



Organic dyes end-capped with perfluorophenyl anchors: Synthesis, electrochemical properties and assessment of sensitization capacity of titania photoanodes

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ARTICLE INFO

Article history:

Received 20 June 2017

Received in revised form

28 July 2017

Accepted 6 September 2017

Available online 7 September 2017

Keywords:

Organic dyes

Perfluorophenyl anchors

Benzothiadiazole-*alt*-carbazole

3,4-ethylenedioxythiophene

DSSCs

Photoelectrochromic devices

ABSTRACT

In the present work, organic sensitizers are synthesized and attached on TiO₂ photoanodes via Ti–O–C bonds. All sensitizers, designed for this purpose are symmetrical and have two perfluorophenyl end groups, which can lead to stable non-hydrolysable bonds on the TiO₂ surface. Broad absorption in the UV–Vis region and low band gap energy levels have been achieved through the alternation of carbazole- and benzothiadiazole-based units. All dyes and their corresponding photoanodes, were characterized via various complementary techniques, including Cyclic Voltammetry measurements and sensitization capacity in Dye-sensitized solar cell tests.

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1. Introduction

Since their discovery, Dye-sensitized solar cells (DSSCs) have inaugurated a very interesting field of research in the general frame of mesoscopic solar cells [1,2]. A great number of different approaches have been employed for their study, but still, the full replacement of standard silicon-based photovoltaics, remains a tough task, even after decades of intensive research and significant progress in the field. Nevertheless, DSSCs show significant advantages, such as low cost and environmentally friendly fabrication process, even if their efficiency is still much lower, compared to inorganic solar cells [3–6]. This has led to increasing efforts for market penetration of DSSCs, over the last years. A typical DSSC consists of two conducting substrates that act as working and

counter electrode, separated by an electrolyte that contains a redox couple. Dye molecules, which are anchored to a semiconductor (usually TiO₂ or ZnO) deposited on the anode, absorb photons, leading to the excitation of electrons from a lower to a higher energy state of the dye (sensitizer) [7,8]. Thus, electrons from the excited state of the dye are injected into the conduction band of the semiconductor. The dye should have suitable anchoring groups to facilitate the formation of stable bonds with the semiconductor. The most commonly used anchor is the carboxylic group, since it can form ester type bonds with the hydroxyl groups on the TiO₂ surface [9,10]. Other groups, such as sulfonic or phosphonic, have also been proven functional [11–13], but have a significant drawback compared to the carboxylic unit: their use is limited in pure organic solvents, since they are not stable in aqueous environments. For this reason, our group has developed an alternative anchoring methodology, which is based on the perfluorophenyl unit. Through this route, the fluorine placed on the para-position can react under mild alkaline conditions with the hydroxyl

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groups of the TiO₂ surface, forming stable, non-hydrolysable Ti–O–C bonds [14,15].

The injected electrons are collected at the transparent conducting oxide (TCO), move through an external circuit towards the counter electrode and are exchanged with a redox couple in solution. This electron transfer is facilitated in the presence of an appropriate electrocatalyst. The redox shuttle finally compensates the holes left in the dye sensitizer and thus the cell functions in a cyclic manner [16–18]. Liquid electrolytes, based in the I[−]/I₃[−] couple, have proven to be the most suitable, between several candidates, even though other couples such as Co³⁺/Co²⁺ have showed higher redox potential which leads to enhanced power conversion efficiencies, but still suffer from slow mass transport and slow regeneration of Co²⁺ at the cathode [19–23]. On the other hand, liquid electrolytes present important disadvantages, such as solvent evaporation and device short lifetime, which has led to the search for viscous variants, such as ionic liquids (ILs) or polymer electrolytes (PEs) [24–28].

Regarding the DSSC operation, two major electrochemical limitations must be taken care of. At first, the lowest unoccupied molecular orbital (LUMO) of the sensitizer, has to be higher than the conduction band of the semiconductor, in order to encourage spontaneous electron injection. Secondly, the dye molecules may be regenerated, when their highest occupied molecular orbital (HOMO) is lower than the redox level of the electrolyte. It is clear, that the energy levels of the dye are very important, and the synthesis of the suitable dye is relevant with the oxide/electrolyte used [29,30].

An additional important feature for the efficiency of dyes employed in DSSCs is the anchoring moiety or moieties used for their connection with the TiO₂ NPs. Two (or more) anchoring groups are mainly used in Ruthenium (or other metal) based sensitizers [3,31], while for most organic sensitizers the synthetic routes typically employed lead to only one anchoring group (D- π -A structure) [32–34]. However, some reports suggest that only one anchor may cause drawbacks in the sensitizer's adsorption geometry on TiO₂ nanoparticles and the overall charge injection [35–37]. In some polymeric dyes on the other hand, the α,ω -end modification of the polymeric chain enables the formation of sensitizers with two anchoring groups, a synthetic strategy also used by us in a previous study [15]. More particularly, those polymeric entities based on the combination of benzothiadiazole and *N*-alkyl-2,7-carbazole have attracted our attention because of the high conjugation level, low bandgap and the good charge carrier transport and mechanical properties they provide, which lead to high power conversion efficiencies in OPVs [38].

