SUPPLEMENTARY INFORMATION

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

*Panagiotis Dallas, Seyyed Shayan Meysami, Nicole Grobert and Kyriakos Porfyrakis**

Department of Materials, University of Oxford, Parks Road Oxford OX1 3PH, UK

Contents

- 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.

Sample	**C_{60}**	**C_{70}**	**C_{76}-C_{78}**	**C_{84}**	**C_{88}-EMF**
Gd-1x	73	23	2.915	4.945	0.815
Gd-2x	1.238	0.797	0.0579	0	0.0724
GdCu-1a	33.81	14	1.389	1.442	2.554
GdCu-2A	15.1	12	0.03	-	7.67
GdCu-1B	~0.016	1.1	0.0381	-	1.741
GdCu-2B	0.821	1.432	-	-	0.1869
Nd-1X	14.1	4.3	0.27	0.33	0.21
NdCu-1B	0.119	0.2324	0.19	-	0.305
NdCu-1A	18.81	7.479	0.327	0.53	3.694

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 ($C_{76\text{-}78}$-C_{84}).

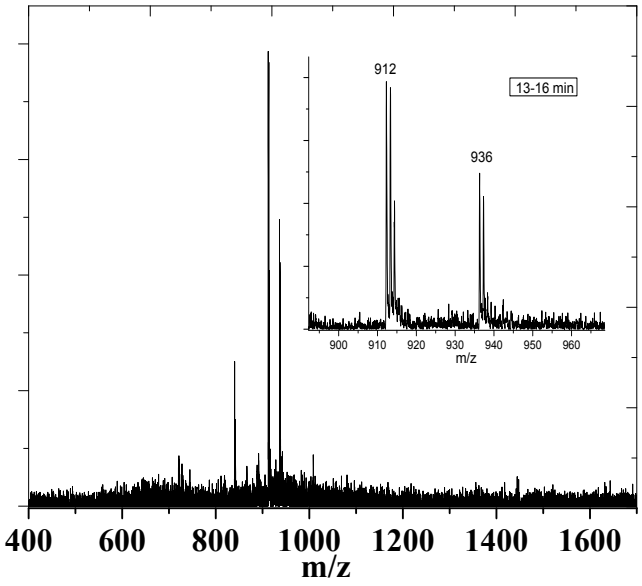


Figure S1. Mass spectrum of the $C_{76\text{-}78}$: 13-16 min retention time.

