

Photovoltaic performance of PPE-PPV copolymers: effect of the fullerene component†

Diana K. Susarova,^a Ekaterina A. Khakina,^a Pavel A. Troshin,^{*a} Andrey E. Goryachev,^a N. Serdar Sariciftci,^b Vladimir F. Razumov^a and Daniel A. M. Egbe^b

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Two conjugated PPE-PPV copolymers were studied as electron donor materials in bulk heterojunction organic solar cells in combination with a library of electron acceptor fullerene derivatives. It was shown that molecular structure and solubility of the fullerene counterpart significantly affect the photovoltaic performance of both polymers. Use of [60]PCBM as an electron acceptor material yielded quite moderate power conversion efficiencies. The best results were achieved when fullerene derivatives with suitable molecular structures and solubilities were applied. The obtained results suggest that every newly designed conjugated polymer should be evaluated in solar cells using a library of fullerene derivatives instead of just conventional PCBM. We believe that only this combinatorial approach might bring the best performing donor/acceptor combinations for future generations of efficient organic solar cells.

Introduction

The past few years are marked by continuous race for development of novel conjugated polymers for use as electron donor materials in organic solar cells.^{1,2} This competition of many research groups worldwide was very successful and brought the efficiency of plastic solar cells from the level of 4% documented as state-of-the-art three years ago up to the level of 7–8% certified very recently.^{3–5} This is quite a breakthrough in the field, proving that organic photovoltaic devices are indeed promising for mass energy production.⁶ Highly efficient solution-based technologies applied to the fullerene/polymer blends should enable industrial production of cheap organic solar cell modules.^{7–9} Grid-connected OPV modules have been demonstrated recently.¹⁰ In addition, some examples of commercially viable devices utilizing small area organic solar cells have been designed.^{11,12}

There are two most promising ways that are currently used to improve photovoltaic properties of conjugated polymers. In the first route, conjugated polymers are modified with some structural blocks that reduce their band gaps and, therefore, enhance their light harvesting properties. These materials give high short circuit current densities (J_{SC}) in solar cells.^{4,5,13–15} According to another approach, the backbones of conjugated polymers are modified in order to lower their HOMO energy levels and

increase open circuit voltages (V_{OC}) of photovoltaic cells.^{3,16,17} Both concepts are equally promising and should be combined to develop the most efficient polymer materials.

It was demonstrated some years ago that conjugated polymers comprising both phenylene-vinylene and phenylene-ethynylene structural blocks have low lying HOMO energy levels and, therefore, give an appreciably high V_{OC} of 900–1000 mV in organic solar cells.¹⁸ Therefore, this is a quite promising group of conjugated polymers that might bring state of the art power conversion efficiencies in solar cells providing their band gaps are lowered sufficiently to reach short circuit currents of 15 mA cm⁻² and higher. The design of such polymers is currently in progress.

Intermolecular interaction of PPE-PPV copolymers with fullerene-based counterparts in the active layers of organic solar cells is also an important issue that should be addressed. It was shown that variation of the side chains attached to the polymer backbone changes physical and electronic properties of these materials and influences significantly their photovoltaic performance when they are combined with [60]PCBM.¹⁹ In this work the same problem was approached from an opposite direction. We have fixed side chains on the polymer backbone and varied organic addends attached to the fullerene cage. Indeed, we observed dramatic effect of the fullerene derivatives structure and solubility on the photovoltaic performance of their blends with PPE-PPV copolymers.

2. Results and discussion

The molecular structures of the investigated polymers and fullerene derivatives are presented in Fig. 1. Synthesis of these materials was described in detail previously.^{20–23} The purpose of

^aInstitute of Problems of Chemical Physics of Russian Academy of Sciences, Semenov Prospect 1, Chernogolovka, Moscow region, 142432, Russia. E-mail: troshin@cat.icp.ac.ru

^bLinz Institute for Organic Solar Cells (LIOS), Johannes Kepler University Linz, Altenbergerstrasse 69, A-4040 Linz, Austria

