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Article

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Injection and Recombination in Dye-Sensitized Solar Cells with a Broadband Absorbance Metal-Free Sensitizer Based on Oligothienylvinylene

Rubén Caballero,[†] Eva M. Barea,[‡] Francisco Fabregat-Santiago,[‡] Pilar de la Cruz,[†] Lourdes Márquez,[‡] Fernando Langa,*[,†] and Juan Bisquert*[,‡]

Instituto de Nanociencia, Nanotecnología y Materiales Moleculares (INAMOL), Universidad de Castilla - La Mancha, Campus de la Antigua Fábrica de Armas, Avda. Carlos III, s/n 45071 Toledo, Spain, and Departament de Física, Universitat Jaume I, 12071 Castelló, Spain

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A new metal-free sensitizer for improved light harvesting with dye-sensitized solar cells (DSC) has been synthesized and fully characterized. The molecular sensitizer was engineered by linking the tiophenes groups by methine units, improving light absorption until 760 nm wavelength. In conventional DSC configuration the dye produces short-circuit current density of 13.4 mA/cm^2 at 1.5 AM illumination (100 mW cm^{-2}) and the incident photon-to-current conversion efficiency (IPCE) of 58%. The causes for the limitation to the photocurrent are investigated by impedance spectroscopy measurements, and it is shown that metal-based and metal-free molecular sensitizers show distinct characteristics concerning the blocking of the TiO$_2$ surface with coadsorbents to prevent electron recombination.

1. Introduction

Dye sensitized solar cells (DSCs) based on molecular-sensitized nanostructured metal-oxides have attracted significant attention as low-cost photovoltaic devices.[1−3] The photosensitizer plays important roles in determining the stability, light harvesting capability and also the total cost of DSCs. Presently the most important photosensitizers are Ruthenium Dyes, such as N719, N3, Black Dye,[4−6] etc, that are well-known and produced in commercial fabrication. Dyes of another kind, called metal free dyes,[7−9] show quite promising characteristics: (1) a large molar extinction coefficient, (2) lower cost than Ru dyes, and (3) control of the absorption wavelength modifying the synthesis method.[10,11] It is well-known that changes in molecular structure and conjugation systems can induce very different optical and physical properties of donor−acceptor π conjugated compounds. When the acceptors or the donor groups, or the linkers between both, are modified, the absorption can be shifted toward the red part of the solar spectrum, which is a future requirement for high performance DSC that should harvest most of the visible and also near IR photons in the solar spectrum. Efficient DSCs have been prepared by using metal free dyes incorporating oligothiophenes (oTs).[12,13]

Here, we present a new metal free dye (RC4-17) sensitizer. The novel metal free organic dye molecule is based on a four units oligothienylvinylene system (4TV) carrying a cyanoacrylic acid moiety as acceptor and as an anchoring unit for the attachment of the dye onto TiO$_2$ nanoparticles. Oligothienylvinylene (oTV) systems have shown to be efficient systems for nanoelectronics showing a decrease of the low HOMO−LUMO gap and better π-electron delocalization respecting to oTs.[14] Finally, alkyl groups were attached to the thiophene in order to enhance the solubility, produce a bathochromic shift on the absorption maximum proportional to the number of alkyl groups, and avoid the aggregation phenomena[13] between molecules due to the alkyl steric impediments (Figure 1).

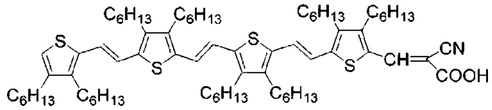

Figure 1. Molecular structure of RC4-17.

We describe in this paper the synthesis, absorbance characteristics of the RC4-17 sensitizer, and the photovoltaic performance in DSCs in a variety of conditions. We also investigate by means of impedance spectroscopy the interfacial energetic and kinetic properties that determine the photocurrent.

2. Experimental Section

2.1. Synthesis of the Organic Dye. Figure 2 shows the synthetic approach for RC4-17 from the previously described 4TV[15,16] by Vilsmeier formylation followed by Knoevenagel condensation with cyanoacetic acid in the presence of pyperidine. RC4-17 was fully characterized by MALDI-TOFF mass spectrometry as well as ^{1}H and ^{13}C NMR, FT-IR, and UV−vis spectroscopies. Further details are given in the Supporting Information.