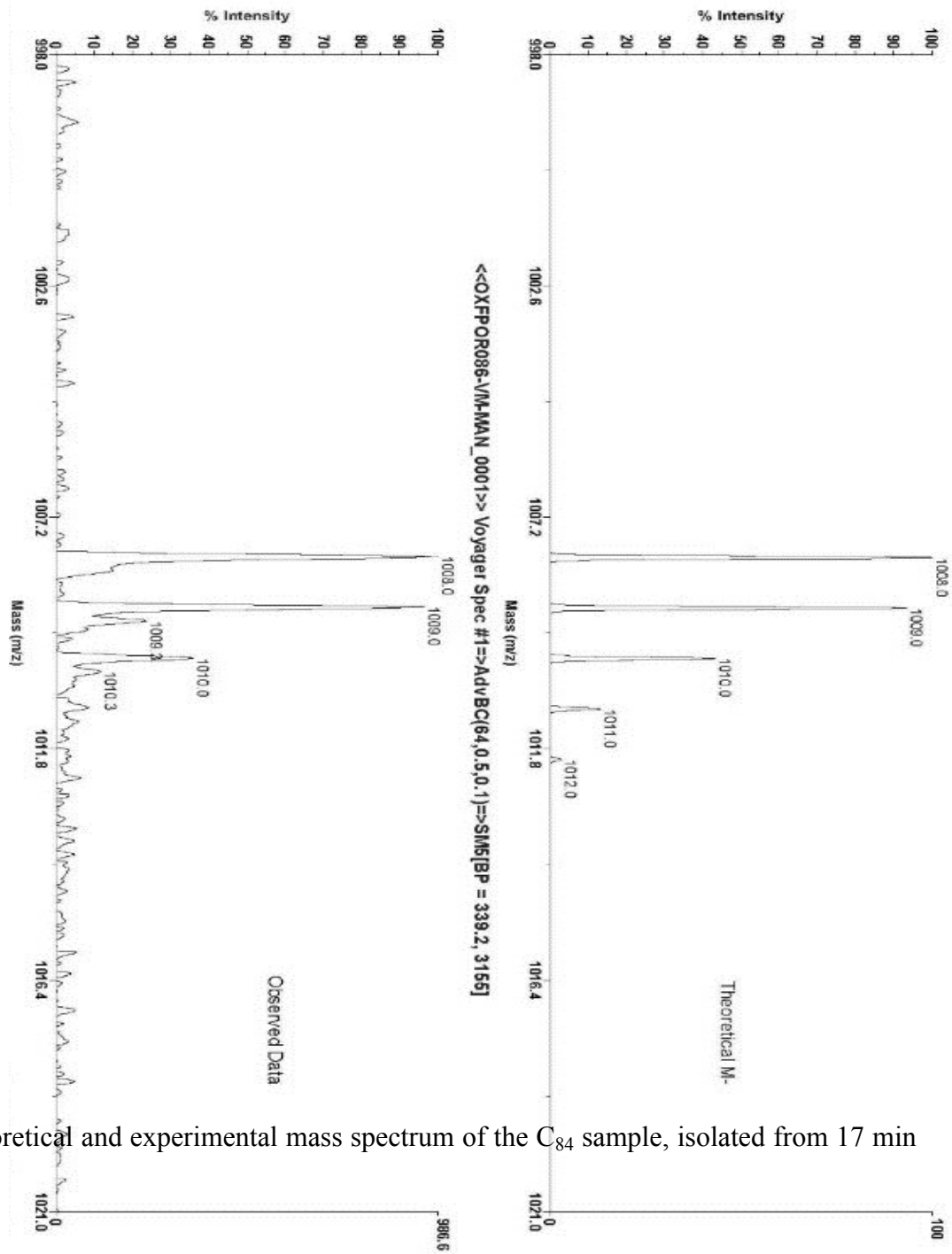


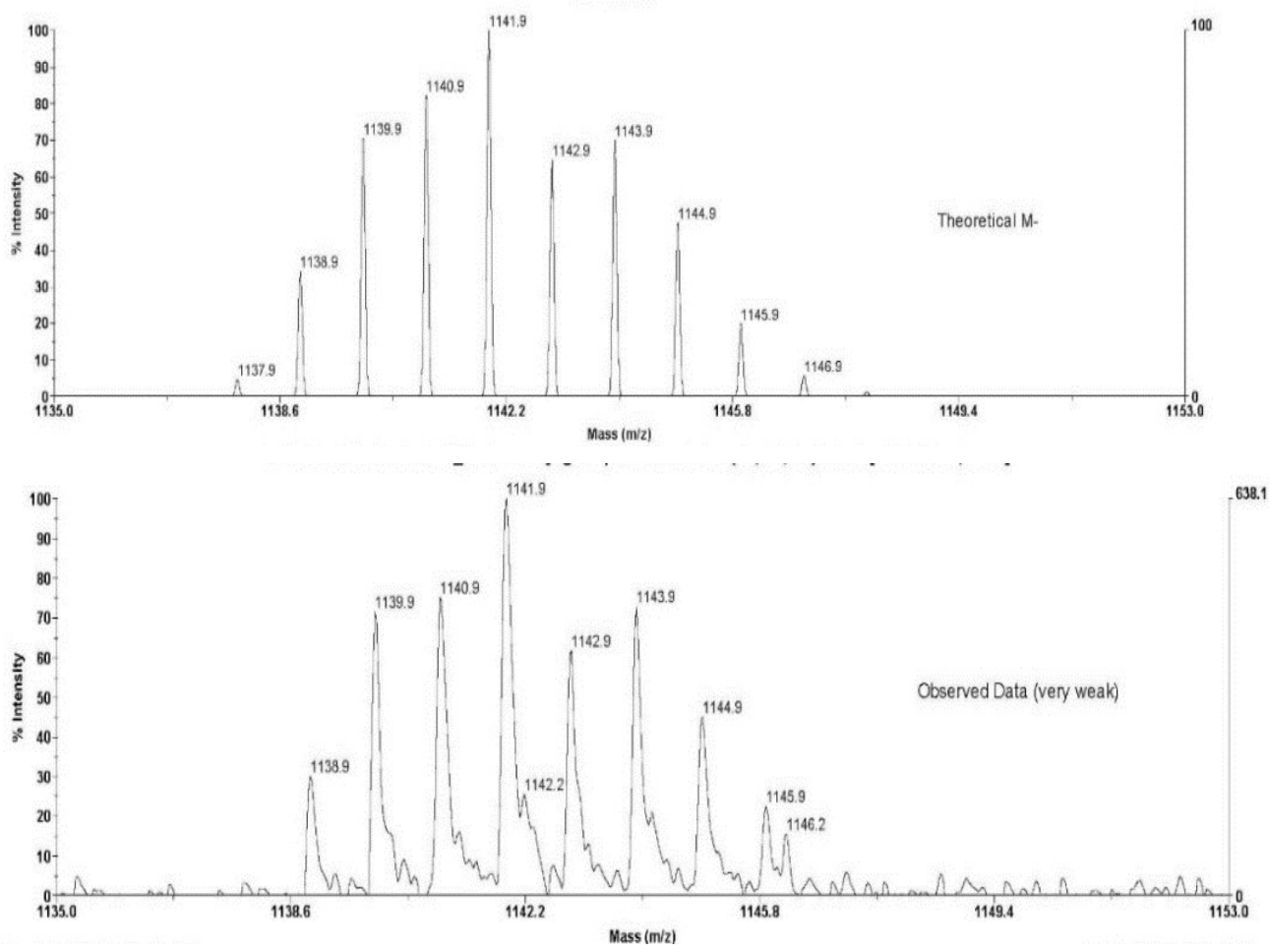
Figure S2. Theoretical and experimental mass spectrum of the C_{84} sample, isolated from 17 min retention time.

- 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 metalofullerenes are observed in higher retention times.



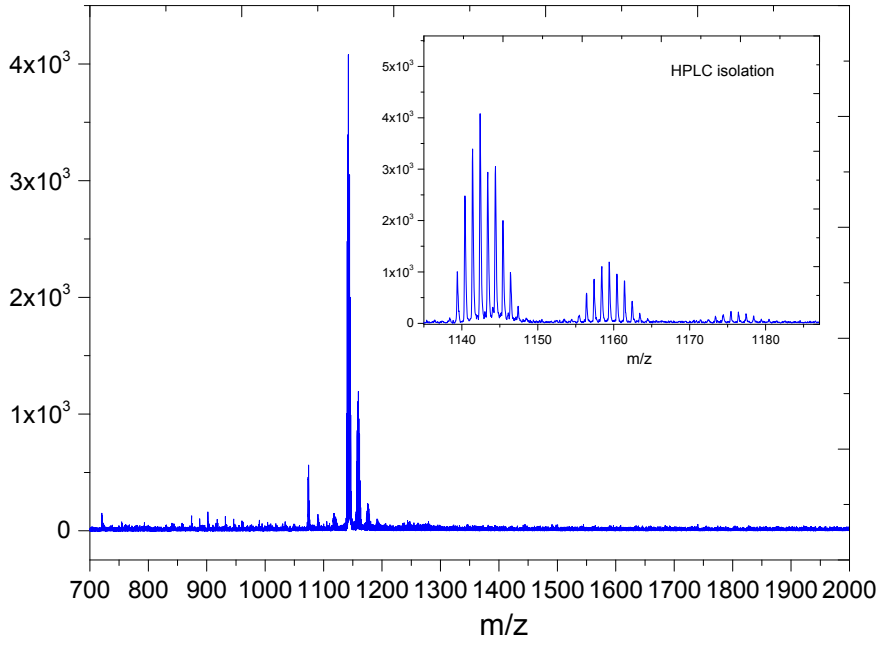


Figure S3. Mass spectra of the extracts derived from carbon soot under the following conditions: 21-25 min retention time in HPLC after toluene extraction (up) with the theoretical and experimental data for the Gd@C_{82} and 21-27 min from DMF extraction (bottom). Sample: Gd-1X. 50 mbar He, 200 amps

