Electronic Supplementary Material (ESI) for ChemComm.

Reactivity Differences of $Sc_3N@C_{2n}$ (2n = 68 and 80). Synthesis of the First Methanofullerene Derivatives of $Sc_3N@D_{5h}$-C_{80}.

Maira R. Cerón,[‡a] Marta Izquierdo,[‡a] Núria Alegret,[b] Juan A. Valdez,[a] Antonio Rodriguez-Fortea,[b] Marilyn M. Olmstead,*[c] Alan L. Balch,*[c] Josep M. Poblet,*[b] and Luis Echegoyen*[a]

a Deparment of Chemistry, University of Texas at El Paso, El Paso, TX 79968, (USA)

b Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Tarragona 43007, (Spain)

c Department of Chemistry, University of California at Davis, Davis, CA 95616 (USA)

SUPPORTING INFORMATION

Contents

General Methodology

All chemicals were reagent grade, purchased from Sigma Aldrich. HPLC experiments were performed on an LC-9130NEXT apparatus (Japan Analytical Industry Co. Ltd.) monitored using a UV detector at 320 nm, and toluene as eluent. Silica gel (Redisep silica, 40-60 μ, 60 Å) was used to separate the products from the pristine fullerene. MALDI-TOF mass spectrometric measurements were conducted on a Bruker Microflex LRF mass spectrometer on reflector positive mode. The NMR spectra were recorded using a JEOL 600 MHz spectrometer. The UV/Vis-NIR spectra were taken using a Cary 5000 UV/Vis-NIR spectrophotometer using toluene solutions. Cyclic voltammetry (CV) were carried out under an Argon atmosphere at room temperature using a CH Instrument Potentiostat. Scan rate for CV experiments was 100 mV/s. A one compartment cell with a standard three-electrode set up was used, consisting of a 1 mm diameter glassy carbon disk as the working electrode, a platinum wire as the counter electrode and a silver wire as the pseudo-reference electrode, in a solution of anhydrous *o*-DCB containing 0.05 M n-Bu_4NPF_6. Ferrocene was added to the solution at the end of each experiment as an internal standard.

Removal of $Sc_3N@C_{68}$: 3.00 mg ($8.0x10^{-3}$ mmol, 11.2 equiv) of tosyl hydrazone **1**, 0.6 mL of anhydrous pyridine and 1.08 mg ($2.00x10^{-2}$ mmol, 2.5 equiv) of NaOMe were stirred under a nitrogen atmosphere at room temperature for 20 min. A sample of 4.30 mg containing 84.0% of $Sc_3N@D_{5h}$-C_{80} and 16.0% of $Sc_3N@C_{68}$, determined by HPLC analysis (Figure 1S), was then dissolved in 5.5 mL of anhydrous *o*-DCB, added to the reaction mixture and heated to 100˚C during 1 h. The crude product was purified by silica gel column chromatography, which afforded pure $Sc_3N@D_{5h}$-C_{80} eluting with CS_2, a minor portion of monoadducts of PCBM-$Sc_3N@D_{5h}$-C_{80} eluting with toluene and multiple adducts of PCBM-$Sc_3N@C_{68}$ eluting with toluene: ethyl acetate 7:3.

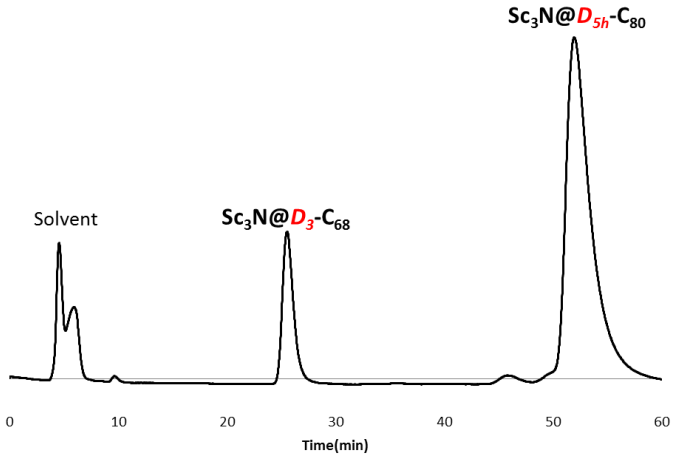

Figure 1S. HPLC profile of a mixture of $Sc_3N@D_{5h}$-C_{80} and $Sc_3N@C_{68}$. Conditions: 5PBB column (ϕ = 4.6 ID x 250 mm); toluene; flow rate: 1.2 $mLmin^{-1}$; λ: 320nm at room temperature.

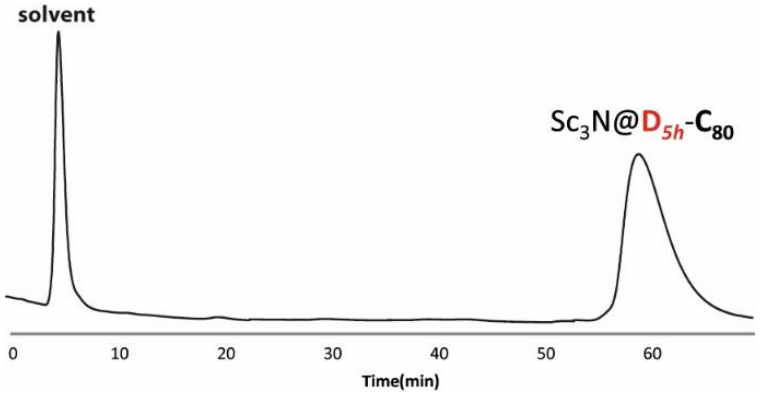

Figure 2S. HPLC profile of pure $Sc_3N@D_{5h}$-C_{80} obtained by silica gel column chromatography after PCBM derivatization of a mixture of $Sc_3N@C_{68}$ and $Sc_3N@D_{5h}$-C_{80}. Conditions: 5PBB column (ϕ = 4.6 ID x 250 mm); toluene; flow rate: 1.2 mLmin^{-1}; λ: 320nm at room temperature.

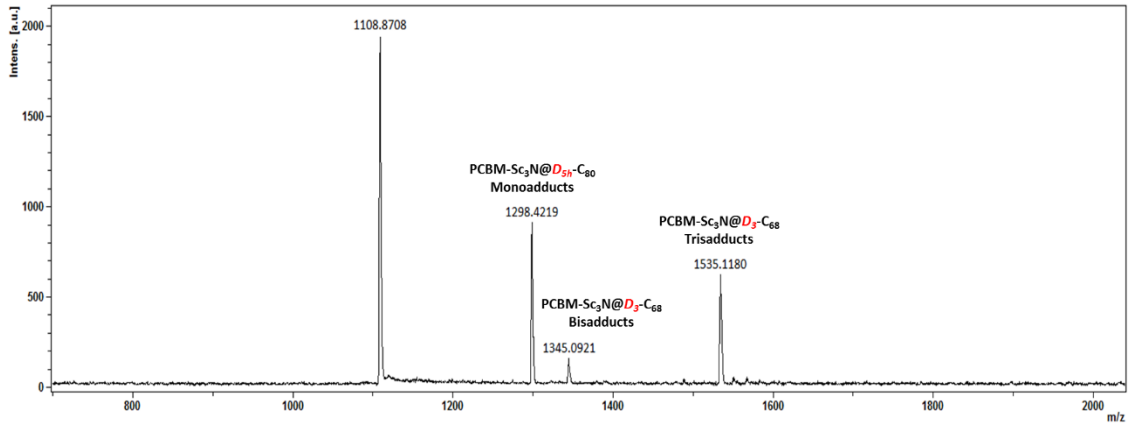

Figure 3S. MALDI TOF spectrum of multiple adducts of $Sc_3N@C_{68}$ and monoadducts of $Sc_3N@D_{5h}$-C_{80} using 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) as a matrix.

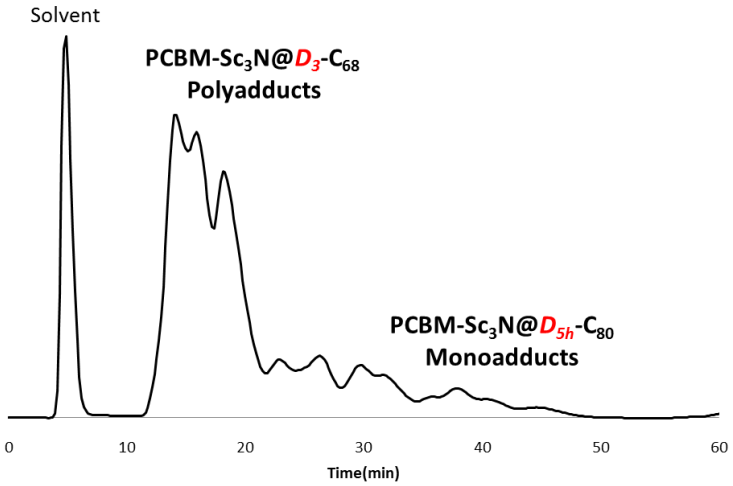

Figure 4S. HPLC profile of the reaction crude after 1 hour heated at 100˚C, PCBM derivatization of the mixture of $Sc_3N@C_{68}$ and $Sc_3N@D_{5h}$-C_{80}. Conditions: 5PBB column (ϕ = 4.6 ID x 250 mm); toluene; flow rate: 1.2 mLmin^{-1}; λ: 320nm at room temperature.

