The spin state of a charged non-IPR fullerene: the stable radical cation of $Sc_3N@C_{68}$†

Shangfeng Yang,*[a] Peter Rapta[ab] and Lothar Dunsch*[a]

Received (in Cambridge, UK) 24th July 2006, Accepted 29th September 2006
First published as an Advance Article on the web 24th October 2006
DOI: 10.1039/b610550e

***In-situ* ESR/UV-vis-NIR spectroelectrochemistry was implemented to probe the spin state of the radical cation of a non-IPR cluster-fullerene $Sc_3N@C_{68}$, which represents the first study on the stable paramagnetic cation of an endohedral fullerene.**

The success in preparing macroscopic quantities of endohedral fullerenes during the past decade has made it possible to characterize their structures and physical properties.[1–4] A great deal of recent interest has arisen on the electrochemistry of endohedral fullerenes which has been recognized as one of the most intriguing properties of endohedral fullerenes because electrochemical characterization could provide direct insight into the electronic structure of endohedral fullerenes.[5–7] In light of the first speculation that single-electron reduction might lead to a one-step valency change of the encapsulated ion of an endohedral fullerene,[8] an NMR study demonstrated that a one-step reduction of $La@C_{82}$ resulted in the formation of stable anions and indeed a diamagnetic closed shell spin system.[6] By means of electrochemical reduction which leads to the generation of the diamagnetic anion, the structures of some paramagnetic endohedral fullerenes could be determined.[9–11] Furthermore, electrochemical reduction of empty fullerenes and their derivatives have been extensively studied and the radical monoanions thus generated turn to be paramagnetic and hence ESR-active, which enables the anions to be accessible for various spectroscopic characterization including *in-situ* ESR/UV-vis-NIR spectroelectrochemistry, and in this way their interesting electronic structures could be revealed.[12–14] On the other hand, little attention has been paid to radical cations of empty fullerenes and endohedral fullerenes which could be generated by electrochemical oxidation. This is presumably because the cations thus generated are generally not as stable as the anions, as revealed in a few reports.[6,11] Besides the stability, there has not been any study on the electronic structure of the paramagnetic cations of endohedral fullerenes despite the fact that the valency change upon formation of cations are similar to that for the anions.

Among the trimetallic nitride endohedral fullerenes (cluster fullerenes),[3,7,15–20] $Sc_3N@C_{68}$ appears unique since it has a non-IPR D_3 (isomer 6140) cage,[15,16,19,20] while up to now only very limited spectroscopic data on it had been reported.[16,19,20] Specifically, the electrochemical properties of $Sc_3N@C_{68}$ has remained unstudied despite its importance. Based on the facile route for high-yield synthesis of $Sc_3N@C_{68}$ which we established very recently,[19] we report here the electrochemical study of $Sc_3N@C_{68}$ with focus on the *in-situ* ESR/UV-vis-NIR spectroelectrochemistry of its oxidation.

The synthesis and structural determination of $Sc_3N@C_{68}$ was previously described elsewhere.[19] For a typical electrochemical and spectroelectrochemical study, $Sc_3N@C_{68}$ dissolved in toluene was dried, transported to a glovebox (oxygen and water content below 1 ppm), and immediately redissolved in 1,2-dichlorobenzene (*o*-DCB, anhydrous, 99%, Aldrich) with the concentration ranging from 1×10^{-4} to 5×10^{-4} mol L^{-1}. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Fluka, dried under reduced pressure at 340 K for 24 h prior to use) was then added as the supporting electrolyte at a concentration of 0.2 mol L^{-1}. The cyclic voltammograms were obtained in a glovebox with a PAR 273 potentiostat (EG&G, US) in a three-electrode system using platinum wires as working and counter electrodes and a silver wire as a pseudo-reference electrode. Ferrocene (Fc) was added as the internal standard after each measurement and all potentials are referred to the Fc/Fc^+ couple. A PG 284 potentiostat (HEKA, Germany) was used as electrochemical equipment in the *in-situ* ESR/UV-vis-NIR spectroelectrochemical studies.[12–14] ESR spectra were recorded by the EMX X-Band ESR spectrometer (Bruker, Germany), and optical spectra were obtained on a UV-Vis-NIR spectrometer system TIDAS (J&M, Aalen, Germany).

