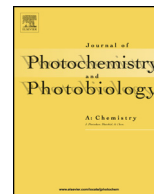




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Incorporation of a fluorophenylene spacer into a highly efficient organic dye for solid-state dye-sensitized solar cells

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ABSTRACT

A new efficient organic dye LEG4F, incorporating a fluorine-substituted phenylene unit in the π -spacer, has been synthesized and tested in dye-sensitized solar cells. Direct comparison with the parent dye LEG4 shows very similar performances in case of liquid electrolyte devices based on iodide/triiodide, yielding a power conversion efficiency of 6.8% under 1 sun and 8.0–8.2% under 0.5 sun illumination. However, LEG4F outperforms its fluorine-free analogue when the liquid electrolyte is replaced by the solid-state hole-transport material Spiro-OMeTAD, reaching 5.3% efficiency compared to 4.8% achieved by LEG4. We show that this improvement is due to the enhancement of the electron lifetime, which reduces recombination at the TiO_2 /dye/Spiro-OMeTAD interfaces.

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1. Introduction

Dye-Sensitized Solar Cells (DSSCs) are an attractive and promising photovoltaic technology for future commercialization, due to their high versatility and low-fabrication costs [1–3]. Since the remarkable breakthrough by O'Regan and Grätzel in 1991 [4], most of the research has been focused on liquid-based electrolyte devices in which a dye-sensitized TiO_2 electrode and a counter-electrode are placed in contact through a liquid solution of the redox mediator. Due to the superior performances recorded with liquid electrolytes, highly efficient and competitive devices have been produced [5–7]. Despite the outstanding performances of liquid DSSCs, a practical disadvantage of this system for future commercialization is the volatile nature of the solvents commonly employed [5–13]. In order to overcome this issue, alternative solid state DSSCs (ssDSSCs) based on hole-conducting small molecules or polymer, have been developed [14–16]. However, the power-to-current efficiency of ssDSSCs is generally lower than that of their liquid counterpart due to incomplete pore-filling of the hole-conducting material into the mesoporous TiO_2 , remarkable sensitivity to moisture of the widely used hole-conductor 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)9,9'-spirobi-fluorene (Spiro-OMeTAD), and the difficulty to control the amount of Spiro-OMeTAD⁺ used as dopant [17–20]. In particular, the pore-filling problem has been addressed as a notable limitation due to

an imperfect contact between the dye and the hole-transport material, which results in increased recombination [21,22].

The introduction of a fluorine atom in organic and metalorganic materials for photovoltaic application has been widely studied in the last years [23–27]. The main advantage of incorporating a fluorine atom in a suitable position is the stabilization of the oxidized form of the material, which leads to reduced recombination in the devices and overall higher performances [27–29]. This property has been tested in ssDSSCs by Chou et al., leading to an enhanced efficiency for the fluorine substituted dye due to higher open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) [30]. Organic dyes based on 4,4-dihexyl-4H-cyclopenta-[2,1-b:3,4-b'] dithiophene (CPDT) segment as conjugated spacer have shown remarkable efficiencies [31,32]. Interestingly, in combination with the CPDT moiety, the introduction of additionally substituted phenyl rings on the triphenylamine donor resulted in organic dyes (Y123, LEG4) with superior performances [13,5], which are currently holding the record efficiency in ssDSSC [18,19]. In particular, Grätzel et al. included additional phenyl rings on the diphenylamine donor of the asymmetric porphyrins SM371 and SM315, breaking the existing record efficiency for liquid-electrolyte DSSCs [6]. In this study, we designed and synthesized a new dye (LEG4F) by adding a phenyl ring with a fluorine substituent in the dye spacer of LEG4, with the aim of improving the dye performance in ssDSSCs.

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2. Experimental details

All chemicals were purchased from Sigma-Aldrich and used as received unless noted otherwise. The organic dye LEG4F (structure in Fig. 1) was synthesized according to a synthetic procedure reported in the SI (Scheme S1). FTO-coated glass substrates were purchased from Pilkington. TEC15 and TEC8 were used for working electrodes and counter electrodes, respectively.

2.1. Optical characterization

Equipment used for the evaluation of the molar extinction coefficient and UV–vis absorption measurements: Varian Cary 50 UV/Vis Spectrometer. The absorption spectra of LEG4F and LEG4 on TiO₂ were recorded on 4 μm thick TiO₂, electrodes fabricated according to the procedure reported in the liquid electrolyte DSSCs fabrication section. The electrodes were placed in a 0.1 mM solution of the dye in acetonitrile:*t*-butanol (1:1 vol ratio) for 3 h and then rinsed with the same solvent mixture.

