

# 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.<sup>[1–13]</sup> 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  $C_{60}$ ,<sup>[11]</sup> which results in two isomeric products such as [5,6]-open fulleroids and [6,6]-closed methanofullerenes.<sup>[2,3]</sup> From an electronic-structure point of view, the [5,6]-open isomers are appealing since they conserve the 60  $\pi$  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,<sup>[2,3,14–16]</sup> 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<sup>[17–19]</sup> and 2) the potential influence of the nitrogen heteroatom of iminofullerenes on the electronic properties of the fullerene cage,<sup>[20]</sup> 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  $\pi$  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

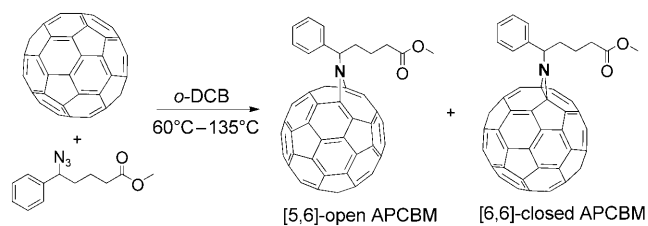
applications such as organic photovoltaics (OPV) as well as organic field-effect transistors (OFETs). Herein, we report the one-pot preparation of two isomeric imino-PCBMs, that is, [5,6]-open azafulleroid ([5,6]-open APCBM; PCBM = [6,6]-phenyl- $C_{61}$ -butyric acid methyl ester, A = aza) and [6,6]-closed aziridinofullerene ([6,6]-closed APCBM; Scheme 1). The characteristics of OFETs with [5,6]-open



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

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.

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.<sup>[18,19]</sup> Depending on the nature of the substituents, the thermal elimination of  $N_2$  affords different ratios of two isomeric imino adducts.<sup>[21–23]</sup> Following previous work,<sup>[23]</sup> 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<sup>[24]</sup> 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  $^1H$  NMR



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

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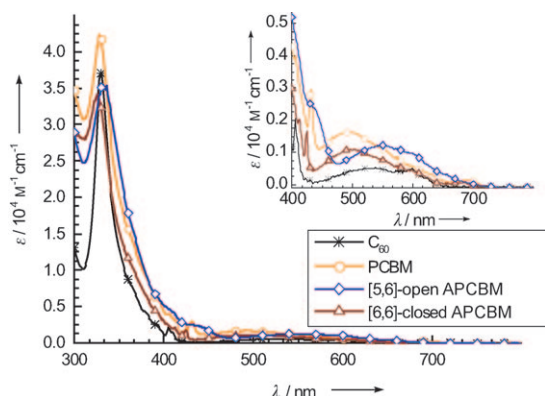
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spectrum of [5,6]-open APCBM shows the tertiary hydrogen atom adjacent to the nitrogen atom as a doublet of doublets at 5.20 ppm ( $J = 9.33$  and  $3.39$  Hz). The  $^{13}\text{C}$  NMR spectrum reveals 42 signals between  $\delta = 148$  and  $132$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

The UV/Vis absorption characteristics of  $\text{C}_{60}$ , PCBM, [5,6]-open APCBM, and [6,6]-closed APCBM in chloroform solution are shown in Figure 1. To identify the features that



**Figure 1.** UV/Vis absorption spectra of solutions of  $\text{C}_{60}$ , PCBM, [5,6]-open APCBM, and [6,6]-closed APCBM in  $\text{CHCl}_3$ .

change through iminofunctionalization on  $\text{C}_{60}$ , the pristine  $\text{C}_{60}$ , 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

**Table 1:** Optical data for compounds in this study.

| Compound           | Absorption [nm]             |
|--------------------|-----------------------------|
| $\text{C}_{60}$    | 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 |

and 423 nm, respectively, which reflects the partially broken symmetry ( $C_{2v}$ ) of the fullerene core relative to pristine  $\text{C}_{60}$  ( $I_h$ ). The UV/Vis spectra of  $\text{C}_{60}$  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  $\text{C}_{60}$  derivatives are governed by the  $\pi$  system of the fullerene. Another noticeable difference occurs in the solution colors, which are purple, brown, dark greenish-brown, and dark wine-red for  $\text{C}_{60}$ , PCBM, [5,6]-open APCBM and [6,6]-closed APCBM, respectively. This observation implies that the optical features of the  $\text{C}_{60}$  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.

