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Syntheses and Structures of Phenyl-C_{81}-Butyric Acid Methyl Esters (PCBMs) from $M_3N@C_{80}$

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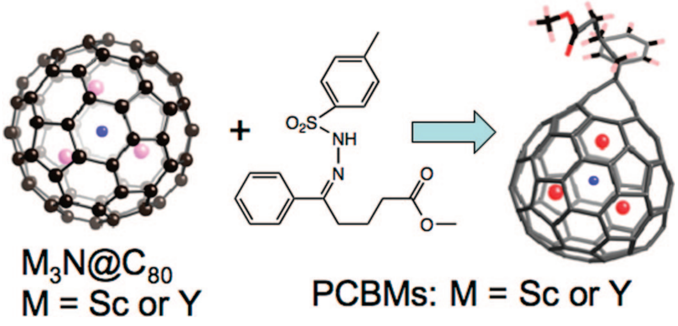
ABSTRACT



Two new 6,6-open phenyl-C_{81}-butyric acid methyl ester metallofulleroids, $M_3N@C_{80}$PCBM (M = Sc, Y), were synthesized by diazoalkane addition reactions and fully characterized. The results demonstrate that the reactive sites are the same for $M_3N@C_{80}$ (M = Sc, Y) but dramatically different from that of C_{60}.

Modified fullerenes and metallofullerenes with good solubility and processability are of great importance for expanding their potential applications in material science.[1] For example, the methanofullerene phenyl-C_{61}-butyric acid methyl ester (C_{60}PCBM)[2] has been widely utilized as an electron-acceptor in bulk heterojunction (BHJ) solar cells.[3] Trimetallic nitride templated (TNT) endohedral metallofullerenes,[4] especially $Sc_3N@C_{80}$, as the most abundant species in the endohedral metallofullerene family, are expected to exhibit novel properties relative to empty cage fullerenes and their derivatives due to the electron-transfer from the endohedral cluster to the carbon cage. However, TNT metallofullerenes are less reactive than empty fullerenes and classical EMFs due to the formal transfer of six electrons from the metal atoms to the fullerene cage, which leads to a closed shell electronic structure and an increase of the HOMO−LUMO gap with a corresponding reduction in reactivity.[5] Herein, we report

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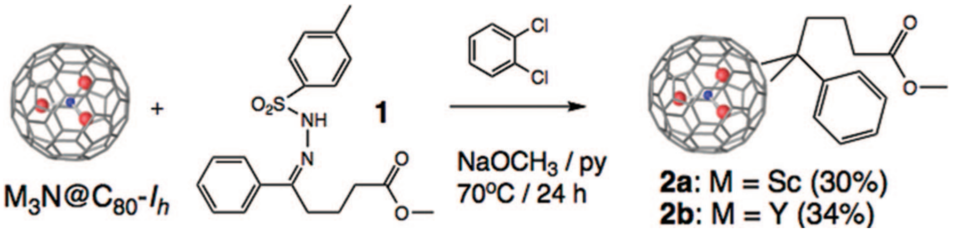
10.1021/ol9002527 CCC: $40.75

Scheme 1. Synthesis of $M_3N@C_{80}$PCBMs



TNT analogues of C_{60}PCBM, which are significantly different from C_{60}PCBM. The demonstration that diazoalkanes are effective reagents for functionalization of TNT EMFs provides an alternative to Diels−Alder,[6] Bingel-Hirsch,[7] Prato[8] and free radical[9] reactions for synthesis of derivatives of these novel species for various applications.

$M_3N@C_{80}$PCBMs were prepared from $M_3N@C_{80}$ and methyl 4-benzoylbutyrate *p*-tosylhydrazone (**1**) (Scheme 1).

