

**Supporting Information for**

**Detection of a Family of Gadolinium-Containing Endohedral Fullerenes:  $\text{Gd}_2\text{C}_{90}$  to  $\text{Gd}_2\text{C}_{124}$  and the Isolation and Crystallographic Characterization of One Member as a Metal-Carbide Encapsulated Inside a Large Fullerene Cage:  $(\text{Gd}_2\text{C}_2)@D_3(85)\text{-C}_{92}$**

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## Experimental Section.

**Synthesis the  $\text{Gd}_2\text{C}_{2n}$  ( $2n = 90$  to  $124$ ) Family.** A 6 x 150 mm graphite rod filled with  $\text{Gd}_2\text{O}_3$  and graphite powder (1:70 atomic ratio) was vaporized as the anode in a DC arc under optimized conditions.<sup>1</sup> The raw soot that formed was sonicated in *o*-dichlorobenzene for eight hours, without special nitrogen protection. After removing the solvent with a rotary evaporator, chlorobenzene was added to re-dissolve the dry powder. The extract was subjected to a three or four-stage HPLC isolation process that did not involve recycling.

The first stage of chromatography was carried out on a Buckyprep-M column with chlorobenzene as eluent while the second stage utilized a Buckyprep column with toluene as eluent. The third stage was performed on a 5PBB column with toluene as eluent for the isolation of  $\text{Gd}_2\text{C}_{94}$  to  $\text{Gd}_2\text{C}_{98}$  and with xylene as eluent for separation of  $\text{Gd}_2\text{C}_{100}$  to  $\text{Gd}_2\text{C}_{106}$ . The fourth stage, which utilized a Buckyprep-M column with toluene as eluent, was needed for purification of  $\text{Gd}_2\text{C}_{100}$  to  $\text{Gd}_2\text{C}_{106}$ . The columns utilized in these chromatographic stages were 10×250 mm (Nacalai Tesque). The flow rate was 4.5 mL/min with a detecting wavelength of 450 nm.

The purity and composition of the samples of  $\text{Gd}_2\text{C}_{94}$  to  $\text{Gd}_2\text{C}_{106}$  were determined by laser desorption time-of-flight mass spectrometry (LD-TOF-MS). Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were obtained through the use of a UV-4100 spectrophotometer (Hitachi High-Technologies Corporation) in toluene or chlorobenzene.

**Crystal Growth.** Co-crystals of  $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$  and  $\text{Ni}^{\text{II}}(\text{OEP})$  were obtained by layering a solution of ca. 0.5 mg of  $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$  in 0.5 mL benzene over a red benzene solution of  $\text{Ni}^{\text{II}}(\text{OEP})$  in a glass tube. Over a 14-day period, the two solutions diffused together and black crystals of  $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}\cdot\text{Ni}(\text{OEP})\cdot 2\text{C}_6\text{H}_6$  formed.

**Crystal Structure of  $\text{Gd}_2\text{C}_2@D_3\text{-C}_{92}\text{Ni(OEP)}\cdot 2\text{benzene}$ .** A black parallelepiped of dimensions  $0.04 \times 0.27 \times 0.36 \text{ mm}^3$  was mounted in the nitrogen cold stream provided by Cryo Industries low temperature apparatus on the goniometer head of a Bruker SMART diffractometer equipped with an ApexII CCD detector. Data were collected with the use of  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). A multi-scan absorption correction was applied using the program SADABS 2008/2.<sup>2</sup> A total of 48440 reflections were collected to  $2\theta_{\text{max}}$  of  $56.4^\circ$ , of which 10532 were unique [ $R(\text{int}) = 0.0493$ ] and 6945 were observed [ $I > 2\sigma(I)$ ]. The structure was solved by direct methods (SHELXS97) and refined by full-matrix least-squares on  $F^2$  (SHELXL97) using 667 parameters and 360 restraints.<sup>3</sup> Both enantiomers of the  $\text{C}_{92}$  cage occur in the structure due to disorder with respect to a crystallographic mirror plane. There are seven sites for Gd atoms in the asymmetric unit. Initially, their occupancies were refined, but in the final cycles of refinement, these occupancies were held fixed at values near the refined values. The most prevalent sites are Gd1 and Gd2 at 0.28 occupancy and Gd3 and Gd4 at 0.16 occupancy. Gd5, Gd6, and Gd7 have occupancies of only 0.06, 0.04 and 0.02, respectively. Anisotropic thermal parameters and a similarity restraint (SIMU) of  $0.01 \text{ \AA}^2$  were used for Gd1 – Gd5. Gd6 and Gd7 were kept isotropic. There are four benzene sites in the structure, and they also exhibit some disorder with a total occupancy of 1.0 in the asymmetric unit. Same distance restraints (SADI) of  $0.01 \text{ \AA}$  were applied to the C-C distances of the 92-carbon atom cage according to their idealized  $D_3$  symmetry. The hydrogen atoms on carbon atoms were treated as riding. The maximum and minimum peaks in the final difference Fourier map were  $1.679$  and  $-0.097 \text{ e\AA}^{-3}$ . Crystal data:  $\text{C}_{142}\text{H}_{56}\text{Gd}_2\text{N}_4\text{Ni}$ , fw= 2191.12, monoclinic,  $C2/m$ ,  $a = 24.2381(14) \text{ \AA}$ ,  $b = 17.6005(10) \text{ \AA}$ ,  $c = 19.7867(12) \text{ \AA}$ ,  $\beta = 97.222(3)^\circ$ ,  $V = 8374.1(8) \text{ \AA}^3$ ,  $T = 90(2) \text{ K}$ ,  $Z = 4$ ,  $R1$

