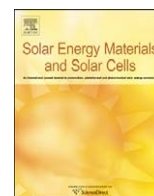




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Dye-sensitized solar cells with natural dyes extracted from achiote seeds

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ABSTRACT

We have explored the application of natural dyes extracted from the seeds of the achiote shrub (*Bixa orellana* L.) in dye-sensitized solar cells (DSCs). The main pigments are bixin and norbixin, which were obtained by separation and purification from the dark-red extract (annatto). The dyes were characterized using ¹H-NMR, FTIR spectroscopy, and UV–Vis spectrophotometry. Solar cells were prepared using TiO₂ and ZnO nanostructured, mesoporous films and the annatto, bixin, and norbixin as sensitizers. The best results were obtained with bixin-sensitized TiO₂ solar cells with efficiencies of up to 0.53%, illustrating the importance of purification of dyes from natural extracts.

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1. Introduction

The dye-sensitized solar cell (DSC) is a third generation photovoltaic device that holds significant promise for the inexpensive conversion of solar energy to electrical energy, because of the use of inexpensive materials and a relatively simple fabrication process [1]. The DSC is based on a nanostructured, mesoporous metal oxide film, sensitized to the visible light by an adsorbed molecular dye. The dye molecules absorb visible light, and inject electrons from the excited state into the metal oxide conduction band. The injected electrons travel through the nanostructured film to the current collector, and the dye is regenerated by an electron donor in the electrolyte solution. The DSC is fully regenerative, and the electron donor is again obtained by electron transfer to the electron acceptor at the counter electrode. The current certified efficiency record is 11.1% for small cells [2], and several large-scale tests have been conducted that illustrate the promise for commercial application of the DSC concept [3,4].

The molecular dye is an essential component of the DSC, and improvements in efficiency over the last 15 years have been achieved by tailoring the optoelectronic properties of the dye. The most successful dyes are based on ruthenium bipyridyl compounds, which are characterized by a large absorption

coefficient in the visible part of the solar spectrum, good adsorption properties, excellent stability, and efficient electron injection [5]. However, ruthenium-based compounds are relatively expensive, and organic dyes with similar characteristics and even higher absorption coefficients have recently been reported; solar cells with efficiencies of up to 9% have been reported [6–12]. Organic dyes with a higher absorption coefficient could translate into thinner nanostructured metal oxide films, which would be advantageous for charge transport both in the metal oxide and in the permeating phase, allowing for the use of higher viscosity materials such as ionic liquids, solid electrolytes or hole conductors. Organic dyes used in the DSC often bear a resemblance to dyes found in plants, fruits, and other natural products, and several dye-sensitized solar cells with natural dyes have been reported [13–21]. In this work, we explore the use of natural dyes obtained from the extract of achiote seeds, which are characterized by a high content of red pigments with a high absorption coefficient in the visible part of the solar spectrum.

Achiote (*Bixa orellana*) is a tropical shrub originating from the American continent that bears an inedible, red fruit containing about 50 red seeds. From the achiote seeds, a dark-red extract is obtained, which is extensively used for food colouring and flavouring. In addition, the dye is used for textiles, varnishes, cosmetics, tattoos, and medicinal purposes. The pericarp of the seeds contains a high concentration of carotenoids, and is composed of up to 80% of the carotenoid *cis*-bixin (methyl hydrogen (9'Z)-6,6'-apocarotene-6, 6'-dioate or 9'-*cis*-bixin or α -bixin); the remaining 20% include *trans*- and *cis*-norbixin

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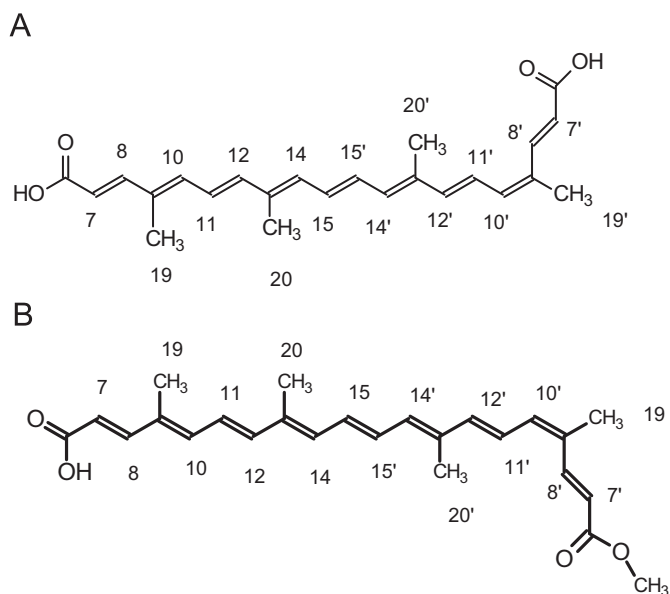


