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Increasing the Open Circuit Voltage of Bulk-Heterojunction Solar Cells by Raising the LUMO Level of the Acceptor

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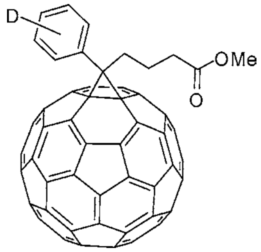
ABSTRACT



We report the synthesis, characterization, and electrochemical properties of ten new fullerene derivatives for usage in organic solar cells. The phenyl ring of PCBM was substituted with electron-donating and electron-withdrawing substituents to study their influence on the LUMO level of the parent fullerene. We varied the LUMO level over a range of 86 mV and show a small but significant change of the open circuit voltage upon application in MDMO–PPV:methanofullerene bulk-heterojunction photovoltaic cells.

The excellent electron-accepting capability of fullerenes has made them interesting materials for organic solar cells.[1] Much work has been done in improving organic solar cells; efficiencies of more then 2.5% have been reached by using a MDMO−PPV:[60]PCBM blend (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-*p*-phenylenevinylene]:phenyl C_{61} butyric methylester).[2] We have reported on organic solar cells with efficiencies of up to 3% using an MDMO−PPV:[70]PCBM blend, while others obtained higher efficiencies by changing the donor polymer to regioregular P3HT (poly(3-hexylthiophene)), and by introducing morphology-improving procedures on the composite film.[3] Several factors are of importance in improving the efficiency of this type of organic solar cell. It is essential that the conjugated polymer has a low band gap (<1.8 eV) to efficiently absorb light in the visible area of the solar spectrum.[4] In the case of the MDMO−PPV:PCBM blend, the solvent from which it is prepared plays an important role. Spin coating from chlo-

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robenzene instead of from toluene led to a threefold increase in the efficiency of the solar cell.[2a] Nevertheless, there is still plenty of room to improve the efficiency of this type of bulk-heterojunction photovoltaic cell. Recently the necessity of improving the V_{oc} has attracted much attention.[5] There is a need for optimizing the electronic match between the donor and acceptor component, in order to minimize unnecessary internal loss of open circuit voltage. We have previously shown that, within certain limits with respect to the electrodes' workfunction (i.e., as long as there are ohmic contacts at both electrodes), the V_{oc} of a bulk-heterojunction PV cell scales linearly with the decrease of the first reduction potential of the acceptor.[6] Later, others confirmed the related relationship, now between the V_{oc} and the first oxidation potential of the donor material.[5a,b] Hence, there is, within certain limits,[7] a linear relationship between the donor-HOMO and acceptor-LUMO energy difference and the V_{oc} of the bulk-heterojunction device. Consequently, the *upper limit* for the V_{oc} of bulk-heterojunction solar cells is determined by the energy difference of the HOMO of the electron donor and the LUMO of the electron acceptor. It should be noted at this point that the fact[8] that for any given donor−acceptor couple as active layer material, minimizing the difference in workfunction of the two metal electrodes leads to a lowering of the V_{oc}, (i.e., now entering the situation where the Fermi levels of one or both electrodes are *not* pinned to the relevant molecular orbital energies, leading to a (also Metal Insulater Metal (MIM) type) device with non-ohmic contacts), is not in conflict with the above-mentioned linear relationship between the orbital levels and the V_{oc}.