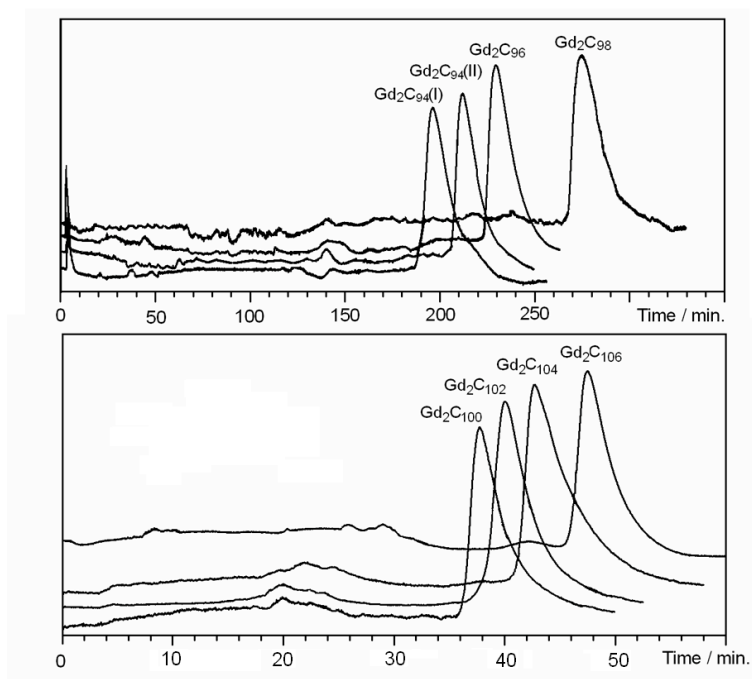
$[I > 2\sigma(I)] = 0.1150$ ,  $wR_2$  (all data) = 0.35761, GOF (on  $F^2$ ) = 1.049.

**Computational Details.** Geometries were fully optimized by non-local density functional calculations at the B3LYP level.<sup>4</sup> The effective core potential and basis set developed by Stevens *et al* were used for gadolinium (CEP-31G),<sup>5</sup> and the split-valence 3-21G basis set was used for carbon. Energies were improved by single-point density functional calculations at the B3LYP level, where a larger 6-31G basis set was employed for carbon. The energy levels of the neutral, tetra-anion and hexa-anion of  $D_{3h}(35)\text{-C}_{92}$  were obtained from single-point density functional calculations at the BLYP. All calculations were carried out with the GAUSSIAN 03 program.<sup>6</sup>

