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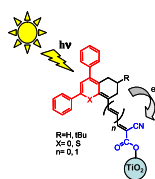
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Graphical Abstract

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**New D- π -A-conjugated organic sensitizers
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New D- π -A-conjugated organic sensitizers based on α -pyranylidene donors for dye-sensitized solar cells

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ABSTRACT

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A series of new push-pull organic dyes incorporating a cyanoacrylic acid group as electron acceptor unit and α -chalcogenopyranylidene group ($X = S ; O$) as electron donor unit has been synthesized, characterized and used as sensitizer for dye-sensitized solar cells (DSSCs). For the first time, α -pyranylidene and thiopyranylidene groups, have been evaluated in DSSC. To obtain the thermodynamic values of the solar cell, an investigation of their electrochemical (CV) and optical properties (UV-vis absorption spectroscopy) is also reported.

Keywords:

D- π -A molecules
 α -pyranylidene
 α -thiopyranylidene
Dye-sensitized solar cell

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Dye-sensitized solar cells (DSSCs), as some of the promising alternatives for the photovoltaic conversion of solar energy, have attracted considerable attention because of their low production cost, easy preparation and relatively high solar-to-electricity conversion efficiency.¹

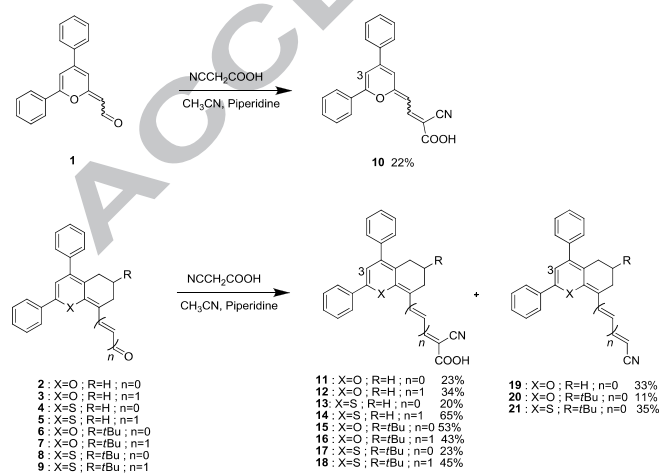
Sensitizers play a key role in the DSSCs and have been extensively studied by researchers throughout the world.² The most typical sensitizers used in DSSCs are the ruthenium(II) polypyridyl complexes, such as the famous dye coded N719.^{1b}

Recently, many organic dyes have been synthesized as alternatives to the Ru-complex to reach higher absorptivities with easier and cheaper synthesis.^{2b-c}

Most organic dyes are characterized by a donor- π -acceptor (D- π -A) structure, so-called push-pull systems, in which the donor group (D) is an electron-rich unit linked through a π -spacer to an electron acceptor group (A). In this context, α and γ pyranilidene fragments, reaching aromatic pyrylium character when intramolecular charge transfer (ICT) occurs, are particularly attracting as donor part in push-pull structures. The use of this proaromatic fragment in D- π -A structure for second order NLO properties has been described by some of us^{3,4} and other groups.⁵

Moreover, to date only few examples of dyes containing γ -pyranilidene as donor moieties for DSSC applications have been described.⁶ In this study, we report, for the first time, the use of α -pyranilidene⁴ and α -thiopyranilidene,⁷ as donor fragments in small organic molecules based dyes and their applications in DSSCs. We focused on the influence of (1) the intracyclic heteroatom (X= O, S Scheme 1) of the donors and (2) the length of the polymethine (-CH=)_n conjugated spacer,⁸ both on the electronic ground state structure and TiO₂ DSSC device performances. In order to determine the Gibbs free enthalpy of the injection (ΔG_{inj}) and dye regeneration reaction (ΔG_{reg}), the electrochemical and optical properties of the dyes were also recorded.

