Towards polymerizable fullerene derivatives to stabilize the initially formed phases in bulk-heterojunction solar cells†

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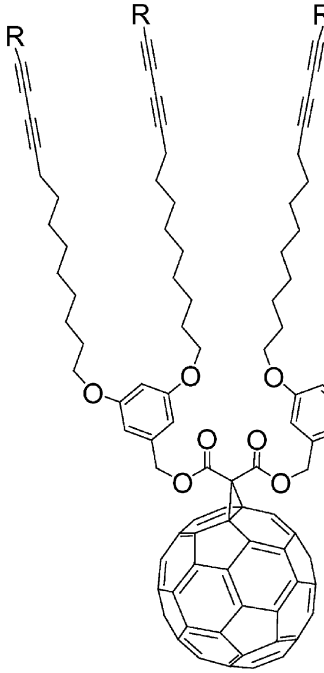
Photovoltaic cells have been prepared with blends of a polymerizable methanofullerene derivative bearing four butadiyne subunits and MDMO-PPV; annealing at 100 °C for 2 hours resulted in an improvement of the performances of the devices and AFM studies suggested that cross-linking polymerization of the fullerene derivative is capable of stabilizing the initially formed phases.

Following the observation of ultrafast photoinduced electron transfer from conjugated polymers to C_{60},[1] a novel approach to the preparation of solar cells has been proposed.[2] It is based on an interpenetrating blend of donor (conjugated polymer) and acceptor (C_{60}) sandwiched between two asymmetric contacts. Remarkably, the efficiency of the bulk heterojunction devices consisting of poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-*p*-phenylene vinylene (MDMO-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61} (PCBM) have been increased up to 3% by the group of Sariciftci.[3] It is worth noting that the performance of this type of solar cell is very sensitive to the morphology of the blend.[3–5] In particular, phase separation and clustering of the fullerene can occur due to the operational heat through illumination, thus reducing the effective donor/acceptor interfacial area and the efficiency of the devices. In order to prevent such undesirable effects, we have recently proposed an all-polymer approach for the preparation of donor/acceptor bulk heterojunction photovoltaic cells.[6] The initially formed phases obtained from the polymer/polymer mixtures are effectively more stable; however, the short circuit current and the open circuit voltage of the first devices are low when compared to the optimized MDMO-PPV/PCBM solar cells. This has been ascribed to the low conductivity of the fullerene polymer due to the presence of the large solubilizing groups necessary to obtain soluble material.[6] As part of this research, we now report the preparation of the fullerene-functionalized monomer **1** allowing polymerization in the bulk and its incorporation in photovoltaic devices.[7] Ideally, a blend of the monomer and MDMO-PPV is prepared first, then the initially formed phases can be fixed by cross-linking polymerization of compound **1**. In this way, the tedious preparation of fullerene-rich polymers is avoided and the size of the solubilizing groups can be dramatically reduced. In the design of compound **1**, it was decided to use butadiyne functions as polymerisable units since the fullerene should not be affected by the polymerization reaction.[8]



1 R = C_5H_{11}

The strategy employed for the preparation of the functionalized methanofullerene derivative **1** is based upon Bingel type chemistry.[9] To this end, malonate **9** was prepared in six steps from 1-heptyne (**2**) and undec-10-ynoic acid (**3**) (Scheme 1). Reaction of **2** and **3** in CH_2Cl_2 under dry air in the presence of an excess of the Hay catalyst (CuCl, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine = TMEDA, dry air) furnished compound **4** in 40% yield. $LiAlH_4$ reduction of **4** followed by treatment of the resulting **5** with *p*-toluenesulfonyl chloride (TsCl) in the presence of pyridine and 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 yielded tosylate **6**. Subsequent reaction with methyl 3,5-dihydroxybenzoate under classical Williamson conditions afforded ester **7** in 71% yield. Reduction with $LiAlH_4$ then gave benzylic alcohol **8** in 75% yield. Treatment of **8** with malonyl chloride in CH_2Cl_2/pyridine finally afforded malonate

