Elsevier Editorial System(tm) for Solar Energy

Manuscript Draft

Manuscript Number:

Title: First examples of pyran based colorants as sensitizing agents of p-type dye-sensitized solar cells

Article Type: Research paper

Section/Category: Photovoltaic materials and systems

Keywords: NiO; Dye-Sensitized Solar Cells; Pyran-based dyes; NIR-Dyes

Corresponding Author: Dr. Matteo Bonomo,

Corresponding Author's Institution: La Sapienza

First Author: Matteo Bonomo

Order of Authors: Matteo Bonomo; Roberto Centore; Aldo Di Carlo; Antonio Carella; Danilo Dini

Abstract: Three different pyran based dyes were synthesized and tested for the first time as photosensitizers of NiO based p-type dye-sensitized solar cells (p-DSSC). The molecules feature a similar molecular structure and are based on a pyran core that is functionalized with electron acceptor groups of different strength and is symmetrically coupled to phenothiazine donor branches. Optical properties of the dyes are deeply influenced by the nature of the electron-acceptor group, so that the overall absorption of the three dyes covers the most of the visible spectrum. The properties of devices based on the NiO electrodes sensitized with the investigated dyes were evaluated under simulated solar radiation: the larger short circuit current density exceeded 1 mA/cm2 and power conversion efficiency as high as 0.04 % could be recorded. The performances of the fabricated p-DSSC have been compared to a reference cell sensitized with P1, a high level benchmark, which afforded a photoelectrochemical activity similar to the best example of our pyran sensitized devices (1.19 mA/cm2 and 0.049 %).

Suggested Reviewers: Claudia Barolo
Claudia.barolo@unito.it
Her wide experience in DSSC (especially in the synthesis of NIR dyes)

Mirko Congiu
mirko.congiu@fc.unesp.br
His wide experience in semiconducting material for PV application.

Alessandro Latini
alessandro.latini@uniroma1.it
His experience in DSSC.

Università degli Studi "La Sapienza" di Roma

DIPARTIMENTO DI CHIMICA

Prof. Danilo Dini

Tel.: -39-06-4991 3335
Fax: -39-06-490324
e-mail: danilo.dini@uniroma1.it

Rome , 12th May 2017

Dear Editor,

the manuscript we intend to submit for consideration of publication in *Solar Energy* reports for the first time the photoelectrochemical properties of p-type dye-sensitized solar cells (p-DSCs), which employ nanostructured NiO photocathodes previously sensitized by pyran based colorants. The series of dye-sensitizers here proposed represents an original choice in the framework of the research on p-DSCs. The light conversion performance of the photoelectrochemical cells here described for the first time compares to the ones of the best performing devices of the same type. For these reasons we believe that the content of the present work fits with the aims of this journal and attracts the interest of a broad audience ranging from organic chemists to electrochemists and materials scientists that are involved in the science of p-DSCs and analogous solar conversion devices.

Thank you for the consideration.

Best regards,

Danilo Dini

First examples of pyran based colorants as sensitizing agents of *p*-type dye-sensitized solar cells

Matteo Bonomo,[a] Roberto Centore,[b] Aldo Di Carlo,[c], Antonio Carella,[b*] Danilo Dini [a*]

a: Dept. of Chemistry, University of Rome "La Sapienza", p.le Aldo Moro 5, 00185 Rome (Italy)

b: Dept. of Chemical Sciences, University of Naples Federico II, Complesso Universitario Monte Sant'Angelo, via Cintia, 80126 Naples (Italy)

c: Centre for Hybrid and Organic Solar Energy (CHOSE), Dept. of Electronic Engineering, University of Rome "Tor Vergata", via del Politecnico 1, 00133 Rome (Italy)

*to whom correspondence should be addressed. e-mail antonio.carella@unina.it and danilo.dini@uniroma1.it

Abstract

Three different pyran based dyes were synthesized and tested for the first time as photosensitizers of NiO based *p*-type dye-sensitized solar cells (*p*-DSSC). The molecules feature a similar molecular structure and are based on a pyran core that is functionalized with electron acceptor groups of different strength and is symmetrically coupled to phenothiazine donor branches. Optical properties of the dyes are deeply influenced by the nature of the electron-acceptor group, so that the overall absorption of the three dyes covers the most of the visible spectrum. The properties of devices based on the NiO electrodes sensitized with the investigated dyes were evaluated under simulated solar radiation: the larger short circuit current density exceeded 1 mA/cm^2 and power conversion efficiency as high as 0.04 % could be recorded. The performances of the fabricated *p*-DSSC have been compared to a reference cell sensitized with **P1**, a high level benchmark, which afforded a photoelectrochemical activity similar to the best example of our pyran sensitized devices (1.19 mA/cm^2 and 0.049 %).

INTRODUCTION

Dye-sensitized solar cells (DSSCs) represent one of the emerging photovoltaic technology which gained a considerable interest in the last twenty years[1–8] as a viable low cost alternative to traditional photovoltaics based on silicon modules[9]. DSSCs technology presents further appealing features as optical transparency, the possibility of being realized in different colours and the possibility to be integrated in architectural elements different from the roof, so paving the way to the so-called building integrated photovoltaics[10,11]. The heart of a DSSC device is a wide bandgap semiconductor oxide, sensitized with a photoactive dye able to inject, upon photoexcitation, electrons (*n*-type) or holes (*p*-type) in the semiconductor substrate. Following the seminal work of Grätzel and O'Regan[12], *n*-type DSSC have been thoroughly investigated and a power conversion efficiency (PCE, η) exceeding 14 % have been reached[13]. Conversely, the number of studies regarding *p*-type DSSCs is significantly lower[14–19] but it is increasing in the last years as it has become clear that efficiency of *n*-type DSSC has reached a plateau: these kinds of devices are in fact extremely interesting because they open the way to the realization of tandem DSSC device[20,21] based on the connection of a *p*-type photoelectrode with a *n*-type photoelectrode, each contributing to the total photovoltage generated by the cell. Applying this concept, photovoltaic devices with a theoretical efficiency up to 40 % could be obtained[22,23]. However, so far, the performances of *p*-DSSCs[24] remain a way lower than the *n*-type counterparts, with a maximum reported PCE of 2.5 %[25]. Different reasons can explain the poor performance of these devices: the typically used photocathode, NiO, suffer from some intrinsic drawbacks, as low hole mobility[26], which is consequential to a stronger bond between the injected hole and electron residing on the dye, thus easing the detrimental charge recombination process, and low dielectric constants[19]. The latter feature lowers the radiation penetration depth (self absorption phenomenon). Moreover, the valence band position of NiO, relatively to the classically used iodide/triiodide redox mediator, limits the maximum attainable V_{OC}[27].

Optimization of both *p*-type semiconductor and electrolyte is undoubtedly required for improving the performance of *p*-DSSC. The sensitizers as well play a very important role[28–32]: absorption in a broad range of the solar spectrum along with high molar extinction coefficients are highly desirable. Moreover, it is essential that, upon photoexcitation, electron density moves away from the anchoring points on NiO surface so that charge recombination occurs at lower rate. The design of novel dyes that fulfil such requirements is then highly demanded in the way for high efficiency *p*-DSSC devices. Pyran based dyes are molecular systems that have shown interesting properties for applications in different field of organic electronics e.g. as red emitters in OLED[33,34] or photovoltaic materials[35,36], and photonics, for their nonlinear optical properties[37–42]. Their synthetic procedure is well established and affords a chemical structure typically based on a pyran core functionalized with an electron acceptor group and symmetrically linked to donor conjugated branches; this kind of structure could be extremely interesting for the application of these molecular systems as photosensitizers in *p*-DSSCs because it is in principle possible design chromophores with an electron acceptor core placed far away from peripheral groups acting as anchoring units for binding the dye to NiO surface. Their use in *p*-DSSC is, up to our knowledge, not yet reported while in the literature some examples of their application as photosensitizers in *n*-type DSSCs can be found[43–45]. In particular, in a recent work[45], some of us prepared the dyes reported in Figure 1 and used them as photosensitizers for classical Grätzel cells.

The functionalization of the same molecular core (pyran) with electron acceptor groups of increasing strength (moving from dyes **CB1** to **CB3**) resulted in the tuning of the optical absorption properties of the dyes and in the obtainment of chromophores the colour of which ranged from orange to blue, so covering most part of the visible spectrum. A moderate efficiency, up to 2.8 %, was reported in this paper[45]. One of the factors limiting the efficiency of these photosensitizers in *n*-DSSC is that, upon photoexcitation, electron density moves away from the peripheral carboxylic groups (representing the anchoring points of the dyes on TiO_2 surface). This feature hinders the

electron injection process from the dye to the semiconductor oxide thus limiting the overall efficiency.

