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Novel 4*H*-pyranylidene organic dyes for dye-sensitized solar cells: Effect of different heteroaromatic rings on the photovoltaic properties

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ABSTRACT

Eight novel Ruthenium-free dyes consisting of a 4*H*-pyranylidene donor, a 2-cyanoacrylic acid acceptor and several heterocyclic rings with different electronic properties are designed and synthesized. The photovoltaic performances of the related dye-sensitized solar cells are discussed and compared, obtaining the best results with the thiophene followed by the mismatched-oriented thiazole. Dyes containing a pyrrol or a matched-oriented thiazole lead to the lower efficiencies of all the series. Charge extraction (CE) and transient photovoltage (TPV) measurements were conducted in order to investigate the recombination resistance and the difference in voltage for the devices. In order to get further insight in the electronic and optical properties of the studied compounds, theoretical calculations using TD-DFT and the CPCM have been carried out.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are among the most efficient molecular devices in converting sun light into electrical current [1]. In fact, under low light conditions (so called indoor conditions) this type of solar cells is capable to surpass the efficiency of most common solar cells based on polycrystalline silicon. Efficiencies as high as 13% under standard measurement conditions (100 mW/ cm² sun simulated 1.5 AM G spectrum) have been recently reported [2]. Such high efficiencies have been possible with the use of the so called Ruthenium-free DSSCs, which are organic sensitizers with unique physical and chemical

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http://dx.doi.org/10.1016/j.orgel.2014.09.003 1566-1199/© 2014 Elsevier B.V. All rights reserved. properties. Indeed, one of the key components for such efficient DSSC is the photosensitizer, which is not only the responsible to harvest the light and inject electrons into the conduction band of the TiO_2 semiconductor, but also to act as a first barrier to prevent back electron transfer from the photo-injected electrons at the TiO_2 and the oxidized electrolyte due to excellent molecular packing at the TiO_2 surface [3].

Based on the pioneering work of Feldt et al. [4] and Wang et al. [5] most of the organic sensitizers have a typical electron Donor- π -Acceptor structure (D- π -A) [6], that leads to an intramolecular charge transfer (ICT) absorption band with high molecular extinction coefficient in the visible region of the sun light. Recently, several groups have proposed different configurations as D-A- π -A [7], D- π - π -A [8], D-D- π -A [9] or 2D- π -A [10] with good results. Triarylamines moieties are commonly used as electron donating groups because of its excellent





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electron-donating capability and good stability [11]. While the 4*H*-pyranylidene ring has proved to be a very good donor system in NLO applications [12], it has scarcely explored in DSSCs [13]. The main feature relies on its pro-aromatic character that improves the charge transfer process through the gain in aromaticity. Moreover, the donor character can be modulated by incorporating substituents with different electronic properties. We think that this system can be an interesting alternative to other common donor unities, like triarylamines.

Most of the studies carried out in DSSCs using these type of sensitizers have been focused on the molecular π -bridge as it plays an important role in tuning the main photochemical properties of the sensitizer [14]. The use of electron-excessive heteroaromatic systems like thiophene, furan [15] or pyrrole [16] is a common strategy to expand the solar cell absorption spectrum to the red region of the sun light, by acting as efficient donor auxiliary systems and affording a greater photo- and chemical stability. Moreover, other important roles on the π -bridge such as the polarizability (the formation of molecular dipoles at the surface of the semiconductor metal oxide), the presence of moieties that may enhance or retard the recombination reaction mentioned above, among others, must be also taking into account to design efficient dyes.

Although the thiophene moiety is among the most used conjugated linkers in organic sensitizers for DSSCs, the number of comparative studies involving in the same series, heterocyclic rings with different electronic properties (donor and electron-accepting characteristics) is truly scarce [17].

In this work, we aim to evaluate the potential of 8 novel Ruthenium-free dyes consisting of a 4*H*-pyranylidene donor, a 2-cyanoacrylic acid acceptor and different heteroaromatic rings acting as the π -bridge, i.e., *N*-methylpyrrole, furan (electron-excessive) and thiazole (electron-deficient). In fact, to our best knowledge, there are not many examples of DSSCs based on this latter heterocyclic system [17b,18], for which, due to its unsymmetrical nature, two regioisomers should be considered (matched and mismatched) [19].

The photovoltaic performances of the related DSSCs are discussed and compared with other previously thiophene reported systems [13] allowing a complete understanding of the dyes molecular structure device efficiency relationship for this new approach towards Ruthenium-free DSSCs.

2. Experimental section

2.1. General information

Infrared measurements were carried out in KBr using a Perkin–Elmer Fourier Transform Infrared 1600 spectrometer. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. ¹H and ¹³C 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), br s (broad singlet), d (doublet), t

(triplet), q (quartet) and m (multiplet). ¹H-¹H COSY and ¹H-¹³C-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 Micro-ToF-Q spectrometer; accurate mass measurements were achieved using sodium formate as external reference. UV-Visible spectra were recorded with an UV-Vis UNICAM 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 CH₂Cl₂, with Bu_4NPF_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. 5-((2,6-Di-tert-butyl-4H-pyran-4ylidene)methyl)thiazole (5b)

A solution of (2.6-di-tert-butyl-4H-pyran-4yl)tributylphosphonium perchlorate 1b (607 mg, 1.23 mmol) in anhydrous THF (10 mL) was prepared, purged with argon and cooled to -78 °C. To this solution, n-BuLi (1.6 M in hexanes) (0.77 mL, 1.59 mmol) was added dropwise and the resulting mixture was stirred for 15 min. Then thiazole-5-carbaldehyde 4 (86 mg, 0.94 mmol) in anhydrous THF (7 mL) was added dropwise and the mixture was progressively heated to reach 0 °C during 4 h. Saturated NH₄Cl solution was added to quench the reaction and the solvent was evaporated under reduce pressure. The organic layer was extracted with dichloromethane, washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the product was purified by alumina column chromatography (30% ethyl acetate in hexanes). Yield: orange solid (219 mg, 0.75 mmol; 88%).

Mp 60–61 °C. IR (KBr): cm⁻¹ 1577 (C=C). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 8.52 (s, 1H), 7.63 (s, 1H), 6.23 (d, *J* = 2.0 Hz, 1H), 5.81 (s, 1H), 5.69 (d, *J* = 2.0 Hz, 1H), 1.24 (s, 9H), 1.20 (s, 9H). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) 165.7, 163.2, 148.8, 140.2, 137.2, 131.9, 104.6, 99.9, 98.9, 36.2, 35.7, 28.2, 28.1. HRMS (ESI⁺): *m/z* calcd for [C₁₇H₂₄NOS]⁺: 290.1573, found: 290.1577.

