Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry C

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High LUMO energy pyrrolidinofullerenes as promising electron-acceptor materials for organic solar cells

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We report the synthesis and investigation of four novel pyrrolidinofullerenes bearing electron donating alkoxyphenyl substituents. Cyclic voltammetry studies revealed that the designed fullerene derivatives have reduced electron affinity compared to the conventional material [60]PCBM. The organic bulk heterojunction solar cells based on the pyrrolidinofullerenes and P3HT revealed impressive open-circuit voltages of 700-780 mV and enhanced light power conversion efficiencies with respect to the reference PCBM/P3HT devices. The designed materials demonstrated also reasonably good compatibility and decent photovoltaic performances in combination with the carbazole-thiophene-benzothiadiazole copolymer PCDTBT.

Introduction

Organic solar cells have been intensively investigated during the last decade in many research laboratories all over the world. Conjugated polymers (p-type) and fullerene derivatives (n-type) are usually used as semiconductor materials in organic solar cells. Design of novel electron donor conjugated polymers resulted in the increase in the solar light power conversion efficiency up to 10% and beyond.[1] In contrast to the conjugated polymers, much less attention is paid to the design of fullerene-based materials with improved electronic properties. Theoretical calculations have shown that the application of fullerene derivatives with reduced electron affinity can increase the open-circuit voltage (V_{OC}) and, consequently, the efficiency of organic solar cells based on P3HT and vast majority of other existing conjugated polymers.[2] The electron affinity of the fullerene sphere can be reduced by opening two or several double bonds in the carbon cage and attaching appropriate number of addends. Indeed, organic solar cells based on biscycloadducts (e.g. bis-PCBM, ICBA) show 150-200 mV higher V_{OC}'s as compared to the reference devices comprising classical [60]PCBM as an electron acceptor component.[3-5] The main disadvantage of the fullerene derivatives with two attached cyclic organic addends is their complex isomeric composition. The formation of complicated mixtures of ~20 regio- and stereoisomers of biscycloadducts based on C_{60} and C_{70} creates a considerable disorder in their thin films inhibiting charge transport and affecting badly the photovoltaic performance of these materials.[6] It is notable that

biscycloadducts work well only in combination with crystalline polymers such as P3HT, PBDTBDD and other.[3,7-13] The crystallization of the polymer during the film formation induces also ordering of the fullerene phase. Furthermore, different isomers of biscycloadducts have rather different LUMO energies which induce energetic disorder in the material represented by a complex isomer mixture.[14,15]

Therefore, it is not surprising that vast majority of highly promising low band gap conjugated polymers give insufficient solar cell performances in combination with biscycloadducts.[16] Another family of the fullerene-based materials with reduced electron affinity is represented by endohedral compounds such as $Lu_3N@C_{80}$-PCBH. Application of such materials in P3HT-based organic solar cells improved their open-circuit voltages and light power conversion efficiency.[17] However, further development and practical implementation of functionalized endohedral fullerene derivatives is limited by their extremely poor availability.[18-20]

The most promising and, at the same time, the least explored approach to lowering the electron affinity of the fullerene core is the attachment of a single organic addend loaded with the electron donating substituents. Preparation and investigation of functionalized derivatives of [60]PCBM comprising multiple RO- or RS- substituents in the phenyl ring was reported previously.[21] The synthesized compounds demonstrated an increase in the V_{OC} by ~50 mV, while the efficiency of the photovoltaic cells was not improved. Furthermore, some examples of diphenylmethanofullerenes showed improved V_{OC} in organic solar cells as compared to the conventional [60]PCBM.[22-24] A number of silicon-containing 1,4-adducts of C_{60} and Diels-Alder-type cycloadducts with reduced electron affinity were also reported.[25-27] Pyrrolidinofullerenes represent other promising family of fullerene derivatives with reduced electron affinity demonstrating enhanced open circuit voltages and power conversion efficiencies in organic solar cells.[28-29]

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The presented examples strongly suggest that fullerene monocycloadducts with the reduced electron affinity represent a promising group of n-type materials for organic solar cells. However, their potential is not explored sufficiently by now. In particular, up to the best of our knowledge, none of the reported fullerene derivatives with reduced electron affinity showed decent photovoltaic performances with the low crystalline or amorphous conjugated polymers, e.g. PCDTBT.[30]

In the present work we pursued the design and investigation of a novel group of the fullerene derivatives whose electron affinity is lowered considerably due to the electron donating nature of a single organic addend attached to the fullerene cage.

Results and discussion

Here we explored a potential of the pyrrolidinofullerene core structure in the design of promising n-type semiconductor materials with lowered electron affinity as compared to the conventional [60]PCBM. First of all, it is known that nitrogen atom donates its electron density to the fullerene cage thus increasing its LUMO energy.[31] Moreover, there are indications in the literature that substituents in the positions 2 and 5 of the pyrrolidine ring can interact directly with the fullerene cage.[32] Additionally, a successful application of the pyrrolidine type fullerene derivatives in organic solar cells was reported.[28-29]

The synthesis of the target fullerene derivatives **F1-F5** required the preparation of N-alkylamino acids **3-4** by treatment of appropriate bromoacetic acids **1** and **2** with 2-ethyl-1-hexylamine as shown in Scheme 1.
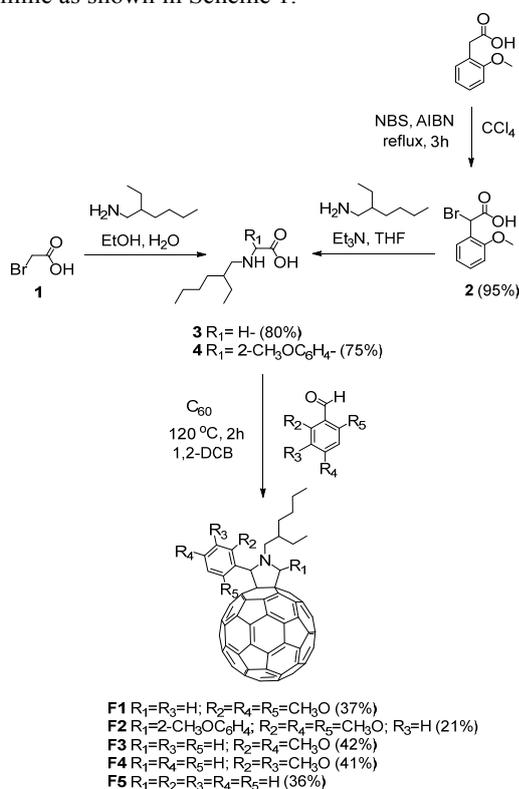
The precursor 2-bromo-2-(2-methoxyphenyl)acetic acid **2** was synthetized by bromination of 2-(2-methoxyphenyl)acetic acid with NBS in the presence of catalytic amount of AIBN.

Pyrrolidinofullerenes **F1-F4** and also the reference compound **F5** were synthesized using a standard reaction based on the [3+2]cycloaddition of azomethine ylides to the fullerene cage.[33] Compounds **F1-F5** were isolated and purified by column chromatography. High purity of the obtained products was confirmed by HPLC.

The compositions and molecular structures of the synthesized fullerene derivatives were revealed using the 1D and 2D NMR spectroscopy and mass spectrometry (Figs. S1-S12, Electronic supplementary information, ESI). The NMR spectra revealed the formation of two stereoisomers of pyrrolidinofullerenes **F1** and **F3-F5** due to the hindered nitrogen inversion. Pyrrolidinofullerene **F2** was isolated as a mixture of 5 stereoisomers formed due to the *cis-trans* isomerism of the addends in 2- and 5- positions of the pyrrolidine ring, their restricted rotation due to the proximity of the bulky fullerene cage and also the hindered nitrogen inversion. These stereoisomers showed very similar characteristics which did not allow us to permit their separation and spectroscopic characterization as individual species. We would like to emphasize that each of the synthesized pyrrolidinofullerenes **F1-F5** represented a single regioisomer with 58 π-electron system in the carbon cage (one double bond is opened and functionalized on the C_{60} sphere). Therefore, these compounds are isoelectronic with conventional [60]PCBM and differ significantly from biscycloadducts such as bis[60]PCBM or [60]ICBA.[3,11-13,34-36]

