

Derivatization of Fullerenes

[5,6]-Open Methanofullerene Derivatives of I_h -C₈₀**

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The synthesis of novel endohedral metallofullerene (EMF) derivatives has attracted considerable attention, mainly because of their exceptional electronic properties.^[1–3] The exploration of new derivatization protocols to increase their solubility and processability is crucial to expand the range of potential applications of these compounds.^[4–6] In general, EMFs show low reactivity owing to the pronounced stabilization that results from extensive charge transfer between the encapsulated metal cluster and the carbon cage.^[7] It is well-known that cycloaddition reactions, such as 1,3-dipolar cycloaddition reactions of azomethine ylides,^[8] Diels–Alder reactions,^[9] and [2+2] cycloaddition reactions,^[10] proceed well with trimetallic nitride endohedrals only if a large excess of the reagents and long reaction times are used. An interesting observation concerning the most studied EMF, Sc₃N@I_h-C₈₀, is its lack of reactivity under regular Bingel–Hirsch conditions.^[11] Sc₃N@I_h-C₈₀ reacts only in the presence of dimethyl formamide.^[12]

Cyclopropanation-type reactions have been used to modify EMFs to yield methanofullerenes^[13] and recently, azafulleroids^[14] and silylene-bridged derivatives.^[15] There are two distinct addition sites available on the I_h isomer of C₈₀ fullerenes: C–C bonds at [6,6] ring junctions (pyrene-type sites) and C–C bonds at [5,6] ring junctions (corannulene-type sites). In 2005, Poblet and co-workers^[16] reported that the corannulene [5,6] bonds closest to the Sc atoms have the highest strain of all bonds in the I_h -C₈₀ cage. Reactions at this bond can relieve some of the strain and produce the thermodynamically more stable derivative; therefore, the [5,6] bond is more reactive toward exohedral functionalization. This hypothesis was experimentally corroborated for

reactions such as Diels–Alder^[17] and 1,3-dipolar cycloaddition reactions.^[8,18] However, the [6,6] junction is favored for methano-bridge formation on I_h -C₈₀.^[13,19,20] Although nitrogen^[14] and silicon bridges^[15] at [5,6] bonds have been reported, the corresponding methano adducts have remained elusive.

Phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) are well-known electron acceptors that exhibit reasonable efficiencies in organic photovoltaic (OPV) devices;^[21] thus, the methano bridge is a useful anchor for the preparation of fullerene derivatives, partly because of its stability at high temperatures. There are many examples of methano derivatives of EMFs;^[11,13,19] the most commonly reported are derivatives of Sc₃N@I_h-C₈₀, because it is the third-most-abundant fullerene after C₆₀ and C₇₀. To the best of our knowledge, all reported cyclopropane derivatives of I_h -C₈₀ were formed by addition exclusively to [6,6] bonds.

The diphenylmethane (DPM) addend was first reported by Martín et al. on C₆₀, and these derivatives showed promising properties in organic photovoltaic (OPV) devices.^[22] Some methanofullerene derivatives of endohedral fullerenes have already shown high open-circuit voltage (V_{oc}) with reasonable efficiencies in OPV devices.^[6] Herein, we report the synthesis and characterization of six diphenylmethano derivatives of Sc₃N@I_h-C₈₀ in good yields under mild conditions. Three of the compounds, **2a–c**, are the first examples of [5,6]-open methanofullerenes derived from an I_h -C₈₀ cage. The structures of compounds **2c** and **3c** were confirmed by X-ray crystallography.