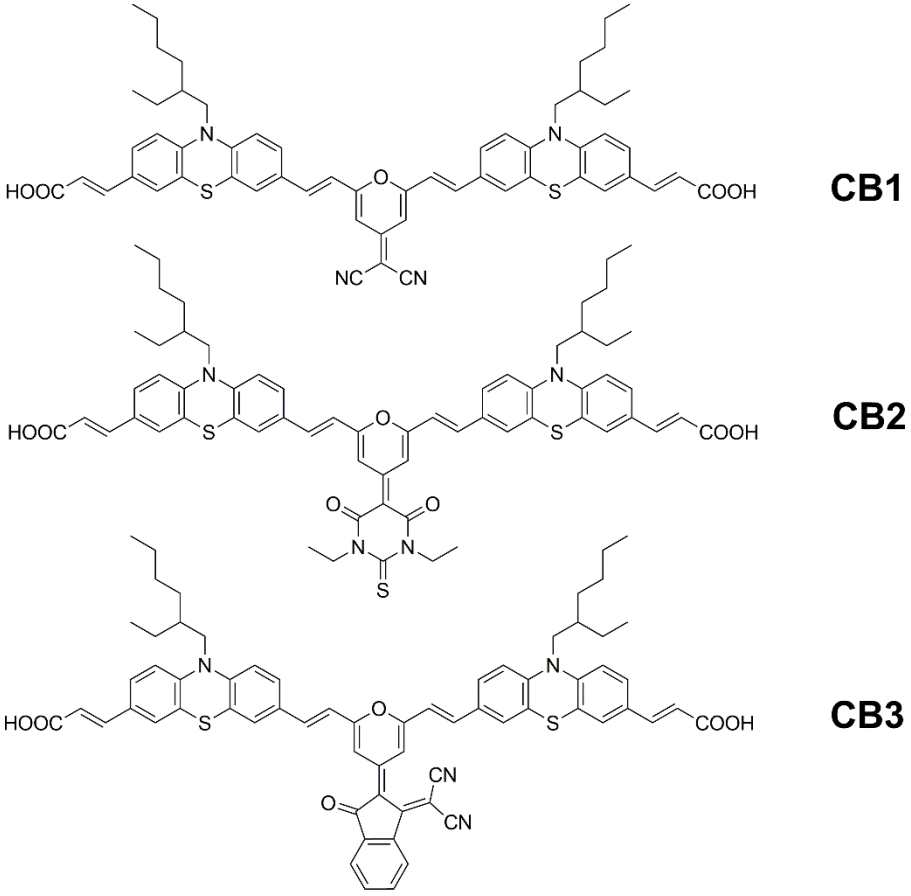

Figure 1. *Chemical structures of the reported pyran based photosensitizers*

At the same time, as previously mentioned, this behaviour is highly desirable if the dyes must be used as photosensitizers for *p*-DSSC[46]. This consideration prompted us to explore the potentiality of these molecular systems in the field of *p*-DSSC: the devices have been prepared by sensitizing NiO thin film and using iodide/triiodide as redox mediator[47].The fabricated devices have been photoelectrochemically characterized under simulated solar radiation and the contribution to current generation by each single wavelength was determined by the analysis of the IPCE (incident photon-to-current conversion efficiency) spectra.

EXPERIMENTAL

The details regarding the synthesis of the dyes as well as the their optical, electrochemical and the computed electronic properties, have been previously reported elsewhere[44,45]. For what concerns the preparation of the photocathode, we adopted a procedure described in previous works from us[46,48]. As far as the preparation of screen-printed NiO electrodes is concerned, preformed NiO nanospheres (with a diameter smaller than 50 nm) have been grinded in a mortar and hydrochloric acid (1 mL), H_20 (5 mL), ethanol (30 mL), terpineol (20 mL) and ethylcellulose (10% w/w in ethanol solution) were added. All chemicals employed were purchased from Sigma-Aldrich or Fluka at the highest degree of purity available and they were used without any further purification. Both addition and grinding of the various mixtures have been performed at room temperature. After the addition of terpineol and ethylcellulose the solution has been homogenized by stirring and ultrasonic treatment. Then the mixture has been heated at 50 °C under continuous stirring till the paste had the appearance of a viscous slurry. Anhydrous terpineol was used as a mixture of enantiomers. The ultrasonic homogenization was performed with a Ti-horn-equipped sonicator (Vibracell 72408 from Bioblock scientific). The resulting paste was spread onto a FTO-covered glass via screen-printing and after a pre-drying period of 15 minutes at 120 °C in oven it was sintered at 450 °C for half an hour (heating ramp of 15 °C/min). The thickness of the resulting electrodes (~ 2 μm) was measured with a Dektat 150® profilometer from Veeco.

Sensitization of NiO photocathodes was obtained by electrodes dipping in a 0.2 mM dye-sensitizer solution with THF as solvent. All electrodes were sensitized at room temperature for 16 hours.

Pt-counter electrodes were prepared by screen-printing onto FTO-coated glass as reported elsewhere[49].

NiO photocathodes and Pt-FTO counter-electrodes were assembled in a sandwich configuration using a Bynel® (a thermoplastic polymeric film) as sealant. Bynel® also acts as a spacer that determines the thickness of the cell. The iodine-based electrolyte solution (HSE from Dyesol) was

injected inside the device by vacuum backfilling technique. The hole for injection was finally sealed with a commercial glass/glass glue. The photoactive area of the samples was 0.25 cm^2.

The measurements of optical transmittance were made with a double ray spectrometer (model UV-2550 from Shimazdu). Photoelectrochemical performances were evaluated using a solar simulator Solar Test 1200 KHS (class B) at 1000 W/m^{-2} with artificial solar spectrum AM 1.5 G. The IPCE curves were recorded using a computer controlled set-up consisting of a Xe lamp (Mod.70612, Newport) coupled to a monochromator (Cornerstone 130 from Newport), and a Keithley 2420 light-source meter.

RESULTS AND DISCUSSION

The chemical physical characterization of the dyes has been previously reported[45]. For sake of clarity, in Table 1 the main optical parameters of wavelength of maximum absorption (λ_{max}) in THF solution, corresponding molar extinction coefficient (ε), and the energies of the frontier's molecular orbitals of the dyes are summarized[45]. The energy levels of the highest-occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) have been estimated by a combined optical-electrochemical approach.

Table 1. *Optical and electrochemical properties of the synthesized chromophores*

Dye	λ_{max} /nm[a]	ε /L·mol^{-1}·cm^{-1} [a]	HOMO /eV[b]	LUMO / eV[b]
CB1	464	$4.1 \cdot 10^4$	-5.51	-3.51
CB2	521	$4.3 \cdot 10^4$	-5.51	-3.69
CB3	582	$3.8 \cdot 10^4$	-5.59	-3.95

a) Scan rate 200 nm/min, in THF solution; b) determined, as reported in ref. 38, by a combined electro-chemical and optical approach on thin film of the dyes,.

The dyes are characterized by a similar chemical structure (see Figure 1) and differ only for the nature of the electron acceptor group which functionalizes the pyran core. The electron-withdrawing strength of this group exerts a strong influence on the optical properties of these dyes

as evinced from the data of Table 1 and the absorption spectra of Figure 2. The absorption spectra of the dyes in solution were recorded. Upon increasing the strength of the electron withdrawing character of the electron acceptor group that functionalizes the pyran core, the larger is the red shift of the characteristic absorption of the dye so that the colour of the dye is tuned from orange (dye **CB1**) to magenta (dye **CB2**) and to blue (dye **CB3**).

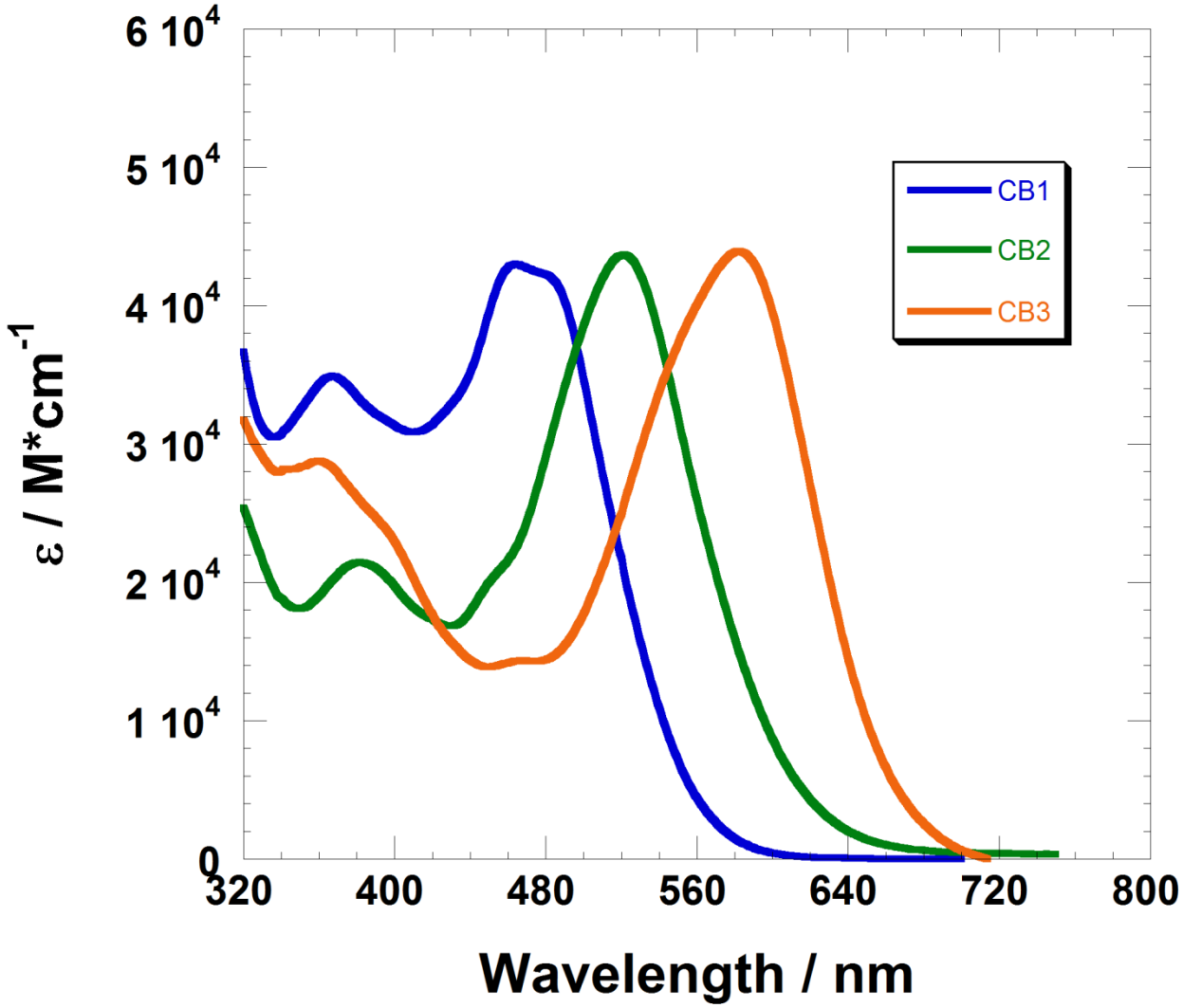

Figure 1. Molar absorptivity of the reported dyes in THF solution

The coverage of a such large part of the visible spectrum along with a high molar extinction coefficients presented by all the dyes (up to $4.3 \cdot 10^4$) represent important properties in view of the use of the reported dyes as photosensitizers for DSSC of *p*-type. Energetic levels of the frontier's molecular orbital, estimated by a combined optical-electrochemical approach in the previous paper

