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# COMMUNICATION

# Metal-free organic sensitizers with a sterically hindered thiophene unit for efficient dye-sensitized solar cells<sup>†</sup>

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Two new organic sensitizers for dye solar cells containing a sterically hindered moiety have been synthesized. The introduction of a 3,4-dibutyl-thiophene ring into D– $\pi$ –A dyes reduces the sensitizer aggregation and allows the preparation of solar cells with PCE of 7.17% and 6.27% without the use of coadsorbant agents.

#### Introduction

In recent years environmental issues have led to the search of sustainable energy generated from renewable sources like solar cells. Organic photovoltaics have attracted considerable academic and industrial attention as potential candidates for the market due to the low cost technology and flexible devices.1 Among organic photovoltaic cells, dye sensitized solar cells (DSCs) show power conversion efficiency up to  $11\%^2$  and are undergoing an intense development towards efficient, cheap, long-term stable devices.3 In DSCs the light harvester component, the dye sensitizer, is anchored to a wide bandgap n-transporter semiconductor in the presence of an electrolyte. Since the beginning in 1991,<sup>4</sup> many sensitizer compounds have been developed in the dye class of ruthenium complexes or in the class of metal-free organic donor-acceptor dyes.1 The organic sensitizers show certain advantages over ruthenium-based dyes, such as the high molar extinction coefficient, easy molecular tailoring of the electronic properties and the low cost.5 A large number of studies have been devoted to the molecular engineering of organic chromophores to direct their interaction with the wide band-gap semiconductors and to improve the light-harvesting of the cell. The organic sensitizer is

anchored on the n-semiconductor, usually titania nanocrystals, to promote energy alignments and stacking, which influence the charge generation, the charge collection, and the rectification at the semiconductor/dye/electrolyte interface.<sup>6</sup> The organic dye aggregation has been suggested to induce unwanted intermolecular energy transfer processes or nonradiative pathways, thus reducing the electron injection efficiency from the dye into the semiconductor. Coadsorbants, such as deoxycholic acid (DCA), are usually added into the dye solution to suppress the dye aggregation, resulting in improved performances of the solar cells.7 Another strategy to prevent the sensitizer aggregation, and the consequent low photovoltaic performance, is to design organic dyes with a chemical structure able to avert the dye intermolecular interaction on TiO2 surface. An easy way to reduce the aggregation in conjugated systems like conducting polymers or D- $\pi$ -A dye sensitizers consists in increasing the steric hindrance of the chemical structure.8 In organic dye sensitizers the introduction of moieties containing a hydrophobic alkyl chain in a  $\pi$ -conjugated bridge can increase the steric hindrance and thus decrease the dye aggregation and enhance the tolerance towards water in the electrolyte.9

In this communication we demonstrate that a sterically hindered thiophene ring can be advantageously incorporated into the  $\pi$ -spacer of D- $\pi$ -A dyes with the aim of preventing organic chromophore aggregation. This allows the assembling of efficient solar cells without the common use of DCA coadsorbant that prevents the dye  $\pi$  stacking, but also decreases the loading of the sensitizer on titania. This concept is exemplified by the synthesis and the characterization of two new metal-free organic dyes, DEK1 and DEK2, shown in Fig. 1. The combination of thiophene-based conjugated units with



Fig. 1 Normalized absorption spectra in chloroform of DEK1 and DEK2 and their molecular structures.

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the triphenylamine and cyanoacrylic acid fragments has been already demonstrated as a good strategy to produce stable and efficient organic sensitizers.<sup>10</sup> DEK1 and DEK2 contain the same donor and acceptor groups, while the length and structure of the thiophenic bridges differ. The DEK1 spacer is a tetrathiophene, while DEK2 contains a dithieno[3,2-*b*:2',3'-*d*]thiophene condensed ring with a high intermolecular  $\pi$  stacking and aggregation tendency, inserted between thiophene rings.<sup>11</sup> The conjugated bridge of both dyes contains 3,4-dibutyl-thiophene ring with high sterical hindrance.

In the literature,  $D-\pi$ -A dyes containing 3-alkyl-thiophene moieties<sup>12</sup> and a disubstituted ring<sup>9</sup> in the spacer giving efficient solar cells are reported, but these sensitizers have different donor and acceptor groups with respect to DEK1 and DEK2. The introduction of a dialkyl substituted moiety enhances the dye solubility and hinders both intermolecular interaction and aggregation allowing the preparation of a DSC without a coadsorbant agent.

## Experimental

Both dyes have been prepared using classical reactions: the synthetic procedures and the characterization are described in the ESI<sup>†</sup> (Fig. S1).