Fig. 1 shows the cyclic voltammograms of $Sc_3N@C_{68}$ in *o*-DCB/$TBAPF_6$ performed in both the cathodic (curve b) and anodic (curve c) potential regions. The cyclic voltammogram of $Sc_3N@C_{68}$ (curve a) exhibits two electrochemically irreversible but chemically reversible reduction steps similar to the reduction steps of $Dy_3N@C_{80}$ (I, I_h),[7] for which a double-square reaction scheme was proposed to explain the observed redox reaction behavior, involving the charge-induced reversible rearrangement of the $Dy_3N@C_{80}$ monoanion.[7] In contrast to the reduction step, in the anodic potential region two reversible oxidation steps are observed for $Sc_3N@C_{68}$ at a scan rate of 100 mV s^{-1}, suggesting the formation of the stable monocation and dication. The redox potentials of $Sc_3N@C_{68}$ and $Sc_3N@C_{80}$ (I_h) are compared in ESI† (Table S1).[17,21,22] The first reduction potential ($E_{1/2}$, red(1)) of

---

[a] *Group of Electrochemistry and Conducting Polymers, Leibniz-Institute for Solid State and Materials Research (IFW) Dresden, D-01171, Dresden, Germany. E-mail: s.yang@ifw-dresden.de; l.dunsch@ifw-dresden.de; Fax: +49(351)4659 745; +49(351)4659 811; Tel: +49(351)4659 713; +49(351)4659 660*
[b] *Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinskeho 9, 81237, Bratislava, Slovak Republic*

† Electronic supplementary information (ESI) available: Table S1: Redox potentials and electrochemical energy gap of $Sc_3N@C_{68}$ in comparison with the data of $Sc_3N@C_{80}$ (I_h); Fig. S1: *In-situ* spectro-cyclovoltammogram of $Sc_3N@C_{68}$: (a) UV-Vis-NIR spectra recorded in the potential range −0.2 to 0.8 V *vs.* Fc/Fc^+; (b) UV-Vis-NIR spectrum of $Sc_3N@C_{68}$ recorded before and after the CV scan. See DOI: 10.1039/b610550e

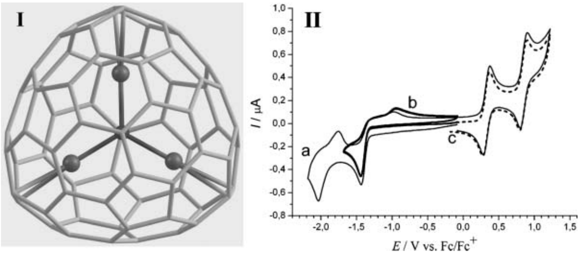

Fig. 1 I: Schematic structure of $Sc_3N@C_{68}$ along the C_3 axis. The central atom is N and the others are Sc_3. II: Cyclic voltammograms (CV) of $Sc_3N@C_{68}$ in $TBAPF_6$–*o*-DCB solution. (a) CV taken for both cathodic and anodic region; (b) redox cycling in the range of the first reduction step (two consecutive scans are shown); (c) CV taken only in anodic part (dotted line). Scan rate: 100 mV s^{-1}.

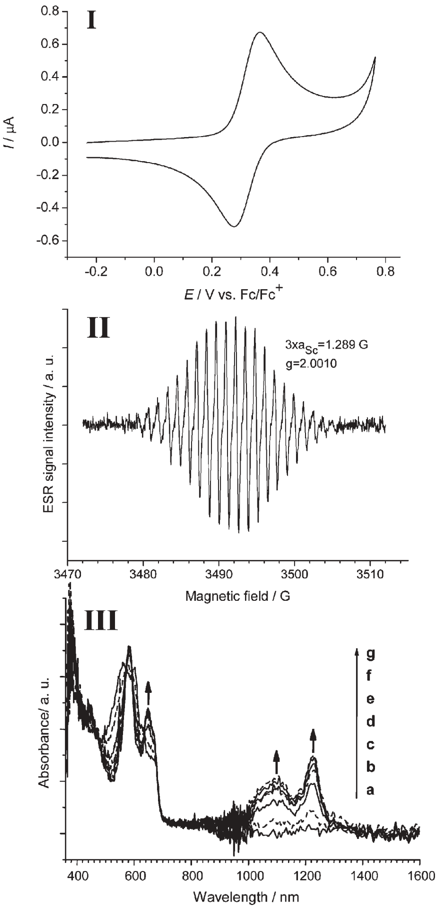

Fig. 2 I: Voltammogram of $Sc_3N@C_{68}$ in $TBABF_4$–*o*-DCB in the oxidation range. Scan rate: 3 mV s^{-1}. II: Representative ESR spectrum of $[Sc_3N@C_{68}]^{+\bullet}$ observed in the *in-situ* oxidation in $TBAPF_6$–*o*-DCB at the first oxidation peak and room temperature (inset: simulation parameters estimated using the SimFonia package). III: UV-vis-NIR spectra of $[Sc_3N@C_{68}]^{+\bullet}$ simultaneously taken in the forward scan at a potential of 0.17 V (a); 0.27 V (b); 0.37 V (c); 0.47 V (d); 0.57 V (e); 0.67 V (f); 0.77 V (g).