2.2.2. 2-((2,6-Di-tert-butyl-4H-pyran-4-

ylidene)methyl)thiazole (7b)

A solution of (2,6-di-*tert*-butyl-4*H*-pyran-4yl)tributylphosphonium perchlorate **1b** (607 mg, 1.23 mmol) in anhydrous THF (10 mL) was prepared, purged with argon and cooled to -78 °C. To the solution, *n*-BuLi (1.6 M in hexanes) (0.76 mL, 1.23 mmol) was added dropwise and the resulting mixture was stirred for 15 min. Then thiazole-2-carbaldehyde (86 mg, 0.94 mmol) in anhydrous THF (7 mL) was added dropwise and the mixture was progressively heated to reach room temperature during 18 h. Saturated NH₄Cl solution was added to quench the reaction and the solvent was evaporated under reduce pressure. The organic layer was extracted with ethyl acetate, washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the product was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: dark yellow oil (250 mg, 0.86 mmol, 91%).

IR (KBr): cm⁻¹ 1666 (C=C). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.66 (d, *J* = 3.3 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.04 (d, *J* = 3.3 Hz, 1H), 5.84 (s, 1H), 5.76 (d, *J* = 1.8 Hz, 1H), 1.27 (s, 9H), 1.22 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂): δ (ppm) 167.9, 166.9, 164.9, 143.3, 135.4, 115.0, 104.6, 102.5, 100.8, 36.3, 36.0, 28.2, 28.1. HRMS (ESI⁺): *m/z* calcd for [C₁₇-H₂₄NOS]⁺: 290.1573, found: 290.1589.

2.2.3. 5-((2,6-Diphenyl-4H-pyran-4-ylidene)methyl)-1methyl-1H-pyrrole-2-carbaldehyde (8a)

A solution of 2,6-diphenyl(4H-pyran-4ylidene)diphenylphosphine oxide **1a** (706 mg, 1.63 mmol) in anhydrous THF (14 mL) was prepared, purged with argon and cooled to $-78 \,^{\circ}$ C. To the solution, *n*-BuLi (1.6 M in hexanes) (1.1 mL, 1.79 mmol) was added dropwise and the resulting mixture was stirred for 20 min. Then 1-methyl-5-(5,5dimethyl-1,3-dioxan-2-yl)-1H-pyrrole-2-carbaldehyde (363 mg; 1.63 mmol) in anhydrous THF (9 mL) was added dropwise and the mixture was progressively heated to reach room temperature during 24 h (TLC monitoring using 30% ethyl acetate in hexanes). The reaction was quenched with HCl (2.4 N) (10 mL) and the mixture was stirred for 30 min at room temperature. The organic layer was extracted with dichloromethane, washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (10% ethyl acetate in hexanes). Yield: red solid (253 mg, 0.71 mmol: 44%).

Mp 174–175 °C. IR (KBr): cm⁻¹ 1645 (C=O), 1581 (C=C). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 9.43 (s, 1H), 7.82–7.78 (m, 4H), 7.50–7.43 (m, 6H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 4.2 Hz, 1H), 6.55 (d, *J* = 1.6 Hz, 1H), 6.50 (d, *J* = 4.2 Hz, 1H), 5.88 (s, 1H), 3.93 (s, 3H). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) 178.4, 154.3, 152.2, 142.0, 133.5, 133.3, 133.2, 131.8, 130.2, 130.0, 129.2, 129.2, 125.5, 125.5, 125.1, 109.6, 108.7, 103.0, 100.7, 32.8. HRMS (ESI⁺): *m/z* calcd for [C₂₄H₂₀NO₂Na]⁺: 376.1308, found: 376.1290.

2.2.4. 5-((2,6-Di-tert-butyl-4H-pyran-4-ylidene)methyl)-1methyl-1H-pyrrole-2-carbaldehyde (8b)

A solution of (2,6-di-tert-butyl-4H-pyran-4yl)tributylphosphonium perchlorate 1b (714 mg, 1.44 mmol) in anhydrous THF (12 mL) was prepared, purged with argon and cooled to -78 °C. To the solution, *n*-BuLi (1.6 M in hexanes) (1.00 mL, 1.60 mmol) was added dropwise and the resulting mixture was stirred for 15 min. Then 1-methyl-5-(5,5dimethyl-1,3-dioxan-2-yl)-1H-pyrrole-2-carbaldehyde (248 mg, 1.11 mmol) in anhydrous THF (10 mL) was added dropwise and the mixture was progressively heated to reach room temperature during 24 h (TLC monitoring using 30% ethyl acetate in hexanes). The reaction was quenched with HCl (1 N) (75 mL) and the mixture was stirred for 10 min at room temperature. The organic layer was extracted with dichloromethane, washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (30% ethyl acetate in hexanes). Yield: brown oil (276 mg, 0.88 mmol; 79%).

IR (KBr): cm⁻¹ 1653 (C=O), 1578 (C=C). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 9.35 (s, 1H), 6.88 (d, *J* = 4.2 Hz, 1H), 6.31 (d, *J* = 4.2 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 5.77 (d, *J* = 2.0 Hz, 1H), 5.37 (s, 1H), 3.86 (s, 1H), 1.22 (s, 9H), 1.21 (s, 9H). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) 177.9, 166.0, 163.8, 143.0, 135.0, 131.3, 125.7, 108.9, 105.2, 99.4, 97.2, 36.2, 35.8, 32.7, 28.2, 28.1. HRMS (ESI⁺): *m/z* calcd for [C₂₀H₂₈NO₂]⁺: 314.2115, found: 314.2104; calcd for [C₂₀H₂₇NO₂Na]⁺: 336.1934, found: 336.1911.

2.2.5. 5-((2,6-Diphenyl-4H-pyran-4-ylidene)methyl)furan-2carbaldehyde (9a)

A solution of 2,6-diphenyl(4H-pyran-4ylidene)diphenylphosphine oxide 1a (1.55 g, 3.57 mmol) in anhydrous THF (30 mL) was prepared, purged with argon and cooled to $-78 \,^{\circ}$ C. To the solution, *n*-BuLi (1.6 M in hexanes) (2.5 mL, 4.00 mmol) was added dropwise and the resulting mixture was stirred for 20 min. Then 5-(1,3-dioxolan-2yl)furan-2-carbaldehyde (600 mg, 3.57 mmol) in anhydrous THF (20 mL) was added dropwise and the mixture was progressively heated to reach 0 °C during 4 h (TLC monitoring using 50% ethyl acetate in hexanes). The reaction was quenched with HCl (2.4 N) (10 mL) and the mixture was stirred for 15 min at room temperature. The organic layer was extracted with dichloromethane, washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: red solid (750 mg, 2.20 mmol; 62%).

Mp 134–135 °C. IR (KBr): cm⁻¹ 1648 (C=O), 1580 (C=C). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 9.50 (s, 1H), 7.94–7.91 (m, 2H), 7.84–7.80 (m, 2H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.55–7.44 (m, 6H), 7.26 (d, *J* = 3.8 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 6.36 (d, *J* = 3.8 Hz, 1H), 5.75 (s, 1H). ¹³C NMR (100 MHz, CD₂Cl₂): δ (ppm) 175.4, 161.4, 154.5, 153.0, 151.2, 133.8, 133.1, 132.9, 130.2, 130.0, 129.2, 129.1, 125.5, 125.2, 125.0, 110.0, 108.3, 103.8, 100.4. HRMS (ESI⁺): *m/z* calcd for [C₂₃H₁₇O₃]⁺: 341.1172, found: 341.1168; calcd for [C₂₃H₁₆O₃Na]⁺: 363.0992, found: 363.0999.

