

Exohedral Derivatization of an Endohedral Metallofullerene Gd@C₈₂Takeshi Akasaka,^a Shigeru Nagase,^b Kaoru Kobayashi,^b Toshiyasu Suzuki,^c Tatsuhisa Kato,^d Kazunori Yamamoto,^e Hideyuki Funasaka^e and Takeshi Takahashi^e^a Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan^b Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan^c Fundamental Research Laboratories, NEC Corporation, Miyukigaoka, Tsukuba 305, Japan^d Institute for Molecular Science, Myodaiji, Okazaki 444, Japan^e Nuclear Fuel Technology Development Division, Tokai Works, Power Reactor & Nuclear Fuel Development Corporation, Tokai, Ibaraki 319-11, Japan

Photochemical and thermal reactions of an endohedral metallofullerene Gd@C₈₂ with disilirane afford an exohedral adduct.

Endohedral metallofullerenes [fullerenes with metal(s) inside the cage] are currently of great interest because they could give rise to new chemical entities with novel properties.¹⁻³ Most work has concentrated on the production and characterization of these compounds,³ and recent successes include the purification and isolation of La@C₈₂^{4,5} and Gd@C₈₂^{6,7} in milligram quantities. However, little is known about the physical properties⁸ and there have been no reports concerning the chemical properties of these species. Very recently, we have reported the first chemical derivatization of an endohedral metallofullerene La@C₈₂ giving an exohedral adduct.⁹ In this context, it is interesting to see how the chemical properties change with different encapsulated metal atoms. Here we report the chemical derivatization of Gd@C₈₂ in comparison with La@C₈₂.

Gd@C₈₂ was prepared and purified according to our recently developed method.⁷ A toluene solution of Gd@C₈₂ and 1,1,2,2-tetramesityl-1,2-disilirane [(Mes₂Si)₂CH₂] **1** was photoirradiated at 20 °C with a tungsten-halogen lamp (cutoff <400 nm) in a degassed sealed tube (Scheme 1).^{10,11} The reaction product was analysed by FABMS using *m*-nitrobenzyl alcohol as the matrix. The positive ion FABMS of the product shows the presence of Gd@C₈₂(Mes₂Si)₂CH₂ **2** (*m/z* 1685–1693), as shown in Fig. 1. No molecular ion peaks ascribable to multiple-addition products such as Gd@C₈₂-[(Mes₂Si)₂CH₂]₂ were observed. The observed ion intensity ratio of a group of peaks for **2** agrees with the carbon and silicon isotope distributions.¹² The ion peak of Gd@C₈₂ at *m/z* 1139–1146 due to a loss of exohedral functional group [(Mes₂Si)₂CH₂] from **2** is a base peak similar to that observed with the exohedral adduct of La@C₈₂(Mes₂Si)₂CH₂.⁹ It is noteworthy that Gd@C₈₂ is also derivatized by the photochemical reaction with **1** to afford the adduct Gd@C₈₂(Mes₂Si)₂CH₂, as with La@C₈₂.⁹

In order to investigate further the interesting properties of Gd@C₈₂, the thermal reaction with **1** has also been examined. Although disilirane **1** did not add thermally to empty fullerenes such as C₆₀, C₇₀ and C₈₂,⁵ a facile thermal addition to Gd@C₈₂ took place. When a toluene solution of Gd@C₈₂ and **1** was heated at 80 °C for 1 h, formation of the adduct **2** was verified by FABMS. In an attempt to explain the high thermal reactivity of Gd@C₈₂ toward **1**, its characteristic electronic properties, *i.e.* electron donor and acceptor characteristics, were examined. The CV of Gd@C₈₂ in 1,2-dichlorobenzene shows a set of one reversible and one irreversible oxidations, and two reversible and one irreversible reductions (Fig. 2). The differential pulse voltammogram (DPV) also displays five well-defined peaks (Fig. 2). The first oxidation and reduction potentials of Gd@C₈₂

are almost the same as those of La@C₈₂,⁸ implying that Gd@C₈₂ is a stronger electron donor and acceptor than empty fullerenes such as C₆₀,⁸ C₇₀⁸ and C₈₂ (Table 1).

A non-local density function calculation[†] was carried out to help understand the redox behaviour of Gd@C₈₂. It predicts that the ionization potential (*I*_p ≈ 6.25 eV) and electron affinity

