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Synthesis and Electrochemical Studies of Bingel–Hirsch Derivatives of $M_3N@I_h$-C_{80} (M = Sc, Lu)

Julio R. Pinzón, Tianming Zuo, and Luis Echegoyen*[a]

Abstract: Bingel–Hirsch derivatives of the trimetallic nitride template endohedral metallofullerenes (TNT-EMFs) $Sc_3N@I_h$-C_{80} and $Lu_3N@I_h$-C_{80} were prepared by reacting these compounds with 2-bromodiethyl malonate, 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate bromide, and 9-bromo fluorene. The mono-adducts were isolated and their ^{1}H NMR spectra showed that the addition occurred with high regioselectivity at the [6,6] bonds of the I_h-C_{80} fullerene cage. Electrochemical analysis showed that the reductive electrochemistry behavior of these derivatives is irreversible at a scan rate of 100 mV s^{-1}, which is comparable to the behavior of the pristine fullerene species. The first reduction potential of each derivative is either cathodically or anodically shifted by a different value, depending on the attached addend. Bis-adducts containing EtOOC-C-COOEt and HC-COOEt addends were isolated by HPLC and in the case of $Sc_3N@I_h$-C_{80} the first reduction potential exhibits a larger shift towards negative potentials when compared to the mono-adduct. This observation is important for designing acceptor materials for the construction of bulk heterojunction (BHJ) organic solar cells, since the polyfunctionalization not only increases the solubility of the fullerene species but also offers a promising approach for bringing the LUMO energy levels closer for the donor and the acceptor materials.

Keywords: Bingel reaction · electrochemistry · fullerenes · reduction · organic solar cells

Introduction

Trimetallic nitride template endohedral metallofullerenes (TNT-EMFs)[1,2] have received the attention of many research groups, since they offer the possibility of encapsulating diverse metals inside fullerene cages to yield novel materials with potential applications in medicine,[3–5] organic solar cell device construction[6–10] and nanomaterials science. Exohedral functionalization is important for increasing the solubility and/or tuning the electronic properties of these fullerenes in order to expand the range of potential applications.

$Sc_3N@I_h$-C_{80}, initially discovered by Dorn and co-workers,[11] is the third most abundant fullerene obtained as a single isomer. It is prepared in a Krätschmer–Huffman reactor by arcing graphite rods packed with Sc_2O_3 in an ammonia or nitrogen containing atmosphere.[11,12] Recent advances in the arcing process have allowed the preparation of soot extracts containing up to 96% of this fullerene[13] and the separation of the icosahedral isomer is easily achieved by diverse chemical methods,[14–18] avoiding tedious and expensive HPLC separations.

Contrasting the easy preparation and purification of $Sc_3N@I_h$-C_{80}, its low reactivity is an obstacle for the preparation of useful derivatives. A formal transfer of six electrons from the metal cluster towards the fullerene cage produces a closed shell structure with a consequential decrease of reactivity.[19–21] A newer member of the TNT-EMF family, $Lu_3N@I_h$-C_{80},[22] has been proposed as an X-ray contrast agent[5] and because of its high first reduction potential, its phenyl-C_{61}-butyric acid methyl ester (PCBM) and phenyl-C_{61}-butyric acid hexyl ester (PCBH) derivatives were prepared and evaluated in photovoltaic cells. These devices exhibit large open circuit voltages when compared to the ones based on C_{60}-PCBM, demonstrating that the use of TNT-EMFs can lead to more efficient organic photovoltaic devices.[8] $Lu_3N@I_h$-C_{80} can also be obtained in good yields and its reactivity is analogous to that of $Sc_3N@I_h$-C_{80}.

The Bingel–Hirsch reaction[23–25] is one of the most used fullerene functionalization strategies. It is very attractive

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[a] J. R. Pinzón, Dr. T. Zuo, Prof. Dr. L. Echegoyen
Department of Chemistry, Clemson University
219 Hunter Laboratories, Clemson, SC 29634 (USA)
Fax: (+1) 864 656 6613
E-mail: luis@clemson.edu

