Article

Natural Dyes from Mortiño (*Vaccinium floribundum*) as Sensitizers in Solar Cells

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Abstract: Photovoltaic energy presents environmental advantages; however, these advantages are limited by the cost of manufacturing solar cells and in many cases, scarce or dangerous materials are incorporated. Therefore, the use of natural dyes from mortiño (*Vaccinium floribundum*) as sensitizers in solar cells is proposed. The dyes were extracted by maceration in acidified methanol (HCl, citric acid and trifluoroacetic acid TFA) and were characterized by High-Performance Liquid Chromatography (HPLC), Thin-Layer Chromatography (TLC) and spectrometric methods (UV-Vis, IR and MS-MALDI). The construction and characterization of cells were in standard conditions. The study confirms that pigments in mortiño are flavonoids of the anthocyanidin group as: cyanidin-3-galactoside, and cyanidin-3-arabinoside. The efficiency of solar cells was between 0.18–0.26%; the extraction with TFA in methanol leads to the best performance. Although they have low power conversion efficiency, mortiño dyes could be an alternative to artificial sensitizers for solar cell technologies because they are harmless and abundant substances.

Keywords: anthocyanins; dye; efficiency; mortiño; solar cells; sensitizer

1. Introduction

According to the International Energy Agency (IEA) [1], the energy generation implicates 68% of global greenhouse gases (GHG), where the principal source corresponds to non-renewable resources. Clean energies like solar energy have been developed to decrease GHG emissions. Solar cells could incorporate scarce and hazardous materials [2]. Also, GHG can be emitted in steps of many production materials e.g., poly-crystalline and mono-crystalline silicon [3,4]. Dye Sensitized Solar Cells (DSSC) have emerged as an alternative to conventionally solar cells because they offer some advantages: (a) Low-light performance, DSSC works in a wide array of lighting conditions, without suffering from angular dependence of sunlight or light. (b) Optimized performance, DSSC materials and dyes can be tuned for optimization in a variety of lighting conditions making it suitable for indoor applications and outdoor applications. (c) Higher temperature performance, DSSC efficiency does not degrade with increased temperature, meaning it possible to continue to efficiently harvest energy in direct sunlight. (d) Low energy manufacturing process, DSSC are manufactured using low-energy consumption, high-efficiency, and roll-to-roll manufacturing technique. (e) Ecologically friendly, DSSC uses inexpensive and eco-friendly nano-materials without concern about shortage of resources. (f) Variety of substrates, DSSC is produced on a thin film, flexible, robust, plastic substrate. DSSC can also be applied to metal and glass substrates. (g) Versatile product integration, DSSC indoor modules are highly flexible, durable and lightweight [5–7]. However, some disadvantages of the DSSC must be

taken into account, such as: (a) the use of liquid electrolyte could affect the stability of the cell when there are temperature changes (the electrolyte can freeze at low temperatures and can expand at high temperatures). In addition, electrolyte solutions usually contain volatile organic compounds, solvents that must be carefully sealed, because they are hazardous to human health and environment. This, together with the fact that solvents impregnate plastics, has prevented large-scale outdoor application and integration in a flexible structure. (b) The materials for the construction of this type of cell could become very expensive, e.g., platinum (catalyst), ruthenium (dye) and glass or plastic conductive (contact), etc. (c) [7].

On the other hand, the sensitizer is a fundamental variable in any DSSC and its characteristics respond to DSSC performance. Desirable requirements of the sensitizer are: It generates an efficient injection of electrons toward the semiconductor conduction band, provides functional groups for chelating to the semiconductor, and has a high molar extinction coefficient [8,9]. Natural dyes are attractive alternatives to synthetic sensitizers due to their low cost, facile obtention, abundance, and being harmless to the environment [10,11]. Among natural pigments, anthocyanins have remarkable characteristics to incorporate in solar cells [12,13]. In order to improve the efficiency of DSSC, anthocyanins were combined with graphene as a co-adsorbent to improve charge transferring at the photoanode [14], organic acids [13], and others additives to avoid dye agglomerates [15]. Applications of anthocyanins from natural sources have been studied, however, there is not enough information about the characterization of the pigment from the natural dyes used [12,15,16].

