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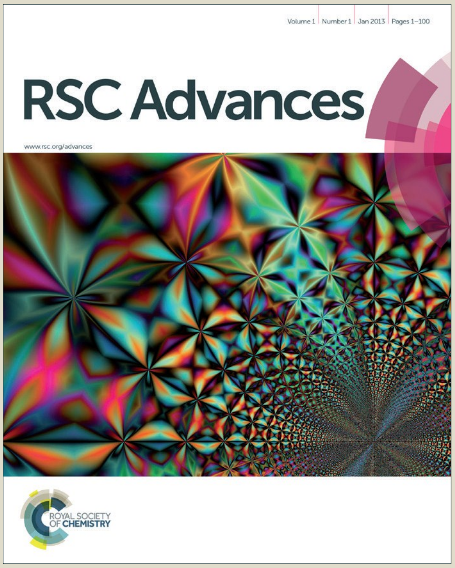

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COMMUNICATION

New efficient *Tert*-butyldiphenyl-4*H*-pyranylidene sensitizers for DSSC

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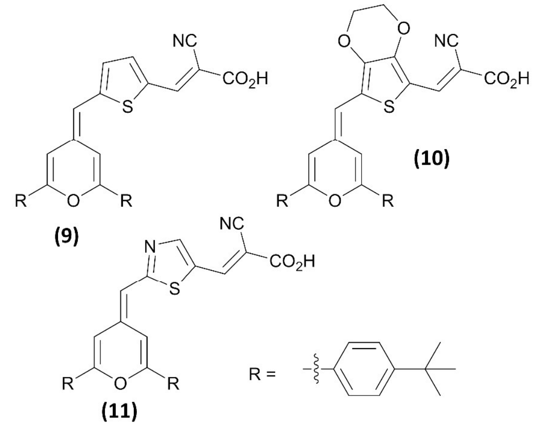
Three new triarylamine-free sensitizers for DSSC containing a *tert*-butyldiphenyl-4*H*-pyranylidene as the donor unit are reported. Devices have been carefully optimized resulting in high J_{sc} values. An efficiency of 5.80% has been obtained for a sensitizer with a thiophene ring in the π spacer. Solvent, dipping time, thickness and photoanode structure have been optimized.

Dye sensitized solar cells (DSSC)[1, 2] constitute an interesting alternative to silicon-based devices due to their lower cost, lightweight, greater flexibility in molecular design and aesthetic features, like color and transparency. Although for a long time the best performances were obtained with Ruthenium-based dyes, efficiencies above 12% have been recently achieved with free-metal organic dyes,[3-5] opening the possibility for further improvement on results. A Donor-π-Acceptor (D-π-A) configuration is usually used in the design of organic sensitizers. This architecture assures an appropriate intramolecular charge transfer (ICT) from donor to acceptor moieties, facilitating the injection of electrons on the semiconductor following light absorption.

A great number of promising donor units have been reported in the literature, including carbazole,[6-9] triphenylamine (TPA),[10-13] phenothiazine,[14-16] indoline,[17-20] dithiafulvene,[21, 22] coumarin[23-25] and indenoperylene,[3] among others. However, the syntheses of dyes containing these units are not always straightforward. TPA based metal free organic dyes present several advantages, like an excellent electron-donating capability and a non-planar structure which suppresses the formation of aggregates on the TiO_2 surface. For these reasons triarylamines are, probably, one of the most popular donors in DSSC. However, this unit is limited by its relatively narrow absorption range and low molar extinction coefficients. The absorption bandwidth can be extended by introducing auxiliary donor groups in the donor unit, but these changes often conduce to more unstable dyes and more complicated syntheses. In this context, to broaden the range of possibilities is therefore necessary to develop novel organic dyes containing triarylamine free donors.

Recently, we have reported the usefulness of 4*H*-pyranylidene-based dyes with silyl bulky groups on the thiophene spacer, as efficient sensitizers for DSSC.[26] The 4*H*-pyranylidene is a more powerful donor group than TPA and it has scarcely employed in DSSC. The properties of this donor system can be modified by the incorporation of different substituents at the 4- and 6- positions of the pyranylidene ring, modulating its donor capability and exercising a good control on the aggregates formation. In this communication we present three new 4*H*-pyranylidene dyes with two bulky *tert*-butylphenyl groups in the donor unit. These bulky groups assure a good solubility and, at the same time, can reduce the recombination processes on the semiconductor surface. As it is well known, the π linker can greatly affect the photovoltaic performance of sensitizers and for this reason, three common spacers based on heterocyclic systems (thiophene and thiazole) have been chosen.



