Supporting Information

New Egg-Shaped Fullerenes: Non-Isolated Pentagon Structures of $Tm_3N@C_{84}$ and $Gd_3N@C_{84}$

Tianming Zuo,[c] Marilyn M. Olmstead,*[a] Frederic Melin,[b] Luis Echegoyen,*[b] Harry C. Dorn,*[c] Manuel Chaur,[b] Christopher J. Chancellor,[a] Christine M. Beavers[a] and Alan L. Balch*[a]

Preparation and Purification of Isomer II of $Tm_3N@C_{84}$. A sample of $Tm_3N@C_{84}$ was synthesized in an arc-discharge generator by vaporizing the composite graphite rods recessedly packed with the mixture of Tm_2O_3, graphite powder, and Fe_xN in a weight ratio of 2.09:1.0:0.4, respectively, in a low pressure He/N_2 static atmosphere. The raw soot was extracted for 20 hours with toluene in a Soxhlet device. The first stage HPLC of the flash elution after chemical separation using cyclopentadiene-functionalized Merrifield peptide resin (CPDE-MPR) demonstrated seven thulium-containing fractions on 5PBB column similar to those of the terbium-based elution using same method. The forth fraction contains $Tm_3N@C_{84}$ (isomers I and II), $Tm@C_{90}$ (I, II) (See supporting information). The first isomer of $Tm_3N@C_{84}$ is much less abundant than the second isomer, as the situations of our reported $Tb_3N@C_{84}$ (I, II). The structural work reported here was done on the second and more abundant isomer, $Tm_3N@C_{84}$(II), isolated in the second HPLC stage using a 5PYE column. The HPLC chromatogram, negative ion LD-TOF MS spectrum, and the UV/Vis absorption spectrum of the pure $Tm_3N@C_{84}$(II) are shown below.

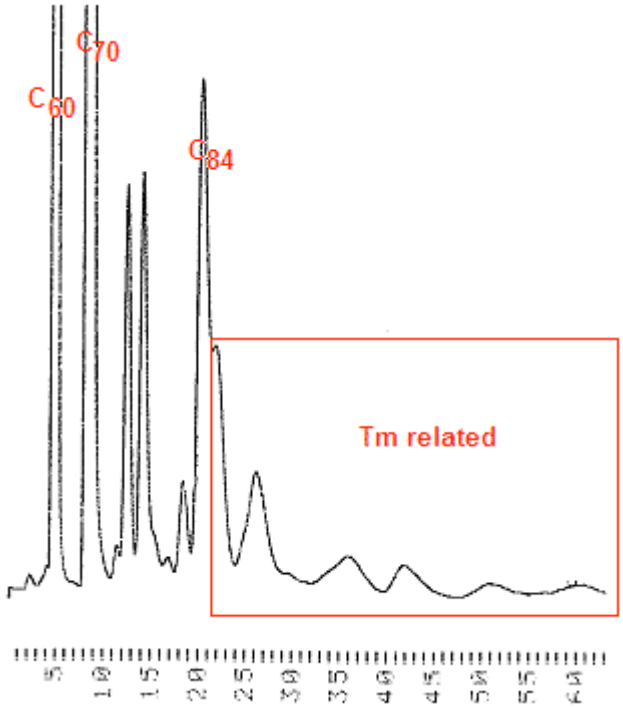

Figure 1S. HPLC trace of the extract on 5PBB column (4.6mm x 250mm). Mobile phase: toluene; Flow rate: 2.0 mL/minute; Detection wavelength: 390nm.

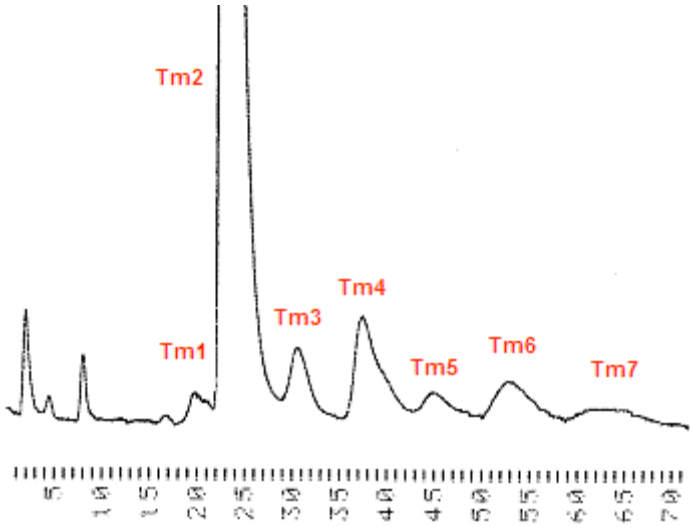

Figure 2S. The first stage HPLC of the flash elution after chemical separation using cyclopentadiene-functionalized Merrifield peptide resin (CPDE-MPR). Column: 5PBB(4.6 mm x 250 mm); Mobile phase: toluene; Flow rate: 2.0 mL/minute; Detection wavelength: 390nm.

