

SUPPORTING INFORMATION

Understanding the Relative Abundances of TNT-based Endohedral Metallofullerenes from Aromaticity Measures

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Computational Details

All Density Functional Theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) program.¹ The molecular orbitals (MOs) were expanded in an uncontracted set of Slater type orbitals (STOs) of double- ζ (DZP) quality containing diffuse functions and one set of polarization functions. In order to reduce the computational time needed to carry out the calculations, the frozen core approximation has been used.² In this approximation, the core density is obtained and included explicitly, albeit with core orbitals ($1s$ for C and N, $1s2s2p$ for Sc, and $1s2s2p3s3p4s3d$ for Y) frozen during the SCF procedure. It was shown that the frozen core approximation has a negligible effect on the optimized equilibrium geometries.³ Scalar relativistic corrections have been included self-consistently using the Zeroth Order Regular Approximation (ZORA).⁴ Energies and gradients were calculated using the local density approximation (Slater exchange) with non-local corrections for exchange (Becke88)⁵ and correlation (Perdew86)⁶ included self-consistently (i.e. the BP86 functional). The actual geometry optimizations and transition state (TS) searches were performed with the QUILD⁷ (QUantum-regions Interconnected by Local Descriptions) program, which functions as a wrapper around the ADF program. The QUILD program constructs all input files for ADF, runs ADF, and collects all data; ADF is used only for the generation of the energy and gradients.⁸

B3LYP/6-31G//BP86/DZP level of theory, using the Becke's multicenter integration scheme and the topological fuzzy Voronoi (TFVC)⁹ atomic partition scheme as implemented in APOST-3D program,¹⁰ and ESI-3D program¹¹ were used to compute the aromaticity electronic normalized multicenter index, I_{NB} index.¹²⁻¹⁴ I_{NB} is a normalized version of multicenter index (MCI),^{15,16} which is a particular extension of the I_{ring} index.¹⁷

$$I_{ring}(A) = 2^N \sum_{i_1, i_2, \dots, i_N}^{OCC} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_N i_1}(A_N) \quad (1)$$

being $S_{ij}(A)$ the overlap between molecular orbitals i and j in the atom A . The MCI index¹⁶ is defined as the sum of all I_{ring} values resulting from the permutations of indices A_1, A_2, \dots, A_N :

$$MCI(A) = \frac{1}{2^N} \sum_{P(A)} I_{ring}(A) = \frac{1}{2^N} \sum_{P(A)} \sum_{i_1, i_2, \dots, i_N}^{OCC} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_N i_1}(A_N) \quad (2)$$

where $P(A)$ stands for a permutation operator which interchanges the atomic labels A_1, A_2, \dots, A_N to generate the $n!$ permutations of the elements in the string A .¹⁶ As a result of the large amount of permutations that needs to be computed, this index has associated a high computational cost that limits its use to rings up to nine members. The normalized version of MCI, the I_{NB} index was proposed by Cioslowski, Matito and Solà in 2007.¹⁴

$$I_{NB}(A) = \frac{C}{N N_\pi} [2^N \cdot MCI(A)]^{1/N} \quad (3)$$

where N is the total number of atoms in the ring, N_π is the total number of π electrons, and $C \approx 1.5155$, which is a proportionality constant.

Figure S1. On top: Quantitative HPLC chromatograms of the arc reactor carbon sample of a typical scandium based TNT EMFs synthesis (from Echegoyen's Lab, ref. 18); Bottom: ALA_N values (in e^-), sorted by increasing cage size.