2.2. Dye Solar Cells (DSC) preparation. Several RC4-17 DSCs were prepared using TiO$_2$ nanocrystalline paste prepared by hydrolysis of titanium tetraisopropoxide[1] with the addition of ethyl cellulose as a binder in α-terpineol. The TiO$_2$ layers were deposited with doctor blading technique on transparent conducting glass (TCO glass; Pilkington TEC15, ∼15 Ω/sq resistance). The resulting photoelectrodes of 10 μm thickness were sintered at 450 °C and then immersed in 0.04 M TiCl$_4$ solution for 30 min at 70 °C followed by calcination at 450 for 30 min. When the temperature decreased until 40 °C, the electrodes were immersed into dye RC4-17 solution (0.3 mM in dichloromethane) overnight (16 h). After the adsorption of the dye, the electrodes were rinsed with the same solvent. As the treatment with the dye solutions is the same for all prepared

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* To whom correspondence should be addressed. E-mail: Fernando.LPuente@uclm.es (F.L.); bisquert@fca.uji.es (J.B.).

[†] Universidad de Castilla - La Mancha.

[‡] Universitat Jaume I.

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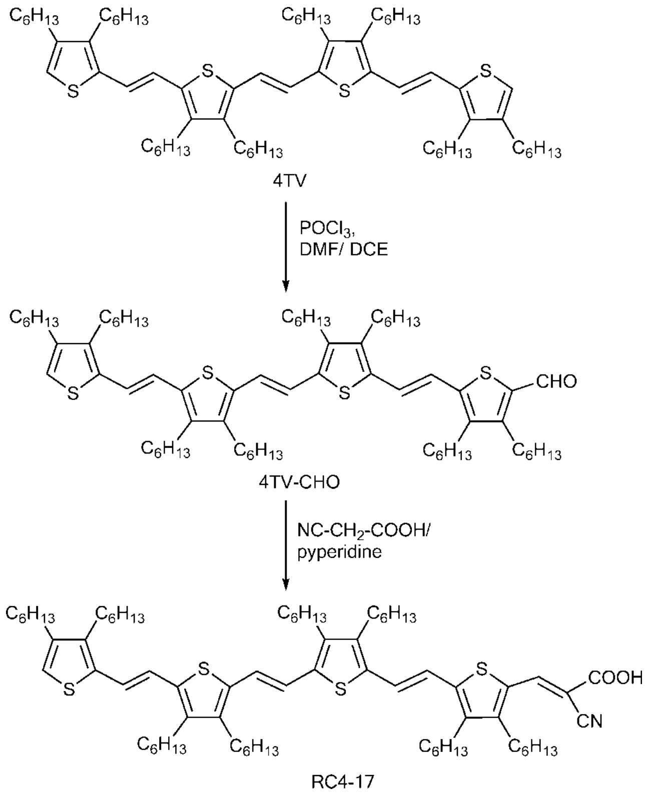

Figure 2. Synthesis of RC4−17.

photoelectrodes (10 μm thickness), the amount of absorbed dye is similar, and this is confirmed with the results of the different DSCs measured. The solar cells were assembled with a counter electrode (thermally platinized TCO) using a thermoplastic frame (Surlyn 50 μm thick). Redox electrolyte (as detailed below) was introduced though a hole drilled in the counter electrode that was sealed afterward. Prepared solar cells (0.5 cm^2 size, masking solar cell to 0.2 cm^2) were characterized by current−voltage characteristics, IPCE and impedance spectroscopy. Photocurrent and voltage were measured using a solar simulator equipped with a 1000 W ozone-free xenon lamp and AM 1.5 G filter (Oriel), where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sunlight intensity (100 mW cm^{-2}). For each dye and electrolyte used, seven cells were prepared using this methodology to check the consistency of the results and their reproducibility was confirmed.

3. Results and Discussion

3.1. Dye Characterization. Figure 3 shows the UV−vis spectra of the RC4-17 sensitizer, that presents absorption until 760 nm with an absorption maximum at 557 nm in Dichloromethane (DCM) (ε = 26 302 M^{-1} cm^{-1}). In addition, the compound shows a band in the UV region (around 290 nm), and two light bands due to the π−π* transitions of the conjugated molecule in the visible region at 350 and 430 nm.

Taking into account that the dye cannot be dissolved in the electrolyte (3-methoxypropionitrile) used for making the cells, the range of the spectrum where the dye attached on TiO$_2$ film is absorbing light is between 380 until 700 nm wavelength (Figure 4a). Remarkably, when dye is absorbed in the film, the maximum absorption band is shifted toward the red part of the solar spectrum, around 600 nm wavelength, compared to the monomeric species in the solution, due to the close packing[17,18] onto TiO$_2$.

