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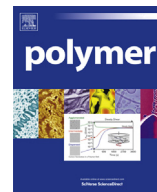
Cyanine dye polyelectrolytes for organic bilayer solar cells

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ABSTRACT

Polyelectrolytes composed of an anionic sulfoethyl methacrylate/methacrylate backbone and cationic cyanine dyes counter ions are synthesized. The effective reaction sequence is confirmed by NMR spectroscopy and consists of a thermal radical copolymerization to obtain the polymer backbone ($M_n \sim 40$ kg mol^{-1}), followed by deprotonation of the sulfoethyl group and a salt metathesis reaction with elimination of silver halide to incorporate the dye. With increasing cyanine content (20–50% of polymer repeating units) polyelectrolytes become insoluble in apolar solvents. This allows the fabrication of simple solution-processed bilayer organic solar cells, where an electron acceptor fullerene layer is coated from the orthogonal solvent chlorobenzene onto an underlying polyelectrolyte electron donor layer. The optimization of solar cells is described, and photo-CELIV measurements are used to identify the low hole mobility in the polyelectrolyte layer as the main reason that currently limits solar cell performance to ~0.9%.

1. Introduction

Polyelectrolytes (PEs) contain a backbone with pendant groups capable of ionizing in high dielectric media. Their solubility in polar solvent allows fabrication of multilayer organic electronic devices by solution coating techniques in combination with neutral semiconducting materials that are soluble in orthogonal nonpolar solvents [1].

The best-known PE for organic electronic device applications is probably poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS, that is coated as a thin film from a water suspension. PEDOT:PSS has widely been used as buffer layer on transparent conducting oxide electrodes in organic devices in which light enters or exits [2].

PEs (and other highly polar polymers [3,4]) have been successfully used as interfacial layer materials in thin-film transistors [5], organic light-emitting devices [6] and organic solar cells [7,8]. PEs as active layers have been applied in single-component light-emitting electrochemical cells [9] and light-emitting devices [10].

A double-layer structure was fabricated by using a cationic PE with fluoride anions coated on top of a neutral polymer containing anion-trapping groups. Application of a bias leads to charge injection and fluoride displacement into the neutral layer, where covalent bond formation takes place. Thereby, a stable p-n rectifying heterojunction and fast-responding light-emitting electrochemical behavior was obtained [11].

In a similar manner, ionic charge was exploited in cyanine dye organic solar cells. Cyanine dyes are charged semiconducting molecules that are accompanied by a counter anion. Therefore, cyanines have intrinsic built-in ionic and electronic charge conductivity. It has been demonstrated that the counter anions are relatively mobile and could be displaced within the cyanine layer and into adjacent layers. Thereby, ionic charge could be used to control the flow of electronic current [12,13].

Cyanine dyes have a number of interesting property characteristics for organic solar cell applications, such as tunable redox levels and wavelengths of absorption [14], very high light extinction coefficients, aggregate formation that facilitates exciton transport and good film forming properties from organic solvents [15].

Due to excessive phase separation resulting in coarse film morphology, efficient bulk heterojunction devices using blends of cyanines and soluble fullerenes could not be fabricated so far [14]. Regular bilayer electron donor cyanine/acceptor C_{60} solar cells with

power conversion efficiencies (PCE) of 2.9–3.6% have been demonstrated [16,17]. In these cases, the C_{60} film was deposited by evaporation, because no orthogonal solvent for the soluble fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) exists that would leave the cyanine layer unaffected during the coating step.

Clean bilayer C_{60} or PCBM/cyanine solar cells in the inverted geometry with PCE = 3.7% were also fabricated [18,19]. In contrast to the regular device architecture, in these cases the cyanines could be coated onto the underlying acceptor from alcohols, where the fullerenes are completely insoluble.

Here we demonstrate the first solution processed bilayer cyanine/PCBM regular solar cells. To this end, cyanine PEs were synthesized where the cationic dyes are electrostatically bound to an anionic polymer backbone. This is a different synthetic approach from the concept where the light-absorbing dye core constituted the PE backbone [20]. We describe the synthesis of the anionic PE backbone, followed by incorporation of the cyanine. The cyanine PEs showed a strongly decreased solubility in chlorinated solvents, which allowed the fabrication of solution-processed regular cyanine/PCBM solar cells. The optimization of solar cells is described and the low hole mobility in cyanine PEs films is identified as the main reason that currently limits the performance of these devices.

2. Experimental

2.1. Materials and methods

Unless stated otherwise, chemicals and solvents were used without further purification. Methyl methacrylate (MMA, distilled before use, Aldrich), 2-sulfoethyl methacrylate (H-MES, ABCR), 2,2′-azobis(2-methylpropionitrile) (AIBN, recrystallized from diethyl ether (Sigma−Aldrich) before use, Fluka), silver(I) oxide (Ag$_2$O, Sigma−Aldrich), methanol and ethanol (MeOH and EtOH, Sigma−Aldrich), dichloromethane (DCM, Sigma−Aldrich), tetrahydrofuran (THF, Merck), 1,3,3-trimethyl-2-[5-(1,3,3-trimethyl-1,3-dihydro-indol-2-ylidene)-penta-1,3-dienyl]-3H-indolium chloride (Cy5-Cl, FEW Chemicals), 1-ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium iodide (Cy3-I, FEW Chemicals), indium tin oxide-coated glass substrates (Glass/ITO, Thin Film Devices, 140 nm, resistivity 20 Ω square^{-1}), 2,2,3,3-tetrafluoropropanol (TFP, Sigma−Aldrich), chlorobenzene (CB, Sigma−Aldrich), molybdenum(VI) oxide (MoO$_3$, Aldrich), aluminum (Al, Lesker), calcium (Ca, CERAC), PCBM (Solenne).