Since the LUMO levels in MDMO−PPV and [60]PCBM (**1**; Figure 1) are estimated to be at 2.8 and 3.7 eV below the vacuum level, respectively[1e] (i.e., a 0.9 eV difference!), we expect that the LUMO level of the acceptor can still be raised substantially before the efficiency of the forward electron transfer from MDMO−PPV to the acceptor is lowered to a significant extent. (In the extreme case, if the two LUMO levels, involved in the photoinduced electron transfer, become too close in energy, the driving force would be lost.) State-of-the-art MDMO−PPV:[60]PCBM cells show V_{oc} values up to 850 mV, while the (donor) HOMO−(acceptor) LUMO gap of this pair is around 1.3 eV. This V_{oc} value might be close to what can be maximally expected from this pair, since a loss of 0.2 V at each electrode is assumed to happen in these specific devices.[7b] In other words, we estimate that the V_{oc} of MDMO−PPV:methano[60]fullerene cells could, in principle, be increased to ∼1.3 V (i.e., by ∼50%), upon diminishing the donor−acceptor LUMO−LUMO gap from 0.9 to 0.5 eV, which would still allow for efficient charge generation. An increased V_{oc} raises the efficiency of the solar cells even in a more than linear way by increasing the fill factor.[8] The main challenge, however, is how to alter the methanofullerene by means of substituent effects in such a way that the LUMO is significantly raised, still fully located on the fullerene moiety, and without introducing concomitant *intra*molecular photoinduced electron transfer (or hole transfer) from an electron-rich addend moiety to the fullerene moiety. This process was previously observed by Verhoeven et al. in a similar compound, a 4-dialkylaminophenyl-substituted fulleropyrrolidine.[9]

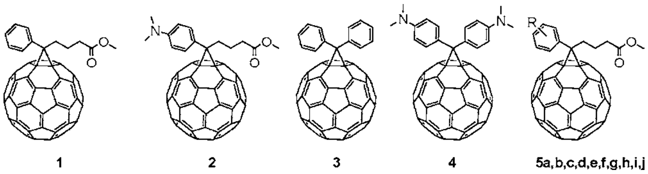

Figure 1. Structures of [60]PCBM (**1**), 4-*N*,*N*-dialkylamino[60]-PCBM (**2**), diphenylmethano[60]fullerene (**3**), bis-4-*N*,*N*-dialkyl-amino-diphenylmethano[60]fullerene (**4**) and substituted PCBM compounds (**5**): R = 4-OMe (a), 3,4-OMe (b), 2,3,4-OMe (c), 2-OMe (d), 2,5-OMe (e), 2,4,6-OMe (f), 3,4-methylenedioxy (g), 2-SMe (h), 4-SMe (i), and pentafluoro (j).

In this paper, we report on our efforts to influence the LUMO level of PCBM by placing electron-donating (methoxy and methyl thioether) and electron-withdrawing (fluorine) substituents on the phenyl ring of PCBM.

Wudl et al. have found that para substituents on the phenyl rings in diphenylmethano[60]fullerenes (**3**; Figure 1) have a negligible effect on the reduction potential of the fullerene moiety.[10] Subsequently, it was claimed that in spiromethanofullerenes a better interaction between the aromatic substituent and the fullerene cage occurred through "periconjugation". The difference in the first reduction potential between a spirofluorene derivative and the corresponding bis-4-dialkylamino derivative (**4**; Figure 1) was found to be ∼70 meV.

In contrast to their two approaches we aimed for a possible direct through space effect of a *substituent* itself on the carbon cage. We hypothesized that an electron-donating substituent on the phenyl ring of PCBM should be at closest proximity to the fullerene cage when connected to the 2-position of the phenyl ring. Subsequent alkoxy or thioether groups on the phenyl ring could then add to the effect of the

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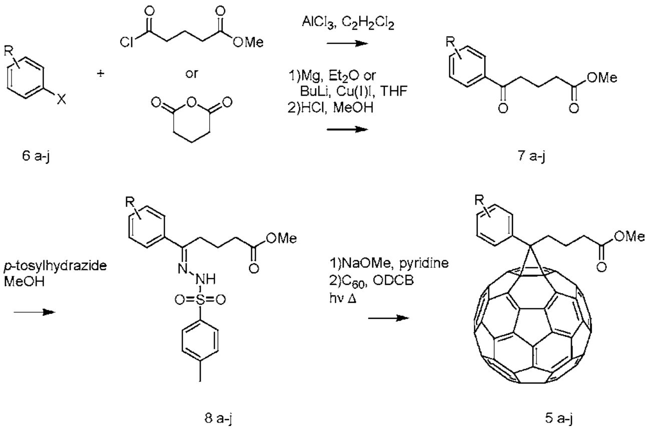
ortho substituent by resonance through the phenyl ring, if at the right position with respect to the ortho substituent (i.e., ortho or para, relative to the ortho substituent). In total, a series of two isomeric monosubstituted, three isomeric bis-substituted, two isomeric tris-methoxy-substituted, two isomeric mono-methyl thioethers, and a pentafluoro[60]PCBM derivative was synthesized (see Figure 1 and Scheme 1, **5a**−**j**).