Synthesis of PCBM-$Sc_3N@D_3$-C_{68}: 0.90 mg ($2.40x10^{-3}$ mmol, 1 equiv) of tosyl hydrazone **1**, 0.4 mL of anhydrous pyridine and 0.32 mg ($6.00x10^{-3}$ mmol, 2.5 equiv) of NaOMe were stirred under a nitrogen atmosphere at room temperature for 20 min. A sample of 4.63 mg containing 90.7% of $Sc_3N@D_{5h}$-C_{80} and 9.3% of $Sc_3N@C_{68}$, determined by HPLC analysis, was then dissolved in 6.0 mL of anhydrous *o*-DCB, added to the reaction mixture and stirred 24 hours at room temperature to yield monoadducts of PCBM-$Sc_3N@C_{68}$. The crude was purified by silica gel column chromatography, using initially CS_2 as eluent to recover the unreacted $Sc_3N@D_{5h}$-C_{80}, followed by toluene to recover the monoadducts of PCBM-$Sc_3N@C_{68}$ and PCBM-$Sc_3N@D_{5h}$-C_{80}.

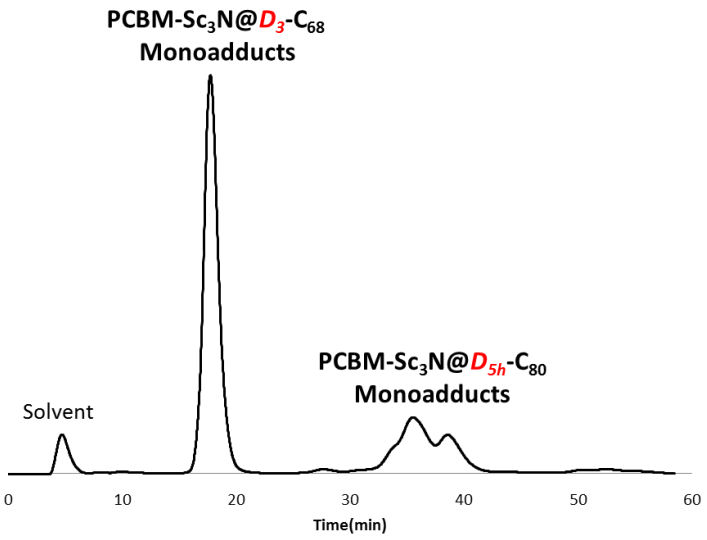

Figure 5S. HPLC profile of the reaction crude after 24 hours at room temperature, PCBM derivatization of the mixture of $Sc_3N@C_{68}$ and $Sc_3N@D_{5h}$-C_{80}. Conditions: 5PBB column (ϕ = 4.6 ID x 250 mm); toluene; flow rate: 1.2 $mLmin^{-1}$; λ: 320nm at room temperature.

Characterization of PCBM-$Sc_3N@C_{68}$ (2 and 3): ^{1}H-NMR (600 MHz; CS_2:$CDCl_3$ 1:1, 298 K); PCBM-$Sc_3N@C_{68}$-**2:** δ 7.35 (d, 2H, *J* = 7.14 Hz), 7.23 (m, 1H), 7.16 (m, 2H), 3.66 (s, 3H, COO-C<u>H</u>$_3$), 2.33 (t, 2H, *J* = 7.24 Hz, CH_2-C<u>H</u>$_2$-CO), 2.12 (m, 4H, C<u>H</u>$_2$-C<u>H</u>$_2$-CH_2) ppm.

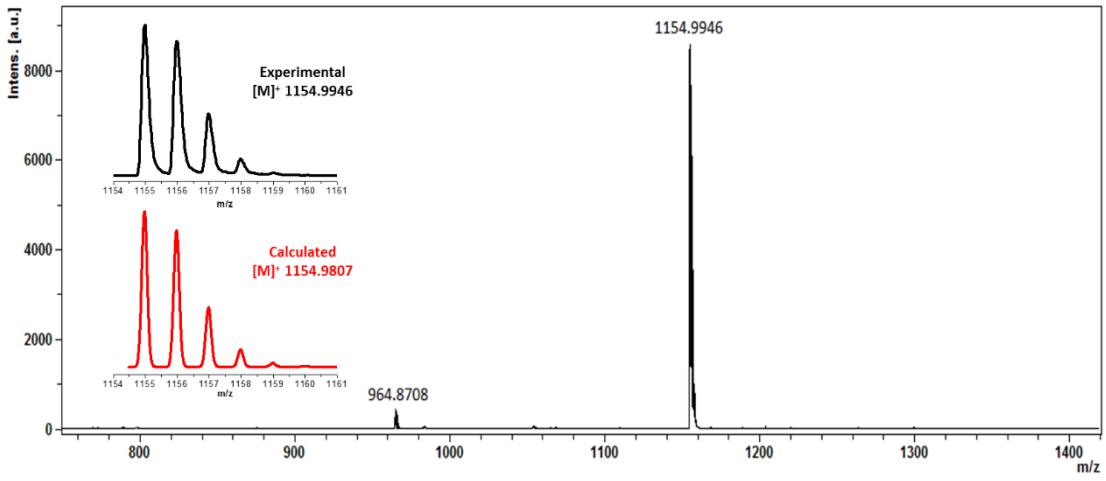

Figure 6S. MALDI TOF spectrum of PCBM-$Sc_3N@C_{68}$-**2** using TPB as matrix.

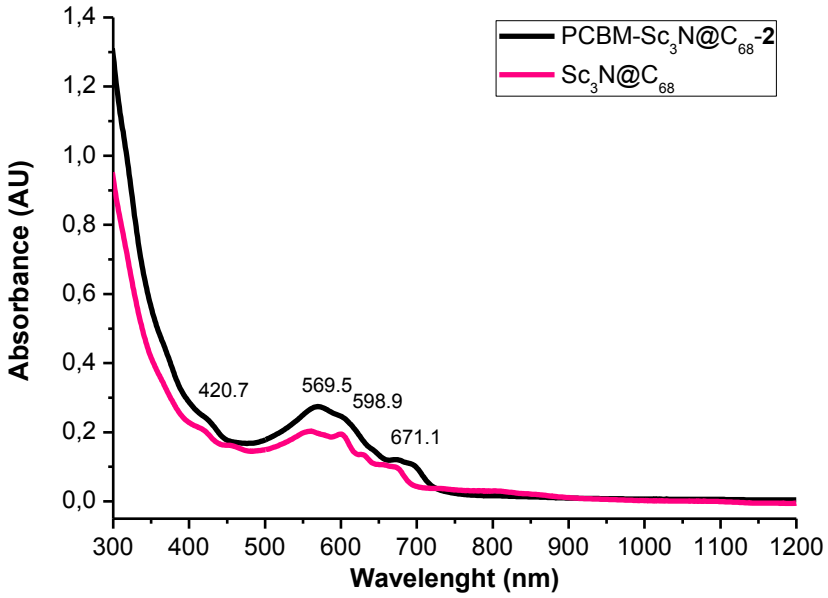

Figure 7S. UV-vis spectrum of PCBM-$Sc_3N@C_{68}$-**2** in toluene.

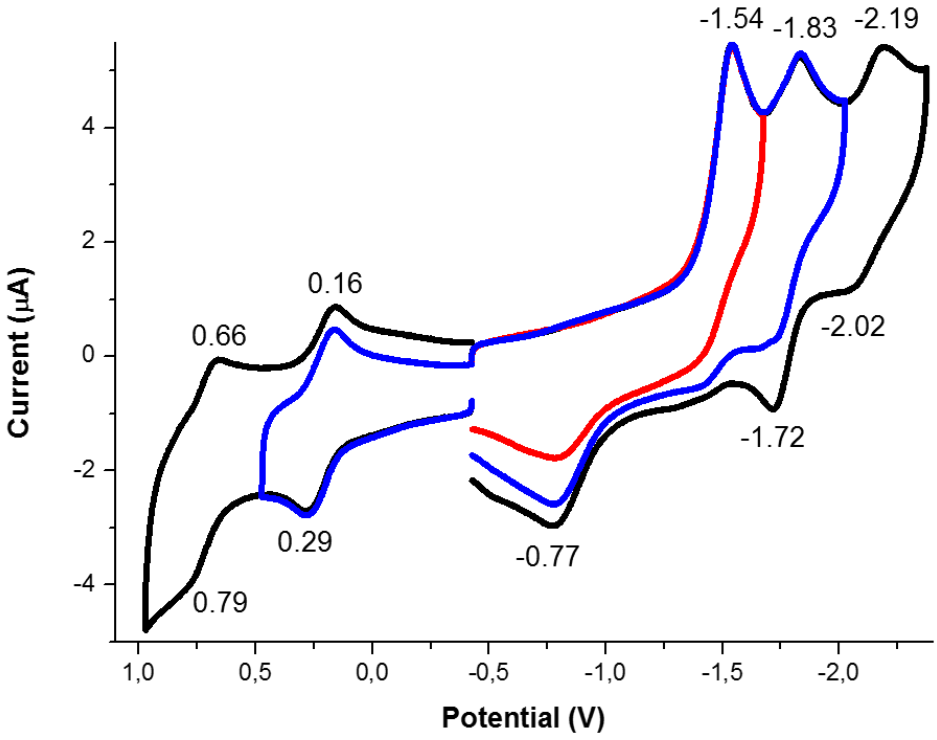

Figure 8S. Cyclic voltammetry of PCBM-$Sc_3N@C_{68}$-**2** (*o*-DCB containing 0.05 M n-Bu_4NPF_6; using the redox couple Fc/Fc^+ as internal reference).

^{1}H-NMR (600 MHz; CS_2:$CDCl_3$ 1:1, 298 K); PCBM-$Sc_3N@C_{68}$-**2:** δ 8.32 (d, 2H, *J* = 7.64 Hz), 7.66 (m, 1H), 7.44 (t, 2H, *J* = 7.27 Hz), 3.51 (s, 3H, COO-C<u>H</u>$_3$), 2.33 (t, 2H, *J* = 7.22 Hz, CH_2-C<u>H</u>$_2$-CO), 2.24 (m, 2H, C<u>H</u>$_2$-CH_2-CH_2), 2.04 (m, 2H, CH_2-C<u>H</u>$_2$-CH_2) ppm.

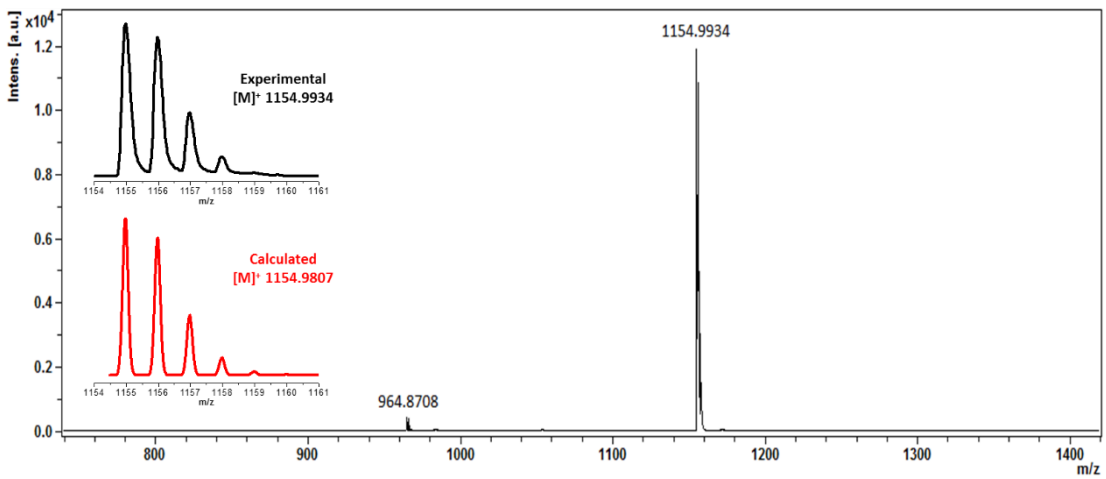

Figure 9S. MALDI TOF spectrum of PCBM-$Sc_3N@C_{68}$-**3** using TPB as matrix.

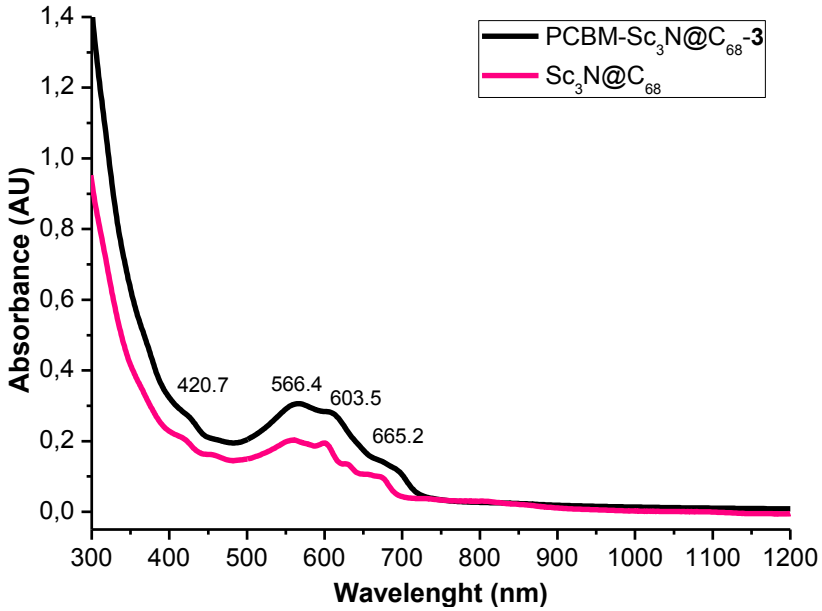

Figure 10S. UV-vis spectrum of PCBM-$Sc_3N@C_{68}$-**3** in toluene.

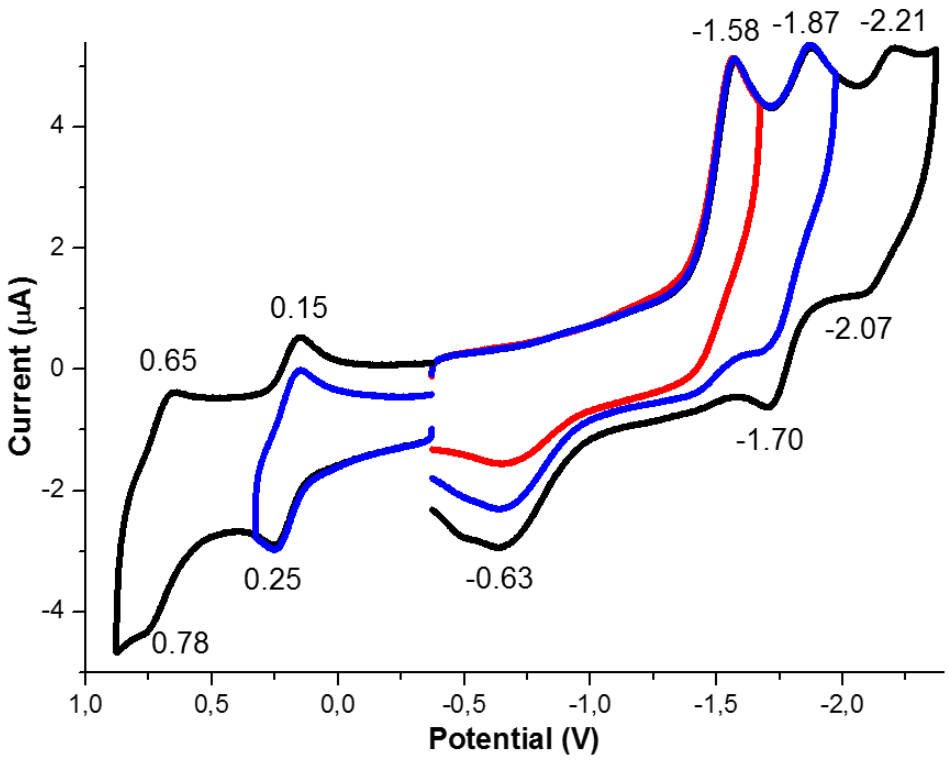

Figure 11S. Cyclic voltammetry of PCBM-$Sc_3N@C_{68}$-**3** (*o*-DCB containing 0.05 M n-Bu_4NPF_6; using the redox couple Fc/Fc^+ as internal reference).

Synthesis of PCBM-$Sc_3N@D_{5h}$-C_{80}: 21.42 mg ($5.71x10^{-2}$ mmol, 1 equiv) of tosyl hydrazone **1**, 3.0 mL of anhydrous pyridine and 7.71 mg (0.14 mmol, 2.5 equiv) of NaOMe were stirred under a nitrogen atmosphere at room temperature for 20 min. A sample of 4.22 mg of $Sc_3N@D_{5h}$-C_{80}, was then dissolved in 5.0 mL of anhydrous *o*-DCB, added to the reaction mixture and heated to 80˚C. The reaction was stopped after 3½h when bisadducts were detected by MALDI-TOF. The crude was purified by silica gel column chromatography, using initially CS_2 as eluent to recover the unreacted endohedral pristine fullerene, followed by toluene to recover the monoadducts of PCBM- $Sc_3N@D_{5h}$-C_{80}, and finally toluene: ethyl acetate 7:3 to recover a small fraction of multiple adducts of PCBM- $Sc_3N@D_{5h}$-C_{80}.

Characterization of PCBM-$Sc_3N@D_{5h}$-C_{80} (4, 5, 6, 7 and 5): ^{1}H-NMR (600 MHz; CS_2:CD_2Cl_2 1:1, 298 K); PCBM-$Sc_3N@D_{5h}$-C_{80}-**4:** δ 8.29 (d, 2H, *J* = 7.42 Hz), 7.61 (t, 2H, *J* = 7.25 Hz), 7.56 (dd, 1H, *J* = 8.05, 14.69 Hz), 3.69 (s, 3H, COO-C<u>H</u>$_3$), 3.15 (m, 2H, C<u>H</u>$_2$-CH_2-CH_2), 2.49 (t, 2H, *J* = 7.20 Hz, CH_2-C<u>H</u>$_2$-CO), 2.15 (m, 2H, CH_2-C<u>H</u>$_2$-CH_2) ppm.

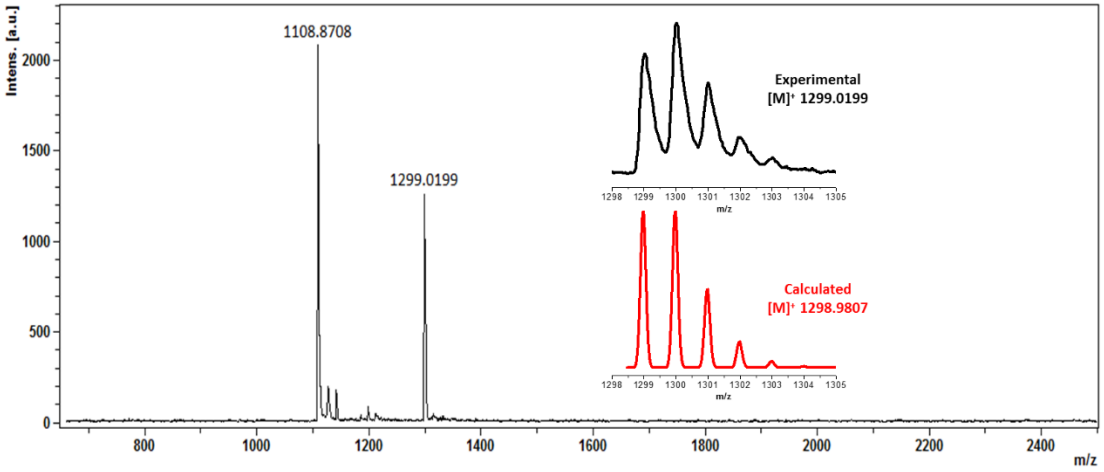

Figure 12S. MALDI TOF spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**4** using TPB as matrix.

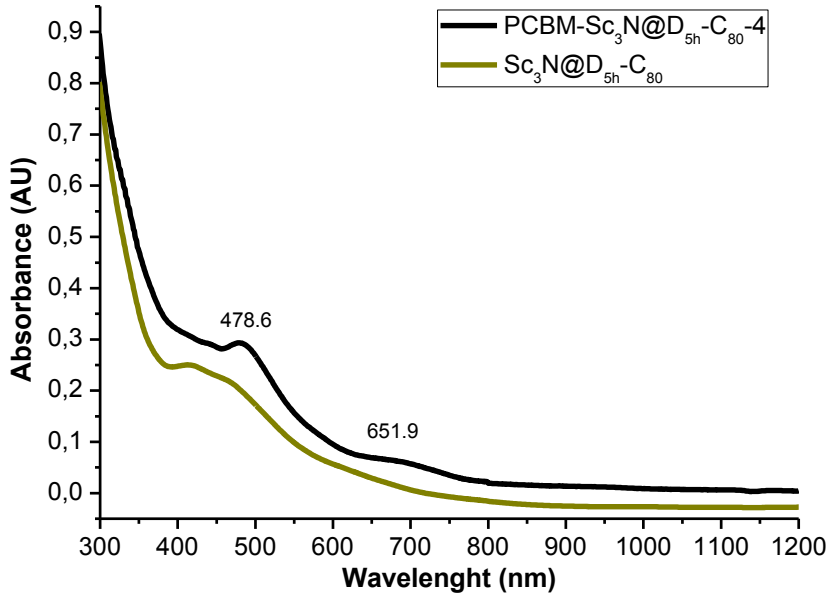

Figure 13S. UV-vis spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**4** in toluene.

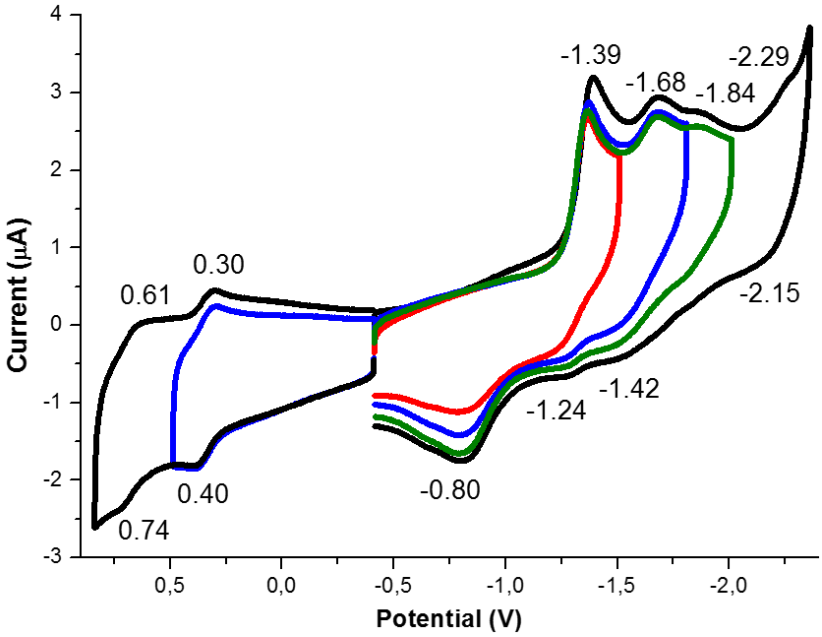

Figure 14S. Cyclic voltammetry of PCBM-$Sc_3N@D_{5h}$-C_{80}-**4** (*o*-DCB containing 0.05 M n-Bu_4NPF_6; using the redox couple Fc/Fc^+ as internal reference).

^{1}H-NMR (600 MHz; CS_2:$CDCl_3$ 1:1, 298 K); PCBM-$Sc_3N@D_{5h}$-C_{80}-**5:** δ 7.91 (d, 2H, *J* = 7.24 Hz), 7.48 (m, 2H), 7.44 (m, 1H), 3.67 (s, 3H, COO-C<u>H</u>$_3$), 2.70 (m, 2H, C<u>H</u>$_2$-CH_2-CH_2) 2.55 (t, 2H, *J* = 7.23 Hz, CH_2-C<u>H</u>$_2$-CO), 2.41 (m, 2H, CH_2-C<u>H</u>$_2$-CH_2) ppm.

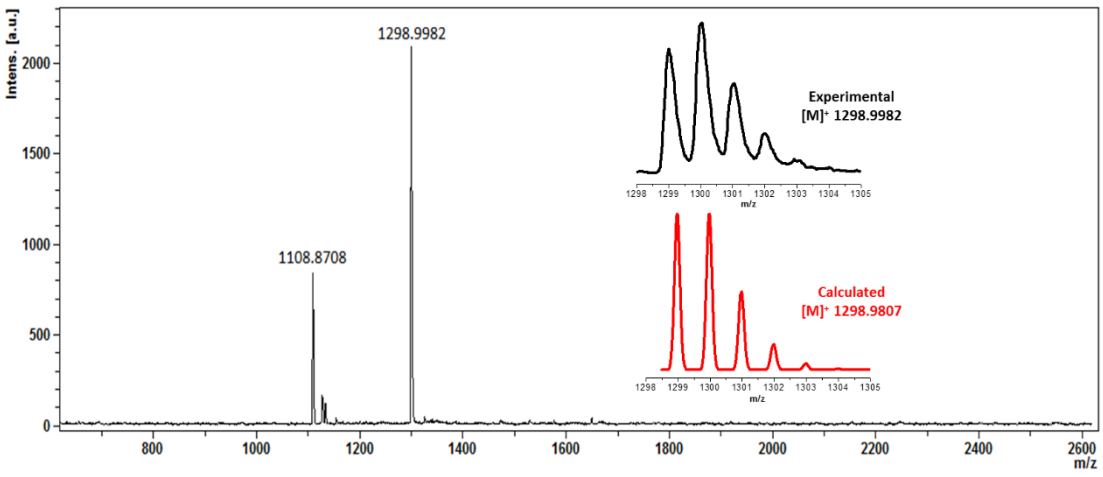

Figure 15S. MALDI TOF spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**5** using trans-2-[3-(4-t-butyl-phenyl)-2-methyl- 2-propenylidene]malononitrile (DCTB) as matrix.

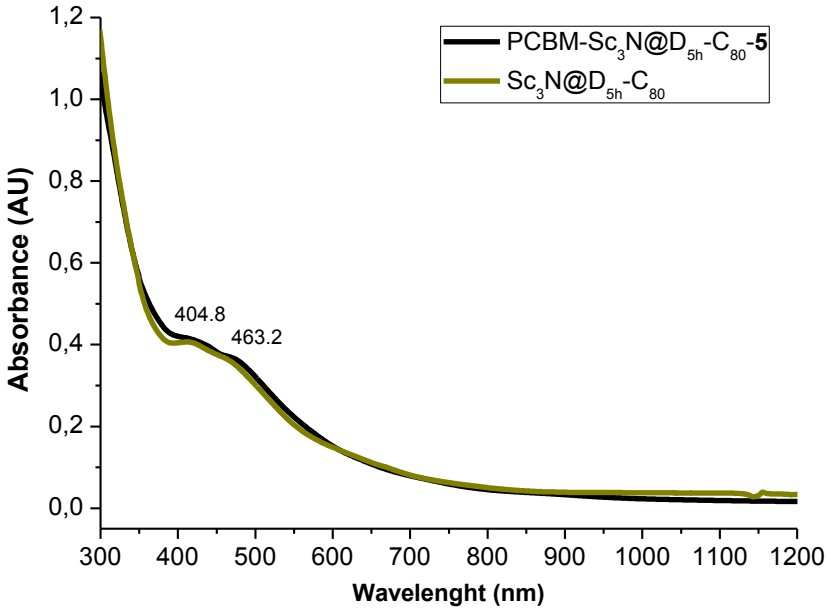

Figure 16S. UV-vis spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**5** in toluene.

^{1}H-NMR (600 MHz; CS_2:CD_2Cl_2 1:1, 298 K); PCBM-$Sc_3N@D_{5h}$-C_{80}-**6:** δ 8.09 (d, 1H, *J* = 7.85 Hz), 7.96 (m, 2H), 7.54 (d, 1H, *J* = 7.28Hz), 7.46 (m, 1H), 3.52 (s, 3H, COO-C<u>H</u>$_3$), 2.21 (t, 2H, *J* = 7.57 Hz, CH_2-C<u>H</u>$_2$-CO), 1.88 (m, 2H, CH_2-CH_2-C<u>H</u>$_2$), 1.71 (m, 2H, CH_2-C<u>H</u>$_2$-CH_2), ppm.

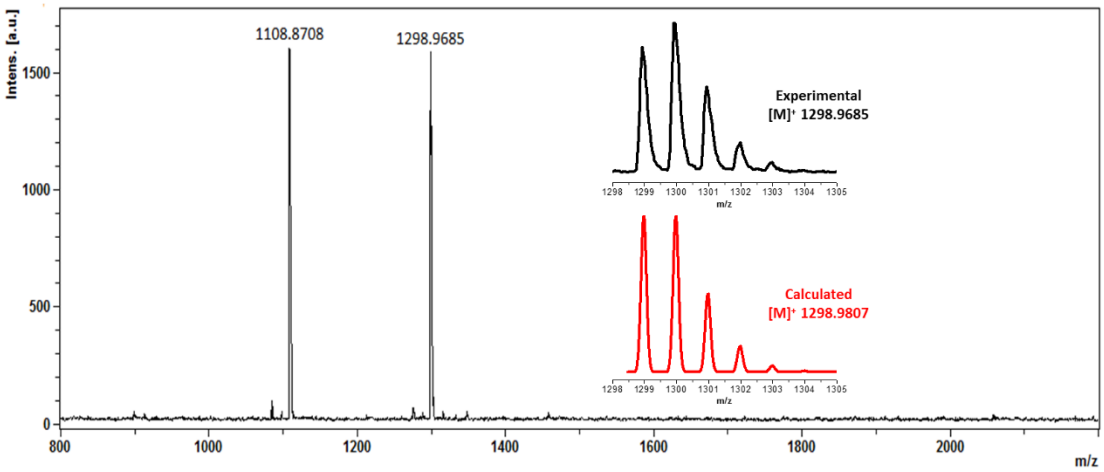

Figure 17S. MALDI TOF spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**6** using DCTB as matrix.

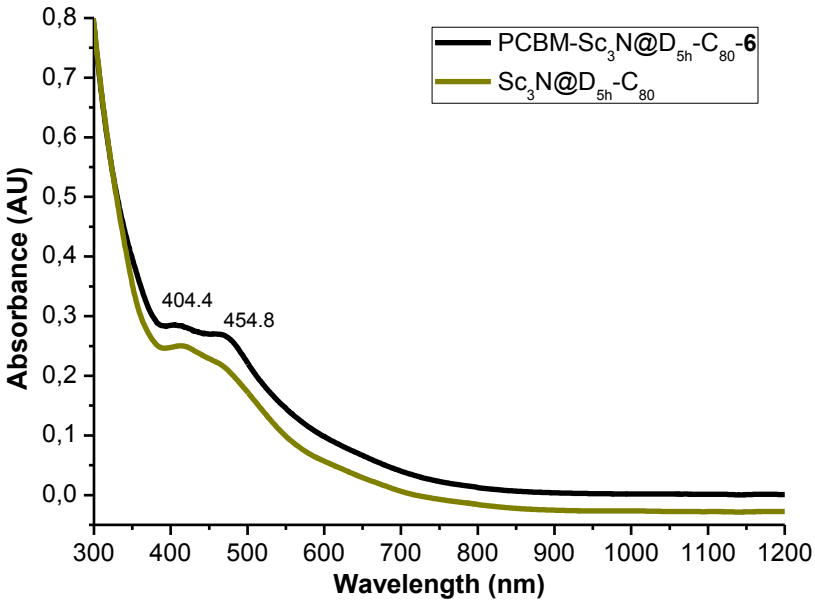

Figure 18S. UV-vis spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**6** in toluene.

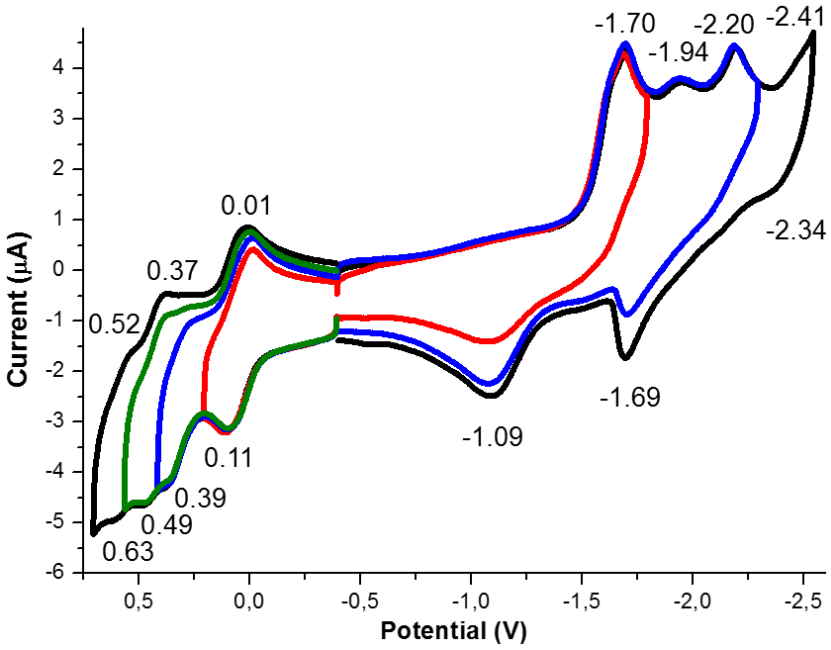

Figure 19S. Cyclic voltammetry of PCBM-$Sc_3N@D_{5h}$-C_{80}-**6** (*o*-DCB containing 0.05 M n-Bu_4NPF_6; using the redox couple Fc/Fc^+ as internal reference).

^{1}H-NMR (600 MHz; CS_2:CD_2Cl_2 1:1, 298 K); PCBM-$Sc_3N@D_{5h}$-C_{80}-**7:** δ 7.28 (m, 1H), 7.23 (m, 2H), 7.15 (m, 2H), 3.68 (s, 3H, COO-C<u>H</u>$_3$), 2.75 (m, 2H, C<u>H</u>$_2$-CH_2-CH_2), 2.47 (t, 2H, *J* = 7.24 Hz, CH_2-C<u>H</u>$_2$-CO), 2.01 (m, 2H, CH_2-C<u>H</u>$_2$-CH_2) ppm.

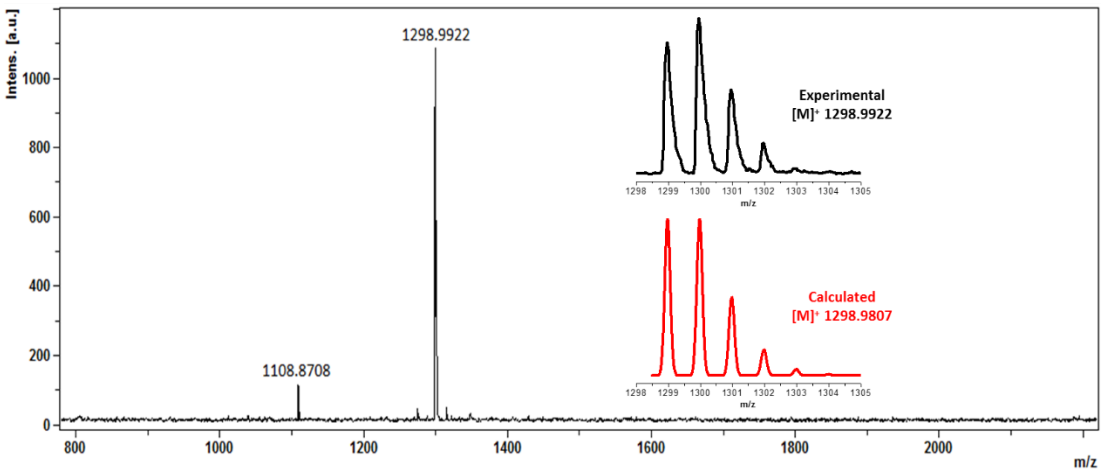

Figure 20S. MALDI TOF spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**7** using DCTB as matrix.