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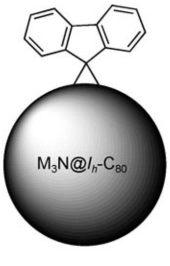
due to the easy accessibility of the malonic acid derivatives. However, previous attempts to prepare Bingel–Hirsch adducts of $Sc_3N@I_h$-C_{80} under the same conditions as used for $Y_3N@I_h$-C_{80} and $Er_3N@I_h$-C_{80} failed[26,27] and this difference of the reactivity was attributed to the nature of the encapsulated metal cluster. A similar behavior was described for $Lu_3N@I_h$-C_{80}.[28] A more recent report has shown that when the reaction is conducted in the presence of Mn^{III} acetate dehydrate, the resulting free radicals can react with these endohedral metalofullerenes and the diethylmalonate Bingel–Hirsch adducts are obtained for $Sc_3N@I_h$-C_{80} and $Lu_3N@I_h$-C_{80}.[29]

Here, we report the preparation of Bingel–Hirsch adducts in high yield for $Sc_3N@I_h$-C_{80} and $Lu_3N@I_h$-C_{80} by using more typical conditions, but with dimethyl formamide (DMF) in the solvent mixture. The presence of DMF has made it possible to prepare these adducts routinely and in reasonably high yields without the need to generate the intermediate radicals. Electrochemical studies of the prepared adducts showed that the reduction potentials can be conveniently tuned and that poly-additions enhance the solubility and cathodically shift the first reduction potential, thus, bringing the LUMO level closer to that of the typical donor polymers, such as poly-3-hexylthiophene (P3HT)[30] or MDMO-PPV[31].

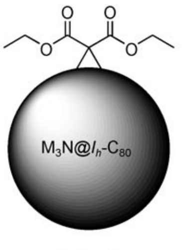
Results and Discussion

Synthesis of the compounds: 9-Bromofluorene and NaH were allowed to react with $Sc_3N@I_h$-C_{80} by using the same experimental conditions as those reported originally by Bingel.[23] Compound **1** was isolated for the first time with an overall yield of 11%. Another experiment was made by using 1,8-diazabicycloundec-7-ene (DBU) instead of NaH and the formation of compound **1** was almost immediately observed by HPLC. However, the reaction mixture was stirred overnight under argon to allow the completion of the reaction. These were determined to be the best conditions for the preparation of compound **1** (See the Supporting Information).

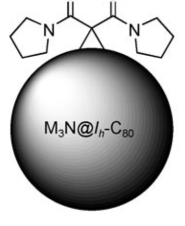
The ^1H NMR spectrum of compound **1** is shown in Figure 1b. It displays only a set of signals for the fluorene moiety. There are two types of double bonds in the I_h-C_{80} fullerene cage; they are designated as a [5,6] bond if it is located between a five- and a six-membered carbon ring or as a [6,6] bond when it is located between two six-membered carbon rings. Based on symmetry considerations, the observed NMR signals are consistent with a [6,6] addition pattern, but it is not clear whether the compound is a cyclopropane derivative or an open cage fulleroid. The low solubility of the sample precluded acquisition of a ^{13}C NMR spectrum. The protons at positions 1 and 1′ of the fluorene ring appear at $\delta = 8.70$ ppm. They are shifted downfield by $\delta = 1.0$ ppm compared to 9-fluorene (Figure 1a) because the rigidity of the molecule keeps them in a fixed position very close to the fullerene cage. Similar deprotecting effects have been previously observed for C_{60} derivatives and are attributed to the aromatic currents over the fullerene sphere.[32]



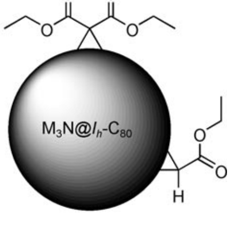
1: M = Sc



2: M = Sc
5: M = Lu



3: M = Sc
6: M= Lu



4: M = Sc
7: M = Lu

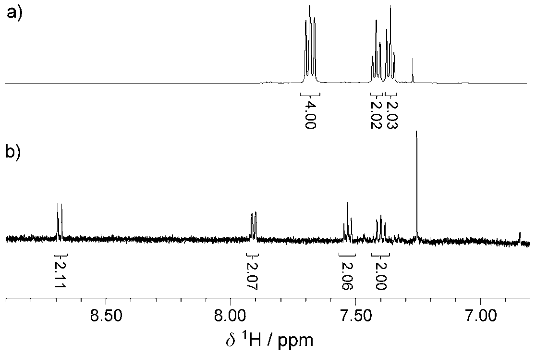


Figure 1. 500 MHz ^1H NMR spectra of a) 9-bromofluorene in $CDCl_3$ and b) compound **1** in $CS_2/CDCl_3$ (4:1). The protons in the positions 1 and 1′are deprotected because of the ring currents on the fullerene cage surface.

Similar reactions between 2-bromodiethyl malonate and $Sc_3N@I_h$-C_{80} or $Lu_3N@I_h$-C_{80} at room temperature by using NaH as the base in *ortho*-dichlorobenzene (*o*-DCB) yielded the desired products. In the case of $Sc_3N@I_h$-C_{80} formation of the desired adduct was observed with 15% yield along with the $Sc_3N@I_h$-C_{80}-HC-COOEt adduct resulting from hydrolysis followed by decarboxylation.[29] By heating the reaction mixture to 60 °C and adding an extra amount of 2-bromodiethyl malonate the reaction was accelerated and the yield of compound **2** increased, but then compound **4** and a complex mixture of poly-adducts were formed (see Figure 2). Replacing the 2-bromodiethyl malonate by 2,2-dibromodiethyl malonate prepared by bromination of 2-bromodiethyl malonate produced identical results. This result is noteworthy, because both the 2-bromo and the 2,2-dibromo malonates can be used for the preparation of these adducts when NaH is chosen as the base. There exists the possibility

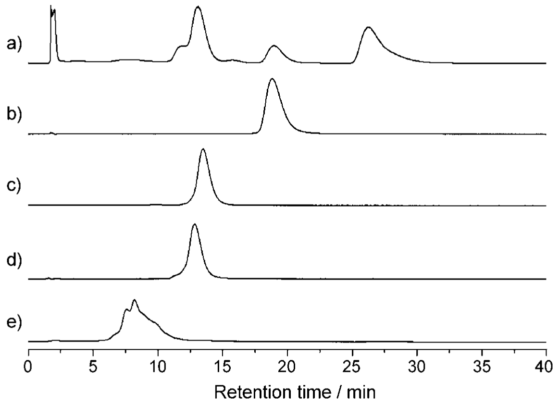


Figure 2. HPLC chromatograms of the reaction of 2-bromodiethylmalonate with $Sc_3N@I_h$-C_{80} by using NaH as the base and heating to 60 °C (PBB column (4.5×250 mm), toluene/*o*-DCB 5% 2 mL min^{-1}). a) Reaction mixture. The peak at 26.2 min corresponds to unreacted $Sc_3N@I_h$-C_{80}. b) $Sc_3N@I_h$-C_{80}-HC-COOEt adduct. c) Compound **2**. d) Compound **4**. e) Bis-adducts fraction.

that a carbene intermediate is formed when the 2,2-dibromo compound is used.

The conversion of $Lu_3N@I_h$-C_{80} under the same conditions as used for $Sc_3N@I_h$-C_{80} gave similar results (see Figure 3a), but due to poly-adduct and hydrolysis product formation, the use of NaH as the base is not optimal for the preparation of the desired mono-adduct. When DBU was used, no reaction was observed with either $M_3N@I_h$-C_{80} (M = Sc, Lu) even after several hours at room temperature, but addition of DMF induced the reaction. When $Lu_3N@I_h$-C_{80} is stirred overnight under argon with 2-bromodiethyl malonate in a 4:1 mixture of *o*-DCB/DMF in the presence of DBU, compound **5** is obtained in 40% yield with high selectivity, and only a minor fraction of the $Lu_3N@I_h$-C_{80}-HC-COOEt adduct is observed. (see Figure 3b) Thus, the combination of DBU with an *o*-DCB/DMF solvent mixture offers a valuable alternative to NaH, since it inhibits the formation of hydrolysis–decarboxylation products.

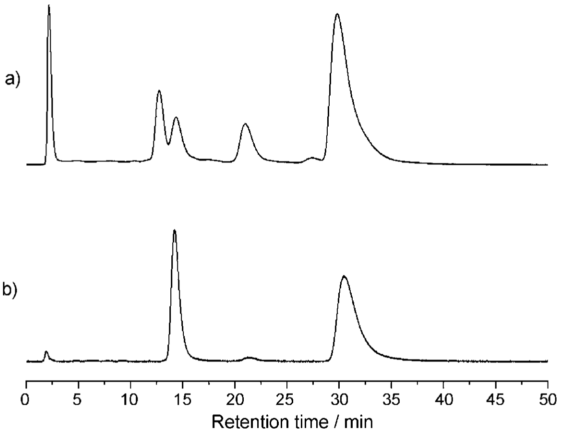


Figure 3. HPLC chromatograms of the reaction of 2-bromodiethylmalonate with $Lu_3N@I_h$-C_{80} (PBB column (4.5×250 mm), toluene/*o*-DCB 5% 2 mL min^{-1}). a) Reaction mixture by using NaH as the base and heating to 60 °C. The peak at 21.0 min corresponds to the $Lu_3N@I_h$-C_{80}–HC-COOEt adduct, the peak at 14.2 min corresponds to compound **5** and the peak at 12.7 min corresponds to compound **7**. b) Reaction mixture by using DBU as the base and *o*-DCB/DMF as solvents at room temperature.

The ^{1}H NMR spectrum of compound **2** in a CS_2/CD_2Cl_2 mixture (4:1) shows a single set of signals, which also suggests a [6,6] addition pattern at the I_h-C_{80} cage. The methylene groups exhibit a quartet centered at $\delta = 4.89$ ppm, whereas the protons of the methyl group are observed at $\delta = 1.43$ ppm (see Figure S4 in the Supporting Information). ^{1}H NMR spectrum of compound **2** in $CS_2/CDCl_3$ (4:1) shows the methylene group signal at $\delta = 4.55$ ppm and the methyl groups at $\delta = 1.45$ ppm in excellent agreement with the previously reported values that were shown to correspond to an open cage (fulleroid) structure.[29] The difference in chemical shifts in different solvents can be attributed to the different solvent anisotropies. For compound **5** the ^{1}H NMR spectrum in a CS_2/CD_2Cl_2 mixture (4:1) shows a single set of signals comparable to those for compound **2** (see Figure S20 in the Supporting Information). The protons of the methylene unit are observed at $\delta = 4.64$ ppm and the protons of the methyl groups appear at $\delta = 1.56$ ppm.

To prevent the hydrolysis and decarboxylation reactions observed with the 2-bromodiethyl malonate, 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate bromide[33,34] was prepared and reacted with $Sc_3N@I_h$-C_{80}. The use of either NaH or DBU gave the same results. The reaction did not work in *o*-DCB or in *o*-DCB/toluene mixtures, but addition of DMF led to the formation of the desired products. At room temperature, it took about three hours to detect the formation of bis-adducts by TLC. If heated to 60 °C the formation of bis-adducts was observed in less than 15 min. The desired mono-adduct was formed in a yield of 54% and easily isolated by column chromatography.

The ^{1}H NMR spectrum of compound **3** is more complex that those of compounds **1** and **2**, because the five-membered pyrrolidine rings are very close to the fullerene sphere that results in hindered rotation, which in combination with the well-known resonance effects of the amide groups produces a complex NMR splitting pattern. The protons connected to the four CH_2 groups next to the pyrrolidine nitrogen atom are observed as broad signals in the region between $\delta = 4.5$ and 3.5 ppm, whereas the remaining protons gave broad signal at $\delta = 2.02$ ppm. In the case of $Lu_3N@I_h$-C_{80} (**6**) the ^{1}H NMR spectrum is almost identical, showing broad signals within the same regions. The correlation among the different signals is clearly observed in the ^{1}H COSY spectrum indicating that they all belong to the same spin system (see Figures S17 and S23 in the Supporting Information).

According to recently reported theoretical calculations[35] the first step of the Bingel mechanism (addition/elimination) is an exothermic barrierless process, but the energy of the transition state during the elimination process is strongly affected by the polarity of the solvent. The presence of a polar solvent lowers the energy of this transition state,[35] which may explain why the presence of DMF favors the reaction. The presence of only the [6,6] isomer further supports the idea that the reaction proceeds through an addition/elimination mechanism instead of a carbene addition because carbene additions to fullerenes have low regioselectivity.

Electrochemical studies: Cyclic voltammetry experiments were done with compounds **1** to **7** and compared with those of the pristine fullerene species. As displayed in Figure 4 (**1**–**4**) and Figure 5 (**5**–**7**), all compounds show an electrochemically irreversible behavior comparable to that of the pristine fullerenes, following the same trend previously observed for other TNT-EMFs.[27] For the $Sc_3N@I_h$-C_{80} compounds **2** and **3**, cathodic shifts of 80 and 110 mV, respectively, are observed for the first reduction potential compared to $Sc_3N@I_h$-C_{80}. An even higher shift of 120 mV is observed for compound **4**, whereas for compound **1** the opposite effect occurs and an anodic shift of 20 mV for the first reduction potential is observed. This anodic shift of compound **1** is likely a consequence of periconjugation,[32,36] because the aromatic rings in the fluorene moiety are held rigidly on the $Sc_3N@I_h$-C_{80} surface, so that the π orbitals on the fluorene can interact with the orbitals of the fullerene cage (see Table 1).

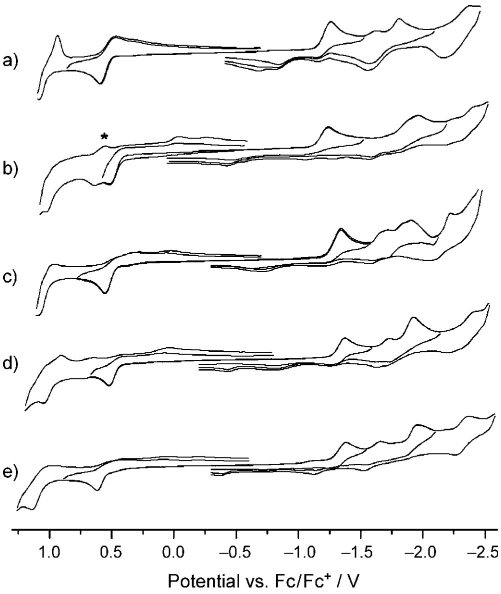


Figure 4. Cyclic voltammograms of a) pristine $Sc_3N@I_h$-C_{80}, b) compound **1** (the asterisk denotes the first oxidation of $Sc_3N@I_h$-C_{80} present as impurity), c) compound **2**, d) compound **3**, and e) compound **4**. The voltammograms were recorded in a 0.05 M solution of tetrabutylammonium hexafluorophosphate in *o*-dichlorobenzene with a glassy carbon electrode as working electrode, silver wire as pseudo reference and platinum wire as counter electrode with a scan rate of 100 mV s^{-1}.

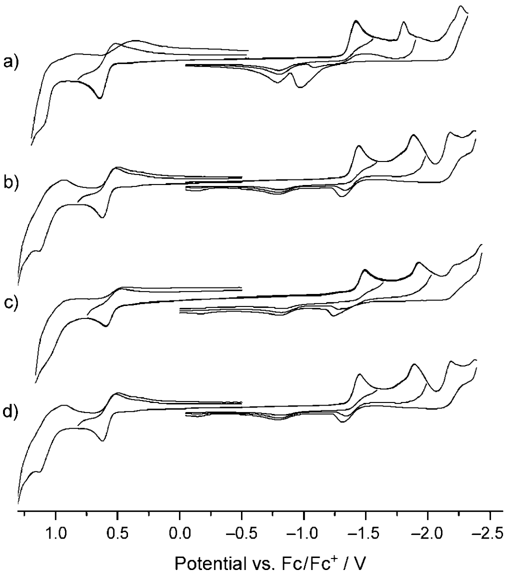


Figure 5. Cyclic voltammograms of a) pristine $Lu_3N@I_h$-C_{80}, b) compound **5**, c) compound **6**, and d) compound **7**. The voltammograms were recorded in a 0.05 M solution of tetrabutylammonium hexafluorophosphate in *o*-dichlorobenzene with a glassy carbon electrode as working electrode, silver wire as pseudo reference and platinum wire as counter electrode with a scan rate of 100 mV s^{-1}.

Table 1. Redox potentials of $Sc_3N@I_h$-C_{80} and compounds **1**–**4** versus Fc/Fc$^+$.

	$E^{+/2+}$ [V]	$E^{0/+}$ [V]	$E^{0/-1}$ [V]	$E^{-1/-2}$ [V]	$E^{-2/-3}$ [V]
$Sc_3N@I_h$-C_{80}[a]	+1.09[c]	+0.59[c]	−1.26[b]	−1.62[b]	−2.37[b]
1	+1.03[c]	+0.52[c]	−1.24[b]	−1.96[b]	−2.41[b]
2	+1.08[c]	+0.56[c]	−1.34[b]	−1.90[b]	−2.22[b]
3	+1.05[c]	+0.52[c]	−1.37[b]	−1.93[b]	−2.41[b]
4	+1.14[c]	+0.62[c]	−1.38[b]	−1.95[b]	−2.37[b]

[a] From reference [14]. [b] Peak potentials. [c] Quasi-reversible process.

The $Lu_3N@I_h$-C_{80} compounds **5** to **7** have higher reduction potentials than the pristine $Lu_3N@I_h$-C_{80}, but in compound **7** the extra addend does not increase the reduction potential when compared to compound **5** but it does increase solubility (see Table 2).