We have designed and synthesized nine new promising D- π -A conjugated organic sensitizers (**10-18**) with fused or non-fused ring α -pyranilidene groups, containing oxygen or sulfur atoms as donors, unsaturated polymethine fragments as spacers and cyanoacrylic acid as an acceptor. The choice of fused ring α -pyranilidene was motivated by a gain of stability of these molecules and by the control of stereochemistry of the aldehyde precursors.^{9c}



Scheme 1. Synthesis of dyes **10-18**

The target chromophores (**10-18**) were prepared from Knoevenagel condensation of heterocyclic aldehydes (**1-9**), easily obtained according to published procedure,⁹ and cyanoacetic acid in the presence of a catalytic amount of piperidine in CH_3CN ,

yields ranging from 20 to 65 % (Scheme 1). The color of the solid products (**10-18**) was dark blue. During the reaction, an additional red product was observed by TLC. It results from a concomitant decarboxylation reaction (compounds **19-21**). To the best of our knowledge, this consecutive reaction has not been previously mentioned for other organic sensitizers containing cyanoacrylic acid.

All new compounds (**7, 9, 10-21**) were fully characterized by FT-IR, ¹H NMR, ¹³C NMR as well as HRMS spectroscopy.

The absorption spectra of the dyes recorded in CH_2Cl_2 show large absorptions in the range 400-800 nm (Figures S1- S2). The first region (under 500 nm) is composed of localized π - π^* transitions and the second region exhibits a strong absorption band up to 500 nm which can be ascribed to ICT processes (**Table 1**). All compounds exhibited good absorption properties with high molar extinction coefficients ϵ_{max} (1.1 to $2.4 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). In the present case, the substitution of the oxygen atom by sulfur in the α -pyranilidene series (**10-18**) slightly red-shifts the λ_{max} values. In addition, an increase of the molar extinction coefficient ϵ occurs in the α -thiopyranilidene series (except for **18**) (**Table 1**).

Increasing the size of the chalcogen atom (O to S) may give a red-shift of λ_{max} , as previously reported for chalcogenopyrylium¹⁰ and chalcogenoxanthylum dyes.¹¹ This red shift was due to the concomitant increasing and lowering of π (HOMO) and π^* (LUMO) levels respectively, as the nature of the heteroatom varies. Such behavior was observed by some of us for organometallic γ -chalcogenomethylenepyran.^{3d} As observed for other push-pull molecules,^{8c-d,12} increasing conjugation length (n=0 to n=1) led to a red shift and **to an increase of the molar absorption coefficient ϵ_{max} (except for 18)**, which are desirable for harvesting the solar spectrum.^{8c} Red-shifting the absorption spectra is an important consideration in the design of efficient organic dye photosensitizers as long as the potential levels of the dye in its ground and excited states matched to the CB level of the TiO₂ electrode and to the redox potential of the I/I₃⁻ electrolyte (*vide infra*).¹³

To obtain information about the pyrylium character of the α -chalcogenopyranilidenes ((6,7-dihydro-5H-benzopyran-8-ylidene) and (6,7-dihydro-5H-thiobenzopyran-8-ylidene) series) two NMR spectroscopic criteria were taken into account: (i) the differences in ³J_{H,H} values ($\Delta^3 J_{\text{H,H}}$) across adjacent C=C and C-C bonds of the unsaturated chain and (ii) the chemical shift value of the proton in position 3 (**H3**). (Scheme 1). **The analysis of the coupling constant (³J_{H,H}) of the ethylenic spacer for compounds 12, 14, 16 and 18, showed that in all cases the CH=CH bonds have an E configuration (14.0 Hz-14.4 Hz).** Moreover, it has been previously emphasized that the variation of ³J_{H,H} values along a conjugated polyene chain provides a good estimation of the C-C bond lengths (or bond orders).¹² In push-pull molecules containing a similar donor (acceptor), the so-called bond length alternation (BLA) depends on the strength of the acceptor (donor).¹⁴ As a consequence: the difference $\Delta^3 J_{\text{H,H}}$ between coupling constants (³J_{H,H}) of concomitant C-C bonds ranges from 6.5 Hz for molecules with alternating C=C and C-C bonds to 0 Hz for molecules in which all C-C bond lengths are equal (the polymethine limit).^{3c} **Compounds 12, 16 and 18 show $\Delta^3 J_{\text{H,H}}$ values in the range 2-2.7 Hz in acetone-d₆.** As well, chemical shifts of the polymethine protons showed an oscillatory behavior, reflecting an alternation of the electron density of the carbon atoms to which they are bonded. This is a characteristic of polarized molecules like merocyanines dyes.¹⁵