Scheme 1

The optimization process of photovoltaic measurements for new dyes in DSSC is not a simple issue because a great number

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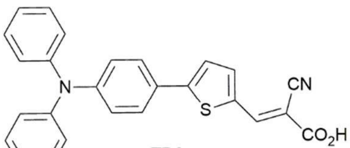
of factors are involved, including structure and thickness of the TiO_2 electrode, solvent and soaking time, electrolyte composition, co-absorption additives, device construction, etc. We have realised that in most cases the optimization process is not detailed. In this communication we can also cover the optimization steps from the synthesis to the final measurement of the photovoltaic properties of the new dyes.

The synthesis of the sensitizers can be carried out in a simple three step protocol from a pyrylium salt. The sequence consists in a Wittig coupling, from a phosphonium salt, and a Knoevenagel condensation of the corresponding aldehydes with cyanoacetic acid. In all cases, dyes precipitated in the reaction medium and further purification processes were not required. The new sensitizers and all intermediates were characterized by ^1H, ^{13}C NMR and mass spectrometry (see supporting section).

The absorption spectra of the dyes in CH_2Cl_2 and onto TiO_2 electrodes are shown in Figure 1. All of them exhibit a strong absorption band from 400 to 650 nm, which can be ascribed to ICT processes. Their molar extinction coefficients are relatively high, at the same level than other previously reported 4*H*-pyranylidene dyes.[27] When dyes are adsorbed onto TiO_2, absorption peaks are blue-shifted around 80 nm, probably due to deprotonation of the dyes or H aggregates formation during the adsorption. In order to compare the properties of the new dyes, the data and spectra of a **TPA** sensitizer[28] (by changing the 4*H*-pyranylidene ring in dye **9** with a triarylamine) are also provided.



TPA

Scheme 2

Table 1. Optical and electrochemical properties of dyes **9**-**11** and **TPA**.

Dye	λ_{abs}, nm (ε, M^{-1} cm^{-1})^a	λ_{abs}, nm^b	E_{ox},^{c} V (vs NHE)	$E_{o\text{-}o}$,^{d} eV	$E_{ox}{}^*$,^{e} V (vs NHE)
9	573 (41587)	480	+0.80	+1.95	−1.15
10	594 (29955)	508	+0.75	+1.89	−1.14
11	543 (42342)	474	+0.80	+2.06	−1.26
TPA	437 (10832)	416	+1.17	+2.40	−1.23

[a] Absorption maxima in CH_2Cl_2 (10^{-5} M). [b] Absorption maxima on TiO_2 films (14 μm). [c] First oxidation potentials were measured from a three electrode electrochemical cell in CH_2Cl_2 (10^{-3} M) containing 0.1 M $TBAPF_6$. A glassy carbon, Ag/AgCl (KCl 3 M), and Pt were used as working, reference, and counter electrode respectively. Calibration was done using ferrocene as standard [d] Zeroth-zeroth transition energies estimated from the intersection between absorption and emission spectra. [e] Excited-state oxidation potentials of the dyes obtained from $E_{ox} - E_{0\text{–}0}$.

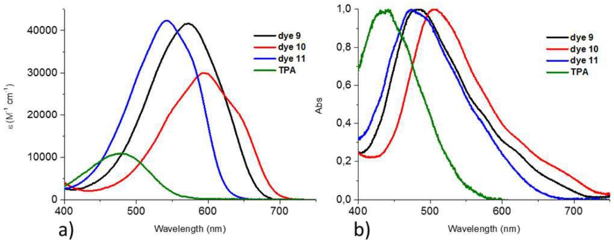


Fig. 1. a) Absorption spectra of dyes **9**-**11** and **TPA** in CH_2Cl_2 solution and b) normalized absorption spectra of dyes **9**-**11** and **TPA** adsorbed onto TiO_2 electrodes.

The first oxidation potentials (E_{ox}) *vs* NHE of the new dyes were determined by Differential Pulse Voltammetry (DPV) in CH_2Cl_2 using a graphite working electrode, an Ag/AgCl reference electrode and a platinum counter electrode. The oxidation potential of the excited state ($E_{ox}{}^*$) was calculated from $E_{ox} - E_{0\text{-}0}$. The measured E_{ox} were in all cases lower than **TPA**, pointing to a better donor capacity for the 4*H*-pyranylidene unit. The obtained values for E_{ox} and $E_{ox}{}^*$ assure in all cases the regeneration of the oxidized dyes (E_{ox} electrolyte I^-/I_3^- = +0.40V) and the injection from the excited states to the TiO_2.

Before carrying out the photovoltaic measurements of the three new sensitizers, it was necessary to optimize the following parameters: solvent, time of dipping and structure and thickness of the titania electrodes.