Fig. 1. Chemical structure of the apocarotenoids *cis*-norbixin (A) and *cis*-bixin (B), which are the main pigments in the pericarp of the achiote seeds.

(6,6'-diapocarotene-6,6'-dioic acid and 9'-*cis*-6,6'-diapocarotene-6,6'-dioic acid); the chemical structures are shown in Fig. 1. *cis*-Bixin ($C_{25}H_{30}O_4$) is insoluble in water and consists of a chain of alternating double conjugated bonds, with a carboxylic acid group at one end of the chain and a methyl ester group at the other. Norbixin ($C_{24}H_{28}O_4$) is a water-soluble carotenoid with only difference the presence of a carboxylic acid moiety in the position of the methyl ester group in bixin. In this work, we have extracted the apocarotenoids from the achiote seeds, and obtained bixin and norbixin in pure form. The extract, called annatto, and the two purified pigments have been applied in the dye-sensitized solar cell, using both ZnO and TiO_2 as substrate materials.

2. Experimental

2.1. Extraction, separation, and characterization of the dyes

Achiote seeds (20 g) were immersed in 200 mL of ethyl acetate in an Erlenmeyer flask and sonicated for 1 h in an ultrasonic bath at a temperature below 60 °C. The ethyl acetate solution was concentrated in vacuo at 40 °C to give 1.2 g of crude residue (6%). The crude residue was chromatographed over silica gel 60 Å (70–230 mesh) using hexane, mixtures of hexane–ethyl acetate (9:1, 8:2, 7:3, 6:4, 1:1), acetone, a mixture of acetone–methanol (1:1), and methanol. Eluates were collected, monitored by thin layer chromatography, and combined in major fractions. Bixin (0.42 g) was obtained from the last fractions.

Norbixin was obtained by saponification of bixin. Achiote seeds (10 g) were added to a flask with 200 mL of aqueous 0.1 M NaOH, and sonicated for 30 min. The solution was filtered, and adjusted to pH 2 with 0.27 M HCl. The resulting suspension was kept and filtered under nitrogen atmosphere, and the solid product was stored under nitrogen.

The purified bixin and norbixin dyes were analysed using 1H -NMR, FTIR spectroscopy, and UV–Vis spectrophotometry. NMR spectra were recorded in $(CD_3)_2CO$ on a Bruker Avance 400 spectrometer with a dual probe of 5 mm. The chemical shifts are given in δ (ppm) with residual $(CD_3)_2CO$ as internal reference, and coupling constants are reported in Hz. FTIR spectroscopy was

performed on a Nicolet Nexus model 670 FT-IR and the samples were measured in powder form mixed with KBr powder. UV–Vis spectra were obtained in chloroform using an Agilent 8453 diode array spectrophotometer.

2.2. Preparation of dye-sensitized solar cells

Dye-sensitized solar cells were prepared by doctor blading using Ti-nanoxide-T paste (Solaronix) and TEC15 FTO-covered glass (Libby-Owens-Ford, Hartford Glass) as follows. The FTO substrate was ultrasonically cleaned in water–isopropanol, and heated at 450 °C for 30 min prior to film deposition. The FTO was then pre-treated by immersion in a 40 mM $TiCl_4$ solution in water at 70 °C for 30 min, which was freshly prepared from a 2 M stock solution. The stock solution was prepared by slowly adding $TiCl_4$ to crushed ice, and was stored in a refrigerator. After the pre-treatment, the film was sintered at 450 °C for 30 min. Mesoporous TiO_2 films were deposited by doctor blading using Scotch Magic tape as a masking material. Two films were subsequently deposited, and between the two steps the electrode was sintered at 500 °C for 1 h. As a final step, the film was again treated in 40 mM $TiCl_4$ solution at 70 °C for 30 min, and heated to 560 °C for 15 min. The final film thickness was approximately 8 μm . After cooling to about 80 °C, the electrode was removed from the furnace and immersed in a concentrated dye solution in acetone for 30 min; the concentrations used were 3.0 g L^{-1} (7.6 mM) for bixin, 6.0 g L^{-1} (15.8 mM) for norbixin, and 4.0 g L^{-1} for annatto.

