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## COMMUNICATION

# Regioselective synthesis and molecular structure of the first derivative of praseodymium-containing metallofullerenes

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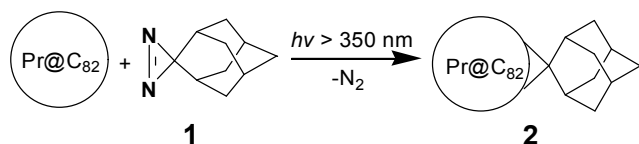
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**Regioselective cycloaddition of adamantylidene carbene to Pr@C<sub>2v</sub>(9)-C<sub>82</sub> affords the first derivative of praseodymium-containing metallofullerenes. X-ray single crystallographic data in combination with theoretical studies demonstrate that the addition is dictated by the single metal ion encapsulated inside the fullerene cage.**

Endohedral metallofullerenes (EMFs) are new family of metal-carbon hybrid molecules.<sup>1</sup> They feature intrinsic electron transfer from metal to cage, uncertain metal locations and strong metal-carbon interactions. Accordingly, they also show a great deal of potential applications in the fields of photovoltaics, nanoelectronics and biomedicine, etc.<sup>2</sup>

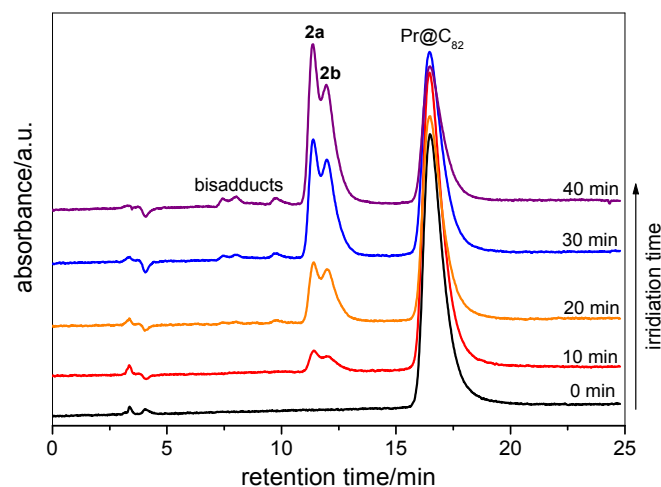
The simplest prototypes of EMFs are these compounds encapsulating only one metal ion, which are particularly suitable for elucidating the unique metal-cage interactions in EMFs. Pr@C<sub>2v</sub>(9)-C<sub>82</sub> was first isolated in 1996.<sup>3</sup> Until 2002, however, its cage structure has been determined with NMR spectroscopy performed on the electrochemically reduced mono-anion.<sup>4</sup> Thereafter, to the best of our knowledge, this compound has not received further attention.

**Scheme 1** Photochemical reaction of Pr@C<sub>2v</sub>(9)-C<sub>82</sub> with **1**.



During the past two decades, great efforts have been devoted to studying the chemical properties of EMFs, paying special attention to the mutual influences between the internal single metal ion and the carbon cage.<sup>5</sup> One of the reactions that have been performed on EMFs is the cycloaddition of adamantylidene carbene (Ad, **1**), which behaves as an electrophilic reagent under photoirradiation or heating.<sup>6</sup> The reactions between **1** and M@C<sub>2v</sub>(9)-C<sub>82</sub> (M = Y, La, Ce, Gd) have been investigated.<sup>6-9</sup> Although in principle, up to 35 different regioisomers should be generated, only two monoadduct isomers were obtained. The high selectivity is attributed to the unique location of the single metal ion and its strong interaction with the nearby cage carbons. It thus appears that the chemical properties

of M@C<sub>2v</sub>(9)-C<sub>82</sub> species are independent on the type of the encapsulated metal ion. However, this is not always true because the reaction between **1** and Sc@C<sub>2v</sub>(9)-C<sub>82</sub> gave rise to four monoadduct isomers.<sup>10</sup> Theoretical results proposed that the small ionic radius of Sc<sup>3+</sup> makes the metal-cage interaction much stronger than the situations in other EMFs. Thus, it is particularly meaningful to study the chemical properties of M@C<sub>2v</sub>(9)-C<sub>82</sub> encapsulating a different metal atom.



