Styryl and phenylethynyl based coumarin chromophores for dye sensitized solar cells

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ABSTRACT

A set of coumarin dyes with styryl and phenylethynyl π-bridge at the 3-position were tested for dye-sensitized solar cells (DSSCs). The natural product 6,7-dihydroxycoumarin (Esculetin) was used as starting material. Crucial steps for extension of the conjugated system involved Sonogashira and regioselective Heck arylation reactions, yielding highly fluorescent molecules. The photophysical characterization showed that the extension of conjugation via the alkynyl bridge resulted in redshifted absorption and emission spectra relatively to the parent compound. Electrochemical studies revealed that this derivatization resulted in a marked decrease in HOMO energy levels, which had a marked effect on sensitized solar cell performance. The overall conversion efficiency of the phenylethynyl derivatives proved to be significantly superior (ca. 45%) to the vinyl derivatives, with **6a** showing a 2% conversion.

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1. Introduction

Coumarins are a well-known class of compounds of natural occurrence in several plant families, which have aroused a growing interest in last decades due to their pharmacological activity [1–3], and photophysical properties [4]. They constitute one of the largest classes of fluorescence sensors [5–7], which accounts for its increased application as fluorescent probes [8,9] and are also widely used in emission layers in organic light-emitting diodes (OLED) [10]. Organic solar cells arise nowadays days as a highly promising and cost-effective alternative for traditional photovoltaics, as they intend to simulate the photosynthesis concept. For this reason, in the last two decades a huge amount of work on the application of organic dyes as photosensitizers for DSSCs (Dye-sensitized solar cells) has been reported [11,12]. Thus far, the application of coumarins as sensitizers for DSSCs has been hindered due to their colour spectra falling in the UV range and the relatively low intensity of their absorption bands. One solution to this problem arises from increasing the delocalization of the conjugated π-electron system. Additionally, a recurring strategy

that became essential for the development of new sensitizers for DSSCs and that can be applied for coumarins involves Donor–π–bridge–Acceptor molecules. This further extends dye absorption bands to longer wavelengths and increases their molar extinction coefficients. A rational selection of substituents and derivatization positions in the chromophore allows a further decrease in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [13–15]. For coumarins, this effect has been observed mainly when electron-donating substituents are introduced in position 7 and electron-withdrawing moieties in position 3 [13,14]. Since the work of Hara et al. [16,17] where they developed coumarins having thiophene moieties for DSSCs with a conversion efficiency (η) of 7.7%, several authors devoted their attention to elaborate on the coumarin scaffold [18–20]. More recently, Brites et al. [18] reported the synthesis of coumarin dyes with ethynyl groups as a π-spacer with an efficiency of 2.2%. The introduction of an ethynyl π-bridge into conjugated donor–acceptor systems has not been the subject of intensive study although it was observed that the incident photon-to-current conversion efficiency reveals that the electron transfer yield ($\Phi(\nu)$ET) becomes larger with the introduction of a triple bond [21]. This ethynyl bridge can be seen as a "highway" for conducting electrons and at the same time reduces charge recombination. Coumarins present themselves as promising candidates due not only to its good photoelectric

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conversion properties, but also for their good long-term stability and an adequate energy level of LUMO appropriate to the conduction band of TiO$_2$. Thus, the structural design of coumarin-based chromophores to tune their light absorption in a way to control the electron transfer processes is of great scientific and technological interest. In recent years, we have developed novel coumarin chromophores with particular emphasis on their syntheses and photophysical properties [14,22,23]. This way, applying our knowledge on the conjugation extension of coumarins at position 3, here we report a new set of 6,7-dihydroxycoumarin (Esculetin, a natural lactone present in chicory and in many toxic and medicinal plants[24]) derivatives with a styryl or phenylethynyl bridge separating the donor and acceptor parts. We expected that excitation by light will induce a pronounced "push-pull" effect. The performance of the coumarin derivatives thus synthesized was evaluated as dyes for dye-sensitized solar cells and the effect of double bond and triple bond as π-bridges was compared.

2. Experimental

2.1. General information and instruments

All the details concerning the instrumental description and measurements are available in the ESI.† The supporting electrolyte used was a commercial electrolyte from Solaronix with reference Iodolyte AN-50, Switzerland. The redox couple was iodide/triiodide with concentration of 50 mM.

