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Effect of the bridge substitution on the efficiency of dye-sensitized solar cells

Beatriz Pelado^a, Pilar de la Cruz^a, Victoria González-Pedro^b, Eva M. Barea^{b,*}, Fernando Langa^{a,*}

^a 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

^b Photovoltaic and Optoelectronic Devices Group, Physics Department, Universitat Jaume I, 12071 Castelló, Spain

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ABSTRACT

We have designed and synthesized a novel D– π –A dye based on zinc porphyrin as the donor, cyanoacrylic acid as the acceptor and *trans*-bis(3,4-ethylenedioxythiophene)vinylene as the bridge. Under standard global AM 1.5 solar conditions, the Zn-porphyrin-2-EDOT sensitizer based cell gave a J_{SC} of 7.28 mA cm⁻², V_{OC} of 0.438 V was obtained with a FF of 0.514, corresponding to an overall conversion efficiency $\eta = 1.64\%$. The reasons for this low efficiency are analyzed to try to develop knowledge for future dye designing.

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Dye-sensitized solar cells (DSCs) based on nanocrystalline TiO₂ electrodes have received considerable attention because of high incident solar light-to-electricity conversion efficiency and low cost of production.¹ Recently, much research has focused on the development of new metal-free organic dyes as a cheap alternative to Ru dves as the feasible modification of their structure, the large molar extinction coefficients and moreover, their electrochemical and photophysical properties can be tunable by synthesis. In this sense, porphyrins are one of the most widely studied sensitizers for DSCs because of their strong Soret (400-450 nm) and moderate O bands (550–600 nm). Elongation of the π conjugation and loss of symmetry in porphyrins cause broadening and a red shift of the absorption bands together with an increasing intensity of the Q bands relative to that of the Soret band. On the basis of this strategy, the cell performance of porphyrin-sensitized solar cells has been improved intensively² and efficiencies up to 12.7% have been achieved.3

As part of our research on developing new organic sensitizers,⁴ we recently described a new dye **1** (Zn-Por-2TV-COOH, Chart 1),⁵ carrying a Zn-porphyrin conjugated to a thienylenevinylene oligomer (TV) carrying alkyl chains. The solar cell prepared with dye **1** provided a threefold enhancement of the photocurrent (η = 4.77%) with respect to the parent dyes (Zn-Por-COOH and 2TV-COOH), as a consequence of the additional strong light absorption in the region of 400–650 nm leading to a IPCE of 60%.

3,4-ethylenethiophene (EDOT) has been widely studied as a building block for the synthesis of functional π -conjugated



Chart 1. Structures of dyes 1 and 2.

systems, due to a unique combination of strong electron donor properties and self-structuring effects.⁶ EDOT unit has been used for the design of polymers with low band gap or specific electrochemical properties and PEDOT occupies a prominent position among conducting polymers due, among other things, to the multiple well-established technological applications of its various conducting forms.⁷ Finally, in the last years, EDOT has been employed as a spacer in D– π –A push–pull systems, some of them applied in the development of DSCs.⁸



^{*} Corresponding authors. Tel.: +34 925 268 843; fax: +34 925 268 840 (F.L.). *E-mail address:* fernando.langa@uclm.es (F. Langa).

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Herein, we describe the synthesis of the new D– π –A dye **2** (Chart 1), in which, different to dye **1**, the 3,4-dihexylthiophene rings were substituted by 3,4-ethylenedioxythiophene (EDOT). Their optical and electrochemical properties were studied and, additionally, dye **2** has been tested in DSC.

The synthesis of dye 2 has been accomplished according to Scheme 1. Phosphonate 3 was prepared by the quantitative reduction of 3,4-ethylenedioxythiophenecarbaldehyde⁹ with NaBH₄ followed by in situ reaction with triethylphosphite in the presence of iodine. After removing in vacuo the excess of triethylphosphite, **3** was purified by column chromatography (silica gel, hexane:AcOEt, 1:1) and obtained in 95% yield, improving significantly the described procedure.¹⁰ Horner–Wadsworth–Emmons (HWE) reaction between **3** and 3.4-ethylenedioxythiophenecarbaldehyde, vielded *trans*-bis-(3.4-ethylene-dioxythiophene)-vinylene (**4**) as a vellow solid in 88% vield, showing that to be a better procedure than the method previously described (49%) from a Grignard reagent.¹¹ Double Vilsmeier formylation reaction of **4** afforded bisaldehyde 5, in quantitative yield. The crucial step was the HWE olefination between the corresponding phosphonate-Zn-porphyrin¹² and 4under careful stoichiometry control giving monoaldehyde 6 in 42% yield as a red solid (mp >300 °C), purified by column chromatography (silica gel, hexane:dichloromethane, 3:7). The measured coupling constant (1) values in the ¹H NMR spectrum of **6** clearly show the *E* geometry of both, the double bond between the porphyrin ring and the thiophene (J = 16 Hz) and the double bond between both thiophene rings (J = 16 Hz). Finally, Knoevenagel condensation of 6 with cyanoacetic acid in the presence of piperidine yielded, after purification by column chromatography (chloroform:methanol 9:1) dye 2 as a purple solid (mp >300 °C) in 74% vield. All new compounds were fully characterized by MALDI-TOF mass spectrometry as well as ¹H and ¹³C NMR, FT-IR, and UV-Vis spectroscopies.¹³