(see Table 1) are well suited for the application of the dyes in NiO based device (*p*-type DSSCs). In fact, the HOMO energy level of the dyes are placed below the upper edge of NiO valence band (VB) located at -5.0 eV[50,51], while the LUMO energy level of the sensitizer lies above the redox potential of the redox couple I^-/I_3^-(4.8 eV). The latter two features are mandatory to ensure efficient hole injection into the semiconductor VB and regeneration from the redox species. Moreover, the dyes are characterized by the presence of two anchoring groups that allow a firm adhesion of the molecules on an oxide surface as previously shown by the stability measurement of the *n*-DSSC devices with TiO_2 electrodes sensitized with the compounds of Figure 1. A further appealing aspect of the dyes here reported is that the electron withdrawing groups (EWGs) are located far away from the carboxylic anchoring groups. By virtue of this spatial arrangement the EWGs are expected to be oriented far from NiO surface and disfavor kinetically electronic recombination if one assumes that the site of triiodide reduction is mostly localized at the EWG[20,52]. By means of a computational analysis at DFT level it was shown that upon photoexcitation in all the dyes electron density moves from the peripheral part to the core and LUMO of the molecules is localized on the pyran core[45]. This aspect could be of great interest in the application of such dyes as photosensitizers for *p*-DSSC because it results in a minimization of recombination phenomena the LUMO of the dyes being far from NiO surface. At the same time, the localization of the LUMO far from NiO surface can induce the acceleration of the electron transfer (*et*) from the excited dye to the redox shuttle.

All these features suggest an efficient use of these dyes in *p*-DSSC. First of all, we tested the goodness of sensitizers chemisorption onto NiO surface. NiO was sensitized as described in Experimental Section. In Figure 3 the transmittance spectra of the sensitized photocathodes are reported: the sensitization provokes a depletion of electrodes transmittance in the absorption region typical of the dyes, as compared to bare NiO. This evidence is a key proof of a good sensitization: all the tested dyes experimented a very good binding.

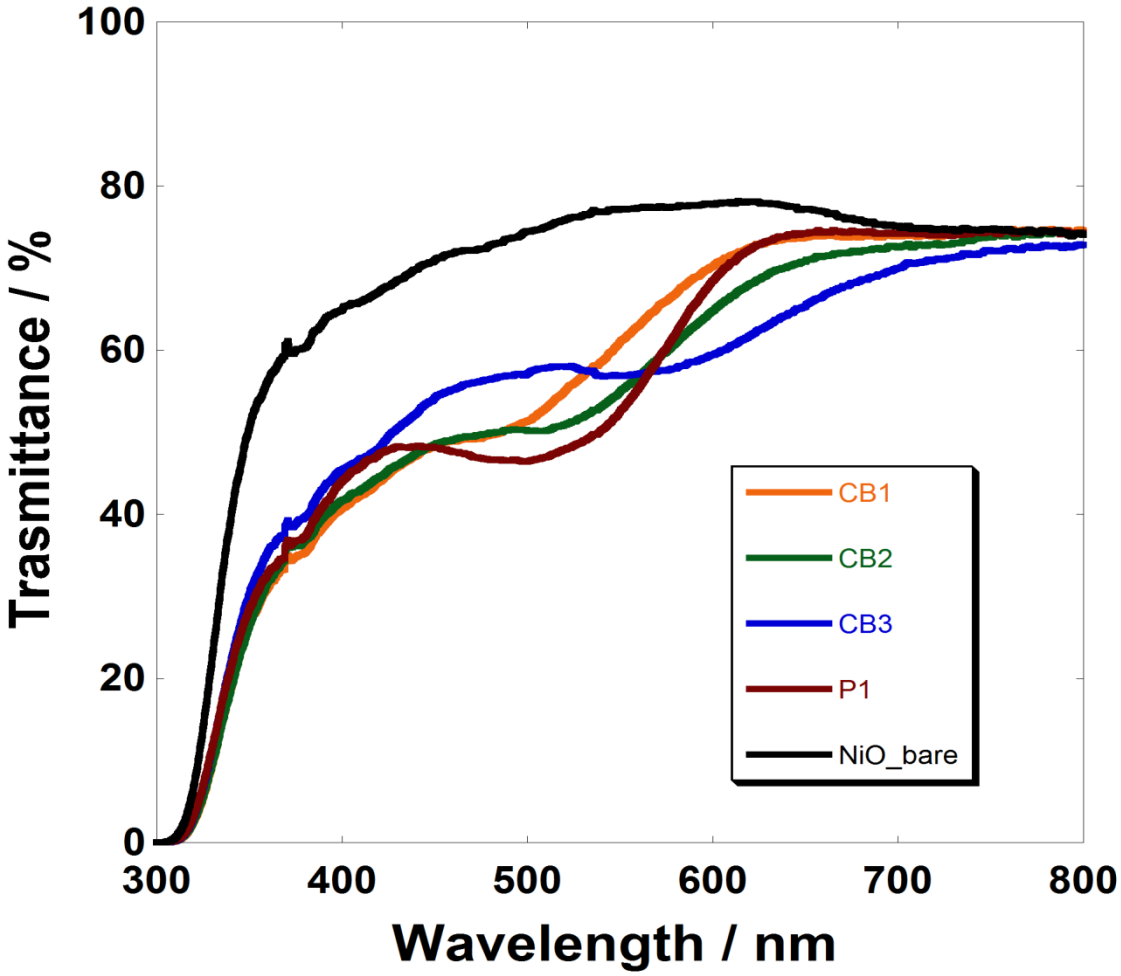

Figure 2. Trasmittance spectra of NiO sensitized with four different dye compared with NiO/P1. Black line refers to the unsensitized electrode.

The electrical characterization of the fabricated devices has been performed under simulated solar radiation and the characteristic *JV* curves are shown in Figure 4. A reference cell sensitized with a high level benchmark as P1 dye[52] has been fabricated and tested as well: its electrical characterization is reported in Figure 4. From *JV* curves some key parameters as open circuit voltage (V_{OC} in mV), short circuit density (J_{SC} in mA·cm^{-2}), fill factor (FF, %) and overall efficiency (η, %) could be obtained. The values of these parameters, averaged on five nominally equal devices have been reported in Table 2.

All the devices based on the reported dyes present interesting photoelectrochemical activity proving their efficiency as photosensitizers for *p*-DSSC. The best performing device is the one based on dye

CB2 with a power conversion efficiency of 0.040 %. The devices based on dyes **CB1** and **CB3** afforded similar performances showing PCE values of 0.032 and 0.034 %, respectively. The obtained performances are only slightly lower that of the reference cell based on **P1** (η = 0.049 %).

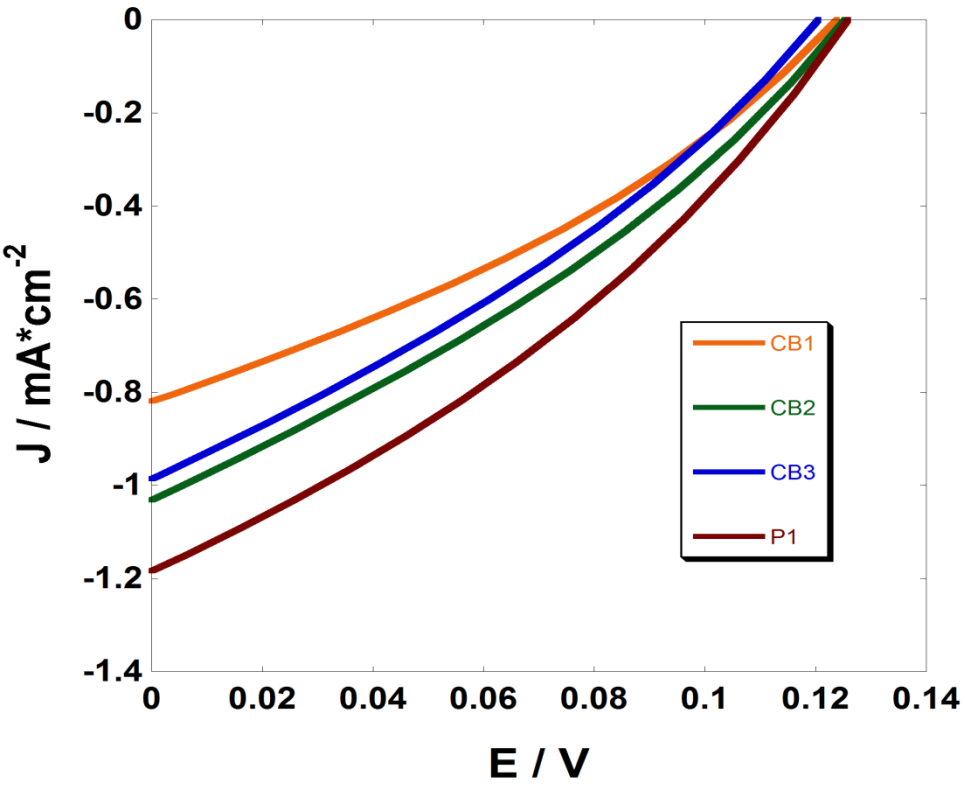

Figure 3. JV curves of NiO-based device sensitized with four different sensitizer and compared with a reference cell NiO/P1. The reported curves refer to the most performing device for each dye.