The standard mesoporous double layer titania film was employed for solar cell fabrication.<sup>13</sup> A 100 nm TiO<sub>2</sub> compact layer was preliminarily spray pyrolized on the fluorine-doped tin dioxide (FTO) conducting glass electrode, to inhibit charge recombination between the FTO and the electrolyte. A 6  $\mu$ m thick film of TiO<sub>2</sub> nanoparticles (Solaronix HT, 20 nm in size), was first tape cast on the FTO conducting glass. After 15 min drying at 150 °C, a 4  $\mu$ m thick second layer of light scattering particles, with bimodal size distribution (20 nm and 400 nm in diameter, Solaronix D paste) was added. Firing in ambient atmosphere at 450 °C for 30 min followed. The TiO<sub>2</sub> electrode was sensitized by a 20 h immersion into a dye solution (10<sup>-4</sup> M in toluene for both the dyes). A platinized FTO conducting glass was applied as the counter electrode. The cell was assembled by separating the electrodes by a 25  $\mu$ m thick plastic spacer and injecting the electrolyte by means of capillary force.

The cell performances were measured by using a ABET 2000 solar simulator at AM 1.5G (100 mW cm<sup>-2</sup>). The impedance spectroscopy was done using a SOLARTRON 1260A Impedance/Gain-Phase Analyzer, with an AC signal 20 mV in amplitude in the frequency range between 10 mHz and 300 kHz. The applied bias was between 0 V and 100 mV above the open circuit voltage of the solar cell.

#### **Results and discussion**

DEK1 and DEK2 show absorption maxima in the visible region (477 nm and 465 nm respectively) and have high molar extinction coefficients ( $\varepsilon = 53.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\varepsilon = 57.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  respectively) which are extremely important for DSC applications since they will allow the use of thinner TiO<sub>2</sub> films contributing to a better charge separation and lower charge recombination. Moreover, the comparison of UV spectra in the solid state and in solution evidences similar maxima for both DEK1 and DEK2, suggesting a poor aggregation in film. The cyclic voltammogram of both DEK1 and DEK2 shows a reversible oxidation wave at 1.09 V and 1.03 V respectively *versus* NHE due to the oxidation of the triphenylamine moiety. The LUMO energy levels of DEK1 and DEK2 are -3.55 eV and -3.50 eV, respectively and are higher than the conduction band

edge of titania, assuring the electron injection from the excited dyes to the metal oxide semiconductor. In addition, the ground-state oxidation potentials of these sensitizers are higher than the redox potential (0.35 V vs. NHE) of the electrolyte iodine/triiodide couple, which could lead to a fast dye-regeneration.

Dye loading on  $TiO_2$  surface was quantitatively evaluated by UV-Vis spectrophotometry (see ESI† Fig. S3).

The adsorbed dyes were completely removed by means of a triethylamine/chloroform (9/1, v/v) solvent mixture. DEK1 was found to be loaded onto the titania surface with average values of about  $4.4 \times 10^{-7}$  mol mm<sup>-3</sup>, a higher amount than the loading of  $3.5 \times 10^{-8}$  mol mm<sup>-3</sup> found for DEK2.

Interaction of DEK1 and DEK2 with the titania surface was investigated by diffuse reflectance infrared spectroscopy (DRIFT) (see ESI† Fig. S4). Spectral features of dye-loaded photoanodes suggest a unidentate coordination of carboxylic groups towards the titania surface. The cyanide group is not involved in the dye anchoring on the titania surface, its stretching vibration is completely preserved in shape and position in both unloaded and loaded dye spectra.

J-V characteristic curves of solar cells under simulated sunlight irradiation are reported in Fig. 2 for DEK1 and DEK2 dyes with the addition of DCA at various concentrations. As a comparison, the functional properties of a cell fabricated using the same photoanode sensitized by the commercial N719 dye is reported. The short-circuit current density ( $J_{SC}$ ) linearly increases with the light power density, while a logarithmic behaviour has been found for the open-circuit voltage ( $V_{OC}$ ), as expected for a well operating DSC (see ESI† Fig. S5 and S6). Photoconversion efficiency (PCE) values up to 7.17% and 6.27% have been obtained for the DEK1 and DEK2 molecules respectively, without DCA. Addition of DCA has no beneficial effect



**Fig. 2** (a) J-V characteristic curve of DEK1 and DEK2 solar cells under simulated sunlight irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>) at different DCA concentrations. Solid line: no DCA; dashed line: 50 mM; dash/ dotted line: 100 mM.