2.2.6. 5-((2,6-Di-tert-butyl-4H-pyran-4-

ylidene)methyl)furan-2-carbaldehyde (9b)

A solution of (2,6-di-tert-butyl-4H-pyran-4yl)tributylphosphonium perchlorate 1b (589 mg, 1.19 mmol) in anhydrous THF (10 mL) was prepared, purged with argon and cooled to -78 °C. To the solution, n-BuLi (1.6 M in hexanes) (0.74 mL, 1.19 mmol) was added dropwise and the resulting mixture was stirred for 15 min. Then 1-methyl-5-(5,5-dimethyl-1,3-dioxan-2-yl)-1H-pyrrole-2-carbaldehyde (154 mg, 0.91 mmol) in anhydrous THF (7 mL) was added dropwise and the mixture was stirred for additional 30 min (TLC monitoring using 30% ethyl acetate in hexanes). Amberlyst® 15 ionic exchange resin was then added to quench the reaction and the mixture was stirred for 30 min at room temperature. The resin was filtered off and washed with dichloromethane. The organic layer was dried over MgSO₄ and the solvent was evaporated under reduced pressure. Pure compound was obtained by alumina column chromatography (30% ethyl acetate in hexanes). Yield: brown oil (100 mg, 0.33 mmol; 36%).

IR (KBr): cm⁻¹ 1655 (C=O), 1583 (C=C). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 9.40 (s, 1H), 7.20 (d, J = 3.8 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.20 (d, J = 3.8 Hz, 1H), 5.78 (d, J = 2.0 Hz, 1H), 5.46 (s, 1H), 1.28 (s, 9H), 1.22 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂): δ (ppm) 175.1, 167.1, 165.2, 162.3, 150.9, 136.0, 124.9, 108.5, 105.0, 100.7, 97.4, 36.4, 36.0, 28.2, 28.1. HRMS (ESI⁺): *m/z* calcd for [C₁₉H₂₅O₃]⁺: 301.1798, found: 301.1792; calcd for [C₁₉-H₂₄O₃Na]⁺: 323.1618, found: 323.1620.

2.2.7. 5-((2,6-Di-tert-butyl-4H-pyran-4-

ylidene)methyl)thiazole-2-carbaldehyde (10b)

A solution of 5-((2,6-di-tert-butyl-4H-pyran-4-ylidene)methyl)thiazole 5b (199 mg, 0.69 mmol) in anhydrous THF (13 mL) was prepared, purged with argon and cooled to -78 °C. To the solution, *n*-BuLi (1.6 M in hexanes) (0.76 mL, 1.22 mmol) was added dropwise and the resulting mixture was stirred for 1 h. Then DMF (161 µl; 2.1 mmol) was added dropwise and the mixture was then warmed to room temperature (TLC monitoring using 30% ethyl acetate in hexanes). Saturated NH₄Cl solution was added to quench the reaction and the solvent was evaporated under reduce pressure. The organic layer was extracted with dichloromethane and dried over anhydrous MgSO₄. After removal of the solvent, the aldehyde was purified by alumina column chromatography (30% ethyl acetate in hexanes). Yield: deep red solid (150 mg, 0.47 mmol; 69%).

Mp 143–144 °C. IR (KBr): cm⁻¹ 1661 (C=O), 1564 (C=C). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 9.84 (s, 1H), 7.80 (s, 1H), 6.38 (d, *J* = 2.0 Hz, 1H), 5.91 (s, 1H), 5.87 (d, *J* = 2.0 Hz, 1H), 1.29 (s, 9H), 1.23 (s, 9H). ¹³C NMR (75 MHz, CD₂Cl₂): δ (ppm) 183.7, 165.4, 159.7, 146.4, 143.3, 136.6, 105.8, 100.5, 100.0, 36.5, 36.0, 28.2, 28.1. HRMS (ESI⁺): *m/z* calcd for [C₁₈H₂₄NO₂S]⁺: 318.1522, found: 318.1518; calcd for [C₁₈H₂₃NO₂SNa]⁺: 340.1342, found: 340.1337.

2.2.8. 2-((2,6-Di-tert-butyl-4H-pyran-4ylidene)methyl)thiazole-5-carbaldehyde (11b)

A solution of 2-((2,6-di-tert-butyl-4H-pyran-4-ylidene)methyl)thiazole 7b (247 mg, 0.85 mmol) in anhydrous THF (16 mL) was prepared, purged with argon and cooled to -45 °C. To this solution, n-BuLi (1.6 M in hexanes) (0.90 mL, 1.43 mmol) was added dropwise and the resulting mixture was stirred for 1 h. Then DMF (199 µl; 2.56 mmol) was added dropwise and the mixture was warmed to room temperature overnight (TLC monitoring using 20% ethyl acetate in hexanes). Saturated NH₄Cl solution was added to quench the reaction and the solvent was evaporated under reduce pressure. The organic layer was extracted with ethyl acetate and dried over anhydrous MgSO₄. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: deep orange solid (192 mg, 0.60 mmol; 71%).

Mp 166–169 °C. IR (KBr): cm⁻¹ 1651 (C=O), 1591(C=C). ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 9.87 (s, 1H), 8.32 (s, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 5.93 (s, 1H), 5.92 (d, J = 1.8 Hz, 1H), 1.30 (s, 9H), 1.25 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂): δ (ppm) 181.9, 175.4, 169.4, 167.6, 154.2, 141.0, 134.6, 105.6, 102.5, 102.10, 36.7, 36.3, 28.2, 28.1. HRMS (ESI⁺): m/z calcd for $[C_{18}H_{24}NO_2S]^+$: 318.1522, found: 318.1505.

2.2.9. 3-(5-((2,6-Diphenyl-4H-pyran-4-ylidene)methyl)-1methyl-1H-pyrrol-2-yl)-2-cyanoacrylic acid (12a)

To a solution of 5-((2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)-1-methyl-1*H*-pyrrole-2-carbaldehyde **8a** (120 mg, 0.33 mmol) and 2-cyanoacetic acid (45 mg, 0.53 mmol) in chloroform (12 mL) was added piperidine (219 μ l; 2.19 mmol). The mixture was refluxed for 5 days under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (70% AcNH₄, 20 mM in acetonitrile). Yield: deep red solid (88 mg, 0.21 mmol; 63%).

