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Isolation and characterization of [5,6]-pyrrolidino-$Sc_3N@I_h$-C_{80} diastereomers†

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Reactions of $Sc_3N@I_h$-C_{80} with aziridine derivatives were conducted to afford the corresponding mono-adducts. A pair of diastereomers of the mono-adduct [5,6]-pyrrolidino-$Sc_3N@I_h$-C_{80} was isolated and characterized by means of mass spectrometry, vis-NIR absorption spectroscopy, and electrochemical measurements. Structural analysis of the mono-adducts was conducted by NMR and single-crystal X-ray structure determinations.

Recent developments in the chemistry of endohedral metallofullerenes (EMFs) have led to increasing efforts to elucidate how the chemical reactivity and selectivity of empty fullerenes are changed by endohedral metal doping and how the electronic properties of metallofullerenes affect chemical functionalization.[1] The preparation and isolation of trimetallic nitride template endohedral metallofullerenes ($M_3N@C_n$) in macroscopic quantities have facilitated the study of their structures, properties, and chemical reactivities.[2] To date, the functionalization of $Sc_3N@I_h$-C_{80} has been widely performed using the Diels–Alder reaction,[3] [2+2] cycloaddition,[4] carbene addition,[5] hydroxylation,[6] disilirane addition,[7] radical addition,[8] azide addition,[9] and so on. 1,3-Dipolar cycloaddition of azomethine ylides is one of the most successful reactions in fullerene chemistry. Azomethine ylides are organic 1,3-dipoles possessing a carbanion next to an immonium ion and can be readily produced upon decarboxylation of the immonium salts derived from the condensation of α-amino acids with aldehydes or ketones.[10] Notably, functionalized aldehydes lead to the formation of 2-substituted fulleropyrrolidines, whereas the reaction with *N*-substituted glycines leads to *N*-substituted fulleropyrrolidines. Recently, the chiral control of fulleropyrrolidine of C_{60} was achieved.[11] In this context, the advantages, such as good yields, the high regioselectivity, and availability or easy preparation of the starting materials in reactions of $Sc_3N@I_h$-C_{80}, encourage the synthesis of functionalized materials to open the materials science of metallofullerenes.[12]

Alternatively, fulleropyrrolidines can be obtained *via* the thermal ring opening of aziridines.[13] Moreover, the addition of aziridines has been extended to carbon nanotubes, which upon thermal reaction with 2-alkoxycarbonylaziridine, afforded the corresponding pyrrolidino-derivatives.[14] Since custom-synthesized aziridines, carrying groups with advanced functionality, can be prepared from commercially available reagents in high yields through only a few steps, the applicability of this kind of functionalization deserves more attention. Herein, we report the synthesis of [5,6]-pyrrolidino-$Sc_3N@I_h$-C_{80} from $Sc_3N@I_h$-C_{80} and aziridine derivatives as well as the formation and isolation of a pair of diastereomers. In addition, the structural characterization of pyrrolidino-$Sc_3N@I_h$-C_{80} was obtained from electronic absorption, NMR spectroscopy and X-ray crystallography, while the redox properties of pyrrolidino-$Sc_3N@I_h$-C_{80} were evaluated by electrochemical means.

The reaction of $Sc_3N@I_h$-C_{80} with **1a** was conducted at 180 °C in *o*-dichlorobenzene (ODCB) for 1 h (Scheme 1). Subsequent preparative HPLC separation afforded products **2a** and **3a** in 26% and 18% yields, respectively (Fig. S1 and S2, ESI†). The conversion yields of **2a** and **3a** were calculated from the HPLC peak area assuming that $Sc_3N@I_h$-C_{80} and the mono-adducts have the same absorption coefficients. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of **2a** and **3a** clearly displayed the molecular ion peaks at *m*/*z* 1267, as expected for the 1 : 1 adducts of $Sc_3N@I_h$-C_{80} and 1a

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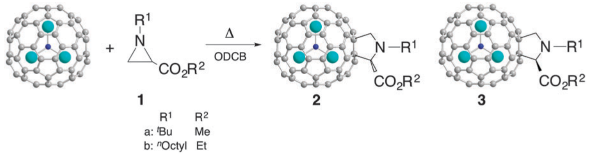

Scheme 1 Reaction of Sc$_3$N@I_h-C$_{80}$ with **1**.

