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Article

Pyranoflavylium Derivatives Extracted from Wine Grape as Photosensitizers in Solar Cells

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Derivados piranoflavinílicos, nomeadamente cianidina-3-glucósido, malvidina 3-*O*-glucósido, malvidina 3-*O*-comaroilglucósido, derivado pirúvico da cianidina-3-glucósido e derivado pirúvico da malvidina-3-glucósido, extraídos de uvas tintas foram usados como sensibilizadores em células solares sensibilizadas por corantes (DSSCs). Com estes corantes naturais, a eficiência das células chegou até 0.08%. Os corantes baseados em cianidinas foram mais eficientes que os baseados em malvidinas, os que não possuíam o grupo do ácido pirúvico foram também mais eficientes. Além disso, o uso direto de gotas de vinho do Porto na produção de DSSCs resultou numa eficiência de 0.025%. Apesar das eficiências obtidas ainda precisarem der ser melhoradas para uma aplicação industrial, os resultados obtidos demonstram que corantes do vinho podem converter luz solar em eletricidade num processo que mimetiza a fotossíntese.

Pyranoflavylium derivatives, namely cyanidin-3-glucoside, malvidin 3-*O*-glucoside, malvidin 3-*O*-coumaroylglucoside, cyanidin 3-glucoside-pyruvic acid adduct and malvidin 3-glucoside-pyruvic acid adduct, extracted from red grapes were used as sensitizers in dye-sensitized solar cells (DSSCs). With these natural dyes, cell's efficiencies ranged up to 0.08%. The cyanidin based dyes were more efficient as sensitizers than the malvidin molecules and the presence of the pyruvic acid adduct decreased efficiency. Furthermore, the use of drops of Port wine in the production of DSSCs resulted in an efficiency of 0.025%. Although the obtained efficiencies still need improvements for an industrial application, it is given further evidence that wine dyes can harvest and convert sunlight into electricity through a process that mimics natural photosynthesis.

Keywords: natural dyes, anthocyanins, anthocyanin-pyruvic acid adducts, dye-sensitized solar cells, wine dyes

Introduction

The energetic dependency on non-renewable energy sources is still an unsolved problem. Photovoltaics is a rather elegant solution, since the use of the virtually inexhaustible energy from the closest star to Earth is conceptually simple and environmentally friendly. Dye-sensitized solar cells (DSSCs) are one of the emerging photovoltaic technologies that have been receiving widespread attention since its early development more than two decades ago.[1-3] These cells aim to mimic photosynthesis whereas the photoreceptor, chlorophyll, is of a different nature of the photocarrier. DSSCs advantages include low-cost high power conversion efficiencies under cloudy and artificial light conditions, semi-transparency and multi-color range possibilities.[2] Recently, their efficiency raised up to a record of 15% without sacrificing stability and exceeding the power conversion efficiencies of conventional amorphous silicon-based solar cells.[4] The conceptual design of a DSSC is simple and includes a semi-conductor working as a photocarrier – the most commonly used is the titanium oxide (TiO_2), two glass plates or flexible substrates (thus including a counter-electrode with a catalyst), which are coated with a transparent conductive oxide (TCO), and a electrolyte connecting both electrodes.[1,2] All these cell elements have been the subject of intensive research.[2]