In the present work, we have synthesized novel small organic dyes of defined chemical structures and length based on thiophene derivatives, carbazole electron donating groups and benzothiadiazole electron accepting groups. Two end-perfluorophenyl units have been incorporated as anchoring groups for the subsequent sensitization of TiO₂ for DSSCs. The synthesis of the herein reported dyes was accomplished via two different synthetic paths. Furthermore, their optical and electrochemical characterization is presented. Finally, initial DSSC tests of the four novel chromophores have been performed, comparing the effect of the different structural motives of the new chromophores and of the side solubilizing chains employed.

2. Experimental section

2.1. Materials

4,7-Di-2-thienyl-2,1,3-benzothiadiazole (di-thien-BTZ) [39], 4,7-di-(5-bromothiophene-2-yl)-2,1,3-benzothiadiazole (di-Br-di-

thien-BTZ) [40], 2,7-dibromo-*N*-heptadecan-9-yl-carbazole (di-Br-HD-carbazole) [38], 2,7-dibromo-*N*-2-ethylhexyl-carbazole (di-Br-EH-carbazole) [41], 2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-*N*-2-ethylhexyl-carbazole (di-boronic ester-EH-carbazole) [38], 2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-*N*-heptadecan-9-yl-carbazole (di-boronic ester-HD-carbazole) [38] and the catalyst palladium (II)tetrakis triphenyl phosphine [Pd(PPh₃)₄] [42] were prepared according to literature.

All solvents and reagents were purchased from Sigma Aldrich, Alfa Aesar or Acros Organics and were used without further purification unless otherwise stated. All reactions were carried out under argon atmosphere. Tetrahydrofuran (THF) was dried and distilled just before use over sodium wire in the presence of benzophenone. Commercial nanocrystalline titania Degussa P25 (specific surface area 50 m²/g) was used in all cell constructions and Millipore water was used in all experiments. SnO₂:F transparent conductive electrodes (FTO, Resistance 8 Ω /square) were purchased from Pilkington. ITO transparent conductive electrodes ($R_{\text{sheet}} < 15 \Omega$ /square) were purchased from Aldrich. TiO₂ nanoparticles prior to their reactions with the perfluorophenyl functionalized moieties were calcined at 400 °C for 3–4 h to remove all hydrogen-bonded water molecules [43].

2.2. Characterization methods

¹H, and ¹⁹F NMR spectra were recorded on Bruker Advance DPX 400.13, and 376.5 MHz spectrometers, respectively, with CDCl₃ as solvent containing TMS as internal standard.

Thermogravimetric analysis (TGA) was carried out on 8 mg samples contained in alumina crucibles in a Labsys TM TG apparatus of Setaram under nitrogen and at a heating rate of 10 °C min^{−1}.

IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer and on an ALPHA-P diamond ATR spectrometer of Bruker Optics GmbH.

UV–Vis spectra in solution were recorded using a Hitachi U-1800 spectrophotometer. Photoluminescence (PL) spectra in solution were recorded using a Perkin-Elmer LS45 luminescence spectrometer, after excitation at the UV–Vis absorption maxima.

UV–Vis absorption spectra and diffuse reflectance spectra (DRS) of sensitized photoanodes were recorded with a Shimadzu UV-2600 spectrophotometer equipped with integration sphere.

The electrochemical behavior of the fabricated materials was investigated using cyclic voltammetry (CV thereafter). CV experiments were carried out in a three electrode cell [44,45]. Two kinds of working electrodes have been used. An ITO/Glass with the synthesized sensitizers to be measured drop-casted on the ITO conductive side and a dye-sensitized TiO₂/FTO/Glass. An Ag/AgCl electrode served as reference and a platinum wire was used as the counter electrode. Thin films of the fabricated materials were drop casted on ITO coated glass slides, ($R_{\text{sheet}} < 15 \Omega$ /square), preheated at 80 °C for 20 min, from precursor solutions of chloroform. The resulting films were further annealed at 80 °C for 15 min. Dye sensitized TiO₂/FTO/Glass was synthesized as described below. An Autolab PGSTAT 302 N electrochemical analyzer connected to a personal computer running the NOVA 1.8 software was used for data collection and analysis. All experiments were carried out at a scan rate of 0.1 V/s. Tetrabutylammonium hexafluorophosphate (TBAPF₆) 0.1 M in Acetonitrile (CH₃CN) was used as supporting electrolyte. Before carrying out the measurements the cell was purged with pure argon for 20 min to remove diluted gasses. The reference electrode potential was calibrated against Ferrocene/Ferrocenium (Fc/Fc⁺) after each voltammetry run.

The corresponding HOMO, LUMO energy levels and the energy gap (E_g) were calculated with use of the redox potentials by the

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