

Catechol versus carboxyl linkage impact on DSSC performance of synthetic pyranoflavylum salts

Authors: Ana Lucia Pinto,^a Luis Cruz,^b Vânia Gomes,^b Hugo Cruz,^a Giuseppe Calogero,^c Victor de Freitas,^b Fernando Pina,^a A. Jorge Parola,^a J. Carlos Lima^{a,*}

^aLAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal.

^bLAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal.

^cCNR, Istituto per i Processi Chimico-Fisici, Sede di Messina, Salita Sperone, C. da Papardo, I-98158 Faro Superiore Messina, Italy.

Keywords: dye-sensitized solar cells, pyranoflavylum dyes, bio-inspired DSSCs

Abstract

Anthocyanins are the main polyphenolic dyes found in young red wines, which are transformed into more stable structures such as pyranoanthocyanins, during wine ageing and maturation. While anthocyanins practically lose their red color between pH 1 and 5, as a result of the formation of colorless hemiketals, pyranoanthocyanins practically do not change their color intensity. For that they constitute a photosensitizer family with great potential for bio-inspired dye-sensitized solar cells (DSSCs). In this work, a series of pyranoanthocyanin derivatives were designed, synthesized and applied for the first time as dye sensitizers in DSSCs. A relation was established between dye structure and cell efficiency. Specifically, the influence of different linker units, carboxyl and catechol, was studied in terms of their influence in the various parameters related to DSSC efficiency. The presence of the catechol unit was shown to be essential for efficient electron injection of the dye into the TiO₂ semiconductor, since carboxylic units showed a deleterious effect in electron injection due to their electron withdrawing character. An overall efficiency of 1.15% was obtained for the best performing compound, 10-catecholpyrano-3',4',5,7-tetrahydroxyplavylium, with no further optimization.

Introduction

Dye-Sensitized Solar Cells (DSSC), as described by Brian O'Regan and Michael Grätzel¹, are photovoltaic devices based on the sensitization of wide band-gap semiconductor electrodes with dyes absorbing visible light. These devices have attracted a lot of attention since they display a large flexibility in shape, colour and transparency, compatibility with flexible substrates and a large variety of designs to facilitate market entry.¹⁻³ Following the pioneering work of Grätzel, the

57
58
59 fundamentals of the working principles of DSSCs are basically understood using several types of
60 dyes such as the original ruthenium dyes,⁴⁻⁶ but also porphyrins,⁶⁻¹⁰ anthocyanins^{6-8,11,12} and, in
61 recent years, perovskite materials.¹³⁻¹⁵ Until recent years, DSSCs exhibiting higher energy
62 conversion yields were based on functional ruthenium or osmium(II)-polypyridyl complexes,
63 which are expensive and toxic.¹⁶ In the last years, however, porphyrin dyes and perovskites
64 challenged these compounds in terms of performance, demonstrating the importance of exploring
65 systematically other types of dyes. To this regard, natural anthocyanin dyes and their synthetic
66 derivatives were shown to have promising properties as efficient photosensitizers for DSSCs.^{6,7,11,17-}
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112

Flavylium compounds represent a family of natural , which includes anthocyanins, anthocyanidins and 3-deoxyanthocyanins, responsible for the colours seen in a broad variety of flowers, fruits, vegetables and roots.²² From pink to red, violet and blue, anthocyanins present themselves as versatile compounds that can change their colour (by means of structural variations) depending on external stimuli such as pH, temperature and light. In fact, they share in common the same chemical equilibrium network in acid to neutral medium (Figure 1). In the case of anthocyanins, flavylium cation (**AH⁺**) is the only species present in very acidic medium. Once the pH is raised two parallel reactions can take place: deprotonation of phenol groups in the flavylium structure to form the blue quinoidal base (**A**) and/or hydration to form a colorless hemiketal (**B**). Since hemiketal formation occurs from the hydration of the flavylium cation and not from the quinoidal base, these two reactions are competitive. Consequently, upon pH increase, **A** appears as a kinetic product, but since it is fairly unstable at equilibrium, it gradually disappears with time to form hemiketal through the flavylium cation. The hemiketal undergoes tautomerization which leads to the formation of the pale yellow *cis*-chalcone (**Cc**), and finally (in a longer timescale) *cis*-chalcone isomerizes and gives the *trans*-chalcone (**Ct**).²²

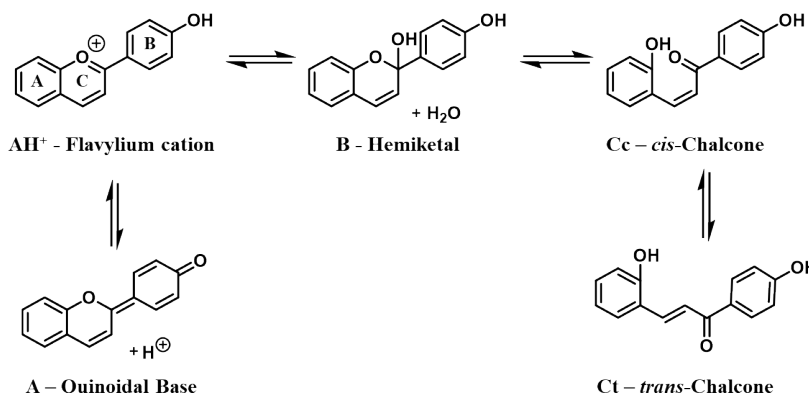


Figure 1 - Flavylium network of chemical reactions exemplified from 4'-hydroxyflavylium.