The optical and electrochemical properties of dye **2** have been analyzed by UV–Vis absorption spectroscopy, fluorescence emission spectroscopy and cyclic (CV) and Osteryoung (OSWV) voltammetries.

The UV–Vis absorption spectrum of dye **2**, recorded in dichloromethane (Fig. 1 and Table 1), exhibits an intense Soret band



Figure 1. UV-Vis spectrum of dye 2 (in dichloromethane).

characteristic of the porphyrin at 422 nm (log ε = 4.99) and a continuous absorption in the visible region, up to 650 nm, due to the presence of the oligothienylenevinylene moiety, with maxima corresponding to the Q bands of the porphyrin at 552 nm (log ε = 4.32) and 595 nm (log ε = 4.09).

Figure 2 shows the steady-state fluorescence spectra of dye **2** in dichloromethane (solid line) exciting at the Soret band of the porphyrin (λ_{exc} = 422 nm) and the typical porphyrin emission at 603 nm and 649 nm is observed. However, in the presence of TiO₂ (dotted line) the fluorescence of the porphyrin is totally quenched indicating efficient electron injection from the sensitizer into the conduction band of the TiO₂ semiconductor through the conjugated bridge; a similar quenching is observed when excited at 554 nm wavelength where the absorption of the oligothienyl-enevinylene bridge is predominant.

The electrochemical properties of dye **2** were investigated in solution by cyclic and Osteryoung square wave voltammetries at



Scheme 1. Synthesis of dye 2.

Table 1				
Data of UV-Vis and fluorescence emission and electrochemical data (OSWV, V	vs Fc/Fc ⁺) for dyes	1, 2, and precursor	rs 3 and ZnPor-Br	
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λ _m ,	_{ax} ^a (nm)	$\log^{a}(\varepsilon)$	$\lambda_{em}^{a,b}(nm)$	$E^{1}_{ox^{c}}(V)$	$E^2_{ox^c}(V)$	$E^{3}_{ox^{c}}(V)$	$E_{\rm HOMO^d}$ (eV)
1 29 2 29 4 36 7nPor-Br 42	3, 422, 553 2, 423, 552, 595 1 1 550, 589	4.6, 5.4, 4.7 4.08, 4.99, 4.32, 4.09 4.47	602, 648, 705 603, 649, 712 422	0.25 0.24 0.28 0.26	0.45 0.37 0.61 0.66	0.65 0.63 	-5.08 -5.04 -5.08 -5.06

^a 10⁻⁵ M, in dichloromethane.

^b 10^{-5} M, in dichloromethane, λ_{exc} = 422 nm.

^c [10⁻³ M] in o-DCB-acetonitrile (4:1), Ag/AgNO₃ (0.01 M in CH₃CN) electrode was used as reference and checked against the ferrocene/ferrocenium coupled (Fc/Fc+), glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu₄NClO₄, scan rate = 100 mV s⁻¹.

^d Calculated respecting to ferrocene, E_{HOMO} : -4.8 eV.



Figure 2. Emission spectra of dye **2** (dichloromethane, λ_{exc} = 422 nm) in the absence () and presence (–) of TiO₂.

room temperature in o-dichlorobenzene-acetonitrile (4:1) as the solvent containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolite (Table 1). The comparison with those of dye $\mathbf{1}^5$ and the model compounds $\mathbf{4}$ and Zn-Por-CH₂-Br is shown in Table 1.

