Organic Solar Cells

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1,4-Fullerene Derivatives: Tuning the Properties of the Electron Transporting Layer in Bulk-Heterojunction Solar Cells**

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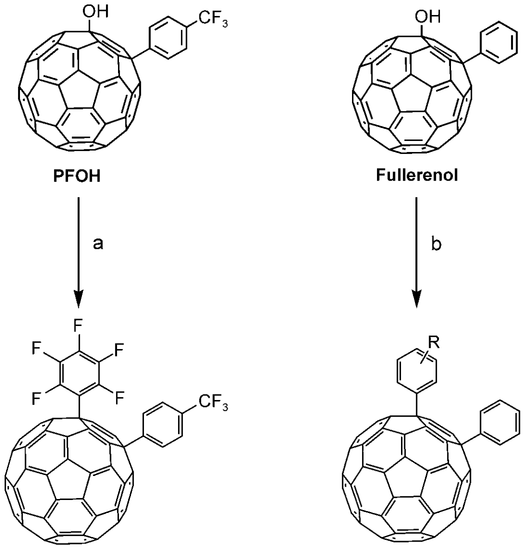
Light and flexible photovoltaic devices based on organic materials are extensively studied as an alternative to expensive and fragile silicon-based solar cells.[1] The efficiency of these devices is rapidly increasing with the most recent power conversion efficiency (PCE) of greater than 8% bringing them closer to commercial viability.[2] Further improvements are needed and can be achieved by optimizing the ratio between donor and acceptor, modifying the electronic properties of the materials,[3] and optimizing the morphology of the resulting bulk heterojunction (BHJ).[4]

A direct way to increase the efficiency is to lower the band gap of the donor material in order to absorb a greater fraction of the solar spectrum.[5] This concept has been explored through the synthesis of a series of new low band gap polymers, which exhibit a decreased band gap as a result of lowering the lowest unoccupied molecular orbital (LUMO).[6] An emerging challenge is the need for electronically compatible acceptors with sufficiently low LUMO levels so that charge separation is efficiently promoted. Optimum miscibility of a specific polymer and fullerene combination to create the optimum degree of phase separation is also a feature to take into account. Typically, the approach used to test new donor materials is to fabricate devices using $PC_{61}BM$ ([6,6]-phenyl-C_{61}-butyric acid methyl ester), a well-studied benchmark acceptor. Only a limited number of other fullerene derivatives have been successfully employed.[1,7] Although these fullerene derivatives bear different functional groups, they are related by the positioning of the substituents on carbons 1 and 2 of a six-membered ring. From literature studies it is apparent that even subtle modification of the nature and especially position of substituents can drastically alter the electronic properties of fullerene derivatives. For example, $PC_{71}BM$ has reduced symmetry that increases visible light absorption and has a positive effect on current generation in polymer BHJ cells.[8]

Here we report the synthesis of a series of novel fullerene derivatives functionalized through the “1,4” position and their use in organic photovoltaics (OPVs). Features that distinguish this class of fullerene derivatives are: 1) straightforward synthesis which includes versatility of functionalization with different substrates starting from the same material (fullerenol, Scheme 1); 2) tunable LUMO energy by appending electron-donating or electron-withdrawing groups; 3) lower symmetry which decreases the optical gap and produces an increased absorption in the visible (the extinction coefficient at 480 nm of a 1,4-adduct is approximately 8 times larger than that of PCBM) ; 4) tunable solubility which influences the morphology of the BHJ. Like $PC_{71}BM$, 1,4-addends have increased light absorption at ca. 500 nm (Figure 1) with the advantage that all the C_{60} derivatives



Scheme 1. Synthesis of the derivatives from fullerenols. a) Pentafluorobenzene, TsOH, 70 °C, 12 h. b) Substituted benzene (trialkyloxybenzene, 2-ethylhexylbenzene, phenylvaleric acid methylester, aniline, anisole), TsOH, 80 °C, 12 h.