Anthocyanins are, as well, the main polyphenolic dyes found in young red wines, which can be transformed into more stable structures such as pyranoanthocyanins, during wine ageing and maturation. Pyranoanthocyanins display different chromatic hues with a wide range of colors from

113
114
115 yellow to blue. Furthermore, pyranoanthocyanins have been shown to display higher color intensity
116 and stability at a wider pH range comparatively to their anthocyanin precursors.^{23,24} In fact, while
117 anthocyanins practically lose their red color between pH 1 and 5, as a result of the formation of
118 colorless hemiketals, pyranoanthocyanins practically do not change their color intensity.^{23,24} For
119 these reasons, these dyes are interesting for a wide range of potential applications namely as food
120 colorants, hair dyes, laser dyes, as well as photosensitizers for medical applications namely in
121 photodynamic therapy and for energy applications such as DSSCs.^{25,26}
122
123

124 However, these natural occurring dyes develop through Nature's evolution process, optimizing and
125 rearranging according to its needs. In fact, some natural flavylum derivatives, such as cyanidin,
126 delphinidin and petunidin, can anchor efficiently to TiO₂ through the catechol unit in the B ring, but
127 do not have the donor-acceptor pattern optimized for electron transfer. So, for DSSC purposes, for
128 example, it is possible to follow a bio-inspired strategy and with the adequate structural
129 modifications prepare quasi-natural biomimetic compounds. With simple, non-toxic and
130 environmentally safe synthetic procedures it is possible to design and prepare compounds with
131 similar properties of natural occurring anthocyanins while tailoring desired energy levels,
132 absorption properties and linker units. In fact, recently a yield of 2.2% was obtained with the
133 compound 7-diethylamino-3',4'-dihydroxyflavylium (and upon device assembly optimization an
134 efficiency of 3.0% was achieved, using the same compound).^{17,27} Anchoring to TiO₂ is one of such
135 traits that can be optimized and can greatly influence the overall cell efficiency. In flavylum
136 derivatives, TiO₂ anchoring is expected to happen through the quinoidal base form.^{17,27,28} But
137 different linker units have different impacts on dye adsorption and electron injection.
138
139

140 In this work, a series of pyranoanthocyanin derivatives were designed, synthesized and applied as
141 dye sensitizers in DSSCs, Figure 2. The spectral response and current *vs.* potential properties of
142 photoanodes using these dyes were measured. A relation was established between dye structure and
143 cell efficiency. Specifically, the influence of different linker units, carboxyl and catechol, was
144 studied in terms of their influence in the various parameters related to DSSC efficiency.
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168

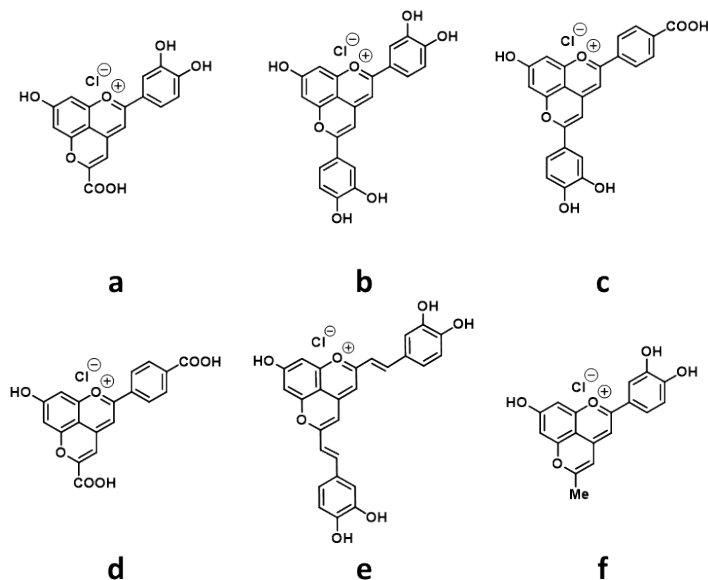


Figure 2 – Chemical structures of the six pyranoflavilyum dyes studied in this work.

Experimental

General information and instruments

All solvents and chemicals employed for synthesis and for preparation of samples were of reagent or spectrophotometric grade and were used as received.

Synthesis – The syntheses of compounds **a** and **d**²³, **b** and **f**²⁴ and **e**²⁹ were previously described.

Pyrano-4'-carboxy-7-hydroxyflavilyum-10-catechol (c) Caffeic acid (1.6 mmol, 10 eq.) was added to a solution of 4'-carboxy-5,7-dihydroxyflavilyum (0.132 mmol, 50 mg) previously obtained,²³ in a mixture of H₂O/EtOH (60:40) (v/v) (50 mL) and pH was set to 3.5. The reaction mixture was left at 60 °C for 5 days. Then, the ethanol was evaporated, and the crude product was pre-purified in a Buchner funnel loaded with C18 silica gel and eluted with acidified aqueous solution containing 30–60% of MeOH. The product was isolated by column chromatography using C18 silica gel with 50% of acidified MeOH. A dark orange powder was obtained with 8% yield.

¹H NMR (600 MHz, DMSO-d₆/TFA 9:1) δ 8.26 (d, J = 8.4 Hz, 2H, H2' and H6'), 8.16 (d, J = 8.4 Hz, 2H, H3' and H5'), 7.82 (s, 1H, H3), 7.68 (dd, J = 8.5, 2.1 Hz, 1H, H6''), 7.63 (s, 1H, H9), 7.61 (d, J = 2.2 Hz, 1H, H2''), 7.25 – 7.21 (m, 2H, H6 and H8), 7.01 (d, J = 8.5 Hz, 1H, H5''). ¹³C NMR (151 MHz, DMSO-d₆/TFA 9:1) δ 168.77 (C10), 167.62 (C7), 166.83 (4'-COOH), 164.58 (C2), 153.80 (C5 or C8a or C4''), 153.70 (C5 or C8a or C4''), 153.44 (C5 or C8a or C4''), 151.04 (C4), 146.91 (C3''), 135.25 (C4'), 133.92 (C1'), 130.57 (C3' and C5'), 127.75 (C2' and C6'), 122.41 (C6''), 120.82 (C1''), 117.08 (C5''), 114.90 (C2''), 108.17 (C4a), 104.12 (C3), 101.97 (C9), 100.99 (C6 or C8), 100.88 (C6 or C8). LC-DAD/ESI-MS: [M]⁺ m/z 415, calculated for C₂₄H₁₅O₇⁺: 415.1.