Mortiño is an endemic fruit of the Andes that grows widely in moorland heights between 2800 and 4000 m above sea level [17,18]; in Ecuador, this fruit is part of food heritage [19]. It is a great source of polyphenols and flavonoids such as anthocyanins derived from cyanidin and delphinidin [20]. Mortiño showed antioxidant, anti-inflammatory and adipogenesis inhibiting properties due to a high content of available photoactive components [21], also it has showed applications in the synthesis of photocatalytic nanocomposites [22]. Anthocyanins have several hydroxyl groups that bind with TiO₂ nanoparticles via metal complexation, and it has been shown that excited anthocyanin molecules are able to inject electrons into the conduction band of TiO₂ very efficiently [23,24]. Besides, several authors have demonstrated that the mixture of natural dyes could improve the energy conversion efficiency of natural DSSC [24–26]. According to Strauch et al., there is significant variation in the anthocyanin composition in the population of red cabbage, therefore, the plausible anthocyanin content in mortiño fruit is different from others fruits and flowers studied previously [27]. Finally, it is expected to obtain devices that provide good photovoltaic characteristics and lower environmental impact, as a result of the application of pigments from mortiño, for sensitizers in solar cells. This work focuses on the characterization of pigments from mortiño (*Vaccinium floribundum*) extracted with different acids and the evaluation as natural sensitizers in solar cells.

2. Materials and Methods

2.1. Reagents and Materials

Samples of mortiño (*V. floribundum*) were purchased in popular markets of Quito; fresh fruit was selected and washed with distilled water. The samples were oven-dried at 50 °C during 72 h and grinded with a mortar. This material was collected and stored in polyethylene containers at −20 °C.

Methanol (99.5%), trifluoroacetic acid (TFA, 99.8%), ethyl acetate (99.8%), and acetone (99%) ACS grade were purchased from J.T. Baker (Pensilvania, United States of America USA). Other ACS grade reagents such as: fuming hydrochloric acid (37%), formic acid (98–100%), phosphoric acid (85%), sodium hydroxide, citric acid and 2-propanol (≥99.8%), methanol, and acetonitrile (HPLC) were obtained from Merck (Darmstadt, Germany). Cyanidia-3-glucoside standard (>97%) was obtained from Phytoflan (Heidelberg, Germany). C18 cartridges (Cromabond® C18ec, 500 mg/6 mL) were obtained from Mancherrey Nagel (Düren, Germany). Silica gel TLC chromatographic plates with fluorescence indicator (10 × 10 cm, 254 nm) and cyanidinium chloride (≥95%) standard were purchased

from Sigma Aldrich (St. Louis, MO, USA). The α -cyano-4-hydroxycinnamic acid matrix (>99.0%) for MALDI was obtained from Fluka (Buch, Switzerland).

For DSSC construction, a transparent conductor substrate of fluorinated-doped tin dioxide (FTO) of 2.2 mm, 15 Ω /sq; nanoparticulate TiO_2 paste (D/SP); electrolyte solution (Iodolyte AN-50, 50 Mm); Pt precursor (Platisol T); and thermoplastic sheet (Meltonix 60 μm SX 1170-60PF) were purchased from Solaronix (Aubonne, Switzerland).