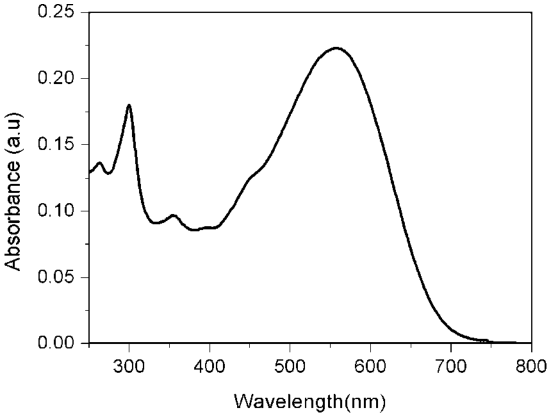

Figure 3. UV−vis absorption spectrum of RC4−17.

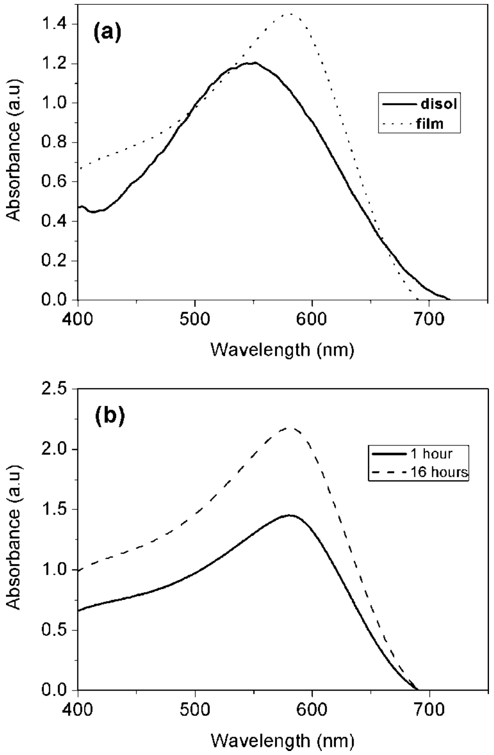

Figure 4. UV−vis spectrum of RC4-17. (a) UV−vis spectrum of the dye solution (solid line) compared with the absorption spectrum of the dye attached to TiO$_2$ (dashed line). (b) Different sensitizing time of TiO$_2$ electrodes, 1 h (solid line) and 16 h (dashed line) in DCM as solvent. The spectra have been vertically offset for clarity of display.

It is well-known that the aggregation phenomena[19−21] during the TiO$_2$ sensitization time decrease the injection of electrons and the overall performance of the DSC. In order to prevent this effect reducing aggregation, the dye has been engineered introducing C$_6$H$_{13}$ to substitute the thiophene moiety. To confirm this feature the immersion time of the TiO$_2$ film in the sensitizing solution has been varied from 1 to 16 h. The UV−vis spectra and the performance of the cell did not present any change (Figure 4b). To further confirm that no significant aggregation occurs on the metal-oxide surface, in a parallel experiment 3 mM chenodeoxycholic acid was added in the dye solution to prevent the dye aggregation on the TiO$_2$ surface and the UV−vis spectra (not shown) matches exactly the spectrum shown in Figure 4a dotted line.

It is well established in the literature[22] that push−pull chromophores based on thienylvinylene present intense solva-

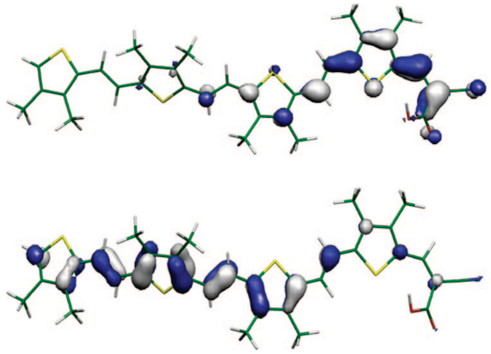

Figure 5. Frontier orbitals LUMO (top) and HOMO (bottom) of RC4-17 optimized at the B3LYP/6-31G* level.

TABLE 1: Photovoltaic Performance of RC4-17[a]

dye	electrolyte[b]	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)
RC4-17	0% MBI	13.4	0.50	0.57	3.84
RC4-17	100% MBI	9.21	0.55	0.57	2.89
N719-refer	100% MBI	16.3	0.71	0.44	6.41

[a] Values are obtained using an average over 7 DSC for each electrolyte, prepared with the same methodology. Photovoltaic performance of DSC based on RC4-17 and N719 under AM 1.5 irradiation. J_{sc} is the short circuit photocurrent density, V_{oc} is the open-circuit voltage, ff is the fill factor, and η is the power conversion efficiency. [b] The amount of MBI is modified in the electrolyte solution.