225
226
227 *Physico-chemical characterization of the compounds* – Optical measurements: The UV-Vis
228 absorption spectra of the solutions and the dyes adsorbed to TiO₂ in transmittance mode were
229 recorded by a Varian Cary 5000. All the spectra were collected at room temperature.
230

231
232 Electrochemical measurements: Cyclic voltammetry (CV) and differential pulse voltammetry
233 (DPV) measurements were performed on a μ Autolab Type III potentiostat/galvanostat, controlled
234 with GPES software version 4.9 (Eco-Chemie), using a cylindrical 5 mL three-electrode cell. A Pt
235 wire was used as counter-electrode. To perform the measurements on the I⁻/I₃⁻ system, a glassy
236 carbon electrode (MF-2013, $r=1.6$ mm, BAS inc.) was used as the working electrode. Prior to use,
237 the working electrode was polished in aqueous suspensions of 1.0 and 0.3 μ m alumina (Beuhler)
238 over 2–7'' micro-cloth (Beuhler) polishing pads, then rinsed with water and ethanol. This cleaning
239 procedure was always applied before any electrochemical measurements. The electrolyte
240 composition was 0.1 M tetrabutylammonium tetrafluoroborate, 10 mM LiI in
241 acetonitrile:valeronitrile (85:15, % v/v). To perform the measurements on the dye-coated TiO₂
242 films, the films themselves were used as working electrode. A fresh sample was used for each scan
243 to avoid uncertainty due to degradation between scans. The electrolyte composition was 0.1M
244 tetrabutylammonium tetrafluoroborate in acetonitrile:valeronitrile (85:15, % v/v). All potentials
245 refer to an SCE (Saturated KCl) reference electrode (Metrohm). CV measurements were performed
246 between 0 and +1V, with a scan rate of 50 mV/s. DPV measurements were performed between 0
247 and +1V, using scan rate 5 and 10 mV/s and a pulse amplitude of 50 mV. The samples in the
248 electrochemical cell were de-aerated by purging with nitrogen for 10 minutes prior to, and during,
249 the electrochemical measurements.
250
251

252
253 *Photoelectrochemical Measurements* – Current-Voltage curves were recorded by a digital Keithley
254 SourceMeter multimeter (PVIV-1A) connected to a PC. Simulated sunlight irradiation was provided
255 by an Oriol solar simulator (Model LCS-100 Small Area Sol1A, 300 W Xe Arc lamp equipped with
256 AM 1.5 filter, 100 mW/cm²).
257

258 The thickness of the oxide film deposited on the photoanodes and the oxide film used for UV-Vis
259 absorption experiments were measured using an Alpha-Step D600 Stylus Profiler (KLA-Tencor).
260

261 **DSSCs fabrication and photovoltaic characterization**

262 The conductive FTO-glass (TEC7, Greatcell Solar) used for the preparation of the transparent
263 electrodes was first cleaned with detergent and then washed with water and ethanol. To prepare the
264 anodes, the conductive glass plates were immersed in a TiCl₄/water solution (40 mM) at 70 °C for
265 30 min, washed with water and ethanol and sintered at 500°C for 30 minutes. The TiO₂
266 nanocrystalline layers were deposited on the FTO plates by screen-printing the transparent titania
267 paste (18NR-T, Greatcell Solar) using a frame with polyester fibres having 43.80 mesh per cm².
268 This procedure, involving two steps (coating and drying at 125 °C), was repeated two times. The
269 TiO₂ coated plates were gradually heated up to 325 °C, then the temperature was increased to 375
270 °C in 5 minutes, and afterwards to 500 °C. The plates were sintered at this temperature for 15 min,
271 and finally cooled down to room temperature. Afterwards the TiO₂ film was treated with the same
272 TiCl₄/water solution (40 mM), following the procedure previously described. A coating of reflector
273 titania paste (WER2-O, Greatcell Solar) was deposited by screen-printing and sintered at 500 °C.
274 Each anode was cut into rectangular pieces (area: 2 cm × 1.5 cm) having a spot area of 0.196 cm²
275
276
277

281
282
283 with a thickness of 15 μm . The titanium oxide film employed for UV-Vis absorption experiments
284 was prepared by doctor blade: two edges of the glass plate were covered with stripes of an adhesive
285 tape (3 M Magic) in order to obtain a transparent ultrathin TiO_2 film with an estimated thickness of
286 about 6 μm . Dye solutions of the pyranoflavylium salts (0.5 mM) were prepared in ethanol. The
287 photoanodes were prepared by soaking the screen-printed glasses overnight ($\sim 17\text{h}$) in the different
288 dye solutions, at room temperature in the dark. The excess dye was removed by rinsing the
289 photoanodes with the same solvent as that employed in the dye solution.
290

291 Each counter-electrode consisted of an FTO-glass plate (area: 2 cm \times 2 cm) in which a hole (1.5
292 mm diameter) was drilled. The perforated substrates were washed and cleaned with water and
293 ethanol in order to remove any residual glass powder and organic contaminants. The Pt transparent
294 catalyst (PT1, Grealcell Solar) was deposited on the conductive face of the FTO-glass by doctor
295 blade: one edge of the glass plate was covered with a stripe of an adhesive tape (3 M Magic) both to
296 control the thickness of the film and to mask an electric contact strip. The Pt paste was spread
297 uniformly on the substrate by sliding a glass rod along the tape spacer. The adhesive tape stripe was
298 removed, and the glasses heated at 550 $^\circ\text{C}$ for 30 min. The photoanode and the Pt counter-electrode
299 were assembled into a sandwich type arrangement and sealed (using a thermopress) with a hot melt
300 gasket made of Surlyn ionomer (Meltonix 1170-25, Solaronix SA).
301

302 The electrolyte was prepared by dissolving the redox couple, I^-/I_2 (0.8 M LiI and 0.05 M I_2), in
303 acetonitrile/valeronitrile (85:15, % v/v) mixture. The electrolyte was introduced in to the cell via
304 backfilling under vacuum through a hole in the back of the cathode. Finally, the hole was sealed
305 with adhesive tape.
306