Compounds **2** and **3** were obtained by photoirradiation of the appropriate carbene precursor **1** (5 equiv) in a solution of Sc₃N@I_h-C₈₀ in *o*-dichlorobenzene (*o*-DCB) at 0 °C for 10 min (Scheme 1, route A; see the Supporting Information). The modified endofullerenes **2** and **3** were obtained in over 40% yield in all cases (> 70% as based on the unreacted pristine starting material). The crude reaction product was purified by column chromatography on silica gel with CS₂/hexanes (7:3) as the eluent to yield a monoadduct fraction and with CS₂/toluene (1:4) to yield a small fraction of bisadducts (see the Supporting Information). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra

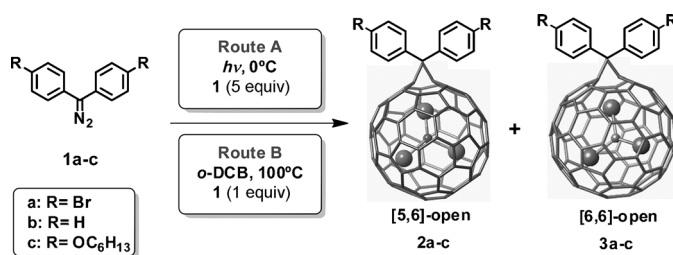
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Scheme 1. Synthesis of compounds **2a–c** and **3a–c**.

confirmed the presence of the molecular-ion peak for the monoadduct products (m/z 1430.7875 for $(p\text{-Br})_2\text{DPM-Sc}_3\text{N@I}_h\text{-C}_{80}$; m/z 1274.0074 for $\text{DPM-Sc}_3\text{N@I}_h\text{-C}_{80} [M-\text{H}]^-$; and m/z 1475.0458 for $(p\text{-C}_6\text{H}_{13}\text{O})_2\text{DPM-Sc}_3\text{N@I}_h\text{-C}_{80}$; see Figures 4S, 7S, and 16S, respectively, in the Supporting Information).

The ^1H NMR spectra in most cases clearly showed the presence of two products with different symmetry. Purification of the mixture by preparative recycling HPLC (with a Buckyclutcher column; Figure 1) enabled the isolation of **2** and **3** in different ratios, depending on the *para* substituent on the aromatic ring (**2a/3a** 1:6; **2b/3b** 1:5; **2c/3c** 1:3).

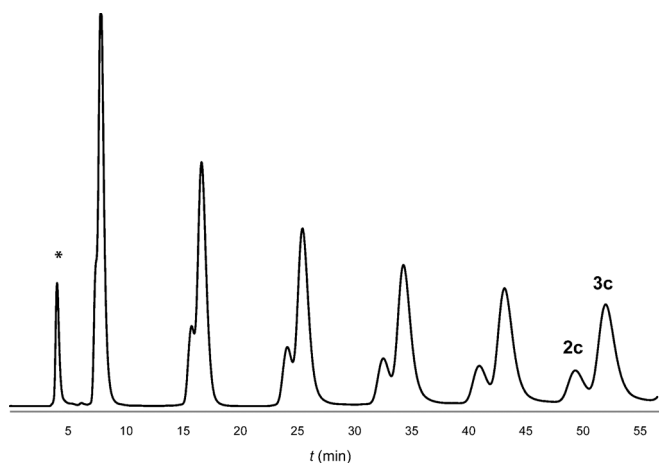


Figure 1. Recycling-HPLC profile of the monoadduct fraction **2c** and **3c** on a Buckyclutcher column ($\phi=25\text{ cm}\times 10\text{ mm}$) in toluene at room temperature; flow rate: 4 mL min^{-1} ; wavelength: 320 nm ; asterisk: solvent.

