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Organic Dyes Incorporating Oligothienylenevinylene for Efficient Dye-Sensitized Solar Cells

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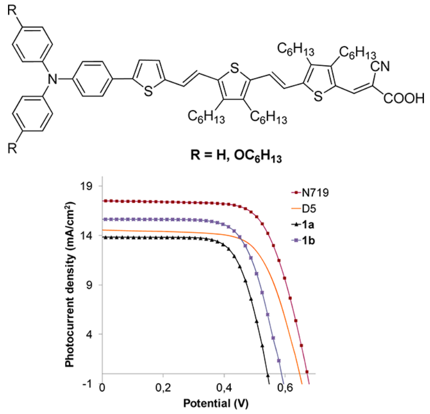
ABSTRACT



Two new organic dyes incorporating triphenylamine as a donor and oligothienylenevinylene as a bridge have been synthesized. The new dyes cover the entire visible region and have a power conversion of up to 6.25%.

Dye-sensitized solar cells (DSCs) represent one of the most promising and environmentally friendly photovoltaic devices because of their low material cost, flexibility and ease of manufacture.[1] The best efficiencies have been recorded on ruthenium complexes (validated energy conversion efficiencies up to 11.7%), but the shortage and high cost of ruthenium metal hampers their commercial applicability. Furthermore, the low molar extinction coefficients of these dyes have led to great efforts to substitute these sensitizers with metal-free organic dyes based on a donor–acceptor (D–A) system;[2] with the aim of preventing charge recombination, a π-bridge can be introduced between the donor and the acceptor (D-π-A).[3] In this respect, many D-π-A-substituted organic dyes have been prepared and used as sensitizers in DSCs.[4] These dyes have large molar extinction coefficients due to the allowed $\pi-\pi^*$ transitions, and they give rise to high conversion efficiency (around 10%).[5]

Triphenylamine (TPA) has been widely investigated as an electron donor in DSC devices[4b] because of its electron-donating capabilities[6] and because it stabilizes

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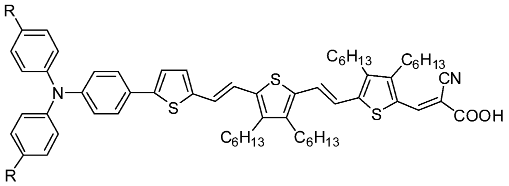
the separated hole generated from the exciton, thus improving hole-transport.[7] Regarding the bridge, in recent years we have developed a series of sensitizers in which oligothienylenevinylenes (oTVs)[8] with different lengths were employed as donors[9] or bridges[10] between the donor and the acceptor. These units were chosen because of the excellent wire behavior of oTVs.[11]



1a R = H
1b R = OC_6H_{13}

Figure 1. Molecular structures of dyes **1a**,**b**.

We report here the synthesis of two new dyes with strong absorption in the visible/near IR region of the spectrum (Figure 1) and their application in DSCs. The new sensitizers are based on TPA as a donor, a three-unit oTV, bearing hydrophobic alkyl chains to impart solubility and prevent aggregation (and thus to avoid self-quenching of the dye excited state),[12] as the π-connector, and 2-cyanoacrylic acid as the electron acceptor.

Sensitizers **1a**,**b** were obtained in good yields by the synthetic protocol shown in Scheme 1.

Aldehydes **2a**,**b** were obtained by palladium-catalyzed Stille coupling of the corresponding triphenylamine bromide derivatives and 5-formylthiophene-2-yl-2-boronic acid in 75% yield in both cases. Subsequent reduction of the corresponding aldehydes **2a**,**b** with $NaBH_4$ and reaction with triethylphosphite gave phosphonates **3a**,**b** in good yields. Careful stoichiometric Horner–Wittig reaction between **3a**,**b** and 2TV-2CHO afforded **4a**,**b** in 64 and 60% yield, respectively. The final dyes **1a**,**b** were obtained by Knoevenagel condensation of **4a**,**b** with cyanoacetic acid as dark blue solids in good yields (**1a**: 71% and **1b**: 85%). All compounds were characterized by ^1H and ^{13}C NMR, FT-IR and MALDI-MS spectrometry (see Supporting Information).

