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Carbazole-based hole transporting material for solid state dye-sensitized solar cells: Influence of the purification methods

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ABSTRACT

The synthesis and properties of a glass-forming carbazole compound 9-(ethyl)-3,6-bis(4,4'-dimethoxydiphenylaminyl)-carbazole are reported. The thermal, optical and electrochemical properties of the hole-transporting molecule were studied by differential scanning calorimetry, thermogravimetric analysis, UV/Vis spectroscopy and cyclic voltammetry. The molecular glass exhibits a thermal stability as high as 370 °C and a glass transition temperature of 68 °C. The synthesized compound absorbs in the 250–400 nm range and possesses an optical band gap of 2.76 eV, avoiding any screening effect with the dye. The solid state ionization potential (IP_{ss}) of the molecule, estimated by cyclic voltammetry is around 4.77 eV, higher than the standard spiro-OMeTAD hole-transporting material. The compound was finally assessed as hole-transporting material in the solid state dye-sensitized solar cells with (5-(1,2,3,3 a,4,8b-hexahydro-4-[4-(2,2-diphenylvinyl)phenyl]-cyclopenta[b]indole-7-ylmethylene)-4-oxo-2-thioxo-thiazolidin-3-yl)acetic acid (D102) as sensitizer. The effect of the purity of the glassy molecule on photovoltaic performances is discussed and showed a two-fold increase of the power conversion efficiency after purification by sublimation, going from 0.82% to 1.62% under standard AM 1.5 G solar irradiation (100 mW/cm²).

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1. Introduction

Among the promising photovoltaic technologies, dye-sensitized solar cells (DSSCs) have received much attention during the past two decades due to their low cost and high efficiency [1–3]. Usually, DSSCs are based on a photoelectrode sensitized by a dye where photo-induced electron transfers are occurring [4–6]. A liquid electrolyte and a counter electrode complete the cell. High efficiencies over 13% have been reached by employing a metal complex redox couple, namely Co(II/III)tris(bipyridyl), and organic dyes [7,8]. In order to avoid potential leakage issues associated with the corrosive and volatile nature of the liquid electrolyte, 2,2',7,7'-tetrakis-(N,N-di-pmethoxyphenyl-amine)-9,9'-spiro-bi-fluorene (spiro-OMeTAD) as hole transporting material (HTM) has been successfully applied in solid state dye-sensitized solar cells (ssDSSCs) [9,10]. Since a few years, spiro-OMeTAD is showing increasing performances when associated with organic dyes such as D102 (4.2%) [11] or Y123 (7.2%) [12] dyes. More recently, high power conversion efficiencies over 17% have been achieved by combining perovskite materials and spiro-OMeTAD as HTM [13,14], opening the way for viable commercial applications of

solid-state approaches. However, nowadays, the reference spiro-OMeTAD remains still too expensive for large-scale applications, and properly controlling its doping state under ambient conditions is tricky [15]. This is why the development of cheaper and more stable hole-transporting molecular glasses for ssDSSCs is a crucial challenge. Although, in the literature, only few alternatives able to compete with the spiro-OMeTAD are described, our group and others have recently reported promising amorphous low-molecular-mass compounds based on carbazole moieties [16–20].

In this article, we present a simple synthesis of a 9-ethyl-carbazole derivative for the preparation of solid-state DSSCs. The thermal, optical and electrochemical properties of the synthesized compound have been studied, and its performances as hole-transporting material have been assessed in FTO/TiO₂/D102/molecular glass/Au ssDSSC and discussed according to the purity grade of the molecular glass.

2. Experimental

2.1. Materials

9-(ethyl)-carbazole, 4,4-dimethoxydiphenylamine, potassium iodate, potassium iodide, palladium acetate, titanium (IV)

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isopropoxide (97%), lithium bis(trifluoro-methanesulfonyl)imide salt, titanium tetrachloride, *ter*-butylpyridine, acetonitrile, *tert*-butanol, anhydrous toluene, anhydrous dimethylformamide, chlorobenzene and ethanol were purchased from Sigma Aldrich, Alfa Aesar, Fluka and used as received. 2,2,7,7-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene was received from Merck KgaA (Germany) and used without further purification. 3,6-diiodo-9-(ethyl)-carbazole was synthesized as previously reported [21].

2.1.1. 9-(ethyl)-3,6-bis(4,4'-dimethoxydiphenylaminyl)-carbazole (1)

A suspension of 3,6-diiodo-9-(ethyl)-carbazole (2.5 g, 5 mmol), bis(4-methoxyphenyl)amine (2.3 g, 10 mmol), Pd(OAc)₂ (22 mg, 0.1 mmol) and P(^{*t*}Bu)₃ (20 mg, 0.1 mmol) was stirred in toluene (50 mL) under argon at room temperature for 15 min. The NaO^{*t*}Bu (1.25 g, 13 mmol) was added and the reaction mixture was refluxed at 110 °C overnight under argon. The Pd(OAc)₂ and inorganic salts were removed by filtration of the hot reaction mixture through celite. The crude product was purified by column chromatography on silica gel, eluting with petroleum ether/ethylacetate (7:3) to afford **1** as a yellow powder (4.5 g, 70%): ¹H NMR (300 MHz, Acetone-D₆, ppm) δ 1.41 (t, *J* = 7.1 Hz, 3H), 3.93 (s, 3H), 6.83–6.80 (m, 8H), 6.96–6.93 (m, 8H), 7.15–7.11 (m, 2H), 7.25–7.20 (m, 4H), 7.53–7.50 (m, 2H), 7.68 (s, 2H); ¹³C NMR (75 MHz, Acetone-D₆, ppm) δ 39.18, 56.61, 56.64, 111.49, 116.29, 118.47, 125.20, 126.04, 138.93, 142.68, 144.50, 144.52, 156.72, 156.74; MS *m/z* (rel. intensity) 649 (100) [M⁺]; Elem. Anal. Calcd. for C₄₂H₃₉N₃O₄: C 77.63, H 6.05, N 6.47, O 9.85. Found: C 77.53, H 6.17, N 6.28, O 10.12.