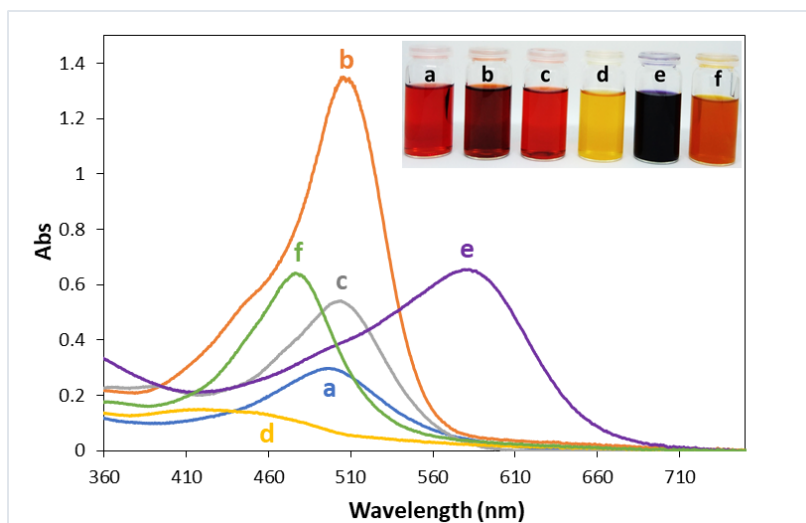
307 For each compound, three cells were assembled under the same conditions, and the efficiencies
308 were measured 10 times for each one resulting in 30 measurements *per* compound, in order to
309 calculate average and standard deviation values.
310

311 **Results and Discussion**

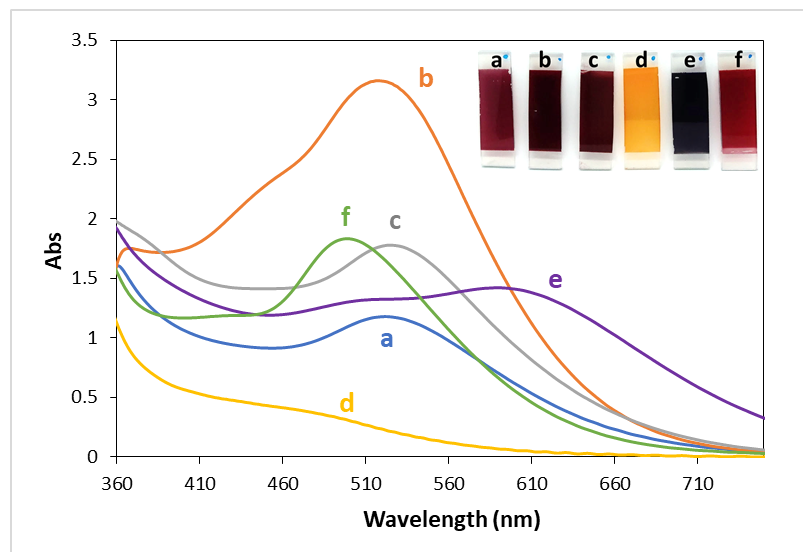
312 **UV-Vis absorption**

313
314
315
316 Dye sensitization plays a crucial role in DSSCs. A dye for DSSC should ideally absorb solar
317 radiation strongly with absorption bands in the visible and NIR region, preferably covering a wide
318 range of wavelengths. The absorption spectra of compounds **a** - **f** in ethanol (0.05 mM) are shown
319 in Figure 3. Compound **d** has the most blue-shifted absorption maximum (458 nm) followed by
320 compounds **f** (476 nm), **a** (495 nm), **b** (503 nm) and **c** (504 nm). Compound **e** exhibits an absorption
321 maximum at lower energies (582 nm) when compared with the other compounds, reflecting the
322 effect of extending the conjugation through a styryl unit to the catechol groups. In addition, since it
323 has a broader band, absorbing a wider range of visible frequencies, it gives rise to a darker colored
324 solution and film (see insets in Figures 3 and 4, respectively). Since these solutions were prepared
325 in ethanol, with no addition of acid, some of these absorption maxima may already have a
326 contribution from the presence of quinoidal base species. Upon adsorption onto TiO_2 (Figure 4) all
327 compounds show red-shifted absorption maxima (between 8 and 27 nm for compounds **e** and **a**,
328 respectively), maintaining however the same qualitative behaviour. This is an indication that TiO_2
329 adsorption involves coordination to the Ti(IV) *via* a quinoidal base formed upon deprotonation of
330 the flavylium cation. The interaction of flavylium cations with some metal ions such as aluminium,
331
332
333
334
335
336

337
338
339 iron and titanium, is known to involve deprotonation and formation of metal complexes with the
340 quinoidal bases, displacing the flavylum-quinoidal equilibrium toward the complexing quinoidal
341 form.^{12,30,31} Five of the six studied compounds (**a**, **b**, **c**, **e**, **f**) exhibited strong absorptions in the
342 Visible region and this characteristic makes them potential candidates for light harvesting in
343 DSSCs.
344
345



362 **Figure 3** - UV-Vis absorption spectra of compounds **a** - **f** 0.05 mM in ethanol. Inset: solutions of the
363 compounds.
364



381 **Figure 4** - UV-Vis absorption spectra of compounds **a** - **f** 0.5 mM in ethanol, adsorbed on a thin (ca. 6 μm)
382 TiO₂ film on FTO glass. Inset: picture of the films.
383
384

385 Electrochemical properties

386
387
388
389
390
391
392

Cyclic and Differential Pulse Voltammetry were used to characterize the compounds electrochemically (see Supplementary Information for full CV and DPV voltammograms). The anodic oxidation peaks obtained from DPV data are presented in Table 1. The minimum value of E_{pa} = 0.332 V was obtained for compound **e** containing two styryl moieties and two catechol groups, one in each styryl unit. Compound **b** comes next with two catechol units and E_{pa} = 0.366 V. Compounds **a**, **c** and **f**, containing only one catechol group and carboxylic acid or methyl groups, are characterized by higher E_{pa} values. These results are a consequence of the electron-donor/acceptor character of the substituents on the pyranoflavylum core. Compounds possessing catechol units, which are electron-donating substituents, and extended conjugation (styryl moieties) are easier to oxidize, resulting in lower oxidation potentials. The presence of the methyl group, a mild electron-donor through hyperconjugation, or of electron-withdrawing carboxylic acid groups contribute to increase the oxidation potential.

Table 1 – First anodic oxidation potentials of dyes **a** - **f** adsorbed to TiO₂, obtained through Differential Pulse Voltammetry (E vs. SCE) in acetonitrile:valeronitrile (85:15, % v/v).

Dye	E_{pa} (V)
a	0.527
b	0.366
c	0.645
d	~ 0.6 ^a
e	0.332
f	0.508

^a The low intensity of the signal prevents a better definition of E_{pa} .

