesized by a Wadsworth-Emmons reaction [29] of the aldehyde (**ALD**), which was prepared following the method described in the literature, and the phosphonate (**P**). Then, a lithiation with *n*-BuLi of compound (**7**) was carried out followed by the addition of *N,N*-dimethylformamide to obtain aldehyde (**8**) [30].

Finally, the Knoevenagel reaction of the aldehydes (**4**), (**8**), (**5**) and (**6**) with cyanoacetic acid in basic media gave, respectively, the dyes (**AT-SIL**), (**AT-L-SIL**), (**ABTZ-SIL**) and (**ABTZ-Ph-SIL**), prepared with the desired D-π-A structure (Chart 1).

2.2. Optical properties

The UV–visible study of the solutions (10^{-4} M THF) of the dyes (**AT-SIL**), (**AT-L-SIL**), (**ABTZ-SIL**) and (**ABTZ-Ph-SIL**) has been carried out and the spectra are shown below.

Fig. 1 shows the higher energy band, which is attributed to $\pi \rightarrow \pi^*$ electronic transitions from the conjugated chain. The spectral range at lower energies shows the charge transfer band between 400 and 550 nm for compounds (**AT-SIL**) and (**ABTZ-Ph-SIL**). The compound (**AT-L-SIL**) presents a broad band which spreads up to 600 nm and, finally, the dye (**ABTZ-SIL**) shows a broad but less intense absorption band.

The molar extinction coefficient (ε) of the compounds was determined in THF solutions 1.10^{-4}-2.10^{-6} M. (Supporting Information, Figs. S1-S4). Table 1 depicts the optical parameters of the dyes.

As concerns the dyes with thiophene in the π-spacer, the extra double bond (**AT-L-SIL**) produces a batochromic shift and a slight decrease of the molar extinction coefficient as compared to the shorter (**AT-SIL**) dye.

With respect to the effect of benzothiadiazole (BTZ) as π-spacer, when this ring is directly linked to the acceptor, compound (**ABTZ-SIL**), a batochromic shift is observed as compared with (**AT-SIL**) dye. However, a phenyl ring just before the acceptor produces a hypsochromic shift of the charge transfer band in (**ABTZ-Ph-SIL**) and, also, the increase of its molar extinction coefficient as compared to (**ABTZ-SIL**).

The emission spectra of solutions (10^{-5} M THF) of the dyes (**AT-SIL**), (**AT-L-SIL**), (**ABTZ-SIL**) and (**ABTZ-Ph-SIL**) were measured. In every case, Stokes shifts ($\Delta\lambda$) are higher than 100 nm which mean that there is a charge transfer in the excited state. The highest $\Delta\lambda$ value corresponds with the compound (**ABTZ-Ph-SIL**). However, the dye (**AT-SIL**) has the smallest Stokes shift among all (Table 1) [31]. These results will be explained in Section 2.4. The quantum yield of these dyes has been determined and the following values were obtained: $\Phi_{\text{AT-SIL}} = 0.10$, $\Phi_{\text{ABTZ-SIL}} = 0.01$, $\Phi_{\text{ABTZ-Ph-SIL}} = 0.06$.

Moreover, a study of the solvatochromism was carried out. Since polarities of the ground and excited states of a chromophore are different, a change in the solvent polarity will lead to different stabilization of such electronic states, and thus, a change in the energy gap between them. Variations in the position, intensity, and shape of the absorption spectra give information about the specific interactions between the solute and solvent molecules. 1,4-dioxane, tetrahydrofurane (THF), acetonitrile (ACN), dichloromethane, methanol (MeOH), *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were used as solvents. Once the solutions were prepared (10^{-4} M), the absorption was measured. Fig. 2 presents the spectra of the four compounds (**AT-SIL**), (**AT-SIL**), (**ABTZ-SIL**) and (**ABTZ-SIL**) in hydrogen bonding acceptor (HBA) solvents: 1,4-dioxane, THF, DMF and DMSO. The normalized UV–Vis spectra of the complete serie of solvents are depicted in the Supporting Information (Fig. S5).

This study shows that the dyes with thiophene in the π-spacer present an analogous behavior, showing a shift to longer wavelengths as the solvent polarity is increased (Fig. 2 a and Fig. 2 b). A clear tendency has not been observed for (**ABTZ-SIL**) (Fig. 2 c) while (**ABTZ-Ph-SIL**) dye shows a slight solvatochromism (Fig. 2 d).

In order to obtain further information about the ground state structure of dyes (**AT-SIL**), (**AT-L-SIL**), (**ABTZ-SIL**) and (**ABTZ-Ph-**