Table 2. *Characteristic values of the parameters characterizing the photoelectrochemical performance of the p-DSSCs sensitized with the pyran based dyes of Figure 1 and P1 benchmark.*

	Jsc / mA cm^{-2}	*Voc /mV*	*FF / %*	*η / %*
CB1	-0.780 ± 0.017	124.3 ± 0.3	32.6 ± 0.5	0.032 ± 0.002
CB2	-1.000 ± 0.033	124.1 ± 0.4	32.3 ± 0.3	0.040 ± 0.002
CB3	-0.844 ± 0.027	122.7 ± 1.1	31.0 ± 0.6	0.034 ± 0.002
P1 (ref)	-1.188	125.6	32.9	0.049

From the examination of the various electrical parameters reported in Table 2, it seems evident that V_{OC} values are not strongly dependent on the dye used to sensitize NiO. This is quite expected since all the dye own similar molecular structures that differ just for the acceptor group (Figure 1). Nevertheless, this unit is quite far away from the NiO surface and it should hardly influence the

energetic modulation of the semiconductor valence band. The same explanation could be used to justify the similarity in FF values. In fact, FF is deeply linked to open circuit potential value[53]. In this case, the higher the latter the higher the former. The different overall efficiency values reported in Table 2 are mainly controlled by the differences in the photocurrent produced by each device. **CB2**/NiO device is the sole cell able to supply a current density higher than 1 mA/cm^{-2}. **CB1**/NiO and **CB3**/NiO cells provide slightly lower current density that led to overall efficiency of 0.032 % and 0.034 %, respectively. This behaviour is consistent with the different molar absorption coefficients of the dyes: the higher is the latter, the higher is the efficiency of the cell. Therefore, we could hypothesize that the here reported difference are mainly due to the light harvesting efficiency (LHE) of each dye whereas the photo-injection efficiency is unvaried no matter of the sensitizer employed.

The results obtained by *JV* curves have been strengthen by IPCE spectral measurements (Figure 5).

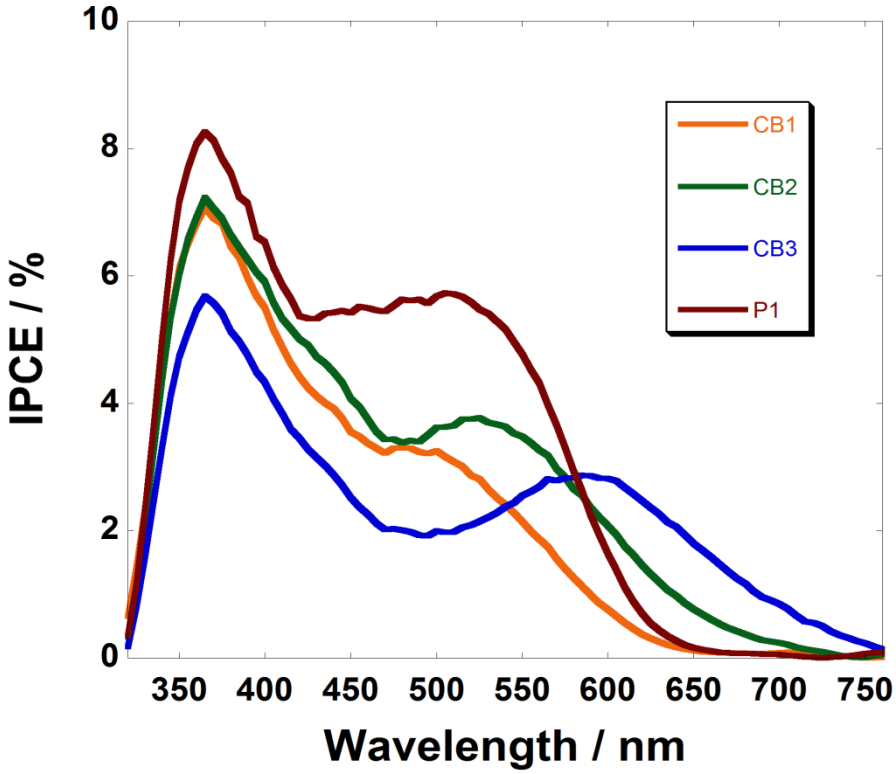

Figure 4. IPCE spectra of NiO-based devices sensitized with the different dyes and compared with a reference cell NiO/P1. The reported spectra refer to the most performing device for each dye.

The IPCE profiles directly provides the percentage of incident photons that are converted into electrons for each wavelength of the incident radiation. In our case, the peak at shorter wavelengths (λ < 420 nm) is due to the intrinsic photoactivity of NiO (especially Ni^{3+} available sites)[48,54] whereas the broad peak at longer wavelength is characteristic of each sensitizer. IPCE spectra give us some additional information with respect to *JV* curves. Interestingly, the intensity of the IPCE peak characteristic of NiO decreases with the increase of the steric hindrance of the acceptor group. At this regard we expect that the bulkiness of the EWG might influence the extent of dye-loading with the larger groups preventing the anchoring of dye-sensitizers at large surface concentrations with respect to the colorants with relatively smaller size. Nevertheless, the goodness of each device performances is mainly linked to the dye peak. Better efficiencies have been recorded when the sensitizer IPCE peak is high and/or broad.

It is well know that non stoichiometric NiO promotes triiodide reduction even in dark conditions[54]. In order to prove the magnitude of the dark reduction of triiodide to iodide ($I_3^- + 2e^- \rightarrow 3\ I^-$) dark *JV* curves measurements (Figure 6) were conducted on the most performing devices. The dark reduction process occurs at both NiO/electrolyte and at the FTO/electrolyte interfaces. The FTO can participate in the electrochemical process if some channels are present through the porous film of NiO semiconductor. This morphological characteristic allows the penetration of the electrolyte till the substrate of charge collection. In our case, we are not going to consider the charge transfer process at the FTO/electrolyte interface. In dark conditions, the *p*-DSSC devices here characterized feature a higher open circuit voltage as compared to devices based on unsensitized NiO cathode. Therefore, we could state that a part of the NiO/dye surface charge arise either from a dark charge transfer process between the sensitizer and the semiconductor film or from the spontaneous adsorption of some anion[55,56]. The extent of the latter phenomenon depends on the surface concentration of the sensitizer, its anchoring geometry and the nature of the adsorbed anion.

Some further information could be obtained by the analyses of dark J_{SC} on the nature of the dye (Table 3). The sensitization of NiO electrodes with **CCB2** and **CB1** produces cell with a larger value of dark current density with respect to bare NiO cathode.

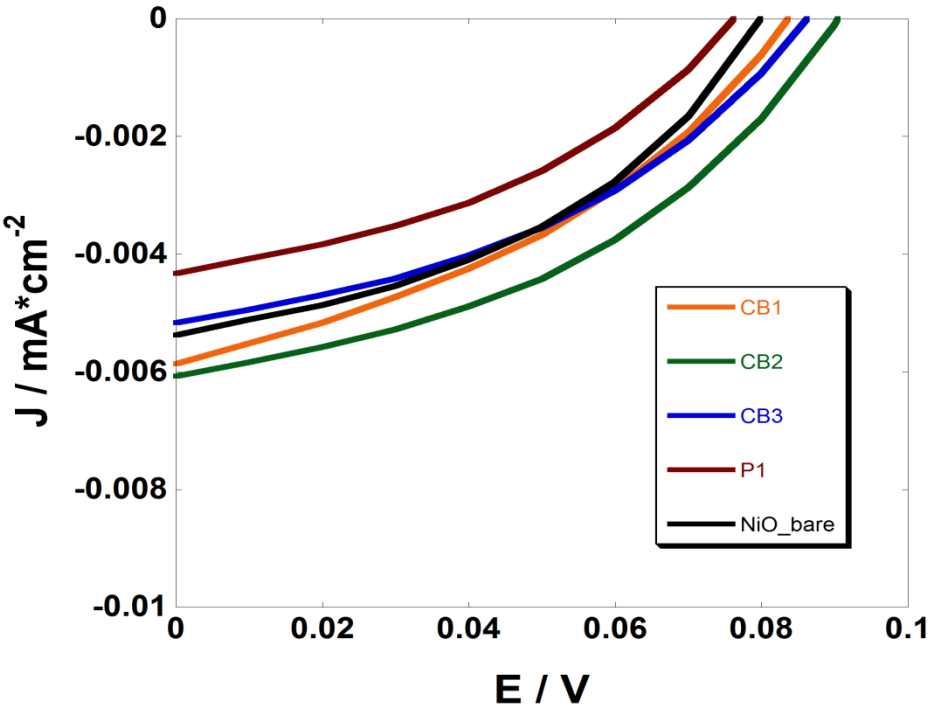

Figure 5. In dark JV curves of NiO-based device sensitized with three different sensitizers and compared with a reference cell NiO/P1 and bare NiO devices. The reported curves refer to the most performing device for each dye.