The ^1H NMR spectroscopic signals for the aryl hydrogen atoms of **2c** appear as four doublets ($\delta=6.82, 6.95, 7.65,$ and 8.16 ppm ; see Figure 10S). In contrast, the corresponding signals for **3c** appear as two doublets ($\delta=6.89$ and 7.91 ppm ; see Figure 12S). Thus, **2c** is the [5,6] addition product, and **3c** is the [6,6] product (Figures 2 and 3c). Compounds **2a-c** and **3a,b** exhibited similar spectra (see the Supporting Information). ^{13}C NMR and UV/Vis spectroscopy were used to establish whether the addition reactions resulted in open- or closed-cage structures. The ^{13}C NMR spectroscopic experiment was only possible for **3c** because it was obtained in reasonable amounts. The ^{13}C NMR spectrum of compound **3c** exhibited 40 signals for sp^2 carbon atoms and two signals for the equivalent sp^2 carbon atoms of the phenyl rings ($\delta=128.47$ and 114.72 ppm ; see Figure 13S), in agreement with the expected symmetry of the [6,6] product. The chemical shift of the methano-bridge carbon atom ($\delta=67.90\text{ ppm}$) is similar to those of other reported open cyclopropyl derivatives.^[23] The UV/Vis absorption spectra of **2c** and **3c** showed similar patterns to those of pristine $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$. The similarity of the spectra suggests that the electronic structure of the C_{80} cage is minimally perturbed and indicates that both compounds probably have open structures (fulleroids; see Figure 17S).

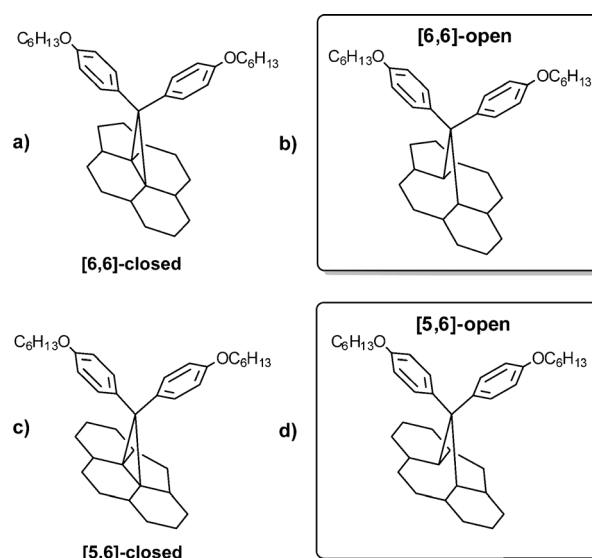


Figure 2. Possible products of cycloaddition to $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$: a) [6,6]-closed adduct; b) [6,6]-open adduct; c) [5,6]-closed adduct; d) [5,6]-open adduct. The phenyl groups are equivalent in (a) and (b) and nonequivalent in (c) and (d).

The diaryl carbene **1c** is remarkably reactive, as evidenced by the formation of **2c** and **3c** (1:3 ratio; Figure 3c) in chlorobenzene at -40°C . The mixture of monoadducts was obtained in 40% yield, which is only slightly lower than that observed when the reaction was carried out at 0°C (48%).

As already mentioned, typical cyclopropanation reactions of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ require a large (sometimes 100-fold)^[24] excess of the carbene reagent and afford the [6,6] adducts exclusively. In the present study, when the reaction was conducted in *o*-DCB (100°C , in the dark, 2 h; route B) only one equivalent of **1** was required for the formation of the products in reasonable yield. The products were obtained in similar ratios to those found for the photochemical reaction, with the exception of **2a** and **3a**, in which case the ratio increased from 1:8 to 1:6 (Figure 3a,b). The substituent group at the *para* position of the aryl group clearly influences the reactivity of the carbene and therefore affects the yield of **2**. When the substituent was electron-withdrawing ($\text{R}=\text{Br}$), less of product **2** was formed than with an electron-donating substituent ($\text{R}=\text{OC}_6\text{H}_{13}$). The new [5,6]-modified compounds exhibited very high stability, even upon heating for long periods (reflux in *o*-DCB, 16 h) or irradiation ($\lambda=350\text{ nm}$, *o*-DCB, 6 h). No evidence of isomerization was observed.

