

## Supporting Information

### An effective retro-cycloaddition of $M_3N@C_{80}$ (M = Sc, Lu, Ho) metallofulleropyrrolidines

Bo Wu,<sup>a</sup> Taishan Wang,<sup>a</sup> Zhuxia Zhang,<sup>a</sup> Yongqiang Feng,<sup>a</sup> Lihua Gan,<sup>b</sup> Li Jiang,<sup>a</sup> and Chunru  
Wang<sup>\*a</sup>

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**Figure S2.** Chromatograms of the isolated (a)  $C_{60}$  and (b)  $C_{70}$  fulleropyrrolidines. HPLC conditions: 10×250 mm Buckyprep column, (a) 6 mL/min and (b) 12 mL/min flow rate with toluene, 330 nm detection.

**Table S1.** The reaction results of the retro-cycloaddition of  $C_{60}$  and  $C_{70}$  fulleropyrrolidines.

**Figure S3.** HPLC profiles of the retro-cycloaddition of (a)  $C_{60}$  and (b)  $C_{70}$  fulleropyrrolidines. HPLC conditions: 10×250 mm Buckyprep column, 12 mL/min flow rate with toluene, 330 nm detection.

**Figure S4.** MALDI-TOF mass spectra of the (a)  $C_{60}$  and (b)  $C_{70}$  fulleropyrrolidine oxides.

**Figure S5.** HPLC profiles of the cycloaddition of  $Sc_3N@I_h-C_{80}$  to get the fulleropyrrolidine nearly 50%. HPLC conditions: 10×250 mm Buckyprep column, 12 mL/min flow rate with toluene, 330 nm detection.

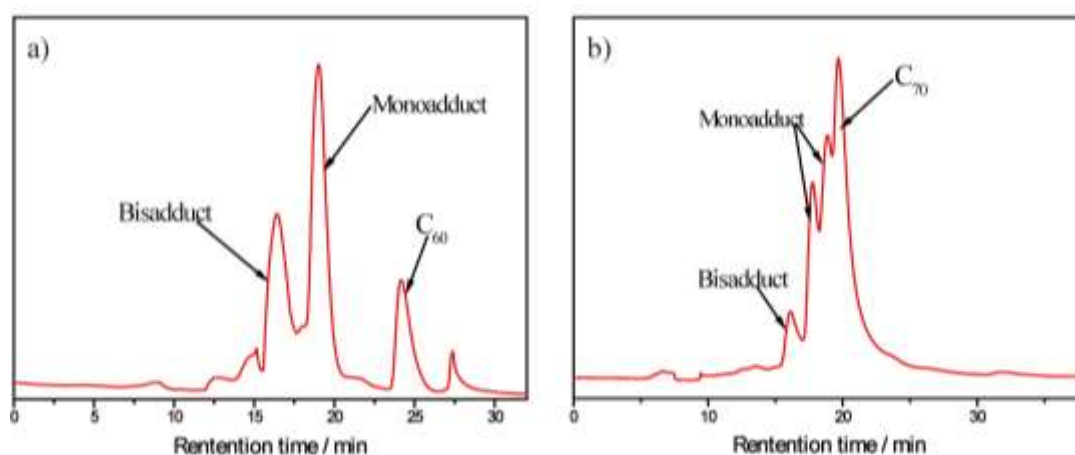
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**Figure S7.** The conceivable reaction mechanism of the formation of fulleropyrrolidines “nitrogen oxide group”.

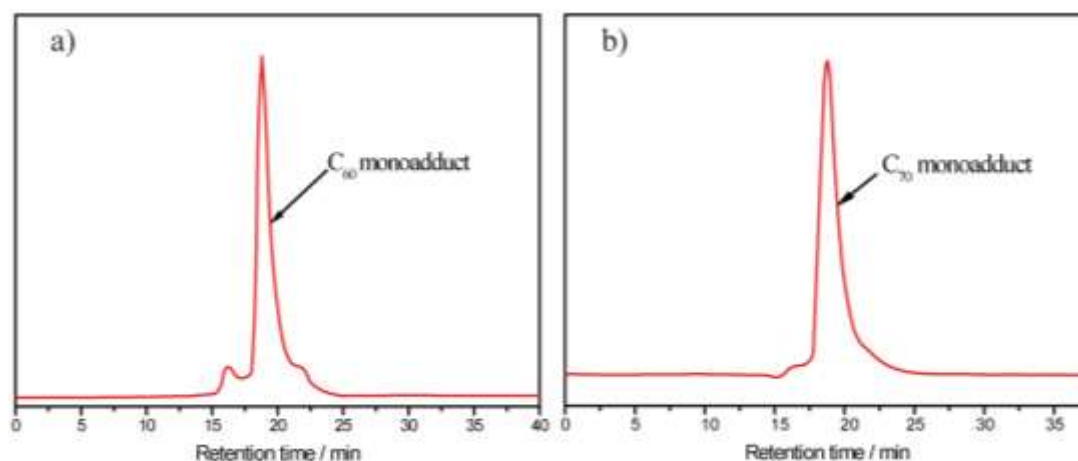
## Experimental Section:

### 1. The synthesis and purification of C<sub>60</sub>, C<sub>70</sub> and Sc<sub>3</sub>N@C<sub>80</sub> fulleropyrrolidines

C<sub>60</sub> and C<sub>70</sub> were heated with *N*-ethylglycine and paraformaldehyde at 120 °C to give corresponding fulleropyrrolidines with yields of nearly 80% and 50% in *o*-dichlorobenzene (*o*-DCB) for 12 and 3 h, respectively. Figure S1 and Figure S2 show the HPLC data of purified C<sub>60</sub> and C<sub>70</sub> fulleropyrrolidines with Buckyprep columns. These fulleropyrrolidines was isolated by silica column chromatography eluted by toluene.



**Figure S1.** HPLC profiles of the cycloaddition of (a) C<sub>60</sub> and (b) C<sub>70</sub>. HPLC conditions: 10×250 mm Buckyprep column, (a) 6 mL/min and (b) 12 mL/min flow rate with toluene, 330 nm detection.



**Figure S2.** Chromatograms of the isolated (a) C<sub>60</sub> and (b) C<sub>70</sub> fulleropyrrolidines. HPLC conditions: 10×250 mm Buckyprep column, (a) 6 mL/min and (b) 12 mL/min flow rate with toluene, 330 nm detection.

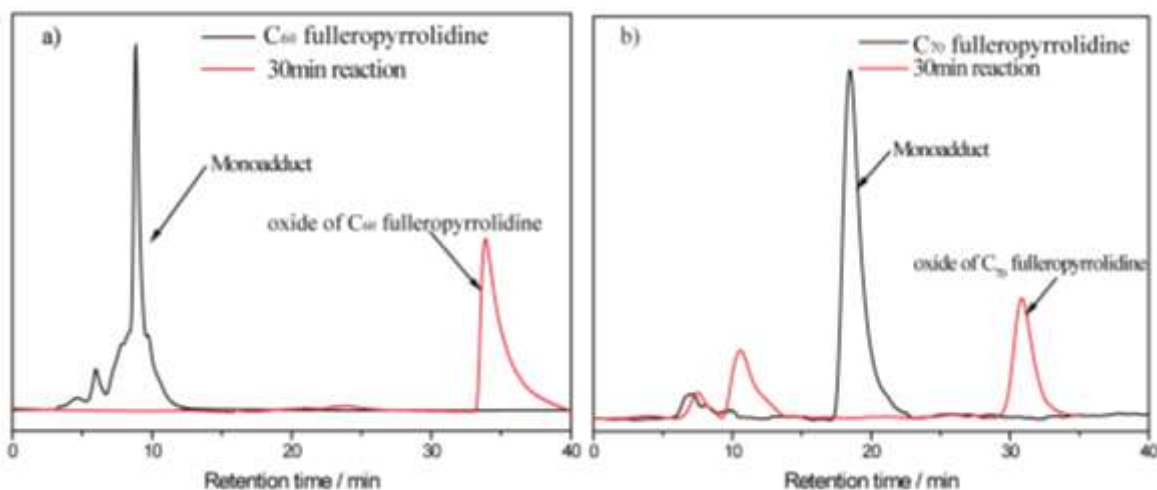
## 2. The retro-cycloaddition of C<sub>60</sub> and C<sub>70</sub> fulleropyrrolidines

C<sub>60</sub> and C<sub>70</sub> fulleropyrrolidines were heated at 40 °C in *o*-DCB for a variable time (0.2–12 h) in the presence of 3-chloroperoxybenzoic acid (MCPBA). The reaction results are listed in Table S1. After stirring for 30 min, the parent fullerenes were not recovered, but generated the oxides of C<sub>60</sub> and C<sub>70</sub> fulleropyrrolidines. Figure S3 shows the HPLC data of retro-cycloaddition products of (a) C<sub>60</sub> and (b) C<sub>70</sub> fulleropyrrolidines.

