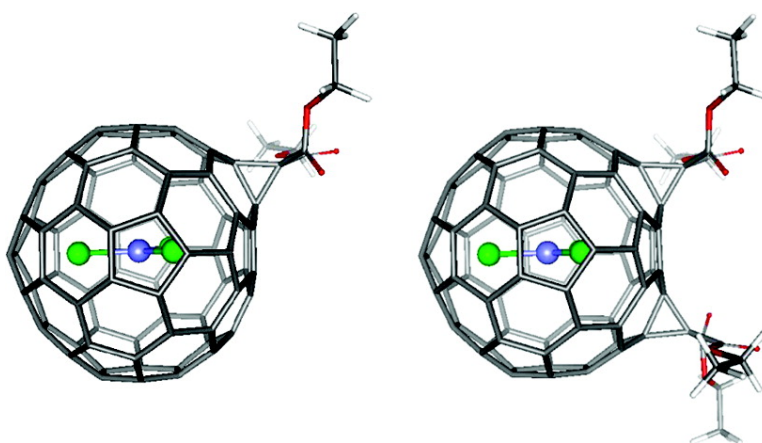


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Selective Formation of a Symmetric Sc₃N@C₇₈ Bisadduct: Adduct Docking Controlled by an Internal Trimetallic Nitride Cluster

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Organic functionalization of endohedral metallofullerenes is essential to construct novel organo-metallofullerene materials for a variety of future applications. Many recent experimental and theoretical studies suggest that the chemical reactivity and regioselectivity of endohedral metallofullerenes are influenced by the encapsulated cluster, metal species, carbon cage size, and symmetry.¹ Trimetallic nitride endohedral metallofullerenes are the most abundant families of metallofullerenes formed in the Krätschmer–Huffmann generator.² As first described in 2001, X-ray crystallographic analysis of Sc₃N@C₇₈ reveals that the C₇₈ cage possesses *D*_{3h} (78:5) symmetry (Figure 1).³ The planar Sc₃N cluster lies on the horizontal mirror plane of the C₇₈ cage with the scandium atoms localized over the three pyracylene patches. Unlike the Sc₃N@C₈₀ I_h isomer, in which the Sc₃N cluster can freely rotate inside the C₈₀ cage, the rotation of the Sc₃N cluster in the C₇₈ cage is restricted to the two-dimensional horizontal mirror plane.⁴ The strong interactions between the Sc₃N cluster and the C₇₈ cage has been demonstrated in several studies.^{4–6}

To date, studies of exohedral derivatization of trimetallic nitride endohedral metallofullerenes have focused on the isolation and characterization of monoaddition products. For example, we recently reported that the 1,3-dipolar cycloaddition sites for two *N*-tritylpyrrolidino Sc₃N@C₇₈ monoadducts were across *c*–*f* and *b*–*d* bonds at elevated temperatures,⁷ consistent with the theoretical prediction by Poblet et al.⁸ Herein, we describe selective kinetic control via a Bingel–Hirsch reaction affording a single monoadduct and more importantly, a dominate symmetric bis(ethyl malonate) adduct derivative of Sc₃N@C₇₈.^{9,10} Thus, the observed single isomers for the mono- and bisadducts demonstrate the remarkable regioselectivity control (adduct docking) exerted by the encapsulated Sc₃N cluster. More importantly, we describe a LUMO electron density surface computational approach that predicts multiadduct docking sites on the fullerene cage surface.

The Bingel–Hirsch cyclopropanation of Sc₃N@C₇₈ was carried out at room temperature with excess diethyl bromomalonate in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in *o*-dichlorobenzene over 5 h under argon (Scheme 1). Surprisingly, under conditions of higher dilution and a larger excess of diethyl bromomalonate only monoadduct **1** and bis-adduct **2** dominate (>70%) the reaction mixture with only relatively minor amounts of the tri-, tetra-, and penta-adducts formed (Figure S1a).¹¹ In contrast, under the same cyclopropanation reaction conditions I_h Sc₃N@C₈₀ does not react.¹² This clearly indicates that *D*_{3h} Sc₃N@C₇₈ has significantly higher reactivity than I_h Sc₃N@C₈₀.