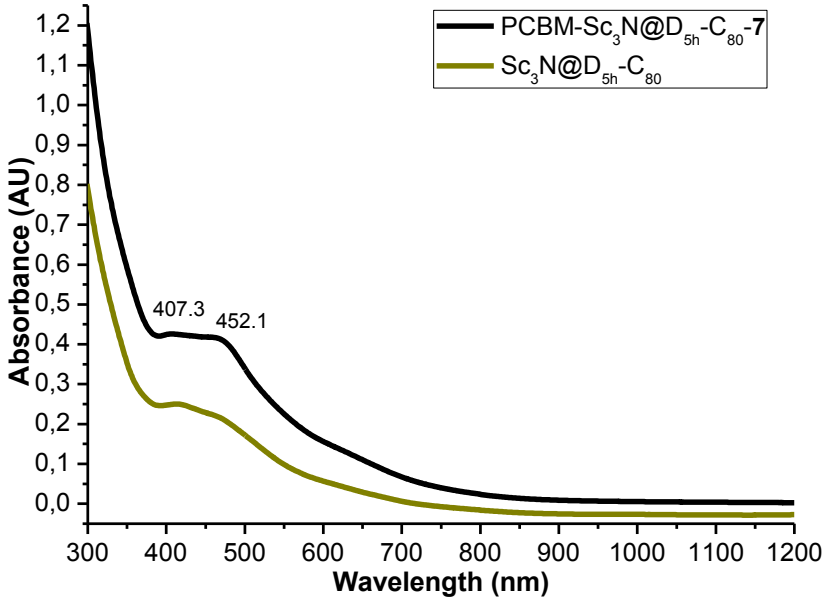

Figure 21S. UV-vis spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**7** in toluene.

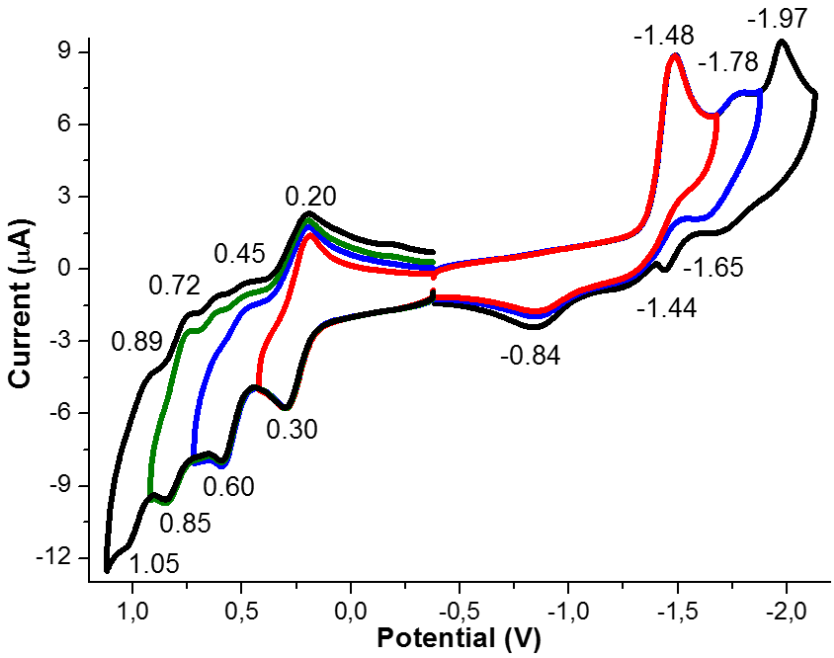

Figure 22S. Cyclic voltammetry of PCBM-$Sc_3N@D_{5h}$-C_{80}-**7** (*o*-DCB containing 0.05 M n-Bu_4NPF_6; using the redox couple Fc/Fc^+ as internal reference).

^{1}H-NMR (600 MHz; CS_2: CD_2Cl_2 1:1, 298 K); PCBM-$Sc_3N@D_{5h}$-C_{80}-**8:** δ 7.72 (d, 1H, *J* = 7.73 Hz), 7.42 (m, 1H), 7.35 (dd, 2H, *J* = 8.12, 15.36 Hz), 7.29 (d, 1H, *J* = 7.28 Hz), 3.57 (s, 3H, COO-C<u>H</u>$_3$), 2.22 (t, 2H, *J* = 7.27 Hz, CH_2-C<u>H</u>$_2$-CO), 1.61 (m, 4H, C<u>H</u>$_2$-C<u>H</u>$_2$-CH_2) ppm.

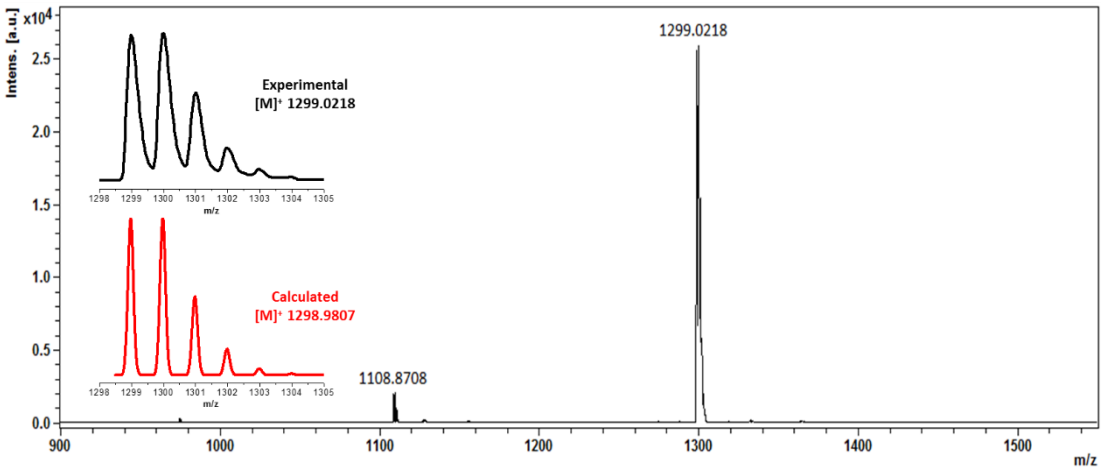

Figure 23S. MALDI TOF spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**8** using TPB as matrix.

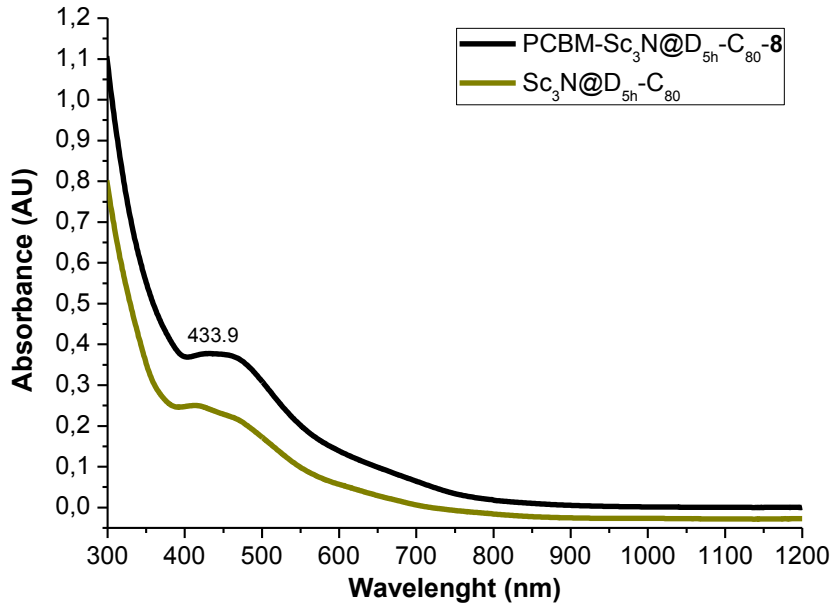

Figure 24S. UV-vis spectrum of PCBM-$Sc_3N@D_{5h}$-C_{80}-**8** in toluene.

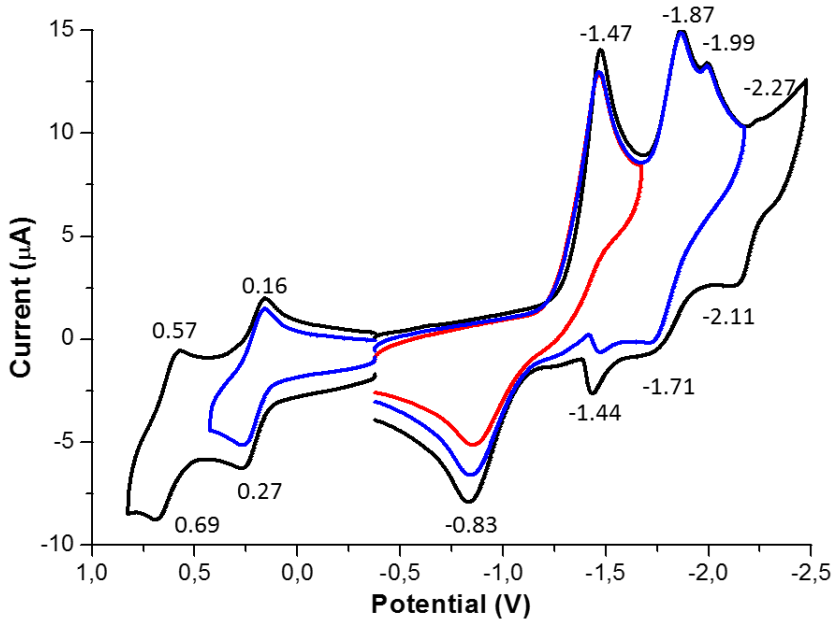

Figure 25S. Cyclic voltammetry of PCBM-$Sc_3N@D_{5h}$-C_{80}-**8** (*o*-DCB containing 0.05 M n-Bu_4NPF_6; using the redox couple Fc/Fc^+ as internal reference).