An important thermodynamic requirement for dyes to be used in DSSC technology is that electron transfer from the excited state of the dye to TiO₂ must be faster than the decay to the ground state. The LUMO of the dye must then be sufficiently high in energy for efficient charge injection into the TiO₂ conduction band (-4.24 eV)². Also, the HOMO level of the sensitizer must be sufficiently low in energy for efficient regeneration of the oxidized dye by the redox couple.^{1,2,17} To experimentally determine the HOMO and LUMO energy levels of the dyes, the first oxidation and reduction potentials obtained from CV experiments may, respectively, be used. Alternatively, the LUMO energy can be obtained by adding the optical absorption energy to the HOMO value.³² In here, we considered the first anodic oxidation peak obtained from DPV performed on the dyes adsorbed on TiO₂, hence determining the HOMO of the dye-TiO₂ complex ($HOMO_{dye@TiO_2}$) (Eq. 1). Addition of the optical absorption energy obtained from the spectra in Figure 4 allowed to obtain the LUMO energy for the dye-TiO₂ complex ($LUMO_{dye@TiO_2}$) (Eq. 2). These results are presented in Table 2.

$$E(HOMO_{dye@TiO_2}) = -(E_{pa} \text{ (vs. SCE)} + 4.44) \text{ eV} \quad (\text{Eq. 1})$$

$$E(LUMO_{dye@TiO_2}) = E(HOMO_{dye@TiO_2}) + E_{\text{absorption edge}} \text{ eV} \quad (\text{Eq. 2})$$

Table 2 – HOMO and LUMO energy levels of the dye-TiO₂ complex calculated from optical and electrochemical data.

Dye	Absorption edge (nm)	Energy (eV)	HOMO _{dye@TiO₂} vs. SCE (V)	HOMO _{dye@TiO₂} vs. Vacuum (eV)	LUMO _{dye@TiO₂} vs. Vacuum (eV)
a	522	2.375	0.527	-4.967	-2.592
b	518	2.394	0.366	-4.806	-2.412
c	525	2.361	0.645	-5.085	-2.724
d	470	2.638	-	-	-
e	590	2.101	0.332	-4.772	-2.671
f	499	2.485	0.508	-4.948	-2.463

$$E(\text{HOMO}_{\text{dye@TiO}_2}) = - (E_{\text{pa}} \text{ (vs. SCE)} + 4.44) \text{ eV} \quad (\text{Eq. 1})$$

$$E(\text{LUMO}_{\text{dye@TiO}_2}) = E(\text{HOMO}_{\text{dye@TiO}_2}) + E_{\text{absorption edge}} \text{ eV} \quad (\text{Eq. 2})$$

Table 2 Since we are determining the HOMO and LUMO energies of the dye-TiO₂ complex, we will consider electron injection into the Fermi level potential of the FTO (-4.4 eV)³², instead of the TiO₂ conduction band (-4.24 eV), when evaluating electron injection ability.³² A schematic representation of the energy levels of the dyes adsorbed onto TiO₂ *versus* the Fermi level potential of the FTO (-4.4 eV) and the calculated redox potential of the redox couple I⁻/I₃⁻ (-4.718 eV) is represented in Figure 5. All the studied pyranoflavylium dye-TiO₂ complexes should be able to inject electrons into the FTO band, given that for every case the difference between the LUMO and the potential of the FTO is ~2 eV. In the case of the HOMO level, it is possible to identify two distinct groups. Although all the pyranoflavylium compounds possess a HOMO energy level below the potential of I⁻/I₃⁻, thus being able to be reduced by the electrolyte, for dyes **b** and **e** this difference is quite small (0.088 and 0.054 eV, respectively). This fact can result in inefficient regeneration of the compounds by the electrolyte, affecting the performance of the cell. In the case of dyes **a**, **c** and **f**, this difference is higher than 0.2 eV, rendering these compounds easy to regenerate by the electrolyte, thus resulting in well-functioning devices.

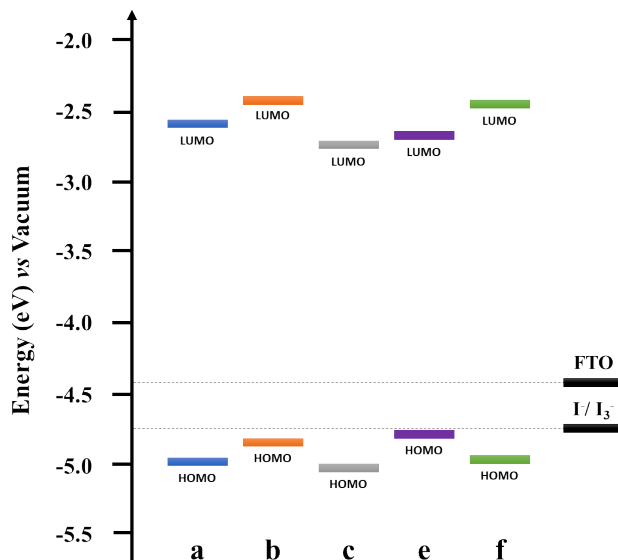


Figure 5 - Schematic representation of the energy level diagram ($\text{HOMO}_{\text{dye@TiO}_2}$ and $\text{LUMO}_{\text{dye@TiO}_2}$) of the pyranoflavylium dyes adsorbed onto the TiO_2 film vs. the FTO and I^-/I_3^- redox potentials.

DSSCs photovoltaic performance

The photocurrent–voltage plots for DSSCs assembled with pyranoflavylium dyes **a - f** are shown in Figure 6. Analysis of these data allowed to determine the short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and overall conversion efficiency (η), summarized in Table 3.

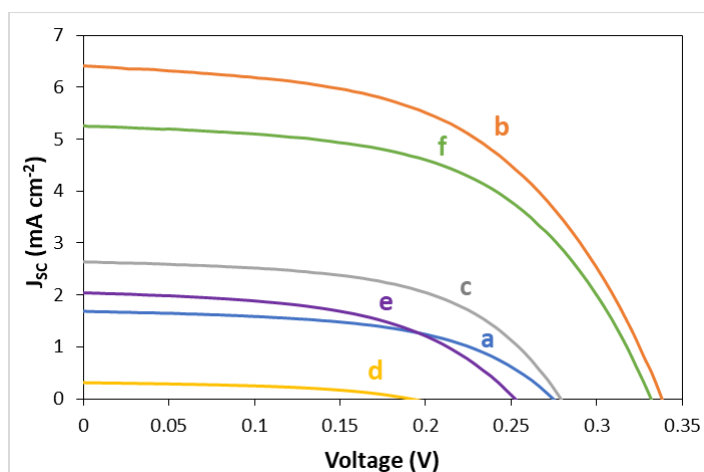


Figure 6 - J–V curves of DSSCs based on dyes **a - f** measured under AM 1.5 solar light (100 mW cm^{-2}), using 0.8 M LiI and 0.05 M I_2 in acetonitrile:valeronitrile (85:15, % v/v) as electrolyte.