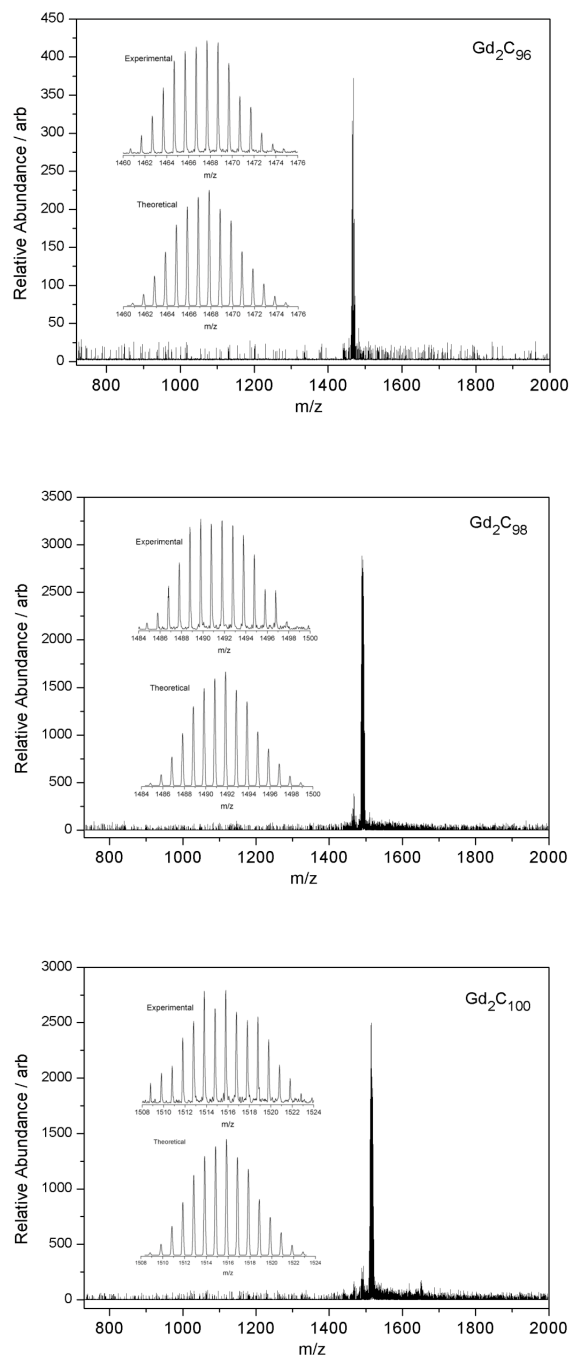
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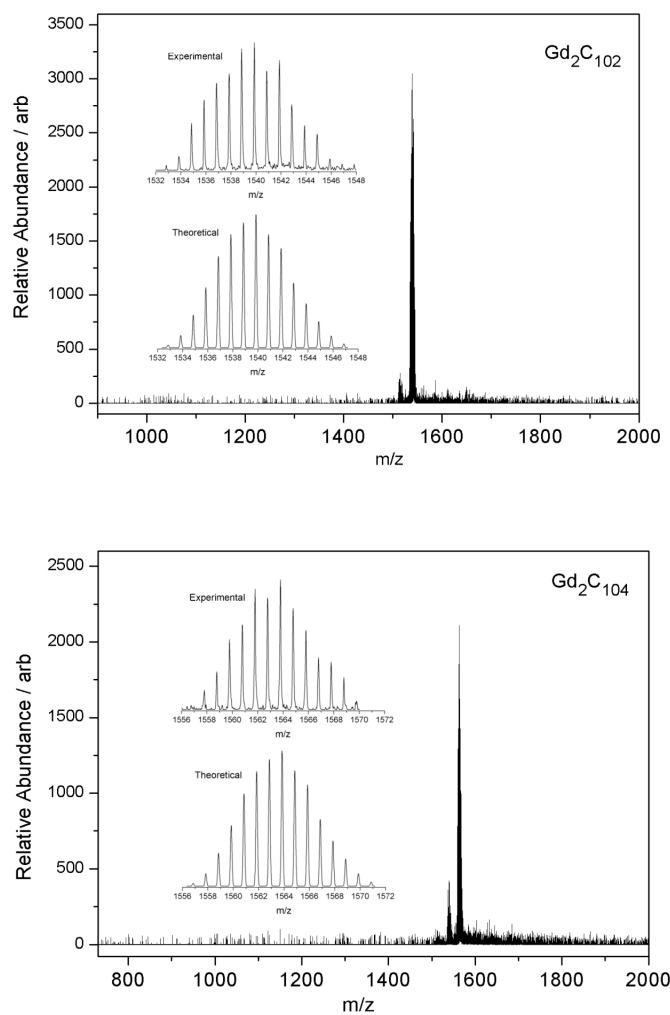
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**Figure SI-1.** Final HPLC profiles of the isolated samples after three-stages of separation. Top: 5PBB column, toluene mobile phase, flow rate 4.5 mL/min, detecting wavelength, 400 nm. Bottom: Buckyprep-M column, toluene mobile phase, flow rate 4 mL/min, detecting wavelength 400 nm.