ZnO electrodes were prepared from commercial ZnO powder (Degussa VP AdNano[®]ZnO20) with an approximate nanoparticle size of 20 nm. The powder was mixed with ethanol and stirred overnight to obtain a colloidal suspension of 30 wt% ZnO. The film was deposited by doctor blading using a Scotch tape mask, and was sintered at 420 °C for 30 min. A second layer was applied in the same manner, and the final thickness was about 18 μm . After cooling to about 80 °C, the films were immersed in the dye solutions for 30 min.

Cells were prepared with areas ranging from 0.1 to 0.5 cm^2 , and it was found that the cell efficiency was independent of cell area in this range. The cell was assembled using a Surlyn 1702 separator, and heating at 180 °C for 5 min. The counter electrode was pre-treated with Platisol (Solaronix) and heated to 400 °C for 5 min; the transparent platinum film with a slightly dark tint was porous and rough, and consisted of aggregates of several hundreds of nanometers. The electrolyte consisted of 0.1 M LiI, 0.6 M DMPII, 0.05 M I_2 and 0.5 M TBP in methoxypropionitrile. All chemicals were ACS reagent grade from Sigma-Aldrich and used as received, except for DMPII which was obtained from Solaronix. The electrolyte was introduced into the cell through a small hole in the counter electrode by vacuum backfilling, and the hole was sealed with a microscope glass cover and Surlyn 1702.

The cell performance was determined using a 450 W ozone-free Oriol Xenon lamp coupled to a water filter and an Oriol AM 1.5G filter. The intensity was measured using a thermopile detector (Oriol). Current–voltage curves were obtained using a variable resistor and an Agilent 34401A multimeter, by means of a LabView program. In order to account for the mismatch between the spectrum of the illumination set-up and the solar spectrum, current–voltage curves were also measured in full sun light in Mérida (México, 21°N), positioning the cell such as to obtain the maximum value for the short-circuit current density.

3. Results and discussion

Fig. 2 shows the results from 1H -NMR characterization of the samples obtained from the separation and saponification methods

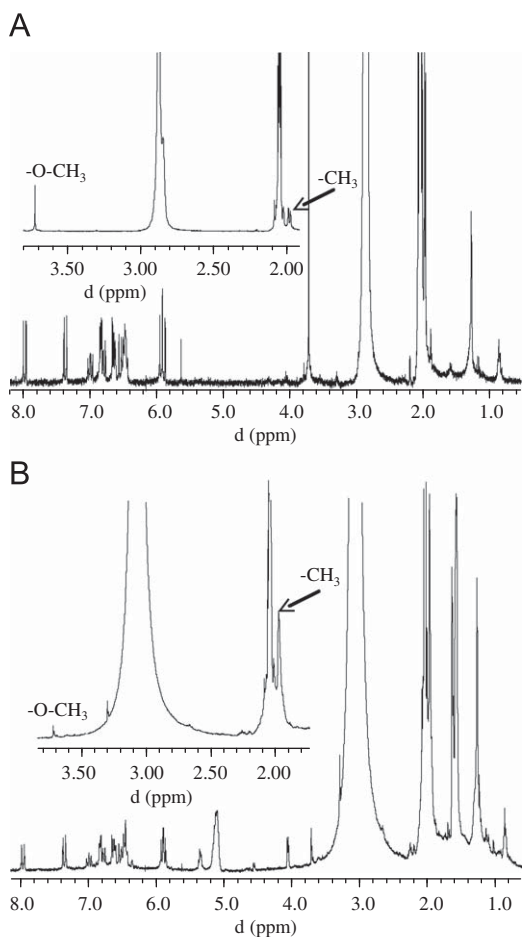


Fig. 2. $^1\text{H-NMR}$ spectra for the purified dyes obtained from the achiote seeds by (A) extraction and column separation resulting in pure bixin, and (B) saponification of the seeds and filtering under nitrogen resulting in norbixin. The peaks corresponding to the characteristic shifts for the methyl groups and the methoxy groups are indicated.

