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Classical or inverted photovoltaic cells: On the importance of the morphology of the organic layers on their power conversion efficiency

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ABSTRACT

Novel organic thiophene derivatives, (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″-terthiophene)vinylene (BSTV) and (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″:3′,2‴-tetrathiophene)vinylene (BOTV), with different numbers of thiophene units, have been synthesized. They are introduced into organic photovoltaic cells as electron donor. The both organic photovoltaic cell configurations are probed: classical, *i.e.* with the ITO used as anode, and inverted, *i.e.* with ITO used as cathode. Whatever the cell configuration, the best results are obtained when a double cathode buffer layer Alq_3/Ca is used. Actually, such double cathode buffer layer allows cumulating the advantages of its both constituents. The Alq_3 blocks the excitons and protects the organic electron acceptor from cathode diffusion during its deposition, while the low work function of Ca induces a good band matching at the interface electron acceptor/cathode. On the other hand, it is shown that the organic layer surface morphology is decisive whatever the cell efficiency. While the BSTV layers are homogeneous those of BOTV are not. It follows that, in the case of classical organic photovoltaic cells, leakage currents limits the performances of the cells using BOTV, and better performances are obtained with BSTV. This difficulty is overcome in the case of inverted organic photovoltaic cells. This configuration allows limiting the effect of the inhomogeneities of the donor layer and better efficiencies are obtained with BOTV, which was expected due to its smaller band gap value.

1. Introduction

In the field of renewable energy, the theme concerning organic photovoltaic cells (OPVCs) is one of the most investigated all over the world. Impressive progresses were done during these last ten years [1–4]. However the power conversion efficiency (η) of the OPVCs stays significantly below that of inorganic cells and effort dedicated to the improvement of the OPVCs must be pursued. If organic semiconductor materials exhibit high absorption coefficient, the domain in which they absorb the light is quite narrow, what limits the reachable maximum value by current density (Jsc). Moreover after light absorption and exciton creation it is necessary, not only to separate the carriers of the excitons, but also to collect these carriers through the electrodes. Therefore, among the possible ways to improve the OPVCs efficiency we can try to widen the domain of absorption of the light and we can use new buffer layers at the interfaces electrode/organic material in order to improve the carrier collection. It was shown that it is possible to improve the performance of OPVCs by using small band gap organic materials [3,4]. Moreover, as said above, the insertion of buffer layers at the interface organic materials/electrodes allows improving significantly the device efficiency [5,6]. Power conversion efficiencies over 5% can be achieved with multilayer planar heterojunctions when a cathode buffer layer is present at the interface electron acceptor/cathode [7]. This layer has been called

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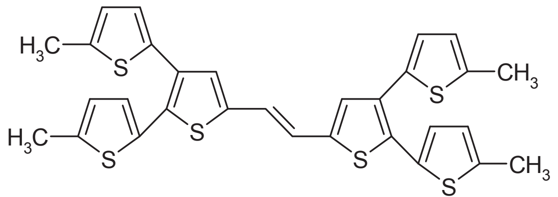
exciton blocking layer (EBL) because its band gap is substantially larger than those of the organic donor and acceptor, which blocks excitons in the organic layer far from the cathode avoiding any quenching effect at the interface cathode/organic. Moreover, it is well known that improving the band matching at the contact electrode/organic material induces significant improvement of the OPVCs performances [8]. In the case of the cathode it is necessary to use a metal with a small work function. Ca has a very small work function but it is quite unstable and usually Ag or Al is used as cathode, while ITO (indium tin oxide) is used as the anode.

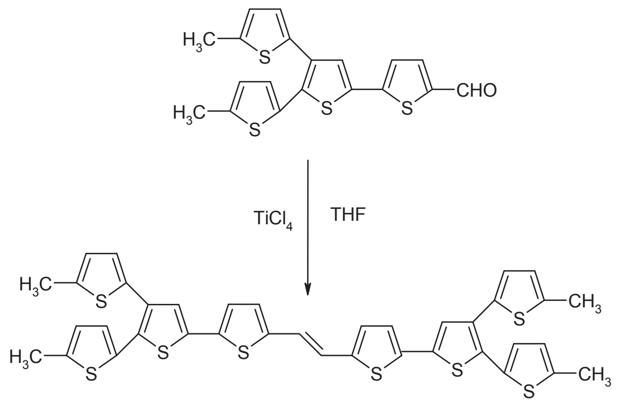
On the other hand, inverted OPVCs (IOPCs) with modified ITO as the transparent cathode and a high W_F metal as the anode were proposed [9–12]. In this architecture the anode is the top electrode. This inverted structure allows improvement of the lifetime of the OPVCs, due to the fact that the C_{60} layer is covered by several layers, which decreases the C_{60} exposure to water vapour and oxygen, moreover, an air stable top electrode can be used [13].