(Fig. S3, ESI†). The fragment peaks were observed at *m*/*z* 1109, which corresponded to the mass of the fragment ion [Sc$_3$N@I_h-C$_{80}$]$^-$. Similarly, the reaction of **1b** and Sc$_3$N@I_h-C$_{80}$ gave two products **2b** and **3b** in 19% and 24% yields, respectively (Fig. S10 and S11, ESI†).

There are two possible position isomers (A–D) for **2** and **3** as shown in Fig. 1 because the I_h-C$_{80}$ cage has two kinds of non-equivalent C–C bonds. Mono-addition occurs at a C–C bond located between a five- and six-membered ring (so-called [5,6]-addition) and the other addition takes place at a C–C bond located between two six-membered rings (so-called [6,6]-addition). When glycine derivatives and aldehydes were used as the starting materials, [5,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$ was obtained. On the other hand, when *N*-triphenylmethyl-5-oxazolidinone was used as the starting material, [6,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$ was obtained as the kinetically controlled product. It was also reported that [6,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$ is converted thermally to the more thermodynamically stable [5,6]-adduct. As previous studies showed that the UV-vis-NIR absorption spectra of C$_{60}$ adducts reflected sensitively the addition pattern rather than the nature of the addends,[15] the UV-vis-NIR spectra can be regarded as powerful tools to determine the addition pattern in fullerene adducts. [6,6]-*N*-Tritylpyrrolidino-Sc$_3$N@I_h-C$_{80}$, [6,6]-Sc$_3$N@I_h-C$_{80}$-(CH$_2$)$_2$NTrt, and the benzyne [6,6]-adduct of Sc$_3$N@I_h-C$_{80}$, [6,6]-Sc$_3$N@I_h-C$_{80}$-(C$_6$H$_4$) exhibited the characteristic absorption peak at *ca.* 800 nm.[4a,b,12a,e] In contrast, [5,6]-Sc$_3$N@I_h-C$_{80}$-(C$_6$H$_4$) showed weak absorption peaks centered *ca.* 950 nm. The absorption spectra of **2** and **3** show the distinctive absorption maxima at around 960 nm. (**2a**: 958 nm, **2b**: 959 nm, **3a**: 959 nm, **3b**: 959 nm). These characteristic absorption spectra suggest that **2** and **3** are [5,6]-addition products (Fig. S4, ESI†).

The molecular structure of **2a** was determined using X-ray crystallographic analysis. The structural drawing shown in Fig. 2 confirms that the addition took place at the [5,6]-bond. The pyrrolidine ring is in an envelope conformation in which the nitrogen atom is above the pentagon ring. The alkoxycarbonyl group is located on the hexagon side on the C$_{80}$ cage (addition pattern: A). Thus, **3a** can be assigned to the stereoisomer of **2a**, which has the alkoxycarbonyl group located at the pentagon side on the C$_{80}$ cage (addition pattern: B).

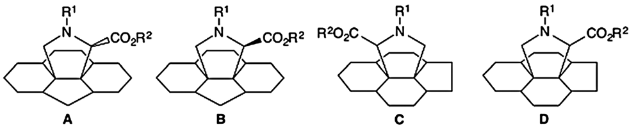

Fig. 1 Possible partial structures of 2-substituted [5,6]- and [6,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$.

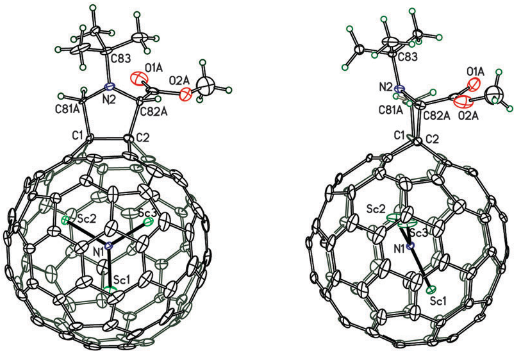

Fig. 2 Front and side views of the crystal structure of **2a** with thermal ellipsoids shown at the 30% probability level.