The optical and electrochemical properties of **1a** and **1b** were analyzed by UV–vis absorption spectroscopy, fluorescence emission spectroscopy and cyclic (CV) and Osteryoung square wave (OSWV) voltammetries, and the data are displayed in Table 1.

In a dichloromethane solution, **1a**,**b** showed strong absorption over the entire visible region (up to 700 nm, Figure 2) with broad peaks (and intense absorption) at 555 nm (log ε = 4.62) and 462 nm (log ε = 4.82), respectively. The higher bathochromic shift observed for **1b** in comparison to **1a** can be attributed to better light harvesting behavior, which improves the photocurrent generation in the DSC (vide infra).

For both dyes **1a**,**b**, a positive solvatochromism of the maximum absorption band was observed on increasing the solvent polarity (Figure S28, Supporting Information), thus confirming the CT character of this band. Moreover, a good correlation (correlation coefficient > 0.97) was found between the absorption maxima and the Kamlet–Taft constants (π^*)[13] (Figure S29 and Table S3–S4, Supporting Information). The slope (S) of the Kamlet–Taft equation ($E = E° + S\pi^*$) is higher, in absolute value, for **1b** (S = −4.98) than for **1a** (S = −4.52) (Table S5, Supporting Information), indicating a higher polarizability for **1b** as a consequence of the higher electron donor ability of the alkoxy-TPA moiety. The dyes exhibited emission bands at 760 nm (**1a**, λ_{exc} = 555 nm) and 770 nm (**1b**, λ_{exc} = 562 nm) (Figures S30–S31, Supporting Information). These bands were totally quenched after adsorption onto TiO_2, indicating an efficient photoinduced electron transfer process from TPA moieties to the TiO_2 nanoparticles. The oligothienylene-vinylene acts as an electron wire, favoring the efficiency between donors and acceptors.[10]

The redox properties of **1a** and **1b** were investigated by cyclic (CV) and Osteryoung square wave (OSWV) voltammetries in *o*-dichlorobenzene:acetonitrile (4:1) (Table 1, Figures S32 and S33, Supporting Information). In the cathodic side, the two compounds show a first reversible oxidation wave at 0.22 V (**1a**) and 0.08 V (**1b**); the presence of the electron-donating alkoxy groups significantly reduces the oxidation potential of **1b** in comparison to that of **1a**. A second reversible oxidation wave is observed at

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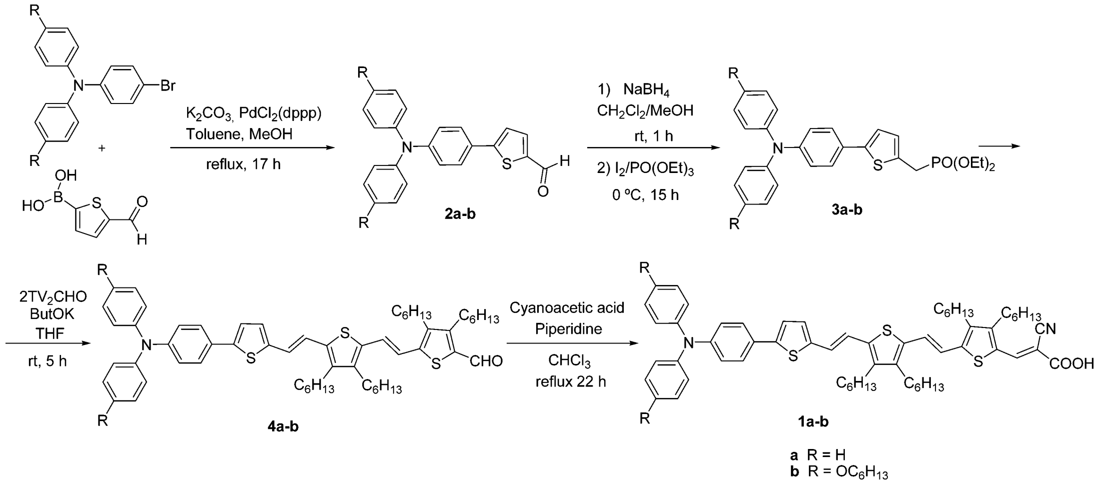
Table 1. Data for UV−vis and Fluorescence Emission Spectroscopies, OSWV for **1a**,**b**