Based in our experience with organic dyes, the starting conditions were defined as: 0.1mM for dye and 0.3mM of chenodeoxicolic acid in CH_2Cl_2 (2 hours of soaking) and a electrolyte based on the classical I^-/I_3^- system (1-butyl-3-methylimidazolium iodide (0.53 M), LiI (0.10 M), I_2 (0.050 M), *tert*-butylpyridine (0.52 M) in acetonitrile). As it can be observed in Table 2, dye **9** obtained the highest efficiency and therefore this sensitizer was chosen for the optimization process.

The first optimized parameter was the solvent. Three solvents were tested, i.e., CH_2Cl_2, acetonitrile/*tert*-butyl alcohol (1:1) and THF. The optimization was carried out after dipping the TiO_2 anodes (made of Ti nanoxide T/SP from Solaronix of 14 μm) at five different immersion times: 2, 3, 4, 5 and 24 hours. Figure 2 shows that CH_2Cl_2 was the best solvent for every studied soaking time, so it was chosen thereafter. Then, two different anode structures were tested: one double layered using Ti nanoxide T/SP and Ti nanoxide R/SP (2 μm) on top of it as scatter, both from Solaronix, and another single layered using 18NR-AO TiO_2 from Dyesol. In addition, two different photoanode thicknesses (4 and 14 μm) were tested for each titania paste. Figure 2 shows that the best performance, for the five studied soaking times, was obtained with the 14 μm Dyesol electrodes, so they were used thereafter. Moreover, 5 hours was found to be the most suitable immersion time. All the corresponding J-V curves and their respective photovoltaic parameters can be found in the supporting information.

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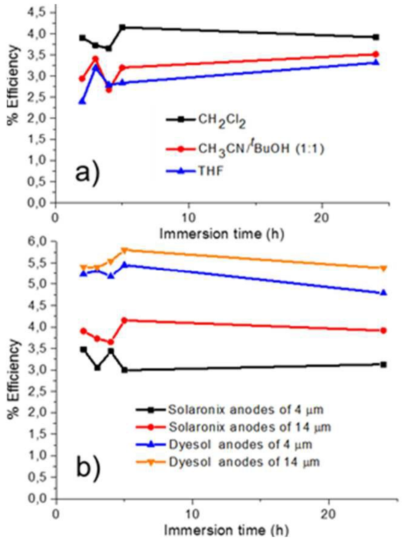


Fig. 2. Efficiencies obtained with dye **9** during the optimization step vs the immersion time modifying a) the solvent and b) the structure and thickness of the TiO_2 layer.

Eventually, the three new dyes were tested and their photovoltaic properties compared at the optimized conditions, under standard A.M. 1.5G simulated solar radiation. We have also included data for the **TPA** device in the same conditions.

As it can be observed in Table 2, the overall efficiency of each dye was significantly increased with respect to the preliminary data and this result can be related to the great increase in the J_{sc} value, whereas V_{oc} is not dissimilar and *ff* decreases a little. In addition, dye **9** obtained the highest efficiency (5.80%), followed by dye **11** (5.30%) and dye **10** (3.85%), the latter very similar to the obtained efficiency for **TPA** devices fabricated at the same conditions (3.91%). Despite a better V_{oc} for the TPA dye, J_{sc} is almost doubled in the case of dye **9**, which compensates the lower V_{oc}. The observed differences can be correlated to the obtained values of molar absorptivity and the amount of dye adsorbed onto the anode (2.29×10^{-7}, 2.11×10^{-7}, 1.76×10^{-7} and 1.75×10^{-7} mol/cm^2 for dyes **9**, **10**, **11** and **TPA** respectively). The higher molecular size of the **TPA** sensitizer leads, probably, to a lower adsorption of this dye on the photoelectrode.[29] The amount of the adsorbed dye was obtained by desorbing the sensitizer with a solution of NaOH:EtOH, 1:1 and measuring the concentration by UV-Vis spectroscopy from the corresponding calibrated curves.

Table 2. Photovoltaic parameters using preliminary (P) and optimized conditions.

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	*ff* (%)	η (%)
9P	10.49	0.570	65.4	3.91
10P	5.89	0.540	69.2	2.20
11P	4.92	0.550	70.0	1.90
9	18.79	0.579	53.4	5.80
10	12.31	0.552	56.6	3.85
11	15.37	0.584	59.1	5.30
TPA	9.65	0.668	60.7	3.91

As it can be observed in the IPCE curves (Fig. 3) dyes **9-11** exhibit a broader range of photon conversion in comparison to **TPA** reference dye. In addition, dye **9** featured a broad IPCE trace spanning a large spectral window spectrum, higher than 70% from 400 to 700 nm, suggesting that electrons are efficiently collected in this region.