2.2. Dye Extraction and Characterization

Mortiño dyes were extracted by maceration, using methanol acidified with HCl (0.01% *v/v*), citric acid (2.5% *w/v*) and trifluoroacetic acid (TFA, 3% *v/v*). Mortiño/methanol ratio was 1:4, the mixture was vacuum filtered (grade 2 filter paper), and the solvent was removed under reduced pressure (rotavapor IKA RV 10) at 35 °C and 200 mbar. The concentrates were centrifuged, and their supernatants were filtered on a membrane (0.5 μm). The extracts were stored at −20 °C. The amount of monomeric anthocyanins in extracts, as cyanidin-3-glucoside (Cy-3-gl), was determined by the pH differential method according to [28]. The characterization of dyes and dye/ TiO_2 (photoanode) was done with UV-Vis spectrophotometer (Varian Cary 50 Bio from Agilent Technologies, California, USA); acidified methanol and TiO_2 /FTO were used as blank respectively. Mortiño extracts were purified by solid phase extraction (SPE) for IR and HPLC analysis with octadecylsilane cartridges (C18), according to [29]. Purified anthocyanins were analyzed with IR spectrophotometer (FT-IR, Perkin Elmer Spectrum One, Massachusetts, USA) using 50 μL of extract that was dried on anhydrous KBr discs (40 °C, 0.5 h). Purified dyes were analyzed by a methodology proposed by [30] with HPLC-Diode Array Detector (DAD, Dionex ultimate 3000) provided with a C18 column (Acclaim[®] 300, 3 μm ; 4.6 $\times$ 150 mm). Binary mobile phase of acetonitrile (A) and H_3PO_4 4% (B) was used; the elution gradient was 6% A-94% B (0–6 min); 25% A-75% B (10–65 min), and 6% A-94% B (65–70 min).

For the separation TLC, a chamber with a ternary mobile phase of 1-butanol, formic acid and water (BAW) in a volume ratio of 60:10:15 was conditioned for 2 h. Extracts seeding was carried out with an atomizer (Camag Liomat 5-WinCats) on silica gel plates. After separation (~1.5 h), solvents were evaporated at room temperature (RT). The fractions were recovered with formic acid (20% *v/v*) and centrifuged at 5000 rpm for 15 min; the supernatants were filtered on a 0.2 μm pore. The filtrates were combined with 10 mg/mL of α -cyano-4-hydroxycinnamic acid (CHCA) matrix dissolved in acetonitrile with 0.01% TFA *v/v* (10:40), these were deposited on stainless steel plates and dried for MALDI-Tof analysis. The spectrometer was built in the Physics Department of Escuela Politécnica Nacional (EPN, Quito, Ecuador) using the guidelines of [31]. A 337-nm nitrogen laser ionization (Spectra-Physics 337201-001) was used, and the signals were recorded in an oscilloscope (Tektronix TDS 5052). The determinations resulted from the average of 20 spectra, each one obtained by 10 pulses.

2.3. DSSC Construction and Characterization

The deposition of anatase TiO_2 paste on FTO was carried out with screen printing using SEFAR PET 1500 mesh with areas of 25 mm^2 . The TiO_2 paste layer on the FTO substrate was homogenized by “spin coating” (Laurell WS-650HZB-23-223NPPB0) for 25 s at 2000 rpm. The deposit was dried by gradually increasing the temperature to 120 °C for 10 minutes on a heating plate (Thermo Scientific CIMAREC, Pennsylvania-USA) and cooled at RT. With this procedure, three layers of paste were placed on FTO and sintered on a plate at 450 °C for 30 min. The FTO/ TiO_2 plates (photoanode) were each immersed in 5 mL of mortiño methanolic extract in closed glass containers and in the dark for 72 h, then the non-adsorbed dye was removed with deionized water and dried at RT. The counter electrode was prepared with a Pt precursor deposited on the FTO with a brush and then sintered at 475 °C on a hotplate for 30 min. The photoanode and the counter electrode were assembled using a polymeric sheet frame heating at $\approx$ 120 °C with a homemade iron. The electrolyte was incorporated by vacuum with syringe through a hole in the counter electrode. Finally, the hole was covered with a piece of hot melt polymer and a piece of glass by heating at 120 °C with a soldering iron. The cells were

illuminated under conditions of 1000 W/m^2 and AM 1.5 by means of a solar simulator and coupled to a source unit of measurement (KEITHLEY 2400).