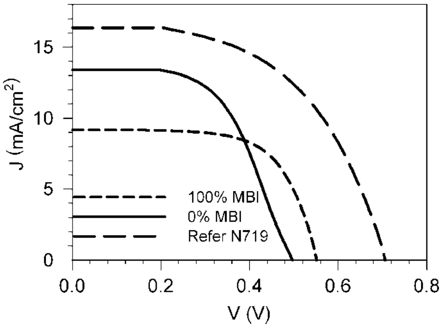

Figure 6. current−potential (*J*−*V*) curves for DSCs using RC4-17 and N-719 sensitizers, under AM 1.5 irradiation.

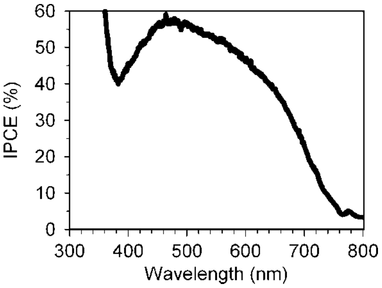

Figure 7. IPCE spectrum for a DSC based on RC4-17 with 100% of MBI.

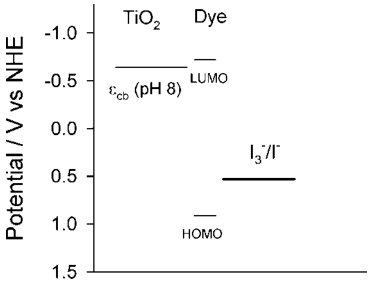

Figure 8. Energy diagram showing HOMO−LUMO levels and band gap of RC4-17.

tochromism; hence, the emission bands can shift in wavelength due to the different solvent polarity. This effect has been checked dissolving RC4-17 in butanol and DCM. The absorption maximum is 531 nm for butanol and 557 nm for DCM (data not shown). In this case the solvent effect is not critical, keeping the absorption range constant with a slight shift of the maximum, from 531 to 557 nm.

Figure 5 shows the calculated molecular structure of RC4-17 at the B3LYP/6-31G* level and the electron distribution of its HOMO and LUMO. Calculations indicate that the HOMO is distributed along the 4TV conjugated system and the LUMO is located over the cyanoacrylic unit through thiophene. This distribution suggests the existence of charge transfer from the donor (nTV) to the acceptor (cyanoacrylate) units, allowing significant charge separation within the dye after photoexcitation. Furthermore the location of the LUMO at the side of the TiO_2 surface and the HOMO at the opposite end of the molecule, eases the electron injection into the semiconductor and prevents back regeneration of the dye with the injected electrons. The distribution of the HOMO along the whole 4TV conjugated chain also improves the regeneration of the dye with the redox couple. Efficient photoinduced electron transfer from nTV to good electron acceptors as C_{60} has been previously observed.[23,24]

3.2. Photovoltaic Performance of DSC. To understand the relationship between dye structure, photophysical and photoelectrochemical properties, we have studied the performance of DSC based on this metal free sensitizer in a variety of conditions.

A DSC with RC4-17 as a sensitizer was prepared, the composition of the standard electrolyte, named 100% MBI (1-methylbenzimidazole) is 0.5 M LiI (99,9%), 0.05 M I_2 (99,9%), 0.5 M MBI (99%) in 3-methoxypropionitrile (98%). As a reference, a N719 DSC was prepared by the same procedure and with the standard electrolyte (100% MBI). In Table 1 are shown the characteristics for these two DSCs prepared and the photocurrent density−voltage (J–V) curves are shown in Figure 6. The overall conversion efficiency (η) for RC4-17, is 2.89%, while under the same conditions the efficiency of N719 is 6.41%. In the range 300 to 800 nm the IPCE (Incident photon-to-current conversion efficiency) of RC4-17 (Figure 7) reached values of about 58%.

It is known that to get an efficient charge separation, the LUMO of the dye from where the electron injection occurs has to be at sufficiently more negative potential than the conduction band edge of the TiO_2 (E_{CB}), and the HOMO has to be more positive than the redox potential of iodine/iodide. Figure 8 shows the energy levels diagram calculated from cyclic voltammetry (CV) of RC4-17 using the methods indicated in ref 25. The HOMO level is sufficiently more positive than the iodine/iodide redox potential value, indicating that the oxidized dyes formed after electron injection to TiO_2 could accept electrons from I^- ions thermodynamically so that inefficient regeneration by the I^- is not expected. The LUMO level is slightly negative to the E_{CB} for acid TiO_2 paste.