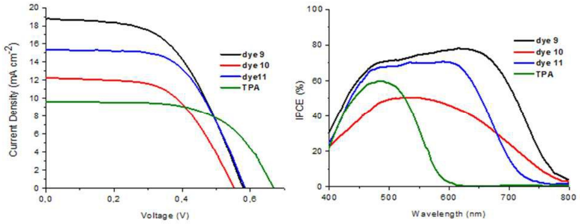
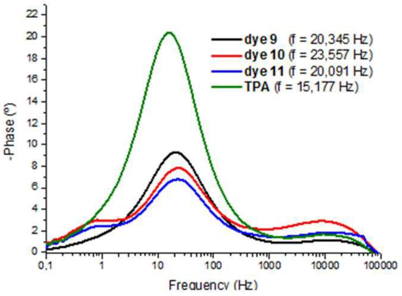


Fig. 3. a) Photocurrent density-voltage curves and b) IPCE curves for dyes **9-11** and **TPA**.

Electrochemical Impedance Spectroscopy (EIS) is a very useful tool to study the electron transport kinetics of a DSSC. The experiments were performed under a forward bias (− 0.65 V) in the dark. Bode phase plots (Fig. 4) were used to estimate the lifetime of electrons (τ) in the conduction band of TiO_2. The lifetimes were calculated following the equation $\tau = 1/2\pi f$ (f = frequency at the maximum of the curve in the intermediate frequency region in the Bode plot). The obtained τ are 7.82, 6.74, 7.92 and 10.5 ms for dyes **9**, **10**, **11** and **TPA**, respectively. Although the value obtained for **TPA** is higher, It is quite noticeable that the electron lifetimes are not dissimilar, but they are in agreement with the V_{oc} observed (V_{oc} **TPA** > V_{oc} **11** > V_{oc} **9** > V_{oc} **10**).

Fig. 4. Bode plot of dyes **9-11** and **TPA** obtained by EIS



In summary, a series of three triarylamine-free new dyes based on a *tert*-butylphenyl-4*H*-pyranylidene ring have been synthesized and successfully used as sensitizers for DSSC.

A quite suitable optimization conditions have been found and used for measuring 4*H*-pyranylidene dyes, which could be employed for other organic systems. The photovoltaic parameters of devices based on these sensitizers have been measured and compared with a TPA-dye used as reference. The obtained results (an efficiency 48% higher than obtained for the **TPA** system in the same conditions) probe that the 4*H*-pyranylidene ring presents new opportunities towards the

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design of efficient triarylamine-free organic dyes. This work is currently underway in our laboratory.