3. Results and Discussions

3.1. Monomeric Anthocyanin Content

The amount of anthocyanins was quantified in mortiño fruit and their methanolic extracts. In fruit, the content as mg Cy-3-gl/100 g was 144 ± 7 , being lower in comparison with results previously reported [20,21]. During the extraction process, methanol acidulated with TFA was the medium with a major content of anthocyanins of $(575 \pm 26) \mu\text{g Cy-3-gl/mL}$, followed by HCl ($444 \pm 22) \mu\text{g Cy-3-gl/mL}$ and citric acid ($329 \pm 18) \mu\text{g Cy-3-gl/mL}$. Differences in the content of anthocyanins evidenced the extraction capacity of distinct acidic media. Variations in chemical properties of the acids would influence the polarity and acidity character of extractant medium. In addition, the pH values in the extracts were about 3, which is appropriate since the acidic medium tends to stabilize anthocyanins as flavylium form [29]. It is also convenient because a too-acidic medium ($\text{pH} \sim 1$) would damage TiO_2 deposit [16].

3.2. UV-VIS Spectroscopy

Absorption spectra of mortiño methanolic extracts acidified with HCl, citric acid and TFA are shown in Figure 1a; these exhibit two absorption bands (λ_{max}) at 280 and 530 nm which are characteristic of anthocyanins. The band absorption with λ_{max} at 530 nm is assigned to derived cyanidins such as 3-glucoside and 3-galactoside dissolved in methanol acidified with HCl, as previously reported [28,32,33]. However, the possibility of finding anthocyanins with different λ_{max} that overlap and contribute to this band must be considered; e.g., anthocyanidins can also present absorption into this wavelength portion [34]. The absorption interval shown in the visible range between 475–550 nm allows the harvesting photons, which is necessary for sensitization in a solar cell. Absorption spectra of the dyes adsorbed on TiO_2 are shown in Figure 1b; their λ_{max} are displaced between 6 and 11 nm in comparison to the absorption band of the dyes alone. This hypsochromic effect shows an interaction between the pigment and the semiconductor; it corresponds to changes in the energy levels in the pigments (HOMO and LUMO), which affect the band gap of TiO_2 . The displacements of λ_{max} are comparable to previous reports where anthocyanin sensitizers were used [35,36], this corroborates the chemical adsorption of anthocyanin on TiO_2 [36].

Figure 1. UV-Vis spectra. (a) Mortiño pigments diluted in methanol (DF = 100). (b) Pigments adsorbed on TiO_2/FTO (counter electrode).

3.3. Infrared Spectroscopy

The infrared spectra of the anthocyanin dyes (Figure 2) showed important bands in the fingerprint region ($600\text{--}1400\text{ cm}^{-1}$), an intense absorption in 1030 cm^{-1} that is assigned to the C-O alcohol group stretch and a band at 1262 cm^{-1} of phenolic Aryl-O stretch. In the range of $1400\text{--}3600\text{ cm}^{-1}$, there are C=C aromatic stretches (1642 and 1463 cm^{-1}), signals of saturated C-H bonds (2838 and 2946 cm^{-1}), and a wide band centered at 3399 cm^{-1} that originated from the O-H stretching, which belongs to alcohols and phenols. The dyes obtained with citric acid and HCl show very similar spectra, while the spectrum of the dye with TFA is distinguished mainly by a peak in 1716 cm^{-1} and a broad band between 550 and 800 cm^{-1} ; such signals for the other two cases appear as a shoulder and a peak defined at 719 and 619 cm^{-1} , respectively. The bands due to O-H and C-O of phenolic type, together with O-H of aromatic type are assigned to the aglyconic structure, while the bands of saturated C-H and O-H of alcohol belongs to the saccharide portion of the anthocyanins.

Figure 2. FT-IR spectra of purified anthocyanin extracts.