Table 3. *Characteristic values of p-DSSC parameters obtained from the JV curves recorded in dark conditions*

	CB1	CB2	CB3	P1	NiO bare
V_{oc} / mV	83	90	86	76	80
J_{sc} / μA cm^{-2}	5.9	6.1	5.2	4.3	5.3

This evidence implicates that these two dyes mediate the dark process of electron transfer from the semiconductor to triiodide anion. Conversely, **CB3**/NiO device showed a dark current very close to that of the bare NiO device while **P1**/NiO cell afforded a reduced dark current indicating that **P1** behaves actually as an agent of passivation towards the dark reduction process, as already reported

by a previous work realized with different electrodes of mesoporous NiO[54]. Nevertheless, it is mandatory to remark that the dark currents constitute less than 2% of the photocurrent.

CONCLUSIONS

Three custom-made full organic dyes have been employed to sensitize screen-printed NiO photocathodes for *p*-DSSC. The dyes are based on a pyran core that has been functionalized with different electron acceptor groups and symmetrically coupled to two phenothiazine donor moieties. The latter moieties bear carboxylic groups which act as anchoring units. Such a design is based on the placement of the electron acceptor group in a site far away from the anchoring carboxylic groups that bind to the NiO surface. Such a structural feature is highly desirable to reduce the internal recombination between the LUMO of the dye and the VB of NiO with resulting enhancement of the cell performances. The optical properties of the sensitizers in solution and in the NiO immobilized state have been evaluated before their employment in a complete device. All dyes experimented a very good binding onto the electrode surface as evidenced by transmittance spectra. When implemented in a complete device, dye **CB2** showed the best photoelectrochemical performance by displaying a photocurrent density of short circuit larger than 1 mA cm^{-2} and an overall efficiency of 0.04%. These results are just slightly lower than the values reported for a high performing reference cell like the *p*-DSSC employing P1 as benchmark sensitizer. The comparison of the IPCE spectra evidence that dye **CB2** gives the higher efficiency thanks to a more efficient light harvesting efficiency due to its higher molar extinction coefficient with respect to the other sensitizers.

In conclusion, the sensitizers here proposed have showed a very good photoelectrochemical behavior in *p*-DSSCs when screen-printed NiO is the cathode. In future works some similar dyes will be investigated to optimize the molecular skeleton as well as the nature and strength of the electron withdrawing group. The optimization will be conducted in the perspective of applying these dyes as sensitizers of *p*-DSSC device.

REFERENCES

[1] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-Sensitized Solar Cells, Chem. Rev. 110 (2010) 6595. doi:10.1021/cr900356p.

[2] C. Cavallo, F. Di Pascasio, A. Latini, M. Bonomo, D. Dini, Nanostructured Semiconductor Materials for Dye-Sensitized Solar Cells, J. Nanomater. 2017 (2017) 5323164.

[3] M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin, et al., Recent advances in dye-sensitized solar cells: From photoanodes, sensitizers and electrolytes to counter electrodes, Mater. Today. 18 (2015) 155–162. doi:10.1016/j.mattod.2014.09.001.

[4] M.K. Nazeeruddin, E. Baranoff, M. Grätzel, Dye-sensitized solar cells: A brief overview, Sol. Energy. 85 (2011) 1172–1178. doi:10.1016/j.solener.2011.01.018.

[5] A. Mishra, M.K.R. Fischer, P. Büuerle, Metal-Free organic dyes for dye-Sensitized solar cells: From structure: Property relationships to design rules, Angew. Chemie - Int. Ed. 48 (2009) 2474–2499. doi:10.1002/anie.200804709.

[6] J. Gong, J. Liang, K. Sumathy, Review on dye-sensitized solar cells (DSSCs): Fundamental concepts and novel materials, Renew. Sustain. Energy Rev. 16 (2012) 5848–5860. doi:10.1016/j.rser.2012.04.044.

[7] P. Docampo, S. Guldin, T. Leijtens, N.K. Noel, U. Steiner, H.J. Snaith, Lessons learned: From dye-sensitized solar cells to all-solid-state hybrid devices, Adv. Mater. 26 (2014) 4013–4030. doi:10.1002/adma.201400486.

[8] Z. Ning, Y. Fu, H. Tian, Improvement of dye-sensitized solar cells: What we know and what we need to know, Energy Environ. Sci. 3 (2010) 1170–1181. doi:10.1039/c003841e.

[9] M.A. Green, S.P. Bremner, Energy Conversion Approaches and Materials for High Efficiency Photovoltaics, Nat. Mater. 16 (2017) 23–34. doi:10.1038/nmat4676.

[10] S. Yoon, S. Tak, J. Kim, Y. Jun, K. Kang, J. Park, Application of transparent dye-sensitized solar cells to building integrated photovoltaic systems, Build. Environ. 46 (2011) 1899–1904. doi:10.1016/j.buildenv.2011.03.010.

[11] A. Fakharuddin, R. Jose, T.M. Brown, F. Fabregat-Santiago, J. Bisquert, A perspective on the production of dye-sensitized solar modules, Energy Environ. Sci. 7 (2014) 3952–3981. doi:10.1039/c4ee01724b.

[12] B. O'Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films, Nature. 353 (1991) 737.

[13] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa, M. Hanaya, Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes, Chem. Commun. 51 (2015) 15894–15897. doi:10.1039/C5CC06759F.

[14] M. Bonomo, D. Dini, Nanostructured p-type semiconductor electrodes and photoelectrochemistry of their reduction processes, Energies. 9 (2016). doi:10.3390/en9050373.

[15] C.J. Wood, G.H. Summers, E.A. Gibson, Increased photocurrent in a tandem dye-sensitized solar cell by modifications in push–pull dye-design, Chem. Commun. 51 (2015) 3915. doi:10.1039/c4cc10230d.

[16] F. Odobel, Y. Pellegrin, E.A. Gibson, A. Hagfeldt, A.L. Smeigh, L. Hammarström, Recent advances and future directions to optimize the performances of p-type dye-sensitized solar cells, Coord. Chem. Rev. 256 (2012) 2414–2423. doi:http://dx.doi.org/10.1016/j.ccr.2012.04.017.

[17] F. Odobel, L. Le Pleux, Y. Pellegrin, E. Blart, New photovoltaic devices based on the sensitization of p-type semiconductors: Challenges and opportunities, Acc. Chem. Res. 43 (2010) 1063–1071. doi:10.1021/ar900275b.

[18] N. Li, E.A. Gibson, P. Qin, G. Boschloo, M. Gorlov, A. Hagfeldt, et al., Dou ble-layered NiO photocathodes for p-Type DSSCs with record IPCE, Adv. Mater. 22 (2010) 1759–1762. doi:10.1002/adma.200903151.

[19] F. Odobel, Y. Pellegrin, Recent advances in the sensitization of wide-band-gap nanostructured p-type semiconductors. photovoltaic and photocatalytic applications, J. Phys. Chem. Lett. 4 (2013) 2551–2564. doi:10.1021/jz400861v.

[20] A. Nattestad, A.J. Mozer, M.K.R. Fischer, Y.-B. Cheng, A. Mishra, P. Bauerle, et al., Highly efficient photocathodes for dye-sensitized tandem solar cells, Nat Mater. 9 (2010) 31.

[21] D. Xiong, W. Chen, Recent progress on tandem structured dye-sensitized solar cells, Front. Optoelectron. 5 (2012) 371–389. doi:10.1007/s12200-012-0283-9.

[22] W. Shockley, H.J. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, J. Appl. Phys. 32 (1961) 510. doi:10.1063/1.1736034.

[23] Y. Xu, T. Gong, J.N. Munday, The generalized Shockley-Queisser limit for nanostructured solar cells, Sci. Rep. 5 (2015) 13536. doi:10.1038/srep13536.

[24] I. Sullivan, B. Zoellner, P.A. Maggard, Copper(I)-Based p-Type Oxides for Photoelectrochemical and Photovoltaic Solar Energy Conversion, Chem. Mater. 28 (2016) 5999. doi:10.1021/acs.chemmater.6b00926.

[25] I.R. Perera, T. Daeneke, S. Makuta, Z. Yu, Y. Tachibana, A. Mishra, et al., Application of the tris(acetylacetonato)iron(III)/(II) redox couple in p-type dye-sensitized solar cells, Angew. Chemie - Int. Ed. 54 (2015) 3758. doi:10.1002/anie.201409877.

[26] L. D'Amario, L.J. Antila, B. Pettersson Rimgard, G. Boschloo, L. Hammarström, Kinetic evidence of two pathways for charge recombination in NiO-based dye-sensitized solar cells, J. Phys. Chem. Lett. 6 (2015) 779–783. doi:10.1021/acs.jpclett.5b00048.

[27] T. Jiang, M. Bujoli-Doeuff, Y. Farré, Y. Pellegrin, E. Gautron, M. Boujtita, et al., CuO nanomaterials for p-type dye-sensitized solar cells, RSC Adv. 6 (2016) 112765. doi:10.1039/C6RA17879K.

[28] X. Li, F. Yu, S. Stappert, C. Li, Y. Zhou, Y. Yu, et al., Enhanced Photocurrent Density by Spin-Coated NiO Photocathodes for N-Annulated Perylene-Based p-Type Dye-Sensitized Solar Cells, ACS Appl. Mater. Interfaces. 8 (2016) 19393. doi:10.1021/acsami.6b04007.

