HPLC elution behavior of heavy lanthanide metallofullerene: Ln@C$_{82}$ (Tb, Dy, Ho, Er, Lu) on pyrenyl stationary phase

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Metallofullerene (MF) is a clathrate compound encapsulating metal atoms in a fullerene molecule. Lanthanide (Ln) EMF, Ln@C$_{82}$, have two or three charge transferred electrons on the C$_{82}$ cage from the encapsulated Ln atom, and their electronic states reflect the number of charge transfer electrons.[1] From the view point of inorgnic chemistry, it is interesting to probe the effect of the electronic state for the series of the ten lanthanide elements (La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu) with the electronic states of $(Ln^{3+})@(C_{82}{}^{3-})$ on the electronic state of the Ln@C$_{82}$ molecule from the difference in interaction with pylenyl stationary phase. To this end, we have determined the retention time in the pyrenyl stationary phase for five types of Ln@C$_{82}$ from La to Gd by using radio chromatography with ten Ln metal atoms activated by the thermal neutron activation method. Moreover, the retention times in the High Performance Liquid Chromatography (HPLC) of Ln@C$_{82}$ with heavy lanthanide elements have not been obtained, because the half-lives of the radionuclides produced by thermal neutron irradiation such as ^{165}Dy and ^{171}Er are very short. Moreover, the production of Ln$_2$@C$_{82}$ and Ln$_2$C$_2$@C$_{80}$, whose production rate increase competitive products, inteferes with the detection of Ln@C$_{82}$ with increasing atomic number of Ln. In this paper, we report the HPLC retention time of Ln@C$_{82}$ encapsulating heavy lanthanides evaluated from HPLC data of already purified Ln@C$_{82}$ and ^{139}Ce@C$_{82}$, where ^{139}Ce was produced using the RIKEN AVF cyclotron as a comparative standard of HPLC analysis.

Cerium-139 produced by ^{139}La$(d, 2n)^{139}$Ce reaction using a ^{nat}La target irradiated with 5 μA of 24 MeV deuterons for 5 h at the RIKEN AVF cyclotron was purified from the target material of La by a solvent extraction method. The studied heavy Ln@C$_{82}$ in this work were produced and separated by a previously reported method.[2] The separated metallofullerene solutions were purified by HPLC with a Buckyprep-M column (flow rate: 3.2 mL min^{-1}, developing solvent: toluene) from other interfering metallofullerenes such as Ln$_2$@C$_{82}$. These purified Ln@C$_{82}$ with ^{139}Ce@C$_{82}$ were injected into a buckyprep column, whose stationary phase is silicate modified with propylpylenylsilyl (flow rate: 3.2 mL min^{-1}, developing solvent: toluene), monitored by UV absorption. Then, the elution components were fractionated every 20 seconds. The HPLC retention times of ^{139}Ce@C$_{82}$ and Ln@C$_{82}$ were evaluated from the gamma-ray measurement of each sample

with a Ge detector and HPLC chromatogram monitored by the UV absorption, respectively.

Here, we define the HPLC retention time of Ln@C$_{82}$ obtained in this study and the void retention time corresponding to the void volume of column as t_{Ln} and t_0, respectively, and the retention ratio of k_{Ln} of Ln@C$_{82}$ is given by $k_{Ln} = (t_{Ln} - t_0)/t_0$. The separation coefficient (α) can be expressed as the ratio of the retention ratio for Ln@C$_{82}$ (k_{Ln}) to that for ^{139}Ce@C$_{82}$ (k_{Ce}). The HPLC retention time t_{Ln} and the evaluated separation coefficient of the studied Ln@C$_{82}$ are shown in Table 1. Figure 1 shows the separation coefficient for each heavy lanthanide Ln@C$_{82}$ as a function of the spin multiplicity of Ln, together with those for previously reported α of light lanthanide Ln@C$_{82}$. Since a very good correlation can be seen between $2S + 1$ and α of Ln@C$_{82}$ (Ln: La to Er), it is presumed that the small difference in the interaction between the pyrenyl stationary phase and Ln@C$_{82}$ is caused by the 4f electronic state of the encapsulated lanthanide atom. For Lu@C$_{82}$, the large separation coefficient cannot be explained. In the near future, it is necessary to investigate the properties of Lu@C$_{82}$ in detail.

Table 1. HPLC retention time and separation coefficient α of studied Ln@C$_{82}$.

	Tb	Dy	Ho	Er	Lu
k_{Ce}	10.17	10.16	10.11	9.196	9.303
k_{Ln}	10.38	10.20	10.19	9.307	9.453
α	1.021	1.004	1.008	1.012	1.016

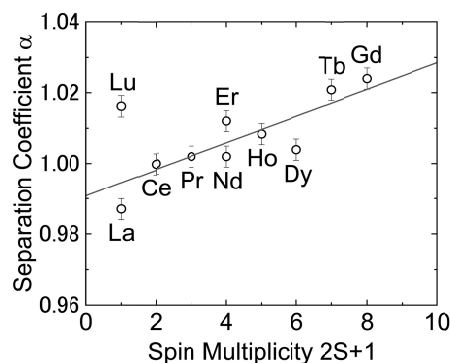Error of t and α is estimated to be less than 0.3%

Fig. 1. Relation between spin multiplicity of Ln and separation coefficient α.

References
1) H. Shinohara, Rep. Prog. Phys. **63**, 843 (2000).
2) K. Akiyama *et al.*, RIKEN Accel. Prog. Rep. **53**, 194 (2019).

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