Under our experimental conditions, dye 2 undergoes two reversible oxidation processes (see Fig. S13) at 0.24 and 0.63 V centered on the porphyrin moiety as revealed by the comparison with model compound ZnPor-Br (0.26 and 0.66 V, see Table 1). An additional non-reversible oxidation is also observed at 0.37 V. The latter is centered on the bis-3,4-ethylenedioxythienylvinylene bridge. In model compound 4 this oxidation process appears at 0.28 V. The observed shift can be explained by the strong acceptor character of the cyanoacrylic moiety attached to conjugated oligomer in compound 2. Importantly, the HOMO orbital of dye 2 is located on the ZnPorphyrin moiety showing that the compound posseses the requested oxidation potential for an efficient photoinduced electron transfer from the porphyrin to the semiconductor through the conjugated bridge as reported for compound **1**. In addition, the first oxidation of **2** is perfectly reversible indicating the formation of a stable radical cation. This is an important issue for the photovoltaic applications. In the reduction side, the voltammogram of dye **2** showed two reduction processes, at -1.50 eV (reversible) is attributable to the EDOT fragment (by comparison to that of **4**); and another reversible wave, at -1.82 eV, corresponding to the model ZnPor-Br, were observed.

To gain insight into the geometry and the electronic structures of the frontier orbitals, the more stable conformation and the electron density distributions of HOMO and LUMO have been calculated using DFT on B3LYP 6-31G level in gas phase with Gaussian 03 W.¹⁴



Figure 3. Optimized structure by DFT on B3LYP 6-31G of dye 2.



Figure 4. Theoretical energy levels and electron density distribution of the frontier orbital of dye 2.

The phenyl ring of the porphyrin unit and the EDOT bridge are almost in a coplanar conformation (calculated dihedral angle is 0.25°). Nevertheless, the electron donor fragment is in an orthogonal conformation, the dihedral angle between the porphyrin and the π -conjugated bridge is over 89.12° (Fig. 3).

The BLA (bond length alternation)¹⁵ value was calculated for the dye **2** according with the theoretical bond distances. The small value of BLA (0.05 Å) suggests a partially quinoid character and a possible zwitterionic contribution to the ground state.¹⁶

Figure 4 shows the energy levels and the electronic distribution of the HOMO-1. HOMO. LUMO. and LUMO+1. The electron density of the HOMO is located along the oligomeric fragment and the HOMO-1 (E = -5.17 eV), close in energy to the HOMO (E = -4.95 eV), is located in the porphyrin. This fact is in sharp contrast with the experimental results obtained by electrochemistry, where HOMO is located in the porphyrin fragment and the HOMO-1 in the oligomeric fragment; this difference can be explained by the fact that theoretical calculations were performed in vacuo and the electrochemical analyses were carried out in solution. On the other hand, the LUMO (E = -2.77 eV) is located over the cyanoacrylic unit and the oligomeric system, suggesting the possibility of charge transfer from the donor (EDOT) to the acceptor (cyanoacrylate) units. The calculated LUMO energy levels lie above the conduction band edge of TiO_2 (\approx -4.0 eV vs vacuum), which should ensure sufficient driving force for electron injection from the dye into the conduction band of the semiconductor. Finally, the calculated HOMO-LUMO gap was evaluated in 2.18 eV, similar to that found for dye 1.

The performance of the cell fabricated with dye **2** was measured under standard conditions (100 mW cm⁻², 1.5 AM G) a current of J_{sc} = 7.28 mA cm⁻² and a voltage of V_{oc} = 0.438 V were obtained with a fill factor (FF) of 0.514 (Fig. 5).

These values afford an efficiency of $\eta = 1.64\%$, lower than that previously obtained for dye **1** ($J_{sc} = 15.6 \text{ mA cm}^{-2}$, $V_{oc} = 0.63 \text{ V}$, FF = 0.49 and $\eta = 4.77\%$) with a similar structure but carrying hexyl chains instead of 3,4-ethylenedioxyl substituent in the thiophene rings. Both, the voltage and, particularly, the current are lower for dye **2** than for dye **1**. The better behavior as sensitizer of dye **1**, than that of dye **2**, can be attributed to the presence of the alkyl chains (**1**) instead of the 3,4-ethylenedioxyl bridge (**2**). On one



Figure 5. Density current versus voltage response for dye 2 under 100 mW $\rm cm^{-2}$ sun simulation.

hand, the alkyl chains, besides affording a better solubility to the dye, should better prevent the aggregation of the dye (it is known that the aggregation during the TiO₂ sensitization time decreases the injection of electrons and the overall performance of the DSC).¹⁷ On the other hand, the non polar alkyl chains should prevent, more than the polar and with lower size (3,4-ethylenedioxyl moiety), the close proximity of the electrolyte to TiO₂ surface making more difficult the charge recombination between the semiconductor and the electrolyte. Also the hydrophobic chains block the possible interaction between dye cation molecule and iodine, preventing the electron back recombination process at the titania/dye/electrolyte interface given better DSC performance.