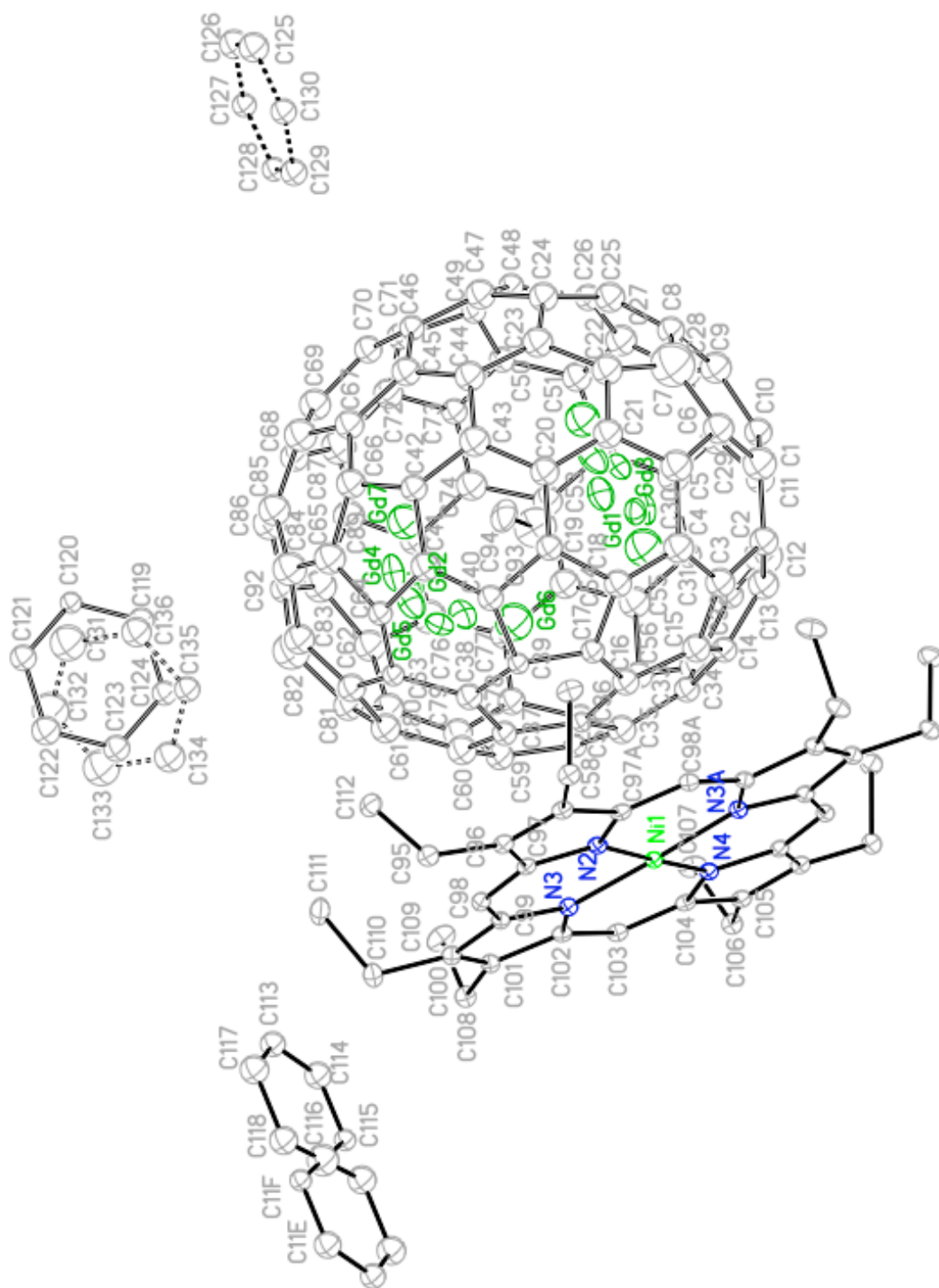
**Figure SI-2.** LD-TOF mass spectra obtained from purified samples of  $\text{Gd}_2\text{C}_{96}$ ,  $\text{Gd}_2\text{C}_{98}$ , and  $\text{Gd}_2\text{C}_{100}$ . The insets show expansions of the experimental and theoretical spectra for the parent ions.



**Figure SI-3.** LD-TOF mass spectra obtained from purified samples of  $\text{Gd}_2\text{C}_{102}$  and  $\text{Gd}_2\text{C}_{104}$ .

The insets show expansions of the experimental and theoretical spectra for the parent ions.





**Figure SI-4.** Complete numbering scheme for  $\text{Gd}_2\text{C}_2@D_3(85)\text{-C}_{92}$ .