3.4. High Performance Liquid Chromatography (HPLC)

Chromatographic HPLC-DAD profiles of the dyes are shown in Figure 3. Seven main peaks were obtained between 22 and 37 min, which are similar in each case. The peaks two (24.6 min) and five (27.7 min) were predominant in all the extracts with similar intensities. In different chromatographic analyses of *Vaccinium floribundum* in reverse phase [20,21], it has been observed that delphinidin derivatives are characterized by having shorter retention times than their analogues cyanidin derivatives; where five anthocyanins have been found with the following order of elution: (1) delphinidin-3-galactoside (Dp-3-gl), (2) cyanidin-3-galactoside (Cy-3-gl), (3) delphinidin-3-arabinoside (Dp-3-ar), (4) Cy-3-gl, and (5) cyanidin-3-arabinoside (Cy-3-ar). These antecedents were useful for the identification in the extracts from mortiño dyes by comparison. In addition, the signs of the samples were compared with a standard of cyanidin, demonstrating the presence of this aglycone (peak 7) in all the extracts.

Figure 3. HPLC chromatographic profile of anthocyanins extracted with different acids from mortiño.

3.5. Thin Layer Chromatography (TLC) + MALDI

The combination of TLC and MALDI allowed identifying certain components in mortiño dye extracts. Colored fractions were separated using BAW eluent, resulting in four main fractions (A, B, C, and D), as can be seen in Figure 4a. The R_f values of fraction components were 0.32, 0.39, 0.51, and 0.86 respectively. Anthocyanins with a greater number of -OH groups will present a lower R_f since these reduce the mobility of the components as they are more affined to the stationary phase. This behavior has been observed and generalized in studies of TLC anthocyanins [37]. In this way, delphinidin derivatives are assigned to higher R_f than their equivalent cyanidines, since they differ by an OH group (delphinidin > cyanidin). The separated components were compared with a standard Cy-3-gl whose retention factor (0.44) differs from them, then the presence of Cy-3-gl was discarded. Figure 4 shows the reflectron mode MALDI mass spectra of B and C fraction, in both, one can observe a peak at m/z 287 corresponding to the cyanidin (aglycone) produced in the fragmentation of the anthocyanin, which was originally contained in both fractions. In the upper spectrum (b), a peak in m/z 449 is also observed, indicating that the compound in fraction B is a hexoside of cyanidin. Similarly, in the lower spectrum (c), a peak at m/z 419 is assigned to fraction C of cyanidin pentoside. According to [21], cyanidin hexosides can be found as Cy-3-gl and Cy-3-gal, while cyanidin pentoside can be found as Cy-3-ar; the anthocyanin corresponding to fraction B is assigned to Cy-3-gal. In addition, this was corroborated by discarding the means of the TLC standard test (Figure 4a). For the C fraction, the Cy-3-ar is assigned, since this is the only pentoside of cyanidin present in mortiño *V. floribundum* according to [20]. The chromatographic separation by TLC shows that the cyanidins 3-galactoside and 3-arabinoside are the main dyes extracted and these correspond to the most intense peaks (2 and 5) of the HPLC chromatogram (Figure 3).

Figure 4. (a) Anthocyanins separated by TLC from mortiño extract (mobile phase: BAW 40:10:15, stationary phase: silica gel F₂₇₀). MALDI spectra (CHCA matrix) of (b) cyanidin-3-hexoside and (c) cyanidin-3-pentoside fraction.

It is worth mentioning that the spectra of A and D TLC fractions did not show responses corresponding to any anthocyanin. These showed predominantly peaks of the CHCA matrix, thus it was not possible to assign their respective compounds. This difficulty probably arose since their unstable nature and the amount of compounds in these fractions were insufficient. Thus, they were not detected by MALDI under the working conditions.

3.6. Characterization of DSSC

Natural dyes extracted from mortiño with different acids were used as sensitizers of solar cells. The influence of acids on the performance of DSSC was studied through one-factor completely randomized design (acid of extraction) with six replicas. The J-V curves generated are shown in Figure 5, and the analyzed parameters through ANOVA are indicated in Table 1.