	λ_{max} (nm)[a]	log (ε)[a]	λ_{em} (nm)[a]	E^1_{ox} (V)[b]	E^2_{ox} (V)[b]	E_{HOMO} (eV)[c]	E_{0-0} (eV)[d]
1a	555	4.62	760	0.22	0.31	−5.32	1.91
1b	562	4.82	770	0.08	0.23	−5.18	1.92

[a] 10^{-5} M, in dichloromethane. [b] [10^{-3} M] in *o*-DCB:acetonitrile (4:1) vs versus Fc/Fc$^+$, glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu_4NClO_4, scan rate = 100 mV s^{-1}. [c] Calculated with respect to ferrocene, E_{HOMO}: −5.1 eV. [d] Estimated from the intersection between the absorption and emission spectra.

Scheme 1. Synthesis of Dyes **1a**,**b**



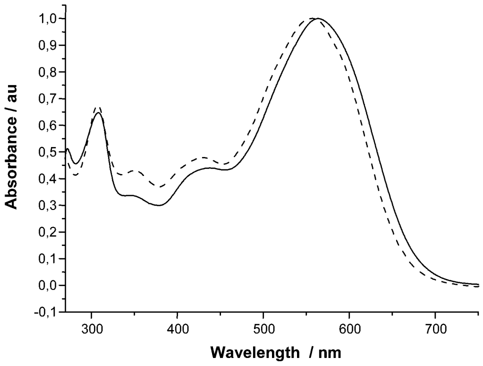


Figure 2. Normalized UV−vis absorption spectra of compounds **1a** (dotted) and **1b** (solid) in dichloromethane.

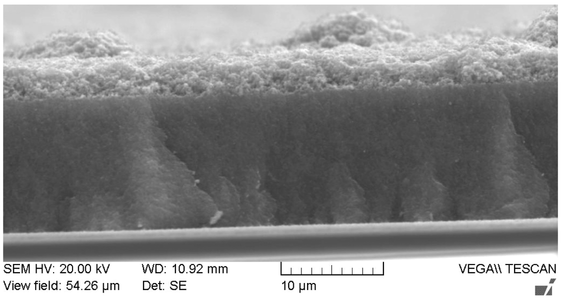


Figure 3. SEM cross section of mesoporous titania photo anode.

0.31 V (**1a**) and 0.23 V (**1b**), and these are assigned to the oTV oligomer.[10a] The E_{HOMO} values (calculated with respect to ferrocene as reference, E_{HOMO}: −5.1 eV)[14] were determined as −5.32 eV (**1a**) and −5.18 eV (**1b**), and these are less negative than the potential of I/I_3^-. This characteristic made it possible to regenerate the dye.

The molecular geometries and frontier molecular orbitals of these new dyes were optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level. The electron distributions of the HOMO and LUMO of dyes **1a** and **1b** are shown in Figures S34−S35, Supporting Information. HOMOs are mainly delocalized from the TPA moiety system to the *o*TV oligomeric part in both compounds (Figures S34−S35, Supporting Information). In both dyes (**1a**,**b**) the LUMO level is localized predominantly on the cyanoacrylic unit and extended to the thiophene rings. This distribution suggests the existence of charge transfer from the TPA to the cyanoacrylic unit

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Table 2. Performance of Dye-Sensitized Solar Cells Fabricated with Dyes **1a**,**b** and References

dye	J (mA/cm^2)	V_{oc} (V)	FF	efficiency (%)
N719	17.52	0.670	0.68	8.06
D5	14.57	0.647	0.67	6.34
1a	13.85	0.542	0.70	5.25
1b	15.64	0.588	0.68	6.25

via the π-spacer group (the *o*TV oligomer), thus allowing significant charge separation within the dye after photoexcitation.