The cyclic voltammetry measurements were used for investigation of the electrochemical properties of the designed fullerene derivatives. The cyclic voltammograms of pyrrolidinofullerenes **F1-F5** exhibited three reversible reduction waves similar to that of [60]PCBM (Fig. 1, Fig. S13, ESI). However, the first reduction (half-wave) potentials were cathodically shifted with respect to [60]PCBM. The magnitudes of this shift were different for 1,2-disubstituted pyrrolidinofullerenes **F1**, **F3**, **F4, F5** (20-70 mV) and 1,2,5-trisubstituted pyrrolidinofullerene **F2** (80 mV, Table 1).

F1 R1=R3=H; R2=R4=R5=CH3O (37%)
F2 R1=2-CH3OC6H4; R2=R4=R5=CH3O; R3=H (21%)
F3 R1=R3=R5=H; R2=R4=CH3O (42%)
F4 R1=R4=R5=H; R2=R3=CH3O (41%)
F5 R1=R2=R3=R4=R5=H (36%)

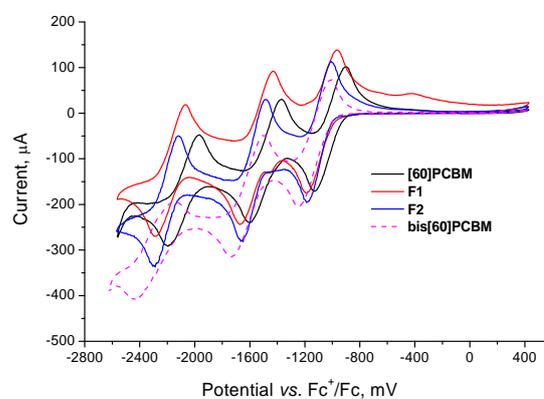**Scheme 1** Synthesis of the fullerene derivatives F1-F5

Figure 1. Cyclic voltammograms of pyrrolidinofullerenes **F1**, **F2**, [60]PCBM and bis[60]PCBM. The cyclic voltammograms of pyrrolidinofullerenes **F3** and **F4** are provided in Fig. S13, Electronic Supplementary Information (ESI).

Table 1 Electrochemical and charge transport characteristics of some fullerene derivatives

Compound	$E^1_{1/2}$, V^a	$E^2_{1/2}$, V^a	$E^3_{1/2}$, V^a	LUMO,^{b} eV	μ_e,^{c} $cm^2V^{-1}s^{-1}$
[60]PCBM	-1.01	-1.49	-2.08	-4.08	1.1×10^{-4}
F1	-1.08	-1.55	-2.18	-4.02	4.3×10^{-4}
F2	-1.09	-1.57	-2.2	-4.01	1.2×10^{-4}
F3	-1.05	-1.52	-2.14	-4.05	1.7×10^{-4}
F4	-1.04	-1.51	-2.14	-4.06	8.0×10^{-4}
F5	-1.03	-1.51	-2.15	-4.06	n/a
bis-[60]PCBM	-1.13	-1.61	-2.29	-3.97	1.07×10^{-5}

^{a}Half-wave reduction potentials are given vs. Fc$^+$/Fc. ^{b}LUMO energies were estimated from the onsets of the first reduction waves using Fermi energy of −5.1 eV for the Fc$^+$/Fc redox couple. ^{c}SCLC mobility was determined in electron-only devices.

It is seen from the Table 1 that fullerene derivatives **F1-F4** have considerably higher LUMO energies with respect to [60]PCBM. Comparing the energy levels of some representative conjugated polymers and fullerene derivatives (Fig. 2) suggests that the solar cells comprising **F1-F4** instead of [60]PCBM can show enhanced open circuit voltages and overall light power conversion efficiencies.

