Fullerenes

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Heteroanalogues of PCBM: N-Bridged Imino-PCBMs for Organic Field-Effect Transistors**

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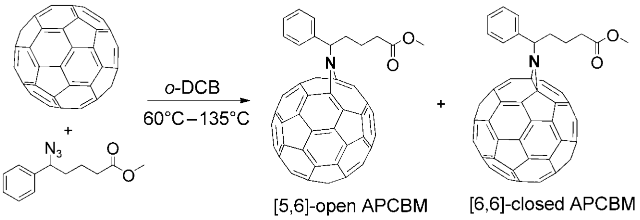
The extraordinary electronic properties of the fullerene C_{60} as an n-type semiconductor with relatively high carrier mobility have evoked continued interest in the development of a wide variety of chemically modified fullerene derivatives.[1–13] One of the most reliable and versatile routes to functionalization has been studied by our research group and involves the addition of diazo compounds to C_{60},[11] which results in two isomeric products such as [5,6]-open fulleroids and [6,6]-closed methanofullerenes.[2,3] From an electronic-structure point of view, the [5,6]-open isomers are appealing since they conserve the 60 π electrons of the parent C_{60}. However, they readily transform into the thermodynamically more stable [6,6]-closed isomers by thermal, electrochemical, pH, and photochemical means,[2,3,14–16] thus making their intrinsic properties in electronic applications difficult to assess.

Therefore, we directed our attention toward the reaction of azides with C_{60} for the following reasons: 1) the possibility of an increased degree of stabilization of the [5,6]-open versus [6,6]-closed isomers[17–19] and 2) the potential influence of the nitrogen heteroatom of iminofullerenes on the electronic properties of the fullerene cage,[20] which can possibly tune the device performance. This is important since it enables us to study the electronic device performance whilst comparing two isomeric configurations, that is, hexagon–pentagon (C_{60}-like) versus hexagon–hexagon junction (PCBM-like; PCBM = [6,6]-phenyl-C_{61}-butyric acid methyl ester), as a function of the perturbation of the fullerene π system. To the best of our knowledge, no examples of performance evaluation between methanofullerene and iminofullerene C_{60} adducts in electronic applications exist.

Of the many monoadducts of C_{60}, PCBM is one of the most successful fullerene adducts in organic electronic applications such as organic photovoltaics (OPV) as well as organic field-effect transistors (OFETs). Herein, we report the one-pot preparation of two isomeric imino-PCBMs, that is, [5,6]-open azafulleroid ([5,6]-open APCBM; PCBM = [6,6]-phenyl-C_{61}-butyric acid methyl ester, A = aza) and [6,6]-closed aziridinofullerene ([6,6]-closed APCBM; Scheme 1). The characteristics of OFETs with [5,6]-open APCBM and [6,6]-closed APCBM in solution-processed devices have been determined and compared with those of PCBM, as part of our study to assess a range of n-type semiconductor properties.

Scheme 1. Structures of PCBM, [5,6]-open APCBM, and [6,6]-closed APCBM.

In our original work, it was shown that 1,3-dipolar [3+2] cycloaddition of azides to C_{60} followed by thermal extrusion of N_2 from the triazoline intermediate leads to [1,6]azafulleroids and [1,2]aziridinofullerenes.[18,19] Depending on the nature of the substituents, the thermal elimination of N_2 affords different ratios of two isomeric imino adducts.[21–23] Following previous work,[23] the preparation of two imino-PCBMs ([5,6]-open azafulleroid; [5,6]-open APCBM and [6,6]-closed aziridinofullerene; [6,6]-closed APCBM) was performed by thermal reaction of methyl 5-azido-5-phenylpentanoate[24] with C_{60}, followed by in situ thermal extrusion of N_2 (Scheme 2). Column chromatography on silica gel yielded [5,6]-open APCBM as a major isomer (45 % yields based on consumed C_{60}) and [6,6]-closed APCBM as a minor adduct (4.8 %; see the Experimental Section). The ^{1}H NMR



Scheme 2. Synthesis of [5,6]-open APCBM and [6,6]-closed APCBM. *o*-DCB = *o*-dichlorobenzene.

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spectrum of [5,6]-open APCBM shows the tertiary hydrogen atom adjacent to the nitrogen atom as a doublet of doublets at 5.20 ppm ($J = 9.33$ and 3.39 Hz). The ^{13}C NMR spectrum reveals 42 signals between $\delta = 148$ and 132 ppm, which are attributable to the fullerene carbon atoms. In the case of [6,6]-closed APCBM, the ^{1}H NMR spectrum shows that the hydrogen atom α to the nitrogen atom not only exhibits a high-field shift from the open isomer to $\delta = 4.56$ ppm, but also the ^{13}C NMR spectrum displays 12 highly symmetrical fullerene resonances (see the Supporting Information).

