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## **New fullerene derivatives for the photovoltaic application**

Hassina Derbal-Habak

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# New fullerene derivatives for the photovoltaic application

Hassina Derbal-Habak,<sup>a,b</sup> Celine Bergeret,<sup>c</sup> Jack Cousseau,<sup>c</sup>  
Jean Jacques Simon,<sup>b</sup> Ludovic Escoubas,<sup>b</sup> and Jean-Michel Nunzi<sup>d</sup>

<sup>a</sup> Université d'Angers, POMA Laboratory, 2 Bd Lavoisier, 49045 Angers, France  
[hassina.derbal@im2np.fr](mailto:hassina.derbal@im2np.fr)

<sup>b</sup> Université Aix-Marseille, Institut Matériaux Microélectronique Nanosciences de Provence,  
CNRS UMR 6242, Domaine Universitaire de Saint-Jérôme, 13397 Marseille, France

<sup>c</sup> Université d'Angers, Laboratoire Moltech Anjou, CNRS UMR 6200,  
2 Bd Lavoisier, 49045 Angers, France

<sup>d</sup> Queen's University, Department of Physics and Department of Chemistry,  
Kingston, Ontario K7L 3N6, Canada

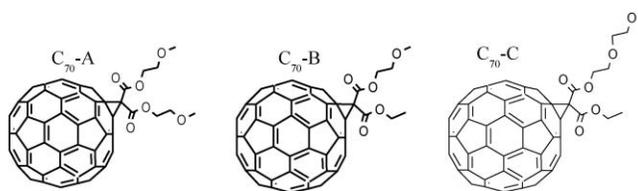
**Abstract.** Cyclopropano[70]fullerenes have been synthesized in the aim of being used as acceptors in blends based on regioregular poly (3,5-Hexylthiophene) *RR*-P3HT for photovoltaic (PV) plastic cells. These molecules used with *RR*-P3HT in bulk heterojunction (BHJ) configuration provided interesting characteristics: 1.5% solar conversion efficiency, 9.29 mA/cm<sup>2</sup> 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](https://doi.org/10.1117/1.3576907)]

**Keywords:** Bulk heterojunction solar cells; organic photovoltaics; C<sub>70</sub> derivatives.

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## 1 Introduction

Since the discovery of photoinduced electron transfer between semiconducting conjugated polymers and fullerenes, several investigations were made.<sup>1</sup> 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.<sup>2-4</sup> 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<sub>70</sub> for the photovoltaic (PV) application besides those already published on the PC<sub>70</sub>BM and the PC<sub>85</sub>BM. Using PC<sub>70</sub>BM into a photoactive layer increases the  $\eta$ % 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<sub>70</sub>BM and the low bandgap polymer PCPDTBT.<sup>5</sup> 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<sup>2</sup> with power efficiency around 7.4%.<sup>6</sup> In our previous work, organic solar cells elaborated from the cyclopropano[60]fullerenes,<sup>7,8</sup> provided promising PV



**Fig. 1** Molecular structure of cyclopropano[70] fullerene derivatives C<sub>70</sub>-A, C<sub>70</sub>-B, and C<sub>70</sub>-C.

performances, with power conversion and current density above 1.2% and 7.2 mA/cm<sup>2</sup>, 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<sub>70</sub> derivatives has a broader absorption in the visible region (see Fig. 1). One should note that this Bingel type approach of fullerene C<sub>70</sub> functionalization is original, and was never studied before.

## 2 Experimental Section

Compounds C<sub>70</sub>-A, C<sub>70</sub>-B, and C<sub>70</sub>-C and C<sub>70</sub> were analyzed in  $7 \times 10^{-4}$  mol l<sup>-1</sup> dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (HPLC grade) solutions containing  $5 \times 10^{-2}$  mol l<sup>-1</sup> *n*-Bu<sub>4</sub>NPF<sub>6</sub> 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<sup>+</sup>/Fc) redox couple. The scan rate used in this study was 100 mV/s.

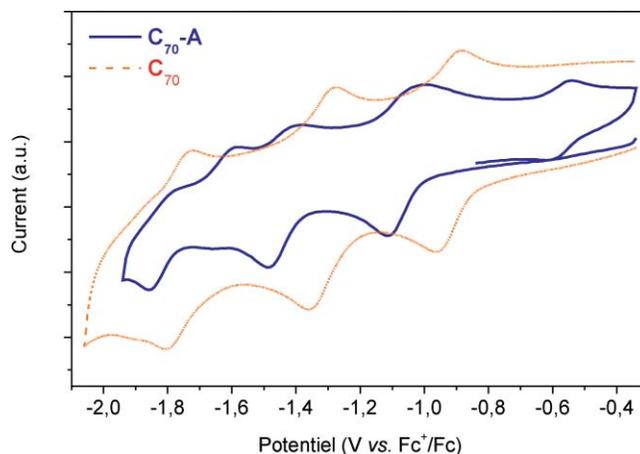
Absorption spectra were recorded at room temperature with a Lambda 19 Perkin–Elmer spectrometer. These measurements were done on thin films based on composite P3HT: C<sub>70</sub> fullerene derivatives.

