

# Chemical oxidation of endohedral metallofullerenes: identification and separation of distinct classes†

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**Chemical oxidation is useful for solubilizing and separating endohedral metallofullerenes, as demonstrated here by a separation of three categories of Gd@C<sub>2n</sub> species and by the solubilization of Tm@C<sub>60</sub><sup>+</sup> and Tm@C<sub>70</sub><sup>+</sup> for the first time.**

Investigations on the properties of endohedral metallofullerenes have often focused on soluble M@C<sub>82</sub> and related species in spite of the fact that they make up only a fraction of the metallofullerenes produced by the arc method.<sup>1</sup> With their solubility in common solvents, M@C<sub>82</sub> can be extracted and separated by chromatography from the much more numerous empty fullerenes and the insoluble endohedral fullerenes. Many endohedrals besides M@C<sub>82</sub> species are formed in the arc process. Working with anaerobically sublimed arc-produced Gd@C<sub>2n</sub>, Diener and Alford noted that soluble Gd@C<sub>82</sub> comprised only *ca.* 4% of the total sublimable Gd@C<sub>2n</sub>.<sup>2</sup> The remaining insolubles include a dominant M@C<sub>60</sub> fraction; of these, Gd@C<sub>60</sub> has been solubilized by electroreduction<sup>2</sup> and various M@C<sub>60</sub> have been solubilized by reactive amine solvents such as aniline and pyridine.<sup>3,4,5</sup> Here we report for the first time chemical oxidation-based procedures to identify and separate new classes of endohedral metallofullerenes that broaden the accessible repertoire of metallofullerenes generated by the arc method.

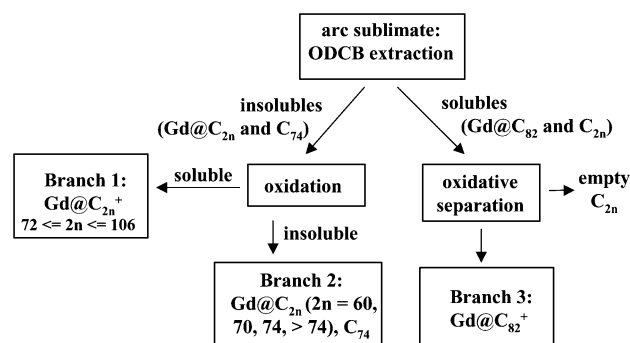
The redox chemistry of empty C<sub>2n</sub> fullerenes is dominated by addition of electrons to form fullerides, while conversely, C<sub>2n</sub> are difficult to oxidize.<sup>6,7</sup> In contrast, endohedral metallofullerene molecules may be expected to oxidize more easily than their empty fullerene counterparts because their interior metals donate electrons to cage-centered orbitals. With soluble M@C<sub>82</sub> species, electrochemical measurements revealed multiple reductions and unlike most C<sub>2n</sub>, these endohedrals also have reversible one-electron oxidations at relatively low potentials. For example, various M@C<sub>82</sub> display reversible one-electron oxidations at *ca.* +0.1 V, as measured by cyclic voltammetry.<sup>1,8</sup> Akasaka *et al.* reported electrochemical synthesis of stable solutions of M@C<sub>82</sub><sup>-</sup> (M = La, Pr) and electrochemical oxidation of M@C<sub>82</sub> species to mono-cations of reportedly lower stability.<sup>9</sup> Following the isolation of fullerene salts of C<sub>76</sub><sup>+</sup> and C<sub>60</sub><sup>+</sup> (with non-reactive anions and the exclusion of nucleophiles)<sup>10</sup> and the much lower first oxidation potentials of M@C<sub>82</sub>, we explored the chemical oxidation of the sublimable arc-generated metallofullerenes containing both trivalent and divalent lanthanide metals.

Trivalent-metal containing Gd@C<sub>2n</sub> fullerenes were investigated first. Gd@C<sub>2n</sub> containing fullerene soot was produced by standard procedures, followed by anaerobic sublimation to liberate the C<sub>2n</sub> and Gd@C<sub>2n</sub> fullerenes from the soot.<sup>2†</sup> The sublimate was anaerobically extracted with *o*-dichlorobenzene (ODCB). Soluble fullerenes, including C<sub>2n</sub>, Gd@C<sub>82</sub> and small amounts of other Gd@C<sub>2n</sub>, are thus separated from the insoluble fullerenes, which are dominated by certain Gd@C<sub>2n</sub> and the small-bandgap fullerene C<sub>74</sub>. This extraction and the oxidative

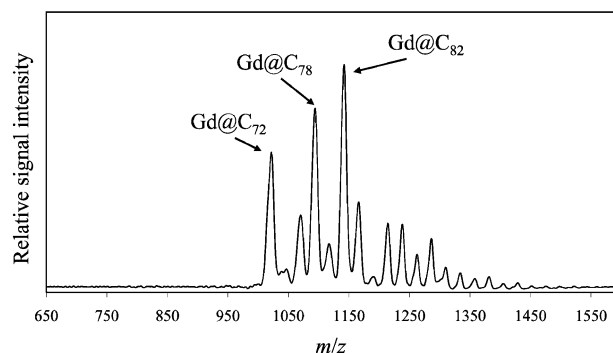
treatments described below reveal at least three separable categories or “branches” of Gd@C<sub>2n</sub> with differing properties (Scheme 1).

A first branch consists of a readily oxidizable Gd@C<sub>2n</sub> class (2n ≥ 72). This branch of metallofullerenes is extractable from the ODCB insoluble Gd@C<sub>2n</sub> mixture by treatment with mild oxidants in CH<sub>2</sub>Cl<sub>2</sub>. A dark brown solution forms quickly containing now-soluble mixed Gd@C<sub>2n</sub><sup>+</sup> species, from which solid salts (see the laser-desorption time-of-flight (LD-TOF) mass spectrum in Fig. 1) can be precipitated by hexane addition. Useful oxidants include Ag<sup>+</sup> salts (as PF<sub>6</sub><sup>-</sup>, SbCl<sub>6</sub><sup>-</sup>, *etc.*) but the Ag<sub>(s)</sub> reduction by-product is mixed in with the remaining insoluble Gd@C<sub>60</sub> material. More convenient is tris(4-bromophenyl)aminium hexachloroantimonate, the reduction by-product of which is organic soluble. Interestingly, the Gd@C<sub>2n</sub><sup>+</sup> material contains Gd@C<sub>82</sub>, possibly as oxidizable cage isomer(s) distinct from the ODCB-soluble Gd@C<sub>82</sub> isomers or as soluble isomer(s) released from entrapment in the matrix of insoluble Gd@C<sub>2n</sub> during the oxidative treatment. Solutions of Gd@C<sub>2n</sub><sup>+</sup> with weakly coordinating anions appear to be stable over at least several days when reductants and nucleophiles are excluded.

After the above mild oxidative treatment a second branch of Gd@C<sub>2n</sub> remains behind, an insoluble Gd@C<sub>60</sub> fraction that also contains C<sub>74</sub>. Treatment of these insolubles with stronger



**Scheme 1** Process flowchart for the separation of three branches of Gd@C<sub>2n</sub> from sublimable fullerenes.



**Fig. 1** LD-TOF mass spectrum of the readily oxidizable fraction of Gd@C<sub>2n</sub>, 2n ≥ 72 (Branch 1, Scheme 1).

† Electronic supplementary information (ESI) available: identification and separation of different classes. See <http://www.rsc.org/suppdata/cc/b3/b301565c/>

oxidants such as excess  $\text{AlCl}_3$  in ODCB extracts additional fullerenes as a dark brown solution. Filtration and rinsing with  $\text{CH}_2\text{Cl}_2$  and hexanes produces a solid material dominated by  $\text{Gd@C}_{60}$ ,  $\text{Gd@C}_{70}$  and  $\text{Gd@C}_{74}$  that is *ca.* 50% depleted in  $\text{C}_{74}$  relative to the starting solids. Mass spectra also reveal decreased quantities of  $\text{Gd@C}_{2n}$  ( $2n \geq 72$ ), particularly  $\text{Gd@C}_{74}$  (see ESI†). Over 500 mg of this enriched  $\text{Gd@C}_{60}$  fraction can be obtained from *ca.* 2.5 g of arc-generated sublimate. Further work will improve this process and characterize the nature of the fullerene products solubilized by  $\text{AlCl}_3$  extraction. This anaerobic process generates a  $\text{M@C}_{60}$  fraction that is largely depleted of  $\text{C}_{2n}$ .

A third branch of  $\text{Gd@C}_{2n}$  dominated by soluble  $\text{Gd@C}_{82}$  isomers resides in the original ODCB-soluble portion along with soluble  $\text{C}_{2n}$  such as  $\text{C}_{60}$ . Selective oxidation of  $\text{Gd@C}_{82}$ , exploiting the *ca.* 1 V difference in the oxidation potential of  $\text{Gd@C}_{82}$  and  $\text{C}_{60}$ , affords a chemical redox-based method for separating  $\text{M@C}_{82}$  from the abundant soluble  $\text{C}_{2n}$  (see ESI†). In bulk, we suggest this process as a useful “pre-enrichment” prior to conventional HPLC for generating larger quantities of ultrapure  $\text{M@C}_{82}$ . Preliminary tests of the processes in Scheme 1 on other trivalent metal-containing  $\text{M@C}_{2n}$  ( $\text{M} = \text{La}, \text{Y}$ ) achieved results similar to those obtained with  $\text{Gd@C}_{2n}$ .