$Sc_3N@C_{68}$ is slightly more negative than that of $Sc_3N@C_{80}$, suggesting a weaker electron accepting ability. On the other hand, the first oxidation potential ($E_{1/2}$, ox(1)) of $Sc_3N@C_{68}$ is much lower than that of $Sc_3N@C_{80}$ (I_h), clearly indicating that $Sc_3N@C_{68}$ has a stronger electron donating ability compared to $Sc_3N@C_{80}$ (I_h). Due to such a significant difference on the first oxidation potential, the electrochemical energy gap ($\Delta E_{gap,ec}$) of $Sc_3N@C_{68}$, which is obtained as the difference between the formal potential of the first oxidation step and the formal potential of the first reduction step, is dramatically smaller than that of $Sc_3N@C_{80}$ (I_h) (see ESI,† Table S1). The fact that $Sc_3N@C_{68}$ has a smaller energy gap compared to $Sc_3N@C_{80}$ (I_h) is consistent with the results obtained for their optical energy gaps, which is 1.1 and 1.7 eV for $Sc_3N@C_{68}$ and $Sc_3N@C_{80}$ (I_h),[17,19] respectively, as determined previously by UV-Vis-NIR spectroscopy.

A noteworthy feature of the cyclic voltammogram of $Sc_3N@C_{68}$ is that the two oxidation steps are electrochemically reversible even at a very slow scan rate such as 3 mV s^{-1} (Fig. 2, I). An intriguing goal is then to characterize the charged states formed in the oxidation. To this purpose, *in-situ* ESR/UV-vis-NIR spectroelectrochemistry, which is established by incorporating the *in-situ* ESR/UV-vis-NIR spectroscopy into the cyclic voltammetric measurement, appears to be the ideal avenue as demonstrated previously by our group.[12–14] Upon oxidation of $Sc_3N@C_{68}$ which is ESR-silent, the generation of the stable radical monocation $[Sc_3N@C_{68}]^{+\bullet}$ is clearly identified by *in-situ* ESR spectroscopy as illustrated in Fig. 2, II, which shows an ESR pattern of 22 lines, indicating three equivalent Sc hyperfine splittings of 1.289 G. No observable N nucleus hyperfine splitting was detected at the experimental conditions used. Simultaneously, the generation of the stable radical cation $[Sc_3N@C_{68}]^{+\bullet}$ is evidenced by *in-situ* UV-vis-NIR spectroscopy, which demonstrates the rise of new NIR absorption bands with maxima at 1100 and 1226 nm (Fig. 2, III). In the voltammetric forward scan the intensities of both new NIR absorption bands, which are absent in the spectrum of the pristine $Sc_3N@C_{68}$,[19] increase with the increase of the applied electrode potential from −0.23 to 0.77 V *vs.* Fc/Fc^+. Interestingly, the electronic absorption spectrum of $[Sc_3N@C_{68}]^{+\bullet}$ studied in the present work seems to resemble the reported cations of the conventional endohedral metallofullerenes $M@C_{82}$ (M = La, Ce, Y) in terms of the characteristic NIR absorptions (*ca.* 1090 and 1270 nm for $[La@C_{82}]^+SbCl_6^-$, 1000 and 1290 nm for $[Y@C_{82}]^+$),[11,23] implying their similarities on the HOMO levels although both the HOMO and LUMO of the pristine $Sc_3N@C_{68}$ appear to be quite different to the conventional metallofullerenes $M@C_{82}$ (M = La, Ce, Y), as concluded according to the strong difference on the electronic absorption spectrum between the pristine $Sc_3N@C_{68}$ and $M@C_{82}$.[1,2,11,19,23]

The dependence of the intensity of both the ESR signal and the absorbance at 1226 nm on the electrode potential (see the corresponding cyclic voltammogram in Fig. 2, I) gives a fairly good coincidence for both the forward and back scans as presented in Fig. 3. Hence, the observed ESR signal as well as the new NIR bands arising in the forward scan can be unambiguously assigned to $[Sc_3N@C_{68}]^{+\bullet}$. The same conclusion could be made based on the results obtained in the back scan (see Fig. 3) where additionally a quantitative recovery of the initial optical spectrum was observed, confirming the stability of the radical cation (see ESI†).

Table 1 compares the ESR parameters calculated for $[Sc_3N@C_{68}]^{+\bullet}$ with the previous ESR results for trimetallic nitride cluster fullerenes which were limited to the radical anions of $Sc_3N@C_{80}$ (I_h) and a pyrrolidine adduct of $Y_3N@C_{80}$

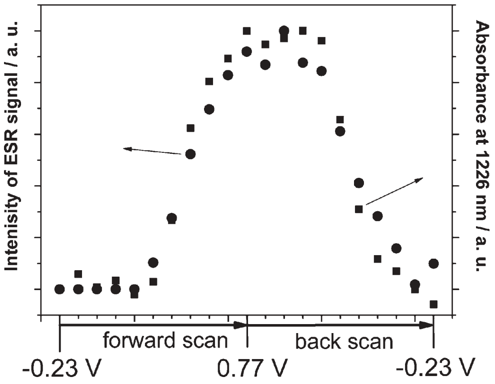

Fig. 3 Relative intensity of the ESR signal (●) and NIR absorbance at 1226 nm (■) of $[Sc_3N@C_{68}]^{+\bullet}$ at different electrode potentials.

Table 1 Scandium isotropic hyperfine splittings (a_{Sc}) and *g*-values of different nitride cluster-fullerenes

Sample	Charge state	a_{Sc}/G	*g*-Value	Ref.
$Sc_3N@C_{68}$	Monocation	1.289	2.0010	This work
$Sc_3N@C_{800}$ (I_h)	Monoanion	55.6	—	24
$Y_3N@C_{80}C_4H_9N$	Monoanion	1.25; 6.26	1.9989	25

$(Y_3N@C_{80}C_4H_9N)$.[24,25] For $[Sc_3N@C_{68}]^{+\bullet}$ we observed very narrow lines and small hyperfine splittings (1.289 G) originating from the encaged cluster. Such a feature is similar to the ESR results of the monoanion of $Y_3N@C_{80}C_4H_9N$ ($[Y_3N@C_{80}C_4H_9N]^{-\bullet}$), for which splittings of 1.25 and 6.26 G and a *g*-value of 1.9989 were reported.[25] On the other hand, based on the large Sc hyperfine splitting of 55.6 G observed in the ESR spectra of the radical anion of $Sc_3N@C_{80}$ ($[Sc_3N@C_{80}]^{-\bullet}$), the exclusive spin localization in the cluster of Sc_3N was proposed.[24] In this sense, however, no exclusive spin distribution on the internal cluster of Y_3N was concluded for $[Y_3N@C_{80}C_4H_9N]^{-\bullet}$ since the splitting of two pairs of hydrogen atoms originated from the side group bound to the cage were observed in the ESR spectra.[25] The analysis of the ESR results obtained for $[Sc_3N@C_{68}]^{+\bullet}$ and literature data discussed above allow us to conclude that the spin density in $[Sc_3N@C_{68}]^{+\bullet}$ is delocalised both on the carbon cage and on the internal cluster of Sc_3N. Indeed, the *g*-value of 2.0010 indicates clearly the strong participation of the carbon cage on the spin delocalisation in $[Sc_3N@C_{68}]^{+\bullet}$. According to the strong correlation of the HOMO with the oxidation potential of the molecule, these results indicate that the HOMO of $Sc_3N@C_{68}$ is not exclusively confined to the internal cluster of Sc_3N and the large part of the unpaired spin is symmetrically delocalised on the carbon cage.

In conclusion, for the first time we have generated the stable radical cation of the non-IPR clusterfullerene $Sc_3N@C_{68}$, $[Sc_3N@C_{68}]^{+\bullet}$, as confirmed by *in-situ* ESR/UV-vis-NIR spectro-electrochemistry. The spin state of such radical cations is probed, indicating the spin density in $[Sc_3N@C_{68}]^{+\bullet}$ is delocalised both on the carbon cage and on the internal cluster of Sc_3N. The magnetic behaviour of the radical cation of $Sc_3N@C_{68}$ studied in the present work appears to be quite different to that of the corresponding anion for which a more complicated redox behavior was found. The detailed spectroelectrochemical studies on the anion of $Sc_3N@C_{68}$ are currently underway in our group.

We cordially thank Ms S. Schiemenz, Ms K. Leger, Mr F. Ziegs and Mrs H. Zöller for technical assistances. S. Y. and P. R. thank the Alexander von Humboldt (AvH) Foundation for financial support. The support of SGA VEGA 1/3579/06 to P. R. is also acknowledged.

