

Characterization of Y@C₈₂ and its bis-silylated

adducts

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The cation and anion of Y@C₈₂ were prepared by controlled potential electrolysis (CPE), and their stabilities were checked by the spectroscopic studies. Since the anion showed higher stability than cation under air atmosphere, the cage structure of Y@C₈₂ was measured by ¹³C NMR in its anionic state. The 125 MHz ¹³C NMR spectrum of [Y@C₈₂]⁻ exhibits a total of 24 distinct lines (17 lines of nearly equal intensity and 7 lines of half intensity), indicating the C_{2v} symmetry. Therefore, Y@C₈₂ has the same molecular symmetry as La@C₈₂-A, Pr@C₈₂-A and Ce@C₈₂,¹⁻³ which is definitely consistent with the similarities among their electronic absorption spectra (UV-Vis-NIR), as well as the theoretical calculations.⁴

In addition, the reactivity of Y@C₈₂ was probed by disilirane, and two isomers of bis-silylated Y@C₈₂ were synthesized and isolated for the first time. Both of them were characterized by mass spectrometry, Vis-NIR absorption and EPR spectroscopy (Figure 1). Their redox behaviors were also investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In general, the addition of disilirane group causes these bis-silylated adducts more negative than the parent Y@C₈₂. The first reduction waves of isomer 1 and 2 appear at -536 mV and -484 mV (vs. Fc/Fc⁺), 180 mV and 128 mV more negative than Y@C₈₂ respectively. Meanwhile their first oxidation waves also negatively shift about 192 mV and 160 mV, and occur at -92 mV and -60 mV, respectively. Furthermore, the stabilities of two isomers have been studied. Interestingly, isomer 1 is much more unstable and more sensitive to oxygen than isomer 2, which might be ascribed to their different addition position.

Reference:

1. Akasaka, T.; Wakahara, T.; Nagase, S.; Kobayashi, K.; Waelchli, M. *J. Am. Chem. Soc.*, **2000**, 122, 9316.
2. Wakahara, T.; Okubo, S.; Kondo, M.; Maeda, Y.; Akasaka, T. *Chemical Physics Letters* **2002**, 360, 235.
3. Wakahara, T.; Kobayashi, K.; Yamada, M.; Maeda, Y.; Akasaka, T. *J. Am. Chem. Soc.* **2004**, 126, 4883.
4. Kobayashi, K., Nagase, S. *Chem. Phys. Lett.* **1998**, 282, 325.

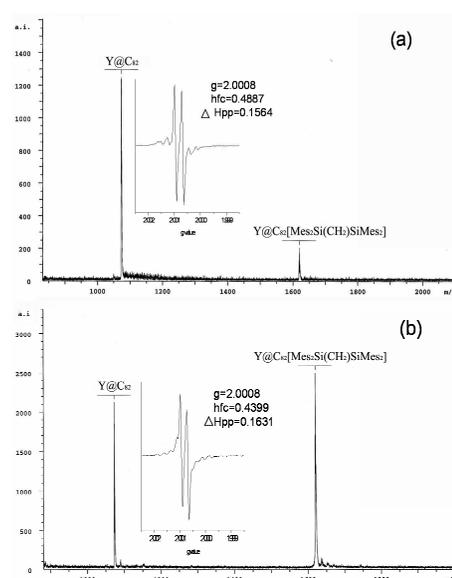


Figure 1. MALDI-TOF mass spectra of the isolated (a) isomer 1, and (b) isomer 2 of the bis-silylated Y@C₈₂. The spectra were recorded in positive mode with 9-NA as matrix. The inset spectra are corresponding X-band EPR spectra of isomer 1 and 2, respectively, which were measured in toluene solution at room temperature.