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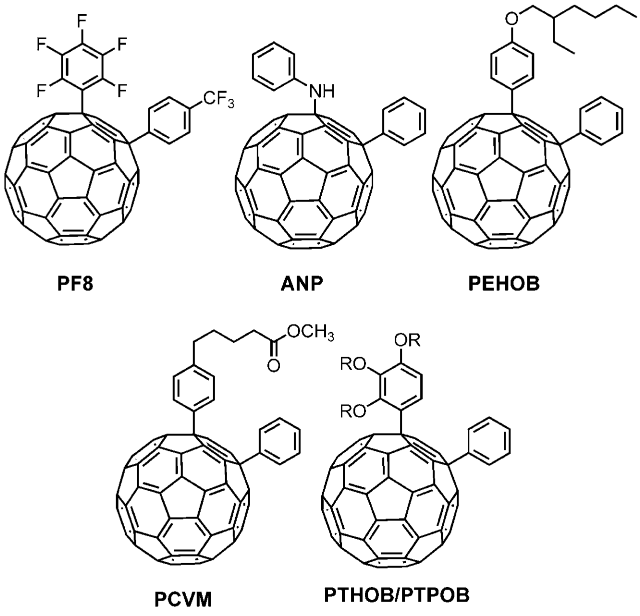
presented here are the same kind of molecules and not a mixture of isomers.[8]

In virtue of all these points we decided to investigate the chemistry to synthesize a large set of 1,4 fullerene derivatives (Schemes 1 and 2) with different LUMO energy levels and different solubility. Then, in order to prove the concept of tunability of their properties, we fabricated BHJ solar cells employing some of these derivatives. We observed a significant change in the photovoltaic (PV) characteristics of the devices that could be predicted from the specific properties of each fullerene (for instance increased open circuit voltage using higher LUMO fullerenes). In addition to study the chemistry of C_{60}, we also tested the reaction on C_{70}, where the ^{1}H NMR spectrum displayed three proton signals of exactly the same intensity corresponding to the alcohol group. We concluded that three isomers formed during this reaction, which is consistent with other C_{70} functionalization such as the synthesis of $PC_{71}BM$.[7] To the best of our knowledge, there is only one example of 1,4-fullerene addend used in solar cells in a p-i-n layered architecture different from the classical BHJ.[9] Nevertheless, in this example the fullerene derivative bears the same functional groups on both carbons and therefore it is more symmetrical. Additionally, it is employed in a non-classical BHJ architecture using an insoluble benzoporphyrin as the organic donor, instead of a polymer.



Scheme 2. Structure of some of the 1,4-addends synthesized and studied. R = propyloxy or hexyloxy.

The synthesis of the novel 1,4-adducts reported herein was achieved by Wang and co-workers by reaction of 1,4-fullerenol with a variety of different aromatic substituents.[10] The procedure developed for the synthesis of the addends was to react the 1,4-aryl fullerenol with a substituted benzene, used as the solvent of the reaction, and in the presence of *p*-toluene sulfonic acid (TsOH).[10a] The identity of the 1,4-fullerene addends was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy (the latter displayed more than 40 signals for the sp^2 carbons on the fullerene, which is consistent with C_2 symmetry) as well as mass spectrometry. The UV/Vis spectrophotometry of these addends displayed an increased and wider absorption compared to traditional fullerenes, with an onset at approximately 500 nm and extinction coefficient of ca. 5000 mol^{-1} cm^{-1} (Figure 1). The energy of the LUMO was estimated by the first peak of the reduction measured by cyclic voltammetry and that of the HOMO by subtracting the value of the optical gap in solution. These values were compared to those obtained by UV photoelectron spectroscopy (UPS), in which the energy of the HOMO was calculated from the binding energy in the solid state and that of the LUMO was estimated using the optical gap of the films on glass. Despite the large difference in the absolute values using these techniques, the relative values are consistent. A summary of the LUMO energy values for the 1,4-fullerene adducts synthesized here and for PCBM can be found in Table 1 (calculation detailed in the Supporting Information). Compared to the PCBM analogues described by Hummelen et al.,[3] the 1,4-fullerene addends with substituents directly appended appear to affect their redox potentials to a greater degree. For instance, one pentafluorophenyl group on PCBM raises the redox potential from −1.08 mV (PCBM) to −1.042 mV (net change 0.038 V), whereas PF8 is increased from −1.02 to −0.910 mV (net change 0.11 V; see Table 1 and reference [3]).