2.2. Synthesis

4-((6,7-dimethoxy-2-oxo-2H-chromen-3-yl)ethynyl)benzaldehyde (4a). To a solution of 3-bromo-6,7-dimethoxycoumarin (**1a**) (130 mg, 0.456 mmol) in 4 mL of dioxane it was added 26 mg (0.0228 mmol, 5 mol%) of tetrakis(triphenylphosphine)palladium (0), 2.9 mg (0.0114 mmol, 2.5 mol%) of triphenylphosphine, 89 mg (0.684, 1.5 eq.) of 4-ethynylbenzaldehyde and 0.096 mL of diisopropylamine. After 10 min stirring under nitrogen atmosphere it was added 6 mg (0.0315 mmol) of CuI. The mixture was stirred at room temperature 16 h and followed by silica-gel thin layer chromatography (dichloromethane/n-hexane (7:3 V/V)). Since the reaction was still showing the presence of **1a** it was added more 20 mg (0.154 mmol, 0.5eq.) of 4-ethynylbenzaldehyde. After completion the reaction mixture was evaporated to dryness and the residue was purified by column chromatography (chloroform). The compound 4-((6,7-dimethoxy-2-oxo-2H-chromen-3-yl)ethynyl)benzaldehyde (**4a**) was obtained (100 mg) in 66% yield. FTIR ν_{max} (KBr): 1716 (C=O), 1689 (CHO), 1615 (Ar C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 3.96 (s, 3H, OCH$_3$), 3.99 (s, 3H, OCH$_3$), 6.88 (bs, 2H, H-5/H-8), 7.73 (d, 2H, J = 8 Hz, H-14/H-15), 7.89 (d, 2H, J = 8.04 Hz, H-14/H-15), 7.94 (s, 1H, H-4), 10.03 (s, 1H, CHO); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 56.4 (OCH$_3$), 56.5 (OCH$_3$), 87.5 (C-11), 93.7 (C-12), 99.9 (C-8), 107.6 (C-5), 108.9 (C-4), 111.4 (C-10 + C-3), 128.7 (C-13), 129.5 (C-15), 132.3 (C-14), 135.8 (C-16), 145.7 (C-6/C-7), 146.9 (C-6), 149.9 (C-7), 153,8 (C-9), 159.8 (CO), 191.4 (CHO).

4-((6,7-bis(decyloxy)-2-oxo-2H-chromen-3-yl)ethynyl)benzaldehyde (4b). Following the above procedure for 3-bromo-6,7-bis (undecyloxy)coumarin (**1b**) (165 mg, 0.3059 mmol) the compound 4-((6,7-bis(decyloxy)-2-oxo-2H-chromen-3-yl)ethynyl)benzaldehyde (**4b**) was obtained (96 mg) in 53% yield, mp 98–101 °C; FTIR ν_{max} (KBr): 2918 (C—H), 2848 (C—H), 1700 (broad, C=O), 1609 (Ar C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 0.90 (m, 6H, CH$_3$), 1.29 (m, 24H, −CH2-), 1.52-1.48 (m, 4H, −CH2), 1.91-1.82 (m, 4H, −CH2-), 4.03 (t, 2H, J = 6.4 Hz, OCH$_2$-), 4.08 (t, 2H, J = 6.4 Hz, OCH$_2$-), 6.84 (s, 1H, H-5/H-8), 6.88 (s, 1H, H-5/H-8), 7.72 (d, 2H, J = 7.8 Hz, H-14/H-15), 7.88 (d, 2H, J = 8.04 Hz, H-14/H-15), 7.91 (s, 1H, H-4), 10.03 (s, 1H, CHO).

2-cyano-3-(4-((E)-2-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)vinyl)phenyl) acrylic acid (5a). To a solution of (E)-6,7-dimethoxy-3-(4-formylstyryl)coumarin (**3a**) (100 mg, 0.299 mmol) in 12.5 mL of acetonitrile it was added 254 mg (2.99 mmol; 10 eq) of cyanoacetic acid and 0.082 mL (0.833 mmol; 2.7 eq) of piperidine. The reaction was put to reflux for 3 h and followed by silica-gel thin layer chromatography (chloroform/MeOH (9:1 v/v)). The compound **5a** began to precipitate as an orange solid that was filtered and dried to give 103 mg in 85% yield. FTIR ν_{max} (KBr): 3407 (COOH), 2927, 2853 (C—H); 2214 (CN); 1710 (C=O); 1615, 1509 (C=C); 1280 (C—O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): 3.82 (3H, s, OCH3), 3.87 (3H, s, OCH3), 7.10 (1H, s, H-8), 7.24 (1H, s, H-5), 7.29 (1H, d, J = 16.0 Hz, H-11), 7.60 (1H, d, J = 16.0 Hz, H-12), 7.70 (2H, d, J = 8.0 Hz, H-15), 7.92 (2H, d, J = 8.0 Hz, H-14), 7.99 (1H, s, H-4), 8.17 (1H, s, H-17 (30%)), 8.20 (1H, s, H-17 (70%)). ^{13}C NMR (100 MHz, DMSO-d6): 55.9 (OCH$_3$), 56.3 (OCH$_3$), 99.8 (C-8), 108.7 (C-5), 111.3 (C-10), 111.9 (C-18), 118.9 (C-3), 120.0 (CN), 125.2 (C-11), 127.0 (C-14), 130.2 (C-15), 130.3 (C-12), 132.4 (C-16), 139.7 (C-13), 140.0 (C-4), 146.2 (C-17), 147.8 (C-9), 148.6 (C-6), 152.8 (C-7), 159.9 (C-2), 163.6 (COOH). HRMS-ESI(+) calcd for C$_{23}$H$_{18}$NO$_6$ [M + H]$^+$ 404.1134 found 404.11130.