The ¹H NMR spectrum of **1** (Figure S7) contains a single triplet at 1.44 ppm and a single quartet at 4.45 ppm, indicating that the ethyl groups of monoadduct **1** are chemically equivalent. Since the

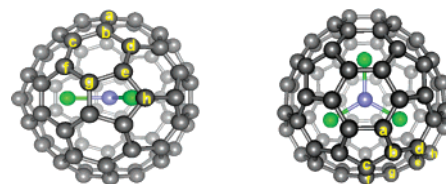
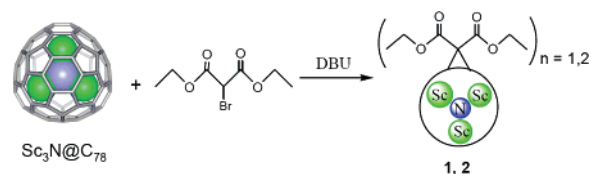


Figure 1. The optimized structure of *D*_{3h} Sc₃N@C₇₈: (left) side view, (right) top view. (Green atoms = Sc; blue atoms = N; a–h labeled for eight different types of carbons.)

Scheme 1



two ethyl group of **1** are equivalent on the basis of the ¹H NMR spectrum, we believe that the *c*–*f* bond is also the cyclopropanation site for the monoadduct **1** on the basis of symmetry considerations, consistent with our earlier results for 1,3-dipolar cycloaddition.¹¹ If the monoadduct had formed at the *b*–*d* bond, nonequivalent ethyl groups would have been observed.

The mirror symmetry of **1** was further confirmed by the ¹³C NMR spectrum (Figure 2a); there are a total of 38 lines in the aromatic region. Two half intensity peaks at 127.08 and 151.54 ppm are due to the two sp²-hybridized carbons on the cage. The remaining 36 peaks represent the other 74 sp²-hybridized carbons on the fullerene cage; the double intensity peak at 142.12 ppm represents four carbons due to coincidental overlap. The other two peaks at 45.54 and 52.49 ppm correspond to sp³-hybridized carbon atoms in the

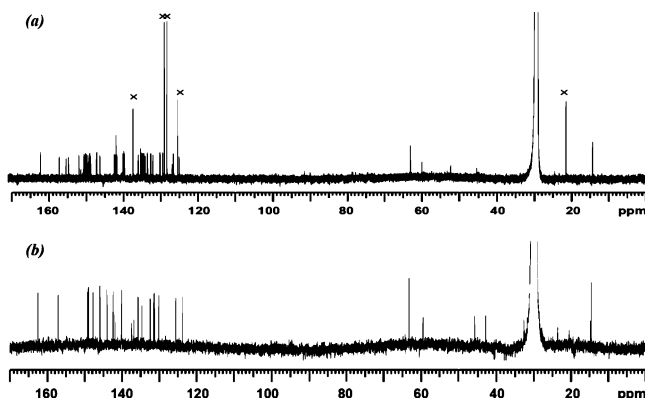


Figure 2. 150 MHz ¹³C NMR spectra of Sc₃N@C₇₈ monoadduct **1** (a) and bisadduct **2** (b) [solvent: CD₃COCD₃/CS₂]. The symbol × denotes toluene peaks.

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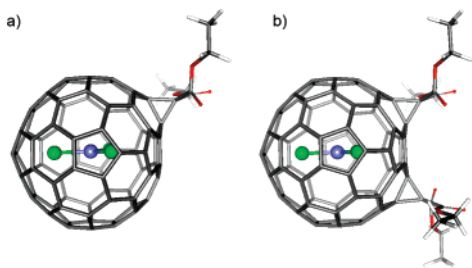


Figure 3. The optimized structure of (a) monoadduct **1**, (b) bisadduct **2**.¹⁵

cyclopropane ring. These data clearly suggest that monoadduct **1** possesses a “closed” cyclopropyl structure (Figure 3a) as opposed to the ring-opened norcaradiene type structure found for the Y₃N@C₈₀¹³ and La@C₈₂ Bingel–Hirsch adducts.¹⁴ The peaks at 14.47, 63.29, and 162.34 ppm correspond to the pairs of equivalent methyl, methylene, and carbonyl carbons, respectively. The peak at 60.21 ppm is assigned to the methano-bridge carbon.