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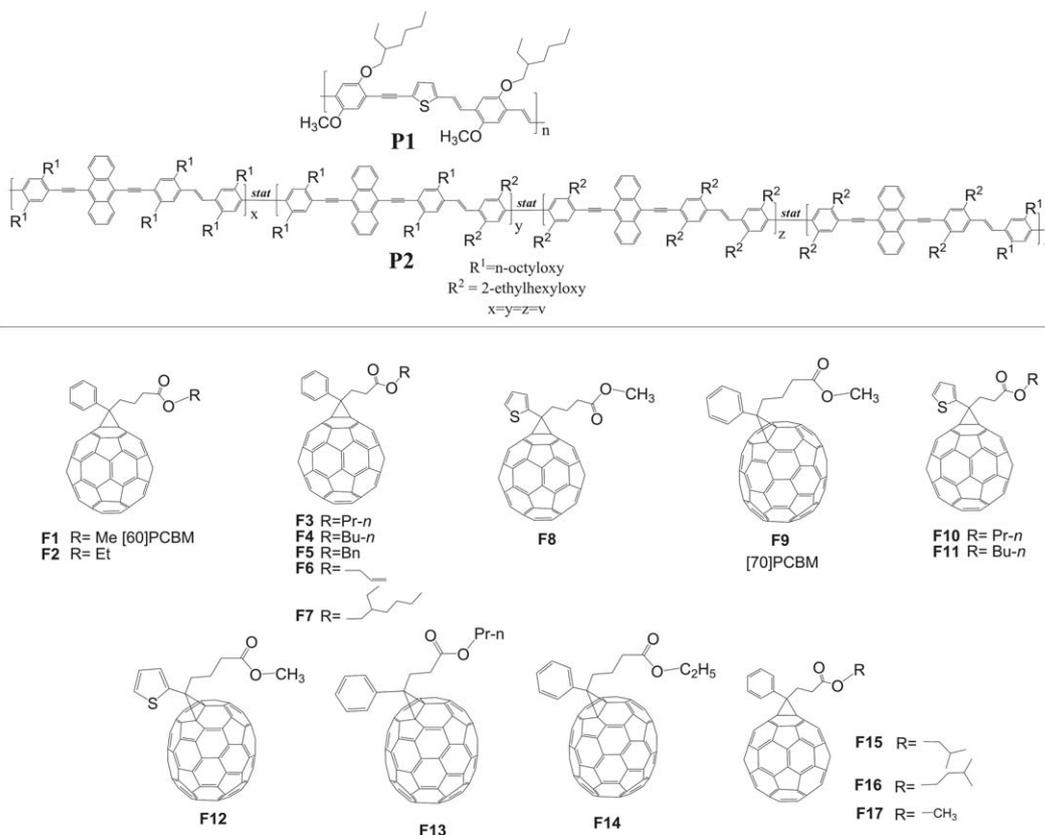


Fig. 1 The molecular structures of the materials used in this work.

this work was to combine polymers **P1** and **P2** with a library of fullerene derivatives and investigate the resulting photoactive blends in bulk heterojunction organic solar cells. The schematic layout of such a cell is shown in Fig. 2.

In the first trials we applied the conventional fullerene derivative [60]PCBM as electron acceptor component. By varying polymer/PCBM ratios from 1 : 1 to 1 : 5 by weight, we obtained optimal blend compositions. Afterwards, PCBM was replaced with other fullerene derivatives. In the test series, we selected a few structurally different fullerene derivatives and performed the same optimisation as it was done for PCBM. This optimisation resulted exactly in the same optimal component ratios that were revealed for the reference PCBM/**P1** and PCBM/**P2** systems. Based on these findings it might be assumed that component ratios are not very sensitive to variations in the molecular structures of our fullerene derivatives. Therefore, all

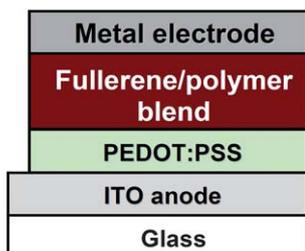


Fig. 2 A schematic layout of an organic bulk heterojunction solar cell.

fullerene derivatives from the library presented in Fig. 1 were processed under fully identical conditions found for reference PCBM-based blends. The obtained results are presented in Table 1. Fig. 3 shows $I-V$ curves for solar cells comprising composites of **P1** and **P2** with various fullerene derivatives used as active layer materials. It is seen from these data that performance of the investigated polymers as electron donor materials in solar cells depends strongly on the choice of fullerene derivative used as electron acceptor counterpart. We emphasize here that all fullerene derivatives involved in this study have virtually equal LUMO level energies as it follows from the very similar first reduction potentials revealed by electrochemical measurements. Cyclic voltammetry data for a number of fullerene derivatives were reported previously.^{21,22} Therefore the observed variations in the open circuit voltages of the devices based on different fullerene derivatives cannot be ascribed to the changes in the energy levels of the materials.