NMR spectra were recorded on a Bruker AV-400 spectrometer. Thermogravimetric analysis was carried out on a Netzsch TG 209 F1, UV−vis spectra were measured on a Varian Cary 50 Scan or using an integrating sphere on a Horiba Jobin Yvon Fluorolog. X-ray fluorescence (XRF) spectra were measured on an ARL Advant XP.

Charge mobilities were measured using the technique of photoinduced charge carrier extraction by a linearly increasing voltage (photo-CELIV). Measurements were carried out under N_2 in a glove box with the commercial Paios system, Fluxim AG. Cy5-Poly/PCBM solar cells were illuminated for 30 μs using a blue LED (430−510 nm) and generated charge carriers were extracted by applying voltage ramps A ranging between 100 and 300 V ms^{-1}. Hole mobilities μ_{Cy5} were calculated using the modified formula [21]

$$\mu_{Cy5} = \frac{2d_{Cy5}(d_{Cy5} + d_{PCBM})}{3At_{max}^2} \cdot \frac{1}{\left(1 + 0.36\frac{\Delta j}{j_0}\right)} \quad (1)$$

where d_{Cy5} and d_{PCBM} are the layer thicknesses of Cy5-Poly and PCBM respectively, t_{max} is the peak position of the current, Δj is the peak height and j_0 is the capacitive displacement current. We assumed equal dielectric constants for Cy5-Poly and PCBM, and the formula accounts for the fact that the voltage is applied over the whole organic layer thickness, but that holes are formed at the heterojunction and have to travel only through the Cy5-Poly layer.

2.2. Polyelectrolyte synthesis

All reaction products were fully characterized with NMR spectroscopy and ^{1}H and ^{13}C chemical shifts were assigned. These data are compiled in the Supplementary Data.

2.2.1. Copolymerization of MMA and H-MES

Synthesis of Poly20. The synthesis of Poly20 is described as a representative example. Copolymers Poly30 and Poly50 were prepared accordingly. MMA (1 mL, 9.35 mmol) and H-MES (454 mg, 2.34 mmol) were dissolved in anhydrous THF (12 mL) under stirring. AIBN (9.7 mg, 0.059 mmol) was then added to the solution under nitrogen flow and the reaction flask was heated to 70 °C under reflux for 20 h. The solution was then cooled to room temperature, poured into diethyl ether (90 mL) and agitated for 5 min. The precipitate was collected by filtration and purified by washing twice with diethyl ether. Poly20 was then dried at 40 °C in vacuum (936 mg, yield 67%).

Synthesis of Poly30. MMA (1 mL, 9.35 mmol), H-MES (779 mg, 4.01 mmol), AIBN (11.0 mg, 0.067 mmol) and THF (14 mL) gave 1350 mg Poly30 (78%).

Synthesis of Poly50. MMA (0.63 mL, 5.89 mmol), H-MES (1.14 g, 5.87 mmol), AIBN (11.0 mg, 0.067 mmol) and THF (20 mL) gave 1233 mg Poly50 (71%).

2.2.2. Incorporation of cyanine dyes into polyelectrolytes

Synthesis of Cy5-Poly20. The synthesis of Cy5-Poly20 is described as a representative example. Other cyanine polyelectrolytes (Cy-Poly) were synthesized accordingly. Poly20 (200 mg containing 0.336 mmol sulfonic acid groups) and Ag$_2$O (117 mg, 0.505 mmol) were mixed in MeOH (15 mL). The reaction flask was covered with aluminum foil to prevent exposure to light and was then stirred at 60 °C for 6 h. Excessive Ag$_2$O was completely removed via a filtration−centrifugation−filtration cycle. Cy5-Cl (148 mg, 0.353 mmol) dissolved in MeOH (5 mL) was then added drop wise to the flask and the reaction mixture was stirred overnight. Subsequently, MeOH was added for dilution, the solution was centrifuged and AgCl was filtered. MeOH was then evaporated under reduced pressure and unreacted Cy5-Cl was removed by washing with EtOH for several times. EtOH was removed under reduced pressure and Cy5-Poly20 was dried under vacuum at 40 °C (170 mg, 52%).

Synthesis of Cy5-Poly30. Poly30 (200 mg containing 0.468 mmol sulfonic acid groups), Ag$_2$O (163 mg, 0.703 mmol), MeOH (20 mL) and Cy5-Cl (206 mg, 0.492 mmol) gave 179 mg Cy5-Poly30 (47%).

Synthesis of Cy5-Poly50. Poly50 (200 mg containing 0.68 mmol sulfonic acid groups), Ag$_2$O (236 mg, 1.02 mmol), MeOH (30 mL) and Cy5-Cl (299 mg, 0.714 mmol) gave 190 mg Cy5-Poly50 (28%).

Synthesis of Cy3-Poly20. Poly20 (200 mg containing 0.336 mmol sulfonic acid groups), Ag$_2$O (117 mg, 0.505 mmol), MeOH (15 mL) and Cy3-I (181 mg, 0.353 mmol) gave 171 mg Cy3-Poly20 (52%). For Cy3-Poly20, Cy3-Poly30 and Cy3-Poly50, unreacted Cy3-I was removed by washing thoroughly with 2-propanol instead of EtOH.

Synthesis of Cy3-Poly30. Poly30 (200 mg containing 0.468 mmol sulfonic acid groups), Ag$_2$O (163 mg, 0.703 mmol), MeOH (20 mL) and Cy3-I (252 mg, 0.492 mmol) gave 170 mg Cy3-Poly30 (45%).