Single crystals of **3c** were grown from a solution in $\text{CS}_2/\text{hexanes}$ by slow diffusion. The asymmetric unit contained one molecule of the open [6,6]- $(p\text{-C}_6\text{H}_{13}\text{O})_2\text{DPM}$ adduct of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ and 0.5 molecules of CS_2 (see Figure 18Sa). The Sc_3N group is positioned such that one Sc (Sc1) atom is nestled close to the extra interior space created by adduct formation (the distance from the centroid of $\text{C1}\cdots\text{C9}$ to Sc1 is 2.220 \AA). If the minor Sc4 disorder is neglected, the trimetallic nitride group is planar, with the sum of the Sc-N-Sc angles equal to 359.8° . The atoms at the open [6,6] junction, C1 and C9, are highly pyramidalized, and the addition of the central methano carbon atom (C81) results in a stretch from

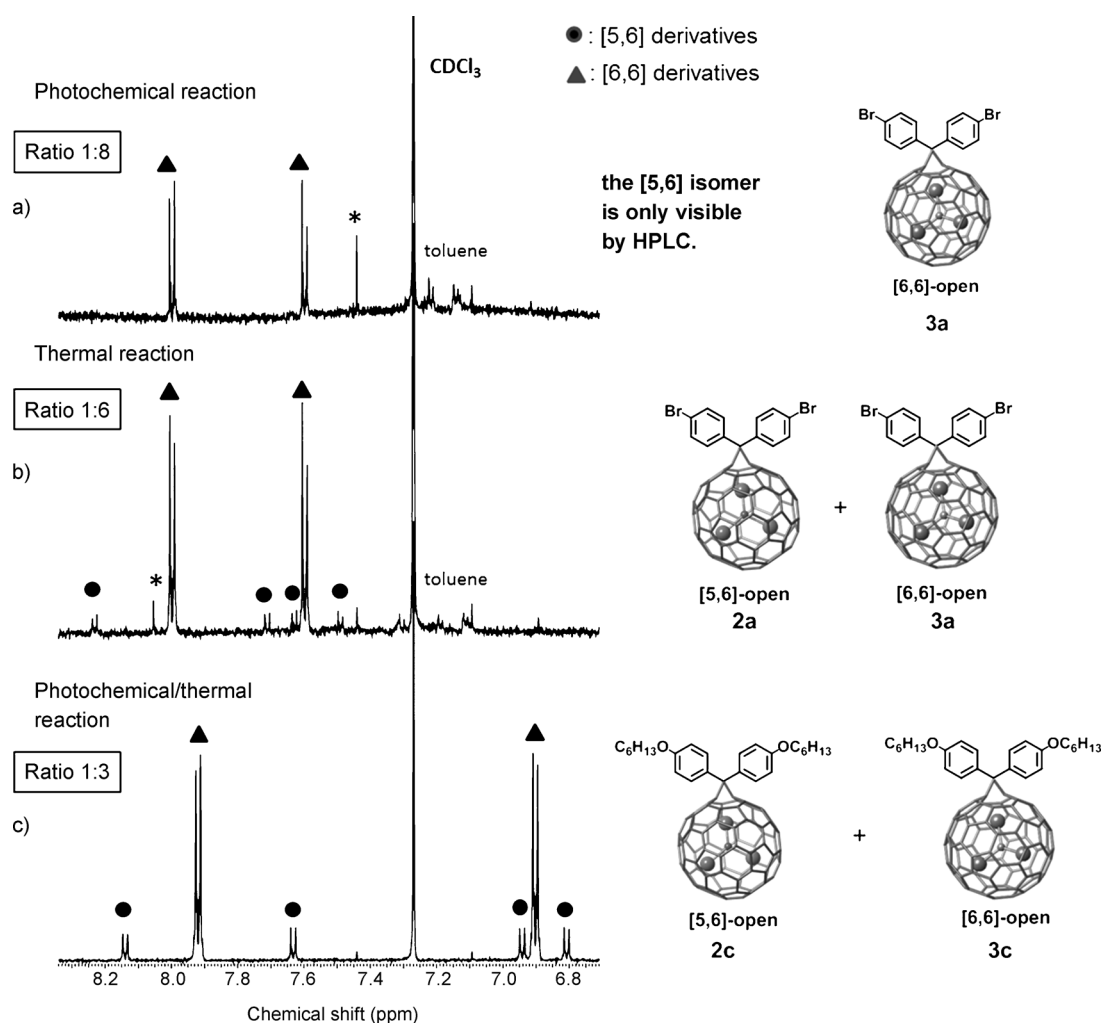


Figure 3. ¹H NMR spectra (600 MHz, CDCl₃, 298 K) of the monoadduct fractions: a) **2a/3a** formed under photochemical conditions (the ratio in this case was calculated by HPLC; see Figure 2S); b) **2a/3a** formed under thermal conditions; c) **2c/3c** (the ratio of the products was the same whether formed under photochemical or thermal conditions); ● signals for the [5,6] derivative; ▲ signals for the [6,6] derivative; asterisks: impurities.

a typical [6,6] distance of 1.42 Å to a distance of 2.12(3) Å between C1 and C9 (see Figure 18Sb). In the crystal structure, a second molecule, generated by the *c* glide, is embraced by the phenyl “arms” of the first molecule through π - π and van der Waals interactions (see Figure 19S).