Additional addends cause a strong shift on the second reduction potentials for the $Sc_3N@I_h$-C_{80} derivatives and cathodic shifts of about 300 mV are observed, whereas in the case of $Lu_3N@I_h$-C_{80} these shifts range from 80 to 120 mV. On the other hand, the third reduction process seems to be unaffected by the addition of the addends.

Table 2. Redox potentials of $Lu_3N@I_h$-C_{80} and compounds **5**–**7** versus Fc/Fc$^+$.

	$E^{+/2+}$ [V]	$E^{0/+}$ [V]	$E^{0/-1}$ [V]	$E^{-1/-2}$ [V]	$E^{-2/-3}$ [V]
$Lu_3N@I_h$-C_{80}	+1.11[b]	+0.64[b]	−1.42[a]	−1.80[a]	−2.26[a]
5	+1.15[b]	+0.62[b]	−1.45[a]	−1.88[a]	−2.22[a]
6	+1.07[b]	+0.59[b]	−1.49[a]	−1.92[a]	−2.23[a]
7	+1.13[b]	+0.62[b]	−1.45[a]	−1.89[a]	−2.21[a]

[a] Peak potentials. [b] Quasi-reversible process.

Finally, the oxidation potential variation for all the compounds is too small and only a cathodic shift is observed for the amide derivatives (compounds **3** and **6**), thus the addends have essentially no effect in altering the energy of the HOMO orbitals. In the case of $Sc_3N@I_h\text{-}C_{80}$ the HOMO orbital has a strong component from the orbitals of the internal trimetallic cluster and a small contribution from the carbon cage.[37] Thus, this observation may indicate that there is a low electronic interaction between the exohedral addend and the internal cluster.

Conclusion

Bingel–Hirsch derivatives of $Sc_3N@I_h\text{-}C_{80}$ and $Lu_3N@I_h\text{-}C_{80}$ with different functional groups were successfully prepared without generating free radical intermediates. The presence of dimethyl formamide (DMF) in the reaction mixture favors the reaction. Cyclic voltammetric (CV) studies showed that the [6,6] addition shifts the reduction potential towards more negative values while preserving the electrochemical irreversibility and chemical reversibility of the pristine TNT-EMFs. This behavior was only different for the 9,9′-([6,6]-$Sc_3N@I_h\text{-}C_{80}$)-spirofluorene (**1**) where the first reduction potential was slightly shifted towards more positive values due to the presence of periconjugation interactions.

These observations are particularly important because the Bingel–Hirsch strategy has been proven to be very powerful for the preparation of poly-adducts either by using excess of reagents and long reaction times or by using tether-directed approaches. It is expected that those TNT-EMF poly-adducts will have similar or more negative reduction potentials than the mono-adducts, but more importantly a much higher solubility that may lead to interesting materials for replacing PCBM in the construction of bulk heterojunction (BHJ) organic solar cells.

Experimental Section

Materials and methods: The I_h isomer of $Sc_3N@C_{80}$ was obtained after purification of the material received from Luna Innovations Inc. by selective chemical oxidation with tris(4-bromophenyl)aminium hexachloroantimonate.[14] The I_h isomer of $Lu_3N@C_{80}$ was prepared as follows: core-drilled half inch graphite rods (12.8 mm in diameter and 153 mm in length) were packed with a mixture of lutetium oxide (Lu_2O_3), graphite powder and iron nitride (Fe_xN, $x=2\approx4$).[38] The total Lu/C molar ratios were about 3:100. The packed rods were preheated at about 1000 °C under N_2 flow for about 10 h to remove air and moisture. The rods were then vaporized in a Krätschmer–Huffman arc-discharge fullerene generator filled with a mixture of N_2 (20 Torr) and helium (280 Torr). The resulting soot was extracted with refluxing toluene to yield a reddish-brown extract. The empty-cage fullerenes in the extract were initially removed utilizing a cyclopentadiene functionalized Merrifield peptide resin (CPDE-MPR), as previously described.[18,39] The polycyclic aromatic hydrocarbons (PAHs) were subsequently removed by using acetone. The pure $Lu_3N@I_h\text{-}C_{80}$ isomer was finally obtained by separating the CPDE-MPR cleaned extract by using a two-stage HPLC process with 5PBB and Buckyprep columns. 9-Bromofluorene, 2-bromodiethyl malonate, 60% sodium hydride oil suspension, *o*-DCB and DMF were bought from Aldrich and used without further purification. 2-Bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate bromide was prepared according to the literature procedures.[33,34] All the reactions were carried out under argon atmosphere with standard Schlenk techniques. The NMR spectra were recorded by using a 500 MHz Bruker spectrometer and a 500 MHz Jeol Instrument; the mass spectra were recorded on a Voyager-DE STR mass spectrometer. The purity of the compounds was verified by HPLC by using a Varian Prostar 210 equipped with a Buckyprep column (10×250 mm) and/or a PBB column (4.5×250 mm) and toluene as eluent with a flow rate of 2 mL min^{-1}.

