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Polymerizable methanofullerene bearing a pendant acrylic group as a buffer layer material for inverted organic solar cells

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Inverted organic solar cells have been designed using an electron-selective buffer layer composed of a blend of a polymerizable methanofullerene with an acrylic pendant group and a quaternized pyrrolidinofullerene as an iodine salt.

Alternative energy resources become more and more important because fossil fuel reserves have declined rapidly.[1] The combustion of oil, coal and gas releases greenhouse gases into the atmosphere. The continuously increasing concentration of carbon dioxide in air leads to a global climate change.[2] In this context, the efficient conversion of wind and sunlight energy into electricity becomes extremely important. Organic solar cells form a promising area of research directed toward the implementation of third-generation photovoltaic technologies.[3] The laboratory prototypes of organic solar cells have already shown power conversion efficiency of more than 10%, and it can be further increased.[4] Practical implementation of organic solar cells requires their long-term stability, which is reachable only for devices with an inverted configuration.[5]

Highly efficient inverted organic solar cells comprise some charge-selective buffer layers in their structure.[6] Many n-type[7] and p-type metal oxides,[8] alkali metal salts,[9] self-assembling monolayers[10] and conjugated polymers[11] are widely used for this purpose. Special attention is paid to the buffer layers based on fullerene derivatives since they can effectively interact with the electron-acceptor components of the photoactive layer of a solar cell.[12]

In this work, we propose electron-selective buffer layers (ETL) in inverted organic solar cells using the blends of a polymerizable acrylate derivative of [60]fullerene (MAF) and pyrrolidinofullerene (FPI) (Figure 1). A fullerene derivative similar to FPI was studied previously as an n-type buffer layer material for solar cells.[13] The synthesis of MAF was reported previously.[14] FPI was synthesized according to a published procedure.[15] The photoactive layer of organic solar cells was composed of the blends of the fullerene derivative [60]PCBM and a conjugated polymer P3HT (Rieke Metals) or PCDTBT,[16] which was synthesized in our laboratory.[17]

The solar cells were fabricated as follows: a glass substrate coated with a layer of indium-tin oxide (ITO) was successively cleaned with water, acetone and isopropyl alcohol in an ultrasonic bath. The precursor solution containing MAF in various concentrations (1.25, 2.5 and 5.0 mg ml^{-1}, respectively) and FPI

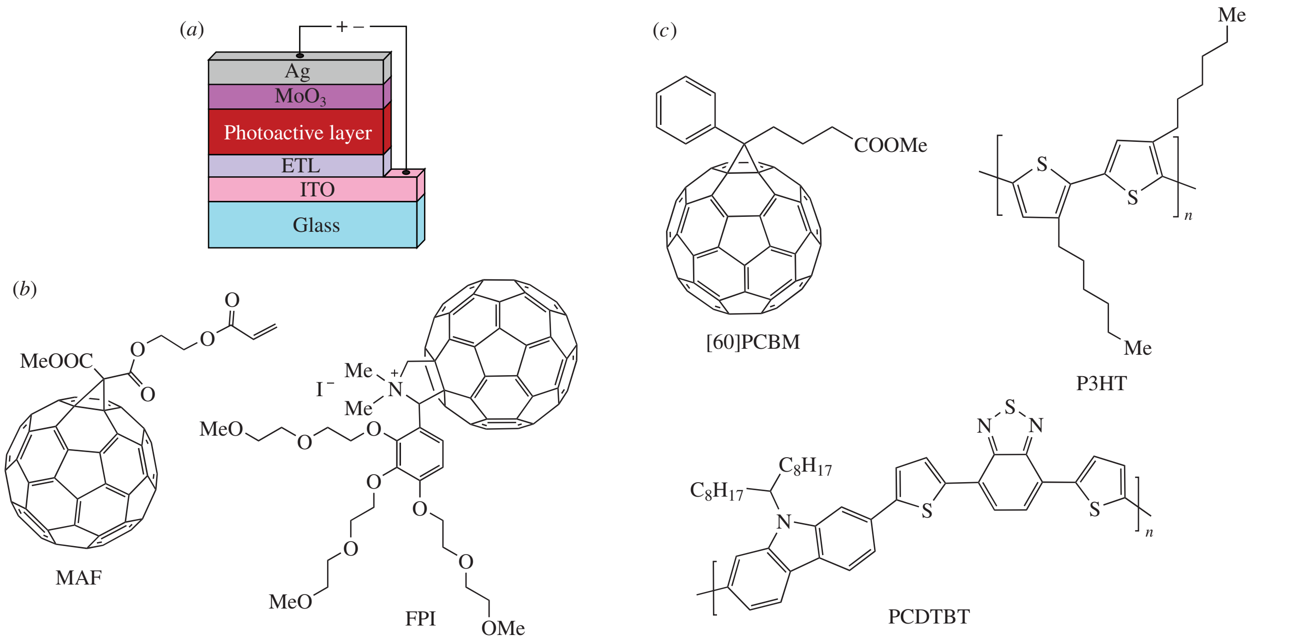

Figure 1 (*a*) Schematic architecture of an inverted organic solar cell. The molecular structures of the materials used to form (*b*) the ETL buffer layer and (*c*) the photoactive layer of the devices.