**Table 1**Functional properties of solar cells sensitized with DEK1 andDEK2 under sunlight irradiation (AM 1.5G, 100 mW cm $^{-2}$ ) with andwithout DCA coadsorbant

Dye	[DCA]/mM	$J_{\rm SC}/{\rm mA~cm^{-2}}$	$V_{\rm OC}/{\rm mV}$	FF (%)	PCE (%)
DEK1	0	14.2	765	66.0	7.17
	50	12.3	777	66.6	6.37
	100	3.5	875	64.8	1.99
DEK2	0	13.5	715	65.0	6.27
	50	13.0	715	62.7	5.83
	100	3.5	875	64.8	1.99
N719	0	16.0	780	67.0	8.36

on the overall cell performances (functional features collected in Table 1). 50 mM DCA induces slight increase of  $V_{\rm OC}$  in DEK1 cell, at the expense of significant decrease of  $J_{\rm SC}$ , while no significant change has been recorded for DEK2 cell. 100 mM DCA noticeably increases  $V_{\rm OC}$  for both dyes, but drastically depresses the current density, resulting in very poor PCE.

The presence of the coadsorbant agent produces a decrease of the dye aggregation, usually leading to an increase of the photovoltaic performances, and a slight decrease of the dye loading on the  $TiO_2$  surface. The DEK1 and DEK2 aggregation is low, as shown in the solid state UV spectra, thus in our case the lower cell performances in the presence of DCA is most likely due only to the decrease of the dye loading.

The transient open circuit photovoltage measurements shown in Fig. 3 indicate slow rate of electron recombination, as deduced by the electron life-time  $\tau_n$  versus  $V_{OC}$ . This is a clear indication of the high capability of both DEK1 and DEK2 to quickly inject the photogenerated electrons inside the TiO<sub>2</sub> network before exciton recombination, inducing high photovoltage, which tends to slowly decrease due to recombination losses.

The constant behavior of PCE and FF as a function of light power density (see ESI<sup>†</sup> Fig. S7) is a sign that the recombination processes inside the cell are almost independent of the concentration of photoexcited electrons, which is one further proof of the good functional properties of the cell; *i.e.*, electron injection is not the process limiting cell efficiency, indicating that both DEK1 and DEK2 exhibit excellent properties from the point of view of their application as light absorbers in DSCs.

**Fig. 3** (a) Transient photovoltage decay and (b) electron lifetime  $\tau_n$  for DEK1 (solid line) and DEK2 (dashed line) solar cells without DCA under simulated sunlight irradiation (AM 1.5G, 100 mW cm<sup>-2</sup>).

Fig. 4 Impedance spectroscopy spectra showing the impedance behaviour of Z at different external applied bias voltages for a cell sensitized with DEK1. On increasing  $V_{\text{bias}}$  the main ark shrinks and permits (inner block) the emergence of small features related to the diffusion process and charge transfer at the back contact.

The electrochemical behaviour of the cells has been investigated *via* electrochemical impedance spectroscopy (EIS) in the dark at bias voltage  $V_{\text{bias}}$  ranging between 0 V and 100 mV above  $V_{\text{OC}}^{14}$  (see Fig. 4). The simplified equivalent circuit applied to elucidate the main features of the transmission line shows for both DEK1 and DEK2 all the physicochemical processes taking place in a properly operating photoelectrochemical device, *i.e.* the effect of the recombination resistance and of the chemical capacitance, the contribution of the transport resistance related to electron diffusion through titanium oxide nanoparticles, the charge diffusion inside the electrolyte, <sup>15</sup>

## Conclusions

Two novel organic dyes containing a sterically hindered moiety that prevents dye aggregation on TiO<sub>2</sub> photoanodes have been synthesized. The introduction of a 3,4-dibutyl-thiophene in the spacer of two D- $\pi$ -A sensitizers prevents the intermolecular  $\pi$  stacking of the organic conjugated molecules responsible for the aggregation in the solid state. This strategy of insertion of a hindered thiophene allows the preparation of efficient solar cells without the need of acid additives coadsorbed on TiO2. Moreover, even in the case of the dithienothiophene containing spacer, which has strongly  $\pi$  stacking and aggregation properties, the presence of a sterically hindered thiophene ring will definitely minimize the dye aggregation. DSCs sensitized by DEK1 and DEK2 demonstrated highly promising PCE values of 7.17% and 6.27%, respectively. Improved photoconversion of DEK1 with respect to DEK2 may be ascribed to enhanced dye loading. DEK1 exhibits dye loading about twelve times higher than DEK2. Addition of DCA negatively affects cell functional properties, since high depression of current density is found, while only small increase of  $V_{\rm OC}$  has been demonstrated.

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