Mp 230–231 °C. IR (KBr): cm⁻¹ 2210 (C≡N), 1653 (C=O), 1558 (C=C). ¹H NMR (300 MHz, dmso-*d*₆): δ (ppm) 7.99 (s, 1H), 7.95–7.86 (m, 4H), 7.67 (d, *J* = 4.4 Hz, 1H), 7.59–7.45 (m, 6H), 7.05 (br s, 1H), 7.01 (bs, 1H), 6.97 (d, *J* = 4.4 Hz, 1H), 6.04 (s, 1H), 3.67 (s, 3H). ¹³C NMR (75 MHz, dmso-*d*₆): δ (ppm) 165.3, 153.5, 150.8, 141.0, 137.4, 132.3, 132.0, 131.9, 130.1, 129.6, 128.9, 128.8, 127.0, 125.1, 124.3, 119.5, 118.7, 112.6, 108.8, 102.1, 101.4, 89.1, 30.2. HRMS (ESI⁺): *m/z* calcd for $[C_{27}H_{20}N_2O_3]^+$: 420.1468, found: 420.1460.

2.2.10. 3-(5-((2,6-Di-tert-butyl-4H-pyran-4-ylidene)methyl)-1-methyl-1H-pyrrol-2-yl)-2-cyanoacrylic acid (12b)

To a solution of 5-((2,6-di-tert-butyl-4H-pyran-4-ylidene)methyl)-1-methyl-1H-pyrrole-2-carbaldehyde (270 mg, 0.86 mmol) and 2-cyanoacetic acid (114 mg, 1.34 mmol) in chloroform (32 mL) was added piperidine (614 µl; 5.52 mmol). The mixture was refluxed for 5 days under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (70% AcNH₄, 20 mM in acetonitrile). Yield: red-pink solid (312 mg, 0.82 mmol; 95%).

Mp 168–169 °C. IR (KBr): cm⁻¹ 2206 (C≡N), 1667 (C=O), 1551 (C=C). ¹H NMR (400 MHz, acetone-*d*₆): δ (ppm) 8.02 (s, 1H), 7.76 (d, *J* = 4.7 Hz, 1H), 6.65 (d, *J* = 4.7 Hz, 1H), 6.36 (d, *J* = 1.8 Hz, 1H), 5.98 (d, *J* = 1.8 Hz, 1H), 5.69 (s, 1H), 3.69 (s, 3H), 1.25 (s, 9H), 1.23 (s, 9H). ¹³C NMR (75 MHz, CD₃COCD₃-*d*₆): δ (ppm) 167.6, 166.8, 165.2, 144.6, 139.4, 136.9, 128.8, 122.0, 120.1, 113.6, 107.0, 101.0, 99.8, 89.6, 37.4, 37.0, 31.6, 29.1, 29.0. HRMS (ESI⁺): *m/z* calcd for $[C_{23}H_{28}N_2O_3]^+$: 381.2173, found: 381.2155; calcd for $[C_{23}H_{28}N_2O_3Na]^+$: 403.1992, found: 403.1965.

2.2.11. 3-(5-((2,6-Diphenyl-4H-pyran-4-

ylidene)methyl)furan-2-yl)-2-cyanoacrylic acid (13a)

To a solution of 5-((2,6-diphenyl-4*H*-pyran-4-ylidene) methyl)furan-2-carbaldehyde **9a** (167 mg, 0.49 mmol) and 2-cyanoacetic acid (65 mg, 0.76 mmol) in chloroform (12 mL) was added piperidine (324 μ l, 3.25 mmol). The mixture was refluxed for 8 h under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography

(50% AcNH₄, 20 mM in acetonitrile). Yield: dark violet solid (133 mg, 0.33 mmol; 66%).

Mp 164–165 °C. IR (KBr): cm⁻¹ 2217 (C≡N), 1687 (C=O), 1546 (C=C). ¹H NMR (300 MHz, dmso- d_6): δ (ppm) 8.09–8.06 (m, 2H), 7.91–7.88 (m, 3H), 7.58–7.49 (m, 8H), 7.05 (d, *J* = 1.5 Hz, 1H), 6.79 (d, *J* = 3.9 Hz, 1H), 5.94 (s, 1H). ¹³C NMR (100 MHz, dmso- d_6): δ (ppm) 164.5, 161.1, 154.8, 152.1, 147.1, 135.9, 133.6, 131.8, 131.6, 130.3, 129.9, 128.9, 128.6, 125.5, 124.5, 122.5, 117.1, 113.1, 108.7, 103.7, 100.6, 92.2. HRMS (ESI⁺): *m/z* Calcd for [C₂₃H₁₈NO₄]⁺: 408.1230, found: 408.1211.

2.2.12. 3-(5-((2,6-Di-tert-butyl-4H-pyran-4-

ylidene)methyl)furan-2-yl)-2-cyanoacrylic acid (13b)

To a solution of 5-((2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl)furan-2-carbaldehyde **9b** (120 mg, 0.40 mmol) and 2-cyanoacetic acid (51 mg, 0.60 mmol) in chloroform (10 mL) was added piperidine (265 μ l, 2.65 mmol). The mixture was refluxed for 24 h under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (50% AcNH₄, 20 mM in acetonitrile). Yield: dark violet solid (81 mg, 0.22 mmol; 55%).

Mp 162–163 °C. IR (KBr): cm⁻¹ 2214 (C≡N), 1664 (C=O), 1539 (C=C). ¹H NMR (400 MHz, acetone-*d*₆): δ (ppm) 7.87 (s, 1H), 7.53 (d, *J* = 4.0 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.52 (d, *J* = 4.0 Hz, 1H), 6.01 (d, *J* = 1.8 Hz, 1H), 5.66 (s, 1H), 1.33 (s, 9H), 1.26 (s, 9H). ¹³C NMR (100 MHz, acetone-*d*₆): δ (ppm) 169.2, 167.0, 165.9, 164.6, 148.7, 138.4, 138.2, 128.6, 118.4, 113.2, 107.3, 103.1, 99.6, 91.1, 38.0, 37.3, 29.3, 29.2. HRMS (ESI⁺): *m/z* calcd for [C₂₂H₂₆NO₄]⁺: 368.1856, found: 368.1847; calcd for [C₂₂H₂₅NO₄Na]⁺: 390.1676, found: 390.1655.

2.2.13. 3-(5-((2,6-Diphenyl-4H-pyran-4-

ylidene)methyl)thiazol-2-yl)-2-cyanoacrylic acid (14a)

To a solution of 5-((2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)thiazole-2-carbaldehyde **10a** (70 mg, 0.19 mmol) and 2-cyanoacetic acid (26 mg, 0.30 mmol) in chloroform (6 mL) was added piperidine (129 μ l, 1.29 mmol). The mixture was refluxed for 3 days under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (70% AcNH₄, 20 mM in acetonitrile). Yield: dark blue solid (60 mg, 0.14 mmol; 47%).