We have previously shown that photovoltaic performance of the fullerene derivative/P3HT blends depends strongly on the solubility of the fullerene derivative.²¹ Use of low soluble fullerene derivatives resulted in a large scale phase separation and poor photovoltaic performance. On the contrary, highly soluble fullerene derivatives were very mixable with poly(3-hexylthiophene) that dramatically decreased percolation of fullerene and polymer phases in the blend and caused charge transport problems. Therefore, fullerene derivative solubility should not be too low and too high. Optimal fullerene derivative solubility range for P3HT-based composite was between 30 and 70 mg ml⁻¹.

Table 1 Output parameters of organic solar cells based on copolymers **P1** and **P2** and various fullerene derivatives

Fullerene derivative	Solubility ^a /mg ml ⁻¹	Polymer P1 ^b				Polymer P2 ^c			
		$J_{SC}/\text{mA cm}^{-2}$	V_{OC}/mV	$FF(\%)$	$\eta(\%)$	$J_{SC}/\text{mA cm}^{-2}$	V_{OC}/mV	$FF(\%)$	$\eta(\%)$
F1	50	6	750	36	1.6	6.1	870	47	2.5
F2	19	6.1	900	38	2.1	7.1	840	58	3.4
F3	43	5	850	38	1.6	5.8	840	43	2.1
F4	30	5.6	900	39	2.0	8.4	840	39	2.7
F5	106	4.5	650	34	1.0	3.7	840	47	1.5
F6	70	4.7	850	35	1.4	—	—	—	—
F7	150	3.2	800	32	0.8	3.8	750	28	0.8
F8	36	6.2	900	37	2.0	3.9	810	51	1.6
F9	80	7	800	40	2.2	—	—	—	—
F10	45	5.7	850	40	1.9	4.9	810	52	2.1
F11	70	5.8	900	40	2.1	7.2	840	56	3.4
F12	70	5.5	850	38	1.8	—	—	—	—
F13	35	5.9	850	36	1.8	—	—	—	—
F14	19	—	—	—	—	4.3	840	41	1.5
F15	48	—	—	—	—	6.3	780	35	1.8
F16	88	—	—	—	—	8.4	810	45	3.1
F17	10	—	—	—	—	3.6	840	47	1.4

^a The solubilities of fullerene derivatives were measured in chlorobenzene. ^b The ratio between the fullerene derivative and the polymer **P1** was 3 : 1 by weight. ^c The ratio between the fullerene derivative and the polymer **P2** was 1.8 : 1 by weight.

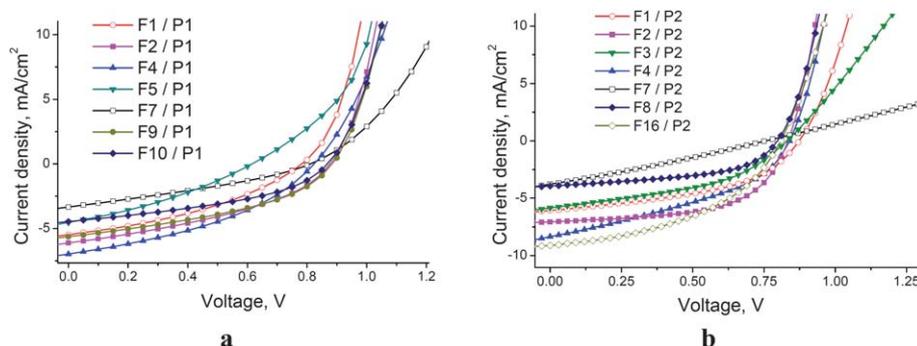
A number of other PCBM-like fullerene-based acceptor materials were developed for solar cell applications recently.^{24,25}

On the base of these previous findings, we expected to observe a strong dependence of photovoltaic performance of copolymers **P1** and **P2** on the solubility and molecular structure of fullerene-based counterparts. Fig. 4 shows plots of short circuit current (J_{SC}) and overall device power conversion efficiency (η) as function of the solubility of the fullerene derivatives. Points corresponding to the systems comprising [60]PCBM as electron acceptor material are outlined with the circles. The positions of all other points are defined by the data presented in Table 1.

All plots presented in Fig. 4 have somewhat strange shapes. For instance, both J_{SC} and η for solar cells comprising copolymer **P1** showed clear double branch behaviour. Higher currents for the systems based on **F9** and **F12** might be attributed to the increased light absorption in the visible range caused by these [70]fullerene derivatives. This is quite possible because copolymer **P1** has quite narrow absorption in the visible range with the band offset at ~ 650 nm (see Fig. S1 in ESI†).