Table 3 - Photovoltaic performance parameters of DSSCs based on pyranoflavylum dyes **a - f**, under 100 mW cm⁻² simulated AM 1.5 illumination. λ_{\max} / A_{\max} refers to the absorption maxima and respective absorbance measured in transmission mode for each dye upon adsorption over TiO₂. The results presented are for the best performing cell.

Dye	λ_{\max} / A_{\max}	J_{SC} (mA cm ⁻²)	V_{OC} (mV)	FF	J_{\max} (mA cm ⁻²)	V_{\max} (mV)	η (%)
a	522 / 1.18	1.68	274	0.54	1.28	194	0.25
b	518 / 3.16	6.43	338	0.53	5.02	229	1.15
c	525 / 1.78	2.63	279	0.56	2.06	199	0.41
d	483 / 0.36	0.31	191	0.46	0.21	129	0.03
e	590 / 1.42	2.03	252	0.51	1.53	172	0.26
f	499 / 1.83	5.26	332	0.56	4.16	233	0.97

Lithium is known to act as a TiO₂ Fermi level stabilizer, thus moving TiO₂ conduction band towards more positive potentials, favouring the photocurrent over the potential.³³ Since the photovoltage generated by the cell under illumination corresponds to the difference between the Fermi level of the electron in the semiconductor and the redox potential of the electrolyte,³ the electrolyte composition is determinant to the V_{OC} values obtained.

Nevertheless, the structural features of the compounds also affect significantly the values obtained. The most relevant observation is that the presence of acidic groups such as -COOH, contributes to the decrease of V_{OC} , as shown in the literature for N3 vs. N719.³⁴ This effect is notorious on the V_{OC} of **a** (274 mV) and **c** (279 mV), possessing one carboxylic group each, when compared with **d** (191 mV) possessing two carboxylic groups or **b** (338 mV) and **f** (332 mV) which have no carboxylic units.

Compound **e**, containing two styryl groups, does not follow this pattern. In this case, a decrease in V_{OC} from 338 to 252 mV with respect to the **b** analogue is observed due to a change in the direction of dipolar moment, as previously shown for ruthenium derivatives.³⁵

On the other hand, for a comparison of the overall performances, we have to take into consideration that J_{SC} is strongly affected by the amount of absorbed light, which is significantly different among the several dyes. A plot of the absorbance at the absorption maximum for each dye (Figure 4) against the short circuit current, yields a straight line (Figure 7), which means that the absorption corrected J_{SC} values would be comparable for the series. Dyes **b** and **f**, possessing only hydroxyl groups, present J_{SC} values slightly higher than the linear correlation defined by the other dyes. This suggests that carboxylates (**a**, **c**, **d**) decrease electron injection and/or increase recombination, conveying them as poorer anchoring groups in these family of dyes.

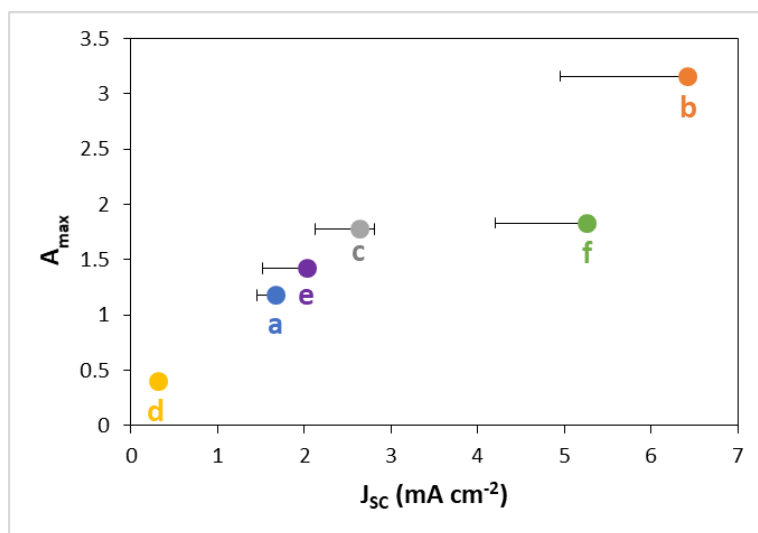


Figure 7 - Relation between the absorbance at λ_{max} for **a - f** dye-TiO₂ complexes and the respective J_{sc} measured for the best efficiency performance. The error bars correspond to the J_{sc} results obtained for 3 DSSCs assembled for each compound, measured 10 times each.

Despite the evident difference in absorbance, with that of **a** being almost 3-fold higher than that for **d** (1.18 vs. 0.36, respectively, as measured by the absorbance at λ_{max}) this difference by itself is not sufficient to account for the ~ 9-fold decrease in overall DSSC efficiency (0.25% vs. 0.03%, respectively). This difference is however mostly justified by the ~ 6-fold decrease in J_{sc} (1.68 vs. 0.31, for **a** and **d** respectively). So, the photocurrent must also reflect, additionally to the higher amount of absorbed light, a better electron injection on the TiO₂ conduction band for compound **a**.