Single crystals of **2c** were grown from a solution in CS₂/CDCl₃/hexanes by slow diffusion. The asymmetric unit contained one molecule of the open [5,6]-(*p*-C₆H₁₃O)₂DPM adduct of Sc₃N@I_h-C₈₀ (Figure 4a). Data collection and structure solution were conducted as for [6,6]-(*p*-C₆H₁₃O)₂DPM-Sc₃N@I_h-C₈₀·0.5(CS₂) (**3c**; see the Supporting Information). The poor agreement factors for this structure are probably the result of several factors: the small crystal size, loss of the solvent CS₂ or disorder of CS₂, 50:50 disorder in the fullerene orientation, and disorder in the alkyl chains. Surprisingly, the structure itself is clear, and we feel that the result is valid. The questions to be answered were 1) whether or not the modification had occurred at a [5,6] junction, at which a pentagon and a hexagon are joined, and 2) whether the [5,6] bond was open or closed. The location of the

modification at a [5,6] junction was apparent from an early stage of the crystal-structure solution, and the methano bridge spans a distance of 2.23(4) Å; thus, the structure is “open”. The structure resembles that of the [6,6] isomer in general. The Sc₃N unit is planar, and one of the three Sc atoms is close to the opening in the cage. The distance from the centroid of C1...C2 to Sc1 is 2.223 Å. The DPM “arms” embrace a neighboring C₈₀ cage in a similar manner to that exhibited by the [6,6] isomer **3c**. A distinct void space is present in which a solvent CS₂ molecule would be expected but was not located. As was true for the [6,6] isomer, there are two rotational orientations for the C₈₀ cage, and their occupancy is close to 50:50 in the case of the [5,6] isomer.

The redox potentials of **2c** and **3c** were measured by cyclic voltammetry (CV) and square wave voltammetry (SWV) in *o*-dichlorobenzene. The SWV results are summarized in Table 1. Previous studies showed that [5,6] adducts resulting from 1,3-dipolar cycloaddition reactions typically exhibit reversible cathodic electrochemical behavior,^[25] whereas [6,6] adducts typically exhibit irreversible behavior,^[12, 23c, 25]

