Supporting Information for

Trapping an unprecedented Ti_3C_3 unit into the icosahedral C_{80} fullerene: A crystallographic survey

Pengyuan Yu‡, WangqiangShen‡, Lipiao Bao‡, Changwang Pan, Zdenek Slanina, and Xing Lu*

State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, P. R. China

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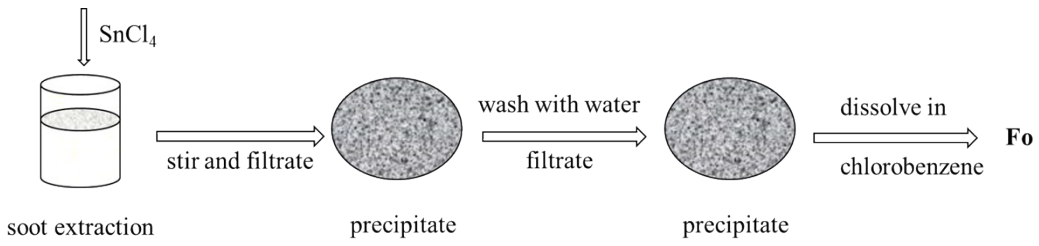
$SnCl_4$ treatment HPLC separation of $Ti_3C_3@I_h$-C_{80}. Ten drops of $SnCl_4$ was added to 500 mL carbon disulfide solution containing empty fullerenes and endohedral metallofullerenes. After stirring for 6 hours, the precipitate was collected. Then the resulting sample was completely recovered with deionized water. Finally, the obtained solid was dissolved in chlorobenzene and subjected to following multi-stage HPLC separation. The first stage of HPLC separation was performed on a 5PBB column (20 mm × 250 mm, Cosmosil Nacalai Tesque) with chlorobenzene as mobile phase. Figure S1 shows the corresponding chromatogram and the mass spectrum of the collected **Fo-7** fraction. Then fraction **Fo-7** was injected in a Buckyprep column (10mm × 250 mm) with toluene as the mobile phase for the second stage separation, and Ti_3C_{83} was finally obtained (Figure S2). The purity of the isolated Ti_3C_{83} was checked by the LDI-TOF mass spectrometry in a positive linear mode (Figure S2b), along with the HPLC chromatogram on a Buckyprep column (4.6 mm×250 mm, Cosmosil Nacalai Tesque) with toluene at a flow rate of 1.0 mL/min (Figure S3).



Scheme S1. The process of separation of Ti-EMFs with $SnCl_4$.

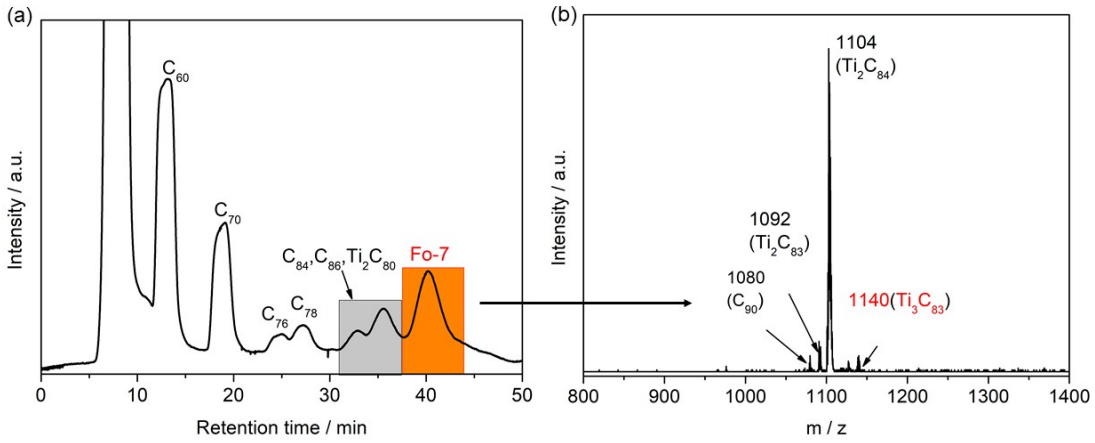


Figure S1. (a) The first stage HPLC chromatogram of **Fo** obtained by $SnCl_4$ treatment. Conditions: 5PBB column, Φ = 20 mm × 250 mm, eluent = chlorobenzene, flow rate = 9.99 mL/min, detection wavelength = 330 nm, room temperature, and (b) mass-spectrum of fraction **Fo-7** containing $Ti_3C_3@I_h$-C_{80}.

