Electronic Supplemental Information:

**Bingel-Hirsch monoadducts of TiSc$_2$N@$I_h$-C$_{80}$ versus Sc$_3$N@$I_h$-C$_{80}$: Reactivity improvement via internal metal atom substitution**

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**Table of Contents**

Experimental section. S2

*Figure S1.* $^{13}$C NMR spectrum of the monoadduct A of TiSc$_2$N@$I_h$-C$_{80}$ S3

*Table S1.* List of chemical shifts of carbon resonance signals of characteristic groups within different NCF-diethyl malonate Bingel-Hirsch monoadducts S4

*Figure S2.* $^1$H NMR spectrum of the monoadduct A of TiSc$_2$N@$I_h$-C$_{80}$ S5

*Figure S3.* $^1$H NMR spectrum of the monoadduct B of TiSc$_2$N@$I_h$-C$_{80}$ S5

*Figure S4.* MALDI-TOF mass spectra of monoadducts A and B of TiSc$_2$N@$I_h$-C$_{80}$ S6

Reference S6
Experimental section

**Synthesis.** TiSc₂N@I₈-C₈₀ was synthesized by a modified Krätschmer-Huffman DC-arc discharging method and isolated as reported previously. In a typical Bingel-Hirsch reaction, cyclopropane derivatives of TiSc₂N@I₈-C₈₀ were synthesized by adding dropwise 5 μl (33 μmol) 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) into a mixture solution of 3.0 mg (2.7 μmol) TiSc₂N@I₈-C₈₀ and 8 μl (50 μmol) diethyl bromomalonate in 10 mL toluene. The mixture solution was stirred at room temperature for 10 min under nitrogen atmosphere. The crude reaction mixture was filtered and injected into an HPLC for analysis and isolation (10 × 250 mm Buckyprep column, toluene as eluent, flow rate 5.0 mL/min, 25°C). If the reaction time was prolonged or amounts of diethyl bromomalonate and DBU were increased, multi-adducts formed and the monoadducts disappeared.

**Characterization.** Laser desorption time-of-flight (LD-TOF) mass spectroscopic analysis was run in both positive and negative ion modes (Autoflex III, Bruker Daltonics Inc., Germany). UV-vis-NIR spectra were recorded on a UV-Vis-NIR 3600 spectrometer (Shimadzu, Japan) using quartz cell of 1 mm layer thickness and 1 nm resolution. The ¹³C NMR spectroscopic study was performed at 125 MHz in a multiprobe head PH 1152Z of an Avance 500 spectrometer (Bruker) at room temperature in carbon disulfide solutions with d₆-acetone as a lock. ESR spectra were measured in toluene solution using a JES-FA200 FT-EPR X-band spectrometer (JEOL, Japan).
Figure S1. $^{13}$C NMR spectrum of monoadduct A of TiSc$_2$N$_@$I$_b$-C$_{80}$. Solvent: CCID$_3$/CS$_2$. Inset: enlarged spectra in the region of 120-170 ppm. $\delta$ = 163.96 (2C), 158.21 (2C), 155.09 (2C), 150.91 (2C), 149.49 (2C), 146.53 (2C), 146.05 (2C), 145.02 (2C), 143.97 (2C), 142.43 (2C), 141.93 (2C), 140.77 (2C), 139.71 (2C), 137.78 (2C), 137.24 (2C), 136.11 (2C), 134.06 (2C), 131.86 (1C), 131.24 (2C), 127.04 (1C), 126.42 (1C), 125.37 (1C), 123.26 (1C), 63.72 (2C), 30.25 (1C), 29.93 (1C), 13.99 (2C).
**Table S1.** List of chemical shifts (ppm) of carbon resonance signals of characteristic groups within different endohedral fullerene-diethyl malonate Bingel-Hirsch monoadducts.