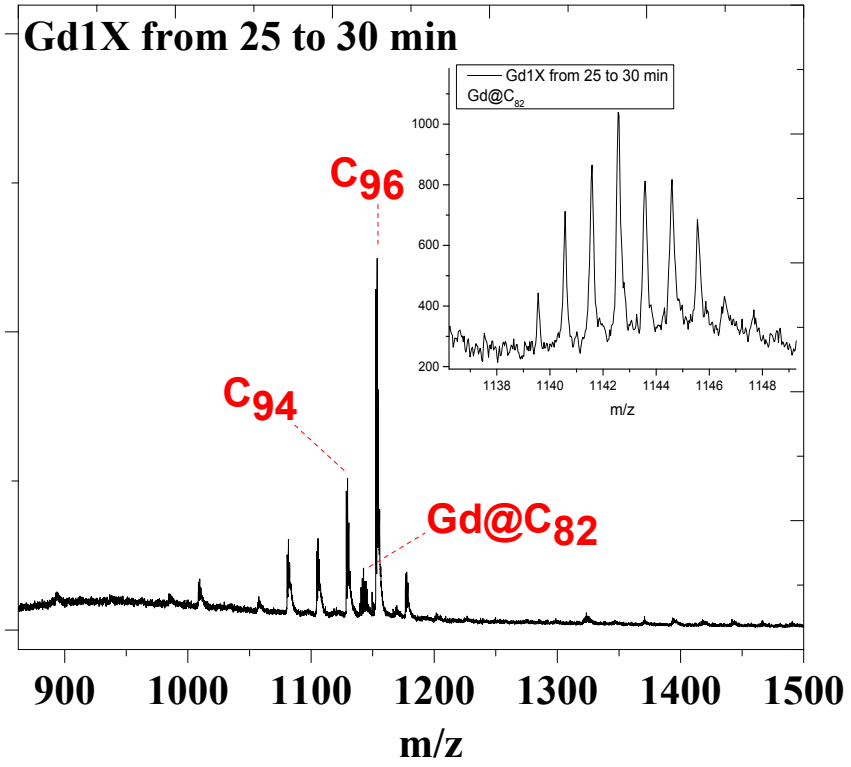


Figure S4. Mass spectrum of the extract with retention time 25 to 30 min from the Gd-1X sample.

Gd-2X:

When the rods where vaporized with lower current and consequently lower temperatures the bimetallic metalofullerenes appear ($Gd_2@C_{80}$).

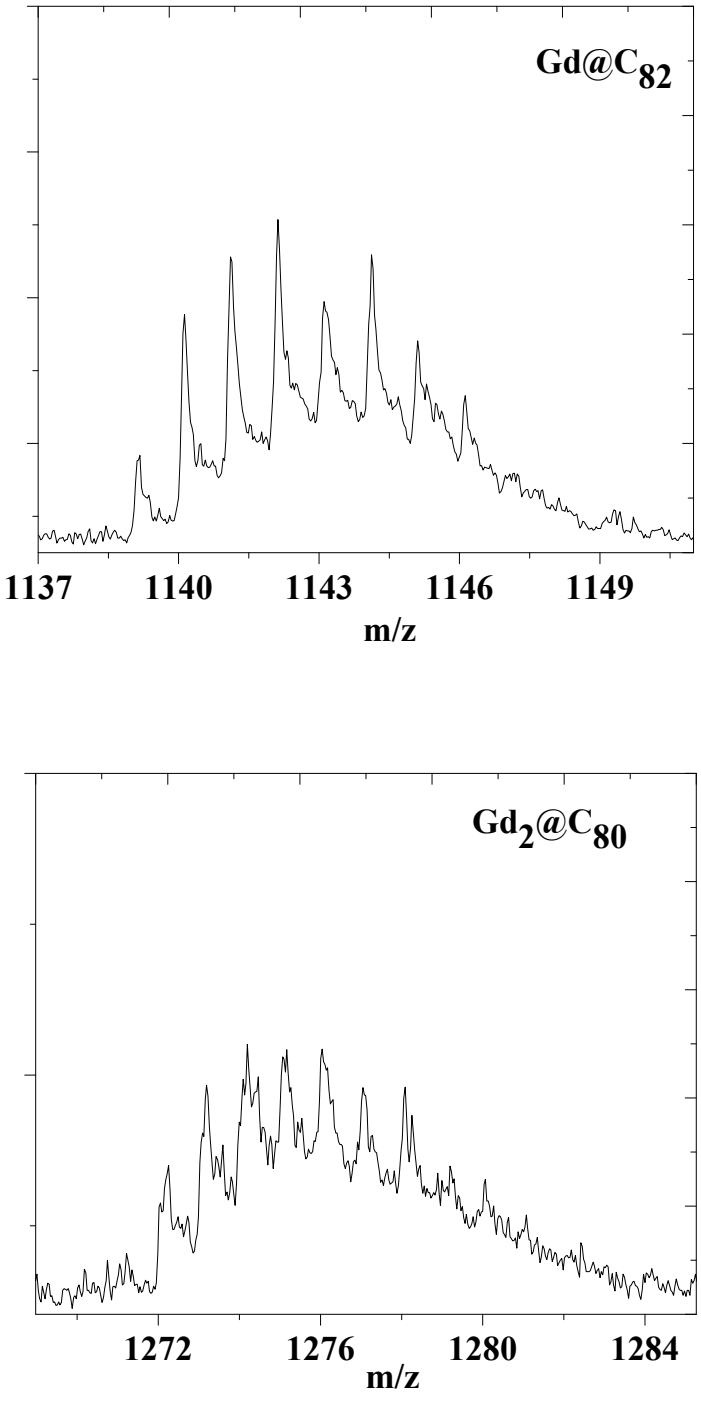


Figure S5. Mass spectrum for the Gd-2X extract from DMF and the predominant Gd@C_{82} and Gd_2@C_{80} peaks

- Section S4.

- Mass spectra for the Gd samples with copper doping:

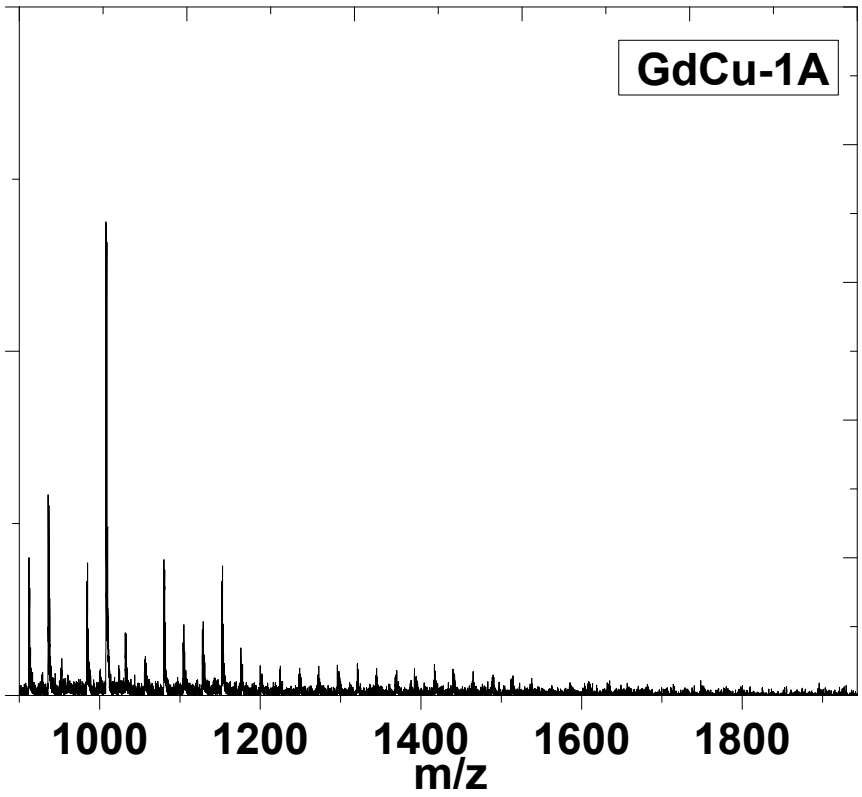
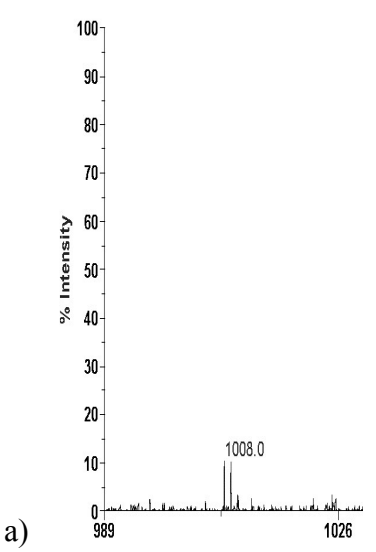
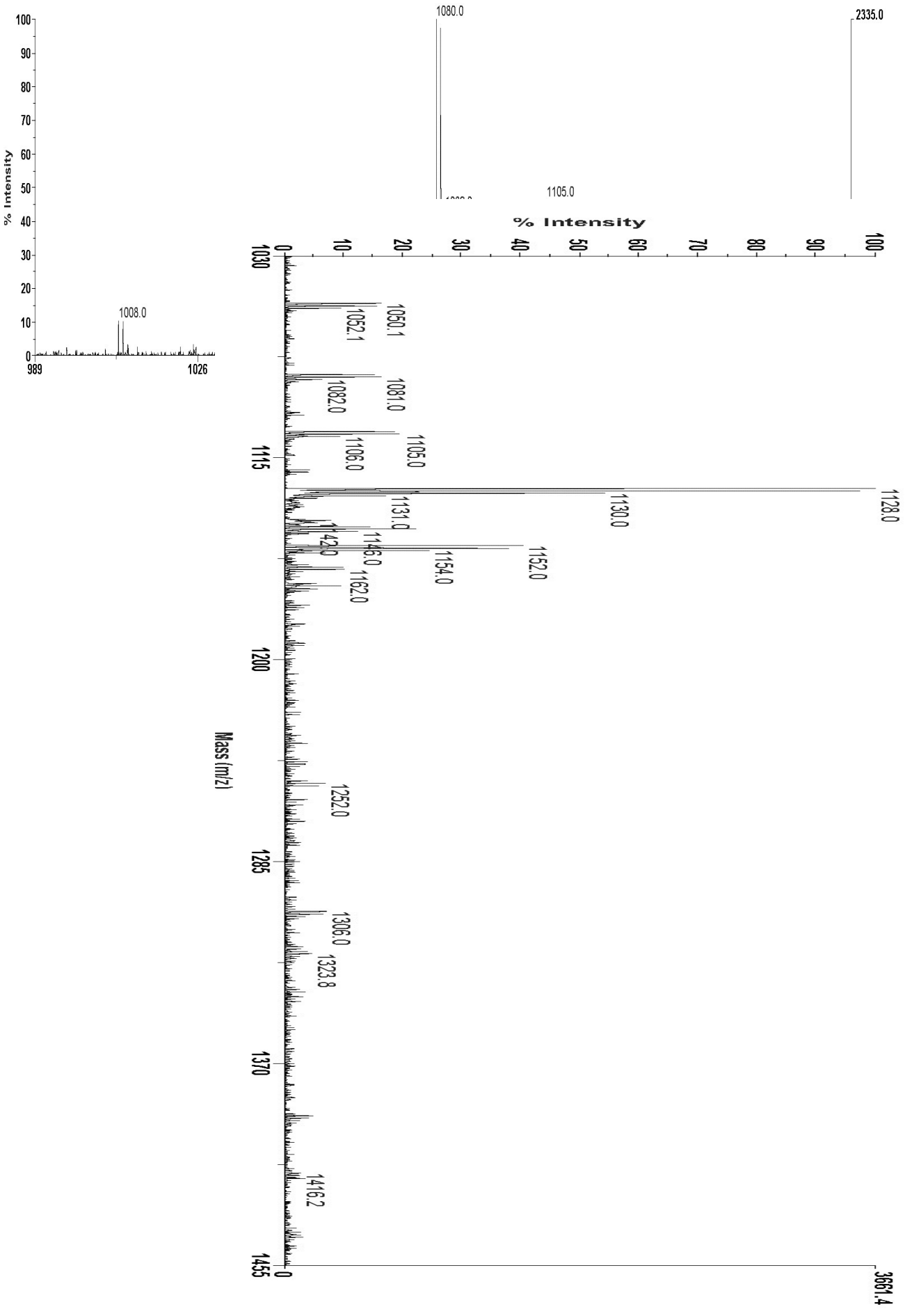


