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Mendeleev Commun., 2015, **25**, 348–349

Mendeleev Communications

Acrylate and methacrylate derivatives of fullerenes as electron-selective buffer layer materials for inverted organic solar cells

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DOI: 10.1016/j.mencom.2015.09.010

Inverted organic solar cells were designed using the acrylic and methacrylic derivatives of C_{60} as buffer layer materials. The highest power conversion efficiency was reached for solar cells comprising the methacrylic derivative {(1-methoxycarbonyl-1-[2-(methacryloyloxy)ethoxycarbonyl]-1,2-methane)}-1,2-dihydro-C_{60}-fullerene.

The development and implementation of alternative energy sources is a problem of considerable current interest because solar energy is environmentally friendly. Organic photovoltaics has a number of advantages over inorganic solar cells. The potentially low cost, high production efficiency and easy recycling are important benefits from a technological point of view.[1] In addition, plastic solar cells are light (important for mobile devices) and flexible, and they can be coated on a curved surface and even integrated into fabrics.[2] The growing interest in this research area is related to a rapid increase in the efficiency of organic solar cells.[3]

New combinations of semiconductor materials based on fullerene derivatives (n-type materials) and electron-donor conjugated polymers (p-type materials) have been actively developed.[4] It is believed that the high efficiency of solar light conversion in organic solar cells can be achieved only by using charge-selective buffer layers.[5] The typical materials for producing such layers include poly(3,4-ethylenedioxythiophene) : polystyrene sulfonate (PEDOT : PSS) and inorganic oxides.[6] PEDOT : PSS exhibits acidic properties and affects severely the operation lifetime of organic solar cells.[7] At the same time, metal oxides in high valence states (MoO_3, V_2O_5 and WO_3) behave as strong oxidizers and damage the photoactive layer materials. This problem is observed even in relatively inert titanium dioxide.[8]

An inverted configuration of organic solar cells has the greatest prospects in terms of practical implementation since it incorporates no highly active metals; this leads to a significantly increased operational stability.[9] However, the construction of these devices requires electron-selective transport buffer layers based on the n-type semiconductors (ETL, Figure 1). Here, we address this problem and propose to apply polymerizable methanofullerenes **1** and **2** comprising unsaturated acrylate and methacrylate fragments [Figure 1(*b*)] for the construction of ETL. The synthesis of these compounds was reported previously.[10]

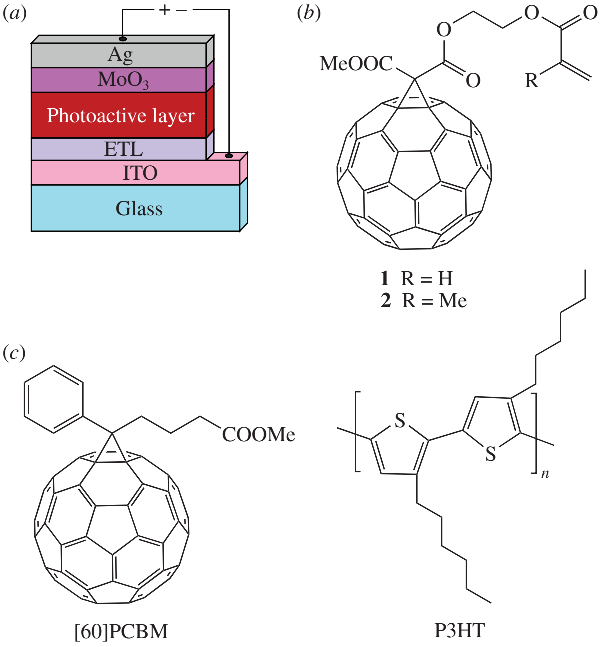

Figure 1 (*a*) Schematic layout of an inverted organic solar cell and the molecular structures of (*b*) methanofullerenes **1** and **2** and (*c*) photoactive materials [60]PCBM and P3HT.

The current–voltage characteristics of organic solar cells[†] were measured under standard conditions using simulated AM 1.5 illumination with an intensity of 100 mW cm^{-2} (a calibrated Si diode was used as a reference) and a Keithley 2400 source-

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[†] The organic solar cells were fabricated as follows: glass substrates coated with an indium–tin oxide layer (ITO, 15 Ohm/sq.) were cleaned by successive sonication in water, acetone and isopropanol. A chlorobenzene solution containing an acrylate or methacrylate fullerene derivative (**1** or **2**, 5 mg cm^{-3}) and azobisisobutyronitrile (0.1 mg cm^{-3}, Aldrich) was deposited on dried substrates by spin coating at 1000 rpm. The obtained films were annealed at 120, 160 and 200 °C (**2**) for 2 h in an inert atmosphere, which resulted in the partial polymerization of fullerene derivatives. After that, the samples were washed with *o*-dichlorobenzene on a spin coater (12 drops on the sample rotating at 6000 rpm) to remove residual monomers from the polymer film surface. Then, with no additional operations, the photoactive composite based on the regioregular poly(3-hexylthiophene) P3HT (Rieke Metals) and the fullerene derivative [60]PCBM was deposited at 900 rpm. A solution of the photoactive components was prepared by stirring P3HT (12 mg) and [60]PCBM (6.75 mg) in 1 ml of chlorobenzene at room temperature for 24 h. The obtained photoactive films were annealed at 165 °C for 3 min under an argon atmosphere. Next, a hole-transport layer of MoO_3 (3 nm) and silver top electrodes (100 nm) were deposited by resistive evaporation *in vacuo* (2×10^{-6} mbar).