The chemical shift of the (H3**) proton linked to the pyranilidene ring may serve to evaluate the pyrylium character of the pyran**

ring and consequently the ground state polarization of the donor fragment.^{16,4} When the H3 chemical shift of the non-fused and fused ring α -pyranylidene **10** and **11** are compared a decrease of the value is observed for **11** suggesting an increase of the donor ability of non fused ring pyranylidene group. We also observed a decrease of the chemical shift of H3 on lengthening the spacer, a finding that suggests a stronger contribution of the zwitterionic canonical form for the shorter dyes in agreement with push-pull compounds containing γ -pyranylidene group.^{3d}

The redox properties of dyes **10-18** were studied by cyclic voltammetry (CV) in CH_2Cl_2 (Table 1).

Table 1. Optical and electrochemical properties of dyes **10-18**

Dye	λ_{max} ^a nm	ϵ_{max} ^a $\text{M}^{-1} \text{cm}^{-1}$	$E(S/S^+)$ ^b V vs NHE	$E(S^*/S^+)$ ^c V vs NHE	ΔG_{inj} eV	ΔG_{reg} eV
10	539	$1.62 \cdot 10^4$	1.26	-0.68	-0.18	-0.91
11	549	$1.11 \cdot 10^4$	1.12	-0.78	-0.28	-0.77
12	604	$1.60 \cdot 10^4$	0.85	-0.86	-0.36	-0.50
13	557	$1.56 \cdot 10^4$	1.11	-0.64	-0.14	-0.76
14	596	$2.44 \cdot 10^4$	0.89	-0.87	-0.37	-0.54
15	548	$1.50 \cdot 10^4$	1.11	-0.79	-0.29	-0.76
16	588	$1.87 \cdot 10^4$	0.88	-0.86	-0.36	-0.53
17	554	$1.93 \cdot 10^4$	1.08	-0.53	-0.03	-0.73
18	597	$1.56 \cdot 10^4$	0.90	-0.71	-0.21	-0.55

^aMeasured in CH_2Cl_2 ; ^b $E(S/S^+)$: redox energy level in the ground state. First oxidation potentials vs NHE, determined by cyclic voltammetry in $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ ^c $E(S^*/S^+)$: Fermi level of excited molecules, calculated from $E(S^*/S^+) = E(S/S^+) + \Delta E_{0-0}(S/S^*)$, ΔE_{0-0} : stored excitation energy, obtained from λ_{onset} ; $\Delta G_{\text{inj}} = E(S^*/S^+) - E_{\text{CB}}$ (TiO_2) with $E_{\text{CB}}(\text{TiO}_2) = -0.5 \text{ V vs NHE}$; $\Delta G_{\text{reg}} = E^\circ(\text{I}^-/\text{I}_3^-) - E(S/S^+)$ with $E^\circ(\text{I}^-/\text{I}_3^-) = 0.35 \text{ V vs NHE}$