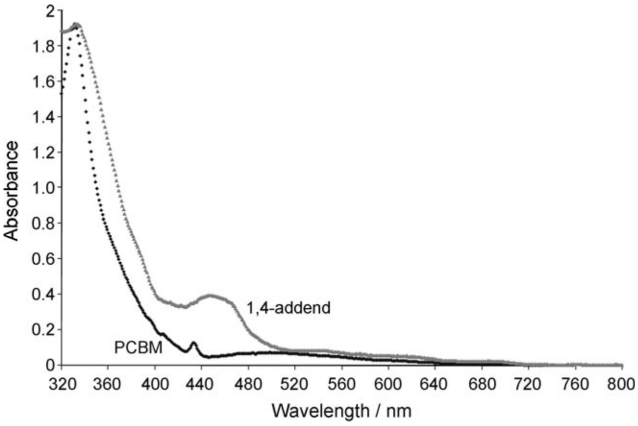


Figure 1. UV/Vis absorption of PEHOB (gray; see Scheme 2) and PCBM (black) in 1,2-dichlorobenzene normalized at 350 nm.

Table 1: Reduction potential of addends calculated from cyclic voltammetry (1,2-dichlorobenzene, scan rate 50 mV s^{-1}).

Addend	E^1_{red}	E^2_{red}	LUMO [eV][a]	LUMO [eV][b]
PFOH	−0.94	−1.46	−3.86	–
PF8	−0.91	−1.37	−3.91	−4.75
ANP	−0.99	−1.53	−3.81	–
PEHOB	−1.06	−1.50	−3.74	−4.30
PCVM	−1.02	−1.48	−3.76	−4.30
PTHOB	−1.15	−1.59	−3.65	−4.24
PCBM	−1.05	−1.47	−3.74	−4.30

[b] Calculated from the onset of the first reduction potential against ferrocene measured from CV. [b] Estimated from the onset of the optical density added to the HOMO value calculated from UPS.

As anticipated above, we decided to focus our attention on tuning various properties of the fullerenes by appending different functional groups to the 1,4-fullerenol. In order to study the reactivity we initially allowed the aryl fullerenol to react with anisole and we observed the formation of the *para* isomer. The appending of the methoxy group did not alter significantly the LUMO energy, compared to other 1,2-addends such as PCBM. This was in agreement with a previous report, where only one alkyloxy group in proximity of PCBM did not alter the LUMO energy.[3] Nevertheless, the HOMO level was higher as the band gap was smaller, which was confirmed quantitatively by UPS. Due to the poor solubility, this derivative was not employed to fabricate photovoltaic devices. In order to make this compound suitable for solution processing, we appended a 2-ethylhexyloxy group yielding PEHOB. The synthetic procedure was analogous to that of the anisole derivative but using 2-ethylhexyloxy benzene. Although the overall yield was low (ca. 10%), more than 60% of fullerenol, as well as the 2-ethylhexyloxy benzene, could be recovered and re-used.