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At present, molecular design of synthetic organometallic sensitizers such as ruthenium(II) polypyridinic complexes and inorganic pigments like perovskite nanocrystals and quantum dots (II-VI and III-V type semiconductor particles small enough to produce confinement effect) is still an active research area in the quest for stable and high efficiency DSSCs. Despite the high cost, scarcity and rather meticulous synthesis process, ruthenium complexes have been the most promising sensitizers for the last two decades due to their excellent stability, high molar extinction coefficient and relatively broad absorption band in the visible spectrum. In addition, the overlap of the dye excited states and the semiconductor conduction band, the favorable regeneration kinetics by the electrolyte redox species and the proper dye excited state lifetime are important features for efficient electron injection, which boosted the overall performance of these sensitizers.[5] Quantum dots recently opened a new window of opportunity as they have very high molar extinction coefficients, fine tuneable absorption/emission spectra as a function of particle size (quantum size effect), and they are likely to perform better in solid state hetero-junction devices where photo-corrosion is less prone to occur.[6] Yet, some of the most efficient quantum dots and ruthenium complexes are very expensive and toxic, which explains the demand for new sensitizers. Energy conversion can, in fact, be achieved by natural available pigments, significantly reducing the overall cost of the cell. Natural pigments can be extracted from natural sources such as fruits, leaves, flowers and bacteria and have the advantages of being low-cost, environmentally friendly, also allowing the use of thinner films of the mesoporous semiconductor.[5] Promising natural compounds are carotenoids, polyphenols, chlorophylls ($\eta > 4.0\%$) and anthocyanins ($\eta > 1.5\%$) as they have the potential to reach similar photoelectrochemical properties as known from dyes based on metal complexes.[7] These pigments, which globally perform poorly in DSSCs because of weak binding energy with the semiconductor and low absorption rate in the entire ultraviolet (UV)/visible (vis)/near infrared (NIR) range[8,9] can, however, be modified at the molecular structure level to adjust the lowest unoccupied molecular orbital (LUMO) energy level of the photosensitizers. This allows a more effective match with the conduction band edges of different semiconductors, thus improving light harvesting efficiency. Moreover, substitution of alkyl groups with carboxyl or hydroxyl groups has been performed to favor chemical bonds with TiO_2 semiconductor films.[9] In fact, due to the presence of carbonyl and hydroxyl groups in the anthocyanin molecule, this can anchor more easily to the surface of TiO_2 nanoparticles acting as favorable electronic pathways between the dye and the semiconductor.[8,10,11] Other studies confirm that as the dye molecules are adsorbed onto the surface of TiO_2 via the interaction between hydroxyl groups on TiO_2 surface and the carboxyl or hydroxyl anchoring groups residing on dye molecules, dye adsorption could also be enhanced via hydroxylation of the semiconductor surface, with a subsequent increase of short-circuit current density and power conversion efficiency of DSSC.[12] It can then be inferred that both approaches tend to favor dye adsorption and enhance the performance of DSSC. We focus on the usage of natural pigments, particularly anthocyanins as light harvesting elements in DSSCs, exhibiting functional groups with the potential to enhance its photosensitizing properties.

Another advantage of anthocyanins and their derivatives over other molecules like chlorophyll is that they commonly exhibit a very broad absorption band in the visible light range.[13] Anthocyanins are natural flavonoids responsible for the red/violet/blue colors of many flowers and fruits.[14] They are also responsible for the color of red wines predominantly young Port wines. These compounds can be used in the food industry as natural food colorants and antioxidants. Depending on their structure and the pH of the medium, they can have different colors from red-blue to orange.[15,16] During red wine aging and maturation, anthocyanins undergo several chemical reactions leading to the formation of more complex compounds with different colors from orange to blue turquoise.[17-20] The main anthocyanin-derived compounds detected by high-performance liquid chromatography (HPLC) in one year-old red wines (particularly red Port wines) are the anthocyanin-pyruvic acid adducts that are formed from the reaction of the anthocyanins with pyruvic acid produced by yeasts during fermentation.[21,22] The color characteristics of these pigments, namely the color stability at a wide pH range and the high resistance to bleaching by bisulfite, as well as their capacity of getting darker with the increasing of the pH are important features for their application in food products.[23] Recently, photoelectrochemical and photophysical measurements showed that some of synthetic analogues of anthocyanins are very promising for DSSC applications.[24,25] The most promising ones were those presenting a diethylamine unit substituted in the position 7 of the ring A of the flavylium moiety. Those results showed that a higher ϖ-conjugation in the dye increased the solar energy-to-electricity conversion efficiency.[24] Thus, this work focus on the identification and usage of anthocyanins extracted from red grapes, in the end of the maturation state thus seizing red wine lees by-products from red wine vinification, and then used to prepare anthocyanin-pyruvic acid adducts as light harvesting elements in DSSC.