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Notes and references

1. B. E. Hardin, H. J. Snaith and M. D. McGehee, *Nature Photon.*, 2012, 6, 162-169.
2. A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, 110, 6595-6663.
3. Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li, P. Wang, Z. Yao and L. Yang, *J. Am. Chem. Soc.*, 2015, 137, 3799-3802.
4. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i. Fujisawa and M. Hanaya, *Chem. Commun.*, 2015, 51, 15894-15897.
5. K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno and M. Hanaya, *Chem. Commun.*, 2014, 50, 6379-6381.
6. G. Tian, S. Cai, X. Li, H. Agren, Q. Wang, J. Huang and J. Su, *J. Mater. Chem. A*, 2015, 3, 3777-3784.
7. J.-F. Huang, J.-M. Liu, L.-L. Tan, Y.-F. Chen, Y. Shen, L.-M. Xiao, D.-B. Kuang and C.-Y. Su, *Dyes Pigm.*, 2015, 114, 18-23.
8. Y. Tan, M. Liang, Z. Lu, Y. Zheng, X. Tong, Z. Sun and S. Xue, *Org. Lett.*, 2014, 16, 3978-3981.
9. Z. S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube and K. Hara, *Chem. Mater.*, 2008, 20, 3993-4003.
10. Z. J. Ning and H. Tian, *Chem. Commun.*, 2009, DOI: 10.1039/b908802d, 5483-5495.
11. W. Gao, M. Liang, Y. Tan, M. Wang, Z. Sun and S. Xue, *J. Power Sources*, 2015, 283, 260-269.
12. Q. Xia, M. Liang, Y. Tan, W. Gao, L. Ouyang, G. Ge, Z. Sun and S. Xue, *Org. Electron.*, 2015, 17, 285-294.
13. W. D. Zeng, Y. M. Cao, Y. Bai, Y. H. Wang, Y. S. Shi, M. Zhang, F. F. Wang, C. Y. Pan and P. Wang, *Chem. Mater.*, 2010, 22, 1915-1925.
14. R. Y.-Y. Lin, T.-C. Chu, P.-W. Chen, J.-S. Ni, P.-C. Shih, Y.-C. Chen, K.-C. Ho and J. T. Lin, *ChemSusChem*, 2014, 7, 2221-2229.
15. J.-S. Ni, W.-S. Kao, H.-J. Chou and J. T. Lin, *ChemSusChem*, 2015, 8, 2932-2939.
16. A. Baheti, K. R. Justin Thomas, C.-T. Li, C.-P. Lee and K.-C. Ho, *ACS Appl. Mater. Interfaces*, 2015, 7, 2249-2262.
17. T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, *J. Am. Chem. Soc.*, 2004, 126, 12218-12219.
18. Y. Wu, M. Marszalek, S. M. Zakeeruddin, Q. Zhang, H. Tian, M. Graetzel and W. Zhu, *Energy Environ. Sci.*, 2012, 5, 8261-8272.
19. S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, 18, 1202-1205.
20. S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Pechy and M. Graetzel, *Chem. Commun.*, 2008, DOI: 10.1039/b809093a, 5194-5196.
21. K. Guo, K. Yan, X. Lu, Y. Qiu, Z. Liu, J. Sun, F. Yan, W. Guo and S. Yang, *Org. Lett.*, 2012, 14, 2214-2217.
22. Z. Wan, C. Jia, Y. Duan, X. Chen, Z. Li and Y. Lin, *RSC Adv.*, 2014, 4, 34896-34903.
23. C. Zhong, J. Gao, Y. Cui, T. Li and L. Han, *J. Power Sources*, 2015, 273, 831-838.
24. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, T. Kyomen and M. Hanaya, *Chem. Commun.*, 2015, 51, 6315-6317.
25. B. J. Song, H. M. Song, I. T. Choi, S. K. Kim, K. D. Seo, M. S. Kang, M. J. Lee, D. W. Cho, M. J. Ju and H. K. Kim, *Chem. - Eur. J.*, 2011, 17, 11115-11121.
26. R. Pérez-Tejada, N. Martínez de Baroja, S. Franco, L. Pellejà, J. Orduna, R. Andreu and J. Garín, *Dyes Pigm.*, 2015, 123, 293-303.
27. S. Franco, J. Garín, N. Martínez de Baroja, R. Pérez-Tejada, J. Orduna, Y. Yu and M. Lira-Cantú, *Org. Lett.*, 2012, 14, 752-755.
28. D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt and L. Sun, *J. Org. Chem.*, 2007, 72, 9550-9556.
29. Z. J. Ning, Q. Zhang, H. C. Pei, J. F. Luan, C. G. Lu, Y. P. Cui and H. Tian, *J. Phys. Chem. C*, 2009, 113, 10307-10313.

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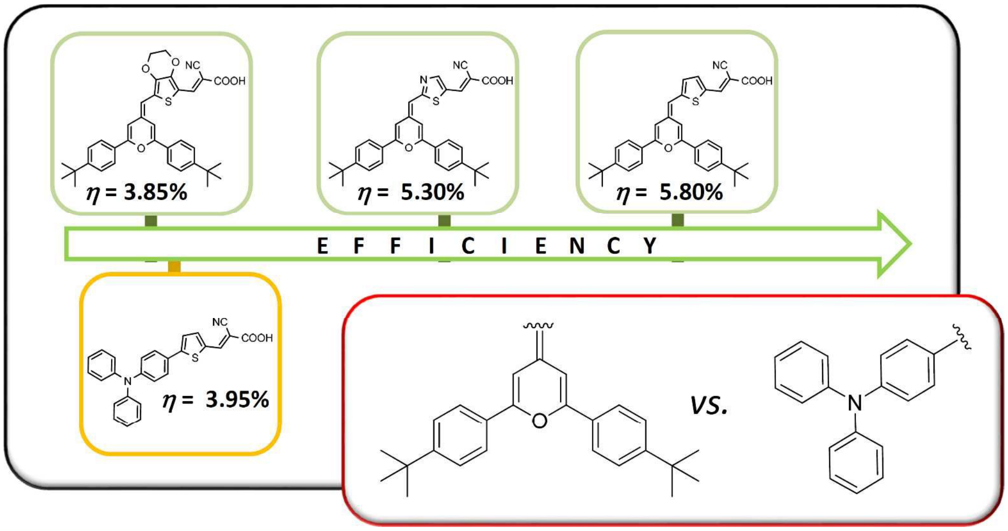

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