[29] T.T.T. Pham, S.K. Saha, D. Provost, Y. Farré, M. Raissi, Y. Pellegrin, et al., Toward Efficient Solid-State p-Type Dye-Sensitized Solar Cells: The Dye Matters, J. Phys. Chem. C. 121 (2017) 129–139. doi:10.1021/acs.jpcc.6b10513.

[30] Y. Farrè, L. Zhang, Y. Pellegrin, A. Planchat, E. Blart, M. Boujtita, et al., Second Generation of Diketopyrrolopyrrole Dyes for NiO-Based Dye-Sensitized Solar Cells, J. Phys. Chem. C. 120 (2016) 7923–7940. doi:10.1021/acs.jpcc.5b12489.

[31] J. Cui, J. Lu, X. Xu, K. Cao, Z. Wang, G. Alemu, et al., Organic sensitizers with pyridine ring anchoring group for p-type dye-sensitized solar cells, J. Phys. Chem. C. 118 (2014) 16433–16440.

doi:10.1021/jp410829c.

[32] Z. Liu, W. Li, S. Topa, X. Xu, X. Zeng, Z. Zhao, et al., Fine tuning of fluorene-based dye structures for high-efficiency p -type dye-sensitized solar cells, ACS Appl. Mater. Interfaces. 6 (2014) 10614–10622. doi:10.1021/am5022396.

[33] B.B. Jung, C. Yoon, H. Shim, L. Do, T. Zyung, Pure-Red Dye for Organic Electroluminescent Devices : Bis-Condensed DCM Derivatives **, Adv. Funtional Mater. 11 (2001) 430–434. doi:10.1002/1616-3028(200112)11:6<430::AID-ADFM430>3.0.CO;2-G.

[34] L. Yang, M. Guan, D. Nie, B. Lou, Z. Liu, Z. Bian, et al., Efficient, saturated red electroluminescent devices with modified pyran-containing emitters, Opt. Mater. (Amst). 29 (2007) 1672–1679. doi:10.1016/j.optmat.2006.09.013.

[35] L. Xue, J. He, X. Gu, Z. Yang, B. Xu, W. Tian, Efficient bulk-heterojunction solar cells based on a symmetrical D-??-A-??-D organic dye molecule, J. Phys. Chem. C. 113 (2009) 12911–12917. doi:10.1021/jp902976w.

[36] Z. Li, Q. Dong, S. Yao, J. Qian, Y. Wang, F. Jiang, et al., An efficient photovoltaic device based on novel D???A???D solution-processable small molecules, J. Mater. Sci. 50 (2014) 937–947. doi:10.1007/s10853-014-8653-x.

[37] A. Carella, F. Borbone, U. Caruso, R. Centore, A. Roviello, A. Barsella, et al., NLO behavior of polymers containing Y-shaped chromophores, Macromol. Chem. Phys. 208 (2007) 1900–1907. doi:10.1002/macp.200700275.

[38] P. Shao, Z. Huang, J. Li, S. Chen, J. Luo, J. Qin, et al., Two-photon absorption properties of two (dicyanomethylene)-pyran derivatives, Opt. Mater. (Amst). 29 (2006) 337–341. doi:10.1016/j.optmat.2005.08.039.

[39] A. Ambrosio, P. Maddalena, A. Carella, F. Borbone, A. Roviello, M. Polo, et al., Two-photon induced self-structuring of polymeric films based on Y-shape azobenzene chromophore, J. Phys. Chem. C. 115 (2011) 13566–13570. doi:10.1021/jp200050h.

[40] D. Dini, M.J.F. Calvete, M. Hanack, Nonlinear Optical Materials for the Smart Filtering of Optical Radiation, Chem. Rev. 116 (2016) 13043–13233. doi:10.1021/acs.chemrev.6b00033.

[41] A. Ambrosio, E. Orabona, P. Maddalena, A. Camposeo, M. Polo, A.A.R. Neves, et al., Two-photon patterning of a polymer containing Y-shaped azochromophores, Appl. Phys. Lett. 94 (2009) 11115. doi:10.1063/1.3058820.

[42] Y. Liu, Y. Liu, D. Zhang, H. Hu, C. Liu, Theoretical investigation on second-order nonlinear optical properties of (dicyanomethylene) -pyran derivatives, J. Mol. Struct. 570 (2001) 43–51. doi:10.1016/S0022-2860(01)00479-3.

[43] S. Franco, J. Garín, N. Martínez De Baroja, R. Pérez-Tejada, J. Orduna, Y. Yu, et al., New D-π-A-conjugated organic sensitizers based on 4 H-pyran-4-ylidene donors for highly efficient dye-sensitized solar cells, Org. Lett. 14 (2012) 752–755. doi:10.1021/ol203298r.

[44] C. Maglione, A. Carella, R. Centore, S. Fusco, A. Velardo, A. Peluso, et al., Tuning optical absorption in pyran derivatives for DSSC, J. Photochem. Photobiol. A Chem. 321 (2016) 79–89. doi:10.1016/j.jphotochem.2016.01.018.

[45] C. Maglione, A. Carella, C. Carbonara, R. Centore, S. Fusco, A. Velardo, et al., Novel pyran based dyes for application in dye sensitized solar cells, Dye. Pigment. 133 (2016) 395–405. doi:10.1016/j.dyepig.2016.06.024.

[46] M. Bonomo, N. Barbero, F. Matteocci, A. Di Carlo, C. Barolo, D. Dini, Beneficial Effect of Electron-Withdrawing Groups on the Sensitizing Action of Squaraines for p-Type Dye-Sensitized Solar Cells, J. Phys. Chem. C. 120 (2016) 16340–16353. doi:10.1021/acs.jpcc.6b03965.

[47] G. Boschloo, A. Hagfeldt, Characteristics of the iodide/triiodide redox mediator in dye-sensitized solar cells, Acc. Chem. Res. 42 (2009) 1819–1826. doi:10.1021/ar900138m.

[48] M. Bonomo, G. Naponiello, I. Venditti, V. Zardetto, A. Di Carlo, D. Dini, Electrochemical and Photoelectrochemical Properties of Screen-Printed Nickel Oxide Thin Films Obtained from Precursor Pastes with Different Compositions, J. Electrochem. Soc. 164 (2017) H137–H147. doi:10.1149/2.0051704jes.

[49] F. De Rossi, L. Di Gaspare, A. Reale, A. Di Carlo, T.M. Brown, Blending CoS and Pt for amelioration of electrodeposited transparent counterelectrodes and the efficiency of back-illuminated dye solar cells, J. Mater. Chem. A. 1 (2013) 12941. doi:10.1039/c3ta13076b.

[50] J. He, H. Lindström, A. Hagfeldt, S.-E. Lindquist, Dye-Sensitized Nanostructured p-Type Nickel Oxide Film as a Photocathode for a Solar Cell, J. Phys. Chem. B. 103 (1999) 8940. doi:10.1021/jp991681r.

[51] G. Natu, P. Hasin, Z. Huang, Z. Ji, M. He, Y. Wu, Valence band-edge engineering of nickel oxide nanoparticles via cobalt doping for application in p-type dye-sensitized solar cells, ACS Appl. Mater. Interfaces. 4 (2012) 5922–5929. doi:10.1021/am301565j.

[52] P. Qin, H. Zhu, T. Edvinsson, G. Boschloo, A. Hagfeldt, L. Sun, Design of an Organic Chromophore for P-Type Dye-Sensitized Solar Cells, J. Am. Chem. Soc. 130 (2008) 8570. doi:10.1021/ja8001474.

[53] T. Daeneke, Z. Yu, G.P. Lee, D. Fu, N.W. Duffy, S. Makuta, et al., Dominating energy losses in NiO p-type dye-sensitized solar cells, Adv. Energy Mater. 5 (2015) 1401387. doi:10.1002/aenm.201401387.

[54] S. Sheehan, G. Naponiello, F. Odobel, D.P. Dowling, A. Di Carlo, D. Dini, Comparison of the photoelectrochemical properties of RDS NiO thin films for p-type DSCs with different organic and organometallic dye-sensitizers and evidence of a direct correlation between cell efficiency and charge recombination, J. Solid State Electrochem. 19 (2015) 975–986. doi:10.1007/s10008-014-2703-9.

[55] M. Bonomo, A.G. Marrani, V. Novelli, M. Awais, D.P. Dowling, J.G. Vos, et al., Surface properties of nanostructured NiO undergoing electrochemical oxidation in 3-methoxy-propionitrile, Appl. Surf. Sci. 403 (2017) 441–447. doi:10.1016/j.apsusc.2017.01.202.

[56] M. Bonomo, D. Dini, A.G. Marrani, Adsorption Behavior of I3- and I- Ions at a Nanoporous NiO/Acetonitrile Interface Studied by X-ray Photoelectron Spectroscopy, Langmuir. 32 (2016) 11540–11550. doi:10.1021/acs.langmuir.6b03695.

Table

Table 1. *Optical and electrochemical properties of the synthesized chromophores*

Dye	λ_{max} /nm[a]	ε /L·mol^{-1}·cm^{-1} [a]	HOMO /eV[b]	LUMO / eV[b]
CB1	464	$4.1 \cdot 10^4$	-5.51	-3.51
CB2	521	$4.3 \cdot 10^4$	-5.51	-3.69
CB3	582	$3.8 \cdot 10^4$	-5.59	-3.95

a) Scan rate 200 nm/min, in THF solution; b) determined, as reported in ref. 38, by a combined electro-chemical and optical approach on thin film of the dyes,.

