



Novel pyran based dyes for application in dye sensitized solar cells



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ABSTRACT

A class of novel pyran based chromophores has been synthesized and characterized for what concerns their optical and electrochemical properties. The electronic structures were investigated in details by means of DFT theoretical computations. The molecular structures of the chromophores are based on a pyran core, functionalized with different electron acceptor groups, symmetrically linked to phenothiazine electron donor moieties. The dyes have different optical absorption properties, affording a set of colors ranging from orange to blue, covering most of the visible spectral region and they are characterized by high molar extinction coefficient, up to a value of $6.4 \cdot 10^4 \text{ cm}^{-1} \text{ M}^{-1}$. The dyes were used as photosensitizers in DSSC and the photovoltaic characterization of these devices was performed under simulated solar radiation. A maximum efficiency of 2.82% has been achieved. The most promising device underwent an accelerated ageing test, performed at 85 °C for 50 days: no variation of the main electrical parameters of the DSSC was observed during the test, indicating an excellent stability for devices based on this class of photosensitizers.

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1. Introduction

Among the classes of dyes more investigated in the last 20 years for applications in organic electronics, pyran containing derivatives hold a relevant position. The versatility of the starting building block of this kind of compounds, 2,6-dimethyl- γ -pyrone, characterized by two kinds of reactive sites (i.e., the ketonic group and the two acidic methyl moieties), has allowed the synthesis of several different molecular structures and led to the preparation of materials featuring different interesting properties. Pyran based chromophores have been in fact reported as interesting compounds in different fields of organic electronics and photonics: they found application as red emitting dyes in OLED technology [1,2] and showed significant photovoltaic activity [3,4]; pyran derivatives endowing second order nonlinear optical activity [5], and two photon absorption properties [6–9], have also been reported in the literature. In the last years, the use of this class of compounds as photosensitizers in dye sensitized solar cells (DSSC) has shown encouraging results [10–12].

In particular, DSSCs have attracted considerable attention in the last 20 years [13–16], as new and promising technology in the field of Photovoltaics which, as a consequence of the rapid consumption of the fossil fuels resources, has been gaining a growing importance in the last years as alternative energy source. As compared to traditional photovoltaics based on silicon, the appeal of DSSCs lies on economical and aesthetic reasons: the fabrication of DSSCs is in fact affordable by using cheap roll-to-roll techniques and, being a thin film technology, the amount of needed active material is reduced so that a significant cost reduction is expected [15,17]: DSSCs can be prepared in a wide range of different colors, are compatible with flexible substrates and offer a better integrability with architectonic elements different from the roof, where silicon based solar cells modules are typically installed. Traditionally, the first molecular systems investigated as possible photosensitizers for DSSC were metallo-organic complexes of ruthenium and iridium and excellent efficiencies, up to 11.7% [18] have been obtained in particular by using ruthenium(II)-polypyridyl complexes as photosensitizers. Ruthenium complexes are, anyway, intrinsically expensive and, moreover, feature moderate molar absorption coefficient (around $20,000 \text{ L mol}^{-1} \text{ cm}^{-1}$). For these reasons, recent years have seen a growing interest in metal free organic dyes for application in DSSCs, typically constituted by a push-pull molecular

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structure [19,20]: the advantages of this kind of system rely on their high molar absorption coefficient and on the tunability of the absorption and electronic properties achievable through a suitable molecular design.

We report here on novel organic photosensitizers based on an electron acceptor pyran core symmetrically linked, through ethylene bridges, to donor phenothiazine moieties. The chemical structures are reported in Scheme 1.

The pyran core of the dyes is functionalized with three different electron withdrawing (EWD) groups: dicyanovinyl (**P**₁), thiobarbituric (**P**₂) and an indandione derivative (**P**₃). As shown in previous works reported in the literature, the use of functionalizing group with different electron acceptor strength on the same molecular fragment results in the tuning of the optical absorption properties of the dyes so that different parts of the visible spectrum can be covered [12,21,22]. The pyran core is symmetrically linked to phenothiazine groups; phenothiazine is a heteroaromatic system characterized by a strong electron donor ability as a consequence of the presence of electron rich nitrogen and sulfur atoms contained in it. It has been widely in organic electronics as donor moiety in donor-acceptor molecular systems in the field of bulk heterojunction solar cells [23–25] and DSSCs [26–29]. In the present work, phenothiazine groups are functionalized with two acrylic acid moieties for allowing binding to the TiO₂ surface in DSSC fabrication. The presence of two carboxyl groups is expected to strengthen the binding of the photosensitizers to titania, possibly resulting in the enhancement of electron transfer and cell performance, as shown in the literature [30–33]. The synthesized chromophores have been characterized by optical and electrochemical measurements; their electronic structure has been analysed by Density Functional Theory (DFT) and their efficiencies in DSSC tested under simulated sun radiation.