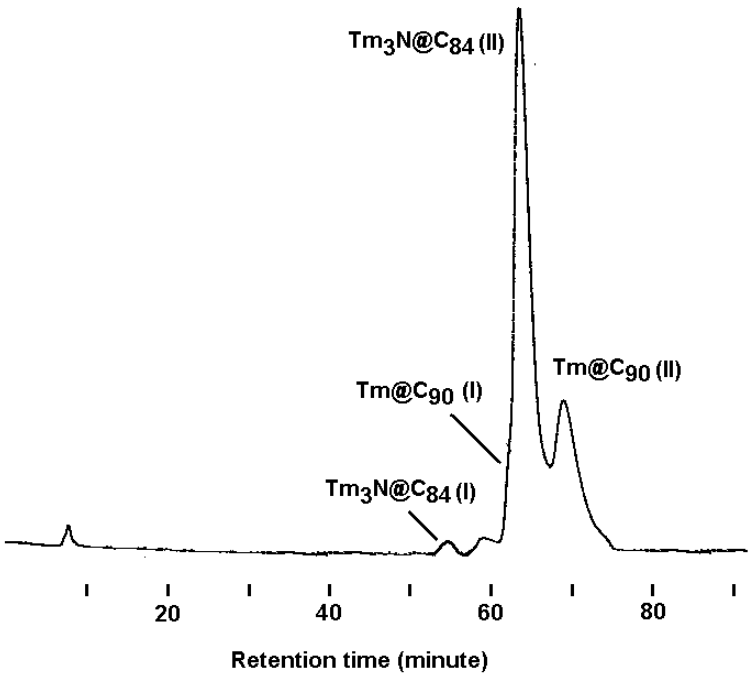

Figure 3S. The second stage HPLC separation for the fraction 4. Column: 5PYE(10 mm x 250 mm); Mobile phase: toluene; Flow rate: 2.0 mL/minute; Detection wavelength: 390 nm.

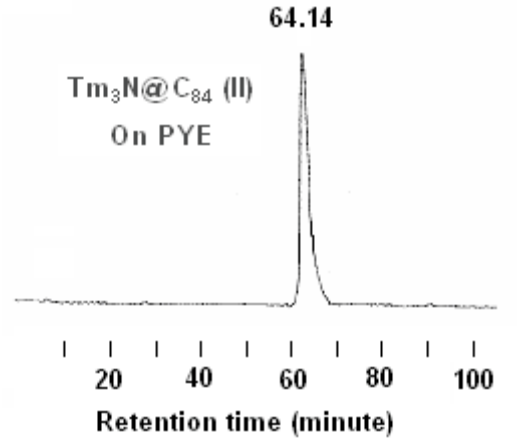

Figure 4S. HPLC of the pure isomer II of $Tm_3N@C_{84}$(II). Column: 5PYE(10 mm x 250 mm); Mobile phase: toluene; Flow rate: 2.0 mL/minute; Detection wavelength: 390 nm.

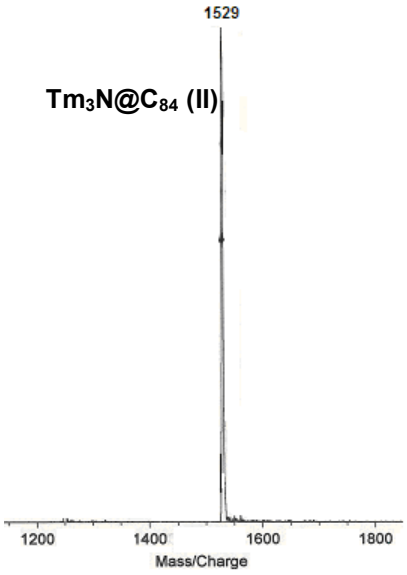

Figure 5S. Negative mode LD-TOF MS spectrum of the pure $Tm_3N@C_{84}$(II).