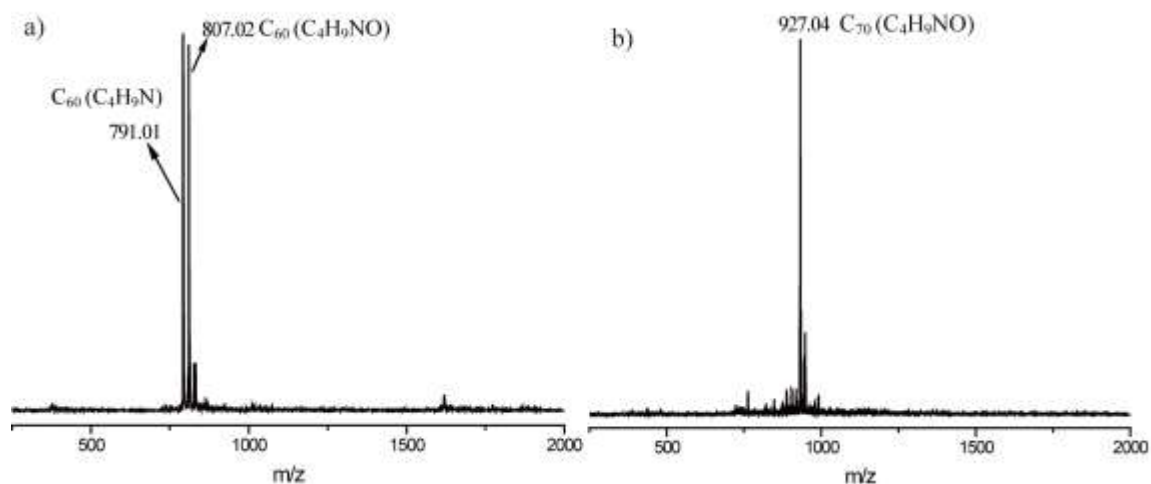
**Table S1.** The retro-cycloaddition of C<sub>60</sub> and C<sub>70</sub> fulleropyrrolidines in the presence of MCPBA at 40 °C for different reaction times.

Entry Compound	Time (h)	Recovered C <sub>60</sub> or C <sub>70</sub> (%)	Product oxide (%) <sup>a</sup>
C <sub>60</sub> mono-adduct	0.2	0	30
C <sub>60</sub> mono-adduct	0.5	0	100
C <sub>60</sub> mono-adduct	1	0	100
C <sub>60</sub> mono-adduct	6	0	100
C <sub>60</sub> mono-adduct	12	0	100
C <sub>60</sub> mono-adduct	24	0	100
C <sub>70</sub> mono-adduct	0.5	0	100
C <sub>70</sub> mono-adduct	1	0	100
C <sub>70</sub> mono-adduct	6	0	100
C <sub>70</sub> mono-adduct	12	0	100

<sup>a</sup> Determined by peak areas of HPLC profiles.



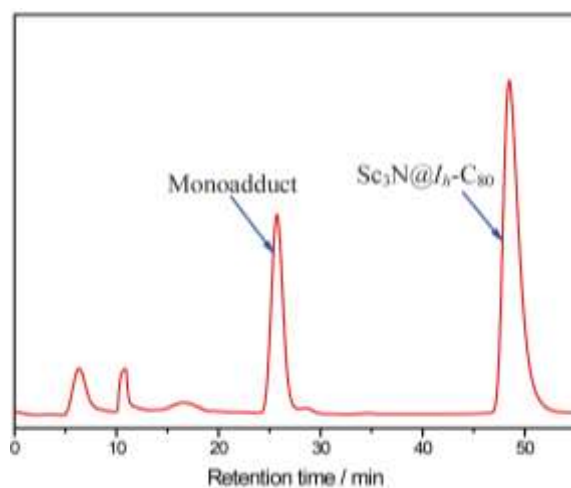
**Figure S3.** HPLC profiles of the retro-cycloaddition products of (a) C<sub>60</sub> and (b) C<sub>70</sub> fulleropyrrolidines. HPLC conditions: 10×250 mm Buckyprep column, 12 mL/min flow rate with toluene, 330 nm detection.



**Figure S4.** MALDI-TOF mass spectra of the (a) C<sub>60</sub> and (b) C<sub>70</sub> fulleropyrrolidine oxides. (m/z = 807.02 is C<sub>60</sub> fulleropyrrolidine oxide, and m/z = 791.01 is C<sub>60</sub> fulleropyrrolidine. m/z = 927.04 is C<sub>70</sub> fulleropyrrolidine oxide.)