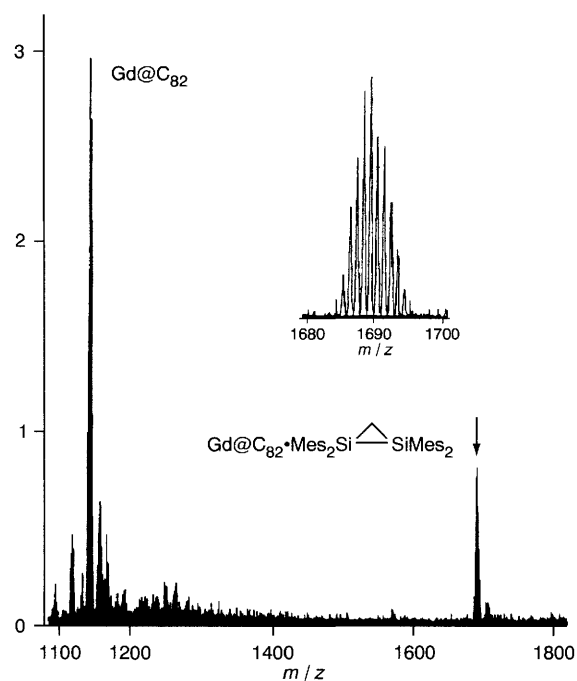


Fig. 1 FABMS of the adduct Gd@C₈₂(Mes₂Si)₂CH₂ **2** from *m/z* 1100 to 1800. Inset: expanded view of the *m/z* 1680–1700 region.

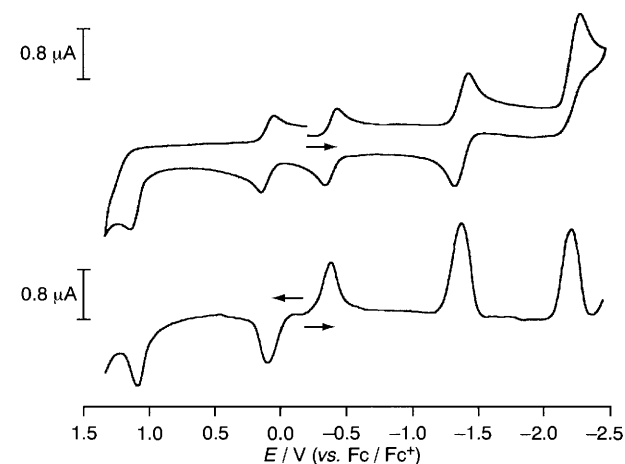
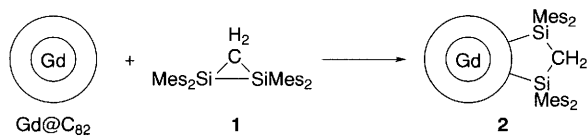


Fig. 2 CV and DPV of Gd@C₈₂ at 20 mV s⁻¹ in 1,2-dichlorobenzene containing 0.1 mol dm⁻³ Buⁿ₄NPF₆.



Scheme 1

Table 1 Reactivities, redox potentials, ionization energies and electron affinities of metallofullerenes and empty fullerenes

	Reactivity ^a		E_{ox}/V^b	E_{red}/V^b	I_p/eV	E_a/eV
	$h\nu$	heat				
Gd@C ₈₂	Yes	Yes	+0.09	-0.39	6.25	3.20
La@C ₈₂	Yes	Yes	+0.07 ^c	-0.42 ^c	6.19 ^d	3.22 ^d
C ₆₀	Yes	No	+1.21 ^{c,e}	-1.12 ^c	7.78 ^d	2.57 ^d
C ₇₀	Yes	No	+1.19 ^c	-1.09 ^c	7.64 ^d	2.69 ^d
C ₈₂	Yes	No	+0.72	-0.69	6.96	3.37

^a Yes implies the formation of a 1 : 1 adduct. No implies no 1 : 1 adduct was formed and no change in the starting fullerene was observed. ^b Half-cell potentials unless otherwise stated. Values are relative to ferrocene-ferrocenium couple. ^c Ref. 8. ^d Ref. 13. ^e Irreversible. Values were obtained by DPV.

($E_a = 3.20$ eV) of Gd@C₈₂ are much smaller and larger, respectively, than those for C₆₀ (7.78 and 2.57 eV) and C₇₀ (7.64 and 2.69 eV).¹⁴ This is consistent with Gd@C₈₂ having both low oxidation and reduction potentials, relative to those of C₆₀ and C₇₀.⁸ Although the E_a of C₈₂ (3.37 eV) is comparable to that of Gd@C₈₂, thermal addition of disilirane to C₈₂ is restrained, as with C₆₀ and C₇₀,¹⁰ due to its higher I_p (6.96 eV). In this context, one of the most important findings is that Gd@C₈₂ can also be exohedrally functionalized with **1** both thermally and photochemically.

In conclusion, the chemical reactivities of Gd@C₈₂ towards functionalization with **1** are almost identical to those of La@C₈₂, supported by their similar redox potentials, I_p and E_a .

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Footnote

† In the spin-polarized calculation, density-gradient corrections developed by Becke^{13a} and Perdew^{13b} were employed for the exchange and correlation functions, respectively. The relativistic effective core potential and basis set by Cundari and Stevens^{13c} were used on Gd: the s and p orbitals were in their quadruple zeta form while the 4f and 5d orbitals were split into double zeta. The split-valence 3-21G basis set was used for C.^{13d}

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