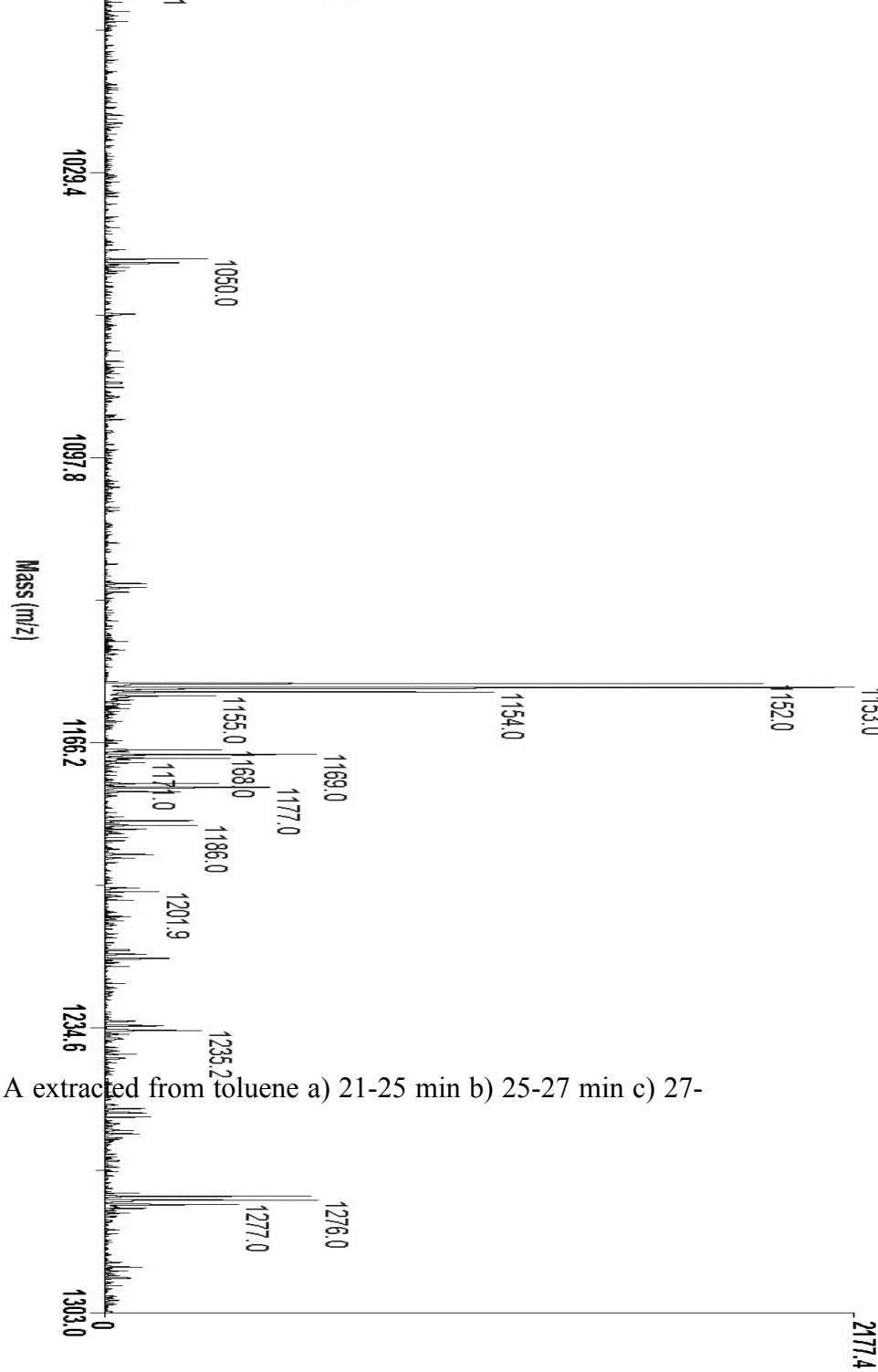
Figure S6. Mass spectrum for GdCu-1A crude extract.


% Intensity
1008.0
989
1026

a)


1080.0
2335.0
1105.0
% Intensity
Mass (m/z)
1030
1115
1200
1285
1370
1455
1050.1
1052.1
1081.0
1082.0
1105.0
1106.0
1128.0
1130.0
1131.0
1142.0
1146.0
1152.0
1154.0
1162.0
1252.0
1306.0
1323.8
1416.2
3661.4

b)



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

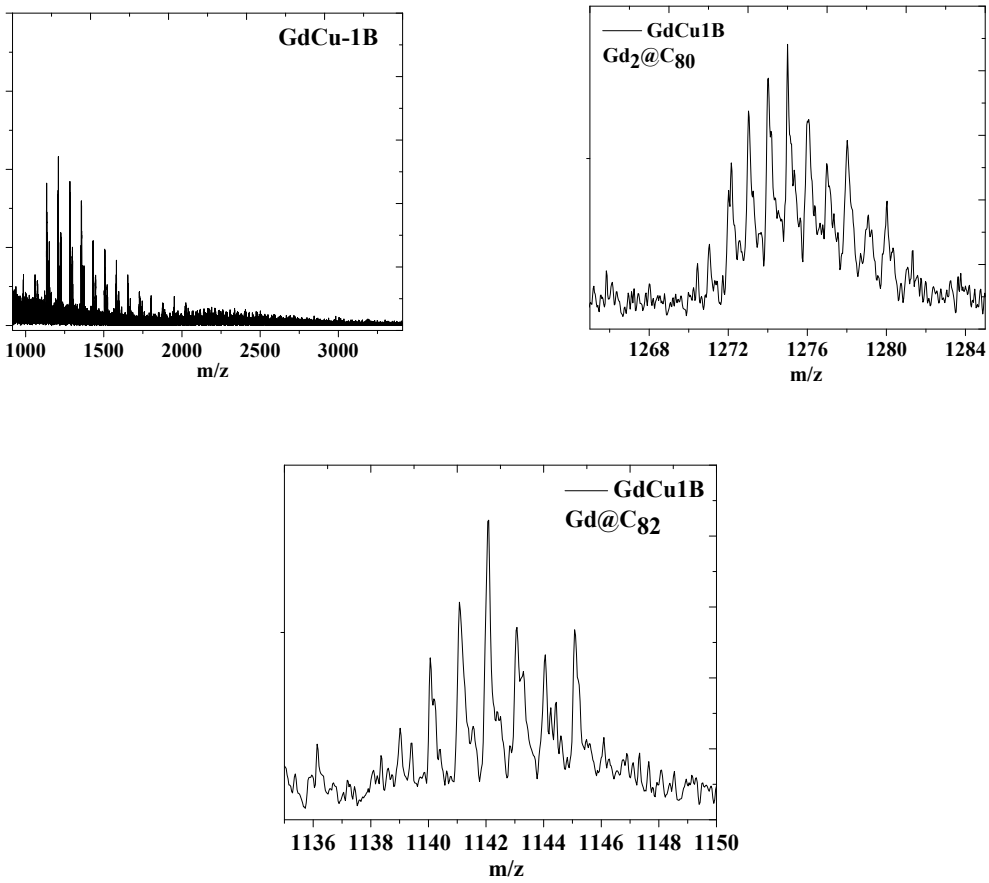


Figure S8. Mass spec for $Gd_2@C_{80}$ and $Gd@C_{82}$ EMFs observed in the mass spec of GdCu-1B.

- Section S5.