Similar and even stronger effect was observed for MDMO-PPV when it was combined with [70]PCBM instead of [60]PCBM.²⁶ However, [60]fullerene derivative **F11** having similar solubility of 70 mg ml⁻¹ also yielded relatively high power conversion efficiency in combination with copolymer **P1** (Fig. 4b). Therefore, appearance of the second branch on the curve shown in Fig. 4b cannot be ascribed only to the use of C₇₀-based materials.

Copolymer **P2** absorbs light quite efficiently in the visible range up to 670–690 nm (see Fig. S1 in ESI†). Therefore, the optical properties of this polymer resemble in some way the optical properties of well-known poly(3-hexylthiophene) P3HT. Therefore, one might expect similar performances from the blends comprising this copolymer and some fullerene derivatives. Indeed, the best power conversion efficiencies of 3.3–3.5% were reached for the blends of **P2** with acceptor counterparts **F2** and **F11**. This is quite close to the values typically reported for P3HT/PCBM based solar cells.²⁷ It is notable that both short circuit current and power conversion efficiency of the solar cells strongly depend on the solubility of the fullerene derivatives applied as

**Fig. 3** I - V curves for solar cells comprising blends of copolymer **P1** (a) and **P2** (b) with various fullerene derivatives.

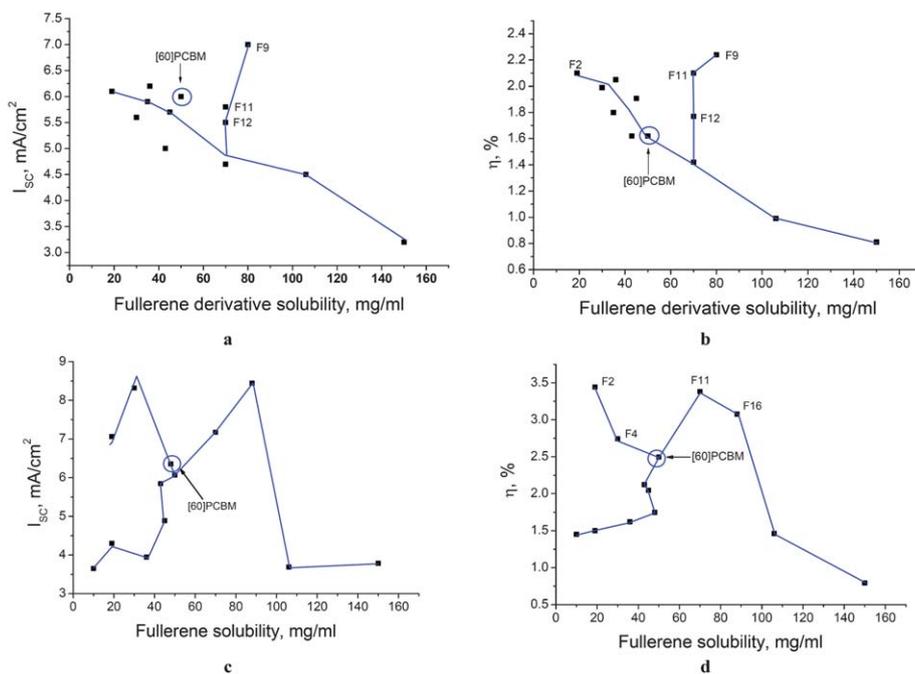


Fig. 4 Dependence of the short circuit current (J_{SC} , a,c) and power conversion efficiency (η , b,d) on the solubility of fullerene derivatives for solar cells comprising copolymers **P1** (a,b) and **P2** (c, d).

electron acceptor materials and mixed together with the copolymer **P2** in the active layer (Fig. 4c,d). These dependences have double-branch shapes resembling in some way analogous plots obtained for copolymer **P1** (Fig. 4a,b). However, the plots obtained for copolymer **P2** clearly show some maxima in the solubility range of 50–90 mg ml⁻¹ where the highest solar cell performances can be reached using fullerene derivatives **F11** and **F16**. This optimal solubility range is shifted by *ca.* 20 mg ml⁻¹ towards higher solubility values in comparison with the P3HT-based systems where optimum gap lies between 30 and 70 mg ml⁻¹.²¹ Fullerene derivatives with solubilities lower than 50 mg ml⁻¹ and higher than 90 mg ml⁻¹ show low performances in combination with **P2** with two exceptions for **F2** and **F4** that form a second branch on the plots shown in Fig. 4c,d. We note that both **F2** and **F4** have rather short and linear alkyl chains attached to the carboxyl groups. These chains might improve compatibility of these two particular fullerene derivatives with copolymer **P2** and thus result in their superior photovoltaic performance.