We believe that the observed decrease in the electron affinity of the designed fullerene derivatives **F1-F4** is related to the through-space electronic interactions between the lone electron pair of the pyrrolidine nitrogen atom and the fullerene cage as well as similar interactions involving the alkoxy groups (lone electron pairs of O) introduced in the phenyl substituents in a close proximity to the fullerene cage. For instance, reference compound **F5** comprising no methoxy groups demonstrates lower electron affinity as compared to PCBM (effect of the pyrrolidine nitrogen) but still higher in comparison with **F1-F4** loaded with different number of methoxy groups. It is notable that compounds **F1** and **F2** with the lowest electron affinity possess two and three methoxy groups at the positions 2'- and 6'- of the phenyl substituents in the pyrrolidine ring, respectively.
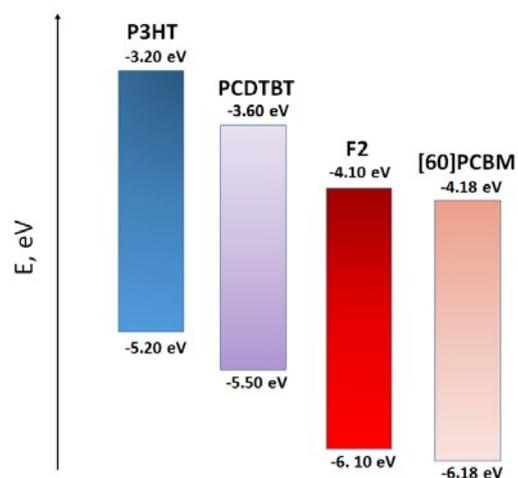

Figure 2. Energy level diagram for P3HT, PCDTBT, **F2** and [60]PCBM showing the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the materials.

It is known that charge transport properties of organic semiconductors affect significantly their photovoltaic performance in devices. In particular, a vast majority of the fullerene bisadducts bearing two cyclic addends randomly distributed on the fullerene cage demonstrate inferior electron transport characteristics. On the contrary, the fullerene derivatives designed in this work comprise a single pyrrolidine-type addend with the well-defined addition pattern to the fullerene cage. However, existence of some stereoisomerism in the structures of **F1-F4** might also affect their charge transport characteristics. The SCLC mobility measurements were performed for the designed compounds and the reference fullerene derivatives [60]PCBM and bis[60]PCBM using electron-only diode devices ITO/Ca/fullerene derivative/Ca/Ag. The obtained results (Table 1) suggest that the fullerene derivatives **F1-F4** have rather good electron mobilities which are similar (**F2-F3**) or even considerably higher (**F1, F4**) as compared to [60]PCBM. On the contrary, fullerene biscycloadducts (e.g bis[60]PCBM) represented by complicated mixtures of isomers demonstrate one order of magnitude lower mobility with respect to [60]PCBM. These results proved that it is possible to achieve the desired reduction in the electron affinity of the fullerene cage while maintaining good charge transport characteristics of the resulting materials.

The designed pyrrolidinofullerenes **F1-F4** were investigated as n-type components of organic bulk heterojunction solar cells in combination with the conjugated polymers P3HT and PCDTBT (Fig. 3a). We would like to emphasize that we utilized inverted device configuration (Fig. 3b) to exclude any possible unfavorable interactions between the pyrrolidinofullerenes and the acidic hole transport layer PEDOT:PSS. The inverted solar cell architecture comprised semitransparent ITO electrode modified with a thin (3 nm) layer of ytterbium collecting the electrons, a photoactive fullerene-polymer blend (60-150 nm) and MoO_3 (3 nm)/Ag (100 nm) hole-collecting electrode. The photoactive composite films were deposited by spin-coating from chlorobenzene (in the case of P3HT) and 1,2-dichlorobenzene (when using PCDTBT) solutions at different spinning frequencies. The polymer : fullerene derivative ratios was also varied from 1:1 to 1:4 in order to find optimal device fabrication conditions. The obtained results are presented in Table 2.
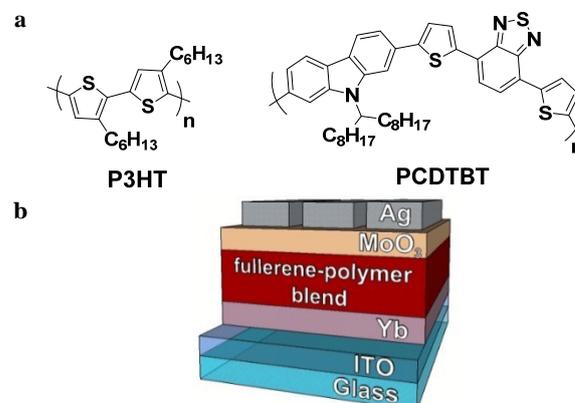