Sublimed compound **1**: Elem. Anal. Found: C 77.59, H 6.12, N 6.34, O 9.95.

2.2. Instrumentation

The synthesized molecule was purified by sublimation using a gradient vacuum oven. To this end, 170 mg of the as-synthesized material were placed in a quartz tube under vacuum (5.10⁻⁵ mbar) and heated gradually within 2 h up to 270 °C. After 4 h at 270 °C, the system was allowed to cool down under vacuum to room temperature. A 120 mg purified fraction of the molecule was finally recovered.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. Mass spectra were recorded on a Finnigan MAT 8500 using a ionization energy of 70 eV (electron impact). Elemental Analysis was performed on an Exeter Analytical CE-400 Elemental analyzer. UV–vis spectra were recorded with Hitachi U-3000 spectrometer. Fluorescence spectra were recorded with a Shimadzu RF-5301PC luminescence spectrometer.

Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-7 (heating/cooling rate 10 K/min). Thermogravimetric analysis (TGA) was fulfilled using Perkin Elmer TAS-409 thermogravimeter at a heating rate 10 K/min under N₂. The purity of the target compound was estimated with a Waters SEC system for oligomers (analytical columns, cross-linked polystyrene gel (Polymer laboratories); length 2 × 60 cm²; width 0.8 cm; particle size 5 μm; pore size 100 Å eluent THF (0.5 ml/min, 80 bar); polystyrene standard). The system included a Waters 486 UV detector (254 nm) and Waters 410 differential refractometer.

Cyclic voltammetry of the carbazole derivative was performed in a 10⁻³ mol L⁻¹ acetonitrile solution with 0.1 mol L⁻¹ tetraethylammonium tetrafluoroborate (TEABF₄) as supporting electrolyte at a scan rate of 50 mV/s. Platinum wire and disk (1 cm diameter) electrodes were used as counter and working

electrodes, respectively. Silver wire was used as a pseudo-reference electrode. At the end of the measurements, ferrocene has been added as internal reference.

2.3. Preparation of the devices

FTO/TiO₂/dye films were prepared as described below. The F-doped SnO₂ (FTO) glass substrates (TCO2215, 15 Ω/Square from Solaronix, Switzerland) were patterned by acidic treatment, then subsequently sonicated for 10 min in acetone, isopropanol and water, before being treated for 10 min with a UV–ozone cleaner. A compact layer of TiO₂ was deposited by chemical spray-pyrolysis [22] at 450 °C from a solution of titanium isopropoxyde and acetylacetone in ethanol (Sigma-Aldrich). The layers were then annealed at 450 °C for 20 min in air, resulting in approximately 150 nm thick films. A nanoporous layer of TiO₂ was applied by spin-coating from a commercial TiO₂ paste (DSL 18NRT, Dyesol Limited, United Kingdom) containing nano-sized anatase particles, followed by gradual annealing from 250 °C up to 500 °C, over 30 min. The resulting film thickness (2–2.5 μm) was a good compromise for solid-state DSSC based on spiro-OMeTAD, organic dyes and TiO₂, resulting in balanced light absorption and charge collection.

The substrates were then treated in a 0.02 M TiCl₄ aqueous solution for 2 h at room temperature [23,24] and rinsed with water followed by annealing at 500 °C for 45 min. Subsequently, they were sensitized by soaking in a 0.6 mM solution of the indoline D102 dye (Mitsubishi Paper Mills, Japan) in acetonitrile: *tert*-butanol (1:1 vol%, Sigma-Aldrich) overnight at 80 °C and then washed with acetonitrile. The hole conducting layer was deposited by spin-coating from a solution of the synthesized molecule (namely molecule **1**, see the following sections) in chlorobenzene (Sigma-Aldrich) at 200 mg/mL, containing Li(CF₃SO₂)₂N solution (190 mg/mL) in acetonitrile with ratio of Li(CF₃SO₂)₂N:monomer (1:27 vol%) and *ter*-butylpyridine (1:57 vol%). Before spin-coating, the solution deposited onto the dye-sensitized substrates was allowed to fill the TiO₂ pores for 40 s. Gold top electrodes were finally evaporated under vacuum (10⁻⁶ mbar) using shadow masks that define two active areas per substrates (0.18 cm² each).

The current density-voltage (*J*-*V*) characteristics were recorded in air using a Keithley 2400 source-measure unit, in the dark and under simulated solar emission (Atlas Solarconstant 575 PV). The spectral mismatch between the emission of the solar simulator and the global AM1.5G solar spectrum (ASTM G173-03) was corrected using a mismatch factor [25] and the solar simulator irradiance was adjusted accordingly using a certified silicon reference cell in order to achieve an equivalent AM1.5G irradiance of 1 sun (100 mW cm⁻²) on the test cells.

2.4. Estimation of the pore filling

The pore filling fraction of the HTM in mesoporous TiO₂ was estimated using a previously reported method [26]. Films of spiro-OMeTAD and molecular glass **1** were deposited both on a flat glass substrate and on a dye-coated porous TiO₂ substrate by spin-coating, using the same conditions as described above in Section 2.3 for the preparation of the devices. The HTM film thickness on flat glass substrate (*t*_{flat}) and the HTM capping overlayer thickness on TiO₂ (*t*_{overlayer}) were determined from cross-section SEM images. The pore filling fraction (*PFF*) is calculated according to the following equations:

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