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  $4 \times 10^{-7}$  mBar argon pressure, on top of the photoactive layer.<sup>9</sup> The size of the active area is 0.32 cm<sup>2</sup>. 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  $\eta\%$  is calculated using:

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

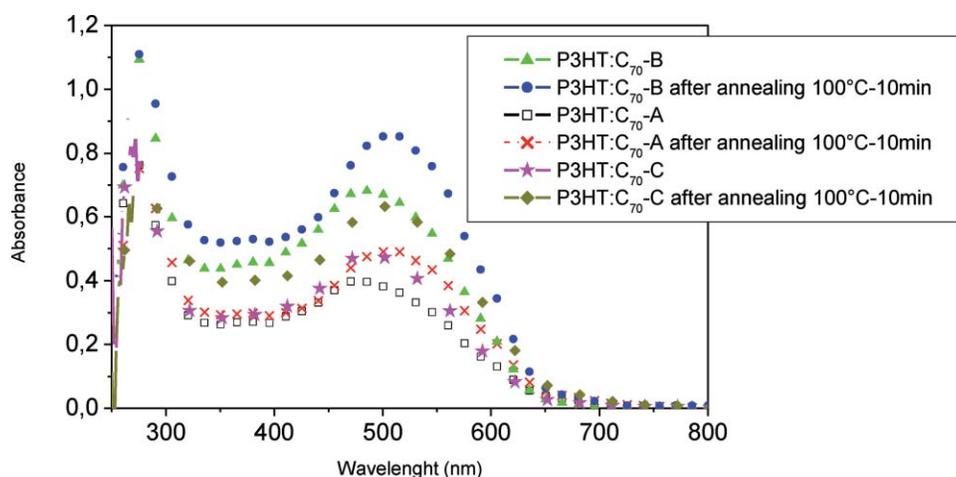
**Table 1** Redox potentials of compounds C<sub>70</sub>-A, C<sub>70</sub>-B, and C<sub>70</sub>-C.

Molecule	E <sup>1</sup> <sub>1/2red</sub> (V)	E <sup>2</sup> <sub>1/2red</sub> (V)	E <sup>3</sup> <sub>1/2red</sub> (V)
C <sub>70</sub>	-1.00	-1.39	-1.80
C <sub>70</sub> -A	-1.07	-1.44	-1.82
C <sub>70</sub> -B	-1.07	-1.44	-1.82
C <sub>70</sub> -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 <sup>-1</sup> )	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	$\eta$ %	$V_{oc}$	$J_{sc}$	ff	$\eta$ %
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  $\lambda$  is given by:

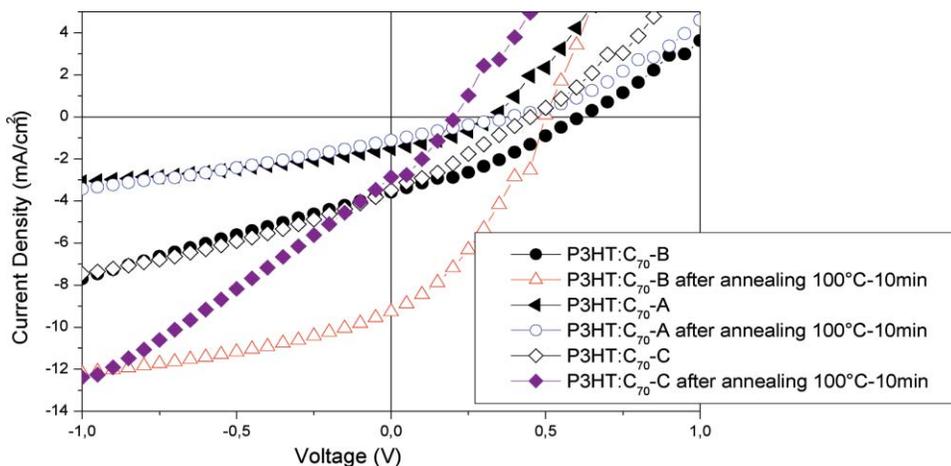
$$IPCE(\%) = 1240 * I_{sc} / (\lambda * I_{inc}). \quad (2)$$