The first oxidation potential E_{ox} measured for the new dyes allows the determination of the redox energy level in the ground state $E(S/S^+)$. Comparison of the α -pyranylidene series with the α -thiopyranylidene one shows that substitution of the oxygen atom in the pyran ring by a sulfur atom did not change the oxidation potential (Table 1) (see for example **12 vs 14**, Figure 1). As well, variation of the R group (H vs tBu) in the fused ring did not modify this potential (table 1) (see for example **13 vs 17**, Figure 1). However, a lowering of $E(S/S^+)$ is noted by comparing **10 vs 11**, which suggests that the non fused ring destabilizes the HOMO energy level (Table 1). Also, lengthening the polyenic chain of the dyes ($n=0$ to $n=1$) facilitates the oxidation process and gives rise to a decrease of the $E(S/S^+)$ value (Table 1) (for example **13 vs 14**, Figure 1), according to the expansion of the π -conjugation system of the dyes.¹²

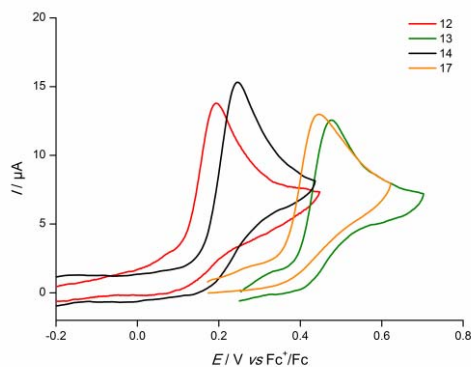


Figure 1. Cyclic Voltammograms of selected compounds **12**, **13**, **14** and **17** showing the variation of the potential with structural

modifications; at a carbon working electrode in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (0.1 M); concentrations of ca. 1 mM; $\nu = 0.1 \text{ V s}^{-1}$.

The redox levels of excited molecules $E(S^*/S^+)$ ¹⁷ can be estimated by subtracting ΔE_{0-0} from the redox energy level of the molecule in the ground state (E_{ox}). The energy of the 0-0 transition between the lowest vibrational levels in the ground and excited states ΔE_{0-0} was obtained from the absorption onset of the dyes. Then, driving forces for electron injection and for regeneration of the oxidized dyes by the electrolyte may be estimated. From these data, we found that the $E(S/S^+)$ levels of the dyes are much more positive (0.85-1.26 V) than the iodine/iodide redox potential value (0.35 V)¹⁸ thus, allowing efficient regeneration of the oxidized dye thermodynamically (ΔG_{reg}) (Table 1). The excited levels of these dyes are more negative $E(S^*/S^+)$ (-0.53 V to -0.87 V) than the conduction-band edge energy level (E_{CB}) of the TiO_2 electrode (-0.5 V vs NHE),¹⁹ which implies that electron injection from the excited dye into the conduction band of TiO_2 is energetically allowed (ΔG_{inj}) (Table 1). But with the assumption that energy gap of 0.2 eV is necessary for efficient electron injection,²⁰ the values of ΔG_{inj} calculated for compounds **10**, **13** and **17** are not negative enough to favorably inject electrons into the conduction band of TiO_2 .

Dye	Jsc (mA/cm^2)	Voc (mV)	FF (%)	PCE (%)
11 ^a	4.62 ± 0.08	565.1 ± 3.2	74.5 ± 1.1	1.95 ± 0.11
12 ^a	2.45 ± 0.08	488.7 ± 1.1	69.0 ± 0.3	0.83 ± 0.03
13 ^a	0.58 ± 0.02	469.0 ± 1.4	69.2 ± 2.1	0.19 ± 0.01
13 ^b	1.13 ± 0.02	381.8 ± 4.9	69.3 ± 0.6	0.30 ± 0.01
14 ^a	1.17 ± 0.11	434.3 ± 3.6	69.3 ± 0.9	0.36 ± 0.03
14 ^b	1.90 ± 0.26	370.7 ± 14.3	65.6 ± 0.1	0.46 ± 0.08
15 ^a	4.53 ± 0.13	598.3 ± 3.4	75.1 ± 2.1	2.03 ± 0.01
16 ^a	1.61 ± 0.02	523.2 ± 2.0	73.1 ± 0.2	0.61 ± 0.01
17 ^a	0.64 ± 0.02	495.4 ± 1.3	72.7 ± 0.1	0.23 ± 0.01
17 ^b	1.02 ± 0.01	386.5 ± 0.9	67.7 ± 0.3	0.27 ± 0.01
18 ^a	0.91 ± 0	484.8 ± 10.5	63.2 ± 7.2	0.28 ± 0.04
18 ^b	1.45 ± 0.09	372.0 ± 1.5	66.2 ± 0.3	0.36 ± 0.03