Figure 3. Molecular structures of conjugated polymers P3HT and PCDTBT (a) and schematic layout of the Inverted solar cell architecture (b)

Table 2 Photovoltaic performance of **F1-F4** in combination with P3HT and PCDTBT

Composite	Ratio *	Annealing conditions	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
P3HT/ [60]PCBM	1:0.5	165 ^{0}C, 3 min	599	8.5	60	3.0
P3HT/ **F1**	1:0.7	90 ^{0}C, 15 min	**747**	7.7	59	3.4
P3HT/ **F2**		140 ^{0}C, 3 min	**772**	8.6	55	3.7
PCDTBT/ [60]PCBM	1:4	90 ^{0}C, 15 min	871	7.8	60	4.1
PCDTBT/ **F3**	1:2		**983**	8.9	47	4.1
PCDTBT/ **F4**	1:3		**957**	8.3	52	4.1

* Optimal polymer to fullerene w/w ratio is provided

The light-on J-V characteristics of the fabricated solar cells based on different material combinations are shown in Fig. 4.
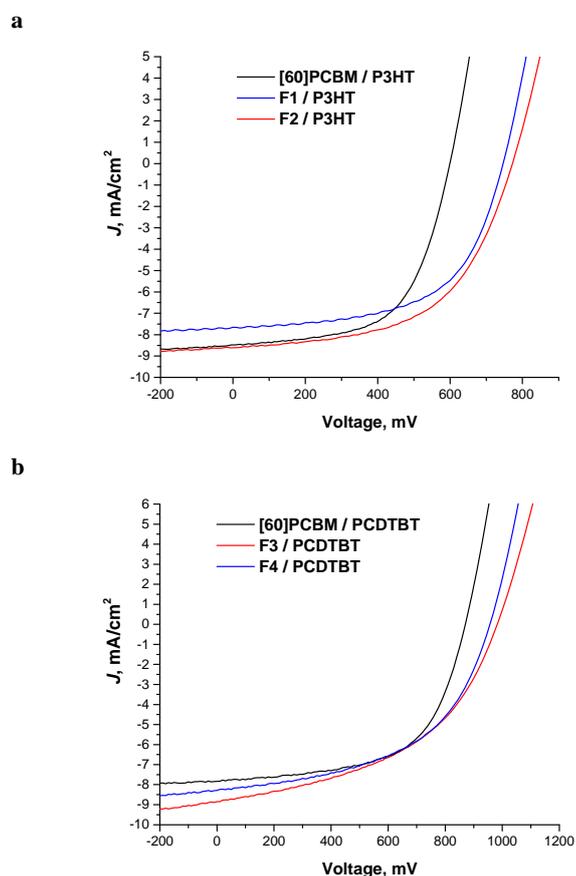

Figure 4. J-V curves of the solar cells based on the composites of the fullerene derivatives **F1**- **F2** with P3HT (a) and the fullerene derivatives **F3**-**F4** with PCDTBT (b) measured under simulated AM1.5 (100 mW/cm^2) illumination

It is notable that organic solar cells comprising the fullerene derivatives **F1-F4** demonstrate strongly increased open circuit voltages as compared to the reference devices with [60]PCBM. We would like to emphasize that the open circuit voltage of 772 mV achieved for the **F2**/P3HT system is even higher than the value obtained for the bis[60]PCBM/P3HT

devices (724 mV, see ref. 3,). The solar cells comprising pyrrolidinofullerenes **F1-F4** and P3HT as a donor polymer demonstrated enhanced power conversion efficiencies in comparison with the reference [60]PCBM/P3HT cells.