The ^{1}H NMR spectra of **2a** and **3a** showed protons in the pyrrolidine rings at 4.81, 4.19, and 4.02 ppm and 4.40, 4.24, and 3.56 ppm, respectively (Fig. S5, ESI†). The diastereotopic geminal protons in the pyrrolidine rings appeared at 4.19 and 4.02 ppm (J = 8.8 Hz) in **2a** and 4.40 and 3.56 ppm (J = 9.5 Hz) in **3a** and are correlated with the carbon atom at 59.8 ppm in **2a** and 62.6 ppm in **3a** in the HMQC spectra (Fig. S8, ESI†). The ^{13}C NMR spectra of **2a** and **3a** showed a total of 78 lines assigned to sp^2-hybridized cage carbons of Sc$_3$N@I_h-C$_{80}$ (Fig. S6, ESI†). In addition, the sp^3-hybridized cage carbon atoms appeared at 62.2 and 57.6 ppm in **2a** and 61.8 and 56.4 ppm in **3a**, which disappeared in DEPT-135 NMR spectra (Fig. S7, ESI†). Echegoyen *et al.* suggested that the large $\Delta\delta$ values for the geminal protons of Sc$_3$N@I_h-C$_{80}$-(CH$_2$)$_2$NR are mainly due to surface ring currents on the C$_{80}$ cage.[12b,d] The chemical shift of the methine proton on the pyrrolidine ring can be used for the simple and concise structural identification of 2-substituted-[5,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$. It is noteworthy that the ^{1}H NMR signals of methine protons of **2a** and **2b** in the pyrrolidine ring appeared downfield compared to those of **3a** and **3b**, respectively. For the assignment of the ^{1}H NMR, the ^{1}H NMR chemical shifts of **2b** and **3b** were calculated by the M06-2X-GIAO method.[16] The calculated chemical shift of the methine proton of **2b** (4.64 ppm) was lower than that of **3b** (3.49 ppm), as shown in Table 1, which strongly supports the structures of **2b** and **3b**. Furthermore, whereas geminal protons of **3a** and **3b** in their ^{1}H NMR spectra showed a large $\Delta\delta$ value ($\Delta\delta$: difference of the chemical shifts of the geminal protons in the pyrrolidine ring, **3a**: $\Delta\delta = 0.84$; **3b**: $\Delta\delta = 1.49$), **2a** and **2b** showed a small $\Delta\delta$ value (**2a**: $\Delta\delta = 0.17$; **2b**: $\Delta\delta = 0.15$). This was also found in the theoretical calculation, as shown in Table 1 (calculated value of the $\Delta\delta$: **2b**: $\Delta\delta = 0.70$; **3b**: $\Delta\delta = 1.68$). Thus, the structure of **2b** (addition pattern A, the

Table 1 Selected ^{1}H NMR chemical shifts of 2-substituted pyrrolidino-I_h-C$_{80}$ adducts

Fullerene	R^1	R^2	H$_{\mathrm{methine}}$^{a}	H$_{\mathrm{geminal}}$^{b}	H$_{\mathrm{geminal}}$$'^b$	$\Delta\delta^c$
Sc$_3$N@I_h-C$_{80}$ **2a**	^{t}Bu	CO$_2$Me	4.81	4.19	4.02	0.17
Sc$_3$N@I_h-C$_{80}$ **3a**	^{t}Bu	CO$_2$Me	4.24	4.40	3.56	0.84
Sc$_3$N@I_h-C$_{80}$ **2b**	^{n}Octyl	CO$_2$Et	4.58	4.05	3.90	0.15
Calculated value **2b**			4.64	4.93	4.23	0.70
Sc$_3$N@I_h-C$_{80}$ **3b**	^{n}Octyl	CO$_2$Et	3.67	4.39	2.90	1.49
Calculated value **3b**			3.49	4.41	2.73	1.68

[a] Methine proton in the pyrrolidine ring. [b] Geminal proton in the pyrrolidine ring. [c] Difference of the geminal protons in the pyrrolidine ring.