used and, taking the results of FTIR spectroscopy and UV-Vis spectrophotometry into account, the spectra in Figs. 2A and B are in agreement with bixin and norbixin, respectively. In Fig. 2A, the characteristic peak at 3.76 ppm indicates the presence of the methoxy group, while the peaks at 1.9 and 2.0 ppm correspond to the methyl groups H-20' and H-20, respectively (see Fig. 1 for the assignments). The doublets at 7.38 and 7.98 ppm integrate to one proton each, and correspond to H-8' and H-8, respectively [22]. The spectrum of *cis*-norbixin in Fig. 2B reveals the presence of traces of *cis*-bixin (small singlet at 3.76 ppm). The doublets confirm the presence of the *cis* bond in both cases [22]. These results illustrate that it is relatively straightforward to obtain pure dyes from the achiote seeds.

In Fig. 3, the FTIR spectra are shown for the bixin and norbixin separation products. The following assignments were made in the bixin spectrum [23]: at 3187 cm^{-1} the O-H stretching vibration is observed, at 3032 cm^{-1} the $=\text{C-H}$ stretch, at 2947 and 2860 cm^{-1} the C-H stretch due to methyl and methylene groups, at 1716 cm^{-1} the carboxylic C=O group, at 1689 cm^{-1} the stretching vibration of the C=O ester group, at 1608 , 1595 and 1564 cm^{-1} the alkene C=C stretch, at 1398 and 1378 cm^{-1} the C-H bending of the methyl groups, at 1287 cm^{-1} the C-O vibrations, at 1254 and 1159 cm^{-1} symmetric and asymmetric vibrations of the C-O-C ester group, and at 964 cm^{-1} the out-of-plane vibration of the $=\text{C-H}$ group. For the norbixin, the spectrum is similar, however, the ester group vibrations are

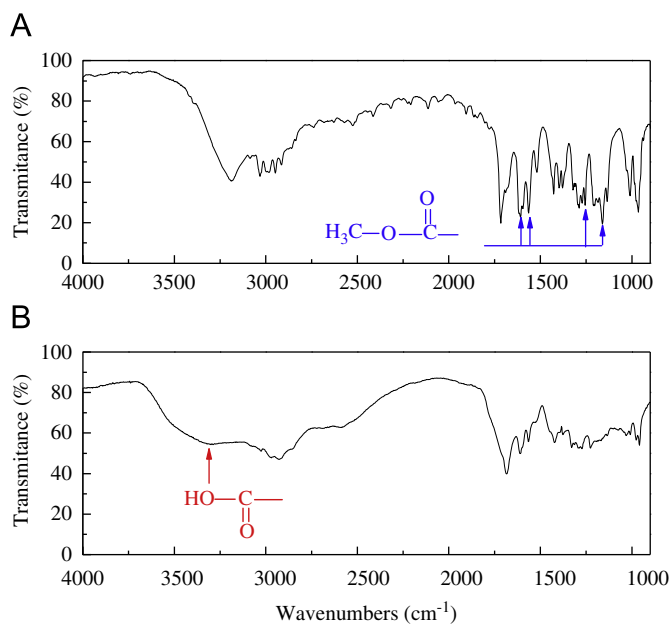


Fig. 3. Fourier-transform infrared spectra for the purified dyes obtained from the achiote seeds by (A) extraction and column separation resulting in pure bixin, and (B) saponification of the seeds and filtering under nitrogen resulting in norbixin. The characteristic vibrations for the carboxyl groups and the methoxy groups are indicated.