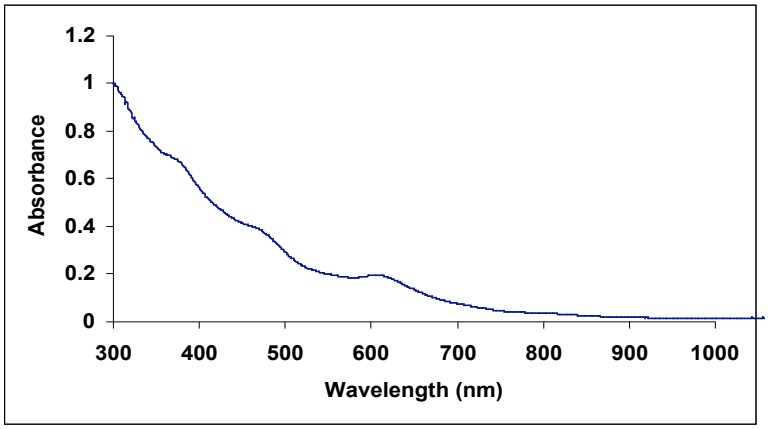

Figure 6S. UV-vis of the pure $Tm_3N@C_{84}$(II) in toluene.

Preparation and Purification of Isomer II of $Gd_3N@C_{84}$. The sample of $Gd_3N@C_{84}$ was synthesized in an arc-discharge reactor by vaporizing graphite rods containing mixture of Gd_2O_3 and graphite powder in a ~400 Torr He/N_2 atmosphere. The raw soot was extracted for ~20 hours with xylene in a custom-built automated extractor/condenser. The extract was treated with cyclopentadiene to remove the empty-cage fullerenes and the higher order species were separated from the $Gd_3N@C_{80}$ via HPLC. The $Gd_3N@C_{84}$ metallofullerene was isolated with purity higher than 95 % by high performance liquid chromatography (HPLC) using a semipreparative 10x250 mm Buckyprep-M column. The composition was established by mass spectroscopy.

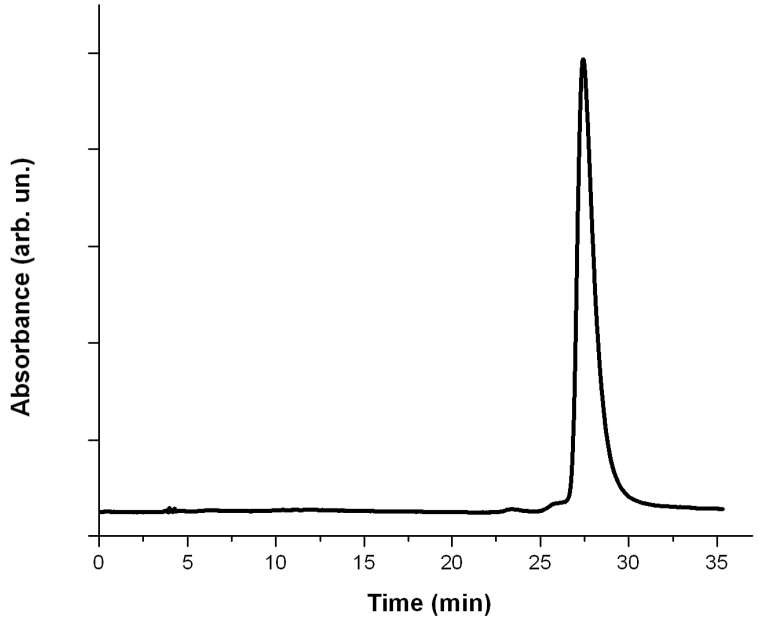

Figure 7S. HPLC of the pure $Gd_3N@C_{84}$ (I). Column: semipreparative 10 x 250 mm Buckyprep-M; Mobile phase: toluene; Flow rate: 4.0 mL/minute; Detection wavelength: 372 nm.

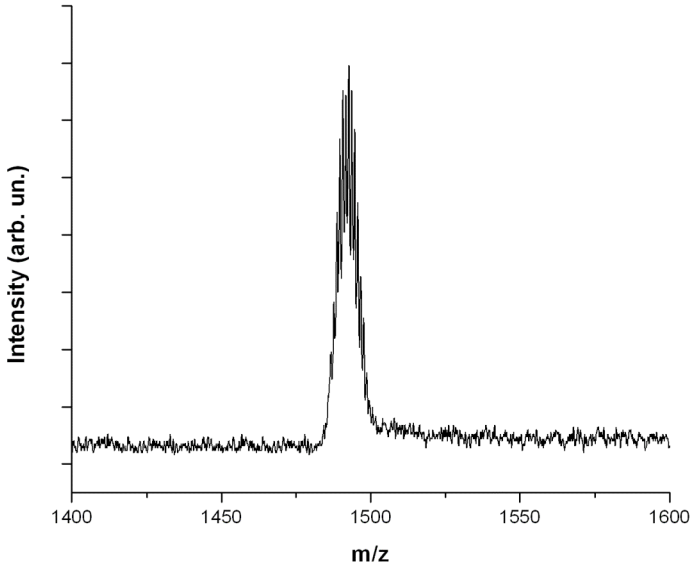

Figure 8S. MALDI-TOF MS spectrum of the pure $Gd_3N@C_{84}$(II).