In the present work, we investigate the two possible configurations, classical (OPVC) and inverted (IOPVC) organic photovoltaic cells and we investigate the two possible ways evocated, the broadening of the absorption domain through the use of oligomers of the same family but with different number of units, *i.e.* with different band gaps and the use of double cathode buffer layer, to improve the charge collection.

Both electron donors (ED) pertain to the same oligomer family: the (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″-terthiophene)vinylene (BSTV) and the (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″:3′,2‴-tetrathiophene)vinylene (BOTV) (Fig. 1) the absorption domain of the former begin at around 540 nm, while that of the latter starts at 660 nm, which corresponds to a smaller band gap. As said above, these two ED were probed in classical and inverted OPVCs. On the other hand, in order to improve the electron collection efficiency, we use a double cathode buffer layer Alq_3/Ca, the cathode being an Al film. We show that, while Alq_3 protect the electron acceptor from Al diffusion, Ca improves the band matching at the interface, which results in a significant improvement of the OPVCs efficiency. About the effect of the decrease of the band gap value on the efficiency of the devices, we show that a significant improvement is obtained only if the organic films morphology is sufficiently homogeneous to prevent high leakage currents.



(a) BSTV



(b) BOTV

Fig. 1. Scheme of the molecules (a) BSTV, (b) BOTV.

2. Experimental

2.1. Electron donor synthesis

We have already presented the synthesis and characterization of (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″-terthiophene)vinylene (BSTV) [13]. We follow a similar process in the case of the (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″:3′,2‴-tetrathiophene)vinylene (BOTV) (Fig. 1), but here the “tetrathiophene” is substituted to the terthiophene in such a way that the final product obtained is the (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″:3′,2‴-tetrathiophene)vinylene (BOTV).

To a solution of 5,5″-dimethyl-2,2′:3′,2″-terthiophene-5′-carbaldehyde (2 mmol) in anhydrous THF (16 mL) is added titanium tetrachloride (0.7 mL) at −18 °C under Argon atmosphere. The mixture is stirred for one hour at −18 °C. To this solution was added Zinc powder (0.79 g, 12 mmol) in small portions for 10–15 min. The mixture was stirred for 40 min at −18 °C and was then gradually warmed to room temperature and then heated at reflux overnight under argon atmosphere. Then, the mixture was cooled in an ice-water bath and aqueous sodium carbonate solution (50 mL) was added. The organic layer was extracted with chloroform (3 × 50 mL). The combined organic layer were filtered and washed with water until neutral pH. The organic layer was dried over anhydrous $MgSO_4$. The product was purified by column chromatography on silica gel using hexane as the eluent, yielding a red solid (0.55 g; 74% yield), UV–Vis $\lambda_{max} = 460$ nm in $CHCl_3$

^1H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7,26 (s, 2H), 7.19–7.00 (m, 3H), 7.01–6.81 (m, 7H), 6.67 (dd, J = 3.4, 1.8 Hz, 4H), 2.55–2.39 (m, 12H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 141.60, 141.57, 140.34, 135.56, 135.07, 134.69, 132.35, 130.76, 127.74, 127.43, 126.80, 126.28, 125.52, 125.37, 124.42, 121.35, 100.01, 15.47, 15.43.

MS (ESI-TOF; $CHCl_3$/MeOH 10:15); m/z 739.9706 $[M+H]^+$ (calcd. for $C_{38}H_{28}S_8$ 739.9986).

2.2. Characterization technique

The morphology and structure cross section were observed through scanning electron microscopy (SEM) with a JEOL 7600F at the “Centre de microcaractéristion de l’Université de Nantes”. The SEM operating voltage was 5 kV. Images were done using secondary electron detector and backscattered electron detector. Optical transmission spectra were recorded by a Carry spectrophotometer. The optical transmission was measured at wavelengths of 1–0.25 μm.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″-terthiophene)vinylene (BSTV) and (*E*)-Bis-1,2-(5,5″-Dimethyl-(2,2′:3′,2″:3′,2‴-tetrathiophene)vinylene (BOTV) were evaluated using cyclic voltammetry. A three electrode cell configuration with Pt as the counter electrode is used for this work. Three-electrode configuration allows one electrode to be studied in isolation without complications from the electrochemistry of the other electrodes. The working electrode (here ITO substrate coated with the sample), dipped in an electrolyte solution (Acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate-$TBABF_4$), is biased with respect to the reference electrode (Ag/AgCl (3 M NaCl)), which has a known potential. When the bias reaches the