Figure 5. Average J-V curves of six DSSC with different extracts.

Table 1. Effect of different extraction acids on the photovoltaic parameters of the DSSC.

Extraction Acid	Efficiency (% η)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF
AC	0.23 ± 0.05 ^{a,b}	0.75 ± 0.15 ^a	0.490 ± 0.007 ^a	0.62 ± 0.03 ^a
HCl	0.18 ± 0.03 ^a	0.68 ± 0.20 ^a	0.475 ± 0.012 ^b	0.57 ± 0.06 ^a
TFA	0.26 ± 0.05 ^b	0.88 ± 0.17 ^a	0.485 ± 0.007 ^{a,b}	0.62 ± 0.04 ^a
ANOVA P	0.027	0.181	0.035	0.156

Average values ± standard deviation of six DSSC. In each column, values that do not share a letter are significantly different with a confidence level of 0.05 according to the multiple comparisons Tukey test. The parameters with $p \leq 0.05$ show a significant difference. ^{a,b} means that there is no significant difference between the variables, and ^a or ^b means that whether there is a significant difference between the variables.

The ANOVA test shows that the efficiency (η) of DSSC is affected by the use of different acids in dye extraction. The differences are significant between the HCl and TFA, while citric acid does not give a significant difference. The highest efficiencies in solar cells belong to TFA and coincide with the dye extracts that have the highest amounts of anthocyanins, as can be seen in 3.1. The greater efficiencies achieved using the extract with TFA might be the result of the greater quantity of disposable anthocyanins to attach on TiO₂, which would help to greater capture photons on the photoanode. In contrast, the lower efficiencies were obtained with HCl, although the lowest anthocyanins content corresponds to citric acid. This disagreement suggests that DSSC performance not only depends on the concentration of dye, but also other characteristics such as the nature of acid in the extraction can affect the performance of DSSC. The best performance is shown when organic acids such as citric acid and TFA are in extraction medium. Those organic acids promote an improvement in the electrical contact of TiO₂ by the addition of carboxylate groups that block recombination processes between TiO₂ and I[−]/I₃[−] electrolyte and enhance J_{sc}, which is similar to that which occurs in treatments with organic acids as co-adsorbents [12,38]. Parameters like short circuit current density (J_{sc}), open circuit potential (V_{oc}) and fill factor (FF) were determined, and their differences in DSSC performance are not considerable.

Chenopy et al. measured the transient absorption signal of cyanin-sensitized nanoparticles of TiO₂ and ZrO₂ and found that charge separation is observed only in TiO₂. Comparing transient absorption of different species of TiO₂-cyanin, they assigned the transient absorption to excited electrons in the conduction band of TiO₂ [23]. DFT calculations show that electron injection from an anthocyanin molecule to the TiO₂ conduction band should be high because: (1) The energy level of the excited state of the dye lies above the conduction band of the semiconductor and this promotes the driving force for

electron injection; (2) the rate constant of the electron injection from the dye to the TiO₂ conduction band is high, which increases the power conversion efficiency; (3) the light-harvesting efficiency is good enough to maximize the photocurrent response; and (4) the dye–electrolyte regeneration energy is negative, inducing the driving force for dye regeneration. [39,40].

4. Conclusions

Dyes extracted from mortiño fruits were used as sensitizers in DSSC and were characterized by chromatography (HPLC and TLC), FT-IR spectroscopy and MALDI mass spectrometry analysis. The most abundant compounds in mortiño extracts correspond to cyanidin derivate anthocyanins. Mortiño dye-sensitized solar cells have a power conversion efficiency between 0.18–0.26%, which is influenced significantly by the acid extraction medium. In this work, the maximum value is obtained using the TFA-acidified methanol.

Further studies of anthocyanins from mortiño dyes and other natural sources are required in order to identify which component gives the best performance. In addition, it is necessary to study factors such as interactions between compounds in the extract dyes (e.g., concentration, co-adsorption and dye aggregated) that would influence the efficiency of a DSSC.

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