Supplementary Information

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

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General $Gd(NO_3)_3 \bullet 6H_2O$ and $Tm(NO_3)_3 \bullet 6H_2O$ (each 99.9%) were purchased from Strem Chemicals and used as received. All other chemicals were purchased from Sigma-Aldrich and used as received. Solvents were distilled and dried under inert atmosphere according to standard procedures. Inert atmosphere manipulations were conducted inside a Vacuum Atmospheres glovebox under argon (O_2, H_2O < 5 ppm). Mass spectrometry was performed with a custom built laser-desorption combination linear and reflectron time-of-flight mass spectrometer. UV-Vis-NIR spectra were recorded using a Perkin-Elmer Lambda 19 spectrometer.

Arc Fullerene Production of Mixed C_{2n}/Gd@C_{2n}. Gd_2O_3 impregnated graphite rods (1/4" diameter Poco Graphite, 40% porosity) doped to a level of ca. 1% Gd were produced according to published procedures (D. W. Cagle, T. P. Thrash, M. Alford, L. P. F. Chibante, G. J. Ehrhardt and L. J. Wilson, *J. Am. Chem. Soc.*, 1996, **118**, 8043). The graphite rods were first evacuated (~ 1 Torr) then soaked in a saturated absolute ethanolic solution of $Gd(NO_3)_3 \bullet 6H_2O$ for 30 min. The solution-saturated rods were air dried and then heated in a quartz furnace at ca. 850°C under vacuum for 3 hours, converting the metal nitrate to the oxide. Gd-containing fullerene soot was generated by the standard direct current (DC) arc-discharge of Gd_2O_3-impregnated 6" graphite rods (ca. 7.75 g per rod) using a custom-built arc apparatus, operating at 150 Torr of helium. Cathode deposit "back-burning" (reverse-polarity arcing) was employed to maximize the yield of fullerenes and metallofullerenes. This consists of periodically briefly reversing the arc polarity so as to arc the solid deposits of material formed on the cathode (relative to the original polarity). Anaerobic sublimation of the raw arc-produced soot onto an isolated, water-cooled cold finger inside of the arc chamber at 750°C separated the fullerenes (a mixture of soluble and insoluble empty fullerenes and Gd@C_{2n} endohedral metallofullerenes) from the non-fullerene carbon soot. Approximately 2.5 g of sublimed fullerenes (the "sublimate") per ten-rod arc run was obtained. Tm@C_{2n} material was arc-generated in a similar fashion.

Separation of the Gd@C_{60} fraction. The sublimable Gd@C_{2n} species have been identified as belonging to at least three distinct classes and separated according to the processes outlined in Scheme 1. Anaerobically collected sublimate, approximately 2.5 g per ten rod arc run (with Gd-impregnated rods) was exhaustively extracted with *o*-dichlorobenzene inside of a glovebox using a continuous-cycling Soxhlet extractor operating at 40 torr and 100ºC, until the washings were almost colorless. This removed essentially all of the dissolvable soluble fullerenes, including C_{60}, C_{70}, etc. and soluble Gd@C_{82}, which were saved for separation of the Gd@C_{82}. The Gd@C_{60} class of endohedral fullerenes, other Gd@C_{2n} and the small-bandgap fullerene C_{74} dominates the remaining insoluble material.

Branch 1. Separation of the ODCB-insoluble oxidizable Gd@C_{2n} class ($2n \geq 72$). ODCB-rinsed insoluble material from above was suspended in CH_2Cl_2 with vigorous stirring. To this was added the oxidant tris(4-bromophenyl)aminium hexachoroantimonate (E^o ~ +0.7 V for tris(4-bromophenyl)amine, vs the Fc/Fc^+ couple) in dichloromethane with stirring, quickly forming a dark brown solution. Periodic measurement of the UV-Vis spectrum of this solution reveals the end point of oxidant addition by monitoring for the persistence of the absorbance of the aminium radical cation (λ_{max} = 730 nm), after which the reaction mixture is stirred for additional period (ca. 30 min). The solution is filtered with a 0.45µm PTFE syringe filter (setting aside the insolubles for use in the next step) and CH_2Cl_2 is removed under vacuum. The solids are then redissolved in ODCB and recrystallized by hexane addition; filtration isolates the mixed $[Gd@C_{2n}^+][SbCl_6^-]$ salts, $72 \leq 2n \leq 106$. Separable yields of salts of the $Gd@C_{2n}^+$ class ($72 \leq 2n \leq 106$) vary, and are on the order of tens of mg for oxidative extraction of 500 mg of ODCB-washed sublimate material. Alternatively, silver salts (e.g. Ag^+ salts of weakly coordinating anions, such as PF_6^-, $SbCl_6^-$, etc.) can be used as an oxidant, but the $Ag_{(s)}$ reduction by-product is then mixed into the insoluble Gd@C_{60} etc. material.