Mp 228–229 °C. IR (KBr): cm⁻¹ 2215 (C≡N), 1650 (C=O), 1578 (C=C). ¹H NMR (300 MHz, dmso-*d*₆): δ (ppm) 8.23 (s, 1H), 8.19 (s, 1H), 7.91–7.86 (m, 4H), 7.55–7.48 (m, 6H), 7.08 (d, *J* = 1.6 Hz, 1H), 7.04 (d, *J* = 1.6 Hz, 1H), 6.40 (s, 1H). ¹³C NMR (75 MHz, dmso-*d*₆): δ (ppm) 163.2, 154.9, 152.5, 152.1, 144.7, 144.4, 143.6, 133.6, 131.6, 131.5, 130.6, 130.0, 129.0, 128.9, 125.0, 124.6, 116.1, 108.6, 103.8, 102.1, 100.7. HRMS (ESI⁺): *m/z* calcd for [C₂₅H₁₇N₂O₃S]⁺: 425.0954, found: 425.0949.

2.2.14. 3-(5-((2,6-Di-tert-butyl-4H-pyran-4-

ylidene)methyl)thiazol-2-yl)-2-cyanoacrylic acid (14b)

To a solution of 5-((2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl)thiazole-2-carbaldehyde **10b** (124 mg, 0.39 mmol) and 2-cyanoacetic acid (52 mg, 0.61 mmol) in chloroform (15 mL) was added piperidine (277 μ l, 2.58 mmol). The mixture was refluxed for 4 days under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (70% AcNH₄, 20 mM in acetonitrile). Yield: dark violet solid (100 mg, 0.26 mmol; 67%).

Mp 219–220 °C. IR (KBr): cm⁻¹ 2212 (C≡N), 1659 (C=O), 1542 (C=C). ¹H NMR (300 MHz, acetone-*d*₆): δ (ppm) 8.31 (s, 1H), 7.98 (s, 1H), 6.52 (d, *J* = 1.9 Hz, 1H), 6.21 (s, 1H), 6.11 (d, *J* = 1.9 Hz, 1H), 1.32 (s, 9H), 1.26 (s, 9H). ¹³C NMR (75 MHz, acetone-*d*₆): δ (ppm) 168.1, 165.0, 162.9, 152.4, 146.1, 145.1, 143.5, 136.1, 120.1, 115.9, 105.6, 101.2, 99.7, 87.4, 35.9, 35.4, 27.1, 27.0. HRMS (ESI⁺): *m*/*z* Calcd for [C₂₁H₂₅N₂O₃S]⁺: 385.1580, found: 385.1578. Calcd for [C₂₁H₂₄N₂O₃SNa]⁺: 407.1400, found: 407.1389.

2.2.15. 3-(2-((2,6-Diphenyl-4H-pyran-4-

ylidene)methyl)thiazol-5-yl)-2-cyanoacrylic acid (15a)

To a solution of 2-((2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)thiazole-2-carbaldehyde **11a** (120 mg, 0.33 mmol) and 2-cyanoacetic acid (44.5 mg, 0.52 mmol) in chloroform (10 mL) was added piperidine (222 µl, 2.22 mmol). The mixture was refluxed for 4 days under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (50% AcNH₄, 20 mM in acetonitrile). Yield: dark red solid (75.5 mg, 0.18 mmol; 53%).

Mp 263–265 °C. IR (KBr): cm⁻¹ 2213 (C≡N), 1649 (C=O), 1545 (C=C). ¹H NMR (400 MHz, dmso-*d*₆): δ (ppm) 8.57 (s, 1H), 8.49 (s, 1H), 8.45 (d, *J* = 1.4 Hz, 1H), 7.95–7.89 (m, 4H), 7.61–7.52 (m, 6H), 7.15 (d, *J* = 1.4 Hz, 1H), 6.37 (s, 1H). ¹³C NMR (100 MHz, dmso-d⁶): δ (ppm) 173.3, 163.4, 156.5, 155.9, 154.4, 144.3, 138.3, 131.6, 131.4, 130.5, 130.2, 129.0, 128.9, 127.0, 125.1, 124.8, 116.4, 108.2, 104.5, 104.1, 97.6. HRMS (ESI⁺): *m/z* calcd for [C₂₅H₁₇N₂O₃S]⁺: 425.0954, found: 425.0954; calcd for [C₂₅H₁₆N₂O₃SNa]⁺: 447.0774, found: 447.0776.

2.2.16. 3-(2-((2,6-Di-tert-butyl-4H-pyran-4-

ylidene)methyl)thiazol-5-yl)-2-cyanoacrylic acid (15b)

To a solution of 2-((2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl)thiazole-2-carbaldehyde **11b** (190 mg, 0.60 mmol) and 2-cyanoacetic acid (80 mg, 0.93 mmol) in chloroform (25 mL) was added piperidine (397 µl, 3.97 mmol). The mixture was refluxed for 4 days and a half under argon atmosphere and then cooled down to room temperature. Pure compound was obtained by reverse C18 column chromatography (70% AcNH₄, 20 mM in acetonitrile). Yield: red-pink solid (181.6 mg, 0.47 mmol; 79%).

Mp198–202 °C. IR (KBr): cm⁻¹ 2214 (C≡N), 1660 (C=O), 1549 (C=C). ¹H NMR (300 MHz, acetone- d_6): δ (ppm) 8.45 (s, 1H), 8.44 (s, 1H), 7.83 (d, J = 1.4 Hz, 1H), 6.19 (d, J = 1.4 Hz, 1H), 6.12 (s, 1H), 1.32 (s, 9H), 1.29 (s, 9H). ¹³C NMR (75 MHz, acetone- d_6): δ (ppm) 168.8, 167.2, 163.3, 156.7, 144.7, 140.9, 126.8, 116.3, 106.2, 105.4, 102.2, 102.1, 97.2, 35.9, 35.6, 27.2, 27.1. HRMS (ESI⁺): m/z calcd for $[C_{21}H_{25}N_2O_3S]^+$: 385.1580, found:

384.1560; calcd for $[C_{21}H_{24}N_2O_3SNa]^{\ast}{:}$ 407.1400, found: 407.1380.

2.3. Device preparation and characterization

The working and counter electrodes consisted of TiO₂ and thermalized platinum films, respectively, and were deposited onto F-doped tin oxide (FTO, Pilkington Glass Inc., with 15 Ω sq⁻¹ sheet resistance) conducting glass substrates. DSC devices were made using 8 µm thick films consisting of 20 nm TiO₂ nanoparticles (Dyesol[©] paste) and a scattering layer of 4 µm of 400 nm TiO₂ particles (Dyesol© paste). Prior to the deposition of the TiO₂ paste, the conducting glass substrates were immersed in a solution of TiCl₄ (40 mM) at 70 °C for 30 min and then dried. The TiO₂ nanoparticle paste was deposited onto a conducting glass substrate using the screen-printing technique. The TiO₂ electrodes were gradually heated under airflow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 15 min. The heated TiO₂ electrodes were immersed again in a solution of TiCl₄ (40 mM) at 70 °C for 30 min and then washed with ethanol. The electrodes were heated again at 500 °C for 30 min and cooled before dye adsorption. The active area for devices was 0.16 cm². The counter electrode was made by spreading a 5 mM solution of H₂PtCl₆ in isopropyl alcohol onto a conducting glass substrate containing a small hole to allow the introduction of the liquid electrolyte using vacuum, followed by heating at 390 °C for 15 min. Films were sensitized in 0.3 mM dye solutions in dichloromethane containing 0.2 mM for 3 h at room temperature. Finally, the working and counter electrodes were sandwiched together using a thin thermoplastic (Surlyn) frame that melts at 100 °C. The electrolyte for all devices measured was the LP1 as described later on this work.