We have also shown that pyrrolidinofullerenes can be used successfully as electron donor components in solar cells with push-pull donor-acceptor copolymers such as PCDTBT. In particular, the devices comprising **F3** and **F4** in combination with PCDTBT showed high open circuit voltages of 960-980 mV and reasonable power conversion efficiencies exceeding 4% (Table 2). It should be emphasized that pyrrolidinofullerenes **F3** and **F4** represent virtually the first fullerene derivatives with the reduced electron affinity showing decent photovoltaic performances in combination with the amorphous conjugated copolymers such as PCDTBT. The data provided in Table 2 suggest that dramatically reduced fill factor limits the photovoltaic performance of the **F3**/PCDTBT and **F4**/PCDTBT blends. It is possible that unbalanced fullerene-polymer blend morphology is responsible for the observed low fill factors. The AFM images shown in Fig. 5 do not reveal strong phase separation between donor and acceptor components of the blend. Moreover, the **F3**/PCDTBT and **F4**/PCDTBT composite films showed rather featureless morphology, which is an indication of too strong intermixing between the donor and acceptor components. Therefore, it is very likely that insufficient phase separation between the fullerene derivatives and PCDTBT prevents the formation of efficient percolation pathways required for delivering photogenerated charges towards the respective electrodes. We believe that morphology problems are even more severe in the case of **F1**/PCDTBT and **F2**/PCDTBT blends delivering lower photovoltaic performances (Table S1, ESI).
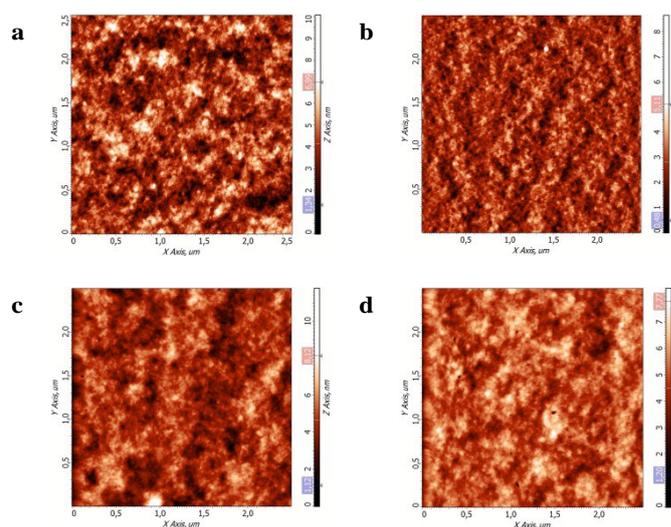

Figure 5. AFM images of thin films of **F1**/P3HT (a), **F2**/P3HT (b), **F3/**PCDTBT (c) and **F4**/PCDTBT (d) blends

At the same time, we have shown that pyrrolidinofullerenes **F1-F4** quench the photoluminescence of PCDTBT in thin films with virtually the same efficiency as [60]PCBM (Fig.

S15-S16, ESI). This observation suggests that lowered electron affinity of **F1-F4** does not prevent efficient charge separation in their blends with PCDTBT. Therefore, inefficient charge collection due to unbalanced active layer morphology seems to be the main factor limiting the performance of the pyrrolidinofullerene/PCDTBT solar cells. Our future research efforts will be aimed to overcome the morphology issues revealed here for the pyrrolidinofullerenes **F1-F4**. In particular, designing novel compounds capable of efficient self-assembling in thin films and/or undergoing stronger segregation from the polymer will be pursued.

Conclusions

Four novel 1,2-disubstituted and 1,2,5-trisubstituted pyrrolidinofullerenes loaded with the electron donor methoxy groups have been synthesized and systematically investigated. It has been shown that introduction of methoxy groups in a close proximity to the carbon cage results in a noticeable decrease in its electron affinity presumably due to direct through-space electronic interactions between the lone electron pairs of the oxygen atoms and the fullerene π-system.

