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Abstract. Cyclopropano[70]fullerenes have been synthesized in the aim of being used as acceptors in blends based on regioregular poly (3,5-Hexylthiophene) *RR*-P3HT for photovoltaic (PV) plastic cells. These molecules used with *RR*-P3HT in bulk heterojunction (BHJ) configuration provided interesting characteristics: 1.5% solar conversion efficiency, 9.29 mA/cm^2 current density, 0.51 V open circuit voltage, and 0.34 fill factor. The IPCE spectrum for P3HT: cyclopropano[70]fullerene cells shows a peak around 430 nm with 71% external quantum efficiency. This result justifies the increased current density. © *2011 Society of Photo-Optical Instrumentation Engineers (SPIE)*. [DOI: 10.1117/1.3576907]

1 Introduction

Since the discovery of photoinduced electron transfer between semiconducting conjugated polymers and fullerenes, several investigations were made.[1] Bulk heterojunction plastic cells (BHJs) based on composites of semiconducting polymers (as electron donors) and fullerene derivatives (as electron acceptors) were studied for their performances. The BHJ devices exhibit a vast interfacial area dispersed throughout the bulk. However, the overall conversion efficiency of these devices is limited by the carrier collection efficiency, which is greatly influenced by the morphology and the phase separation within the active film.[2–4] Generally the morphology optimization of the active layers is of primary importance to improve the exciton dissociation efficiency, the transport of free charge carriers, and their extraction from the photoactive layer. To date, there were not many studies made on the functionalization of C$_{70}$ for the photovoltaic (PV) application besides those already published on the PC$_{70}$BM and the PC$_{85}$BM. Using PC$_{70}$BM into a photoactive layer increases the η% of the cells in both BHJ samples and tandem cases where it was permitted to reach 6%. In 2008, Heeger and co-workers obtained a 5.6% conversion using a photoactive layer based on PC$_{70}$BM and the low bandgap polymer PCPDTBT.[5] Improved photovoltaic properties were obtained for solar cells based on copolymer {thieno[3,4-b]thiophene and benzodithiophene polymers (PTBs)} by Luping Yu's team. The broad absorption of this copolymer increased the short circuit current density (J_{SC}) of cells to 14.5 mA/cm^2 with power efficiency around 7.4%.[6] In our previous work, organic solar cells elaborated from the cyclopropano[60]fullerenes,[7,8] provided promising PV
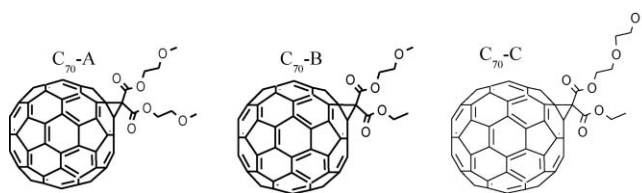
Fig. 1 Molecular structure of cyclopropano[70] fullerene derivatives C_{70}-A, C_{70}-B, and C_{70}-C.

performances, with power conversion and current density above 1.2% and 7.2 mA/cm^2, respectively. The effects of molecular structure on morphology and PV characteristics of *RR*-P3HT {poly (3,5 Hexylthiophene): cyclopropano[60]fullerenes} were studied. Along the same lines, cyclopropano[70]fullerenes were synthesised in order to study PV characteristics, keeping in mind that this family of fullerene C_{70} derivatives has a broader absorption in the visible region (see Fig. 1). One should note that this Bingel type approach of fullerene C_{70} functionalization is original, and was never studied before.

2 Experimental Section

Compounds C_{70}-A, C_{70}-B, and C_{70}-C and C_{70} were analyzed in 7×10^{-4} mol l^{-1} dichloromethane (CH$_2$Cl$_2$) (HPLC grade) solutions containing 5×10^{-2} mol l^{-1} n-Bu$_4$NPF$_6$ as a supporting electrolyte. Electrochemical experiments were performed in a dry, oxygen-free (<0.1 ppm), argon glove box at room temperature with a platinum working electrode. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat-galvanostat. Reduction potential was measured using a silver wire pseudo-reference electrode in reference with internal standard ferrocenium ion/ferrocene (Fc$^+$/Fc) redox couple. The scan rate used in this study was 100 mV/s.

Absorption spectra were recorded at room temperature with a Lambda 19 Perkin–Elmer spectrometer. These measurements were done on thin films based on composite P3HT: C_{70} fullerene derivatives.