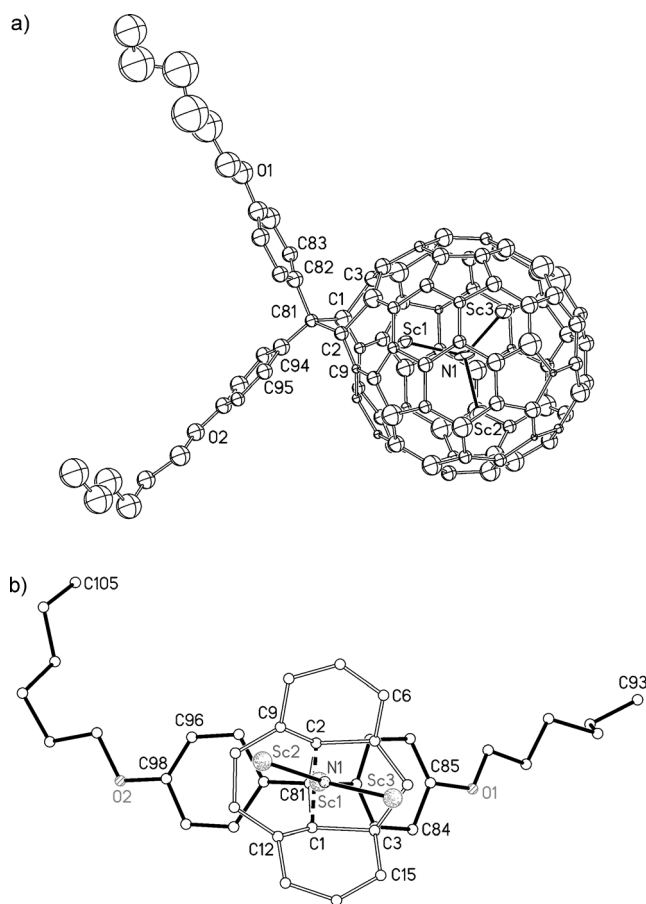


Figure 4. a) A view of the asymmetric unit of **2c**. The disorder in the C_{80} orientation is omitted for clarity. Displacement parameters are shown at the 35% probability level. b) A view from inside the I_h cage of **2c** in the vicinity of the open [5,6] junction. The DPM adduct spans C1...C2 at a distance of 2.23(4) Å. Another orientation is present, but the two atoms C1 and C2 belong to both parts of the molecule. The expected [5,6] distance in I_h-C_{80} is approximately 1.45 Å.

analogous to that observed for the unfunctionalized parent compound. CV of compound **2c** gave five irreversible reduction waves, and no oxidation processes were observed (see Figure 10S). The first, second, and third reduction peak potentials of the [5,6]-methanofullerene derivative **2c** were shifted anodically (by 70, 110, and 450 mV, respectively) relative to those of $Sc_3N@I_h-C_{80}$. The CV spectrum of **2c** also showed two new reduction processes at -2.25 and -2.35 V. In contrast to **2c**, the [6,6]-methanofullerene derivative **3c** showed the same number of reduction processes as the pristine compound, with electrochemical quasireversible cathodic behavior. The first reduction was shifted cathodically (by 250 mV) relative to that of $Sc_3N@I_h-C_{80}$, and the third

reduction was shifted anodically (by 140 mV). Only one oxidation process was shifted cathodically (by 70 mV) relative to that for the parent compound.

There is only one reported example of an endohedral fullerene in an OPV device: PCBH- $Lu_3N@I_h-C_{80}$ (phenyl- C_{81} -butyric acid hexyl ester) which exhibited a photoconversion efficiency of 4.2% with a very high open-circuit voltage (890 mV). The first reduction potential of PCBH- $Lu_3N@I_h-C_{80}$ is -1.51 V and the first oxidation potential is 0.56 V versus ferrocene.^[6] Compound **3c** has the same reduction-potential value as PCBH- $Lu_3N@I_h-C_{80}$ and a very similar oxidation potential. Although it is difficult to predict whether **3c** is a better acceptor than **2c** on the basis of the redox potentials alone, this comparison with PCBH- $Lu_3N@I_h-C_{80}$ suggests that **3c** could potentially be a promising acceptor in OPV devices.

In conclusion, we successfully prepared and characterized the first [5,6] methano adduct of $Sc_3N@I_h-C_{80}$ by using a diaryl diazo compound as a reagent. This reaction exhibits high yields under relatively mild conditions, which is unusual for endohedral fullerenes. We also showed that different substituent groups at the *para* position of the phenyl ring change the reactivity of the carbene formed and alter the ratio of [5,6] and [6,6] isomers obtained. The structures of compounds **2c** and **3c** were confirmed by X-ray crystallography.