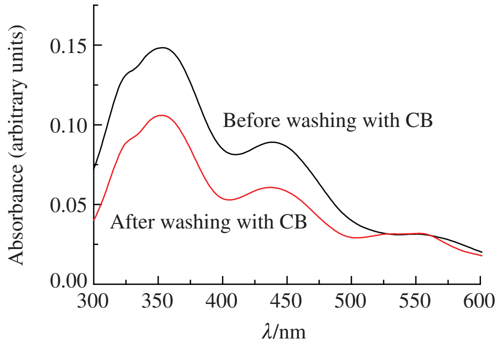

Figure 2 Absorption spectra of the cross-linked MAF+FPI films before and after washing with chlorobenzene (CB); MAF concentration in the precursor solution was 1.25 mg ml^{-1}.

(25 mol% with respect to MAF) was spin-coated on the dried substrates at 1000 rpm. The resulting films were annealed under argon at 230 °C for 30 min. In this case, the thermal polymerization of C_{60} derivatives resulted in the formation of fullerene-based insoluble coatings. Monomer residues were washed away from the surface of the films using chlorobenzene (12 drops applied onto the sample rotating at 6000 rpm).

Figure 2 shows the absorption spectra of the thin films (the spectra were recorded on an Avantes 2048 fiber spectrometer). Washing the films with chlorobenzene reduced their optical density by ~30% thus indicating the removal of unpolymerized MAF and FPI species.

Semiconductor materials P3HT (12 mg) and [60]PCBM (6.75 mg) or PCDTBT (6 mg) and [60]PCBM (24 mg) were dissolved in 1 ml of chlorobenzene or 1,2-dichlorobenzene, respectively, with stirring on a magnetic stirrer at 40–45 °C for 30 h. Photoactive layer was spin coated on the substrates covered with ETL at 600–900 rpm. The obtained films were annealed under an inert atmosphere at 165 °C for 3 min (P3HT/[60]PCBM) or at 90 °C for 15 min (PCDTBT/[60]PCBM). Hole-transport

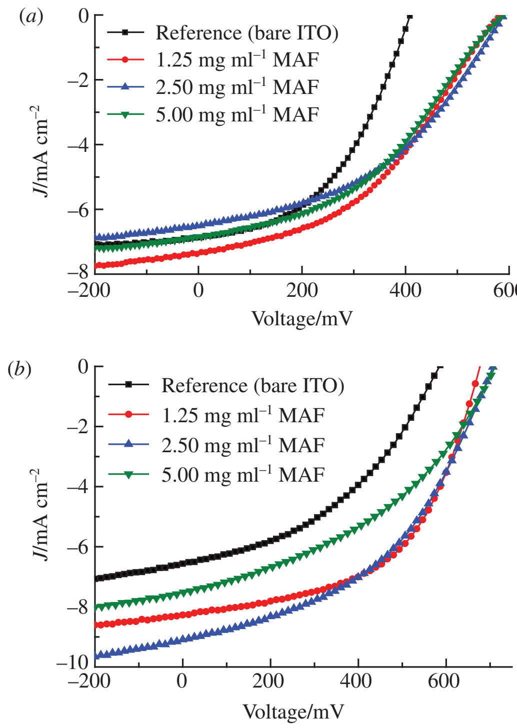

Figure 3 Current-voltage characteristics of (*a*) inverted P3HT/[60]PCBM and (*b*) inverted PCDTBT/[60]PCBM organic solar cells comprising MAF + FPI buffer layers as a function of MAF concentration in the precursor solution.

Table 1 Parameters of the inverted organic solar cells.

Photoactive materials	Concentration of MAF in the precursor solution/ mg ml^{-1} [a]	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF (%)	η (%)
P3HT/[60]PCBM	—	409	6.9	46	1.3
	1.25	582	7.4	42	1.8
	2.50	591	6.5	43	1.7
	5.00	486	7.0	43	1.5
PCDTBT/[60]PCBM	—	585	6.6	42	1.6
	0.625	618	11.1	39	2.7
	1.25	677	8.3	54	3.0
	2.50	707	9.1	46	2.9
	5.00	712	7.5	41	2.2

[a] The concentration of FPI in the precursor solutions was always 25 mol% with respect to the amount of MAF.

layer of MoO_3 (3 nm) and the top silver electrodes were deposited by resistive evaporation in a vacuum (4×10^{-6} mbar).

The current-voltage characteristics of organic solar cells (Figure 3) were measured under standard conditions using simulated solar AM 1.5 illumination (100 mW cm^{-2}, a calibrated Si diode was used as a reference) and a Keithley 2400 source-measurement unit. The main parameters of the solar cells are given in Table 1.

The obtained results suggest that the electron-selective buffer layers based on the blends of the fullerene derivatives FPI and polymerizable MAF can be successfully used for fabricating inverted organic solar cells. The power conversion efficiencies for the inverted devices were only 25–30% lower than the parameters of the standard configuration organic solar cells. However, the latter contain a reactive metal (calcium in our case) cathode that induces inherent instability leading to the rapid deterioration of the device parameters even under an inert atmosphere. Inverted devices showed lower open-circuit voltages (approximately by 100 mV) and fill factors as compared to the standard ones. It is very likely that the electron work function of the fullerene-based buffer layer material is too high with respect to the conduction band (LUMO level) position of the n-type component of the photoactive layer ([60]PCBM). Therefore, a Schottky-type barrier might be formed at the interface between the photoactive and the buffer layers. This might be a plausible reason for the observed reduction of the open-circuit voltages and fill factors of the inverted devices.

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