The UV/Vis absorption characteristics of C_{60}, PCBM, [5,6]-open APCBM, and [6,6]-closed APCBM in chloroform solution are shown in Figure 1. To identify the features that change through iminofunctionalization on C_{60}, the pristine C_{60}, and PCBM data obtained in this study are also listed in Table 1. The absorption features of PCBM and [6,6]-closed APCBM both show a distinguishable sharp band at 430 nm and 423 nm, respectively, which reflects the partially broken symmetry (C_{2v}) of the fullerene core relative to pristine C_{60} (I_h). The UV/Vis spectra of C_{60} and [5,6]-open APCBM are almost identical in shape, with a peak at 330 nm and 332 nm and broad bands at 540 nm and 547 nm, respectively, which are bathochromically shifted compared to the closed forms (PCBM and [6,6]-closed APCBM). These results are clearly suggestive that the absorption characteristics of the functionalized C_{60} derivatives are governed by the π system of the fullerene. Another noticeable difference occurs in the solution colors, which are purple, brown, dark greenish-brown, and dark wine-red for C_{60}, PCBM, [5,6]-open APCBM and [6,6]-closed APCBM, respectively. This observation implies that the optical features of the C_{60} analogues are also affected by the inductive effect of the bridged atoms in the fullerenes, that is, the electron-donating and -withdrawing nature of the corresponding functionalizing addends.

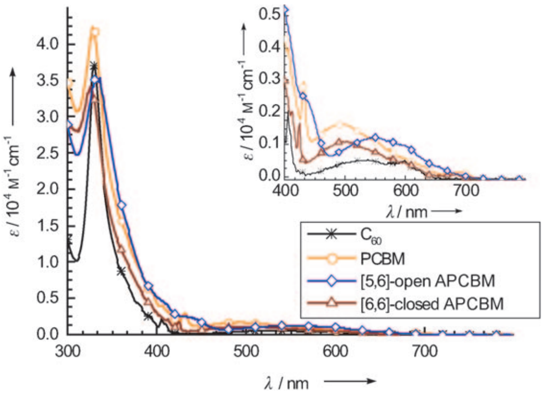

Figure 1. UV/Vis absorption spectra of solutions of C_{60}, PCBM, [5,6]-open APCBM, and [6,6]-closed APCBM in $CHCl_3$.

Table 1: Optical data for compounds in this study.

Compound	Absorption [nm]
C_{60}	330, 405, 540, 600, 623(sh)
PCBM	328, 430, 490, 603(sh), 695
[5,6]-open APCBM	332, 435(sh), 547, 602(sh)
[6,6]-closed APCBM	326, 423, 495, 607(sh), 685

The cyclic voltammograms of [5,6]-open APCBM and [6,6]-closed APCBM not only show three reduction waves but also all reductions exhibit clear quasireversibility (see the Supporting Information). The data for all materials are summarized in Table 2. The reduction potentials of the functionalized C_{60} adducts are shifted toward more negative values with respect to C_{60} because of fewer π electrons and release of strain energy.[25]

Table 2: Electrochemical data for compounds in this study.[a]

Compound	E^1_{red}	E^2_{red}	E^3_{red}
C_{60}	−1.071	−1.484	−1.969
PCBM	−1.158	−1.540	−2.039
[5,6]-open APCBM	−1.114	−1.512	−1.984
[6,6]-closed APCBM	−1.110	−1.504	−2.000

[a] Experimental conditions: values for $0.5(E_{pa}+E_{pc})$ in V versus Fc/Fc$^+$ (Fc = ferrocene) in o-DCB solution (10^{-4} to 10^{-3} mol L^{-1}) with Bu_4NClO_4 (0.1 M) as the supporting electrolyte and Pt wire as the counterelectrode; scan rate = 50 mV s^{-1}.

[5,6]-open APCBM and [6,6]-closed APCBM show less negative reduction values than PCBM. A likely rationale for this redox behavior is the higher electronegativity of the nitrogen atom relative to the analogous carbon atom, which results in slightly reduced electron density in the fullerene shell. It is also interesting to note that the reduction potentials reveal remarkable similarities between [5,6]-open APCBM and [6,6]-closed APCBM, which is in contrast to most all-carbon systems, in which the reduction waves of the open form occur at almost the same potential as in C_{60} since they are isoelectronic analogues of C_{60} (60 π electrons).[3] These results suggest that the reduction potentials of the functionalized C_{60} derivatives stem from a combination of the nature of the bridge atoms and the binding mode in fullerene framework.