<table>
<thead>
<tr>
<th>NCF</th>
<th>methyl (C\textsubscript{a,a'})</th>
<th>methylene (C\textsubscript{b,b'})</th>
<th>methano-bridge carbon (C\textsubscript{d})</th>
<th>fullerenyl sp\textsuperscript{3} carbon (C\textsubscript{e})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSc\textsubscript{2}N@C\textsubscript{80}-monoadduct A</td>
<td>13.99</td>
<td>63.72</td>
<td>30.25</td>
<td>29.93</td>
<td>this work</td>
</tr>
<tr>
<td>Y\textsubscript{3}N@C\textsubscript{80}-\textsuperscript{13}C (CO\textsubscript{2}\textsubscript{13}CH\textsubscript{2}Ph\textsubscript{2})\textsuperscript{[a]}</td>
<td>-</td>
<td>69.54</td>
<td>61.46</td>
<td>-</td>
<td>S2</td>
</tr>
<tr>
<td>Sc\textsubscript{3}N@C\textsubscript{80}-A\textsuperscript{[b]}</td>
<td>-</td>
<td>-</td>
<td>57.3</td>
<td>-</td>
<td>S3</td>
</tr>
<tr>
<td>Sc\textsubscript{3}N@C\textsubscript{78} monoadduct \textsuperscript{[c]}</td>
<td>14.47</td>
<td>63.29</td>
<td>60.21</td>
<td>45.54/52.49</td>
<td>S4</td>
</tr>
<tr>
<td>Sc\textsubscript{3}N@C\textsubscript{68} monoadduct \textsuperscript{[c]}</td>
<td>14.22/14.26</td>
<td>63.77/63.87</td>
<td>53.45</td>
<td>71.08/67.40</td>
<td>S5</td>
</tr>
<tr>
<td>La@C\textsubscript{82}-mono-A\textsuperscript{[d]}</td>
<td>14.13/14.16</td>
<td>63.71/63.99</td>
<td>69.42</td>
<td>60.46</td>
<td>S6</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Synthesized by Bingel-Hirsch reaction of Y\textsubscript{3}N@C\textsubscript{80} with \textsuperscript{13}C-labelled bromo-dibenzylmalonate.

\textsuperscript{[b]} Synthesized by using a free radical reaction of Sc\textsubscript{3}N@I\textsubscript{r}-C\textsubscript{80} with \textsuperscript{13}C-labelled diethyl malonate catalyzed by Mn(III) acetate. This methano monoadduct Sc\textsubscript{3}N@C\textsubscript{80}-A was exactly same to that expected from a corresponding classical Bingel-Hirsch cycloaddition reaction of Sc\textsubscript{3}N@I\textsubscript{r}-C\textsubscript{80} with diethyl bromomalonate if happened (but no reaction happened in fact).

\textsuperscript{[c]} Conventional cycloadduct. Two signal lines for the fullerenyl sp\textsuperscript{3} carbons were observed.

\textsuperscript{[d]} Unconventional singly bonded monoadduct.

Noteworthy, the chemical shifts of both methano-bridge carbon and fullerenyl sp\textsuperscript{3} carbon (C\textsubscript{e}) within A seem to exhibit dramatic high-field shifts compared to those of other analogous Bingel-Hirsch monoadducts including both conventional Bingel–Hirsch cycloadducts of several NCFs and singly bonded monoadducts of La@C\textsubscript{82} (see Table S1).\textsuperscript{S4–S6} This is presumably due to the larger perturbation of the electronic property of TiSc\textsubscript{2}N@C\textsubscript{80} by the Bingel-Hirsch reaction as convinced by the ESR results.
**Figure S2.** $^1$H NMR spectrum of monoadduct A of TiSc$_2$N@I$_{h}$-C$_{80}$. Solvent: CClD$_3$/CS$_2$. The small peaks labeled by asterisks denote unidentified solvent impurities. Insets: enlarged spectra of signals $H_{a,a'}$ (right) and $H_{b,b'}$ (left).

**Figure S3.** $^1$H NMR spectrum of monoadduct B of TiSc$_2$N@I$_{h}$-C$_{80}$. Solvent: CClD$_3$/CS$_2$. The small peaks labeled by asterisks denote unidentified solvent impurities.
**Figure S4.** Positive-mode LD-TOF mass spectra of monoadducts A and B of TiSe$_2$N@I$_n$C$_{80}$. The signal marked with an asterisk (m/z=1286) is assigned to the oxide compound of monoadduct with the loss of bromine atom. The mass peak at m/z=1233 for monoadduct B is due to a fragmentation signal. Inset: enlarged spectrum in the region of m/z=1200-1300.

Reference: