SUPPLEMENTARY INFORMATION

Classification of carbon nanostructure families occurring in a chemically activated arc discharge reaction

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- Section S1

- Methods

The fullerene fractions were isolated through HPLC chromatography using a Buckyprep M silica column, 20 × 250 mm. Toluene was used as the eluent phase and the flow rate was 14 mL/min for all experiments. Scanning electron micrographs were taken on a JEOL JSM-840F with 10 kV acceleration voltage. Raman spectra were recorded on a JY Horiba Labram Aramis imaging confocal Raman microscope using a 532 nm laser. Transmission electron micrographs were taken on a JEOL JEM-2000FX. For transmission electron microscopy (TEM), the samples were dispersed in acetone, sonicated for 10 min and drop casted on carbon grids from a diluted acetone solution. Matrix-assisted laser-desorption ionization time-of-flight mass spectra
(MALDI-TOF MS-negative ionization) were obtained from a Bruker Ultraflex III MALDI-TOF spectrometer using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) or dithranol as a matrix.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C$_{60}$</th>
<th>C$_{70}$</th>
<th>C$<em>{76}$-$C</em>{78}$</th>
<th>C$_{84}$</th>
<th>C$_{88}$-EMF</th>
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</thead>
<tbody>
<tr>
<td>Gd-1x</td>
<td>73</td>
<td>23</td>
<td>2.915</td>
<td>4.945</td>
<td>0.815</td>
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<tr>
<td>Gd-2x</td>
<td>1.238</td>
<td>0.797</td>
<td>0.0579</td>
<td>0</td>
<td>0.0724</td>
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<tr>
<td>GdCu-1a</td>
<td>33.81</td>
<td>14</td>
<td>1.389</td>
<td>1.442</td>
<td>2.554</td>
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<tr>
<td>GdCu-2A</td>
<td>15.1</td>
<td>12</td>
<td>0.03</td>
<td>-</td>
<td>7.67</td>
</tr>
<tr>
<td>GdCu-1B</td>
<td>~0.016</td>
<td>1.1</td>
<td>0.0381</td>
<td>-</td>
<td>1.741</td>
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<tr>
<td>GdCu-2B</td>
<td>0.821</td>
<td>1.432</td>
<td>-</td>
<td>-</td>
<td>0.1869</td>
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<td>Nd-1X</td>
<td>14.1</td>
<td>4.3</td>
<td>0.27</td>
<td>0.33</td>
<td>0.21</td>
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<tr>
<td>NdCu-1B</td>
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<td>0.2324</td>
<td>0.19</td>
<td>-</td>
<td>0.305</td>
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<td>NdCu-1A</td>
<td>18.81</td>
<td>7.479</td>
<td>0.327</td>
<td>0.53</td>
<td>3.694</td>
</tr>
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</table>

**Table S1.** Summary of the reaction yields for all samples. The values are given in mg and have been normalized to total raw soot mass of 17 g.
- **Section S2.**

- **Mass spectra for the empty cage fullerenes, retention time 12-17 min:**

The mass spectra correspond to fraction collected from 12-17 min, the second class of empty cage fullerenes ($C_{76-78}$-$C_{84}$).

**Figure S1.** Mass spectrum of the $C_{76-78}$: 13-16 min retention time.
Figure S2. Theoretical and experimental mass spectrum of the C$_{84}$ sample, isolated from 17 min retention time.

- Section S3.

- Mass spectra for the Gd samples without copper doping:

Gd-1X:
Despite the high gadolinium content in the rods (2 % wt) the spectrum is largely dominated by the monometallic EMF Gd@C_{82} (m/z=1142). Some oxidized species of this metallofullerenes are observed in higher retention times.
Figure S3. Mass spectra of the extracts derived from carbon soot under the following conditions: 21-25 min retention time in HPLC after toluene extraction (up) with the theoretical and experimental data for the Gd@C₈₂ and 21-27 min from DMF extraction (bottom). Sample: Gd-1X. 50 mbar He, 200 amps
**Figure S4.** Mass spectrum of the extract with retention time 25 to 30 min from the Gd-1X sample.

**Gd-2X:**

When the rods were vaporized with lower current and consequently lower temperatures the bimetallic metallofullerenes appear (Gd$_2$@C$_{80}$).
Figure S5. Mass spectrum for the Gd-2X extract from DMF and the predominant Gd@C\textsubscript{82} and Gd\textsubscript{2}@C\textsubscript{80} peaks
- Section S4.

- Mass spectra for the Gd samples with copper doping:

![Mass spectrum for GdCu-1A crude extract.](image)

**Figure S6.** Mass spectrum for GdCu-1A crude extract.
c) Figure S7. Mass spec of the GdCu-1A extracted from toluene a) 21-25 min b) 25-27 min c) 27-30 min. DCTB as matrix.
Figure S8. Mass spec for Gd$_2$@C$_{80}$ and Gd@C$_{82}$ EMFs observed in the mass spec of GdCu-1B.

- Section S5.

- Mass spectra for the Nd samples without copper doping
Figure S9. Mass spectra of the extracts derived from carbon soot under the following conditions: toluene extraction, 21-25 min HPLC retention time. Sample: Nd-1X
Figure S10. Mass spectra of the extracts derived from carbon soot under the following conditions: toluene extraction, 21-28 min HPLC retention time. Sample: Nd-1X

- Section S6

- Mass spectra for the Nd samples with copper doping
Figure S11. Mass spec for the monometallic EMF Nd@C_{82} observed in the mass spec of the NdCu-1A sample.
Figure S12. Mass spec for the trimetallic nitride Nd$_3$N@C$_{82}$ observed in the mass spec of the NdCu-1B sample.
- Section S7

We present additional SEM and TEM images for the CNTs detected in the cathode deposits.

**Figure S13.** SEM images of the GdCu-2A

**Figure S14.** SEM images of GdCu-1B
**Figure S15.** TEM image of GdCu-1B sample.

**Figure S16.** Database analysis of the XRD patterns of the cathode deposits.