In order to increase the LUMO energy of the fullerene derivative, we chose to append the stronger electron-donating group 1,2,3-trialkyloxy benzene (propyloxy benzene yielded PTPOB and hexyloxy benzene PTHOB; see Scheme 2). The tri-alkyloxybenzenes were synthesized according to literature procedures and used in multiple reactions as the solvent.[11] Surprisingly, despite the steric hindrance caused by the alkyloxy groups, we only observed the formation of the product with the benzene appended in *meta* to the central alkoxy carbon. Both ^{1}H (Figure 2) and ^{13}C NMR spectroscopy confirmed the presence of two distinct protons and five carbon atoms. The LUMO energy of PTHOB/PTPOB was 50 to 100 mV higher than that of PCBM, depending whether measured in solution or in the solid phase. In addition to a smaller band gap as other 1,4 derivatives, the trialkyloxy derivatives delivered a higher V_{OC} (detailed below) and tunable miscibility with the polymer by varying the alkyl chain length. The yield was approximately 20% and, once again, both fullerenol and alkyloxy benzene could be re-used.

We then attempted to create a derivative with a further increased LUMO by reacting fullerenol with aniline. The aniline could act as electron-donating group, but under these synthetic conditions we only observed formation of an N-bonded addend directly bound to the C-4 on C_{60} (ANP). In this case, since the nitrogen is more electronegative than carbon, it acted as an electron-withdrawing group and lowered the LUMO by approximately 50 mV. The yield was much higher than for previous derivatives (approximately 40%) and the synthesis is interesting because it showed a simple and straightforward way to create a C–N bond directly on the fullerene.

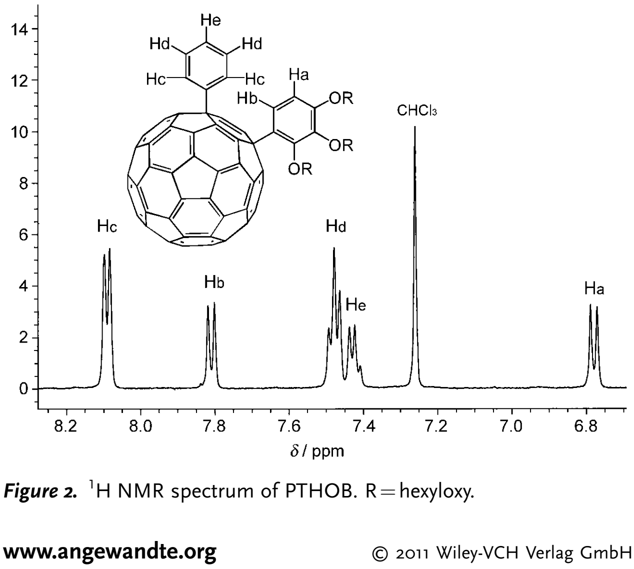


Figure 2. ^{1}H NMR spectrum of PTHOB. R = hexyloxy.

To stabilize the LUMO energy, the fullerenol derivative was allowed to react with pentafluoro benzene, a very strong electron-withdrawing group. The synthesis was performed using a *para*-trifluoromethyl-substituted fullerenol as shown in Scheme 1 (PFOH). The LUMO energy is greatly decreased by more than 200 mV and the HOMO is similarly lowered. This material should be compatible with very low LUMO polymers which cannot transfer charge to PCBM or other acceptors with similar energy levels. Moreover, due to their low surface energy, highly fluorinated compounds tend to self-aggregate on the top of blended films[12] which is favorable for the specific device architecture of OPVs.