In summary, we have successfully synthesized a novel dye with Zn-porphyrin as the donor, bis-(3,4-ethylene-dioxythiophene)vinylene as the bridge and cyanocrylic acid as the acceptor. Its optical and electrochemical properties were studied. A DSC device was fabricated and under standard global AM 1.5 solar conditions, the cell gave a J_{sc} of 7.28 mA cm⁻², V_{oc} of 0.438 V was obtained with a FF of 0.514, corresponding to an overall conversion efficiency $\eta = 1.64\%$ lower to that found for a similar dye with a different substitution in the bridge. The importance of the substitution in the bridge was evaluated.

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Supplementary data

Supplementary data (detailed experimental procedures, synthesis, and characterization of all compounds) associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.tetlet.2012.09.091.

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- Selected spectroscopic data: 5: ¹H NMR (CDCl₃, 400 MHz) δ: 9.91 (s, 2H), 7.14 (s, 2H), 4.37 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz): 179.5, 148.4, 139.7, 126.7, 120.0, 116.6, 65.3, 64.7; UV-Vis (CH₂Cl₂), λ_{max} (nm) (log₂): 427 (4.63), 451.5 (4.61); FT-IR (ATR) v/cm⁻¹: 1635, 1508, 1454, 1363, 1288, 1269, 1215, 1115, 1076, 955, 931, 845, 675; MS (m/z) (MALDI-TOF): 364.86 (M^{*}); calculated for C₁₆H₁₂O₆S₂: 364.00. 6: ¹H NMR (CD₂Cl₂, 400 MHz) δ: 9.81 (s, 1H), 8.90 (d, 2H),

- J = 4.6 Hz), 8.72 (d, 2H, J = 4.6 Hz), 8.68–8.66 (m, 4H), 8.18 (d, 2H, J = 8.1 Hz), 7.83 (d, 2H, J = 8.1 Hz), 7.46 (d, 1H, J = 16 Hz), 7.27 (bs, 7H), 7.23 (d, 1H, J = 15.6 Hz), 7.19 (d, 1H, J = 15.6 Hz), 4.38 (m, 8H), 2.59 (m, 9H), 1.82–1.80 (m, 18H); ¹³C NMR (CD₂Cl₂, 100 MHz): 179.1, 149.9, 149.8, 149.7, 142.3, 141.0, 139.8, 139.3, 139.1, 138.9, 138.2, 137.4, 136.2, 134.9, 132.0, 131.1, 131.0, 130.6, 127.6, 127.2, 124.5, 121.1, 119.7, 118.8, 118.6, 118.1, 117.9, 115.2, 114.9, 65.4, 65.1, 64.9, 64.6, 30.9, 29.7, 21.8, 21.7, 21.5, 14.1; UV–Vis (CH₂Cl₂), λ_{max} (nm) (logε): 422 (5.30); 478 (4.61); 550.5 (4.27); FT-IR (KBr) ν/cm⁻¹: 2980, 2914, 1645, 1440, 1079, 993; MS (m/z) (MALDI-TOF): 1162.47; calculated for C₇₀H₅₈N₄O₅S₂Zn: 1162.31. Compound 2: ¹H NMR (C₆D₆, 400 MHz) δ: 9.11 (d, 2H, J = 4.4 Hz), 9.00 (d, 2H, J = 4.4 Hz), 8.93 (d, 2H, J = 4.4 Hz), 8.89 (d, 2H, J = 4.4 Hz), 8.79 (bs,1H), 8.03 (d, 2H, J = 16 Hz), 7.57 (d, 1H, J = 16 Hz), 7.51 (d, 1H, J = 16 Hz), 7.46 (d, 2H, J = 16 Hz), 7.26 (d, 1H, J = 16 Hz), 7.23 (d, 1H, ¹ = 16 H2, 7.17 (s, 6H), 4.39 (bs, 8H), 3.43–3.37 (m, 8H), 2.41–2.39 (m,9H), 1.96 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz): 149.8, 149.7, 149.6, 141.6, 141.1, 139.8, 139.2, 139.1, 138.9, 138.3, 137.4, 136.1, 135.2, 134.9, 132.0, 131.1, 130.6, 127.6, 125.0, 124.4, 119.7, 118.8, 118.5, 115.5, 110.8, 70.5, 65.6, 64.9, 64.6, 45.8, 32.2, 26.4, 23.5, 21.8, 21.7, 21.5, 8.6; UV-Vis (CH₂Cl₂), λ_{max} (nm) (log ε): 277 (4.36); 422 (4.97); 554 (4.28); FT-IR (KBr) v/cm⁻¹: 2917, 2851, 2362, 1730, 1461, 1371, 1252, 1074; MS (m/z) (MALDI-TOF): 1229.49; calculated for C₇₃H₅₉N₅O₆S₂Zn: 1229.32
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