The differences in the properties of n-channel OFETs that contain the isomeric structures can provide an important guideline for the design of C_{60} derivatives for electronic applications. All n-type OFETs were fabricated on heavily doped Si wafers with a 200 nm thick SiO_2 layer with top contact geometry as shown in Figure 2a. Figure 2b shows the transfer characteristics, I_{ds} against V_{gs} and $I_{ds}^{1/2}$ against V_{gs} ($V_{ds} = 60$ V), of the OFETs fabricated with [5,6]-open APCBM and [6,6]-closed APCBM as an active layer, respectively, compared to the PCBM measured under identical conditions. Both [5,6]-open APCBM and [6,6]-closed APCBM display typical behavior of ideal n-type OFETs as well as excellent output characteristics with clear saturation (Figure 2c,d). Notably, a non-negligible difference between [5,6]-open APCBM and [6,6]-closed APCBM in the plot of I_{ds} against V_{gs} is observed (the plot of $I_{ds}^{1/2}$ against V_{gs} clearly shows this difference), which allows the alternation of OFET performance in the characteristic output curves. The linear plot of $I_{ds}^{1/2}$ against V_{gs} derived from the measurements of I_{ds} against V_{gs} yields electron mobilities of $\mu_1 = 4.1 \times 10^{-2}$ cm^2 V s,

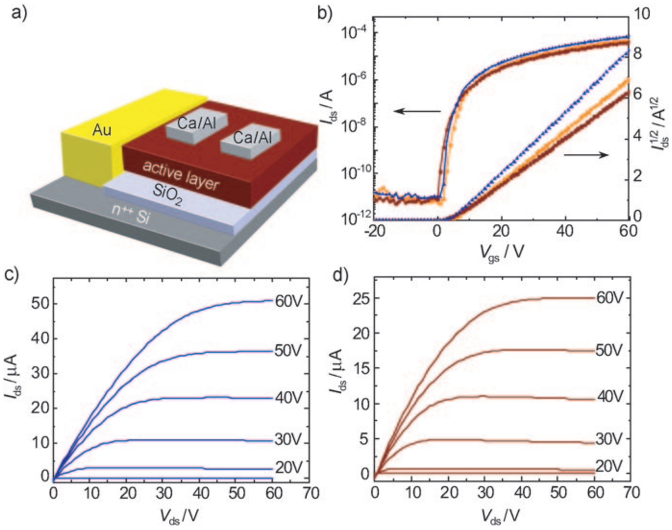

Figure 2. a) Schematic diagram of the n-type OFET structure ($L = 50$ μm, $W = 1.5$ mm). b) Transfer characteristics in the saturated regime (🟥; PCBM, ▲; [5,6]-open APCBM, ●; [6,6]-closed APCBM). Output curves at different gate voltages for c) [5,6]-open APCCM and d) [6,6]-closed APCBM.

$\mu_2 = 2.3\times10^{-2}$ cm^{2}Vs, and $\mu_3 = 2.8\times10^{-2}$ cm^{2}Vs for [5,6]-open APCBM (μ_1), [6,6]-closed APCBM (μ_2), and PCBM (μ_3).[26] The higher electron mobility in the [5,6]-open APCBM OFET can be attributed to its 60π-electron nature, which affords a stronger electron-acceptor strength than that of the [6,6] junctions.[27] On the other hand, the mobility value of the [6,6]-closed APCBM reveals an obvious similarity to the isoelectronic isomer PCBM. These results are indicative that the nature of the bridged heteroatom may not engage with the n-type electronic properties of C_{60} but a perturbation of the π electrons of the fullerene can indeed tune the electron-transfer characters that can be responsible for the mobility variation in OFETs.

In summary, two isomeric stable imino-PCBMs ([5,6]-open APCBM and [6,6]-closed APCBM) have been prepared. The former isomer retains the intact π electron system of the parent C_{60}, whereas the fullerene core of the latter has two π electrons less than C_{60}; this electron loss results in a difference in the electron-accepting properties of the isomers. It is of particular significance that an n-channel OFET that contains [5,6]-open APCBM exhibits a substantial electron mobility ($\mu = 4.1\times10^{-2}$ cm^{2}Vs) in a solution-processed device, which is the first example of a fullerene with mobility that exceeds that of the optimized high performance of PCBM ($\mu = 2.8\times10^{-2}$ cm^{2}Vs). This work augurs well for the future preparation of fullerene derivatives that have improved mobility.