2.2. Electrochemical characterization

Electrochemical experiments were performed in a three-electrode electrochemical cell with a platinum mesh working electrode, glassy carbon counter electrode and Ag/AgNO₃ (10 mM/MeCN) as reference electrode. The samples were dissolved in 0.1 M *t*-Bu₄NPF₆/DCM electrolyte solution in order to obtain dye concentration 10⁻³ M. The counter electrode was kept separate from the main solution by a salt bridge with glass frit tip. All electrochemical measurements were performed using an Autolab PGSTAT302 potentiostat/galvanostat with a GPES electrochemical interface. All experiments were carried out in a glovebox (MBraun) maintained at < 0.1 ppm O₂ and H₂O. The CVs of LEG4F and LEG4 on TiO₂ were recorded on 4 μm thick transparent TiO₂ electrodes, fabricated and sensitized according to the procedure reported in the next section.

2.3. Liquid electrolyte DSSCs fabrication

TEC15 substrates were cleaned in an ultrasonic bath with detergent solution (RBS 25 from Fluka analytical), ethanol (VWR DBH Prolabo purity of 99.9%) and deionized water. The glass substrates were pre-treated in a 40 mM aqueous TiCl₄ solution at 70 °C for 90 min and then rinsed with water and ethanol. After drying in air the substrates were screen printed (active area

0.25 cm²) with a Dyesol 30 NR-D paste, 30 nm particle size (thickness around 8.0 μm after sintering). The substrates were dried at 125 °C for 10 min before being screen-printed with a TiO₂ scattering paste (Dyesol WER2-O). The samples were heated gradually at 180 °C (10 min), 320 °C (10 min), 390 °C (10 min) and 500 °C (60 min) in an oven (Nabertherm Controller P320) in air atmosphere. After sintering the samples were once again treated with 40 mM aqueous TiCl₄ at 70 °C, for 30 min. A final heating step (500 °C for 60 min) was performed. Before immersing the electrodes in the dye bath the electrodes were cooled down to 90 °C. Optimized substrates were screen-printed with a diluted (80% wt. paste, 20% wt. mixture of terpineol/ethyl cellulose) scattering paste (for a total thickness of 12–13 μm), while non-optimized substrates were screen-printed with non-diluted scattering paste (for a total thickness of 11 μm). Dye baths of LEG4 and LEG4F consisted of a 0.2 mM dye solution in acetonitrile:*t*-butanol (1:1 vol ratio). Different molar ratio of dye:chenodeoxycholic acid were added to the dye bath of LEG4F where reported. The films were left in a dye bath overnight (14 h) in the dark, rinsed with ethanol and assembled in a sandwich structure with the counter electrode. A 25 μm thick thermoplastic Surlyn frame was employed (Meltonix 1170-25 from Solaronix). The electrolyte was introduced in the sealed devices through the predrilled hole by vacuum back-filling technique, sealed with a thermoplastic Surlyn cover and a glass coverslip. For counter-electrodes preparation, a predrilled one-hole TEC8 glass was cleaned following the same procedure reported for the working-electrodes, and heated in air at 400 °C for 30 min to remove residual impurities. After cooling down to room temperature, 9 μL cm⁻² of a 4.8 mM H₂PtCl₆ solution in ethanol was deposited on the glass substrate, followed by heating in air at 400 °C for 30 min. Optimized devices were assembled using freshly prepared working electrodes and counter electrodes, while non-optimized devices were assembled using previously prepared working electrodes, stored in air for days/weeks, and re-heated to 90 °C prior to dye-bath immersion.

2.4. Solid state DSSCs fabrication

Fluorine-doped SnO₂ (TEC15) substrates were etched with Zn powder and HCl (4 M) to form the desired electrode pattern. The substrates were cleaned in an ultrasonic bath for half an hour with the following solvents: deionized water, acetone and ethanol. A compact layer of TiO₂, intended to block the recombination current at the FTO support, was prepared on cleaned FTO substrate by spray pyrolysis. The solution used for the spray pyrolysis was

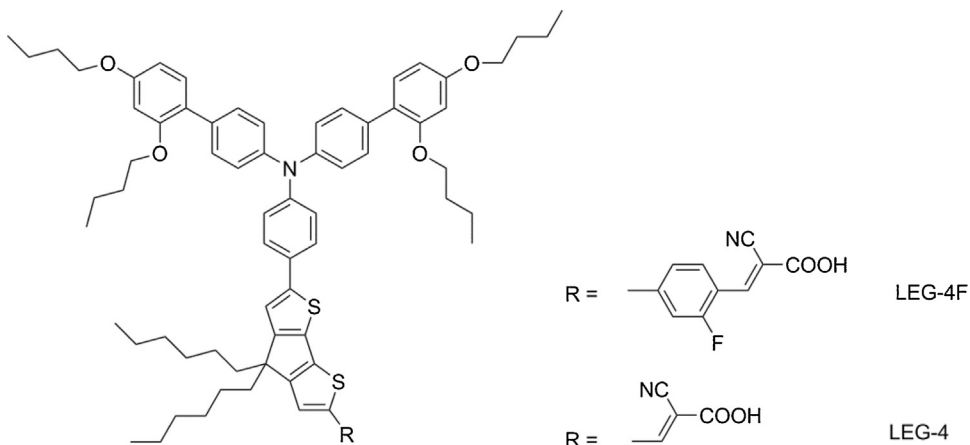


Fig. 1. Molecular structures of LEG4F and LEG4 dyes.

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