Table 1S. Redox Potentials (V) of PCBM-$Sc_3N@D_{5h}$-C_{80} **4**-**8**.

Compound	$E_{pa}^{+/+2}$	$E_{pa}^{0/+}$	$E_{pc}^{0/-}$	$E_{pc}^{-/-2}$	$E_{pc}^{-2/-3}$
$Sc_3N@D_{5h}$-C_{80}[1]	-	0.34	-1.33	-	-
Isomer **4**	0.74	0.40	-1.39	-1.68	-1.84
Isomer **6**	0.39	0.11	-1.70	-1.94	-2.20
Isomer **7**	0.60	0.30	-1.48	-1.78	-1.97
Isomer **8**	0.69	0.27	-1.47	-1.87	-1.99

X-ray Crystallography and Data Collection of 7.

Compound **7** was crystallized by slow diffusion of hexanes into a chloroform and carbon disulfide solution of the complex. Crystal data for **7**, PCBM-$Sc_3N@D_{5h}$-C_{80}·CS_2 (CCDC 1421222). $C_{93}H_{14}NO_2S_2Sc_3$, M = 1376.05, black plate, 0.165×0.053×0.021 mm, λ = 0.7749 Å (synchrotron radiation at Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley Laboratory), orthorhombic, space group $Pna2_1$ (no. 33), a = 19.9442(6), b = 15.7417(6), c = 14.9924(4) Å, T = 100(2) K, V = 4706.9(3) Å^3, Z = 4, 64302 reflections measured, 8566 unique (R_{int} = 0.0730), Bruker ApexII; $2\theta_{max}$ = 55.64°; min/max transmission = 0.635/ 0.756 (multi-scan absorption correction applied); direct methods solution; full-matrix least squares based on F^2 (SHELXS and SHELXL-2014); Final $wR(F_2)$ = 0.4000 (all data), conventional R_1 = 0.1649 computed for 7646 reflections with I > 2σ (F_O), with 901 parameters and 715 restraints. Inversion twin parameter, 0.22(10).

Computational Results

The calculations were performed by means of DFT methodology with the combined use of the ADF-2012 and Gaussian-09 codes.[2] The exchange-correlation GGA density functionals of Becke and Perdew (BP86)[3] were employed to calculate all the minima optimized geometries with ADF-2012. Relativistic corrections were included by means of the ZORA (Zero-Order Regular Approximation) formalism. Dispersion corrections were also incorporated (D3 method by Grimme).[4] Triple-ζ polarization basis sets (TZP) of Slater type were used to describe the valence electrons of the atoms. Frozen cores consisting of the 1s shell were described by means of single Slater functions. All the optimized geometries (BP86-D3/TZP), the energies of the products were recomputed by using the M06 functional,[5] at the M06/6-311G** level with the Gaussian-09 code. Solvent effects were also included by using the polarizable continuum model (PCM) [6] to simulate the effects of *o*-DCB.

The vibrational frequencies and the corresponding normal modes were computed using the harmonic approach. Relative abundances along the range of temperatures were obtained from the rigid rotor and harmonic oscillator (RRHO) and the related free-encapsulating model (FEM). In the FEM model we consider that if at high temperature the cluster rotates freely inside the cage, its contribution to the partition function will be similar for the different cages and will cancel out.

Table 1S. Relative energies for computed PCBM monoadducts for $Sc_3N@D_3$-C_{68} including solvent effects (*o*-dichlorobenzene).

Reacting bond[b]	Bond type	E_{rel} (kcal·mol^{-1})
b-*2**	[6,6] – Pyrene	0.0
b-*a*	[5,6] – Corannulene	4.2
b-*a*[a]	[5,6] – Corannulene	4.9
b-*b*	[5,6] – type F	4.5
b-*b*[a]	[5,6] – type F	4.5
b-*e*	[5,6] – Corannulene	6.8
b-*3*	[6,6] – type B	8.4
b-*5*	[6,6] – type B	11.3
b-*d*	[5,6] – Corannulene	11.1
b-*6*	[6,6] – type B	10.9
b-*g*	[5,6] – Corannulene	14.3
b-*c*	[5,5] – Pentalene	14.3
b-*j*	[5,6] – Corannulene	16.9
b-*i*	[5,6] – Corannulene	19.3
b-*1*	[6,6] – type B	21.5
b-*4*	[6,6] – Pyracylene	17.4
b-*8*	[6,6] – type B	20.3
b-*h*	[5,6] – Corannulene	20.4
b-*f*	[5,6] – Corannulene	21.0
b-*7*	[6,6] – type B	21.8

[a] Second regioisomer for such adduct, with a different position of the non-symmetrical addend. *Bonds that contains a symmetry element; only one possible regioisomer exists. [b] Bonds are labelled without the prefix "b-" in Figure 2.

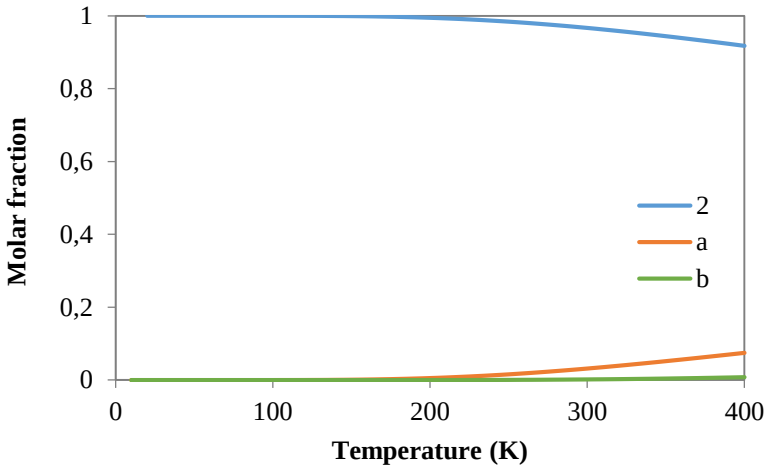

Figure 26S. Representation of the molar fraction as a function of the temperature for the three most stable PCBM monoadducts on $Sc_3N@D_3$-C_{68}.

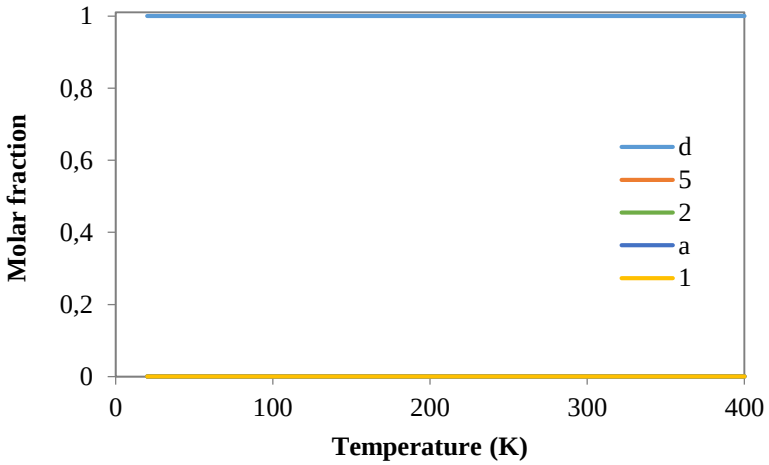

Figure 26S. Representation of the molar fraction as a function of the temperature for five PCBM monoadducts on $Sc_3N@D_{5h}$-C_{80}.