Experimental Section

General: All solvents were purified and freshly distilled prior to use according to literature procedures. The synthesis of methyl 5-azido-5-phenylpentanoate was adapted from literature procedures.[24] Commercially available materials were used as received unless noted. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer and referenced to the solvent signal.

[5,6]-open azafulleroid ([5,6]-open APCBM) and [6,6]-closed aziridinofullerene ([6,6]-closed APCBM): A mixture of 5-azido-5-phenylpentanoate (0.7 g, 3.0 mmol), C_{60} (2.16 g, 3.0 mmol) and *o*-DCB (150 mL) was placed in a round-bottom flask under argon and stirred at room temperature for 15 min. The homogeneous mixture was stirred at 60 °C under argon overnight. The solution was heated to 135 °C and was again stirred overnight. The resulting mixture was concentrated in vacuo to 100 mL, adsorbed onto SiO_2 (40 × 10 cm) and pre-eluted with chlorobenzene (100 mL) and then toluene. The first fraction, which contained the remaining C_{60} (1.35 g, 63 %), was collected. Subsequently, the fraction that contained [5,6]-open APCBM ($R_f = 0.57$) was collected. The solution was concentrated in vacuo, redissolved in a minimal amount of toluene, and transferred to a centrifuge tube. The product was precipitated with MeOH, centrifuged, and decanted. The product was treated with MeOH several times in the same manner. The product (470 mg, 45 % based on consumed C_{60}) was isolated as a brown solid. ^{1}H NMR ($CS_2/CDCl_3$ 1:3, 500 MHz): $\delta = 7.68$ (d, $J = 7.10$ Hz, 2H), 7.43 (t, $J = 7.57$ Hz, 2H), 7.34 (t, $J = 7.57$ Hz, 1H), 5.20 (dd, $J = 9.33$, 3.39 Hz, 1H), 3.64 (s, 3H), 2.41–2.23 (m, 4H) 1.69–1.62 ppm (m, 2H); ^{13}C NMR ($CS_2/CDCl_3$ 1:3, 125.70 MHz): $\delta = 172.13$, 147.03, 144,71, 144.57, 144.40, 144.00, 143.87, 143.75, 143.70, 143.61, 143.49, 143.21, 143.06, 143.04, 142.84, 142.77, 142.68, 142.41, 142.35, 142.30, 142.26, 134.07, 141.94, 141.02, 140.95, 140.56, 140.51, 140.31, 139.74, 139.04, 139.01, 138.96, 138.32, 138.11, 138.03, 137.22, 136.33, 136.25, 136.15, 136.03, 135.95, 133.78, 133.38, 128.50, 128.07, 127.79, 64.10, 50.80, 35.78, 33.38, 20.47 ppm; FABMS (nitrobenzyl alcohol) *m/z*: 926 ($[M+H]^{+\bullet}$); elemental analysis calcd (%) for $C_{72}H_{15}NO_2$: C 93.40, H 1.63, N 1.51, O 3.46; found: C 93.29, H 2.10, N 1.70.

Upon further elution, [6,6]-closed APCBM ($R_f = 0.53$) was collected as a second product fraction and further purified by triple preparative column chromatography (toluene/CS_2 1:1). Workup was carried out as described above (using MeOH). Isolated yield = 50 mg (4.8 % based on consumed C_{60}) as a dark-reddish solid. ^{1}H NMR (CS_2/$CDCl_3$ 1:3, 500 MHz): $\delta = 7.75$ (d, $J = 7.02$ Hz, 2H), 7.48 (t, $J = 7.67$ Hz, 2H), 7.40 (t, $J = 7.67$ Hz, 1H), 4.56 (dd, $J = 7.66$, 5.42 Hz, 1H), 3.66 (s, 3H), 2.51–2.41 (m, 4H) 1.97–1.89 ppm (m, 2H). ^{13}C NMR ($CS_2/CDCl_3$ 1:3, 125.70 MHz): $\delta = 172.62$, 144.76, 144.68, 144.26, 144.18, 144.07, 143.33, 142.61, 142.44, 141.85, 141.67, 140.31, 139.31, 128.48, 127.81, 127.64, 63.54, 50.97, 36.11, 33.63, 21.16 ppm. FABMS (nitrobenzyl alcohol) *m/z*: 926 ($[M+H]^{+\bullet}$). Elemental analysis calcd (%) for $C_{72}H_{15}NO_2$: C 93.40, H 1.63, N 1.51, O 3.46; found: C 93.54, H 1.86, N, 1.71.

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