Table 2. *Characteristic values of the parameters characterizing the photoelectrochemical performance of the p-DSSCs sensitized with the pyran based dyes of Figure 1 and P1 benchmark.*

	Jsc / mA cm^{-2}	*Voc /mV*	*FF / %*	*η / %*
CB1	-0.780 ± 0.017	124.3 ± 0.3	32.6 ± 0.5	0.032 ± 0.002
CB2	-1.000 ± 0.033	124.1 ± 0.4	32.3 ± 0.3	0.040 ± 0.002
CB3	-0.844 ± 0.027	122.7 ± 1.1	31.0 ± 0.6	0.034 ± 0.002
P1 (ref)	-1.188	125.6	32.9	0.049

Table 3. *Characteristic values of p-DSSC parameters obtained from the JV curves recorded in dark conditions*

	CB1	CB2	CB3	P1	NiO bare
V_{oc} / mV	83	90	86	76	80
J_{sc} / μA cm^{-2}	5.9	6.1	5.2	4.3	5.3

Figure

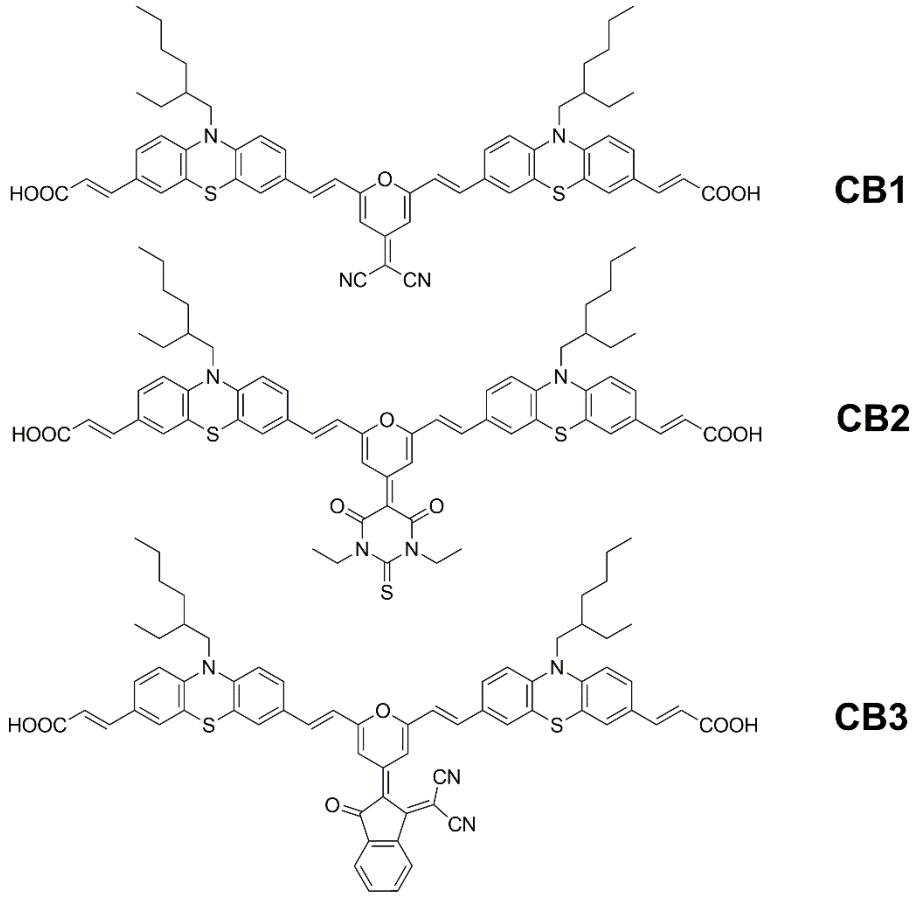

Figure 1. *Chemical structures of the reported pyran based photosensitizers*

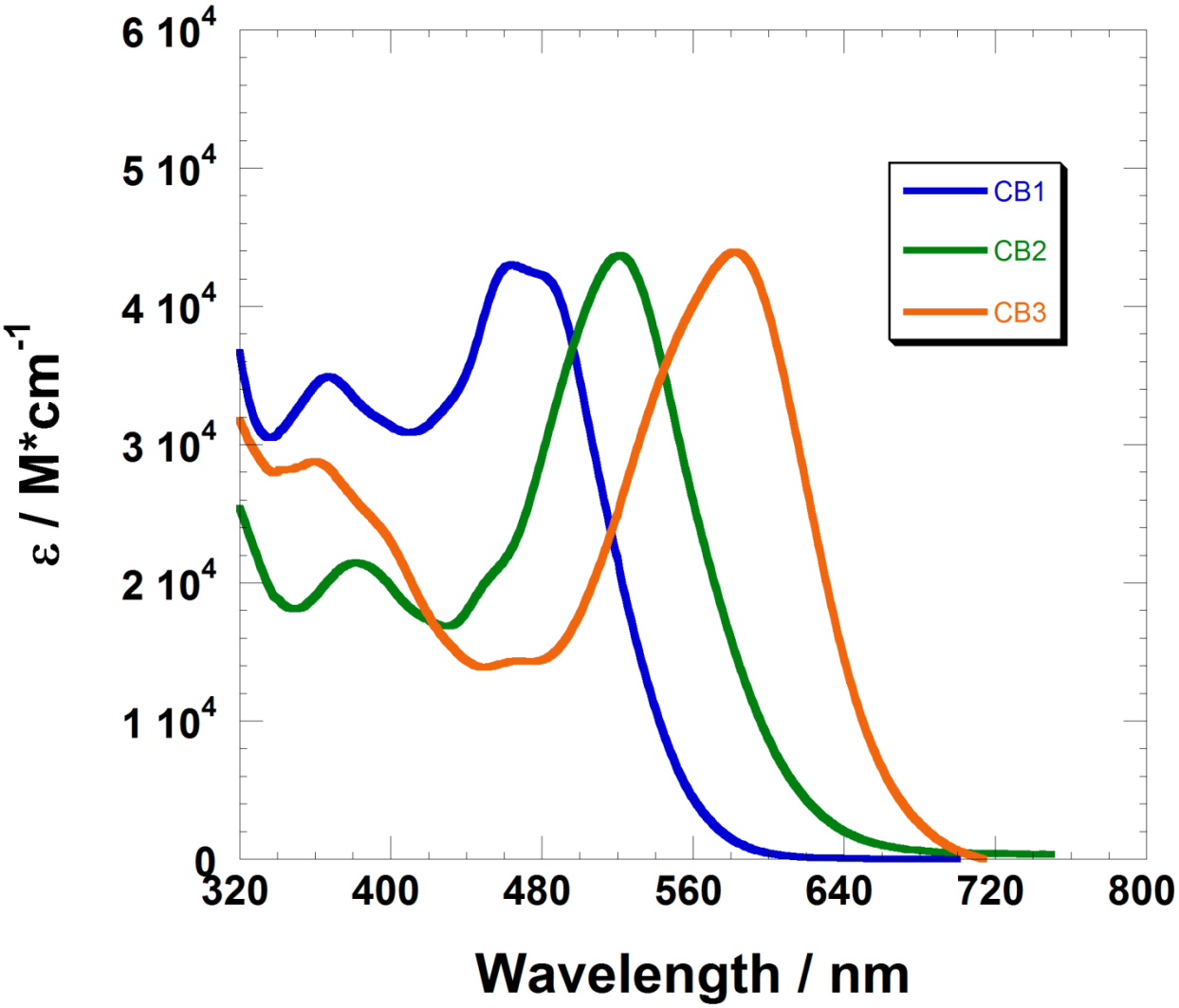

Figure 1. Molar absorptivity of the reported dyes in THF solution

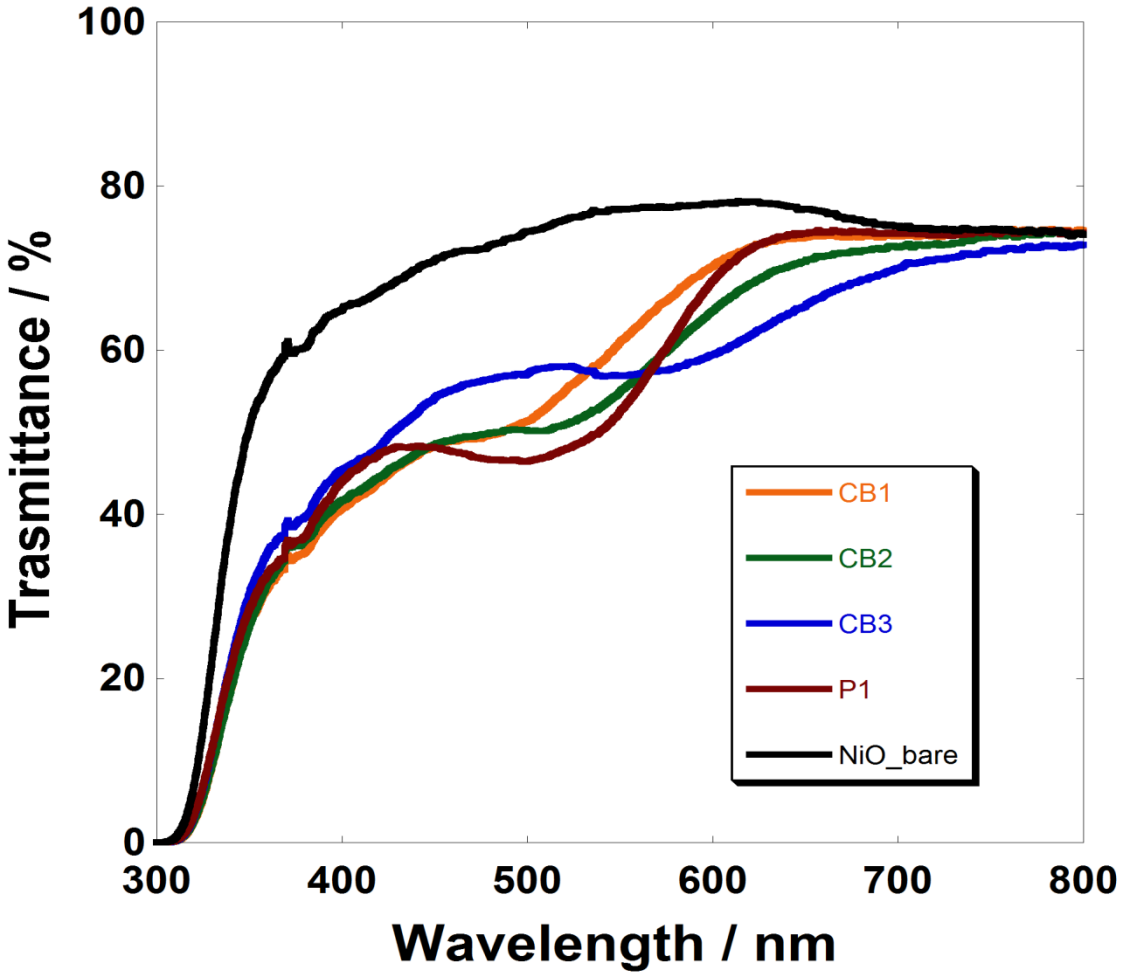

Figure 2. Trasmittance spectra of NiO sensitized with four different dye compared with NiO/P1. Black line refers to the unsensitized electrode.