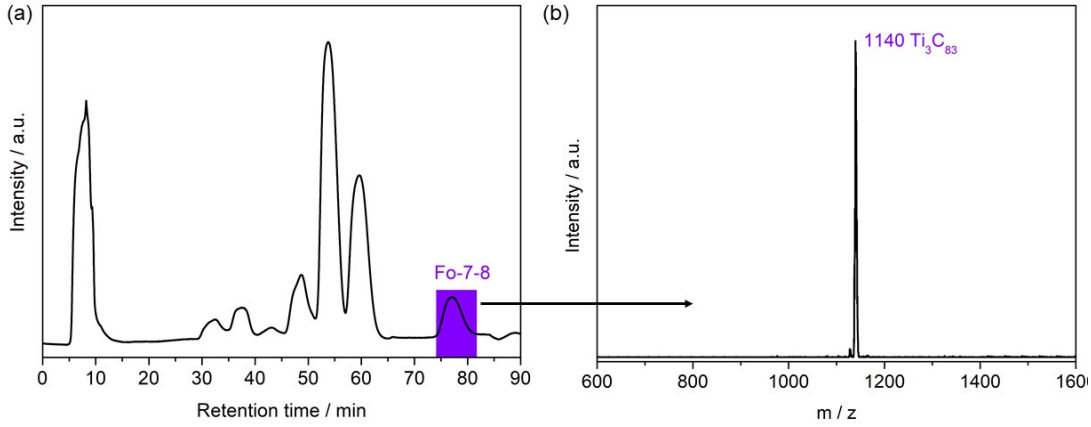


Figure S2. (a) The second stage HPLC chromatogram of fraction **Fo-7**. Conditions: Buckyprep column, Φ = 10 mm × 250 mm, eluent = toluene, flow rate = 4 mL/min, detection wavelength = 330 nm, room temperature, and (b) mass-spectrum of purified Ti_3C_{83}.

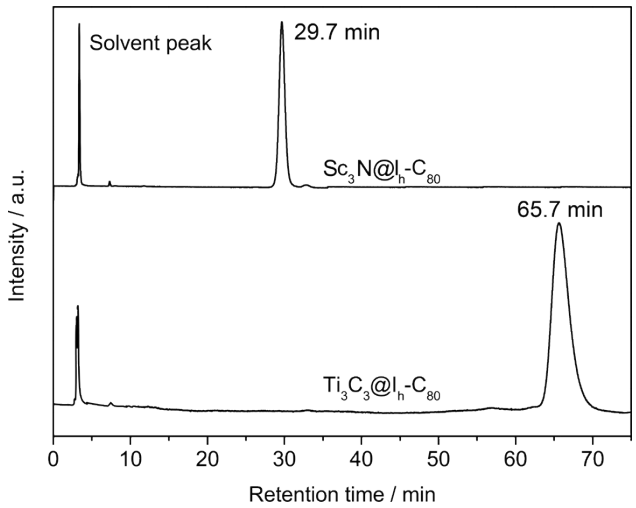


Figure S3. HPLC chromatogram of purified $Sc_3N@I_h$-C_{80} and $Ti_3C_3@I_h$-C_{80}. Conditions: Buckyprep column, 20 μL injection volume, Φ = 4.6 mm × 250 mm, eluent = toluene, flow rate = 1 mL/min, detection wavelength = 330 nm, temperature = 40 °C.

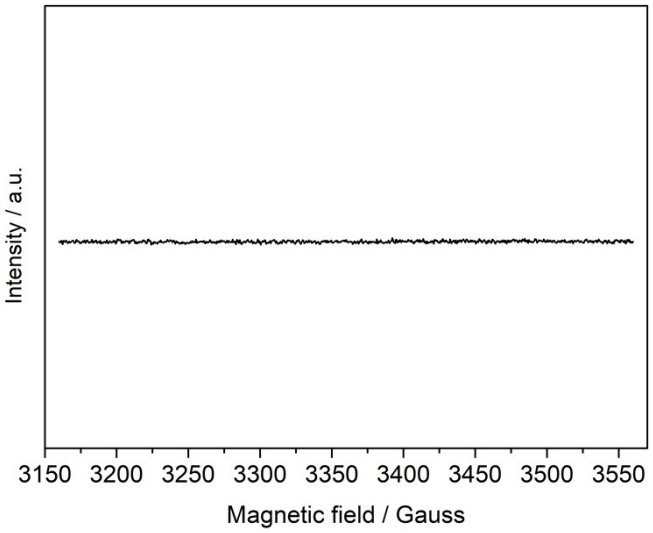


Figure S4. X-band EPR spectrum of $Ti_3C_3@I_h$-C_{80} recorded in toluene at 100 K.