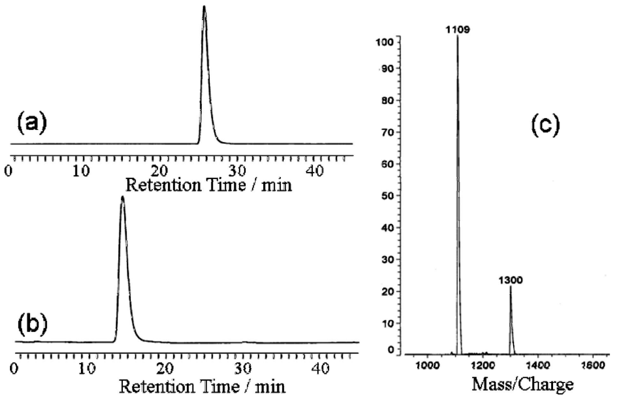


Figure 1. HPLC profiles of $Sc_3N@C_{80}$PCBM (**2a**) on (a) PYE and (b) PBB columns. (c) Positive mode MALDI-TOF MS of **2a**.

$Sc_3N@C_{80}$PCBM (**2a**) was isolated in 30% yield based on consumed $Sc_3N@C_{80}$ after silica gel column chromatography and subsequently purified by high performance liquid chromatography (HPLC) using a PYE [2-(1′-pyrenyl)ethyl silica] column. The HPLC traces of **2a** on PYE and PBB [pentabromobenzyloxypropyl silica] columns consist of single symmetric peaks centered at retention times of 25.2 min (Figure 1a) and 14.0 min (Figure 1b), respectively, revealing pure isomers as confirmed by ^1H and ^{13}C NMR spectroscopy. The MALDI-TOF mass spectrum exhibits a strong molecular ion peak from $\mathbf{2a}^+$ at *m*/*z* 1300 (Figure 1c). The peak at *m*/*z* 1109 is attributed to $Sc_3N@C_{80}$ formed by loss of the exohedral functional groups as usually observed under laser desorption conditions.[9] In similar fashion, $Y_3N@C_{80}$PCBM (**2b**) was synthesized and purified in 34% yield.

In the UV−vis absorption spectrum of **2a** (Figure 2), the lowest energy transition occurs at 736 nm, similar to that of pristine $Sc_3N@C_{80}$,[10] revealing that the C_{80} chromophore is minimally perturbed by the functional group and suggesting an open π-homoaromatic structure.[7a,9a] Similarly, the UV−vis spectrum of the yttrium analog **2b** resembles that of its precursor, $Y_3N@C_{80}$ (Figure 2), with a maximum at 693 nm, again consistent with a fulleroid structure.[7a]

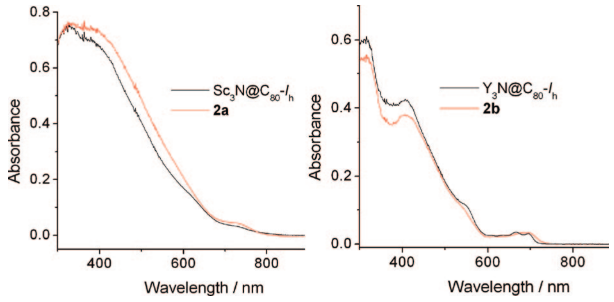


Figure 2. (left) UV−vis spectra (in toluene) of $Sc_3N@C_{80}$PCBM (**2a**, red line) and $Sc_3N@C_{80}$-I_h (black line); (right) $Y_3N@C_{80}$PCBM (**2b**, red line) and $Y_3N@C_{80}$-I_h (black line).

Addition at the 5,6-ring junction of the C_{80} cage results in two sets of nonequivalent hydrogens from the functional groups, since the pentagons and hexagons on the carbon cage provide different chemical environments, but addition at the 6,6-ring junction produces only one set of proton signals.[8a,9a]

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In the ^1H NMR spectra of **2a** and **2b**, only one set of signals was observed: for **2a** 1.98 (2H, m, $J = 7.5$ Hz), 2.41 (2H, t, $J = 7.5$ Hz), 2.73 (2H, m, $J = 5.5$ Hz), 3.65 (3H, s), 7.49 (1H, m), 7.55 (2H, m) and 7.94 (2H, d, $J = 7.0$ Hz) ppm; for **2b** 2.06 (2H, m, $J = 7.0$ Hz), 2.45 (2H, t, $J = 7.0$ Hz), 2.81 (2H, m, $J = 5.5$ Hz), 3.68 (3H, s), 7.50 (1H, m), 7.56 (2H, m) and 8.08 (2H, m, $J = 8.0$ Hz) ppm, revealing that addition of the functional group took place at a 6,6-junction.