The photosensitizing properties of these molecules were assessed and compared with a commercial ruthenium based dye.

Experimental

Dye synthesis and purification

In order to obtain the malvidin-3-*O*-glucoside (Mv-3-Gluc) and the malvidin-3-*O*-coumaroylglucoside (Mv-Cum) pigments, grape skins (*Vitis vinifera*) were subjected to extraction with 50% aqueous ethanol (pH 1.5) for 1 day at room temperature. The grape skin anthocyanin extract was purified by Toyopearl (Tosoh Bioscience, King of Prussia, USA) gel column chromatography and individual Mv-3-Gluc and Mv-Cum were isolated by semi-preparative HPLC according to the procedure described elsewhere.[23] Similarly, the cyanidin-3-*O*-glucoside (Cy-3-Gluc) pigment was obtained from blackberry fruit (*Rubus fruticosus*) using the same procedure.[23]

The formation of malvidin-3-*O*-glucoside-pyruvic acid adduct (Mv-Py) and cyanidin-3-*O*-glucoside-pyruvic acid adduct (Cy-Py) was achieved through the reaction of the respective anthocyanins isolated from red grape skins and blackberry (Mv-3-Gluc and Cy-3-Gluc, respectively) with pyruvic acid (molar ratio pyruvic acid/anthocyanin of 50:1) in water (pH 2.6, 35 °C) during 5 days. The obtained extract was purified by Toyopearl gel column chromatography and the anthocyanin 3-glucoside-pyruvic acid adducts fraction eluted with water/ethanol 20% (v/v) and further purified by semi-preparative HPLC.[23] The purity of the pigments was confirmed by liquid chromatography with diode array detection and mass spectrometry (LC/DAD-MS) and nuclear magnetic resonance (NMR), which confirmed the presence of only the isolated anthocyanin. Five different dyes were tested in solar cells (Figure 1). The solutions of the natural dyes were prepared with absolute ethanol (Merck, Darmstadt, Germany), followed by filtration to remove any solid residues. The pH was adjusted to 1 with 0.1 mol L^{-1} hydrochloric acid (HCl, Merck) solution. The final concentration of each dye was 0.3 mmol L^{-1}.