From the energy diagram (Figure 8), due to the short energy gap between E_{CB} and the LUMO level of RC4-17, additional engineering on the solar cell energetics was developed to improve its performance. It is known that the MBI shifts the E_{CB} of TiO_2 negatively[26,27] and makes more difficult the electron injection from excited dye to TiO_2. And in this case, due to the close position of the LUMO of the dye with respect to the E_{CB} of the TiO_2, the presence of MBI

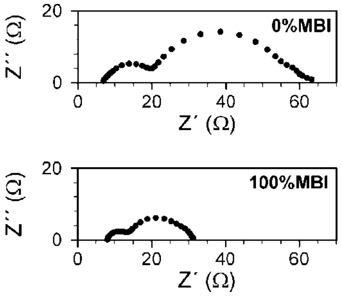

Figure 9. Impedance plot of DSC with different composition of electrolyte: 0% MBI and 100% MBI cells. Measured at V_{oc} potentials under AM 1.5 irradiation.

in the 100% MBI electrolyte composition, could lower the electron injection from the excited dye to the TiO_2, by negative shift of E_{CB}, decreasing the photocurrent. Therefore, the standard electrolyte (100%MBI) composition was modified, removing MBI from the electrolyte. With the new electrolyte composition, 0% MBI, it is observed (Table 1 and Figure 7) that the J_{sc} is higher (13.4 mA/cm^2) because the E_{CB} of TiO_2 is shifted downward, which produces a minimum decrease of the V_{oc}. The increase of efficiency ($\eta = 3.84\%$) in the absence of MBI suggests that at the same time that MBI rises the conduction band[10] and diminishes injection, it may produce another effect not previously observed.[27]

Impedance spectroscopy measurements (Figure 9) were performed on the same cells in order to clarify this effect. All measurements were carried out with an irradiation of AM 1.5 at V_{oc} scanning the frequencies from 1 MHz to 0.1 Hz. These measurements were analyzed using the impedance model developed by Bisquert et al.[28−30] According to this model, the high-frequency arc corresponds to the parallel combination of the charge transfer resistance at the platinized electrode, $R_{\text{ct}_{\text{Pt}}}$ and the Helmholtz capacitance at this interface and the second arc corresponds to the combination between the charge-transfer resistance of the charge recombination process between electrons in mesoscopic TiO_2 film and I_3^- in electrolyte, R_{ct}, and the chemical capacitance of the semiconductor. A third arc present in the model is attributed to diffusion processes, that arc is observed in the present measurements as a small deformation of the second arc and is not taken in account on the value of R_{ct}.

In this particular case, the relevant parameter affecting the response of the cell is R_{ct}.[29] As may be observed in Figure 9, for 0% of MBI, the value of R_{ct} is nearly 3 times larger than in the case of 100% MBI. This means that the electrons injected into the TiO_2 nanoparticles recombine with the electrolyte at lower rate in the absence of MBI than in the case of its addition, preventing the achievement of a higher V_{oc} when MBI is added.

This result diverges from the one obtained in the case DSC with N3 dye[26,27] which is quite general for other Ru based dyes, where besides the shift in the band the MBI coats the parts of TiO_2 uncovered with dye, producing a reduction of the recombination rate. Here this coating is not produced, probably because there is not surface available for massive MBI link. Instead, with the rise of the position of the Fermi level of electrons, the interaction with the acceptor states in the redox couple increases the transfer rate.[30] From this result, the next step for the future studies must be to improve the electrolyte composition, in order to increase the V_{oc} as much as is possible, taking into account the energy levels, and blocking the possible recombination processes with alternative additives, improving the overall performance of the RC4-17 DSC.

4. Conclusions

We have successfully fabricated a novel metal free dye based on four units of thienylvinylene. The obtained dye showed high stability, good short-circuit current density ($J_{\text{sc}} = 13.4$ mA/cm^2) and reproducible solar cell efficiency. This dye presents important properties such as short absorption time on TiO_2 films without any indication of aggregation process, absorption toward the far-red region and chemical stability. The easy of synthesis and future modifications to further extend the absorption range present it as one of the promising metal free dye for the fabrication of efficient and stable dye solar cells.

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Supporting Information Available: Synthetic procedures and characterization details for RC4−17. This material is available free of charge via the Internet at http://pubs.acs.org.

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