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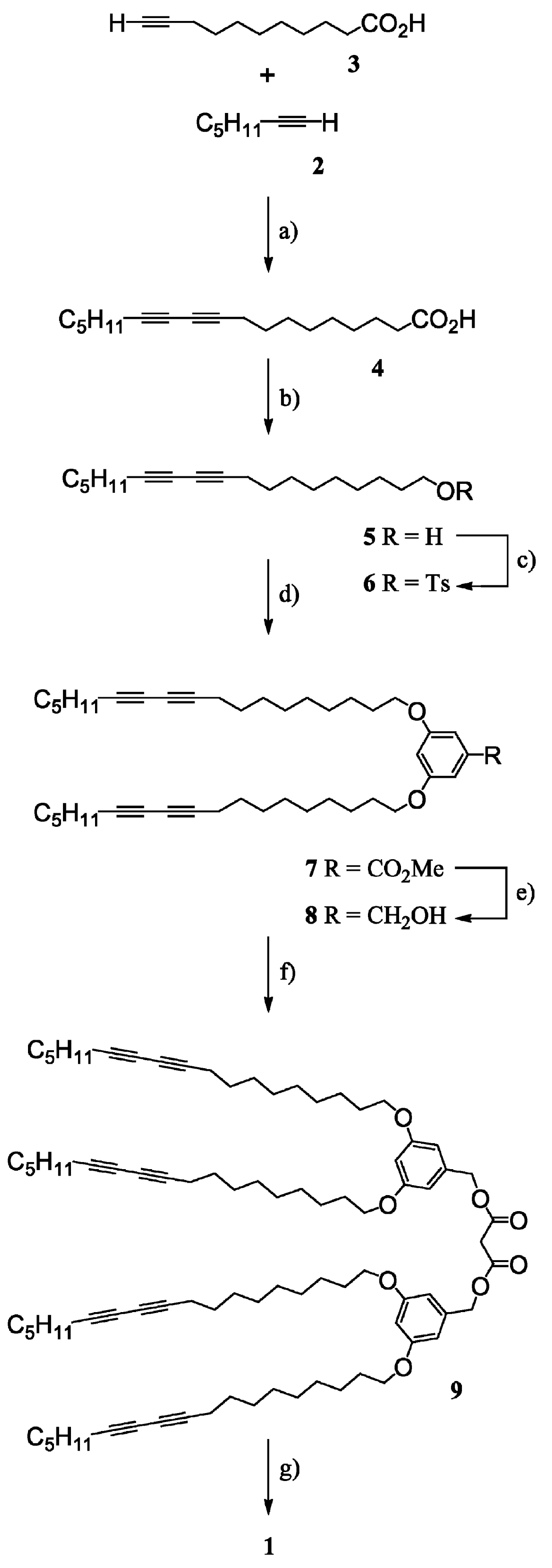
† Part of this work has been reported in a patent (UK patent, application 0413398.9, June 2004).



Scheme 1 Preparation of methanofullerene derivative **1**. Reactant and conditions: (a) CuCl, TMEDA, dry air, CH_2Cl_2, room temp., 24 h (40%); (b) $LiAlH_4$, THF, 0 °C, 4 h (95%); (c) TsCl, pyridine, DMAP, CH_2Cl_2, 0 °C, 18 h (64%); (d) methyl 3,5-dihydroxybenzoate, K_2CO_3, DMF, 70 °C, 24 h (71%); (e) $LiAlH_4$, THF, 0 °C, 3 h (75%); (f) malonyl chloride, pyridine, DMAP, CH_2Cl_2, room temp., 20 h (62%); (g) C_{60}, I_2, DBU, toluene, room temp., 14 h (53%).

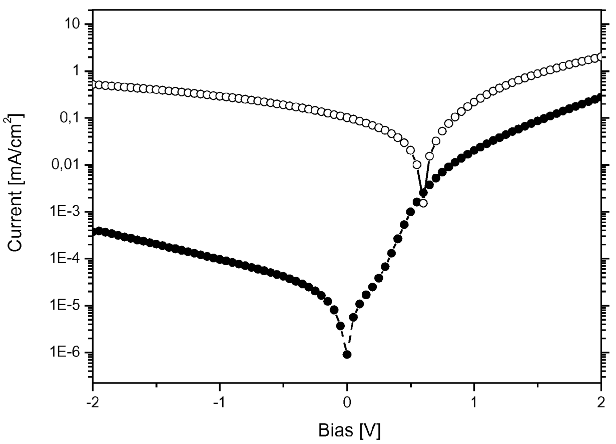


Fig. 1 Current–voltage (I/V) characteristics in the dark (black circles) and under illumination (open circles) of a MDMO-PPV/**1** device with a Ca/Al cathode.