The substrates PEDOT:PSS {Poly(3,4 ethylenedioxythiophene): poly(styrenesulfonate)} coated ITO anode from Merck were first dried in an oven at 150°C during 10 min. The blend of *RR*-P3HT (Rieke): fullerene derivatives was dissolved in chlorobenzene solution. An active layer of *RR*-P3HT:cyclopropano[70]fullerene was deposited by spin coating over the PEDOT: PSS from Baytron P. Therefore, the LiF(Aldrich)-Al (Goodfellow) cathode was deposited by evaporation under a 4×10^{-7} mBar argon pressure, on top of the photoactive layer.[9] The size of the active area is 0.32 cm^2. The cells ITO/PEDOT: PSS (40 nm)/*RR*-P3HT:cyclopropano[70]fullerene(80 nm)/LiF(0.7 nm)/Al(100 nm) were characterized and annealed in the glove box. The PV measurements were carried out before and after heat treatment. The PV properties were measured using a Keithley 236 unit in the dark and under AM 1.5 illumination with 575 Steuernagel solar simulator, through the back side (ITO) of the solar cells. The conversion efficiency η% is calculated using:

$$\eta\% = (\text{ff}^* J_{\text{sc}}^* V_{\text{oc}})/P_{\text{inc}}, \tag{1}$$

Table 1 Redox potentials of compounds C_{70}-A, C_{70}-B, and C_{70}-C.

Molecule	$E^1_{1/2\text{red}}$ (V)	$E^2_{1/2\text{red}}$ (V)	$E^3_{1/2\text{red}}$ (V)
C_{70}	−1.00	−1.39	−1.80
C_{70}-A	−1.07	−1.44	−1.82
C_{70}-B	−1.07	−1.44	−1.82
C_{70}-C	−1.07	−1.44	−1.82
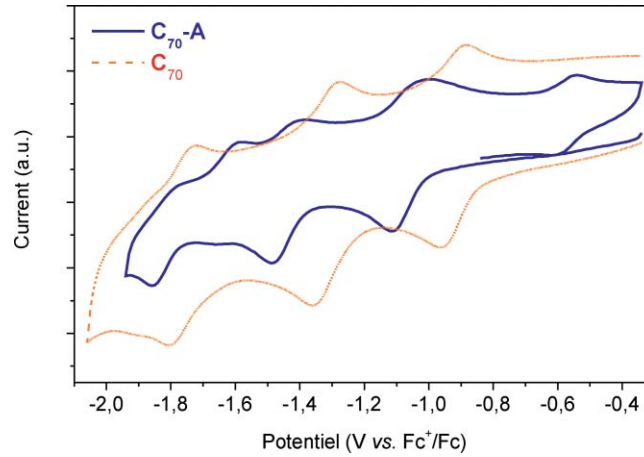
Fig. 2 Cyclic voltammograms of derivatives C_{70}-A and C_{70}.

Table 2 Relative quantities in mass of derivatives C_{70}-A, C_{70}-B, and C_{70}-C used in photoactive layer.

Fullerene compound C	Molecular weight M_C (g mol^{-1})	Compound molecular weight ratio M_C/M_{PCBM}	X mass used in mixtures (P3HT: X) (10 mg: X mg)
C_{70}-A	1058	1.16	11.6
C_{70}-B	1028	1.13	11.3
C_{70}-C	1072	1.18	11.8
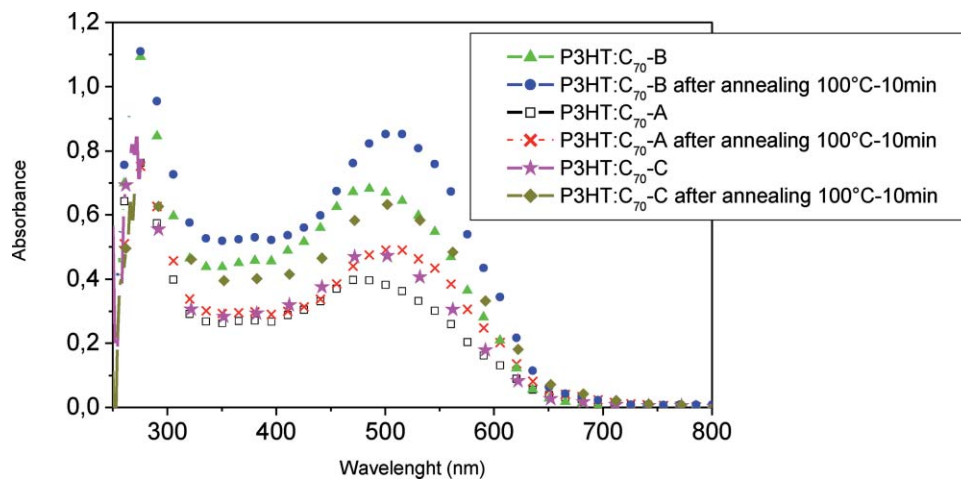
Fig. 3 Absorption spectra of various composites *RR*-P3HT: C_{70}-A, *RR*-P3HT: C_{70}-B, *RR*-P3HT: C_{70}- C.