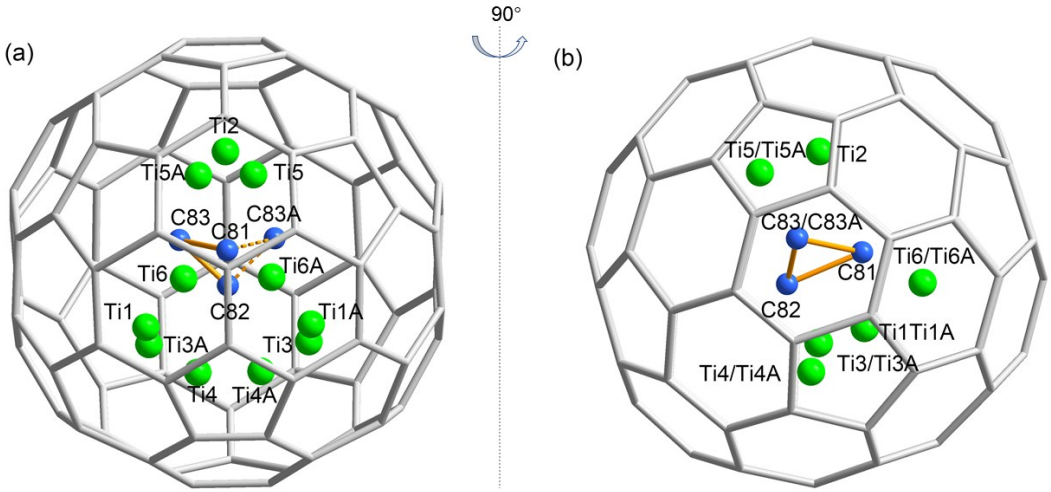


Figure S5. Perspective drawings showing the disordered titanium and carbon atoms of the internal Ti_3C_3 cluster in $Ti_3C_3@I_h$-C_{80}.

Table S1. The occupancy values of the titanium atoms inside $Ti_3C_3@I_h$-C_{80}.[a]

Metal site	Ti1/Ti1A	Ti2	Ti3/Ti3A	Ti4/Ti4A	Ti5/Ti5A	Ti6/Ti6A
Occupancy	0.5056	0.5049	0.2082	0.1268	0.2476	0.1573

a. The atoms labelled 'A' are generated by the crystallographic operation.

Table S2. Bond Distances[a] (Å) within the major Ti_3C_3 site and the closest Ti-cage contacts[b] in $Ti_3C_3@I_h$-C_{80} (Å).

Ti_3C_3 cluster structure parameters	Bond distance	Ti-cage contacts	Bond length
C81-Ti1	2.014(4)	Ti1-C17A	2.060(4)
C81-Ti1A	2.014(4)	Ti1-C18A	2.181(5)
C81-Ti2	1.979(6)	**Average**	**2.12**
C82-Ti1	2.193(4)		
C82-Ti1A	2.193(4)	Ti1A-C17	2.060(4)
C82-Ti2	2.463(6)	Ti1A-C18	2.181(5)
C83-Ti1	2.109(8)	**Average**	**2.12**
C83-Ti1A	3.090(6)		
C83-Ti2	1.838(7)	Ti2-C35	2.129(4)
C81-C82	1.474(8)	Ti2-C35A	2.129(4)
C81-C83	1.470(9)	**Average**	**2.13**
C82-C83	1.195(8)		

a. Measured by X-ray crystallographic study. b. The Ti-cage contact was based on the major site of the Ti_3C_3 cluster.

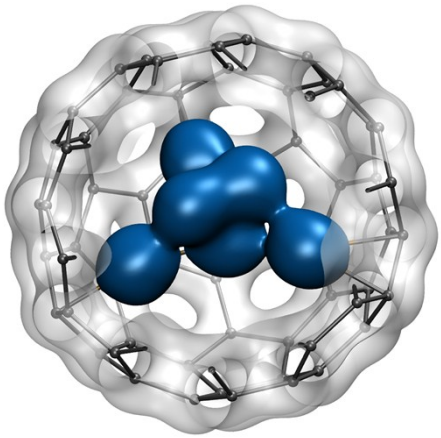


Figure S6. The $Ti_3C_3@I_h$-C_{80} isosurface of electron density of 0.086 a.u. at the B3LYP/3-21G~SDD level (colored blue and gray, partially transparent and with cut cage, for better visibility).

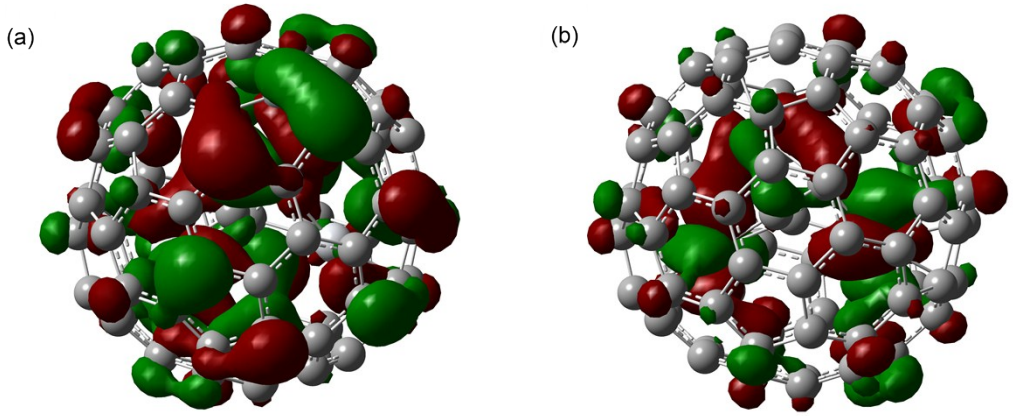


Figure S7. (a) HOMO and (b) LUMO orbitals of $Ti_3C_3@I_h$-C_{80}.