9. The reaction of C_{60} with compound **9**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under Bingel conditions then gave methanofullerene **1** in 53% yield. The structure and purity of compound **1** were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and elemental analysis. Compound **1** could be stored for several months in the freezer without significant degradation. It is also reasonably stable at room temperature in the neat state. In contrast, when compound **1** is heated at 100 °C for 1 h, an insoluble dark red material is obtained suggesting that polymerization occurred. It can be noted that the UV/Vis spectra of a spin coated thin film of compound **1** before and after heating at 100 °C for one hour are similar. The latter observation shows that the fullerene chromophore is not affected by the polymerization of the butadiyne subunits. In addition, it also reveals that the solid state reaction of the butadiyne moieties does not produce polydiacetylene (PDA) polymers. This is expected since the reactive subunits are not pre-organized to allow the formation of extended conjugated PDA chains.

In order to test the potential of fullerene derivative **1** for photovoltaic applications, solar cells were prepared with blends of **1** and MDMO-PPV, then characterized before any thermal treatment. A mixture of MDMO-PPV and **1** (1 : 5 by weight) was spin coated from a chlorobenzene solution on top of a 100 nm (surface profiler (Veeco Dektak 3ST)) thick layer of poly(ethylene dioxythiophene)-polystyrene sulfonate (PEDOT:PSS, Baytron P)-covered indium-tin oxide (ITO) substrate. The resulting thickness of the layer was determined with a surface profiler to be 90 nm. Calcium (15 nm) and aluminium (150 nm) were evaporated on the composite layer. The devices were measured under nitrogen in a glove box. The current/voltage (I/V) characteristics in the dark and under illumination (standard AM1.5 conditions) are depicted in Fig. 1. These cells exhibit a short circuit current (I_{sc}) of 0.1 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.59 V and a fill factor (FF) of 0.27.

In a second set of experiments, the Ca/Al cathode was replaced by silver (150 nm). To study their thermal stability, these devices were annealed at 100 °C for 2 hours in the glove

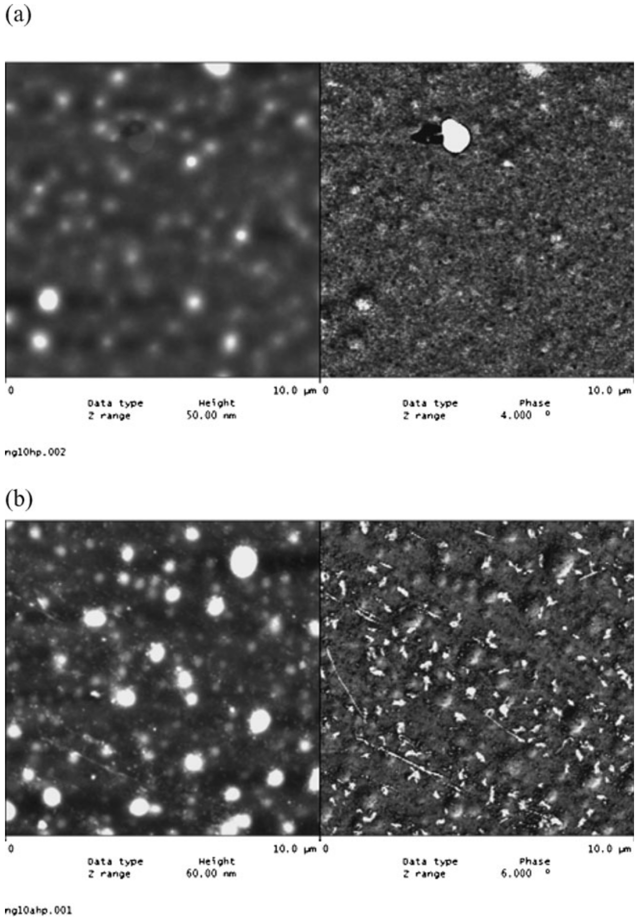


Fig. 2 AFM pictures of MDMO-PPV/**1** before (a) and after annealing (b).

box. During this treatment, polymerization of **1** might occur. In addition, the influence of the remaining solvent present in the active layer on the cathode is thus reduced. Interestingly, the annealing resulted in a slight improvement of the performances (before annealing: $I_{sc} = 0.034$ mA cm^{-2}, $V_{oc} = 0.6$ V, FF = 0.22; after annealing $I_{sc} = 0.037$ mA cm^{-2}, $V_{oc} = 0.61$ V, FF = 0.26). This effect has also been observed for polythiophene/PCBM composites,[10] but it can be noted that the MDMO-PPV/PCBM devices degrade upon annealing.