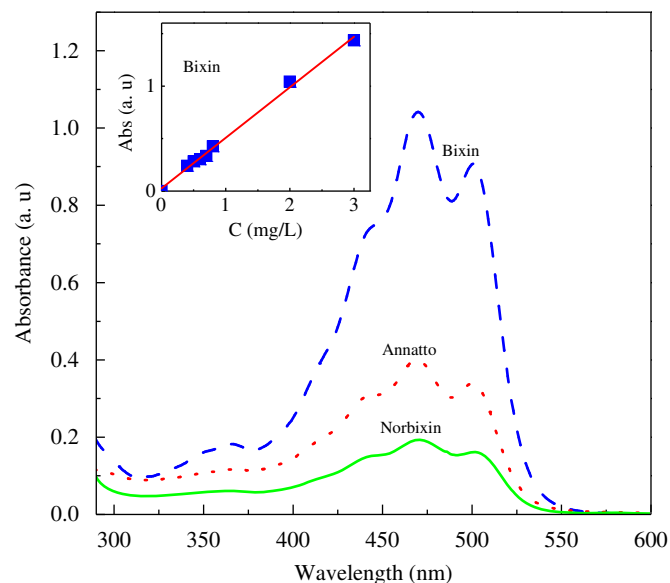


Fig. 4. UV-Vis absorbance spectra for the three pigments extracted and purified in chloroform. The concentrations were 2.0 mg/L for bixin, 3.0 mg/L for the annatto extract, and 4.0 mg/L for norbixin. The inset shows the absorbance of bixin at the peak at 470 nm as a function of concentration.

absent, and stronger carboxylic acid vibrations are observed in agreement with the structure of norbixin (see Fig. 1).

In Fig. 4, the UV-Vis absorbance spectra are shown for the bixin, norbixin, and the annatto pigments in chloroform; note that annatto is a mixture of dyes and, for that reason, it was not analysed with FTIR spectroscopy and $^1\text{H-NMR}$. Fig. 4 shows that the peak signatures are remarkably similar for the three pigments, illustrating that annatto does not contain dyes with an absorption spectrum significantly different from bixin or norbixin. The absorption maxima for bixin are expected at 502, 474.5 and 443 nm, while for norbixin, the maxima are at 501, 471.5, and

442 nm, respectively [24], in good agreement with the experimental results. The absorption coefficients were determined by obtaining the spectra as a function of the dye concentration, and were found to be as follows: bixin: $480 \text{ L g}^{-1} \text{ cm}^{-1}$ at 470 nm ($1.9 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$); norbixin: $38 \text{ L g}^{-1} \text{ cm}^{-1}$ at 471 nm ($1.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$); and annatto: $140 \text{ L g}^{-1} \text{ cm}^{-1}$ at 469 nm. These results show that bixin is the strongest absorbing dye. Bixin has a maximum absorption coefficient that is about 13 times higher than that of the N-719 dye, which is generally used in high efficiency DSCs. The maximum absorption coefficient of norbixin is similar to that of the N-719 dye [1]. Note that the absorption coefficient in the red is low, which is a disadvantage of these dyes.

The solar cells prepared with TiO_2 and ZnO acquired a deep red colour upon immersion in the annatto and bixin sensitizing solution, and an orange to red colour with norbixin. Upon increasing the immersion time, the coloration became weaker, and the best cells were prepared using 30 min immersion times. This may be due to dye aggregation and a weak interaction between the dye and the metal oxide surface, indicating that the surface chemistry requires optimization. Fig. 5 shows a current–voltage curve for a cell based on a TiO_2 substrate using bixin as a sensitizer, measured in sunlight, resulting in an efficiency of 0.53%. Table 1 shows the results for the three pigments and two substrates obtained with the illumination set-up, resulting in somewhat lower efficiencies due to the spectral mismatch between the lamp and sunlight. It can be concluded that for TiO_2 substrates, bixin gives the highest efficiency followed

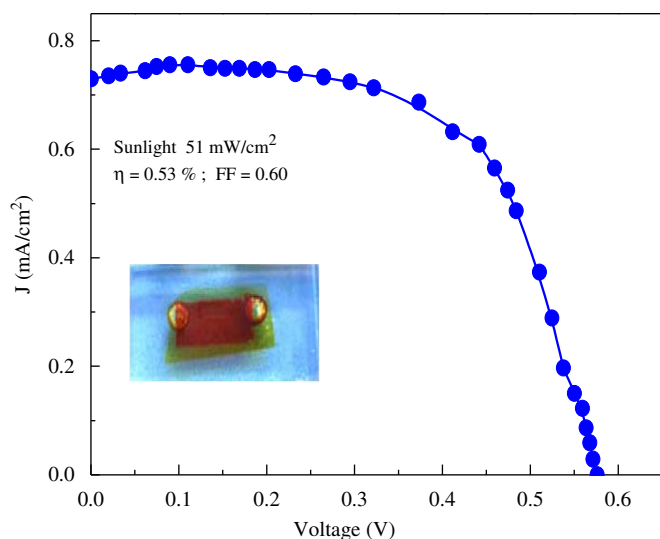


Fig. 5. Current–potential curve for a dye-sensitized solar cell prepared with a TiO_2 substrate and bixin as sensitizer, measured in sunlight (Mérida, México at 21°N) with an efficiency of 0.53%. The inset shows a photo of a TiO_2 -based cell with an active area of 0.5 cm^2 against a light blue background, illustrating the dark red colour of the cell.

