Organic sensitizers bearing a trialkylsilyl ether group for liquid dye sensitized solar cells

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Raquel Pérez-Tejada [a], Natalia Martínez de Baroja [a], Santiago Franco [a, *], Laia Pellejà [b, **], Jesús Orduna [a], Raquel Andreu [a], Javier Garín [a]

[a] Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza — CSIC, E50009 Zaragoza, Spain
[b] Institute of Chemical Research of Catalonia (ICIQ), Avda Països Catalans 16, Tarragona E-43007, Spain

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ABSTRACT

In this work we present the synthesis, optical characterization and performance of five metal-free sensitizers for dye-sensitized solar cells (DSSC). All dyes include, for the first time, a trialkylsilyl ether group in the π-conjugated bridge (a thiophene ring). The influence of different donor unities, like tri-arylamine (TPA), 4H-pyranylidene and dithiafulvene has been evaluated in DSSC with a liquid I_3^-/I^- electrolyte, obtaining the best results with the 4H-pyranylidene moiety. The size and the position of the bulky group have a great importance in the efficiency of the final devices.

In order to explain the recombination processes and electron life-time, charge extraction (CE) and transient photovoltage (TPV) experiments have been carried out.

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1. Introduction

Solar energy offers a clean, well-spread and inexhaustible energy source. Although the market is dominated by silicon-based photovoltaic devices, in recent years the interest on alternatives more environment-friendly has increased, specially focused on reducing mass during cell manufacture processes and the thickness of the final device.

Organic Photovoltaic Cells (OPVs) [1,2] and particularly Dye Sensitized Solar Cells (DSSCs) [3,4] constitute an interesting alternative due to their low manufacturing cost, flexibility of molecular design, light-weight and great esthetic features, like color and transparency. The key element in a DSSC device is probably the sensitizer dye and over the last years, thousands of new dyes have been investigated. The most efficient organic sensitizers are based on Donor—π spacer—acceptor (D—π—A) structures [5], a type of push—pull systems which lead to effective photoinduced intramolecular charge-transfer (ICT). In these systems small variations in the different parts of the molecule (mostly in the donor and the π-bridge) may result in significant changes in the photovoltaic properties. Triphenylamine (TPA)-based metal free organic dyes are one of the most common donor groups in DSSCs [6,7], as it presents several advantages, like a non-planar structure, which suppresses the formation of aggregates. Furthermore, the physical properties can be easily modulated by introduction of bulky or donor groups [8—13]. Recently, proaromatic systems like 4H-pyranylidene [14—17] and dithiafulvene [18—20] have been introduced as alternative and efficient donor unities in DSSCs, but no studies comparing their properties have been reported.

When designing a new sensitizer, one important factor to take into account is related to the minimization of aggregates by π—π stacking. This may be performed by using additives, such as deoxycholic acid (DCA) [21,22] or by the introduction of bulky groups both, in the donor or in the π-bridge [12,23—26]. However, it is relatively difficult to synthesize dyes with bulky chains in the conjugated spacer, requiring tedious and multiple reaction steps.

Silicon-based dyes have been very promising for DSSCs due to its photo and thermal stability [27,28]. Examples of organic sensitizers bearing a dithienosilole (DTS) as a π-linker have been reported with high efficiencies [29—34]. However, to the best of our knowledge, organic dyes featuring a trialkylsilyl ether
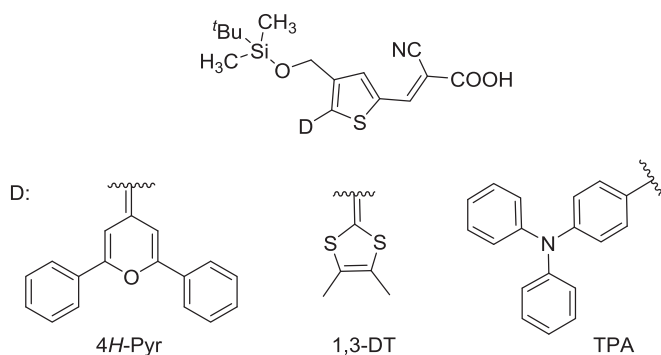
Fig. 1. Molecular structures of TBDMS organic sensitizers.

$R_1 = CH_2OTBDPS$ or $CH_2OTBDMS$, $R_2 = H$
$R_1 = H$, $R_2 = CH_2OTBDPS$
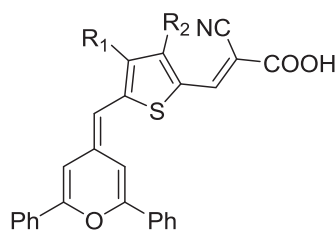
Fig. 2. Molecular structures of 4*H*-pyranylidene organic sensitizers.

$(R_1R_2R_3SiO-)$ were never used to preclude the π-aggregation on the TiO$_2$ in DSSCs. This popular protecting group can be easily introduced from alcohols [35] and the overall size and the stability depend on the nature of the R_1, R_2 or R_3. Moreover, the silyl ether group greatly enhances the solubility of the sensitizer that facilitates its adsorption on the TiO$_2$ surface.

In the present work, a series of five new metal-free organic sensitizers for DSSCs with a trialkylsilyloxy group have been designed, synthesized and characterized. In order to evaluate the donor influence on the photovoltaic properties a TPA and two proaromatic donor unities (4*H*-pyranylidene and dithiafulvene) have been used (Fig. 1).