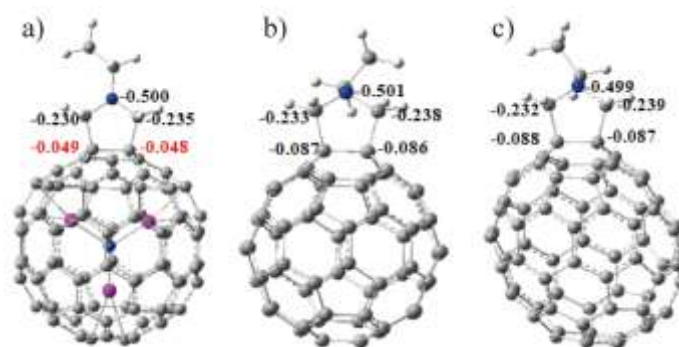
### 3. The cycloaddition and retro-cycloaddition of Sc<sub>3</sub>N@C<sub>80</sub> fulleropyrrolidine

Sc<sub>3</sub>N@C<sub>80</sub> was heated with *N*-ethylglycine and paraformaldehyde at 120 °C to give metallofulleropyrrolidine with a yield of nearly 50% in *o*-DCB for 1 h. Figure S5 shows the HPLC data of purified Sc<sub>3</sub>N@C<sub>80</sub> fulleropyrrolidine with Buckyprep columns. The retro-reaction of Sc<sub>3</sub>N@C<sub>80</sub> fulleropyrrolidine (1 mg) in *o*-DCB solution (8 ml) was executed in the presence of MCPBA (0.5 equiv) stirring at 40 °C for 20-60 min. The resulted products were analysed by HPLC (Buckyprep-column) and separated by silica column chromatography.



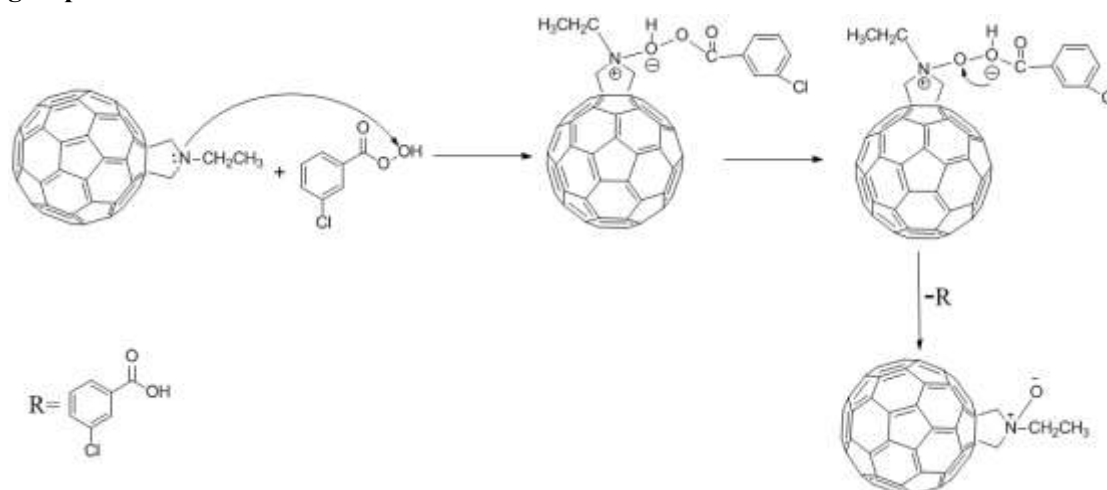
**Figure S5.** HPLC profiles of the cycloaddition of Sc<sub>3</sub>N@I<sub>h</sub>-C<sub>80</sub> to get the fulleropyrrolidine nearly 50%. HPLC conditions: 10×250 mm Buckyprep column, 12 mL/min flow rate with toluene, 330 nm detection.

#### 4. Partial NBO charge distributions of the three fullerene derivatives



**Figure S6.** Partial NBO charge distributions of (a)  $\text{Sc}_3\text{N}@C_{80}$  fulleropyrrolidine, (b)  $C_{60}$  fulleropyrrolidine, and (c)  $C_{70}$  fulleropyrrolidine.

#### 5. A conceivable reaction mechanism of the formation of fulleropyrrolidines “nitrogen oxide group”



**Figure S7.** The conceivable reaction mechanism of the formation of [60]fulleropyrrolidines “nitrogen oxide group”.