2. Materials and methods

2.1. Synthesis

All the intermediates used in the synthetic procedures described below, have been purchased by Sigma Aldrich, TCI Europe or Acros Organics, and used without further purification with the exceptions of 3-dicyanovinylindan-1-one that has been prepared according to reported a procedure [34].

2.1.1 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile (**A**₁)

2,6-dimethyl- γ -pyrone (12.50 g, 0.100 mol) and malononitrile

(6.90 g, 0.104 mol) were dissolved in 50 mL of acetic anhydride; the solution was refluxed, under nitrogen flowing, for 5 h. The system was then slowly cooled down to room temperature and the crystallization of a brown compound occurred. The compound was recovered by suction filtration and recrystallized by chloroform-hexane. Light brown needle-shape crystals were obtained. The yield was 60%.

¹H NMR (CDCl₃, 200 MHz); δ = 2.31 (s, 6H, –CH₃); 6.53 (s, 2H, pyran CH).

Mp: 192 °C.

2.1.2. 2-(2,6-Dimethyl-4H-pyran-4-ylidene)-thiobarbituric acid (**A**₂)

The same synthetic strategy used for the preparation of **A**₁ was followed; the only difference is that thiobarbituric acid was used instead of malonitrile in the condensation reaction with the pyrone derivative. Yellow needles were recovered after crystallization in chloroform-hexane. The yield was 68%.

¹H NMR (CDCl₃, 200 MHz); δ = 1.30 (t, 6H, J = , –CH₃); 2.46 (s, 6H, –CH₃), 4.57 (q, 4H, J = , –CH₂); 8.82 (s, 2H, pyran CH).

Mp: 195 °C.

2.1.3. 2-(2-(2,6-Dimethyl-4H-pyran-4-ylidene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**A**₃)

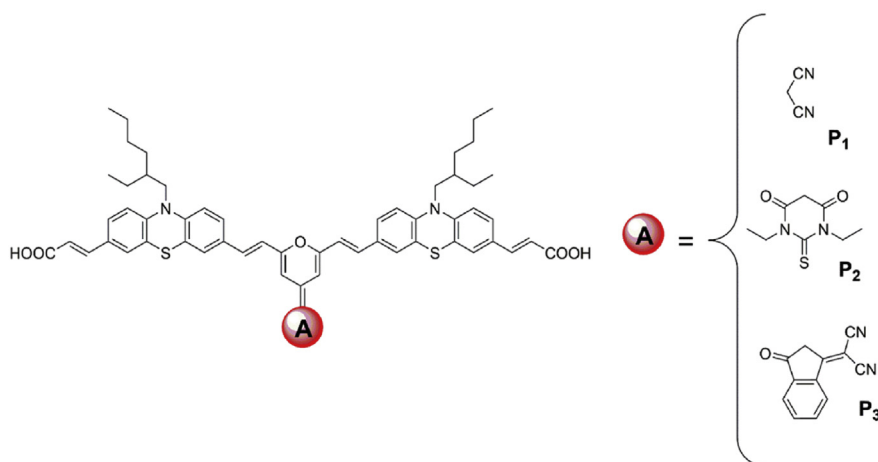
The compound was synthesized following the same procedure used for **A**₁, except that 3-dicyanovinylindan-1-one was used instead of malononitrile. A brown crystalline solid was obtained after recrystallization (CHCl₃-hexane). The yield was 58%.

¹H NMR (CDCl₃, 400 MHz); δ = 2.50 (s, 6H, –CH₃), 7.50 (broad, 1H); 7.60 (m, 3H, Ar–H); 7.74 (d, 1H, J = 7.0 Hz); 8.44 (d, 1H, J = 7.0 Hz, Ar–H).

Mp: 212 °C.

2.1.4. 10-(2-Ethylhexyl)-10H-phenothiazine (**1**)

Sodium hydride (4.8 g, 60% wt in mineral oil corresponding to 0.120 mol of NaH) was suspended in 50 mL of dry DMF at 0 °C and in nitrogen atmosphere. Phenothiazine (19.9 g, 0.100 mol) solved in 50 mL of dry DMF was added dropwise to this suspension and kept under stirring for 1 h. Then, 2-ethylhexylbromide (23.2 g, 0.120 mol) solved in 25 mL of dry DMF was added dropwise. The system was left to warm up to room temperature and kept under stirring overnight. Then, it was neutralized with a diluted HCl aqueous solution (300 mL 5% wt) and extracted with hexane (2 × 200 mL). The organic layer was then washed with brine and water and finally dried over Na₂SO₄. After the removal of the



Scheme 1. Chemical structure of the synthesized dyes.

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