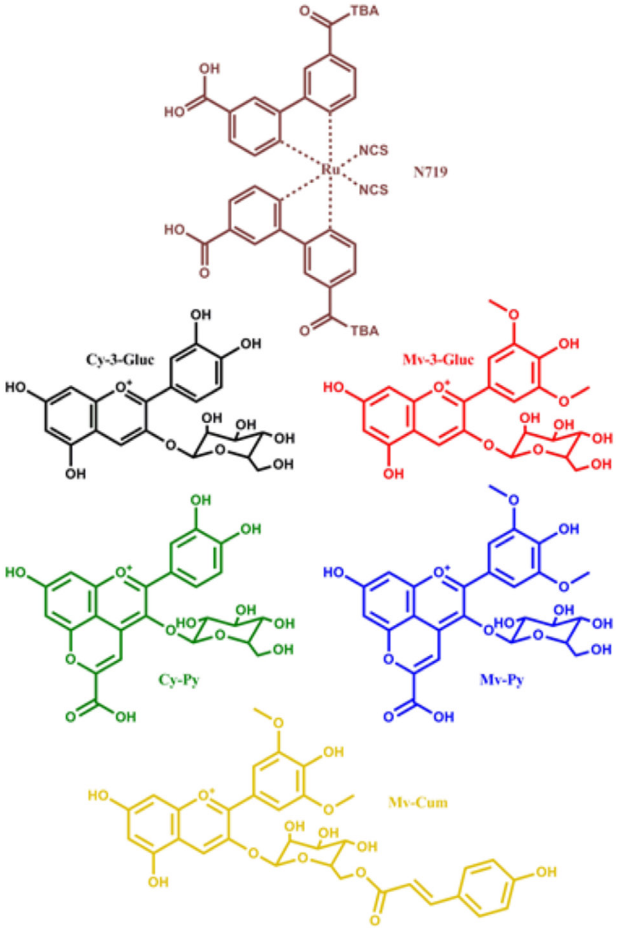

Figure 1. Chemical structure of the natural dyes and the standard N719 ruthenium based complex dye used for the preparation of DSSCs.

Assembly of DSSCs

The electrodes were prepared by coating clean transparent conducting glass substrates (TCO, fluorine-doped SnO_2, 15 Ω *per* square sheet resistance from Pilkington, St. Helens, UK) with a nanocrystalline TiO_2 paste (Ni-Nanoxide T/SP, from Solaronix, Aubonne, Switzerland) by the doctor blade technique to form a ca. 8 μm-thick uniform layer (Figure 2). Following calcination at 450 °C for 30 min, the electrodes were soaked in 0.3 mmol L^{-1} ethanolic solution of the natural dyes (Cy-3-Gluc, Mv-3-Gluc, Cy-Py, Mv-Py and Mv-Cum) for 24 h at room temperature – this time was not optimized and was based on literature.[26,27] The sensitized electrodes were then rinsed with anhydrous ethanol and dried for a few seconds under an air stream at 50 ºC. Finally, they were sandwiched with platinum-coated (Platisol T/SP, Solaronix) counter electrodes using a thermomechanical process and a polymer-based hot-melt seal foil (Meltonix 1170-25 Series, Solaronix). A thin layer of iodolyte AN-50 electrolyte (I^-/I_3^- based electrolyte, Solaronix) was injected into the interelectrode space from the counter-electrode side through a predrilled hole, which was then sealed with the same polymeric material and a glass lamella. The active cell area was typically 0.196 cm^2. A photograph of the photoanodes is shown in Figure 3.

A standard cell (Std Ru) was also prepared for comparison using the reference materials for DSSCs and ruthenium(II) bis(tetrabutylammonium) cis-diisothiocyanato-bis(2,2’-

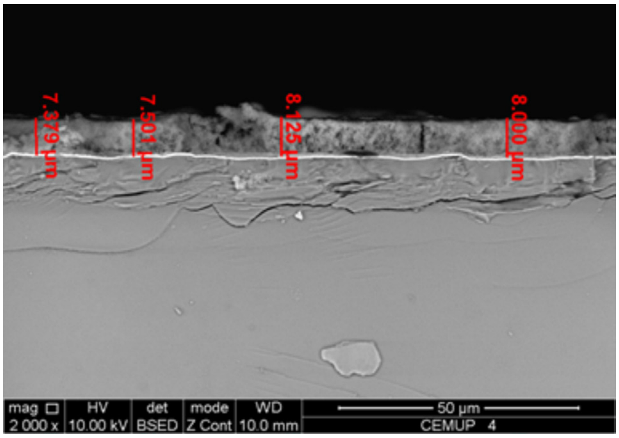

Figure 2. Cross-section field emission scanning electron micrography (FE-SEM) image of TiO_2 electrode sintered at 450 °C for 30 min.