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  $\text{C}_{60}$  adducts are shifted toward more negative values with respect to  $\text{C}_{60}$  because of fewer  $\pi$  electrons and release of strain energy.<sup>[25]</sup>

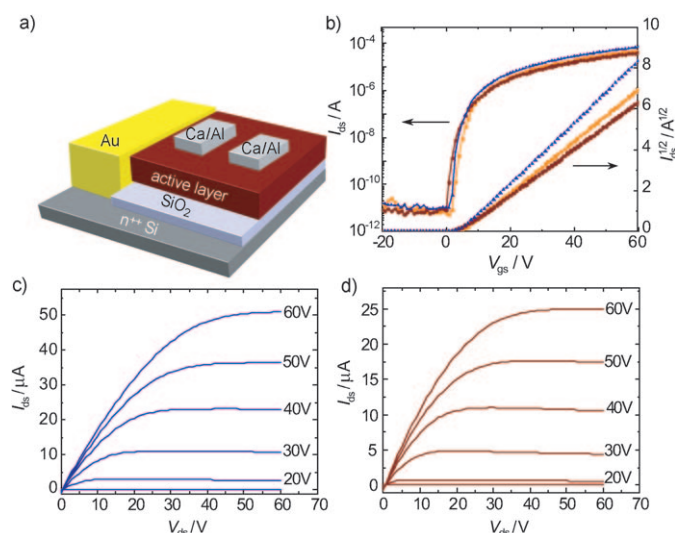
**Table 2:** Electrochemical data for compounds in this study.<sup>[a]</sup>

| Compound           | $E_{\text{red}}^1$ | $E_{\text{red}}^2$ | $E_{\text{red}}^3$ |
|--------------------|--------------------|--------------------|--------------------|
| $\text{C}_{60}$    | −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  $0.5(E_{\text{pc}} + E_{\text{pc}})$  in V versus  $\text{Fc}/\text{Fc}^+$  ( $\text{Fc}$  = ferrocene) in *o*-DCB solution ( $10^{-4}$  to  $10^{-3}$  mol  $\text{L}^{-1}$ ) with  $\text{Bu}_4\text{NClO}_4$  (0.1 M) as the supporting electrolyte and Pt wire as the counterelectrode; scan rate = 50  $\text{mVs}^{-1}$ .

[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  $\text{C}_{60}$  since they are isoelectronic analogues of  $\text{C}_{60}$  (60  $\pi$  electrons).<sup>[3]</sup> These results suggest that the reduction potentials of the functionalized  $\text{C}_{60}$  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  $\text{C}_{60}$  derivatives for electronic applications. All n-type OFETs were fabricated on heavily doped Si wafers with a 200 nm thick  $\text{SiO}_2$  layer with top contact geometry as shown in Figure 2a. Figure 2b shows the transfer characteristics,  $I_{\text{ds}}$  against  $V_{\text{gs}}$  and  $I_{\text{ds}}^{1/2}$  against  $V_{\text{gs}}$  ( $V_{\text{ds}} = 60$  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  $I_{\text{ds}}$  against  $V_{\text{gs}}$  is observed (the plot of  $I_{\text{ds}}^{1/2}$  against  $V_{\text{gs}}$  clearly shows this difference), which allows the alternation of OFET performance in the characteristic output curves. The linear plot of  $I_{\text{ds}}^{1/2}$  against  $V_{\text{gs}}$  derived from the measurements of  $I_{\text{ds}}$  against  $V_{\text{gs}}$  yields electron mobilities of  $\mu_1 = 4.1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,



**Figure 2.** a) Schematic diagram of the n-type OFET structure ( $L = 50 \mu\text{m}$ ,  $W = 1.5 \text{ mm}$ ). 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 APCBM and d) [6,6]-closed APCBM.