Finally, a state of the art cell was prepared with several titania photo anodes (0.36 cm^2) printed on FTO glass (2.2 mm thick and 15 Ohm/sq). The layering used was as follows (see SEM cross section in Figure 3): around 11 μm of 18 nm TiO_2 nanoparticles (Solaronix' Ti-Nanoxide T/SP) and 3 μm of over 100 nm TiO_2 nanoparticles (Solaronix' Ti-Nanoxide R/SP).

$TiCl_4$ pre- and a post-treatments were performed to optimize the adhesion, porosity and specific area of the titania. The counter electrode was prepared by paint brushing three layers of Solaronix' Platisol T, leading to the formation of a platinized catalytic layer after firing at 400 °C. The photoanodes were then sensitized using the various dyes. Usually 0.5 mM solutions in ethanol in the presence of chenodeoxycholic acid (5 mM) were prepared, but in the cases of dyes **1a** and **1b**, chenodeoxycholic acid was found to compete with dye adsorption. Solutions containing dyes **1a**,**b** were prepared in dichloromethane without any coadsorbent.

The working and counter electrodes were joined together using a 25 μm spacer to minimize any mass transport limitation. The cells were then backfilled with an electrolyte based on acetonitrile containing 0.5 M of dimethyl propyl imidazolium iodide, 0.5 M of 4-*tert*-butylpyridine, 0.1 M of lithium iodide and 50 mM of iodine. For accurate measurement the cells were masked. The total active area was 0.36 cm^2.

The characteristics of the cells made under the above conditions and using dye **1b** were found to be V_{oc} = 588 mV, J_{sc} = 15.64 mA/cm^2 and FF = 68%, with a photon to current efficiency (PCE) of 6.25%, which is similar to the organic dye D5 used as a reference in this study.

In comparison with the previously published[11a] dye FL-7, shortening the bridge between the TPA moiety and anchoring group led to a dramatic increase in the overall cell efficiency. The increase is mainly due to a better fill factor and an improved voltage, which can be attributed to the difference in oxidation potential or to slower recombination dynamics with oxidized electrolyte. The $J_{sc}-V$ performance of these cells measured in full sun (1000 W/m^2, AM 1.5 G) is represented in Figure 4, and the values are listed in Table 2.

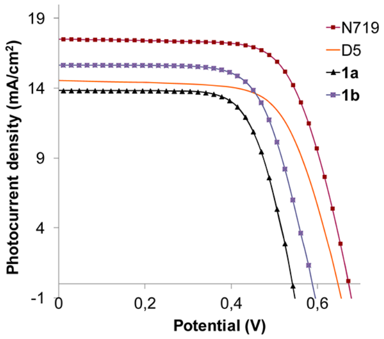

Figure 4. Comparison of $J_{sc}-V$ curves under full AM 1.5 solar intensity.

In summary, we have developed two new organic sensitizers that incorporate triphenylamine or alkoxytriphenylamine as the donor, a cyanoacrylic acid moiety as the acceptor and a three-unit oTV as a bridge. The introduction of alkoxy groups in the TPA donor enhances considerably the efficiency of the cell, with over 6.25% power conversion efficiency achieved. We have also shown that shortening the bridge between the TPA moiety and anchoring group leads to a dramatic increase in the overall cell efficiency. We believe that the development of highly efficient dyes with these types of components is possible through molecular modifications. Work is in progress to achieve this aim.

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Supporting Information Available. General experimental methods, synthetic procedures, ^1H and ^{13}C NMR, MALDI-MS, FT-IR and UV–vis spectra; computational details, details of cell construction and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.