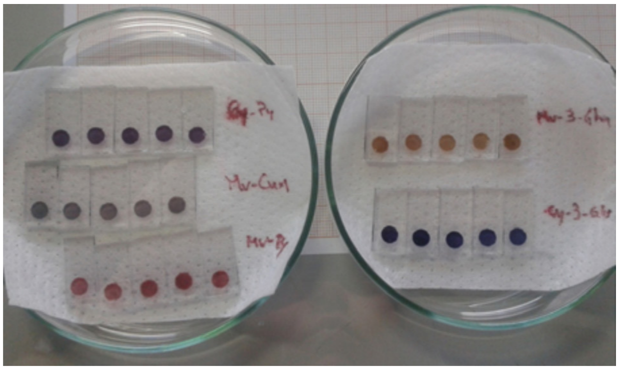

Figure 3. Photographs of the photoanodes prepared with pyranoflavylian derivatives dyes. From top to bottom, left column: Cy-Py, Mv-Cum and Mv-Py; and right column: Mv-3-Gluc and Cy-3-Gluc.

bipyridyl-4,4'-dicarboxylato) (Ruthenizer 535-bisTBA – N719, Solaronix) as sensitizer.

UV/Vis spectroscopy and photocurrent-voltage (*I-V*) measurements

The absorption spectra of the dye solutions and dyes adsorbed on TiO_2 surface were recorded using a UV/Vis spectrophotometer (UV-1700, Shimadzu, Kyoto, Japan). The adsorption of the dyes onto the semiconductor surface was done by soaking the electrode in the dye solution (concentration of 0.3 mmol L^{-1}) at room temperature for 24 h. The photocurrent-voltage (*I-V*) measurements were carried out using a 7 W day light lamp (Philips, Eindhoven, The Netherlands) as irradiation source (Figure 4). Light intensity was calibrated to ca. 0.6 sun (60 mW cm^{-2}, 25 °C) using a single crystal Si photodiode (Newport, USA) before the experiments. The applied bias voltage and ac amplitude were set to open circuit potential (V_{OC}) of the cell and 10 mV, respectively. The measurements were carried out at open circuit voltage conditions under a bias illumination of 60 mW cm^{-2}. Before measurements, each cell was left to stabilize at room temperature and light intensity for ca. 5 min.

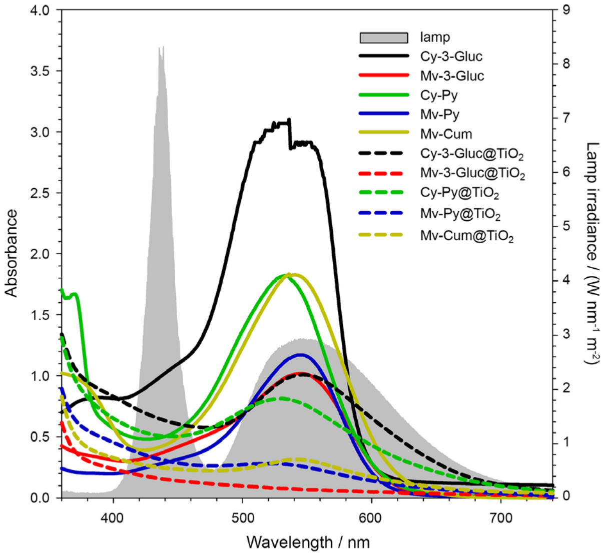

Figure 4. Light absorption spectra of dye in solution, 0.3 mmol L^{-1} and adsorbed onto the TiO_2 film (@TiO_2), and the lamp irradiance spectrum shaded in grey.

Results and Discussion

The most widely used dyes employed in DSSCs are ruthenium-based dyes, which have fairly wide optical absorption spectra ($\Delta\lambda \approx 350$ nm) but low molar extinction coefficients ($\varepsilon \approx$ 5,000-20,000 mol^{-1} L cm^{-1}). Recently, synthesized organic dyes reached higher absorptivities ($\varepsilon \approx$ 50,000-200,000 mol^{-1} L cm^{-1}) but still have quite narrow spectral bandwidths ($\Delta\lambda \approx 250$ nm). The quest today is to set a dye cocktail (the use of several dyes with different spectral responses simultaneously) exhibiting high extinction coefficients and broad absorption overlapping the solar spectra as much as possible to obtain high performance dye solar cells.