Branch 2. The ODCB-Insoluble Gd@C_{60} Class. The Gd@C_{60}-class of fullerenes remains insoluble in ODCB after the Soxhlet extraction and the above oxidative treatment; this material, in addition to Gd@C_{60}, Gd@C_{70}, Gd@C_{74} and small amounts of other Gd@C_{2n} ($2n > 72$) also contains the empty, small-bandgap fullerene C_{74} (along with small amounts of other misc. empty C_{2n}). Depletion of the empty small-bandgap fullerene C_{74} and other Gd@C_{2n} ($2n \geq 72$) from this material is accomplished by treatment with excess $AlCl_3$ (E^o approximately +1 V) in ODCB, producing a dark brown solution. The insolubles were collected by filtration, rinsed with ODCB and dichloromethane (to remove excess $AlCl_3$) followed by hexane rinsing, and then dried under vacuum. This process depleted the content of C_{74} by ca. 50% (see Fig. S1). The resulting material is composed of the Gd@C_{60}-dominated fraction of fullerenes, including chiefly Gd@C_{60} with smaller amounts of Gd@C_{70}, Gd@C_{74}, other higher Gd@C_{2n} and C_{74} (with negligible amounts of C_{60} and C_{70}, small amounts of which may be physically trapped in the solid matrix of insoluble Gd@C_{60}).

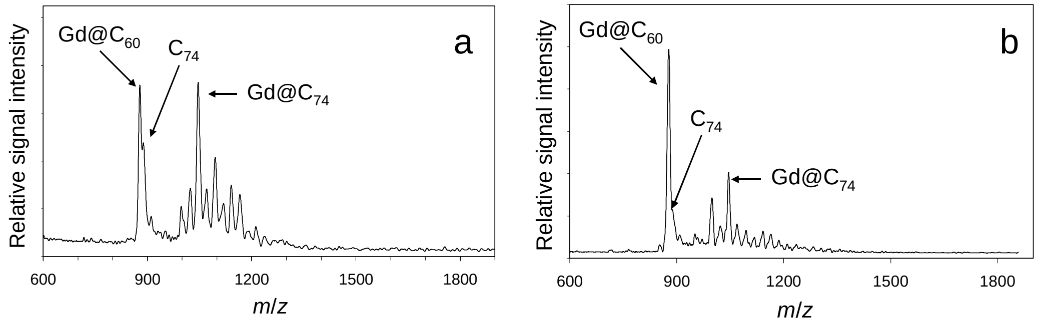

Fig. S1 (a) LD-TOF mass spectrum of the ODCB-insoluble Gd@C_{60} class prior to $AlCl_3$ treatment. **(b)** LD-TOF mass spectrum of the ODCB-insoluble Gd@C_{60} class after $AlCl_3$ treatment.

Branch 3. ODCB-Solubles: Oxidative Separation of Gd@C_{82} fraction from soluble empty C_{2n}. The ODCB solvent is removed from the soluble fullerenes under reduced pressure. The resulting solid mixture of fullerenes is dispersed in CH_2Cl_2, to which is added excess $AgSbF_6$. After stirring for ca. 2 hours, the solubles are filtered, and the CH_2Cl_2 is removed from the filtrate under reduced pressure. These solids (containing a mixture of [Gd@C_{82}^+][SbF_6^-] and traces of empty C_{2n} species) are stirred overnight with a 1:1 toluene:hexane mixture, filtered, rinsed with hexane and dried under reduced pressure. The near-infrared electronic spectrum of this Gd@C_{82}^+ material confirms its oxidized nature (λ_{max} = 1280 nm, ODCB solution), in agreement with previous measurements on electrochemically generated Ln@C_{82}^+ species. The mass spectrum of this material (Fig. S2) reveals small amounts of empty higher C_{2n} fullerenes and other Gd@C_{2n} species (likely also oxidized by the aminium oxidant) present in this non-chromatographed material. 10 mg of enriched Gd@C_{82}^+ material can be generated from 300 mg of starting material in this process. Optionally, the Gd@C_{82}^+ salt can be reduced with decamethylferrocene and recrystallized to generate enriched Gd@C_{82}.

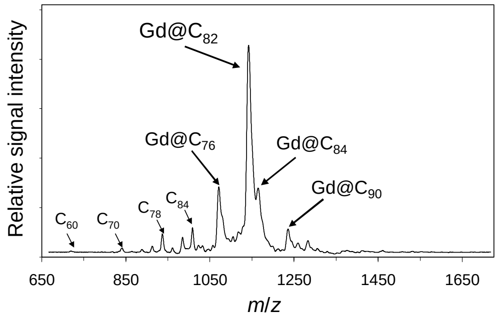

Fig. S2 LD-TOF mass spectrum of the oxidatively-separated Gd@C_{82}^+-dominated material.

Oxidizable Tm@C_{2n} Class. Tm@C_{2n}-containing fullerene sublimate was produced by the arc method and sublimed according to the procedure described for Gd@C_{2n} sublimate above. The sublimate was stirred in ODCB for several days (this removed most soluble C_{2n} and Tm@C_{2n}, etc.), after which the insolubles were filtered off and rinsed with hexane. The insolubles were treated with excess $AgPF_6$ in ODCB for 12 hours. The resulting dark brown solution was filtered with a 0.45μm PTFE syringe filter and added dropwise to stirring hexane, inducing immediate precipitation. This precipitate containing Tm@C_{60}^+ and Tm@C_{70}^+ was collected by filtration, rinsed with hexanes and dried under reduced pressure. The Ag^+ oxidation dissolves only a portion of the ODCB-insoluble Tm@C_{2n} sublimate (less than 50%, varying with conditions).