In order to gain more insight into the morphological changes occurring during the thermal treatment, tapping mode atomic force microscopy (TM-AFM) studies have been carried out. The TM-AFM pictures of the MDMO-PPV/**1** film (see Fig. 2) show features of 0.2–0.6 µm widths and a height difference of 60 nm. Through annealing the roughness of the surface increases (height difference of 70 nm). Additionally, new features with a diameter of 0.1–0.4 µm can be observed in the height and phase picture. The morphological changes observed after annealing the MDMO-PPV/**1** are however much smaller than the observed separated phases in the MDMO-PPV/PCBM composites. This is a clear indication that cross-linking of compound **1** is capable of stabilizing the initially formed phases.

A new methanofullerene derivative bearing four butadiene subunits has been prepared. Preliminary studies indicate that this compound is able to form a polymeric film upon heating without affecting the fullerene chromophore. The potential of this new fullerene derivative for the preparation of bulk heterojunction photovoltaic cells has been evaluated. The results obtained with our first devices are quite promising. Further investigations are still underway for a complete characterization of the polymer obtained after thermal treatment and to optimize the performances of these solar cells.

Experimental

Compound 9

Malonyl dichloride (85 mg, 0.60 mmol) was added to a stirred degassed solution of **8** (0.76 g, 1.20 mmol), pyridine (0.098 mL, 1.21 mmol) and DMAP (40 mg, 0.30 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The solution was warmed slowly to room temperature (over 1 h) and stirred for 20 h. The resulting CH_2Cl_2 solution was washed with water, dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2) yielded **9** (490 mg, 62% yield) as a colourless glassy product. ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.90$ (t, $^3J = 6$ Hz, 12H), 1.20–1.85 (m, 80H), 2.25 (t, $^3J = 6$ Hz, 16H), 3.49 (s, 2H), 3.91 (t, $^3J = 6$ Hz, 8H), 5.10 (s, 4H), 6.40 (s, 2H), 6.46 (s, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 13.88$, 19.11, 22.11, 25.96, 27.99, 28.27, 28.75, 28.98, 29.18, 29.28, 29.33, 30.94, 41.44, 65.19, 65.23, 67.16, 67.98, 77.41, 77.49, 101.08, 106.28, 137.14, 160.40, 166.17.

Compound 1

DBU (0.3 mL, 1.8 mmol) was added to a stirred solution of C_{60} (325 mg, 0.45 mmol), I_2 (177 mg, 0.7 mmol) and **9** (600 mg, 0.45 mmol) in toluene (450 mL). The solution was stirred for 14 h, then filtered through a short plug of SiO_2, eluting first with toluene (to remove unreacted C_{60}) and then with CH_2Cl_2. Column chromatography (SiO_2, toluene–hexane 7 : 3) yielded **1** (490 mg, 53%). Dark red glassy product. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 0.90$ (t, $^3J = 6$ Hz, 12H), 1.20–1.85 (m, 80H), 2.24 (t, $^3J = 6$ Hz, 16H), 3.89 (t, $^3J = 6$ Hz, 8H), 5.43 (s, 4H), 6.40 (s, 2H), 6.58 (d, $^4J = 2$ Hz, 4H); ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 13.96$, 19.10, 22.08, 26.01, 27.96, 28.24, 28.76, 28.96, 29.18, 29.29, 29.34, 30.91, 51.75, 65.27, 65.31, 67.93, 68.71, 71.30, 77.36, 77.45, 101.48, 106.70, 136.49, 138.89, 140.69, 141.71, 142.00, 142.78, 142.86, 143.65, 144.31, 144.39, 144.49, 144.71, 144.82, 144.95, 145.00, 145.05, 160.37, 163.18; IR (CH_2Cl_2): 1749 cm^{-1} (C═O); Elemental analysis calc. for $C_{149}H_{126}O_8$: C 87.53%, H 6.21%; found C 82.97%, H 5.96%; FAB (MS): 2044.8 (10%, M$^+$, calc. for $C_{149}H_{126}O_8$: 2044.63); 720.0 (100%, $[C_{60}]^+$, calc. for C_{60}: 720.00).

Acknowledgements

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