Several lanthanide  $\text{M@C}_{2n}$  ( $\text{M} = \text{Sm}, \text{Eu}, \text{Tm}, \text{Yb}$ ) are reported to contain metals donating two electrons to the fullerene cage, with properties differing from corresponding trivalent-metal  $\text{M@C}_{2n}$  species.<sup>1,11–13</sup> We find the oxidation behavior of  $\text{Tm@C}_{2n}$  species also differs from the trivalent lanthanide-containing  $\text{M@C}_{2n}$  such as  $\text{Gd@C}_{2n}$ .  $\text{Tm@C}_{2n}$  containing arc-sublimate (pre-extracted with ODCB to remove most soluble  $\text{C}_{2n}$  and  $\text{Tm@C}_{2n}$ ) was treated with excess  $\text{AgPF}_6$  in ODCB. The resulting dark brown solution contained soluble cationic  $\text{Tm@C}_{2n}$  species, including most unexpectedly  $\text{Tm@C}_{60}^+$  and  $\text{Tm@C}_{70}^+$ , in contrast to the results seen above with  $\text{Gd@C}_{2n}$ . The mass spectrum of hexane-precipitated  $\text{Tm@C}_{2n}^+$  solid salt is shown in Fig. 2. We note that the oxidation dissolves only a portion of the ODCB-insoluble  $\text{Tm@C}_{2n}$  sublimate; possibly there are other  $\text{Tm@C}_{2n}$  structures with higher oxidation potentials and/or their intermolecular polymerization is more difficult to surmount.

The natures of the metallofullerene oxidations shown above are of particular interest. Among trivalent metal containing  $\text{M@C}_{2n}$ , the first oxidations involve the removal of the unpaired cage electron, as first proposed for  $\text{M@C}_{82}$ ,<sup>1,8</sup> with the different cage sizes (and structures) controlling the oxidation potentials. The first oxidation of the divalent metal containing  $\text{Tm@C}_{2n}$  may have different origins. A tentative explanation is that it is metal-centered, with conversion of  $\text{Tm}^{2+}$  to  $\text{Tm}^{3+}$ . Future studies will investigate this possibility with  $\text{Tm}$  and the other divalent lanthanide-containing  $\text{M@C}_{2n}$ . The extant complexity of the chemical properties of the different classes of  $\text{M@C}_{2n}$  species (with respect to metal and cage identities) is enriched by the study of their chemical oxidation.

In summary, chemical oxidation allows separation of at least three distinct classes of trivalent-metal containing  $\text{M@C}_{2n}$ ,

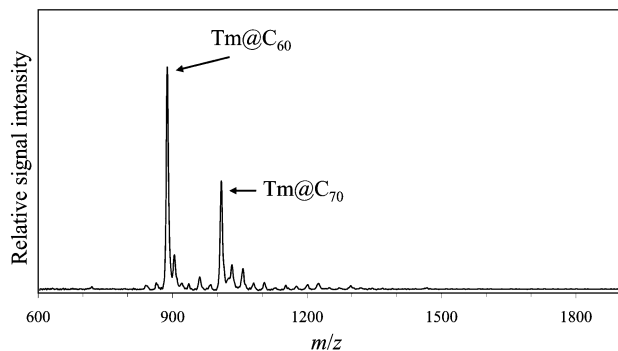


Fig. 2 LD-TOF mass spectrum of the oxidizable fraction of  $\text{Tm@C}_{2n}$ .

including  $\text{M@C}_{60}$  without using coordinating and potentially reactive amine solvents. Intriguingly, divalent metal-containing  $\text{Tm@C}_{60}$  and  $\text{Tm@C}_{70}$ , etc. are readily oxidized to *soluble* cations. Selective tuning of oxidation reagent potentials may allow separation of specific  $\text{M@C}_{2n}$  species from complex mixtures and the isolation of  $\text{M@C}_{2n}$  with unique cage and electronic structures. The rich oxidation chemistry revealed here expands the accessible realm of endohedral metallofullerenes beyond those previously studied. Increased access to this expanded variety, which previously has gone essentially unused, enhances prospects for using metallofullerenes such as  $\text{M@C}_{60}$  in medicinal applications<sup>14</sup> and may aid further exploration of their intriguing properties (*cf.* evidence for metallic behavior of  $\text{La@C}_{60}$ <sup>15</sup> and light emission by  $\text{Er@C}_{60}$ <sup>16</sup>).

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## Notes and references

† Sublimation of the arc-produced soot was performed inside the quartz arc chamber at 750 °C and 1 mTorr onto a cold finger, which was brought into an argon-filled glove box without atmospheric exposure at any point. The ODCB extraction was performed by a Soxhlet-style extractor operating at 100 °C and 40 Torr inside of the glove box until the washings were colorless. See ESI for more details.†  $E^\circ$  are quoted vs the ferrocene/ferrocenium couple = 0.0 V.

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