Surprisingly, the ¹H NMR spectrum of **2** (Figure S8) is nearly identical to the corresponding ¹H NMR spectrum of monoadduct **1**. It contains only one triplet for the twelve methyl protons at $\delta = 1.43$, and one quartet for the eight methylene protons at $\delta = 4.44$, implying that all four ethyl groups of bisadduct **2** are equivalent. The 150 MHz ¹³C NMR spectrum for $\sim 200 \mu\text{g}$ s of **2** (Figure 2b) exhibits only 20 peaks in the range typical of sp²-hybridized carbon atoms on the fullerene cage ($\delta = 125\sim 160$). This further supports the higher symmetry of bisadduct **2** compared with monoadduct **1**. On the basis of the C_{2v} symmetry of **2** shown in Figure 3b, 17 full intensity peaks ($\delta = 125\sim 160$) account for a total of 68 sp²-hybridized carbon atoms on the cage. Three half intensity peaks at 137.03, 137.63, and 142.15 ppm are consistent for the six *h*-labeled sp²-hybridized carbon atoms in the equatorial plane containing the Sc₃N cluster. Two half intensity peaks at 42.73 and 45.70 ppm correspond to the four sp³-hybridized fullerene carbons in the cyclopropane rings. The carbon chemical shifts of the exohedral functional groups in the bisadduct **2** are very similar to those of monoadduct **1**. Methyl, methylene, carbonyl, and methano-bridge carbons each appear as single signals at 14.47, 63.25, 162.75 and 60.21 ppm, respectively. The UV–vis absorption spectrum of **1** is similar to that of **2** (Figure S9). However, after derivatization, the characteristic Sc₃N@C₇₈ absorption at 614 nm is not observed in **1** or **2**; this indicates significant alteration of the π system of the C₇₈ carbon cage. A cyclic voltammetric study of Sc₃N@C₇₈ and monoadduct **1** exhibits (^{ox}E₁–^{red}E₁) values of 1.637 and 1.560 V, respectively. These values are significantly lower than the Sc₃N@C₈₀ I_h isomer but close to the D_{5h} isomer.⁷ These data are consistent with the higher reactivity of Sc₃N@C₇₈. However, an even lower (^{ox}E₁–^{red}E₁) value for Sc₃N@C₇₈ in toluene was reported by Zhang.¹⁸

Under the conditions of our study, the cyclopropanation of Sc₃N@C₇₈ with diethyl bromomalonate produced only one monoadduct and one dominant symmetric bisadduct. Significantly, the second addition for the major bisadduct **2** occurs at the *anti*-**1** bond instead of *syn*-**1** and *anti*-**2** bonds, which all seems to be equivalent bonds on the Sc₃N@C₇₈ cage (Figure 4a). However, the high regioselectivity is supported by the highest LUMO surface electron density value for the *anti*-**1** bond (Figure 4b), which corresponds to the kinetically preferred site for nucleophilic attack.¹⁶ The novel C_{2v}-adduct **2** represents the first example of a symmetric endohedral metallofullerene bisadduct in which the second reaction site is clearly controlled by the internal trimetallic nitride cluster. In

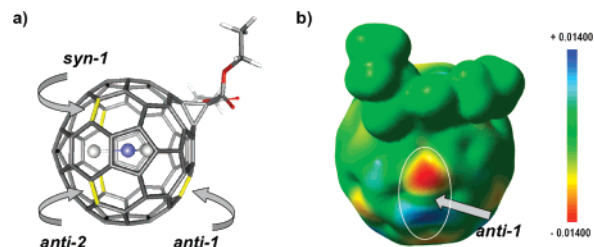


Figure 4. (a) The three most preferred sites for the second addition of the adduct. (b) Projection of the LUMO onto the electron density surface of **1**.

comparison, similar cyclopropanation reactions of C₆₀¹⁰ and C₇₀¹⁷ lead to symmetric bisadducts in lower proportion relative to the other bisadducts. Therefore, the remarkable regioselectivity for bisadduct **2** is attributed to the strong influence of the internal trimetallic nitride cluster. This finding provides new insight and rationale for the synthesis and study of mutiadducts of other endohedral metallofullerenes.

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Supporting Information Available: Experimental details and HPLC and spectroscopic data and theoretical calculations for **1a** and **1b** (S1–S12). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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