- Mass spectra for the Nd samples without copper doping

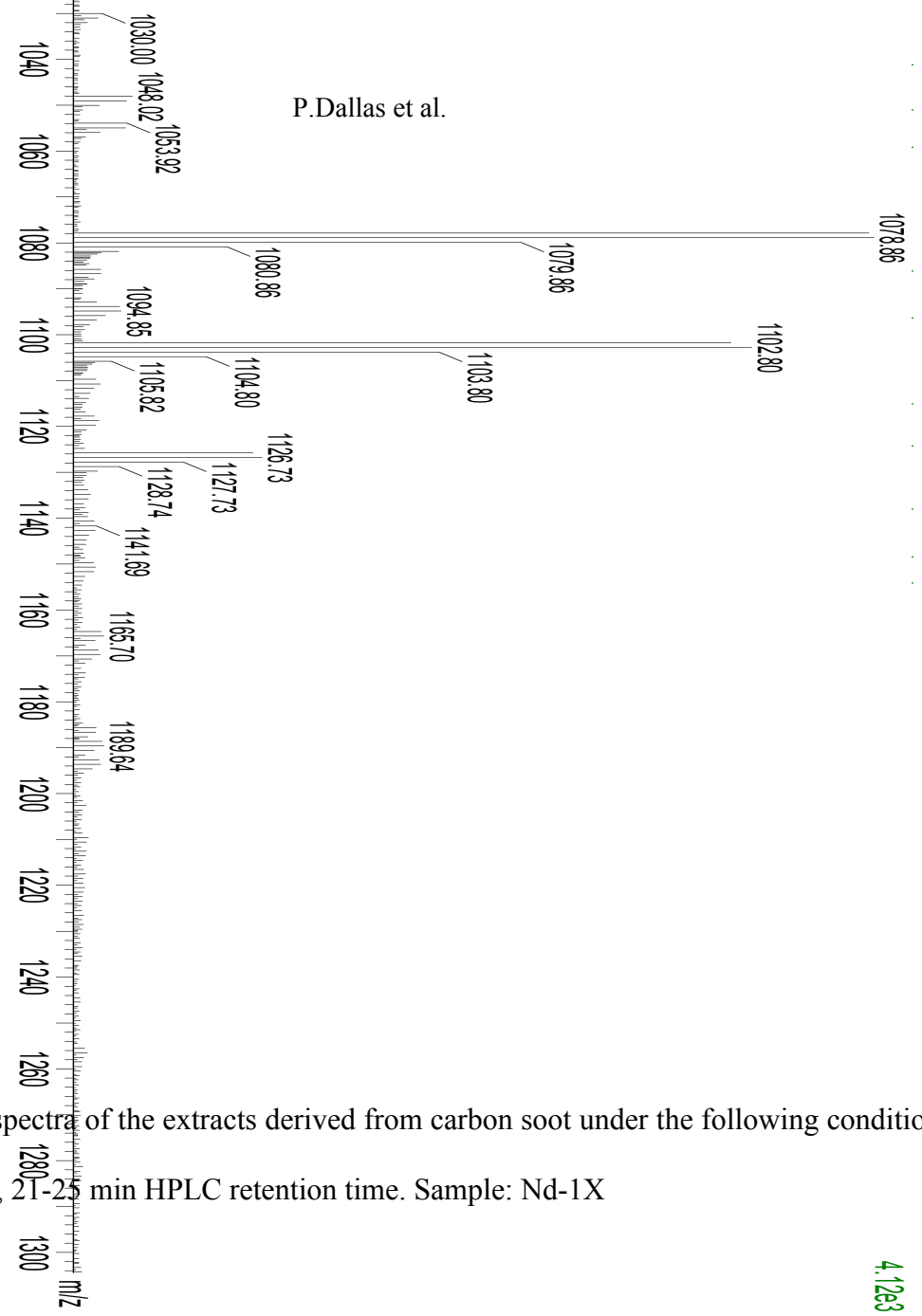


Figure S9. Mass spectra of the extracts derived from carbon soot under the following conditions: toluene extraction, 21-25 min HPLC retention time. Sample: Nd-1X

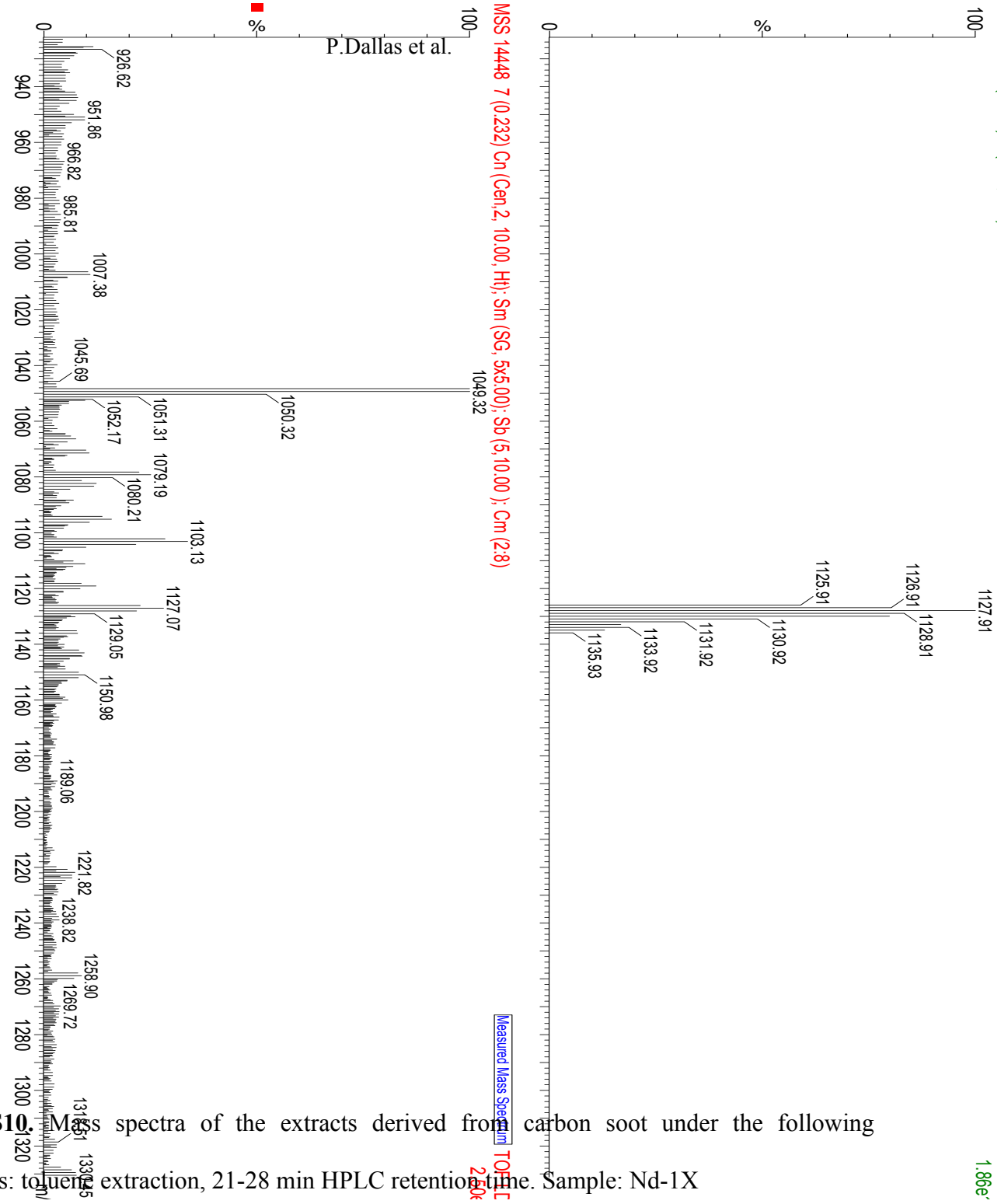


Figure S10. Mass spectra of the extracts derived from carbon soot under the following conditions: toluene extraction, 21-28 min HPLC retention time. Sample: Nd-1X

- Section S6

- Mass spectra for the Nd samples with copper doping

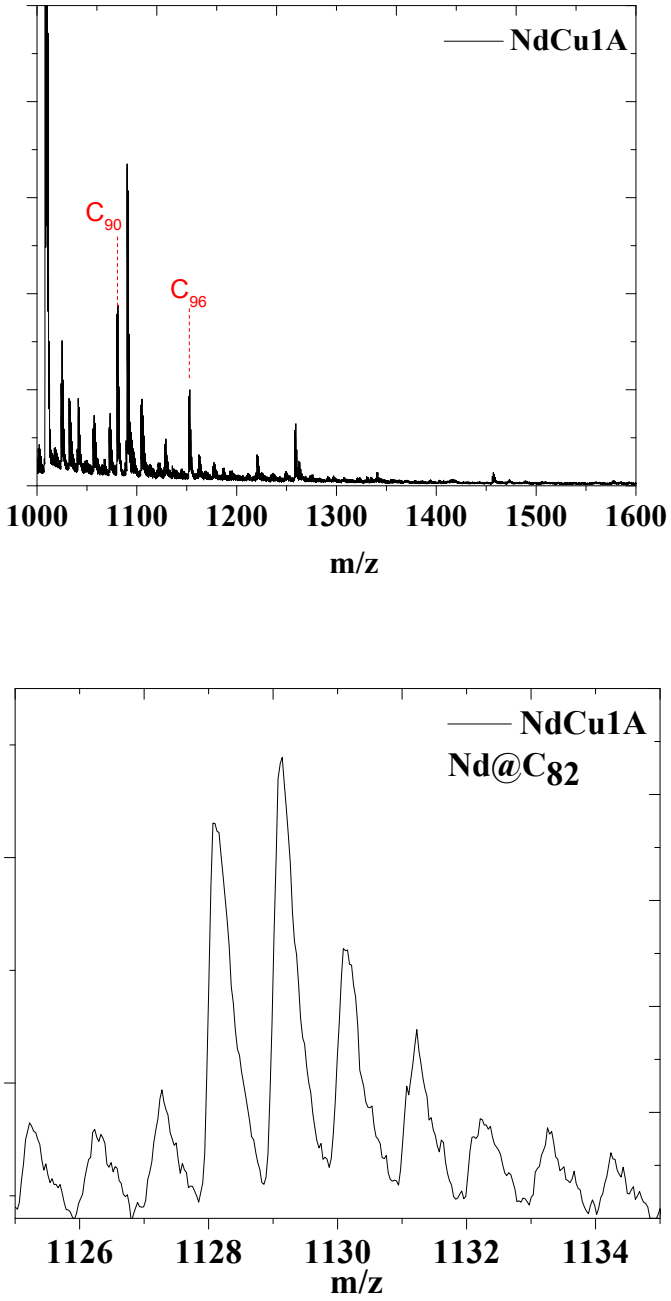


Figure S11. Mass spec for the monometallic EMF Nd@C_{82} observed in the mass spec of the NdCu-1A sample.

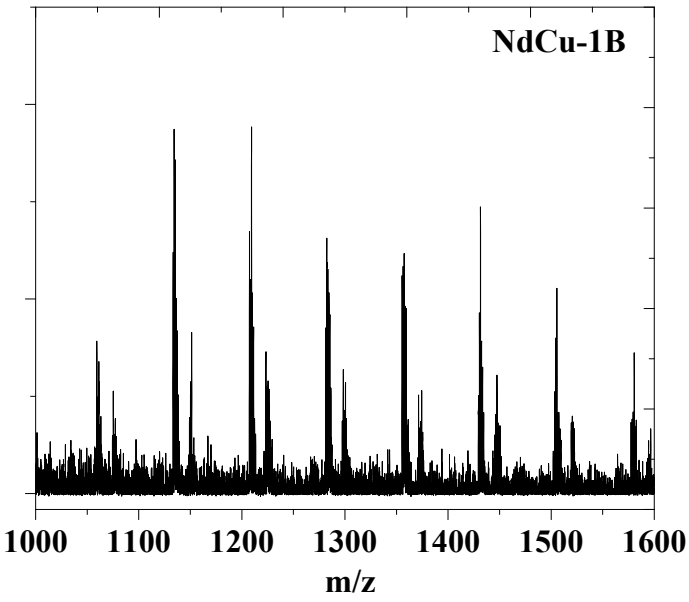


Figure S12. Mass spec for the trimetallic nitride $Nd_3N@C_{82}$ observed in the mass spec of the NdCu-1B sample.