Table 1

Summary of the best results for DSCs based on TiO_2 and ZnO substrates and the natural dyes measured using the illumination set up and at an intensity of 100 mW/cm^2 .

Substrate	Sensitizer	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
TiO_2	Bixin	1.1	0.57	0.59	0.37
	Annatto	0.53	0.56	0.66	0.19
	Norbixin	0.38	0.53	0.64	0.13
ZnO	Bixin	0.087	0.32	0.37	0.010
	Norbixin	0.15	0.34	0.34	0.017

by annatto, related to the high content of bixin in annatto. The efficiency of the norbixin-sensitized TiO_2 -based cells is much lower. For the ZnO substrates, the use of norbixin results in a higher efficiency than for bixin, however, the efficiencies are very low.

The efficiency of the TiO_2 -based cells is correlated to the maximum absorption coefficient of the dye, suggesting that the light harvesting efficiency may limit the cell current. However, taking the high absorption coefficients in the blue and green into account, the cell current would be expected to be much higher, suggesting that the injection efficiency is not optimal. This may be explained by several factors such as a relatively short life-time of the excited state related to the symmetrical structures of bixin and norbixin, limited electronic interaction and overlap between the excited states and the conduction band, or unfavourable dye-regeneration kinetics. In addition, the observation of bleaching upon longer immersion in the dye solution indicates that dye-multilayer deposition and polymerization may occur, leading to a decrease in conjugation and, hence, a lowering of the absorption coefficient in the visible. These effects appear to be of similar importance for bixin and norbixin, indicating that the presence of a second carboxyl moiety in the norbixin structure does not significantly change the interaction of the dye with the metal oxide surface.

The efficiencies obtained with TiO_2 are much higher than for ZnO substrates, in agreement with the general trends observed for these two substrate materials. In previous work, we showed that nanostructured, mesoporous ZnO sensitized with the xanthene dyes eosin-Y and mercurochrome reach efficiencies on the order of 2%, similar to those obtained with ruthenium-based dyes [25]. In addition, the efficiencies obtained with xanthene dyes and TiO_2 substrates based on Degussa P-25 were found to be very similar. Hence, the low efficiencies obtained with bixin and norbixin indicate that the injection yield for ZnO substrates is particularly low, either due to a limited overlap of the excited states of the dye and the ZnO conduction band or due to a very weak adsorption and interaction of the dye with the ZnO surface. Interestingly, the efficiency of the norbixin-sensitized ZnO -based cell is larger than for bixin, in contrast to the trend observed with TiO_2 .

The results for both TiO_2 and ZnO are expected to improve upon optimizing the metal oxide surface chemistry, electrolyte solution, as well as the sensitizing solution. However, in order to achieve a significant increase in the efficiency, the chemical structure of the dye could be altered in order to achieve better separation of the ground and excited states, thus increasing the excited state life-time, to optimize the interaction and overlap with the metal oxide conduction band, and to shift the absorption onset into the red. Molecular engineering of the bixin or norbixin structure is an interesting option due to the low cost and ease of purification of the dye.

4. Conclusions

We have prepared dye-sensitized solar cells using the carotenoids bixin and norbixin, which were obtained from the extract of achiote seeds and simple separation and purification processes. The dyes strongly absorb visible light between 400 and 550 nm, and the maximum absorption coefficient of bixin is about $13 \times$ times higher than that of the ruthenium-based dye N-719, while the maximum absorption coefficient for norbixin is about the same as for N-719. Despite strong light absorption, the cell efficiencies are low, with the best efficiency of 0.53% for bixin-sensitized TiO_2 cells; note that the cells were not optimized. The results for norbixin-sensitized ZnO cells were slightly better than for bixin-sensitized cells, but the efficiencies were much lower

than for the TiO₂-based cells. The low cell efficiencies are related to low injection efficiencies, indicating that the overlap of the dye excited states and the metal oxide conduction band, the dye-regeneration kinetics, and the dye excited state life time are not optimal. In order to enhance cell performance, we propose to use molecular engineering to improve the energetic and kinetic properties of the dyes.

Acknowledgments

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