2-cyano-3-(4-((E)-4-((E)-2-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)vinyl)styryl)phenyl)acrylic acid (5b). Following the above procedure for ((E)-4-((E)-2-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)vinyl)styryl)benzaldehyde (**3b**) (96 mg, 0.299 mmol) the compound (**5b**) was obtained as an orange solid (108 mg) in 82% yield. FTIR ν_{max} (KBr): 3391 (COOH), 2922, 2852 (C—H); 2217 (CN); 1711 (C=O); 1623, 1580, 1510 (C=C); 1279 (C—O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): 3.83 (3H, s, OCH$_3$), 3.88 (3H, s, OCH$_3$), 7.12 (1H, s, H-8), 7.24 (1H, s, H-5), 7.22 (1H, d, J = 16.0 Hz, H-11), 7.35 (1H, d, J = 16.0 Hz, H-18), 7.42 (1H, d, J = 16.0 Hz, H-17), 7.60 (1H, d, J = 16.0 Hz, H-12), 7.61 (2H, d, J = 8.0 Hz, H-15), 7.66 (2H, d, J = 7.6 Hz, H-14), 7.73 (2H, d, J = 8.0 Hz, H-20), 7.89 (2H, d, J = 8.0 Hz, H-21), 7.90 (1H, s, H-4), 8.20 (1H, s, H-23). ^{13}C NMR (100 MHz, DMSO-d_6): 55.9 (OCH$_3$), 56.3 (OCH$_3$), 99.8 (C-8), 108.6 (C-5), 111.9 (C-10), 112.0 (C-24), 119.6 (C-3), 120.4 (CN), 123.1 (C-11), 126.9 (C-20), 127.1 (C-14), 127.3 (C-21), 127.8 (C-17), 129.8 (C-12, C-15), 130.9 (C-18), 132.6 (C-16), 136.6 (C-22), 136.7 (C-19), 139.0 (C-4), 139.3 (C-13), 146.2 (C-23), 146.3 (C-6), 148.4 (C-9), 152.6 (C-7), 160.0 (C-2), 162.8 (COOH). ESI–MS(−): m/z 504.14 [M-H]$^-$, 460.15 [M-H—CO$_2$]. HRMS-ESI(+) calcd for C$_{31}$H$_{24}$NO$_6$ [M + H]$^+$ 506.15981 found 506.15660.

2-cyano-3-(4-((6,7-dimethoxy-2-oxo-2H-chromen-3-yl)ethynyl)phenyl)acrylic acid (6a). Following the above procedure for 4-((6,7-dimethoxy-2-oxo-2H-chromen-3-yl)ethynyl)benzaldehyde (**4a**) (100 mg, 0.299 mmol) the compound **6a** was obtained as an orange solid (65 mg) in 54.3% yield. FTIR ν_{max} (KBr): 3423 (O—H), 2229 (C≡N), 2203 (C≡C), 1723 (C=O); 1682 (COOH), 1617 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.82 (s, 3H, OCH$_3$), 3.90 (s, 3H, OCH$_3$), 7.14 (s, 1H, H-5/H-8), 7.28 (s, 1H, H-5/H-8), 7.66 (d, 2H, J = 8.3 Hz, H-14/H-15), 7.98 (d, 2H, J = 8.3 Hz, H-14/H-15), 8.05 (s, 1H, H-4), 8.34 (s, 1H, H-17). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 56.42 (OCH$_3$), 56.87 (OCH$_3$), 87.55, 93.52, 100.51, 107.62, 109.20, 111.69, 118.72 (CN), 124.78 (C-13), 130.42 (C-14), 132.07, 132.30 (C-15), 133.76, 146.77, 147.41, 148.24, 149.90, 154.11, 159. 62 (CO), 163.07, 165.84 (CO). ESI–MS/MS (402.09): m/z 387.07 [(M+H)-Me]$^+$, 358.10 [(M+H)-CO$_2$]$^+$, 343.08 [(M+H)-CO$_2$-Me]$^+$, 331.09 [(M + H)-CO$_2$-CN)]$^+$. HRMS-ESI(+) calcd for C$_{23}$H$_{16}$NO$_6$ [M + H]$^+$ 402.09721 found 402.09492.

2-cyano-3-(4-((6,7-bis(decyloxy-2-oxo-2H-chromen-3-yl)ethynyl)phenyl)acrylic acid (6b). Following the above procedure for 4-((6,7-bis(decyloxy-2-oxo-2H-cromen-3-yl)ethynyl)benzaldehyde (**4b**) (100 mg, 0.299 mmol) in 5 mL of acetonitrile it was added 83.5 mg (0.983 mmol; 6 eq) of cyanoacetic acid and 0.032 mL (0.327 mmol; 2.0 eq) of piperidine. After reflux for 3 h the