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Table 1 Parameters of the best inverted solar cells fabricated on bare ITO and using buffer layers formed from polymerized **1** and **2**.

Buffer layer	T^a_{polym}/°C	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF (%)	η (%)
–	–	437	7.2	46	1.5
1	120	542	7.5	50	2.0
	160	526	6.8	47	1.7
2	120	608	7.5	55	2.5
	160	652	8.2	50	2.7
	200	528	7.8	38	1.6

[a] Annealing temperature of the buffer layer materials **1** and **2** is provided.

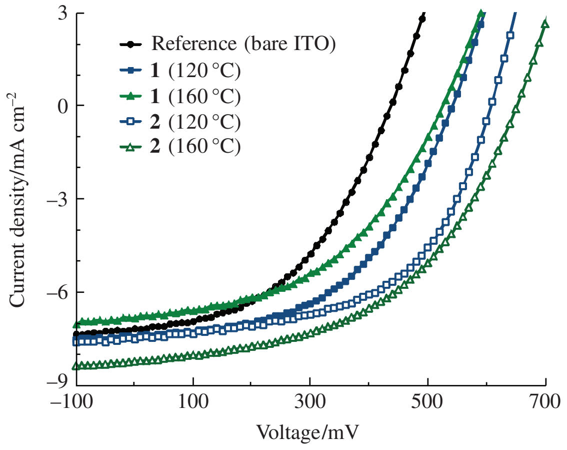

Figure 2 Selected J–V characteristics of the inverted P3HT/[60]PCBM solar cells prepared on bare ITO (reference) and using buffer layers based on the polymerized **1** or **2**.

measurement unit. The current–voltage curves are shown in Figure 2. The device parameters are given in Table 1.

The experimental data clearly demonstrate a positive influence of the buffer layers (polymerized fullerene derivatives **1** and **2**) on the characteristics of the solar cells. Particularly exciting were high open-circuit voltages of 637–652 mV achieved under optimal conditions by the use of polymerized **2** as a buffer layer. Note that these high voltages are very rare for the P3HT–PCBM solar cells.[11]

An increase in the temperature used for inducing the polymerization of **1** and **2** leads to deterioration of the power conversion efficiencies of organic solar cells. This behavior can be explained based on the results of thermogravimetric analysis (Figure 3). Compounds **1** and **2** decompose at temperatures below 200 °C. The weight loss of 16.7 % observed for compound **1** at the first decomposition stage corresponds to the cleavage of the $CH_2{=}CHCOOCH_2CH_2$ unit and methoxycarbonyl group affording methano[60]fullerene-61-carboxylic acid **A1** as a product. This result correlates well with published data.[12] Note that compound **2** decomposes at the first stage (weight loss of 11.8%) with the formation of 1-(methoxycarbonyl)methano[60]fullerene-61-carboxylic acid **A2**.

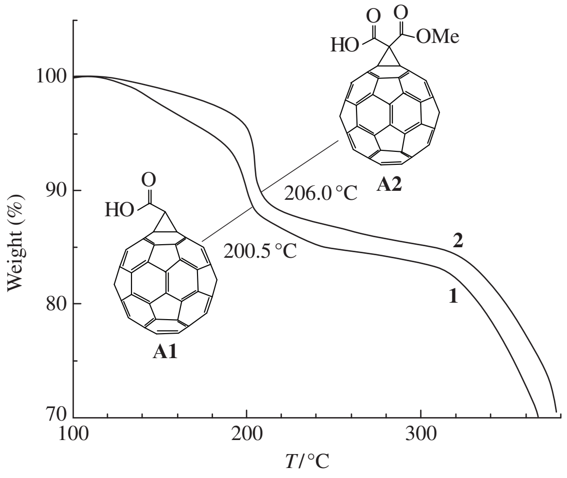

Figure 3 TGA profiles for methanofullerenes **1** and **2**.

The results of the thermogravimetric analysis clearly indicate that methanofullerenes **1** and **2** undergo partial decomposition when they are polymerized at temperatures above 160 °C. The degradation products containing carboxyl groups can act as traps for mobile charge carriers, which might be responsible for the observed decrease in the efficiency of solar cells (Table 1). Therefore, a further research could be focused on the design of new acrylate and methacrylate fullerene derivatives with enhanced thermal stability.

Thus, we have demonstrated the potential of polymerizable acrylate and methacrylate fullerene derivatives for constructing electron-selective buffer layers in inverted organic solar cells. The obtained solar cell parameters, in particular, the unusually high open-circuit voltage reaching 637–652 mV for the P3HT/[60]PCBM system, point to the prospects of further exploration of this research.

This work was supported by the Russian President Science Foundation (grant no. MK-5260.2014.3) and the Russian Foundation for Basic Research (grant nos. 14-03-31913, 14-03-31681 and 14-03-31610).

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Received: 24th February 2015; Com. 15/4571