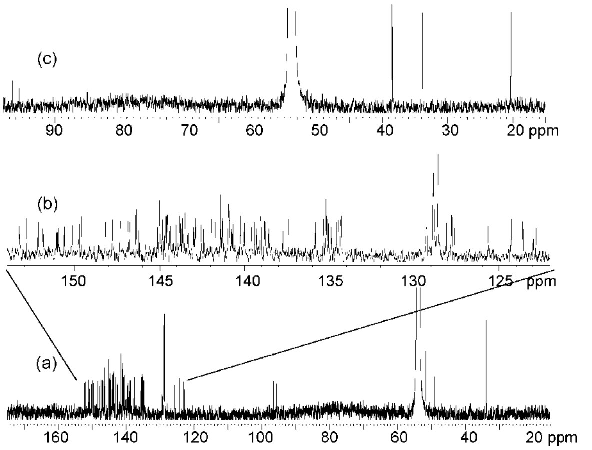

Figure 3. (a) ^{13}C NMR spectrum (150 MHz, $CD_2Cl_2/CS_2 = 20/80$ v/v, doped with chromium acetylacetonate) of $Sc_3N@C_{80}$PCBM (**2a**), and expanded parts from (b) 122 ppm to 154 ppm and (c) 15 ppm to 98 ppm.

The ^{13}C NMR spectrum of **2a** (Figure 3) contains resonances at 172.13 ($\mathit{C}O_2CH_3$), 129.27, 128.91, 128.87 (2C), 128.61 (2C), 51.51 ($CO_2\mathit{C}H_3$), 49.16 (Ph$\mathit{C}CH_2$), 38.46 (PhC$\mathit{C}H_2$), 33.77 ($\mathit{C}H_2CO_2$) and 20.31 ($\mathit{C}H_2CH_2CO_2$) ppm for the functional group and another 80 resonances in the range of 95−155 ppm for the carbon cage, consistent with C_1 symmetry. Notably, the bridged fullerene C-atoms (C1 on a 6-membered ring and C41 on a 5-membered ring in Figure 4 below) are assigned at δ 95.55 and 96.49 ppm in agreement with an "open" methano-bridged transannular bond due to π-homoaromaticity.[5] The structure of this final product is dramatically different from the analogous[2] and similar[11] diazo derivatives of C_{60} (6,6-closed and 5,6-open isomers) formed under the same conditions. Likewise, the ^{13}C NMR spectrum of **2b** is similar to that of **2a**, having resonances at 172.44 ($\mathit{C}O_2CH_3$), 51.09 ($CO_2\mathit{C}H_3$), 52.04 (Ph$\mathit{C}CH_2$), 38.39 (PhC$\mathit{C}H_2$), 33.43 ($\mathit{C}H_2CO_2$) and 19.47 ($\mathit{C}H_2CH_2CO_2$) ppm for the functional group and another 84 resonances in the range of 95−150 ppm for the carbon cage and phenyl group, also in agreement with C_1 symmetry. Notably, the ^{13}C NMR signals of sp^2 hybridized carbons of the C_{80} cage for $Y_3N@C_{80}$PCBM exhibit a larger chemical shift range relative to those of $Sc_3N@C_{80}$PCBM, indicating that the different clusters inside the cage do influence the properties of the molecule.