Experimental Section

The synthesis and purification of $Sc_3N@I_h-C_{80}$,^[26] the experimental details, and the characterization of the products are included in the Supporting Information, as well a diagram showing the numbering scheme for I_h-C_{80} (see Figures 18S and 19S) and X-ray crystallographic files for [6,6](*p*-OC₆H₁₃)₂DPM- $Sc_3N@I_h-C_{80}$ ·0.5 CS₂ and [5,6](*p*-OC₆H₁₃)₂DPM- $Sc_3N@I_h-C_{80}$ in CIF format.

X-ray crystallography and data collection: Black shards of approximately 1 μm thickness of [5,6](*p*-OC₆H₁₃)₂DPM- $Sc_3N@I_h-C_{80}$ (**2c**) and [6,6](*p*-OC₆H₁₃)₂DPM- $Sc_3N@I_h-C_{80}$ ·0.5 CS₂ (**3c**) were selected for data collection on a Bruker D8 diffractometer equipped with an ApexII CCD detector at the Advanced Light Source, Berkeley, CA, beamline 11.3.1. Data was collected at 90(2) K by the use of a cold stream of nitrogen provided by an Oxford Cryostream low-temperature apparatus and silicon(111) monochromated synchrotron radiation ($\lambda = 0.77490$ Å). The data sets were reduced by the use of Bruker SAINT software package,^[27] and a multiscan absorption correction was applied by the use of the program SADABS.^[28] The structures were solved by using the SHELXT software package^[28] and refined by full-matrix least-squares on F^2 (SHELXL-2013).^[28] There are two orientations for the C_{80} cage in both structures, and these orientations were modeled by the use of rigid groups corresponding to well-determined structures of I_h-C_{80} . However, the refinement of carbon atoms in the region of the modification was allowed to proceed. Relative occupancies for the two orientations were 0.50/0.50 (fixed) for the [5,6] isomer and 0.691(4)/0.309(4) (refined) for the [6,6] isomer. The engaged Sc_3N moiety was ordered in the case of the [5,6] isomer and suffered minor disorder with a Sc₂/Sc₄ set at a 0.895(6):0.104(18) ratio in the [6,6] isomer. Crystal data for **2c**: C₁₀₅H₃₄N₂O₂Sc₃, $M_r = 1476.21$, monoclinic, $P2_1/c$, $a = 11.153(8)$, $b = 32.36(2)$, $c = 17.024(12)$ Å, $\beta = 104.054(8)^\circ$, $V = 5960(7)$ Å³, $Z = 4$, $R1 [3740 \text{ reflections with } I > 2\sigma(I)] = 0.292$, $wR2 (\text{all } 4678 \text{ data}) = 0.633$, 319 parameters, 30 restraints. Crystal data for **3c**:

Table 1: Redox potentials^[a] of **2c**, **3c**, and $Sc_3N@I_h-C_{80}$.

Compound	$E^{+/+2}$	$E^{0/+}$	$E^{0/-}$	$E^{-/-2}$	$E^{-2/-3}$	$E^{-3/-4}$	$E^{-4/-5}$
2c	–	–	–1.19	–1.51	–1.92	–2.25	–2.35
3c	–	+0.52	–1.51	–1.61	–2.23	–	–
$Sc_3N@I_h-C_{80}$ ^[b]	+1.09	+0.59	–1.26	–1.62	–2.37	–	–

[a] Values obtained by SWV in volts versus Fc/Fc⁺. [b] Data from Ref. [16].

$C_{105}H_{34}NO_2Sc_3 \cdot 0.5CS_2$, $M_r = 1514.28$, monoclinic, $P2_1/c$, $a = 11.015(6)$, $b = 31.715(17)$, $c = 17.265(9)$ Å, $\beta = 104.090(8)^\circ$, $V = 5850(5)$ Å³, $Z = 4$, R_1 [3646 reflections with $I > 2\sigma(I)$] = 0.149, $wR2$ (all 7294 data) = 0.361, 571 parameters, 640 restraints.

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