Table 2. Performances of TiO_2 based DSSC associated to dyes **11-18** recorded under simulated sunlight AM1.5.

^aThe electrolyte is formulated as such: 30 mM I_2 , 0.1 M LiI, 0.6 M N-tert-N'-ethyl-methylimidazolium iodide, 0.1M guanidinium thiocyanate and 0.1 M 4-terbutylpyridine in acetonitrile. ^b4-terbutylpyridine was removed from the previous electrolyte.

Finally, the dyes **11-18** were tested in dye sensitized solar cells with an iodide based electrolyte (details given in the experimental part). All the dyes strongly adsorbed on TiO_2 as evidenced by the UV-Vis spectra of the photo-electrodes (Figure S1). The performances of the resulting DSSC were subsequently estimated under calibrated AM 1.5 simulated solar irradiance and the results are gathered in Table 2. The incident photon to current efficiency (IPCE) spectra are shown in Figure 2. At first glance, it appears clearly that the nature of the intracyclic heteroatom plays a major role on the photoconversion efficiencies (PCE) of corresponding DSSC. Indeed, dyes where X = O perform significantly better than dyes where X = S. The reason is likely grounded in the lower electron injection driving forces of S-bearing dyes compared to O-bearing ones (Table 1). Among the latter, dyes **11** and **15** are well ahead dyes **12** and **16** owing to a higher Jsc (ca. $4.5 \text{ mA}/\text{cm}^2$). The driving forces for dye

regeneration by the redox mediator are significantly smaller for the latter dyes compared to the former, a likely reason rationalizing the lower performances of dyes **12** and **16** despite their better optical properties (higher extinction coefficients, red shifted absorption, Table 1).

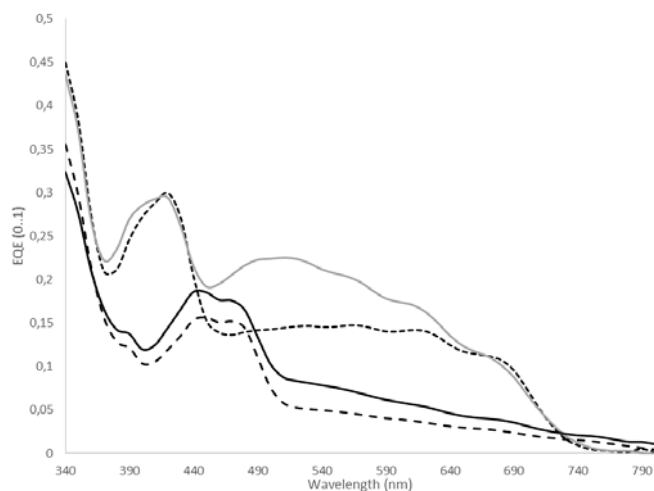


Figure 2. IPCE spectra of DSSC where TiO₂ was sensitized by dyes **11** (grey line), **12** (black line), **15** (black dotted line) and **16** (black dashed line).