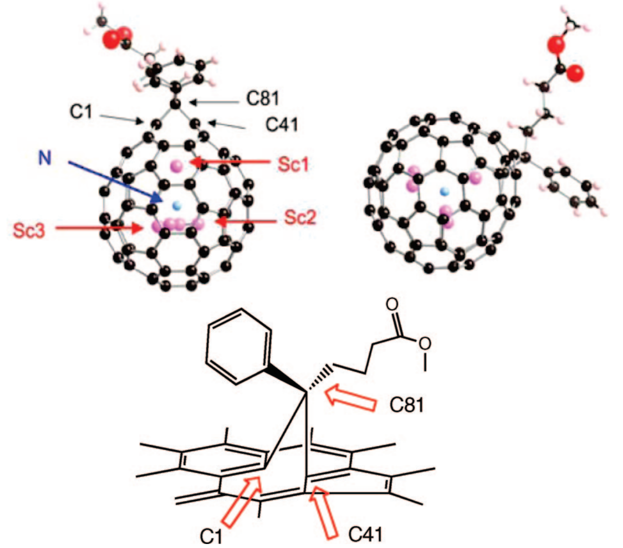

Figure 4. Two views of one enantiomer of $Sc_3N@C_{80}$PCBM (**2a**) showing the two positions of two of the Sc atoms of the disordered Sc_3N cluster. The solvate molecules are omitted for clarity.

Black crystals of **2a**·$(CS_2)_3$ and **2b**·CS_2 suitable for X-ray diffraction were obtained by liquid diffusion of hexane into solutions of **2a** and **2b** in CS_2 at 4 °C. The two enantiomers of **2a**/**2b** present in the crystals lead to apparent disorder in the positions of the cage atoms. And as observed in similar compounds,[7a] the Sc_3N and Y_3N clusters are truly disordered. The Sc2 and Sc3 atoms can be modeled with 2-position disorder with relative occupancies of 0.737(5) and 0.263(5), respectively, but attempts to model Y2 and Y3 of **2b** failed. The structures shown in Figures 4 and 5 represent one enantiomer of **2a** and **2b**, respectively. Both of them prove unambiguously that addition occurred at a 6,6-ring junction. The distance between the bridgehead carbon atoms (C1 and C41) of the cage is 2.116(4) Å for $Sc_3N@C_{80}$PCBM and 2.218 Å for $Y_3N@C_{80}$PCBM, much longer than that of

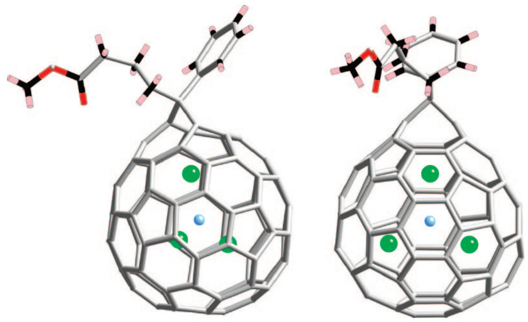

Figure 5. Two views of one enantiomer of $Y_3N@C_{80}$PCBM (**2b**) showing one position of the Y atoms of the disordered Y_3N cluster. The solvate molecules are omitted for clarity.

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$Sc_3N@C_{80}$-I_h [1.421(2) Å].[12] These results are consistent with an open structure and comparable to other metallofulleroids: $Y_3N@C_{80}C(CO_2CH_2Ph)_2$[7a] [2.30(3) Å for one orientation of the cage and 2.28(4) Å in the other] and $La@C_{82}(Ad)$[13] (2.097 Å). The Sc_3N and Y_3N clusters are planar; the sums of the angles are 359.95° (0.74)/359.39° (0.26) for the former and 360.0° for the latter. The planar structure of the Y_3N cluster in $Y_3N@C_{80}$PCBM is consistent with another 6,6-open case derived from a Bingel reaction, $Y_3N@C_{80}C(CO_2CH_2Ph)_2$;[7a] in contrast the cluster geometry is different from that of the pyrrolidino adduct of $Y_3N@C_{80}$ in which the cluster is slightly pyramidal.[14] The Sc1/Y1┅C1 distances are 2.447(3)/2.524(6) Å and the Sc1/Y1┅C41 distances are 2.456(3)/2.544(6) Å, respectively, much longer than in $Sc_3N@C_{80}$-I_h [2.188(9) and 2.170(1) Å],[4] indicating that the functional group leads to distortion of the carbon cage. Notably, under the same conditions, the addition of unsymmetrically substituted diazoalkanes on C_{60} produces two isomers, a 6,6-closed structure (methanofullerene) and a 5,6-open structure (fulleroid);[2,15] the Prato addition on $Sc_3N@C_{80}$[16] and $Y_3N@C_{80}$[8a,17] produces 5,6- and 6,6-pyrrolidino adducts, respectively; the Bingel reaction works well on $Y_3N@C_{80}$ but fails on $Sc_3N@C_{80}$.[8a] However, in this diazoalkane addition reaction, both $Sc_3N@C_{80}$ and $Y_3N@C_{80}$ produce single stable PCBM isomers with 6,6-open structures.