Scheme 1. Synthetic Overview of All New Fullerenes[a]



[a] Key: (a) R = 4-OMe, X = H. (b) R = 3,4-OMe, X = H. (c) R = 2,3,4-OMe, X = H. (d) R = 2-OMe, X = Br. (e) R = 2,5-OMe, X = H. (f) R = 2,4,6-OMe, X = H. (g) R = 3,4-methylenedioxy, X = H. (h) R = 2-SMe, X = Br. (i) R = 4-SMe, X = H. (j) R = pentafluoro, X = MgBr.

We also aimed for a third tris-methoxy PCBM isomer, with a 2,3,5-substitution pattern, because that would have to be the most effective one, according to the above-mentioned hypothesis. Until now, however, we have been unable to prepare the correspondingly substituted methyl benzoylbutyrate derivative.

The ^{13}C NMR spectra of all *o*-methoxy and *o*-methyl thioether substituted phenyl methanofullerene isomers showed *two* resonances in the 80 ppm region for the two cyclopropyl sp^3 carbon atoms of the fullerene cage, instead of the usual one only, clearly indicating a severely hindered rotation of the phenyl ring when ortho substituted with methoxy or methyl thioether groups. We therefore conclude that in the *o*-methoxy and methyl thioether substituted PCBM derivatives the phenyl rings are, with strong preference, in a conformation close to horizontal with respect to the fullerene surface. In principle, this would allow for a good electronic overlap between the oxygen or sulfur lone pairs and the fullerene π-system. This should be visible in cyclic voltammetry. A lowering of the first reduction potentials (with respect to the Fc/Fc$^+$ redox couple) of the ortho-substituted PCBM derivatives when compared to the PCBM derivatives without ortho substitution is expected. Furthermore, a difference between the oxygen and sulfur versions was expected. The first reduction potentials of all PCBM derivatives were measured by cyclic voltammetry. The obtained CV data are presented in Table 1. All reductions were reversible.

Table 1. Cyclic Voltammetry Data

compd[a]	$E_{1/2}$,1,reduction	ΔE (mV)[b]
2-OMe-PCBM	−1.104	76
4-OMe-PCBM	−1.096	76
2,5-OMe-PCBM	−1.106	76
3,4-OMe-PCBM	−1.099	85
3,4-methylenedioxy-PCBM	−1.071	59
2,3,4-OMe-PCBM	−1.118	81
2,4,6-OMe-PCBM	−1.128	73
2-SMe-PCBM	−1.086	73
4-SMe-PCBM	−1.085	73
F5-PCBM	−1.042	87
PCBM	−1.084	83

[a] Experimental conditions: *V* vs Fc/Fc$^+$, Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte, ODCB/acetonitril (4/1) as the solvent, 10 mV/s scan rate. [b] Energy difference between peak potentials (forward and backward sweep).

Since the first reduction potentials of all but one of the methoxy-substituted PCBM derivatives are more negative than the first reduction potential of PCBM, it can be concluded that the LUMO levels of the fullerenes are indeed raised slightly, but significantly, with respect to the LUMO level of PCBM. However, we do not observe a significant difference between either the first reduction potential of 2-OMe-PCBM and 4-OMe-PCBM (8 mV) or the first reduction potential of 2,5-OMe-PCBM and 3,4-OMe-PCBM (7 mV). We therefore conclude that the ortho position of the phenyl substituent does *not* result in the expected direct through space electronic overlap between the oxygen lone pairs and the fullerene π-system. We do observe a significant decrease of the first reduction potentials when going from two to three alkoxy substituents. Hence, it appears that the number of alkoxy substituents is of importance, rather than the position of the substituents. Furhermore, we can conclude that substituting the phenyl ring with methyl-thioether moieties has no effect on the LUMO level of the parent fullerene, indicating that their donating power is insufficient. The electron-withdrawing effect of the fluorine atoms, however, is clearly visible in the first reduction potential of F$_5$-PCBM. The fluorescence spectra of all compounds were qualitatively and quantitatively very similar. Hence, significant photoinduced intramolecular charge transfer does not occur, even in the compounds with the strongest electron-donating groups (see the Supporting Information).