To prove this hypothesis a deeper study has to be carried out using different microscopy techniques. Such work is in progress at the moment with more than one hundred fullerene/polymer composite systems involved in the study. As a preliminary result, Fig. 5 shows AFM images for two differently performing fullerene/polymer composites: **F2/P2** and **F17/P2**. These topography images suggest that the phase separation is much stronger in the blend **F17/P2** compared to the blend **F2/P2**. Improved nanoscale morphology of the **F2/P2** composite results in its superior photovoltaic performance.

3. Conclusion

We have demonstrated that photovoltaic performance of two PPE-PPV copolymers depends strongly on the solubility and molecular structure of fullerene derivatives applied as electron acceptor counterparts in the active layer of organic solar cells. The obtained results clearly show that conventional material [60]PCBM gives just moderate efficiencies in combination with copolymers **P1** and **P2**. The best photovoltaic performances were reached when each copolymer was combined with specific fullerene derivatives with better-suited molecular structures and solubilities in organic solvents. Thus, fullerene derivatives **F2**, **F3** and **F8–F10** were the best electron acceptor counterparts for polymer **P1**. At the same time, fullerene-based materials **F2**, **F4**, **F11** and **F16** yielded the highest solar cell power conversion efficiencies reaching 3.3–3.5% when blended with copolymer **P2**. These examples prove that [60]PCBM and [70]PCBM are not materials of choice for every novel conjugated polymer. Therefore, combinatorial approach using a set of fullerene derivatives with different molecular structures and physical properties has to be applied in order to reach maximal photovoltaic performances from novel generations of low band-gap copolymers.

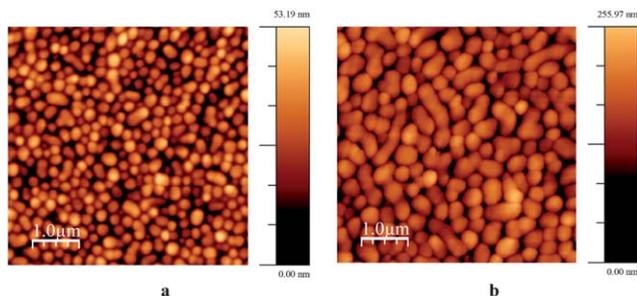


Fig. 5 AFM topography images of the **F2/P2** (a) and **F17/P2** (b) blend films.

4. Experimental

Polymer (5 mg of **P1** and 7 mg of **P2**) was dissolved together with appropriate amount of fullerene derivative (15 mg for **P1** and 12.5 mg for **P2**) in 1 ml chlorobenzene. All blend solutions were filtered through a 0.45 μm PTFE syringe filter just before the film preparation.

ITO glass slides with a size of 15 \times 15 mm were cleaned by successive sonication in toluene, acetone and, finally, in isopropanol. On the clean ITO surface PEDOT-PSS (Baytron PH) solution was spin-coated at 3000 rpm. The PEDOT-PSS films were annealed at 155 $^{\circ}\text{C}$ for 15 min. Afterwards, fullerene-polymer blends were spin-coated at 1000–1200 rpm and immediately transferred inside nitrogen glove-box. The films of the fullerene-polymer blends were dried in vacuum (*ca.* 10^{-3} mbar) at ambient temperature for 30–40 min. Afterwards, top electrodes were deposited in vacuum $\sim 10^{-6}$ mbar. A combination of 0.6 nm of LiF and 120 nm of Al was used as top electrode in the solar cells comprising polymer **P1**. Alternatively, sequential deposition of 10 nm of Ca and 120 nm of Al was used for devices based on copolymer **P2**. Finalized devices were characterized directly inside nitrogen glove box.

I-*V* characteristics of the devices were obtained in dark and under the simulated 100 mW cm^{-2} AM1.5 solar irradiation provided by a KHS Steuernagel solar simulator. The intensity of the illumination was checked every time before the measurements using a calibrated silicon diode with known spectral response. All data given in this paper were not corrected for the mismatch between the solar simulator illumination and the AM1.5 spectrum. The photocurrent spectra were measured with a SRS 830 lock-in amplifier using the monochromated light from a 75W Xe lamp as excitation.

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