$\mu_2 = 2.3 \times 10^{-2} \text{ cm}^2 \text{ V s}$ , and  $\mu_3 = 2.8 \times 10^{-2} \text{ cm}^2 \text{ V s}$  for [5,6]-open APCBM ( $\mu_1$ ), [6,6]-closed APCBM ( $\mu_2$ ), and PCBM ( $\mu_3$ ).<sup>[26]</sup> The higher electron mobility in the [5,6]-open APCBM OFET can be attributed to its  $60\pi$ -electron nature, which affords a stronger electron-acceptor strength than that of the [6,6] junctions.<sup>[27]</sup> 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  $\text{C}_{60}$  but a perturbation of the  $\pi$  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  $\pi$  electron system of the parent  $\text{C}_{60}$ , whereas the fullerene core of the latter has two  $\pi$  electrons less than  $\text{C}_{60}$ ; 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 ( $\mu = 4.1 \times 10^{-2} \text{ cm}^2 \text{ V s}$ ) 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 ( $\mu = 2.8 \times 10^{-2} \text{ cm}^2 \text{ V s}$ ). 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.<sup>[24]</sup> Commercially available materials were used as received unless noted. <sup>1</sup>H

and <sup>13</sup>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),  $\text{C}_{60}$  (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  $\text{SiO}_2$  ( $40 \times 10 \text{ cm}$ ) and pre-eluted with chlorobenzene (100 mL) and then toluene. The first fraction, which contained the remaining  $\text{C}_{60}$  (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  $\text{C}_{60}$ ) was isolated as a brown solid. <sup>1</sup>H NMR ( $\text{CS}_2/\text{CDCl}_3$  1:3, 500 MHz):  $\delta = 7.68$  (d,  $J = 7.10 \text{ Hz}$ , 2H), 7.43 (t,  $J = 7.57 \text{ Hz}$ , 2H), 7.34 (t,  $J = 7.57 \text{ Hz}$ , 1H), 5.20 (dd,  $J = 9.33, 3.39 \text{ Hz}$ , 1H), 3.64 (s, 3H), 2.41–2.23 (m, 4H) 1.69–1.62 ppm (m, 2H); <sup>13</sup>C NMR ( $\text{CS}_2/\text{CDCl}_3$  1:3, 125.70 MHz):  $\delta = 172.13, 147.03, 144.71, 144.57, 144.40, 144.00, 143.87, 143.75, 143.70, 143.61, 143.49, 143.21, 143.06, 143.04, 142.84, 142.77, 142.68, 142.41, 142.35, 142.30, 142.26, 134.07, 141.94, 141.02, 140.95, 140.56, 140.51, 140.31, 139.74, 139.04, 139.01, 138.96, 138.32, 138.11, 138.03, 137.22, 136.33, 136.25, 136.15, 136.03, 135.95, 133.78, 133.38, 128.50, 128.07, 127.79, 64.10, 50.80, 35.78, 33.38, 20.47 \text{ ppm}$ ; FABMS (nitrobenzyl alcohol)  $m/z$ : 926 ( $[M+H]^+$ ); elemental analysis calcd (%) for  $\text{C}_{72}\text{H}_{15}\text{NO}_2$ : 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/ $\text{CS}_2$  1:1). Workup was carried out as described above (using MeOH). Isolated yield = 50 mg (4.8 % based on consumed  $\text{C}_{60}$ ) as a dark-reddish solid. <sup>1</sup>H NMR ( $\text{CS}_2/\text{CDCl}_3$  1:3, 500 MHz):  $\delta = 7.75$  (d,  $J = 7.02 \text{ Hz}$ , 2H), 7.48 (t,  $J = 7.67 \text{ Hz}$ , 2H), 7.40 (t,  $J = 7.67 \text{ Hz}$ , 1H), 4.56 (dd,  $J = 7.66, 5.42 \text{ Hz}$ , 1H), 3.66 (s, 3H), 2.51–2.41 (m, 4H) 1.97–1.89 ppm (m, 2H). <sup>13</sup>C NMR ( $\text{CS}_2/\text{CDCl}_3$  1:3, 125.70 MHz):  $\delta = 172.62, 144.76, 144.68, 144.26, 144.18, 144.07, 143.33, 142.61, 142.44, 141.85, 141.67, 140.31, 139.31, 128.48, 127.81, 127.64, 63.54, 50.97, 36.11, 33.63, 21.16 \text{ ppm}$ . FABMS (nitrobenzyl alcohol)  $m/z$ : 926 ( $[M+H]^+$ ). Elemental analysis calcd (%) for  $\text{C}_{72}\text{H}_{15}\text{NO}_2$ : 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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