

Cerium Endofullerenes: Purification and Spectroscopic Analysis

Mito Kanai*^a, T. J.S. Dennis^a and H. Shinohara^b
a Department of Chemistry, Queen Mary, University of London

b Department of Chemistry, Nagoya University

Cerium is the most common lanthanide element with its valence states is +3 and +4. Cerium endohedral fullerenes, including Ce@C₈₂ and Ce₂@C₈₀, were purified and characterized by TOF-MALDI mass spectrometry, UV-Vis and ¹³C NMR spectroscopy.

EXPERIMENTAL PROCEDURE

Cerium endohedral fullerenes were produced by contact-arc burning of Cerium/graphite composite rods (Ce/C = 1.6 wt%; 30cm in length × 1.5cm in diameter; Φ = 30V; I = 500A; He pressure = 60 Torr) in Apr 2002 in Department of Chemistry, Nagoya University. The soot inside the collection box was collected under unaerobic conditions. The crude soot was then placed to the flask and was refluxed in o-xylene for 4hrs. The dark-brown o-xylene solution was filtered and the residue was dried under vacuum. The dried solid was refluxed in DMF/pyridine for 4hrs and then the solid was filtered and dried. This reflux-treatment in DMF/pyridine was repeated three times. Either o-xylene or DMF/pyridine was evaporated from the sample and replaced by toluene. The sample was then separated into endohedral/hollow fullerenes by so-called multi-stage HPLC technique (JAI co.ltd, LC-908). The HPLC diagram was shown in Figure 1. In the first step, the sample was injected by 20ml (Cosmosil 5PYE column, 20 × 250mm, toluene eluent, 18ml/min. flow) and was separated into 5 fractions by the retention time. Then, the fraction which involves Ce endofullerenes was reinjected to the column and recycled (the recycling step, shown in Figure 1-inset.). This recycling step was repeated until the desired peak was obtained. A single peak corresponds to Ce₂@C₈₀ was observed in the final recycling step and was collected.

The ¹³C NMR spectroscopic measurement of Ce₂@C₈₀ was performed by Brüker AMX600 spectrometer at 600MHz in ULIRS NMR service in Department of Chemistry, Queen Mary. The spectra were recorded from 200 K to 340K by 20K, between 3,000 to 12,300 scans.

RESULTS AND DISCUSSION

Ce₂@C₈₀ has two NMR lines (20 × 1, 60 × 1) and we focused on the main peak at 149ppm (at RT). The nearly linear response in both the shift to the higher frequency and in the broadening was observed. The more results will be discussed in the presentation with the comparison to La₂@C₈₀¹ and Sc₂@C₈₄.²

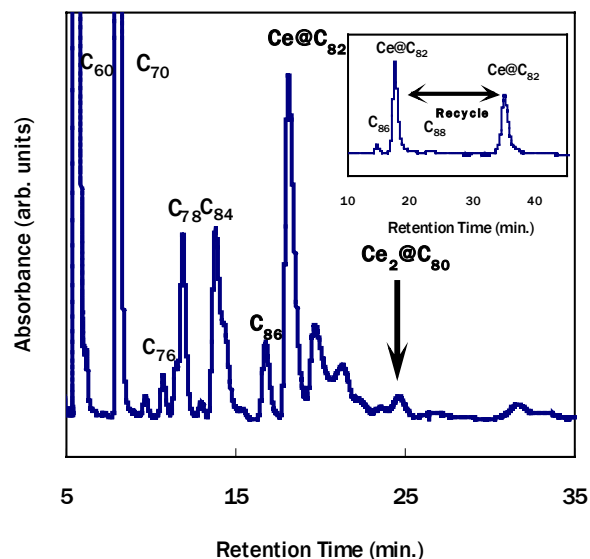


Figure 1. The two-stage HPLC profiles of Ce@C₈₂ (18ml/min. flow, toluene eluent, 20mm × 250mm 5PYE column (Nacalai Tesque)). The peaks correspond to C₈₆ to C₈₈ were collected and recycled. Ce@C₈₂ was finally purified in the recycling stage (inset).

REFERENCES

- ¹ T. Akasaka, S. Nagase, K. Kobayashi, T. Kato, Y. Achiba, K. Yamamoto, H. Funasaka and T. Takahashi, *Angew Chem., Int. Ed. Engl.* **36**, 1643 (1997).
- ² M. Krause, M. Hulman, H. Kuzmany, T.J.S. Dennis, M. Inakuma and H. Shinohara, *J. Chem. Phys.* **111**, 7976 (1999).