Table 3 PV parameters of solar cells based on composites *RR*-P3HT: cyclopropano[70] fullerenes.

Composite	Before Annealing				After Annealing 100°C-10 min			
	V_{oc}	J_{sc}	ff	η%	V_{oc}	J_{sc}	ff	η%
P3HT : C_{70}-B	0.607	3.56	0.332	0.67	0.507	9.29	0.342	1.50
P3HT : C_{70}-A	0.389	1.12	0.248	0.10	0.324	1.48	0.402	0.18
P3HT : C_{70}-C	0.450	3.49	0.285	0.42	0.204	3.12	0.299	0.17

where ff is the fill factor, J_{sc} is the short circuit current, V_{oc} is the open circuit voltage, and P_{inc} is the incident light intensity.

The external quantum yield or incident photon-to-electron conversion efficiency (IPCE) was measured using an Acton Spectra Pro 150 apparatus, by illuminating the solar cells with monochromatic light through the ITO. The relation between IPCE, current I_{sc}, monochromatic intensity $I_{inc,}$ and wavelength λ is given by:

$$\text{IPCE}(\%) = 1240^* I_{sc}/(\lambda^* I_{inc}). \qquad (2)$$

3 Results and Discussion

The electrochemical behavior of cyclopropano[70]fullerene derivatives and parent C_{70} as reference, has been investigated by cyclic voltammetry at room temperature in CH_2Cl_2 solution using $TBAPF_6$ as the supporting electrolyte. The corresponding data are listed in Table 1. All derivatives show very similar voltammograms. The curves displayed by compound C_{70}-A and C_{70} have been chosen as an example (see Fig. 2).

The voltammogram clearly shows 3 one-electron fullerene-based reduction waves at potentials $E^1_{1/2} = -1.07$ V, $E^2_{1/2} = -1.44$ V, and $E^3_{1/2} = -1.82$ V (half-wave potential versus Fc^+/Fc), which are assigned to the generation of the anion radical $C_{70}^{\bullet-}$, the dianion $C_{70}^{\bullet2-}$, and the trianion $C_{70}^{\bullet3-}$, respectively, from the cyclopropanoC_{70} moiety. That is characteristic of the electrochemical behavior of cyclopropano[70]fullerene issued from the Bingel process.[10–12] Table 1 shows that all fullerene derivatives C_{70}-A, C_{70}-B, and C_{70}-C are characterized by almost identical reduction potentials.

It can thus be inferred that the differences observed in the structures of these derivatives, i.e., the ester chain length and/or the overall symmetry or nonsymmetry of the molecule, brings no net influence on the reduction ability of the compounds. On the other hand the redox properties of all cyclopropano[70]fullerenes appear to be close to those of parent C_{70}. Table 2 shows a 70 mV negative shift for the first reduction step of the derivatives of C_{70}-A, C_{70}-B, and C_{70}-C compared to the parent C_{70}. This shift can be reasonably attributed to a partial loss of conjugation and alteration of the electron-accepting ability of C_{70} core further to LUMO energy elevation. These results can be explained by the presence of two $-CO_2R$ groups connected to the cyclopropano ring in C_{70}-A, C_{70}-B, and C_{70}-C compounds. These ester groups are electron acceptors, which obviously increase the reduction potential of the C_{70} core in both series. The fourth oxidation wave at 0.59 V in the case of C_{70}-A was attributed to the Cyclopronano moiety on C_{70}.[10]
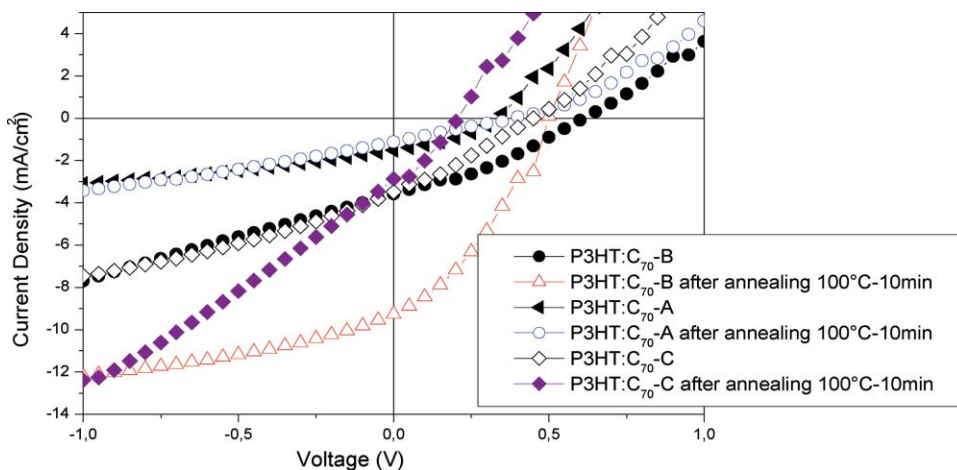