### 3 Results and Discussion

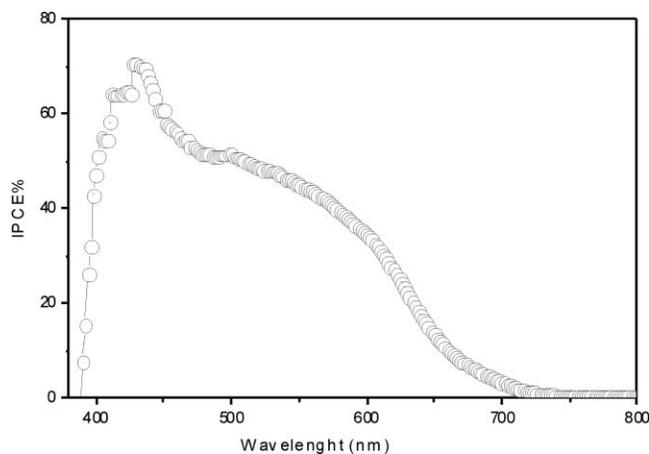
The electrochemical behavior of cyclopropano[70]fullerene derivatives and parent  $C_{70}$  as reference, has been investigated by cyclic voltammetry at room temperature in  $CH_2Cl_2$  solution using  $TBAPF_6$  as the supporting electrolyte. The corresponding data are listed in Table 1. All derivatives 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  $E^{1/2} = -1.07$  V,  $E^{2/2} = -1.44$  V, and  $E^{3/2} = -1.82$  V (half-wave potential versus  $Fc^+/Fc$ ), which are assigned to the generation of the anion radical  $C_{70}^{\bullet-}$ , the dianion  $C_{70}^{\bullet 2-}$ , and the trianion  $C_{70}^{\bullet 3-}$ , respectively, from the cyclopropano $C_{70}$  moiety. That is characteristic of the electrochemical behavior of cyclopropano[70]fullerene issued from the Bingel process.<sup>10-12</sup> 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 Cyclopropano moiety on  $C_{70}$ .<sup>10</sup>



**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<sub>70</sub>-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<sub>70</sub> 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<sub>61</sub>-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  $\eta\%$ . Indeed, the best performances are obtained from cells based on the composite P3HT: C<sub>70</sub>-B, with  $J_{sc}$  3.56 mA/cm<sup>2</sup>,  $V_{oc}$  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<sub>70</sub>BM system already studied by Yamanari et al.,<sup>13</sup> 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<sup>2</sup> 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.  $\eta\%$  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.<sup>14-16</sup> 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<sub>70</sub>-A, C<sub>70</sub>-B, and C<sub>70</sub>-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.<sup>7</sup> The higher  $\eta\% = 1.5\%$  is obtained for devices based on C<sub>70</sub>-B after heat treatment at 100°C during 10 min.

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**Hassina Derbal-Habak** received her PhD at the University of Angers, France in 2009. She made several national and international collaborations. In September 2009, she joined IM2NP laboratory in the "Optoelectronics and photovoltaics components" team as POST-DOC. Her main research interests are photonics, organic solar cells, organic components, bulk nanostructured and nanoplasmonic structures for PV.

**Celine Bergeret** received her PhD at the University of Angers, France in 2009. Her main research interests are the developments of modified fullerenes and carbon nanotubes for organic components and supramolecular structures. She is involved in the setup of new plastic solar cells.

**Jack Cousseau** is retired Professor from the University of Angers.

**Jean Jacques Simon** received his PhD at the University of Marseille in 1996 for a thesis on "Electrical activity of dislocations in silicon." From 1997 to 2000, he worked as a process engineer for IBM Semiconductor at Corbeil-Essonnes, France. He joined the University Paul Cezanne of Marseille in 2000 as a senior lecturer and for his research the Fresnel Institute in the group "Microstructured Optical Components." He joined the IM2NP laboratory in 2007 and his current research interests are photonics for organic and thin film solar cells. He has authored more than 30 papers and communications.

**Ludovic Escoubas** is Professor at the Aix Marseille University and leader of the OPTO-PV group at the Materials, Microelectronics and Nanoscience Institute of Provence (IM2NP). His current research interests are photonic structures in organic solar cells and surface structuration of components for light propagation control. He has authored more than 50 papers in peer-reviewed scientific journals and holds 7 patents.

**Jean Michel Nunzi** is T1 Canada research chair, member of the NSERC Photovoltaic innovation Network. He was at the origin of the renewal of research on plastic solar cells in Europe with the first successfully granted EC project on Organic Solar Cells (EUROSCI) in 1996.