- Section S7

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

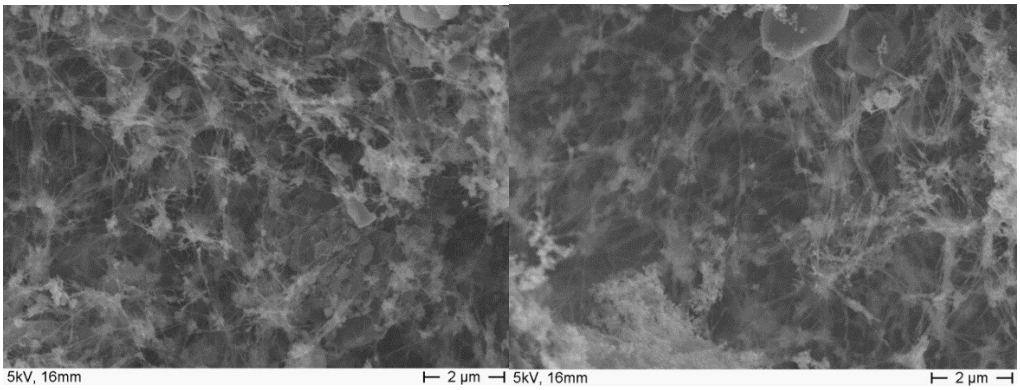


Figure S13. SEM images of the GdCu-2A

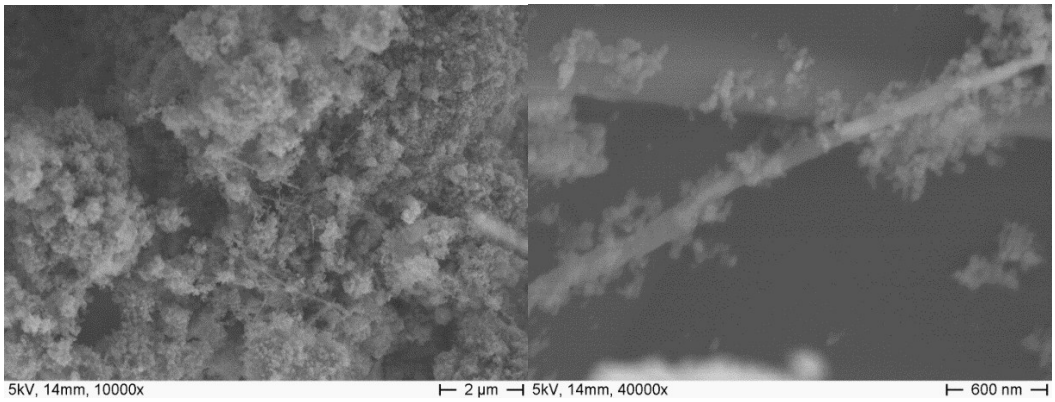


Figure S14. SEM images of GdCu-1B

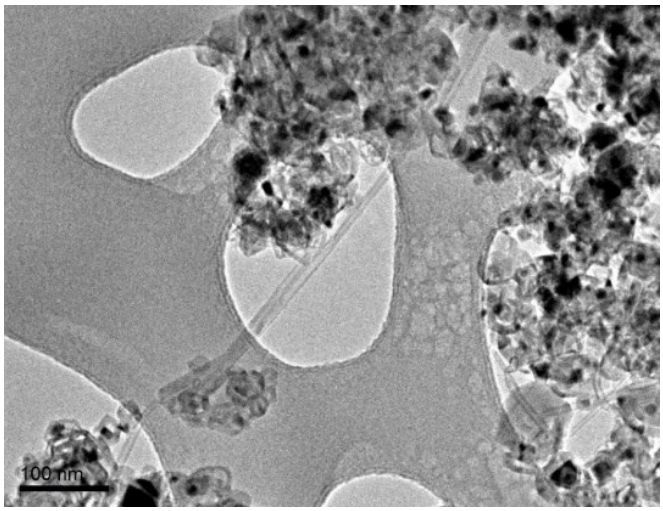


Figure S15. TEM image of GdCu-1B sample.

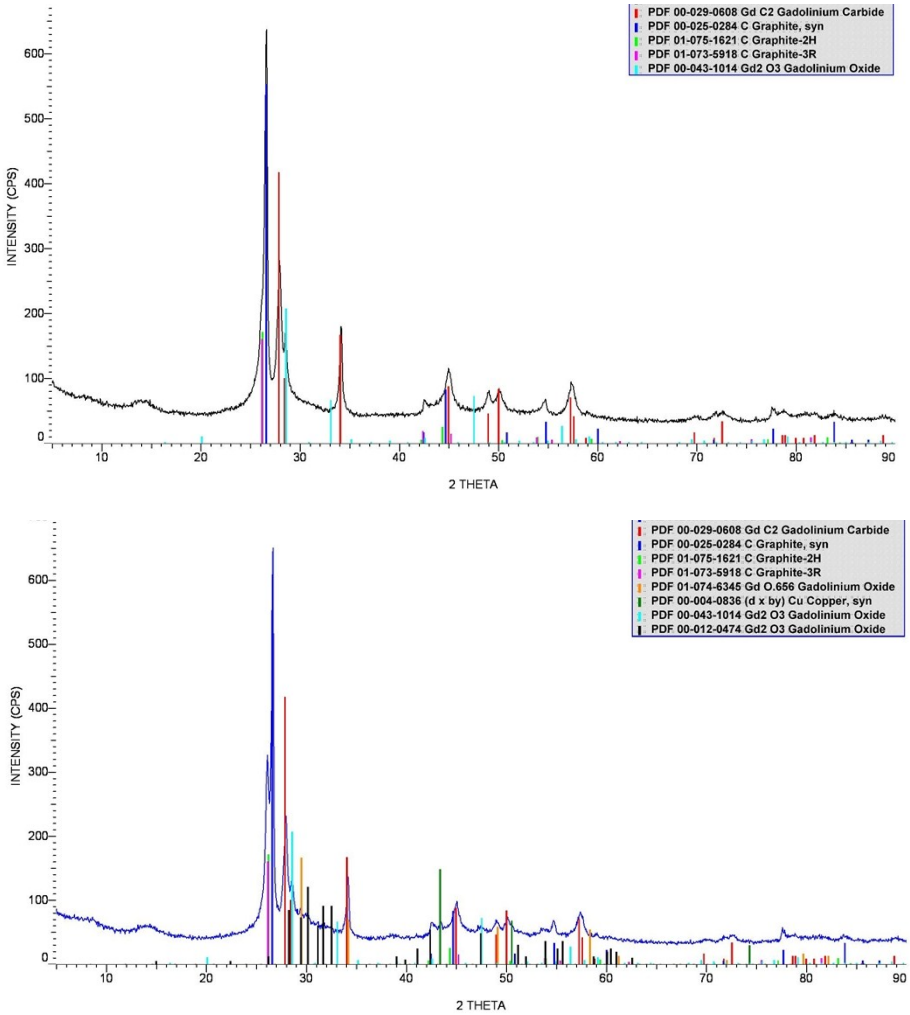


Figure S16. Database analysis of the XRD patterns of the cathode deposits.