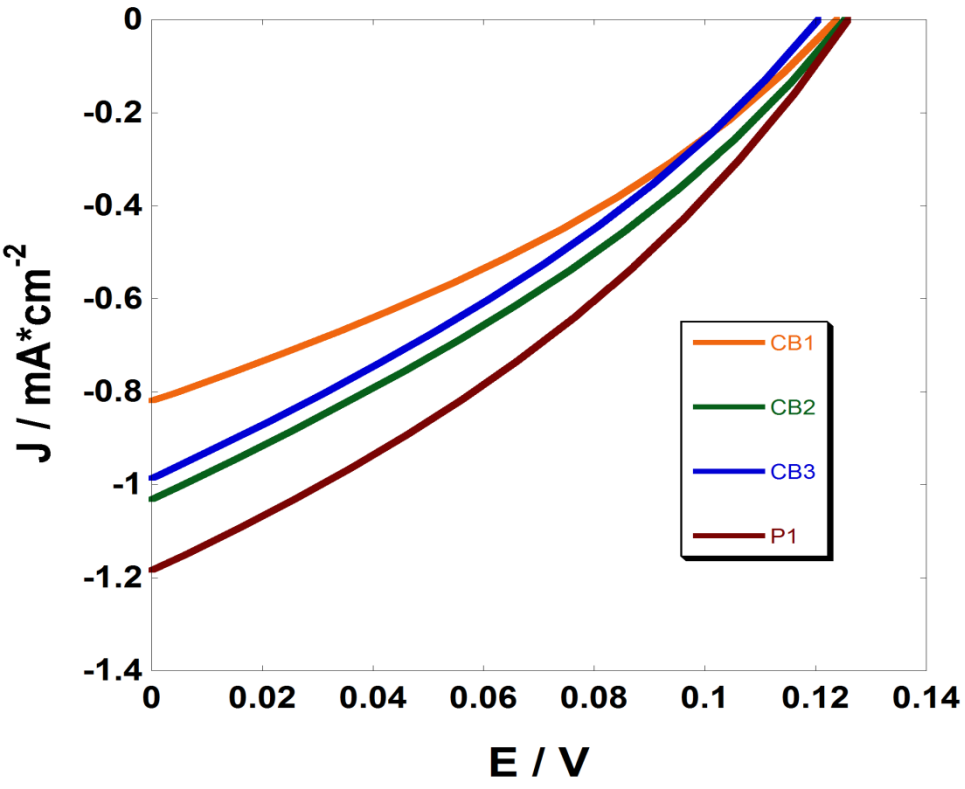

Figure 3. JV curves of NiO-based device sensitized with four different sensitizer and compared with a reference cell NiO/P1. The reported curves refer to the most performing device for each dye.

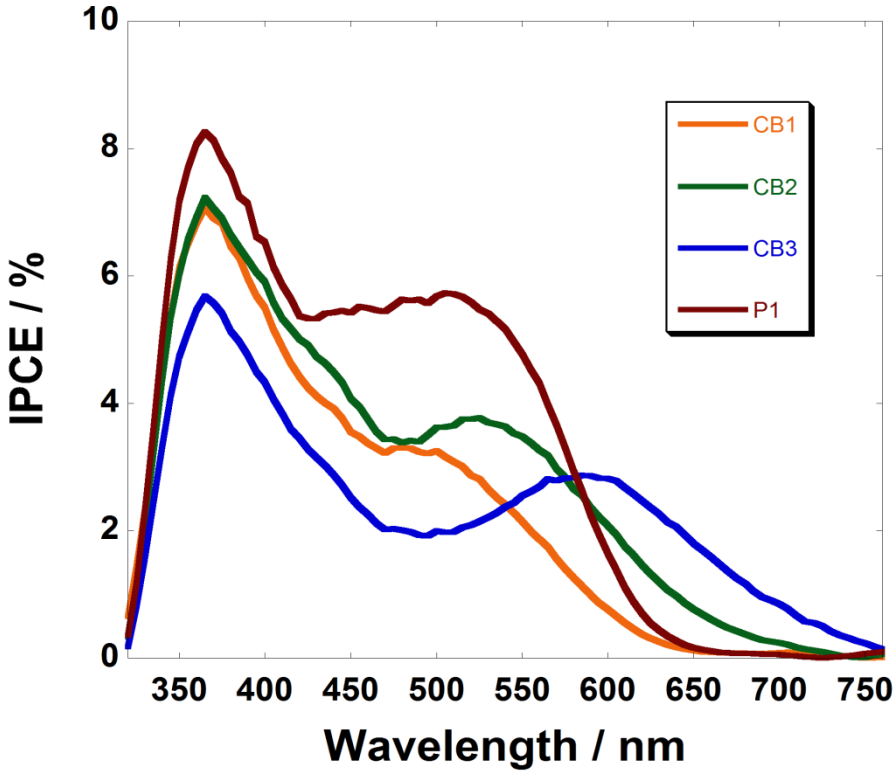

Figure 4. IPCE spectra of NiO-based devices sensitized with the different dyes and compared with a reference cell NiO/P1. The reported spectra refer to the most performing device for each dye.

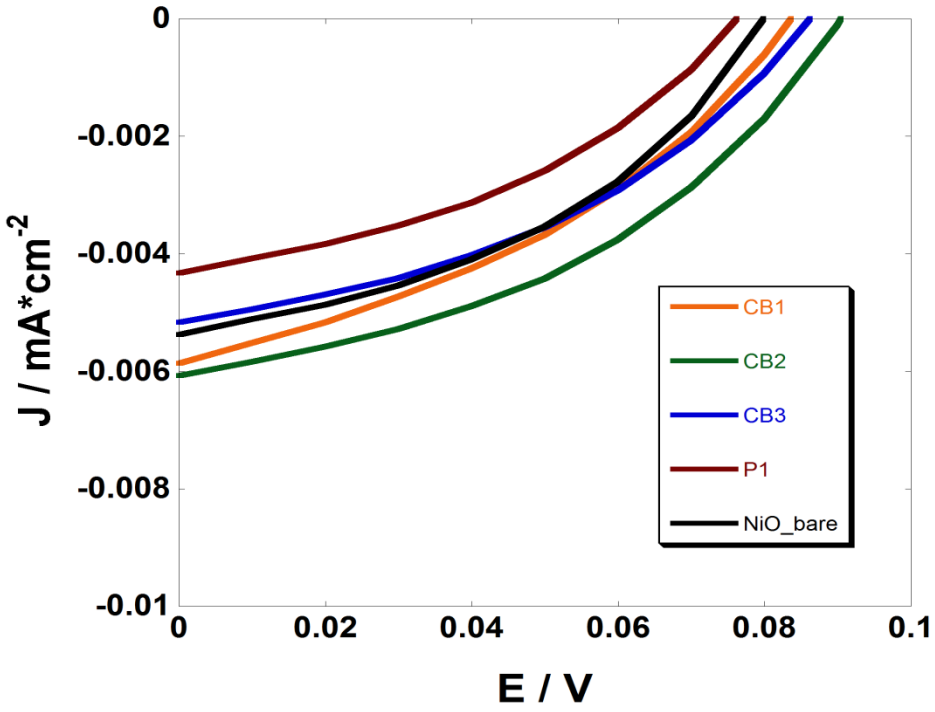

Figure 5. In dark JV curves of NiO-based device sensitized with three different sensitizers and compared with a reference cell NiO/P1 and bare NiO devices. The reported curves refer to the most performing device for each dye.

Highlights (for review)

- Electroactive NiO films are deposited via screen printing with NiO nanoparticles

- Screen-printed NiO is mesoporous

- New Pyran-based dyes has been tested as sensitizers in p-DSSC

- CV measurements reveals a good photoelectrochemical behavior for all the devices

- Overall efficiencies are comparable with P1-based device