The molar extinction coefficient of the natural dyes Cy-3-Glu, Cy-Py, Mv-3-Glu, Mv-Py and Mv-Cum dissolved in ethanol was obtained from the absorbance spectra: $(10.3 \pm 0.5) \times 10^3$ mol^{-1} L cm^{-1} at 531 nm, $(3.4 \pm 0.2) \times 10^3$ mol^{-1} L cm^{-1} at 690 nm, $(6.1 \pm 0.3) \times 10^3$ mol^{-1} L cm^{-1} at 535 nm, $(6.1 \pm 0.3) \times 10^3$ mol^{-1} L cm^{-1} at 536 nm, $(3.9 \pm 0.2) \times 10^3$ mol^{-1} L cm^{-1} at 540 nm, for Cy-3-Gluc, Mv-3-Gluc, Cy-Py, Mv-Py and Mv-Cum, respectively. The molar extinction coefficient of the N719 reference dye in ethanol is 14×10^3 mol^{-1} L cm^{-1} at 515 nm, slightly higher than those obtained for these natural dyes.[28]

In a DSSC, dye molecules absorb the light, the photons cause dye photoexcitation leading to the rapidly release of electrons to the TiO_2. Electrons then circuit from the TiO_2 (photocarrier) toward the conductive glass substrate where they are collected and forwarded to the outer circuit producing usable electricity. Upon reaching the platinized counter-electrode, electrons are forwarded back to the semiconductor/dye interface carried by the I^- ions present in the electrolyte solution. The dye subsequently returns to its ground state through electron donation from iodide ions. A schematic and energy level diagram showing the operation and electron loss pathways of a typical DSSC is shown in Figure 5. Electron recombination may occur upon photoexcitation of the dye molecules, leading to poor performance DSSCs. In fact, electrons may not efficiently go to the conduction band of the semiconductor, instead they may simply return to the ground state releasing energy, they can react with the electrolyte species (iodide reduces the oxidized dye to form $I_2^{\bullet-}$ intermediates that then disproportionate to form I_3^-), and they can even interact with other dye molecules. In a subsequent step, after successful electron injection into the conduction band of the semiconductor, dark current may also generate from direct electron recombination at the TiO_2/electrolyte interface. These complex charge transfer processes, in which electrons choose their pathway, are based on thermodynamics, but are also kinetically driven,[2] where supramolecular interactions are present.[29] Choosing the appropriate sensitizer should therefore take these considerations into account. The ideal dye sensitizer requires properties such as: (*i*) a broad absorption spectrum covering the visible and some of the near-infrared region; (*ii*) strong adsorption at the surface of the semiconductor to allow an efficient injection of the photoexcited electrons; (*iii*) be stable in the fundamental and excited state; (*iv*) be easy to synthesize, and quite importantly; (*v*) should possess several carbonyl or hydroxyl groups capable of chelating to the Ti(IV) sites on the TiO_2 surface (Figure 1).[2,4,30]

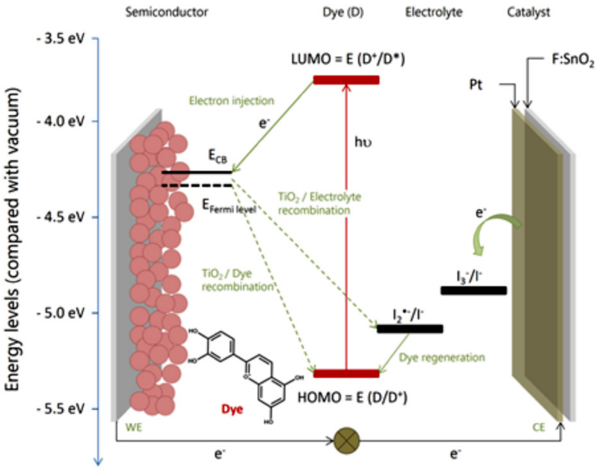

Figure 5. Schematic and energy level diagram showing the operation of a typical DSSC.