Compound **b** is the best performing dye with an efficiency of 1.15%, under the present (non-optimized) conditions, and the highest V_{oc} and J_{sc} , 338 mV and 6.43 mA.cm⁻², respectively. This is also the compound with the highest absorbance at λ_{max} (3.16) and the highest LUMO energy (-2.412 eV). Compound **b** not only is the dye with the highest absorption, but also the compound with the better adjusted LUMO for improved electron injection into the TiO₂ conduction band. Comparing these results with compound **e** (its styryl catechol analogue) we see for the latter an overall worse performance. Despite of the broader and red-shifted absorption band, compound **e** has lower absorbance (1.42), which corresponds to a lower light absorption under the same conditions, with direct impact in J_{sc} (2.03 mA.cm⁻²). Additionally, a reduction of ~100 mV in V_{oc} further reduces the performance of dye **e**. This difference can as well be attributed to the lower LUMO energy of this compound (-2.671 eV), resulting in lower J_{sc} . This can be due to the presence of *cis*- and *trans*-isomers in the styryl units anchored to TiO₂. Probably, for different isomers, molecular orbitals may not always be optimized for electron charge transfer resulting in less effective electron injection.

Compounds **c** and **f** display an interesting “couple” since despite the almost insignificant difference in absorbance (1.78 and 1.83, respectively), the J_{sc} measured (Figure 7) and, consequently the efficiencies, are quite different. Compound **f** has twice the value of J_{sc} (5.26 vs. 2.63 mA.cm⁻², respectively) resulting in twice the efficiency (0.97% vs. 0.41%, respectively). This can be due to the significant difference in LUMO energies between the compounds, with that of compound **f** being higher than that of compound **c** (-2.463 vs. -2.724 eV). Once again, the compound with the

673
674
675 higher LUMO is the one with a better J_{SC} performance due to the higher driving force for electron
676 injection into the TiO_2 conduction band. Once more, the main difference between **c** and **f** is the
677 presence of a carboxylic group in **c** which is absent in **f**. In fact, a closer inspection of Figure 7
678 shows that also **b**, which lacks a carboxylic group, yields a slightly higher photocurrent than
679 expected from the linear correlation with absorption.
680
681

682 In summary, the overall performance of these compounds in DSSCs is clearly dominated by light
683 absorption of the dyes. We can further correlate the resulting efficiency with the nature of the linker
684 units and their electron-donor/acceptor character. In this class of dyes, carboxylic groups seem to
685 have a deleterious effect in electron injection due to their electron withdrawing character.
686 Moreover, this same characteristic reflects in lower J_{SC} results and, consequently, in lower cell
687 efficiencies.
688
689

692 **Conclusions**

693
694 Pyranoanthocyanins display great potential as photosensitizers in bio-inspired DSSCs. The best
695 known efficiency reported so far using this family of compounds is 0.006 % for cyanidin-3-O-
696 glucoside-pyruvic acid adduct.³⁶ In this work, for the first time, six pyranoflavylum salts were
697 synthesized following a bio-mimetic approach, and successfully applied, as light harvesters in
698 DSSCs. An overall efficiency of 1.15% was obtained for the best performing compound, 10-
699 catecholpyrano-5,7,3',4'-tetrahydroxyplavylium (**b**), with no further optimization. When
700 considering naturally occurring dyes, betalains which contain carboxylates as anchoring groups
701 consistently show higher efficiencies compared to anthocyanins.^{8,11,37,38} This led to the idea that
702 carboxylic linkage was essential in order to have strong electronic coupling and rapid forward and
703 reverse electron transfer reactions between the dye and the DSSC.^{8,11} In this work, where both
704 anchoring groups are compared within closely related molecules with the same pyranoflavylum
705 core, it became clear that the presence of catechol unit increases electron injection to the TiO_2
706 semiconductor. The electron withdrawing carboxylic units showed, on the other hand, a deleterious
707 effect in electron injection reflected in lower J_{SC} and, consequently, in lower cell efficiencies. In
708 summary, the overall performance of these compounds in DSSCs is clearly dominated by the nature
709 of the linker units and their electron-donor/acceptor character.
710
711
712
713

714 **Acknowledgements**

715
716 This work was supported by the Associate Laboratory for Green Chemistry, LAQV-REQUIMTE
717 which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by
718 the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265).
719 FCT/MCTES is acknowledged for Project PTDC/QEQ-QFI/1971/2014, grants
720 PD/BD/135087/2017 (ALP), SFRH/BD/136556/2018 (VG) and, a research FCT contract (LC).
721
722
723
724
725
726
727
728

References

1. O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353**, 737–740 (1991).
2. Grätzel, M. Photoelectrochemical cells. *Nature* **414**, 338–344 (2001).
3. Grätzel, M. Solar energy conversion by dye-sensitized photovoltaic cells. *Inorg. Chem.* **44**, 6841–6851 (2005).
4. Nazeeruddin, M. K., Liska, P., Moser, J., Vlachopoulos, N. & Grätzel, M. Conversion of Light into Electricity with Trinuclear Ruthenium Complexes Adsorbed on Textured TiO₂ Films. *Helv. Chim. Acta* **73**, 1788–1803 (1990).
5. Wang, Q., Moser, J.-E. & Grätzel, M. Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells. *J. Phys. Chem. B* **109**, 14945–14953 (2005).
6. Sharma, K., Sharma, V. & Sharma, S. S. Dye-Sensitized Solar Cells : Fundamentals and Current Status. *Nanoscale Res. Lett.* **6**, 381 (2018).
7. Calogero, G. *et al.* Natural dye sensitizers for photoelectrochemical cells. *Energy Environ. Sci.* **2**, 1162–1172 (2009).
8. Calogero, G., Bartolotta, A., Di Marco, G., Di Carlo, A. & Bonaccorso, F. Vegetable-based dye-sensitized solar cells. *Chem. Soc. Rev.* **44**, 3244–3294 (2015).
9. Kay, A. & Grätzel, M. Artificial photosynthesis. 1. Photosensitization of titania solar cells with chlorophyll derivatives and related natural porphyrins. *J. Phys. Chem.* **97**, 6272–6277 (1993).
10. Lu, J., Liu, S. & Wang, M. Push-Pull Zinc Porphyrins as Light-Harvesters for Efficient Dye-Sensitized Solar Cells. *Front. Chem.* **6**, 541 (2018).
11. Calogero, G. *et al.* Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells. *Sol. Energy* **86**, 1563–1575 (2012).
12. Cherepy, N. J., Smestad, G. P., Grätzel, M. & Zhang, J. Z. Ultrafast Electron Injection: Implications for a Photoelectrochemical Cell Utilizing an Anthocyanin Dye-Sensitized TiO₂ Nanocrystalline Electrode. *J. Phys. Chem. B* **101**, 9342–9351 (1997).
13. Wali, Q., Elumalai, N. K., Iqbal, Y., Uddin, A. & Jose, R. Tandem perovskite solar cells. *Renew. Sustain. Energy Rev.* **84**, 89–110 (2018).
14. Kalaiselvi, C. R., Muthukumarasamy, N., Velauthapillai, D., Kang, M. & Senthil, T. S. Importance of halide perovskites for next generation solar cells – A review. *Mater. Lett.* **219**, 198–200 (2018).
15. Ng, C. H., Lim, H. N., Hayase, S., Zainal, Z. & Huang, N. M. Photovoltaic performances of mono- and mixed-halide structures for perovskite solar cell: A review. *Renew. Sustain. Energy Rev.* **90**, 248–274 (2018).