Appending a bulky *tert*-butyl group on the dye structure (**15** and **16**) has surprisingly little impact on the Light Harvesting Efficiency (LHE) and on J_{sc}, indicating that the higher hydrodynamic volume of **15** and **16** does not significantly modify the packing of the dyes on the TiO₂ surface. We notice, however, a slight increase of the Voc: analysis of the J-V curves recorded in the dark reveal that the dark current is diminished for *tert*-butyl bearing dyes (**15** and **16**) compared to naked **11** and **12** (Figure S3). *Tert*-butyl groups probably passivate better the surface of TiO₂, thus preventing counter-productive interfacial charge recombination between injected electrons in TiO₂ and the electrolyte, hence curbing dark current and improving Voc²¹. However, recorded output potentials remain low (600 mV at best), further protection of the left-over naked sites of TiO₂ with bulkier chains would be a positive boon for the future design of such dyes. Importantly, even the best performing dyes among those presented in this contribution feature quite low PCE (Table 2). In order to investigate the extent of dye aggregation at the surface of TiO₂, chenodeoxycholic acid (CDCA) was added in the dyeing bath. While Voc and FF were virtually not affected, J_{sc} severely decreased yielding poorer performances (see figure S9 and table S1). CDCA molecules compete with dye molecules during the chemisorption step, entailing a diminution of the LHE and therefore J_{sc}. All in all these experiments reveal that aggregation of the dye molecules on the surface of TiO₂ is not the major limiting factor for low charge injection because it has no favorable effect on the photocurrent density, whatever its concentration in the dye bath. The broad signals, extending until 720 nm, prove that these organic dyes can display a virtually panchromatic behavior and allow current generation at the edge of near infrared. All these features are highly desirable for efficient light collection and conversion by photovoltaic devices and prove the uttermost interest of this family of dyes. As mentioned above, dyes featuring X = S give poor photoconversion efficiencies because of too small an injection driving force. In order to improve the PCE, 4-*tert*-butylpyridine (TBP) was removed from the electrolyte since it bends upward the conduction band,²² thus lowering the electron injection driving force. A significant improvement of J_{sc} but concomitant decrease of Voc (Table 2) was monitored upon removal of TBP from the electrolyte, confirming that the injection process is the

limiting factor for S-bearing dyes. PCE slightly increased nevertheless, but none surpassed oxygen bearing dyes and the measured IPCE remained much lower (Figure S4). Interestingly, the best dyes of the series are those with the longer linker (n = 1) and therefore the more red-shifted absorption, likely because the other two show the weakest injection driving forces. For the whole series where X = S, the Voc is low regardless the presence of TBP; J-V curves recorded in the dark (Figure S6) clearly prove that the dark current is higher for S-bearing dyes rather than O-bearing ones (Figure S5). A privileged interaction between S and triiodide could entail the accumulation of the latter close to the surface of TiO₂, facilitating charge recombination.²³

In summary, we have successfully synthesized a novel series of dyes with α -chalenomethylenepyran, as donor, methine unit (1 or 3) as bridge and cyanoacrylic acid as the acceptor. Their optical and electrochemical properties were studied and showed that the expansion of π conjugation in the dye structures and the modification of electron-donating property of chromophore skeletons allowed tuning the photophysical and electrochemical properties of the dyes. DSSC devices were fabricated and tested under standard global AM 1.5 solar conditions, the best dye is **15** giving a J_{sc} of 4.5 mA cm⁻² a Voc of about 600 mV corresponding to an overall conversion efficiency of 2.03%. New dyes based on α -pyranilidene displaying higher injection driving forces could most probably exhibit valuable properties in DSSC. We are working in this direction and the results will be reported in due course.

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Supplementary Material

Supplementary data (typical experimental procedures, spectroscopic data, absorption spectra in solution and on TiO₂ films current/voltage characteristics, associated with this article can be found, in the online version, at [http...](http://...)

Highlights :

α -pyranylidene based dyes for DSSC applications are described

Fused ring α -pyranylidene was motivated by a gain of stability of these molecules

The role of the nature of the heteroatom (O, S) on conversion efficiency was studied

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