Fig. 4 Current density/voltage (*I–V*) characteristic of cells based on composites *RR*-P3HT: cyclopropano[70]fullerene derivatives.
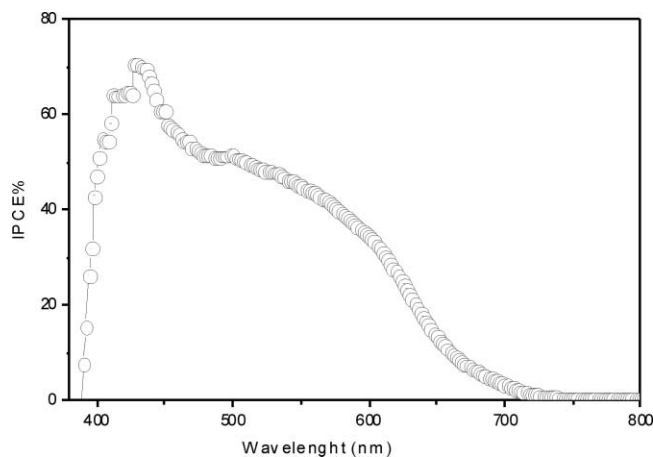
Fig. 5 IPCE spectra of cell: ITO/PEDO:PSS/P3HT: C_{70}-B /LiF/Al, after annealing 100°C for 10 min.

The UV-visible absorption spectra of the mixtures deposited as thin films are presented in Fig. 3. We notice that the absorption spectra have the same shape, with the same bands characteristic of the P3HT and C_{70} derivatives, before and after annealing. Heat treatment improves absorption coefficient of the samples. It involves a 30-nm shift of the spectra toward the highest wavelengths and an increase in absorption intensity with the appearance of shoulders at 565, 610, and 620 nm. This is usually attributed to the crystallization of RR-P3HT, further to phase separation.

Although the molar concentrations of the fullerene derivatives are identical to those in the PCBM {[6,6]-phenyl-C_{61}-butyric acid methyl ester} cell, PV characteristics delivered by the solar devices are not the same. That confirms the dependence of PV performances on the exact molecular structure and more precisely on the difference or similarity between ester side chains. The electrochemical characteristics showed that these derivatives have very comparable electronic properties. The PV characteristics strongly depend on the nature of the interaction between the donor and the acceptor, and on their behavior inside the active layer. However, molecular structure influences the PV parameters as well as η%. Indeed, the best performances are obtained from cells based on the composite P3HT: C_{70}-B, with J_{sc} 3.56 mA/cm^2, V_{oc} 0.607 V, and ff 0.332 (Table 3). These parameters are improved after annealing at 100°C during 10 min (see Fig. 4). These parameters are smaller than in the P3HT:PC$_{70}$BM system already studied by Yamanari et al.;[13] their cells provided a conversion efficiency of 3.8%.

The heating effect causes phase separation and crystallization of the polymer RR-P3HT which allows the improvement of the absorption of the organic layers. Crystallization of the RR-P3HT increases the mobility of the charge carriers and thus we get $J_{sc} = 9.29$ mA/cm^2 and ff $= 0.342$. Figure 5 shows a new peak around 430 nm with 71% IPCE which justifies the large J_{sc}. On the other hand, V_{oc} slightly decreases. It can be caused by interface modification created during annealing. η% reaches 1.5% in that kind of solar cell.

4 Conclusions

In the development of BHJ solar cells containing new fullerenes derivatives, it is clear that optimization alone of electronic and optical properties is insufficient.[14–16] It is essential to take into account the molecular structure of the materials used, which can influence the interaction between donor and acceptor. These compounds C_{70}-A, C_{70}-B, and C_{70}-C put in evidence the importance of the acceptor chemical structure on PV characteristics. They confirm also that synthesis strategies more direct than for the PCBM molecules are promising.[7] The higher η% $= 1.5$% is obtained for devices based on C_{70}-B after heat treatment at 100°C during 10 min.

Acknowledgments

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