The influence of the size and the relative position on the heterocyclic linker of two bulky groups, *tert*-butyldimethyl (TBDMS) or *tert*-butyldiphenyl silyl ether (TBDPS) is also studied (Fig. 2). Finally, the photophysical properties, molecular orbital calculations and the performance of DSSCs based on these organic dyes are reported.

2. Experimental section

2.1. General information

Infrared measurements were carried out in KBr or neat using a Perkin−Elmer Fourier Transform Infrared 1600 spectrometer. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz and 75 or 100 MHz respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), and m (multiplet). ^{1}H–^{1}H COSY and ^{1}H–^{13}C-HSQC experiments were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz in order to establish peaks assignment and spatial relationships. Electrospray mass spectra were recorded on a Bruker Microtof-Q spectrometer; accurate mass measurements were achieved using sodium formate as external

reference. UV−Visible spectra were recorded with a UV−Vis UNI-CAM UV4 spectrophotometer. Pulse differential voltammetry measurements were performed with a μ-Autolab type III potentiostat using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon in CH$_2$Cl$_2$, with Bu$_4$NPF$_6$ as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 0.01 V s^{-1}, modulation amplitude 0.025 V and modulation time 0.05 s^{-1}.

2.2. Synthesis

2.2.1. 4-((tert-Butyldimethylsilyloxy)methyl)-5-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)thiophene-2-carbaldehyde (7)

A solution of 2,6-diphenyl-(4*H*-pyran-4ylidene)-diphenylphosphine oxide **5** (680 mg, 1.56 mmol) in anhydrous THF (12 mL) was prepared, purged with argon and cooled to −78 °C. To this solution, *n*-BuLi (1.6 M in hexanes) (1.2 mL, 2.08 mmol) was added dropwise and the resulting mixture was stirred for 15 min. Then 3-((*tert*-butyldimethylsilyloxy)methyl)thiophene-2-carbaldehyde **4** (472 mg; 1.84 mmol) in anhydrous THF (5 mL) was added dropwise and the mixture was warmed to 0 °C for 3 h (TLC monitoring using 10% EtOAc in hexanes). Saturated NH$_4$Cl solution was added to quench the reaction and the solvent was evaporated under reduced pressure. The organic layer was extracted with EtOAc (2 × 25 mL) and dried over anhydrous MgSO$_4$. After the removal of the solvent, the residue was dissolved in EtOAc/hexanes (3/97) and filtered over silica gel to give the crude *tert*-butyl((2-((2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)thiophen-3-yl)methoxy)dimethylsilane **6** as an intermediate. Then, a solution of 2,2,6,6-tetramethylpiperidine (0.27 mg, 1.58 mmol) in THF (8.4 mL) was prepared, purged with argon and cooled to −78 °C. To this solution, ^{t}BuLi (1.7 M in pentane) (1.01 mL, 1.71 mmol) was added dropwise and the resulting mixture was stirred for 1 h and then a solution of **6** (676.0 mg, 1.41 mmol) in THF (33.6 mL) was added. The resulting mixture was stirred for an additional hour, DMF (0.28 mL, 3.70 mmol) was added dropwise and the mixture was warmed to −30 °C. The reaction was quenched by the addition of saturated NH$_4$Cl solution and the solvent was evaporated under reduced pressure. The organic layer was extracted with EtOAc (2 × 20 mL) and dried over anhydrous MgSO$_4$. After the removal of the solvent, the aldehyde **7** was purified by silica gel column chromatography (6% EtOAc in hexanes). Yield: red oil (583.0 mg, 1.16 mmol; 82%).

IR (neat): cm^{-1} 1648 (C=O), 1573 (C=C). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.81 (s, 1H), 7.90−7.76 (m, 4H), 7.69 (s, 1H), 7.55−7.43 (m, 6H), 7.29 (d, *J* = 2.0 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.07 (s, 1H), 4.75 (s, 2H), 0.96 (s, 9H), 0.14 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 182.1, 155.3, 152.6, 146.6, 139.0, 137.9, 137.0, 132.8, 132.5, 132.5, 130.2, 129.7, 128.9, 128.8, 125.3, 124.7, 109.0, 104.7, 102.9, 59.7, 26.0, 18.4, −5.2. HRMS (ESI$^+$): *m/z* calcd for [C$_{30}$H$_{33}$O$_3$SSi]$^+$: 501.1914, found: 501.1914 [M + H]$^+$; calcd for [C$_{30}$H$_{32}$NaO$_3$SSi]$^+$: 523.1734, found: 523.1721 [M + Na]$^+$.

2.2.2. 4-((tert-Butyldimethylsilyloxy)methyl)-5-((4,5-dimethyl-1,3-dithiol-2ylidene)methyl)thiophene-2-carbaldehyde (10)

A solution of tributyl(4,5-dimethyl-1,3-dithiol-2-yl)phosphonium hexafluorophosphate **8** (317.7 mg, 0.66 mmol) and 3-((*tert*-butyldimethylsilyloxy)methyl)thiophene-2-carbaldehyde **4** (131.0 mg, 0.51 mmol) in anhydrous THF (16 mL) was prepared, purged with argon and cooled to −78 °C. To this solution, Et$_3$N (352.4 μL, 2.51 mmol) was added dropwise and the resulting mixture was stirred for 15 min. After the removal of the solvent, the residue was dissolved in EtOAc/hexanes (1:9) and filtered over neutral aluminum oxide to give compound **9** as an intermediate. Then, a solution of **9** in THF (10 mL) was prepared, purged with argon and cooled to −45 °C. To this solution, *n*-BuLi (1.6 M in hexanes) (0.53 mL, 0.85 mmol) was