The application of the designed pyrrolidinofullerenes as electron acceptor components of organic solar cells resulted in a significant improvement of the device open circuit voltages as compared to the reference systems comprising conventional [60]PCBM. In particular, the V_{OC} of 772 mV achieved for the F2/P3HT blends represents one of the highest values ever reported for the fullerene monocycloadducts. These findings prove that pyrrolidinofullerenes undoubtedly have a big potential as promising n-type materials with reduced electron affinity.

The light power conversion efficiencies of the solar cells comprising pyrrolidinofullerenes were somewhat higher or equal to the parameters of the reference [60]PCBM-based devices. Unfortunately, enhanced V_{OC} was counterbalanced by reduced fill factors related, most probably, to the unbalanced active layer morphology. Overcoming this obstacle by modifying the molecular structures of the pyrrolidinofullerenes and tailoring their physical properties (e.g. solubility) might lead to the development of a novel generation of the fullerene-based n-type materials for highly efficient organic photovoltaics.

Experimental

Synthesis

The synthetic procedures and spectral data are provided in Electronic Supplementary Information (ESI).

Cyclic voltammetry measurements

Cyclic voltammetry measurements were performed for ~1.10^{-3} M solutions of the fullerene derivatives in a 1,2-dichlorobenzene/DMF (3:2) solvent mixture using a cell equipped with a glassy carbon working electrode (2 mm^2),

platinum wire as a counter electrode and a standard Ag/Ag$^+$ pseudo reference electrode. The scan rate was 50 mV/s. A 0.1 M solution of Bu$_4$NPF$_6$ was used as a supporting electrolyte.

Fabrication of inverted photovoltaic devices

The cleaned and patterned ITO glass (see ref. 37) was modified with 3 nm of Yb deposited by thermal evaporation in vacuum. P3HT (15 mg) or PCDTBT (6 mg) and the corresponding amount of the fullerene derivative (following the optimal weight ratios given in Table 2) were dissolved together in 1 mL of chlorobenzene (P3HT) or 1,2-dichlorobenzene (PCDTBT) with addition of 11 mg of silica (ACROS Organics 40-60 A). The resulting polymer-fullerene blend solutions were filtered through a 0.45 μm PTFE syringe filter and spin-coated at 1200 rpm for 40 sec (P3HT) or at 800 rpm for 140 sec (PCDTBT) on the Yb-modified ITO slides. The deposited films were annealed in argon glove box under the conditions specified in Table 2. The top electrode comprising 3 nm of MoO$_3$ and 100 nm of Ag was deposited by thermal evaporation.

Characterization of photovoltaic devices.

The current-voltage (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 integrated in MBraun glove box. The intensity of the illumination was checked every time before the measurements using a calibrated silicon diode with a known spectral response. The I-V curves were recorded in inert atmosphere using Keithley 2400 source-measurement unit. The active areas of all devices were measured with a good accuracy just after the J-V measurements to estimate the short circuit current densities.

SCLC mobility measurements

The electron-only diodes were fabricated using the following procedure. Thin film (15 nm) of Yb was evaporated on the cleaned ITO glass. Afterwards, a solution of fullerene derivative in PhCl-CHCl$_3$ (1:4 v/v) was spin-coated at different spinning rates (from 100 to 1600 rpm) in order to provide a set of film thicknesses ranging typically from 80 to 700 nm. The diode structure was completed by evaporation of 100 nm of Ca and 100 nm of Al on the top of the fullerene layer. The current-voltage characteristics of the fabricated diodes were recorded inside a nitrogen glove box (MBraun) using Keithley 2400 source-measurement unit. The thickness of the films was determined by making scratches near the corresponding electrodes and profiling them using NTEGRA PRIMA microscope (NT-MDT, Russia) operating in a contact mode. The obtained data were analysed according to the standard space charge limited current (SCLC) model. The SCLC mobility depended on the active layer thickness (due to interface effects, in particular) approaching the maximal values at 200-400 nm. The highest reproducible values are provided in Table 1 above.

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Acknowledgements

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TOC entry

Appropriately designed pyrrolidinofullerenes loaded with electron donor alkoxy groups showed enhanced V_{OC} and power conversion efficiencies in organic solar cells