The IV characteristics of cells were measured using a Sun 2000 Solar Simulator (150 W, ABET Technologies). The illumination intensity was measured to be 100 mW/ m^2 with a calibrated silicon photodiode. The appropriate filters were utilized to faithfully simulate the AM 1.5G spectrum. The applied potential and cell current were measured with a Keithley 2400 digital source meter. The IPCE (Incident Photon to Current conversion Efficiency) was measured using a homemade set up consisting of a 150 W Oriel Xenon lamp, a motorized monochromator and a Keithley 2400 digital source meter.

Transient photovoltage and charge extraction measurements were carried out on a home-built system. In charge extraction, white light from a series of LEDs was used as the light source. When the LEDs are turned off the cell is immediately short circuited and the charge is extracted allowing electron density in the cells to be calculated. By changing the LEDs intensity the electron density can be estimated as a function of cell voltage. In transient photovoltage measurements, in addition to the white light applied by the LEDS, constant background voltage is applied to the cells and again, a diode pulse (660 nm, 10 mW) is then applied to the sample inducing a change of 2-3 mV within the cell. The resulting photovoltage decay transients are collected and the τ values are determined by fitting the data to the equation $\exp(-t/\tau)$.

2.4. Computational details

Theoretical calculations were performed using Gaussian 09 [20] and the default parameters provided by this software package. Solvent effects were estimated using a Conductor-like Polarizable Continuum Model (CPCM) [21]. Equilibrium geometries in solution were obtained using the M06-2x hybrid meta-GGA exchange correlation functional [22] and the medium size 6-31G^{*} basis set [23] both for ground and first excited states. Excitation energies were calculated by time-dependent single point calculations using the M06-2x/6-311+G (2d,p) model chemistry. Absorption spectra were calculated from the vertical excitations at the optimized ground state geometry, emission spectra from the vertical excitations at the optimized excited state geometry and adiabatic excitation energies (E_{0-0}) were calculated subtracting the ground state energy from the excited state energy both calculated at their optimized geometry. Molecular Orbital contour plots were obtained using the Avogadro software [24] at 0.04 isosurface value.

3. Results and discussion

3.1. Synthesis and structural characterization

Aldehydes (**8**–**9**)**a** were prepared by a Horner reaction of (2,6-diphenyl-4*H*-pyran-4-yl)diphenylphosphine oxide **1a** [25] with the reported monoprotected aldehydes **2** [26] and **3** [27] respectively. Thiazole aldehydes **10a** and **11a** were prepared from a procedure previously reported in our laboratory [19] (see Scheme 1).

Tert-butyl aldehydes **8b**, **9b** were obtained by a Wittig reaction from the phosphonium salt **1b** [28] and the corresponding monoprotected aldehydes as described before. Concerning aldehydes bearing a matched **10b** or a mismatched thiazole ring **11b**, they were also prepared in two steps from phosphonium salt **1b** with the commercially available thiazolecarbaldehydes **4** or **6** and then, followed by lithiation and reaction with anhydrous DMF. Finally, the desired dyes **(12–15)a,b** were obtained by Knoevenagel condensation of the aforementioned aldehydes with 2-cyanoacetic acid in the presence of piperidine as shown in Scheme 2. All intermediates and the final organic dyes have been confirmed by ¹H NMR, ¹³C NMR and HRMS.

3.2. Optical properties

The absorption spectra of the dyes in CH₂Cl₂ are shown in Fig. 2 and the photophysical data are collected in Table 1. In order to compare with the new systems we are also included in this study data of the previously reported dyes with a thiophene ring in the π -spacer (**16a,b**) [13] (Fig. 1). All dyes exhibit a strong and broad band ranging from 450 to 650 nm that can be assigned to an ICT process. The energy of the ICT band is dependent on the heterocycle employed as spacer and does not follow a general rule. All dyes have molar extinction coefficients (ε) ranging from 24600 to 52,000 M⁻¹ cm⁻¹, higher than those of standard



(12-15)a,b

 R = Ph for series a
 12: $X = N-CH_3$; Y = CH; Z = CH

 $R = {}^{t}Bu$ for series b
 13: X = O; Y = CH; Z = CH

 14: X = S; Y = CH; Z = CH

 15: X = S; Y = N; Z = CH

Scheme 2. Synthesis of 4H-pyranylidene organic dyes (12-15)a,b.

ruthenium dyes N3 [29] and N719 [30] (13,900 and 14,000 M^{-1} cm⁻¹ respectively) except the compound **15a** with a molar extinction coefficients around 11,000 M^{-1} cm⁻¹. It is interesting to note that compound **15b** has the highest molar extinction coefficient of all the series (51,929 M^{-1} cm⁻¹).

When the dyes are attached to TiO_2 surface, the maximum absorption peaks are blue-shifted (in some cases more than 50 nm) as compared to those in solution. In general, the blue shifts of the absorption spectra on TiO_2 could be ascribed to deprotonation and formation of H-aggregates (extended head to tail stacking) [31] of the dyes on

the TiO₂ surface, as it was described for other organic molecules [17d,32].

3.3. Theoretical calculations

In order to get further insight in the electronic and optical properties of the studied compounds, theoretical calculations using TD-DFT (Time Dependent Density Functional Theory) and the CPCM (Conductor-like Polarizable Continuum Model) solvation method have been made. Calculations were first performed at the ground state geometry to obtain the ground state dipole moments (μ_0), orbital

Table 1			
Optical and electrochemical	properties	of the	dyes.

Dye	λ_{abs} , nm (ϵ , M ⁻¹ cm ⁻¹) ^a	$\lambda_{\rm abs}$, nm ^b	$\lambda_{\rm em}$, nm ^c	$E_{\rm ox}$, ^d V (vs NHE)	$E_{0-0,e} eV$	$E_{ox}^{,f}$ V (vs NHE)
12a	514 (37067)	463	587	0.75	2.22	-1.45 (-1.26)
12b	515 (45550)	481	571	0.77	2.27	-1.49 (-1.37)
13a	568 (31194)	491	651	0.77	1.99	-1.22 (-1.10)
13b	538 (26761)	507	621	0.83	2.08	-1.24 (-1.19)
14a	566 (24679)	506	660	0.94	1.98	-1.02 (-0.89)
14b	573 (27785)	508	646	0.97	2.00	-1.02 (-0.95)
15a	533 (10934)	467	611	0.95	2.12	-1.16 (-1.13)
15b	531 (51929)	461	589	1.10	2.19	-1.10 (-1.33)
16a	553 (41071)	487	655	0.81	2.00	-1.19 (-1.17)
16b	544 (33558)	497	588	0.86	2.16	-1.19 (-1.22)

^a Absorption maxima in CH₂Cl₂ solution.

 b Absorption maxima on TiO_2 films (4 μm).