Table 2 Redox potentials (V) and HOMO–LUMO levels (eV) of Sc$_3$N@I_h-C$_{80}$ and its derivatives

Compound	E_2^{ox}	E_1^{ox}	E_1^{red}	E_2^{red}	E_3^{red}	HOMO	LUMO
Sc$_3$N@I_h-C$_{80}$[c]	1.09	0.59	−1.26	−1.62	−2.37	−6.47	−2.58
2a	0.64[b]	0.23[b]	−1.15[a]	−1.57[a]	−2.33[a]	−6.13	−2.79
2b	0.63[b]	0.31[b]	−1.11[a]	−1.51[a]	−2.28[a]	−6.11	−2.80
3a	0.60[b]	0.30[b]	−1.11[a]	−1.50[a]	−2.23[a]	−6.14	−2.79
3b	0.59[b]	0.30[b]	−1.10[a]	−1.49[a]	−2.22[a]	−6.10	−2.80

[a] Half-wave potential, V *vs.* Fc/Fc$^+$ in ODCB containing 0.1 M ^{n}Bu$_4$NPF$_6$. [b] Values are obtained by DPV, a quasi-reversible process. [c] Ref. 12*k*.

alkoxycarbonyl group located at hexagon side) and **3b** (addition pattern B, the alkoxycarbonyl group located at pentagon side) were determined based on the NMR and theoretical calculations.

Dorn *et al.* reported that [5,6]-Sc$_3$N@I_h-C$_{80}$-(CH$_2$)$_2$NTrt was obtained as the thermodynamically favorable product and [6,6]-Sc$_3$N@I_h-C$_{80}$-(CH$_2$)$_2$NTrt was obtained as the kinetically favorable product from the reaction of *N*-triphenylmethyl-5-oxazolidinone *via* the corresponding azomethine ylide.[12e] When an azomethine ylide was prepared from *N*-alkylglycine and an aldehyde, [5,6]-Sc$_3$N@I_h-C$_{80}$-(CH$_2$)$_2$NR (R: Me or Et) was obtained as the thermodynamically favorable product.[12a,b] The relative energy difference between [5,6]- and [6,6]-Sc$_3$N@I_h-C$_{80}$-(CH$_2$)(CHCO$_2$CH$_3$)N^{t}Bu was calculated using the M06-2X method. The results showed that the [5,6]-adduct is the thermodynamically favorable product (Fig. S21, ESI†). Therefore, **2** and **3** were obtained as the thermodynamically preferred mono-adducts under the reflux conditions in ODCB.

The redox properties of **2** and **3** were determined from the results of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements (Table 2 and Fig. S20, ESI†). Compounds **2** and **3** exhibited three reversible reduction and two quasi-reversible oxidation patterns. The reversible cathodic behavior of **2** and **3** is consistent with previously reported results for [5,6]-pyrrolidino-M$_3$N@I_h-C$_{80}$ derivatives.[12d,j,k] The identical electrochemical behavior of **2** and **3** indicates that the position of the alkoxycarbonyl group in **2** and **3** does not affect the electronic properties of pyrrolidino-Sc$_3$N@I_h-C$_{80}$.

In conclusion, we have conducted the reaction of Sc$_3$N@I_h-C$_{80}$ with aziridine, which affords the corresponding [5,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$ as an isolable pair of diastereomers of pyrrolidino-EMF derivatives. Aziridines are effective reagents to introduce two functional groups on Sc$_3$N@I_h-C$_{80}$. Adducts **2** and **3**, which are the first example of an isolated pair of the diastereomers, were characterized on the basis of absorption measurement, NMR analysis, cyclic voltammetry, and X-ray crystallography. The characteristic absorption spectra and cyclic voltammograms afford useful information to determine the addition patterns, [5,6]- or [6,6]-addition. In addition, **2** and **3** show characteristic ^{1}H NMR signals of methine and methylene protons in the pyrrolidine-ring, which give valuable information for the assignment of a pair of [5,6]-pyrrolidino-Sc$_3$N@I_h-C$_{80}$ diastereomers.

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