BHJ solar cells were also fabricated using regioregular poly(3-hexylthiophene) (*rr*-P3HT) as the electron-donating polymer and PTPOB and PTHOB as the electron-accepting 1,4-fullerene adducts. This series was chosen because it allows us to demonstrate both the tunability of the electronic properties (higher LUMO level) and relative degree of phase separation (using different alkyl chain lengths). As anticipated above, this series of materials possesses a higher LUMO and broader absorption as well as tunable solubility with no effect on the energy levels. The ability to separate the relative degree of phase separation from the electronic properties is of particular interest for future studies. These devices were fabricated using a solvent annealing technique (detailed in the Supporting Information). For the fabrication of the devices we used conditions appropriate for P3HT/PCBM BHJ solar cells, but there might be processing conditions that could further optimize the performance of 1,4-addends. Given the different properties of each fullerene, the solar cells would require a large degree of optimization that is beyond the scope of this report. All current–voltage characteristics for the fabricated devices containing the different 1,4-fullerene adducts can be viewed in the Supporting Information. A parallel study was also conducted using PCBM, which has a lower LUMO and does not absorb in the visible. As reported in Figure 3, devices of P3HT:PTPOB combined at a 1:1 w/w ratio and annealed at 165 °C for 10 min yielded devices with a median efficiency of 2.3%. Similarly, devices of P3HT:PTHOB were fabricated with a 1:1.1 w/w ratio (larger fraction of fullerene to compensate for larger weight of insulating alkyl chains) and found to yield devices with a median efficiency of 1.2%, after annealing at 165 °C for 30 min. Increasing the length of alkyl chain from propyl to hexyl (without changing the molar ratio of fullerene to polymer) yielded devices with a lower short circuit current density and fill factor (Figure 3). It is hypothesized that this is due to non-optimal phase separation within the device. These materials provide a means to test important hypotheses with regards to the relationship of the solubility of fullerenes in the

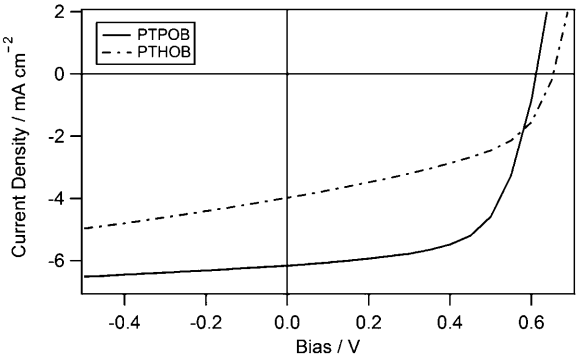


Figure 3. *J–V* curves of solar cells fabricated with PTPOB/P3HT in a 1:1 ratio and PTHOB/P3HT in a 1.1:1 ratio.

polymer to photoconversion efficiency by providing a series of derivatives with similar electronic levels, but varying solubility. This relationship of solubility to efficiency has been previously detailed with a number of different 1,2-fullerene derivatives.[13] Note that devices made from PCBM as the electron acceptor at a ratio of 1:0.8 were found to give median efficiencies of 2.8%. The most notable improvement was that the alkoxylated 1,4-derivatives yielded approximately 70 mV higher V_{OC}, consistent with the observation of higher LUMO energy. However, the increased absorption had little improvement on the short circuit current density, which is attributed to non-optimal active layer morphology and may be more important for polymers that do not strongly absorb light with wavelengths ranging from 400–500 nm.

In conclusion we explored the syntheses of novel fullerene addends based on 1,4-addition, tuned the electronic, chemical and physical properties of the derivatives, and investigated their use in BHJ solar cells. More specifically, we described an approach to increase or decrease the LUMO energy of the 1,4-addends and how its value influences the V_{OC} of the device. The 1,4-derivatives are less symmetrical than previous reported fullerenes and therefore display a stronger absorption in the visible. Finally, the effect of altering the solubility of the fullerene in the polymer has been explored and will be subject of future reports.

Experimental Section

Chemicals were purchased from Sigma–Aldrich, Acros Organics, SES Research, Fisher Scientific, Merck and used as received without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker 500 MHz spectrometer and referenced to the solvent peak. Mass spectrometry was performed by the UC Santa Barbara Mass Spectrometry Laboratory. UV/Vis spectra were recorded on an Agilent 8453 spectrophotometer using 1,2-dichlorobenzene (ODCB) solution of fullerene in 1 cm quartz cuvettes at room temperature. The electrochemical measurements were carried out with a Princeton Applied Research Model 263A Potentiostat/Galvanostat employing Ag/AgCl as reference electrode, a platinum wire as a counter electrode, and an internal ferrocene/ferrocenium standard. Solutions of fullerenes were in dry ODCB containing 0.1M tetrabutylammoniumhexafluorophosphate as the supporting electrolyte.

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