^c Emission spectra were recorded in CH₂Cl₂.

^d First oxidation potentials were measured from a three electrode electrochemical cell in CH_2Cl_2 containing 0.1 M TBAPF₆. A glassy carbon, Ag/AgCl (KCl 3 M), and Pt were used as working, reference, and counter electrode respectively.

^e Zeroth-zeroth transition energies estimated from the intersection of normalized absorption and emission spectra in CH₂Cl₂ solution.

^f Excited-state oxidation potentials of the dyes obtained from $E_{ox} - E_{0-0}$.



Fig. 1. Molecular structures of studied organic dyes **12–15** and analogues **16a,b** previously reported[13].

energies and topologies, absorption wavelengths (λ_{abs}) and oscillator strengths (f), and then, the first excited state geometries were optimized to obtain the emission wavelength (λ_{em}) and the adiabatic excitation energy (E_{0-0}). The results of these calculations are gathered in Table 2. Compared to experimental results, theoretical calculations provide a reasonable accuracy with mean absolute errors of 18 nm (0.09 eV) in λ_{abs} , 12 nm (0.04 eV) in λ_{em} and 0.10 eV in E_{0-0} , and reproduce the experimental trends.

According to the calculations, the first excited state is mainly contributed from a one electron HOMO to LUMO transition. The topology of these orbitals (Fig. 3) accounts for an ICT from the 4*H*-pyranylidene donor to the cyanoacrylic acid acceptor. There is however a large HOMO-LUMO spatial overlap that is responsible for the high oscillator strengths (*f*) and molar extinction coefficients (ε). In good agreement with the experimental trend, the highest excitation energies corresponds to pyrrole derivatives **12** which also display the largest HOMO-LUMO gap followed by the matched thiazole derivatives **15**.

Theoretical calculations also provide useful information on the changes of the geometry and charge distribution when passing from the ground to the first excited state. The studied compounds can be represented by using two limiting resonance structures (Fig. 4) displaying a neutral or a zwitterionic charge distribution.

As previously mentioned, the lowest excitation involves an ICT and therefore, it is expected an increased contribution from the zwitterionic structure on passing from the ground to the first excited state. These changes are not only responsible for a change in charge distribution but also in structural parameters. The excited state displays a more aromatized 4H-pyranylidene ring, a more quinoidal heterocyclic spacer and changes in the alternation of single and double bond lengths. If we take compound **15b** as an example, the sum of Mulliken charges at the donor, the spacer and the acceptor are +0.476, -0.388 and -0.087 respectively in the ground state and +0.674, -0.413 and -0.260 in the excited state and the bond lengths are those depicted in Fig. 5. As expected, both the charge distribution and the changes in bond lengths point to a larger contribution of the zwitterionic structure to the first excited state.

3.4. Electrochemical properties

The electrochemical properties of dyes adsorbed on TiO_2 films were studied by using differential pulse voltammetry (DPV) methods. Representative voltammograms were performed under argon, in CH_2CI_2 using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, a glassy carbon working electrode, a Pt counter electrode and a Ag/AgCl reference electrode. The relevant electrochemical data are listed in Table 1 and in order to establish a comparison we have also included parameters for the previously reported dyes with a thiophene ring [13].

The electronic nature of the heteroaromatic rings in the conjugated spacer affects significantly to the oxidation potential values. It is interesting to note that dyes with a more electron rich ring like pyrrol are the easier oxidized in both phenyl and *tert*-butyl series. The stronger electron-donating ability of this system resulted in a higher HOMO energy level (estimated from its first oxidation potential). Thus, the HOMO energy decreased (more positive E_{ox}) in the order: E_{ox} (pyrrol) < E_{ox} (furan) < E_{ox} (thiophene) < E_{ox} (thiazole matched) < E_{ox} could show a



Fig. 2. Absorption spectra of organic dyes (12-16)a,b in CH₂Cl₂ (top) and on TiO₂ transparent films (bottom).

 Table 2

 Results of DFT Calculations in dichloromethane solution.^a

Dye	$\mu_0^{\mathbf{b}}$	λ_{abs}^{c}	f	$E_{\rm HOMO}^{\rm d}$	E_{LUMO}^{d}	λ _{em} ^c	E_{0-0}^{d}
12a	14.5	483 (2.57)	1.79	-6.39	-1.91	615 (2.01)	1.95
12b	15.5	477 (2.60)	1.59	-6.33	-1.80	569 (2.18)	2.38
13a	8.4	545 (2.28)	0.94	-6.39	-2.18	651 (1.91)	2.03
13b	8.0	528 (2.35)	0.80	-6.34	-2.01	595 (2.09)	2.21
14a	9.2	568 (2.18)	1.24	-6.52	-2.50	673 (1.84)	2.00
14b	10.1	553 (2.24)	1.14	-6.48	-2.38	634 (1.96)	2.08
15a	8.1	521 (2.38)	1.30	-6.69	-2.37	612 (2.03)	2.20
15b	8.8	502 (2.47)	1.20	-6.67	-2.23	569 (2.18)	2.32
16a	9.8	550 (2.25)	1.29	-6.43	-2.30	652 (1.90)	2.08
16b	10.5	533 (2.33)	1.19	-6.39	-2.15	603 (2.06)	2.18

^a M06-2x/6-311+G(2p,d)//M06-2x/6-31G^{*} model chemistry using the CPCM solvation model.

^b In Debye.

^c In nm with parenthesized energy in eV.

^d eV.



Fig. 3. Contour plot of the HOMO (left) and LUMO (right) of compound 15b.



Fig. 4. Resonance structures of compounds 12-16.



Fig. 5. Selected Bond lengths of compound **15b** in the ground (Blue) and first excited (Red) states. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

better performance of the dispositive because of its higher difference with the iodide/triiodide redox couple (+0.42 vs NHE) and then, a better regeneration of the oxidize dye after electron injection into the conduction band of TiO₂. Concerning the thiazole dyes, oxidation potential values for the mismatched ones are slightly higher than their matched isomers, in agreement with the previous results [19]. These results are fairly consistent with the theoretical calculations using a polarizable continuum model. The excited state potential (E_{ox}^*) was deduced from the expression $(E_{\text{ox}}-E_{0-0})$, where the band gap energies (E_{0-0}) were estimated from the intercept of the normalized absorption and emission spectra (Table 2). The E_{ox}^* values were in all cases sufficiently more negative than the energy conduction band edge energy level of TiO_2 (-0.5 V vs NHE) which can indicate that the electrons can be efficiently injected into the TiO₂ from the excited dyes. These results are probably related with the delocalization energies of the heterocyclic rings (furan 16 Kcal mol^{-1} . pyrrole 21 Kcal mol^{-1} and thiazole 25 Kcal mol^{-1}).