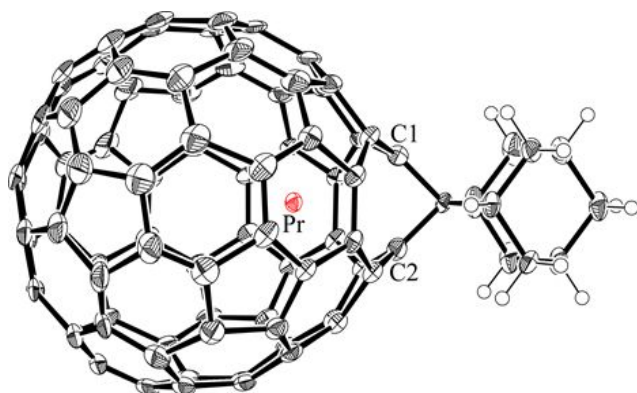
**Fig. 1** HPLC tracing of the reaction between **1** and Pr@C<sub>82</sub> with a PYE column. Conditions: 1.0 mL/min toluene flow; 330 nm detector wavelength; 298 K.

Herein, we report the efficient cycloaddition of 2-adamantane-2,3-[3H]-diazirine (AdN<sub>2</sub>, **1**) to Pr@C<sub>2v</sub>(9)-C<sub>82</sub>. In a typical reaction, 5 mg Pr@C<sub>2v</sub>(9)-C<sub>82</sub> and an excess amount of **1** (ca. 30 fold) were dissolved in 50 mL toluene. The solution was degassed with argon for 20 minutes before it was irradiated with an ultra-high pressure mercury lamp (wavelength > 350 nm). The reaction was monitored with HPLC and the profiles are put in Fig. 1. Before irradiation, a strong peak corresponding to Pr@C<sub>2v</sub>(9)-C<sub>82</sub> appeared at 16.5 min. After the solution was irradiated for 10 minutes, new peaks corresponding to the monoadducts appeared at 11.4 min and 12.0 min, respectively. The content of adducts continued to increase upon irradiation. The reaction was terminated after 40-min-irradiation

when a small amount of bisadducts was formed. After concentration and filtration, preparative HPLC gave rise to two monoadduct isomers of Pr@C<sub>2v</sub>(9)-C<sub>82</sub>Ad (**2a** and **2b**) in a relative ratio of 4:1 (Fig. S1, ESI†).

MALDI-TOF mass spectrometric study concretely verifies the successful formation of 1:1 adducts. The mass spectrum of **2a** and **2b** are nearly identical (Figs. S2&S3, ESI†). Both display a single peak at m/z 1259, verifying the covalent attachment of the Ad moiety onto the fullerene cage. The isotropic distribution agrees perfectly with the calculated result of Pr@C<sub>82</sub>(C<sub>10</sub>H<sub>14</sub>) (insets in Fig. S2). Absence of any fragmentation peak reflects the high stability of the derivatives, even under laser irradiation.

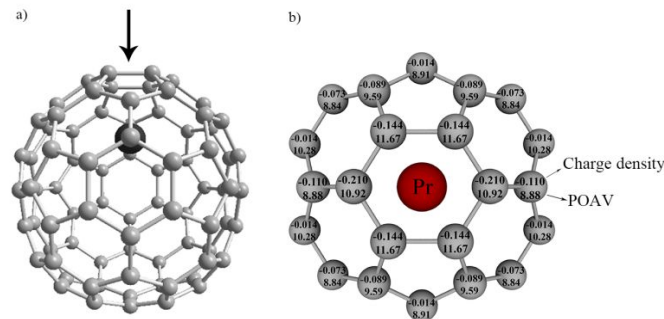
Although NMR spectroscopy is powerful to determine the cage structures of fullerenes/EMFs, it is hard to provide sufficient information about the structures of their derivatives because of the decrease in symmetry.<sup>11,12</sup> Another obstacle for direct NMR measurement is the paramagnetic property of some open-shell EMFs, like Pr@C<sub>2v</sub>(9)-C<sub>82</sub> under study. Accordingly, single crystal XRD crystallography is a better solution for the structures of EMFs and their derivatives. In present study, single crystallization was performed on the derivatives using an interfacial diffusion method. Finally, black single crystals of **2a** were obtained, and its molecular structure was accurately established by XRD crystallography.<sup>‡</sup>



**Fig. 2** Ortep drawing of **2a** showing thermal ellipsoids at the 50% probability level. Only the major cage orientation (0.34 occupancy) and the major metal site (0.88 occupancy) are shown. Solvent molecules, minor cage orientations and minor metal sites are omitted for clarity.