XYZ coordinates for the PCBM regioisomer on bond b-*2* of $Sc_3N@D_3$-C_{68}

C	-3.553310	0.931691	-0.465659
C	1.611561	-0.344327	-3.462560
C	2.345694	-1.514964	-3.107413
C	3.663842	-1.410674	-2.542889
C	4.267916	-0.127665	-2.285271
C	3.543742	1.036559	-2.684701
C	2.255953	0.925076	-3.316612
C	1.495287	2.103171	-2.998471
C	0.065156	2.048381	-2.814285
C	-0.560158	0.776441	-2.978670
C	0.189961	-0.385501	-3.326328
C	-0.485436	-1.525797	-2.773825
C	0.271520	-2.671966	-2.351161
C	1.690230	-2.651482	-2.524705
C	2.577286	-3.229439	-1.535225
C	3.813828	-2.504230	-1.606783
C	3.553812	2.243600	-1.882078
C	2.320066	2.930960	-2.143935
C	-1.725367	0.386889	-2.216751
C	-1.685478	-1.062463	-2.079142
C	-2.161237	-1.817805	-0.951242
C	-1.520579	-3.095289	-0.676609
C	-0.252704	-3.457408	-1.273128
C	0.648011	-3.888894	-0.203235
C	2.085332	-3.718409	-0.278387
C	2.809282	-3.378267	0.946443
C	4.091153	-2.707584	0.827640
C	4.639745	-2.360217	-0.467848
C	5.435006	-1.163758	-0.330459
C	5.155733	-0.003543	-1.155877
C	5.012102	1.147568	-0.262127
C	4.152474	2.274040	-0.576590
C	3.427718	2.923077	0.515650
C	2.218550	3.657261	0.198418
C	1.726491	3.755855	-1.157580
C	0.290290	3.874334	-1.119702
C	-0.535662	2.960463	-1.871709
C	-1.579861	2.465646	-0.987861
C	-2.354392	1.295862	-1.324309
C	-2.769892	0.169288	0.590565
C	-2.480748	-1.222341	0.350296
C	-1.899440	-2.063030	1.382324
C	-1.398339	-3.259589	0.751507
C	-0.067574	-3.728781	1.042243
C	0.627160	-3.179487	2.147324
C	2.058032	-3.060283	2.128831
C	2.398350	-1.923675	2.961744
C	3.588462	-1.167440	2.737174
C	4.531540	-1.681291	1.774861
C	5.394651	-0.764043	1.053799
C	5.140534	0.656096	1.095213
C	4.258841	1.163390	2.077906
C	3.453620	2.323118	1.819514
C	2.251991	2.189958	2.618800
C	1.016589	2.774632	2.202402
C	1.050467	3.663415	1.078980
C	-0.130858	3.824116	0.258760
C	-1.268218	2.924357	0.371172
C	-1.344145	2.084747	1.538528
C	-2.000502	0.785428	1.616907
C	-1.237571	-0.015523	2.551521
C	-1.157310	-1.436741	2.449199
C	0.072740	-2.058360	2.876290
C	1.177045	-1.277923	3.364708
C	3.519585	0.259084	2.932697
C	2.279945	0.907741	3.263667
C	-0.199808	2.048635	2.445856
C	-0.151540	0.754457	3.063848
C	1.085685	0.147544	3.442814
N	1.336936	-0.095358	-0.013800
Sc	-0.010740	-1.537200	0.092917
Sc	0.734027	1.763573	-0.304053
Sc	3.263674	-0.504708	0.167867
C	-4.601428	0.066846	-1.174066
C	-5.440278	-0.753686	-0.408231
C	-4.833882	0.170338	-2.548990
C	-6.474615	-1.472817	-1.005904
H	-5.280768	-0.832355	0.668386
C	-5.870276	-0.547844	-3.150597
H	-4.208278	0.820585	-3.158426
C	-6.690271	-1.375335	-2.383151
H	-7.112746	-2.110001	-0.394944
H	-6.035190	-0.454383	-4.222971
H	-7.496051	-1.938675	-2.852745
C	-4.300493	2.163734	0.115923
C	-4.871165	3.093394	-0.957054
H	-3.642485	2.733604	0.781799
H	-5.108689	1.768653	0.748365
C	-5.533769	4.326727	-0.348469
H	-4.072938	3.419345	-1.640045
H	-5.601734	2.559289	-1.578544
H	-6.352482	4.049020	0.333383
H	-4.823556	4.907399	0.260940
C	-6.100936	5.253273	-1.405681
O	-6.038313	5.079111	-2.605896
O	-6.702985	6.328706	-0.827085
C	-7.277511	7.275857	-1.761141
H	-7.712483	8.066181	-1.143952
H	-6.502075	7.680817	-2.422718
H	-8.048282	6.791420	-2.372961

XYZ coordinates for the PCBM regioisomer on bond b-*4* of $Sc_3N@D_{5h}$-C_{80}

C	2.643552	-2.157057	2.318076
C	3.230652	-2.365831	1.033986
C	1.401156	-2.794813	2.693203
C	2.684745	-0.874199	2.947801
C	3.944922	-1.274710	0.457043
C	2.586461	-3.291095	0.167396
C	3.920955	-1.055841	-0.959235
C	4.005883	0.008279	1.104610
C	1.341261	-3.934567	0.542345
C	2.561545	-3.071611	-1.246731
C	0.681466	-3.627837	1.765898
C	0.583977	-4.140855	-0.654060
C	-0.789395	-3.599681	1.806794
C	0.729307	-1.939119	3.637288
C	3.180976	-1.924734	-1.814160
C	1.300672	-3.577581	-1.756763
C	2.550689	-1.340251	-2.953697
C	3.967111	0.363190	-1.190306
C	1.294388	-1.842544	-3.465781
C	2.576482	0.073268	-3.165382
C	-0.814219	-4.098032	-0.623130
C	-1.510564	-3.857607	0.604711
C	-1.550378	-3.501161	-1.696458
C	0.601603	-2.920361	-2.808750
C	-0.869838	-2.889553	-2.789576
C	0.595555	-0.745075	-4.084563
C	-1.438874	-2.758197	2.791865
C	-0.692605	-1.929882	3.716391
C	-2.624097	-2.019747	2.409683
C	-2.751420	-3.171551	0.277269
C	3.246737	0.949318	-2.266892
C	1.334040	0.456094	-3.793377
C	2.676849	2.243469	-2.079199
C	4.043767	1.020958	0.085309
C	1.421019	2.625392	-2.679614
C	2.780752	2.905353	-0.827098
C	-0.828628	-0.720089	-4.106228
C	-1.548427	-1.793091	-3.451882
C	-1.481401	0.525181	-3.763341
C	0.692559	1.708259	-3.488103
C	-0.761160	1.744211	-3.464432
C	0.763648	3.572266	-1.804672
C	-2.775981	-2.952808	-1.135120
C	-2.715909	-1.210486	-2.823528
C	3.409136	2.274709	0.290547
C	1.654412	3.802024	-0.662827
C	2.820510	2.526417	1.565789
C	1.687424	3.413733	1.711860
C	2.759192	1.522696	2.567240
C	-0.668011	3.599394	-1.772893
C	-1.410068	2.690989	-2.622286
C	-1.496468	3.870813	-0.597850
C	1.264295	4.263373	0.640275
C	-1.024836	4.308749	0.684124
C	0.841532	2.860615	2.771018
C	-2.681729	0.204098	-3.031326
C	-2.662793	2.382305	-1.969825
C	3.328140	0.236412	2.334423
C	1.525994	1.701407	3.299314
C	1.464979	-0.704036	3.701396
C	-0.586393	2.892075	2.797427
C	-1.447347	3.486907	1.776899
C	-1.305984	1.767795	3.359027
C	0.820611	0.578873	3.813497
C	-0.633970	0.613441	3.850481
C	-2.679801	3.044169	-0.713320
C	-2.634967	2.667195	1.682891
C	-2.581659	1.661671	2.683628
C	-1.350486	-0.643279	3.790941
C	-2.575712	-0.734580	3.035397
C	-3.214360	0.406056	2.466317
C	-3.957028	0.205708	1.271930
C	-3.987543	1.219170	0.254869
C	-3.989985	-1.081125	0.624527
C	-3.284670	2.442883	0.432530
C	-3.997943	0.560446	-1.021248
C	-3.294467	1.115807	-2.122735
C	-4.014597	-0.861944	-0.792176
C	-3.350476	-1.768404	-1.666733
C	-3.301045	-2.205735	1.160878
N	-0.127984	0.153264	0.019416
Sc	0.085586	2.135492	0.292137
Sc	-0.229538	-1.043355	1.677721
Sc	-0.276200	-0.501248	-1.913163
C	0.143909	5.271952	0.833869
C	0.155922	5.960570	2.200289
C	-1.045490	6.447565	2.730034
C	1.350839	6.235752	2.873462
C	-1.055907	7.177627	3.918614
H	-1.984769	6.251947	2.211193
C	1.343457	6.967360	4.062718
H	2.299202	5.888395	2.466067
C	0.140402	7.436169	4.591957
H	-2.000756	7.543140	4.318231
H	2.283879	7.172318	4.571909
H	0.134440	8.002296	5.522794
C	0.127965	6.372807	-0.259784
C	1.359984	7.279578	-0.236353
H	-0.785589	6.963881	-0.096854
H	0.030765	5.916300	-1.251158
C	1.318658	8.315530	-1.357722
H	1.435721	7.799389	0.727248
H	2.275928	6.677932	-0.331664
H	1.319243	7.839627	-2.350719
H	0.395620	8.914101	-1.315136
C	2.494995	9.270677	-1.300041

O	3.415499	9.210279	-0.510359
O	2.384292	10.224579	-2.264391
C	3.468007	11.186667	-2.291913
H	3.229499	11.869988	-3.110950
H	3.525135	11.726383	-1.338770
H	4.424690	10.681583	-2.472129

[1] T. Cai, C. Slebodnick, L. Xu, K. Harich, T. E. Glass, C. Chancellor, J. C. Fettinger, M. M. Olmstead, A. L. Balch, H. W. Gibson and H. C. Dorn, *J. Am. Chem. Soc.*, 2006, **128**, 6486-6492.

[2] (a) E. J. Baerends, D. E. Ellis, P. Ros, *ADF 2011.01*, *Department of Theoretical Chemistry*, Vrije Universiteit: Amsterdam; (b) G. T. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931 – 967; (c) Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc, Wallingford CT, **2009**.

[3] (a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 –3100; (b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822 – 8824.

[4] S. Grimme, J. Anthony, S. Ehrlich, and H. Krieg. *J. Chem. Phys.* **2010**, *132*, 154104

[5] Y. Zhao, D. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215 –241.

[6] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999 –3094.