Typically, the overall efficiency (η) of dye cells are evaluated in terms of open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (*FF*) according to:

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \qquad (1)$$

where P_{in} is the power of the incident light. *FF* is defined as follows:

$$FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} \qquad (2)$$

where J_{max} and V_{max} are the photocurrent density and cell voltage obtained at the maximum power output operating conditions. The photoelectrochemical parameters of DSSCs prepared with the different natural dyes, obtained under approximately 0.6 sun illumination are summarized in Table 1.

The natural dyes in cells based on a TiO_2 substrate produced efficiencies ranging from 0.0042 to 0.075% (Figure 6). The low efficiencies of these particular pigments might be possibly explained by the weak binding interaction between the dye and the metal oxide surface and apparent low-charge transfer absorption in the visible range.[6] The highest J_{sc} of 0.33 mA cm^{-2} was obtained from the cell sensitized with Cy-3-Glu, with a V_{oc} of 0.328 V, *FF* of 0.432 and η of 0.075%. The results suggest that even

Table 1. Detailed photovoltaic parameters of DSSCs based on different dyes. Five replicates of each cell were manufactured, the best results are displayed

Dye	V_{oc} / V	J_{sc} / (mA cm^{-2})	*FF*	η / %
Cy-3-Gluc	0.33 ± 0.01	0.33 ± 0.02	0.432 ± 0.008	0.075 ± 0.005
Mv-3-Gluc	0.35 ± 0.04	0.13 ± 0.01	0.47 ± 0.01	0.035 ± 0.002
Cy-Py	0.1965 ± 0.0004	0.051 ± 0.007	0.387 ± 0.003	0.006 ± 0.001
Mv-Py	0.184 ± 0.004	0.029 ± 0.008	0.380 ± 0.007	0.003 ± 0.001
Mv-Cum	0.241 ± 0.001	0.065 ± 0.001	0.430 ± 0.007	0.0108 ± 0.0001
N719	0.691 ± 0.001	12.90 ± 0.09	0.492 ± 0.01	7.1 ± 0.1

V_{oc}: circuit voltage; J_{sc}: short circuit current; *FF*: fill factor.

though the concentration of the dye for immersion was the same, remarkable differences occur in the adsorption (chemical and physical) of the dyes on the TiO_2 film, which is comparable to the photocurrent density of the corresponding DSSC. A larger amount of dye adsorbed onto the TiO_2 film was achieved using Cy-3-Glu as photosensitizer comparing with the other as-prepared dyes, resulting in the highest solar energy conversion efficiency. Moreover, the Cy-3-Glu dye adsorbed onto the TiO_2 surface also denoted the highest absorption peak in Figure 4, which may partially explain the better performance of the cell in terms of photocurrent output.

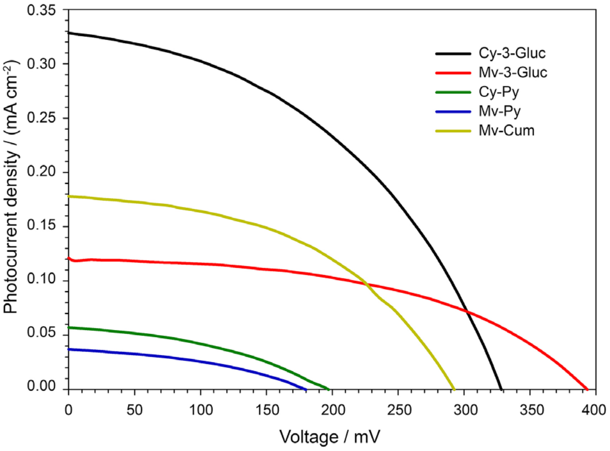

Figure 6. Photocurrent-voltage curves of the DSSCs sensitized with different natural extracts.