The asymmetric crystallographic unit falls into the triclinic P-1 space group which contains a whole molecule of **2a** featuring four disordered cage orientations linking to two disordered Ad moieties, respectively. From the drawings showing the disorders in the crystal structure of Pr@C<sub>82</sub>Ad (Fig. S4, ESI†) observed that the occupancy values for Pr1, Pr2, Pr4 and Pr8 are 0.88, 0.03, 0.03, 0.06, respectively. The populations for the disordered cage are a) 0.34, b) 0.20, c) 0.31, d) 0.15, respectively. Only two disordered positions are found for the Ad group, and their relative ratio is 0.85:0.15. In sharp contrast to those obtained for M@C<sub>82</sub>Ad (M = Y, La, Ce, and Gd), multiple metal sites are found in Pr@C<sub>82</sub>Ad. While in other cases, the metal atom is always fixed, being trapped inside the cavity provided by bond cleavage. Fig. 2 shows the X-ray structure of **2a** consisting of the major cage with the major metal site. The Ad group adds to a [6,6]-bond junction which is close to the encapsulated metal ion. The distance between the two cage carbons at the sites of addition is 2.105 Å, consistent with an open-cage structure. The metal atom is trapped inside the cavity provided by bond cleavage upon Ad cycloaddition. It is proved that the metal ions interact strongly with the cage carbons in EMFs and thus the properties of

the EMF molecules, especially the chemical behaviors of the cage carbons, depend strongly on the type, composition, and even location (motion) of the encapsulated metallic species.<sup>12</sup> Accordingly, the high regio-selectivity found in this reaction is believed to be a sequence of the strong Pr-cage carbon interactions.



**Fig. 3** (a) Optimized structure of Pr@C<sub>2v</sub>(9)-C<sub>82</sub> and (b) POAV and charge density values of selected cage carbons of Pr@C<sub>2v</sub>(9)-C<sub>82</sub>.

We performed DFT calculations to seek theoretical evidences. First of all, we obtained the optimized structure of Pr@C<sub>82</sub> (Fig. 3a). It is not surprising that the metal ion is located steadily beneath a hexagonal ring along the C<sub>2</sub>-symmetric axis of the cage (see the arrow in Fig. 3a), as previously found for other M@C<sub>82</sub> (M = Sc, Y, La, Ce, Gd) compounds. The calculated Mulliken charge of the metal ion is +2.36, indicating that the same amount of electron density has been transferred to the cage. As a geometrical consequence, the extra negative charges are mainly localized on these cage carbons adjacent to the Pr ion. In particular, as shown in Fig. 3b the cage carbons consisting of the hexagonal ring closest to the metal ion have the highest values of negative charges. In addition, the *p*-orbital axis vector (POAV) value is an index of the chemical reactivity of cage carbons of fullerenes. These cage carbons also have higher POAV values than the other cage carbons on Pr@C<sub>82</sub>. Accordingly, it is conclusive that adamantylidene carbene (**1**) selectively attacks the carbon atom with both the highest charge density and POAV value, when reacting with Pr@C<sub>82</sub>. Previous results have demonstrated that the metallic core is critical to the reactivity of the cage carbons. For instance, the M@C<sub>82</sub> (M = Y, La, Ce, Gd) compounds normally gave two isomers with **1**, whereas Sc@C<sub>82</sub> afforded four isomers. Our computational results clarified that the high regioselectivity of the reaction between Pr@C<sub>82</sub> and **1** comes from the dictation effect of the internal metal ion. In addition, the X-ray results of **2a** suggest that the most stable structure of Pr@C<sub>2v</sub>(9)-C<sub>82</sub> requires the metal ion being located steadily under the hexagonal carbon ring along the C<sub>2</sub>-axis of the cage in spite that multiple metal sites are observed.