A series of ten photovoltaic devices was fabricated containing MDMO−PPV as the electron donor and the ten substituted PCBM derivatives shown in Figure 1, respectively, as the electron-acceptor material. The devices were made with the following configuration: ITO/PEDOT/(MDMO−PPV:PCBMX)/LiF/Al. In earlier work it was shown that for the specific combination of MDMO−PPV (from Covion) and PCBM, maximum power conversion efficiencies of 2.5% at standard test conditions (AM1.5, 100 mW/cm^2) could be obtained by using a high content of PCBM (80 wt %) relative to MDMO−PPV and with chlorobenzene as the solvent for spincoating.

However, it turned out that most of the new PCBM acceptor materials were poorly soluble in chlorobenzene, so that devices could not be made in a proper way from that solvent. Only two of the PCBM derivatives, i.e., 3,4-OMe-PCBM and 2,3,4-OMe-PCBM, were soluble enough in chlorobenzene to make working devices. *o*-Dichlorobenzene was therefore chosen as the general processing solvent.

In Figure 2, the V_{oc} values are plotted against the measured reduction potentials (from Table 1) of the methoxy-substituted PCBM derivatives.

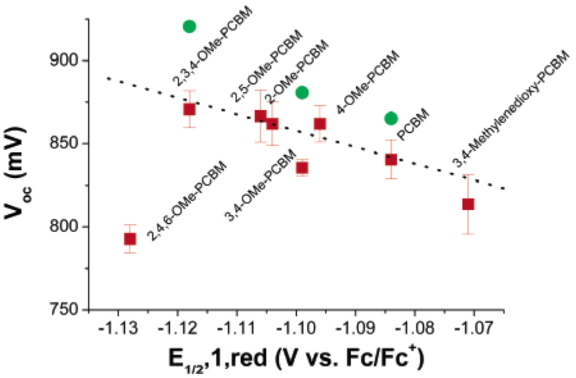


Figure 2. V_{oc} of devices from MDMO−PPV blends vs the first reduction potental, $E_{1/2}$,1,red (V vs ferrocence/ferrocence$^+$) of the PCBM derivatives: squares, from ODCB; circles, from chlorobenzene. The dotted line is to guide the eye for a 1:1 relationship between V_{oc} and $E^{1/1}{}_{red}$.

In a separate experiment, devices were constructed with both thioether substituted PCBMs and the pentafluoro substituted PCBM analogues. We found a slightly lower V_{oc} value of 4-SMe-PCBM to PCBM (20 mV lower). F_5-PCBM gave a value 40 mV lower than that of PCBM, according to expectations. The insolubility of 2-SMe-PCBM in ODCB rendered it impossible to construct a representable device. Similar problems occurred with 2,4,6-OMe-PCBM. We attribute its low V_{oc} to these insolubility problems, leading to at best marginally successful bulk-heterojunction morphology. When the domain sizes in the blend are too big, fewer charge carriers are formed, resulting in a decreased splitting of the quasifermi levels, hence lowering the observed V_{oc} at the same light intensity.

We would like to stress that the presented values are not obtained from fully optimized devices since the optimization of ten new donor acceptor combinations is an extraordinarily time-consuming process. However, the trend is clearly visible, indicating that raising the LUMO level of the acceptor fullerene does give a higher V_{oc} in fullerene:polymer solar cell devices. Moreover, that trend seems to be linear, in agreement with previous results.

In conclusion, we have synthesized a series of ten new PCBM anologues with LUMO levels varying over ∼85 mV, allowing further optimization of the open circuit voltage of polymer:fullerene organic solar cells.

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Supporting Information Available: Experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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