One of the reasons for the quite low efficiencies observed in general may be ascribed to a certain spectral mismatch between the dye absorption spectra and the lamp irradiance (shaded grey in Figure 4). In this work a commercially widely available light source was used instead of one simulating the sun's spectrum. Such light source would better cover all wavelengths, including 460-500 nm and below 400 nm. Therefore, in such case one could expect higher efficiencies.

Analyzing the results achieved, the Cy-3-Gluc efficiency is double of Mv-3-Gluc. The same conclusion is drawn when comparing Cy-Py and Mv-Py, which demonstrates that the cyanidin structure outperforms malvidin as a sensitizer. An explanation for such fact might be that there was an increase of dye anchoring to the TiO_2 surface by the two hydroxyl groups in the ortho position in ring B. This is perceptible when analyzing Figure 4, as the main absorption peak of Mv-3-Gluc and Mv-Py dyes, severely diminishes when they are adsorbed into the TiO_2 surface.

In addition, both dyes with pyruvic acid adducts (Cy-Py and Mv-Py) had lower efficiencies than the corresponding dyes without the pyruvic acid adducts (Cy-3-Gluc and Mv-3-Gluc), which further shows that the presence of the Py adduct with carboxylic acid groups holds no advantage. Also when comparing Mv-3-Gluc with Mv-Cum, the first shows a better efficiency, indicating that the coumaroyl residue is not valuable for the sensitizing process. The presence of carboxylic acid groups in the Py adduct and the coumaroyl residue apparently did not have a direct beneficial impact in the electron injection process between the dye molecule and the conduction band of the semiconductor. Another possible explanation would be related to the fact that alkyl chains or moderately long chain groups, such that of the coumaroyl residue, are often attached to the side of the dye to create a barrier between holes in the redox couple (I^-/I_3^-) and electrons in the TiO_2, thereby inhibiting dark current and improving the performance of the dye cell. In practice, a slight increase in V_{OC} would be observed, which is not the present case. Also, dye aggregation on semiconductor films, arising from long impregnation times, may result in either the nonelectron injection or the steric hindrance preventing dye molecules from efficiently adsorb on the TiO_2 film and transfer the photogenerated electron. However, the monotonic behavior of absorption spectra of all photoanodes (@TiO_2 in Figure 4) evidences no changes in dye attachment to TiO_2. This indicates that the low output of the cells is most probably due to a combined effect of low absorptivity, compared to other conventional dyes.

Worthy of note was the performance of DSSCs sensitized with a few drops of Port wine. The wine was used directly without any purification step. The cell efficiency was 0.025%, with an V_{OC} of 0.385 V, a J_{SC} of 0.150 mA cm^{-2} and a *FF* of 0.412. This is remarkable considering that Port wine has several hundreds of compounds and high water/ethanol content, which are *per se* harmful to the cell's performance.

Conclusions

In this work we have reported an investigation on pyranoflavylium derivatives extracted from wine grapes as natural sensitizers for dye solar cells. The photosensitization effect of these dyes is related to their ability towards adsorption onto the TiO_2 surface. This topic was addressed and, against some expectation arising from the apparent affinity of the pyruvic acid adduct to the semiconductor hydroxyl groups, its presence decreased efficiency. Moreover, cyanidin based molecules were more efficient than the malvidin structures. The DSSCs made using these dyes showed efficiencies of up to 0.08%, open circuit voltages (V_{OC}) ranging between 0.184 and 0.350 V, and short-circuit photocurrents (J_{SC}) varied from 0.029 to 0.35 mA cm^{-2}. Moreover, the direct use of a few drops of

Port wine as sensitizer in these cells resulted in an efficiency of 0.025%. Addition of appropriate co-adsorbants could assist dye loading/attachment resulting in further enhancement of the cells output in terms of open circuit voltage and short circuit current density. Nevertheless, though energy conversion efficiencies are still below the current requirements for large scale practical applications, these natural wine dyes are quite useful for their availability, "green" character, and low cost of production, opening up a whole new window of feasibility for environmentally friendly dye solar cells.

Acknowledgments

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