The absorption spectra of **2a** and **2b** (Fig. S5, ESI†) largely resemble that of pristine Pr@C<sub>2v</sub>(9)-C<sub>82</sub>, all showing distinct absorption peaks at 390 nm, 640 nm and a broad band at 1020 nm. The onsets of all compounds are observed at 1560 nm, corresponding to a small optical bandgap (~0.8 eV). These results confirm again that the electronic structures of open-cage derivatives are normally similar to those of the pristine EMFs, because the  $\pi$ -electron conjugation of the C<sub>82</sub> cage is not changed significantly, despite the C-C bond cleavage due to the carbene addition.

The electrochemical properties of **2a** and **2b** are investigated with cyclic voltammetry. Both show one reversible oxidation step and three reduction reversible processes (Fig. S6, ESI†). In contrast, pristine Pr@C<sub>82</sub> exhibits one reversible oxidation step and four reduction processes along with one irreversible oxidation step.<sup>14</sup> In addition, the corresponding redox potentials of **2a** and **2b** are shifted

cathodically in comparison with the corresponding values of pristine Pr@C<sub>2v</sub>(9)-C<sub>82</sub> (Table 1), indicating an electron-donating ability of Ad.

**Table 1.** Redox potentials<sup>a</sup> (V vs. Fc/Fc<sup>+</sup>) of Pr@C<sub>2v</sub>(9)-C<sub>82</sub>, **2a** and **2b**.

Compound	<sup>ox</sup> E <sub>1</sub>	<sup>red</sup> E <sub>1</sub>	<sup>red</sup> E <sub>2</sub>	<sup>red</sup> E <sub>3</sub>
Pr@C <sub>2v</sub> (9)-C <sub>82</sub> <sup>b</sup>	0.07	-0.39	-1.35	-1.46
<b>2a</b>	0.00	-0.46	-1.47	-1.82
<b>2b</b>	0.00	-0.43	-1.40	-1.76

a. Half-wave potentials on a Pt-working electrode in 1,2-dichlorobenzene containing 0.1M (n-Bu<sub>4</sub>)NPF<sub>6</sub>. b. Ref. 14.

In summary, regioselective cycloaddition of admantylidene carbene (**1**) to Pr@C<sub>2v</sub>(9)-C<sub>82</sub> affords the first derivatives of praseodymium-containing metallofullerenes. Two monoadduct isomers (**2a** and **2b**) were obtained. X-ray crystallographic results of the major isomer **2a** confirm a [6,6]-open structure with multiple metal positions. Theoretical calculations reveal that the negative charges immigrated from the internal metal ion is anisotropically distributed on the cage surface, making one of the cage carbons, which is very close to the metal ion, much more reactive than others. Our study has shed new light on the chemical behaviors of mono-EMFs which are viewed as the simplest prototypes of EMFs. Thus the results will stimulate further investigation on the formation mechanism, the properties and potential applications of these hybrid materials.

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† Electronic Supplementary Information (ESI) available: Experimental details, HPLC, Mass spectra, Drawings showing crystal structure, Vis-NIR and CV spectra. See DOI: 10.1039/b000000x/

‡ Crystal data of a black plate of Pr@C<sub>82</sub>(C<sub>10</sub>H<sub>14</sub>)·2.5(CS<sub>2</sub>): C<sub>94.5</sub>H<sub>14.5</sub>S<sub>5</sub>Pr, FW = 1450.27, 0.67 × 0.22 × 0.13 mm, Monoclinic, *P*2<sub>1</sub>/*n*, *a* = 11.325(2) Å, *b* = 21.950(4) Å, *c* = 20.931(4) Å, *V* = 5100.8(16) Å<sup>3</sup>, *Z* = 4, ρ<sub>calc</sub> = 1.889 g cm<sup>-3</sup>, μ (Mo *K*α) = 1.228 mm<sup>-1</sup>, θ = 3.91–29.21°; *T* = 90 K; *R*<sub>1</sub> = 0.1398, *wR*<sub>2</sub> = 0.2700 for all data; *R*<sub>1</sub> = 0.1087, *wR*<sub>2</sub> = 0.2518 for 49841 reflections (*I* > 2.0 σ(*I*)) with 2692 parameters. Maximum residual electron density 3.000 e/Å<sup>-3</sup>.

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