Notes and references

1 H. Shinohara, *Rep. Prog. Phys.*, 2000, **63**, 843.
2 *Endofullerenes: A New Family of Carbon Cluster* ed. T. Akasaka and S. Nagase, Kluwer Academic Publishers, Dordrecht, 2002.
3 L. Dunsch, M. Krause, J. Noack and P. Georgi, *J. Phys. Chem. Solids*, 2004, **65**, 309.
4 S. F. Yang and L. Dunsch, *Angew. Chem., Int. Ed.*, 2006, **45**, 1299.
5 T. Akasaka, S. Nagase, K. Kobayashi, M. Walchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshito and T. Erata, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1643.
6 T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, R. Nagahata, X. Gao, E. Van Caemelbecke and K. M. Kadish, *J. Am. Chem. Soc.*, 2000, **122**, 9316.
7 S. F. Yang, M. Zalibera, P. Rapta and L. Dunsch, *Chem. Eur. J.*, 2006, **12**, 7848.
8 L. Dunsch, P. Kuran and M. Krause in *Electronic Properties of Novel Materials: Progress in Molecular Nanostructures*, ed. H. Kuzmany, J. Fink, M. Mehring and S. Roth, AIP Conference Proceedings 442, Woodbury, 1998.
9 T. Wakahara, J. Kobayashi, M. Yamada, Y. Maeda, T. Tsuchiya, M. Okamura, T. Akasaka, M. Waelchli, K. Kobayashi, S. Nagase, T. Kato, M. Kako, K. Yamamoto and K. M. Kadish, *J. Am. Chem. Soc.*, 2004, **126**, 4883.
10 M. Yamada, T. Wakahara, Y. Lian, T. Tsuchiya, T. Akasaka, M. Waelchli, N. Mizorogi, S. Nagase and K. M. Kadish, *J. Am. Chem. Soc.*, 2006, **128**, 1400.
11 L. Feng, T. Wakahara, T. Tsuchiya, Y. Maeda, Y. Lian, T. Akasaka, N. Mizorogi, K. Kobayashi, S. Nagase and K. M. Kadish, *Chem. Phys. Lett.*, 2005, **405**, 274.
12 P. Rapta, A. Bartl, A. Gromov, A. Stasko and L. Dunsch, *ChemPhysChem*, 2002, **3**, 351.
13 L. Dunsch, P. Rapta, A. Gromov and A. Stasko, *J. Electroanal. Chem.*, 2003, **547**, 35.
14 L. Dunsch, F. Ziegs, C. Siedschlag and J. Mattey, *Chem. Eur. J.*, 2000, **6**, 3547.
15 For a recent review, see: L. Dunsch and S. Yang, *Small*, in preparation.
16 S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible and H. C. Dorn, *Nature*, 2000, **408**, 427.
17 M. Krause and L. Dunsch, *ChemPhysChem*, 2004, **5**, 1445.
18 (*a*) S. F. Yang and L. Dunsch, *J. Phys. Chem. B*, 2005, **109**, 12320; (*b*) S. F. Yang and L. Dunsch, *Chem. Eur. J.*, 2006, **12**, 413.
19 S. F. Yang, M. Kalbac, A. Popov and L. Dunsch, *Chem. Eur. J.*, 2006, **12**, 7856.
20 M. M. Olmstead, H. M. Lee, J. C Duchamp, S. Stevenson, D. Marciu, H. C. Dorn and A. L. Balch, *Angew. Chem., Int. Ed.*, 2003, **42**, 900.
21 B. Elliott, L. Yu and L. Echegoyen, *J. Am. Chem. Soc.*, 2005, **127**, 10885.
22 Y. Iiduka, O. Ikenaga, A. Sakuraba, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Nakahodo, T. Akasaka, M. Kako, N. Mizorogi and S. Nagase, *J. Am. Chem. Soc.*, 2005, **127**, 9956.
23 Y. Maeda, J. Miyashita, T. Hasegawa, T. Wakahara, T. Tsuchiya, L. Feng, Y. Lian, T. Akasaka, K. Kobayashi, S. Nagase, M. Kako, K. Yamamoto and M. Kadish, *J. Am. Chem. Soc.*, 2005, **127**, 2143.
24 P. Jakes and K.-P. Dinse, *J. Am. Chem. Soc.*, 2001, **123**, 8854.
25 L. Echegoyen, C. J. Chancellor, M. M. Cardona, B. Elliott, J. Rivera, M. M. Olmstead and A. L. Balch, *Chem. Commun.*, 2006, 2653.