9,9′-([6,6]-$Sc_3N@I_h\text{-}C_{80}$)-spirofluorene (1): In a 50 mL Schlenk flask equipped with a magnetic stirrer $Sc_3N@I_h\text{-}C_{80}$ (2.04 mg, 1.83 μmol, 1 equiv) was poured and 9-bromofluorene (1.55 mg, 6.32 μmol, 3.4 equiv). *o*-DCB (10 mL) was added and the reaction mixture was stirred under argon. DBU (1 drop) was added and the whole mixture was stirred overnight at room temperature. The reaction was quenched with glacial acetic acid (100 μL). The solvent was evaporated under a nitrogen stream and the solid residue was redissolved in CS_2 and filtered through a silica plug. The CS_2 was evaporated and the residual solid washed with diethyl ether. Finally, the solid was redissolved in toluene, filtered and separated by HPLC on a Buckyprep column (10×250 mm) with toluene (2 mL min^{-1}) as eluent to give **1** as a black solid (0.96 mg, 41%). $t_R=66.7$ min; ^1H NMR (500 MHz, $CS_2/CDCl_3$ 4:1, 25 °C, TMS): $\delta=8.68$ (dd, 2H; $^3J(H,H)=8.2$ Hz, $^4J(H,H)=0.8$ Hz, H1,H1′), 7.91 (dd, 2H; $^3J(H,H)=7.3$ Hz, $^4J(H,H)=0.8$ Hz, H4,H4′), 7.53 (ddd, 2H; $^3J(H,H)=7.3$ Hz, $^3J(H,H)=7.4$ Hz, $^4J(H,H)=0.8$ Hz, H3,H3′), 7.40 ppm (ddd, 2H; $^3J(H,H)=7.4$ Hz, $^3J(H,H)=8.2$ Hz, $^4J(H,H)=0.8$ Hz, H2,H2′); MALDI-TOF (negative ionization mode 9-nitroanthracene as matrix): *m*/*z*: 1274.90.

81-Di(ethoxycarbonyl)-1,2-methano-[6,6]-$Sc_3N@I_h\text{-}C_{80}$]fullerene (2): $Sc_3N@I_h\text{-}C_{80}$ (6.9 mg, 6.22 μmol, 1 equiv) and NaH (10.0 mg, 60% oil suspension) were charged into a 50 mL Schlenk flask and poured under argon. *o*-DCB (8.0 mL) and DMF (2.0 mL) were added. While stirring, a solution of 2-bromodiethylmalonate (4.0 μL, 5.68 mg, 23.7 μmol, 3.8 equiv) dissolved in toluene (2.0 mL) was added dropwise. The reaction mixture was heated to 60 °C and the reaction progress was monitored by using TLC (first eluting with CS_2, followed by CS_2/CH_2Cl_2 2:1). After stirring for 20 min and when the formation of bis-adducts was evident on the TLC plates, glacial acetic acid was added until the bubbling ceased. The solvent was evaporated under a nitrogen stream and the solid residue was dissolved in toluene. The reaction mixture was separated by HPLC on a PBB column (4.5×250 mm) with toluene/*o*-DCB 5% (2 mL min^{-1}) as eluent to give **2** as a black solid (3.2 mg, 40.5%). $t_R=13.5$ min; t_R (Buckyprep column, toluene 2 mL min^{-1})$=28.6$ min; ^1H NMR (500 MHz, CS_2/CD_2Cl_2 4:1, 25 °C, TMS): $\delta=4.89$ (q, 4H; $^3J(H,H)=7.0$ Hz, $COO{-}CH_2$-, 1.43 ppm (t, 6H; $^3J(H,H)=7.0$ Hz, CH_3); MALDI-TOF (positive ionization mode 9-nitroanthracene as matrix): *m*/*z*: 1267.94.