Interestingly, similar cyclic voltammetric (CV) profiles were observed for **2a** and $Sc_3N@C_{80}$ (Figure 6). The first reduction of **2a** is chemically reversible but electrochemically irreversible, reminiscent of the starting material, $Sc_3N@C_{80}$-I_h, whose ${}^{red1}E_p$ and ${}^{ox1}E_p$ are consistent with previous reports.[10] The ${}^{red1}E_p$ of **2b** (see Supporting Information) is cathodically shifted 40 mV relative to $Y_3N@C_{80}$-I_h, whereas that of Sc analog is cathodically shifted 100 mV relative its precursor. These results demonstrate the large electronic effects of encapsulated metal clusters in the TNT endohedrals vs empty cage systems such as C_{60}.

In conclusion, two new TNT metallofullerene derivatives were synthesized by diazoalkane addition and characterized in detail. The successful demonstration that diazoalkanes are effective reagents for functionalization of these compounds provides an alternative to Diels−Alder, Bingel-Hirsch, Prato and free radical types of reactions for synthesis of derivatives of these novel species for various applications.

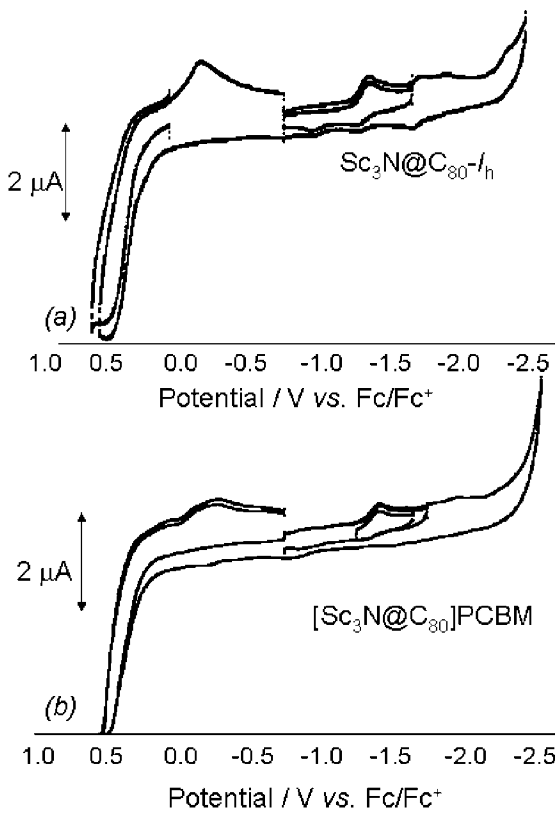

Figure 6. Cyclic voltammograms of (a) $Sc_3N@C_{80}$ and (b) $Sc_3N@C_{80}$PCBM (**2a**). Scan rate, 250 mV/s. Solvent: 1,2-dichlorobenzene. Values are relative to the ferrocene/ferrocenium couple.

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Supporting Information Available: Details of synthesis of **2**; HLPC profiles and MS spectra of **2b**; ^1H, $^1H-^1H$ COSY, HMQC NMR spectra of **2**; ^{13}C NMR spectrum of **2b** and FTIR spectrum of **2a**; cyclic voltammograms of $Y_3N@C_{80}$ and $Y_3N@C_{80}$PCBM (**2b**), electrochemical methods; thermal ellipsoid drawings, crystal data, structure refinement of **2a**/**2b** and crystallographic files for **2a**·$(CS_2)_3$ and **2b**·CS_2 in CIF format; scheme showing formation of racemic **2a**/**2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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