3.5. Photovoltaic properties of DSSCs

The device performance (with an effective area of 0.16 cm²) were measured under sun-simulated AM 1.5 G irradiation (100 mW/cm²). The open-circuit photovoltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (*ff*), and solar-to-electrical energy conversion efficiencies (η) are listed in Table 3. Moreover, current density-voltage (J–V) curves and incident photon- to- current conversion efficiencies (IPCE) of devices based on these dyes are shown in Figs. 6 and 7, respectively. The optimized

Table 3

Photovo	oltaic	properties	of	DSSCs	constructed	using	the c	lyes	(12-	·16)a,	, b .
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Dye	J_{sc} (mA cm ⁻²)	V_{oc} (V)	ff	η (%)
12a	3.10	0.564	65	1.13
12b	5.44	0.554	70	2.13
13a	6.48	0.544	72	2.52
13b	9.06	0.609	72	4.00
14a	2.93	0.569	70	1.16
14b	4.89	0.609	76	2.28
15a	2.11	0.569	60	0.72
15b	10.51	0.689	73	5.35
16a	8.91	0.594	68	3.62
16b	12.06	0.654	74	5.85

conditions for these dyes are determined to be 0.3 mM of dye in dichloromethane solution, 2 h of immersion and LP1 (0.5 M BMII/0.05 M $I_2/0.5$ M TBP/0.1 M LiI in acetonitrile) as electrolyte.

As it can be seen, the IPCE performance of the DSSCs with bulky tert-butyl groups in the donor system is higher than those with phenyl groups (Fig. 6). It should be noted that for dves **15b** and **16b** the IPCE is roughly constant (70-78%) in the range of 400-600 nm, while for the rest of compounds a maximum can be observed around 450 nm. Surprisingly, the performance of the IPCE spectrum of dye **15a** (solar cell efficiency, $\eta = 0.72\%$) is much lower than **15b** (solar cell efficiency η = 5.35%). This result was not observed when comparing the other couples of **a**,**b** compounds. This result can be explained in terms of the lower molar extinction coefficient of the phenyl system (**15a**: $10950 \text{ M}^{-1} \text{ cm}^{-1} \text{ vs}$ **15b**: $51929 \text{ M}^{-1} \text{ cm}^{-1}$) as well as the presence of aggregates of type H (see figure S-53 in supporting information) in the TiO₂ loading conditions for 15a, despite the use of the chenoxycholic acid as co-adsorbent. Our hypothesis has been confirmed by the measurement of the absorption at different concentrations of both dyes. Thus, whereas 15b is linear in the range of measured concentrations (10^{-4} M) **15a** do not show Lamber-Beer behaviour from relatively low concentrations $(0.3 \times 10^{-4} \text{ M})$ (Fig. 8). Finally, it can be noted that electrodes from dye 15a were quickly discolored, even in presence of the electrolyte, which indicates certain instability of the dye **15a** on the TiO₂ surface.

As listed in Table 3, the *tert*-butyl series give higher energy conversion efficiencies than the corresponding phenyl ones. In general, devices from *tert*-butyl substituents in the 4*H*-pyranylidene ring showed a higher open-circuit voltage than their phenyl equivalents. The improvement of V_{oc} can be attributed to the reduction of the charge recombination processes between the photo-injected electrons at the TiO₂ and the oxidized electrolyte. The presence of sterically hindered *tert*-butyl groups reduces the aggregation phenomena and also block the approach of I⁻ to the TiO₂ surface due to the improved molecular packing of the molecules at the surface of the semiconductor metal oxide as reported in other literature examples [33].

In contrast, the lower performances of DSSCs based on the phenyl dyes are mostly due to the lower J_{sc} values compared to *tert*-butyl series.

It is well established that in a DSSC, the V_{oc} is determined by the energy difference between the quasi-



Fig. 6. Photocurrent action spectra of the TiO₂ electrodes sensitized: phenyl series (a), tert-butyl series (b).



Fig. 7. I/V curves recorded under AM 1.5G illumination and in the dark for DSC devices.



Fig. 8. Absorption vs concentration for dyes 15a and 15b.

Fermi-level of the metal oxide semiconductor, which is correlated with its conduction band (CB) edge and the electron density, and the oxidation potential of the electrolyte used. The electron density is itself dependent on rate of recombination between the photo-injected electrons at the semiconductor metal oxide and the oxidized electrolyte species. To investigate the difference in voltage for these devices, charge extraction and transient photovoltage measurements were conducted. Both techniques have been widely used in the study of the limiting interfacial charge transfer reactions in DSSC due to the fast data acquisition which prevents the degradation of the devices during the measurement period. In fact, the use of both techniques implies no more than 20 min for each device. As can be seen in Fig. 9, the experimental data showed a shift for the electron density vs light bias (the solar cell photovoltage when illuminated at different light intensities) of the exponential curve. The shift is more pronounced for the 12a with almost 50 mV when compare to devices made using 16a. This shift corresponds to a change on the position of the TiO₂ conduction band-edge but does not explain by itself the observed differences in V_{oc} (Table 3). Taking into account that all devices are prepared under the same conditions and using the same solvent and electrolyte the shift can only be attributed to the differences on surface molecular dipole promoted by the sensitizers at the surface of the semiconductor nanoparticles. This is in good agreement with the calculated



Fig. 9. Electron density as a function of cell voltage.



Fig. 10. Device electron lifetime τ as function of charge density (e⁻/cm³).

molecular dipole moments of these dyes (Table 2) larger for compounds **12** compared to **16**. Moreover, as depicted in Fig 10, the slower recombination kinetics by the devices made using the sensitizer **16a** also influences the different photovoltage observed. Furthermore, it is worthy to mention that in all cases the **b** series shows slower recombination with the electrolyte than the **a** series as measured by TPV, in good agreement with the better molecular packing of the **b** series that includes bulky groups in each structure acting as an effective barrier preventing the contact between the oxidized electrolyte and the TiO_2 nanoparticles surface.

4. Conclusions

In summary, we have designed and prepared eight new Ruthenium-free dyes with a 4*H*-pyranylidene ring as the donor moiety to evaluate the effects of several aromatic π linkers (pyrrol, furan, thiazole and thiophene) on the electrochemical and photovoltaic properties of DSSCs in D- π -A systems. The most effective bridge has to be found the thiophene, followed by the mismatched-oriented thiazole. These systems lead to a higher recombination

resistance and V_{oc} . The observed values can be attributed to the presence of sterically hindered *tert*-butyl groups and to the differences on molecular dipoles of the sensitizer at the TiO₂ surface. Matched orientation of a thiazole ring in the π -bridge leads to sensitizers less efficient. The lower performance measured for pyrrol derivatives could be due to the higher HOMO energy values for dyes containing this heterocycle.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.09.003.

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