81-Di(pyrrolidine-*N*-carbonyl)-1,2-methano-[6,6]-$Sc_3N@I_h\text{-}C_{80}$]fullerene (3): Following an analogous procedure $Sc_3N@I_h\text{-}C_{80}$ (2.0 mg, 1.80 μmol, 1 equiv), 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate (6.0 mg, 16.3 μmol, 9.0 equiv) and NaH (30.0 mg, 60% oil suspension) were charged into a 50 mL Schlenk flask and poured under argon. *o*-DCB (4.0 mL) and DMF (1.0 mL) were added. Under stirring the reaction mixture was stirred heated to 60 °C and the reaction progress was monitored by using TLC (first eluting with CS_2, followed by CH_2Cl_2/ethyl acetate/triethylamine 7:2:1). After 20 min and when the formation of bis-adducts was evident on the TLC plates, the reaction mixture was cooled to room temperature and glacial acetic acid was added until the bubbling ceased. The solvent was evaporated under a nitrogen stream and the solid residue was dissolved in CS_2 and separated on a silica gel column. CS_2 was used for eluting the unreacted $Sc_3N@I_h\text{-}C_{80}$ followed by a mixture of CH_2Cl_2/ethyl acetate/triethylamine (7:2:1) to give **3** as a black solid (1.2 mg, 54%). t_R (Buckyprep column, toluene 2 mL min^{-1})$=28.6$ min; ^1H NMR (500 MHz, $CS_2/CDCl_3$ 9:1, 25 °C, TMS): $\delta=4.33$ (br s, 1H; N-CH_2), 4.17 (br s, 1H; N-CH_2), 4.00 (br s, 1H; N-CH_2), 3.76 (br s, 3H; N-CH_2), 3.67 (br s, 1H; N-CH_2), 3.56 (br s, 1H; N-CH_2), 2.02 ppm (brs, 8H; N-C-CH$_2$); MALDI-TOF (negative ionization mode 9-nitroanthracene as matrix): m/z: 1318.01.

81-Di(pyrrolidine-*N*-carbonyl)-1,2-methano-[6,6]-Lu$_3$N@I_h-C$_{80}$]fullerene (6): Under the same conditions as used for **3** Lu$_3$N@I_h-C$_{80}$ (1.66 mg, 1.11 μmol, 1 equiv), 2-bromo-1,3-dipyrrolidin-1-ylpropane-1,3-dionate (1.8 mg, 6.24 μmol, 5.6 equiv) and NaH (10.0 mg, 60 % oil suspension) were used to give **6** as a black solid (1.1 mg, 58 %). t_R (PBB column, toluene/*o*-DCB 5 % 2 mL min^{-1}) = 19.4 min; ^{1}H NMR (500 MHz, CS$_2$/CD$_2$Cl$_2$ 4:1, 25 °C, TMS): δ = 4.37 (brs, 1H, N-CH$_2$), 4.22 (brs, 1H; N-CH$_2$), 4.07 (brs, 1H; N-CH$_2$), 3.80 (brs, 3H; N-CH$_2$), 3.69 (brs, 2H; N-CH$_2$), 2.08 ppm (brs, 8H; N-C-CH$_2$); MALDI-TOF (negative ionization mode 9-nitroanthracene as matrix): m/z: 1708.12

81-Di(ethoxycarbonyl)-1,2-methano-[6,6]-Lu$_3$N@I_h-C$_{80}$]fullerene (5): Lu$_3$N@I_h-C$_{80}$ (1.80 mg, 1.20 μmol, 1 equiv) was poured in a Schlenk flask under argon. Dry *o*-DCB (4.0 mL) and DMF (1.0 mL) were added and the material dissolved. 2-Bromodiethyl malonate (10 μL) and DBU (1 drop) were added, after 1 h an extra drop of DBU was added and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with glacial acetic acid (2 drops), the solvent was removed under a nitrogen stream and the remaining solid was dissolved in CS$_2$ and acetone. The solution was filtered through a silica plug and the solvent was evaporated. The solid was dissolved in toluene and separated by HPLC on a PBB column (4.5 × 250 mm) with toluene/*o*-DCB 5 % (2 mL min^{-1}) as eluent to give **5** as a black solid (0.8 mg, 40.0 %). t_R = 14.2 min; ^{1}H NMR (500 MHz, CS$_2$/CD$_2$Cl$_2$ 4:1, 25 °C, TMS): δ = 4.64 (q, 4H; ^3J(H,H) = 7.0 Hz, COO-CH$_2$), 1.56 ppm (t, 6H; ^3J(H,H) = 7.0 Hz, CH$_3$); MALDI-TOF (positive ionization mode 9-nitroanthracene as matrix): m/z: 1656.80

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