- 785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
16. Grätzel, M. Recent Advances in Sensitized Mesoscopic Solar Cells. *Acc. Chem. Res.* **42**, 1788–1798 (2009).
 17. Calogero, G. *et al.* Synthetic analogues of anthocyanins as sensitizers for dye-sensitized solar cells. *Photochem. Photobiol. Sci.* **12**, 883–94 (2013).
 18. Hug, H., Bader, M., Mair, P. & Glatzel, T. Biophotovoltaics: Natural pigments in dye-sensitized solar cells. *Appl. Energy* **115**, 216–225 (2014).
 19. Calogero, G. & Marco, G. Di. Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells. *Sol. Energy Mater. Sol. Cells* **92**, 1341–1346 (2008).
 20. Mohiuddin, O., Obaidullah, M. & Sabah, C. Improvement in dye sensitized solar cells from past to present. *Opt. Quantum Electron.* **50**, 377 (2018).
 21. Tennakone, K., Kumarasinghe, A. R., Kumara, G. R. R. A., Wijayantha, K. G. U. & Sirimanne, P. M. Nanoporous TiO₂ photoanode sensitized with the flower pigment cyanidin. *J. Photochem. Photobiol. A Chem.* **108**, 193–195 (1997).
 22. Pina, F., Melo, M. J., Laia, C. A. T., Parola, A. J. & Lima, J. C. Chemistry and applications of flavylum compounds: a handful of colours. *Chem. Soc. Rev.* **41**, 869–908 (2012).
 23. Sousa, J. L. C. *et al.* Synthesis and equilibrium multistate of new pyrano-3-deoxyanthocyanin-type pigments in aqueous solutions. *Tetrahedron* **73**, 6021–6030 (2017).
 24. Cruz, L., Sousa, J. L. C., Marinho, A., Mateus, N. & de Freitas, V. Synthesis and structural characterization of novel pyranoluteolinidin dyes. *Tetrahedron Lett.* **58**, 159–162 (2017).
 25. Roque, A. *et al.* Photochromic properties of 3-methyl-substituted flavylum salts. *European J. Org. Chem.* 2699–2709 (2002).
 26. Czerney, P., Graneß, G., Birckner, E., Vollmer, F. & Rettig, W. Molecular engineering of cyanine-type fluorescent and laser dyes. *J. Photochem. Photobiol. A Chem.* **89**, 31–36 (1995).
 27. Calogero, G. *et al.* Electronic and charge transfer properties of bio-inspired flavylum ions for applications in TiO₂-based dye-sensitized solar cells. *Photochem. Photobiol. Sci.* **16**, 1400–1414 (2017).
 28. Cherepy, N. J., Smestad, G. P., Grätzel, M. & Zhang, J. Z. Ultrafast Electron Injection: Implications for a Photoelectrochemical Cell Utilizing an Anthocyanin Dye-Sensitized TiO₂ Nanocrystalline Electrode. *J. Phys. Chem. B* **101**, 9342–9351 (1997).
 29. Gomes, V., Mateus, N., de Freitas, V. & Cruz, L. Synthesis and Structural Characterization of a Novel Symmetrical 2,10-Bis-Styryl-1-Benzopyrylium Dye.

- 841
842
843 *Synlett* **29**, 1390–1394 (2018).
844
845 30. Goto, T. & Kondo, T. Structure and Molecular Stacking of Anthocyanins - Flower
846 Color Variation. *Angew. Chemie - Int. Ed. Engl.* **30**, 17–33 (1991).
847
848 31. Bayer, E., Egeter, H., Fink, A., Nether, K. & Wegmann, K. Complex Formation and
849 Flower Colors. *Angew. Chemie Int. Ed. English* **5**, 791–798 (1966).
850
851 32. Kavitha, S., Praveena, K. & Lakshmi, M. A new method to evaluate the feasibility of
852 a dye in DSSC application. *Int. J. Energy Res.* **41**, 2173–2183 (2017).
853
854 33. Jennings, J. R. & Wang, Q. Influence of Lithium Ion Concentration on Electron
855 Injection, Transport, and Recombination in Dye-Sensitized Solar Cells. *J. Phys.*
856 *Chem. C* **114**, 1715–1724 (2010).
857
858 34. Nazeeruddin, M. K., Humphry-Baker, R., Liska, P. & Grätzel, M. Investigation of
859 Sensitizer Adsorption and the Influence of Protons on Current and Voltage of a Dye-
860 Sensitized Nanocrystalline TiO₂ Solar Cell. *J. Phys. Chem. B* **107**, 8981–8987
861 (2003).
862
863 35. Moehl, T. *et al.* High Open-Circuit Voltages: Evidence for a Sensitizer-Induced
864 TiO₂ Conduction Band Shift in Ru(II)-Dye Sensitized Solar Cells. *Chem. Mater.* **25**,
865 4497–4502 (2013).
866
867 36. Santos, C. M. *et al.* Pyranoflavylum Derivatives Extracted from Wine Grape as
868 Photosensitizers in Solar Cells. *J. Braz. Chem. Soc.* **25**, 1029–1035 (2014).
869
870 37. Zhang, D. *et al.* Betalain pigments for dye-sensitized solar cells. *J. Photochem.*
871 *Photobiol. A Chem.* **195**, 72–80 (2008).
872
873 38. Qin, C. & Clark, A. E. DFT characterization of the optical and redox properties of
874 natural pigments relevant to dye-sensitized solar cells. *Chem. Phys. Lett.* **438**, 26–30
875 (2007).
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896