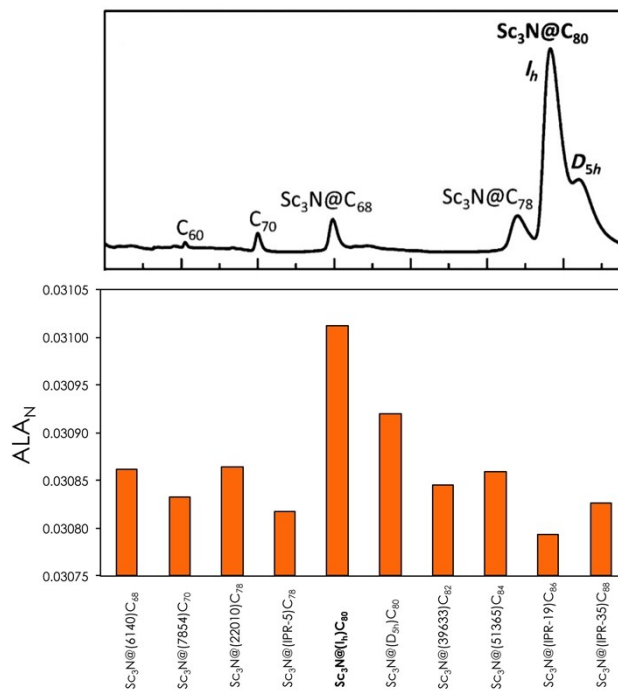
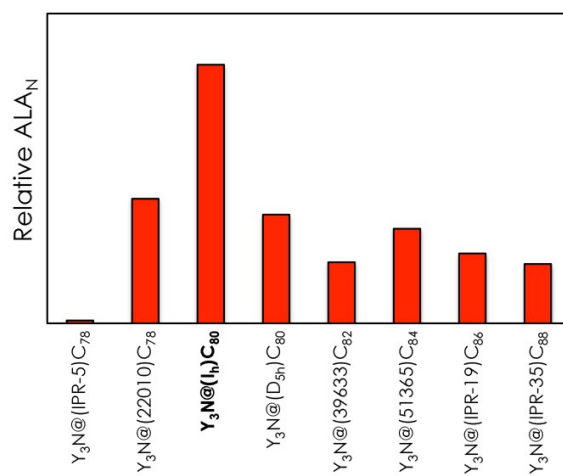
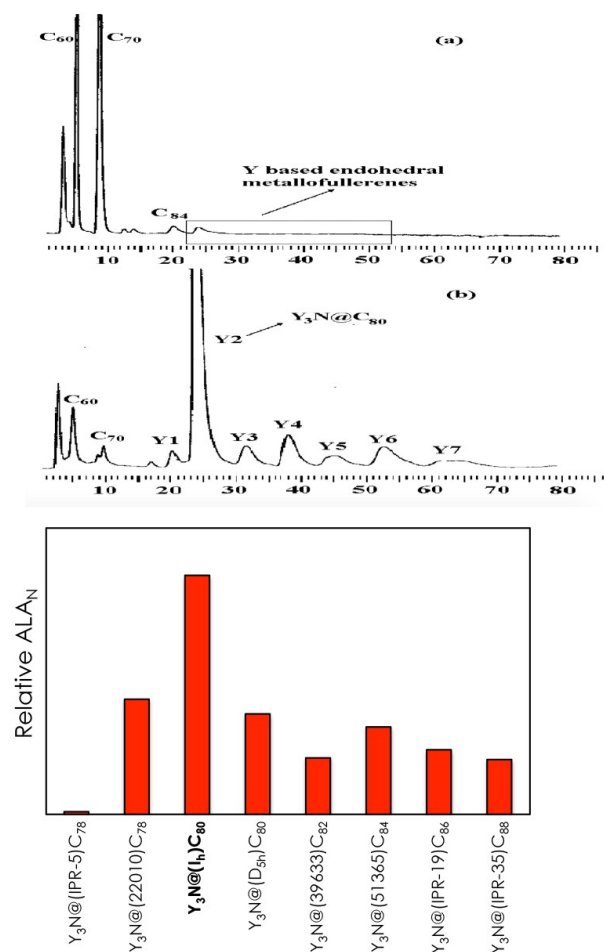


Figure S2. $ALAN$ analysis of Y_3N EMFs relative abundances at B3LYP/6-31G+Y(SDD)//BP86/DZP level of theory



$Y_3N@$	$ALAN \times 10^4$	Relative $ALAN$
$(D_{3h})-C_{78}$	308.26	1
$(22010)-C_{78}$	309.39	48
$(I_h)-C_{80}$	310.60	100
$(D_{5h})-C_{80}$	309.24	42
$(39633)-C_{82}$	308.82	24
$(51365)-C_{84}$	309.12	37
$(IPR-19)-C_{86}$	308.89	27
$(IPR-35)-C_{88}$	308.80	23

Figure S3. Quantitative HPLC chromatograms of the arc reactor carbon sample of a yttrium based TNT EMFs synthesis from J. Am. Chem. Soc. 2009, 131, 11762.



From: J. Am. Chem. Soc, 2009, 131 (33), pp 11762–11769:

The first stage was carried out on a 5PBB column (4.6 × 250 mm). The different fractions (Y1-Y7) from this 5PBB column were collected and further separated with a 5PYE column (10 × 250 mm). The flow rate for both stages was 2.0 mL/min, and the detection wavelength was 390 nm.

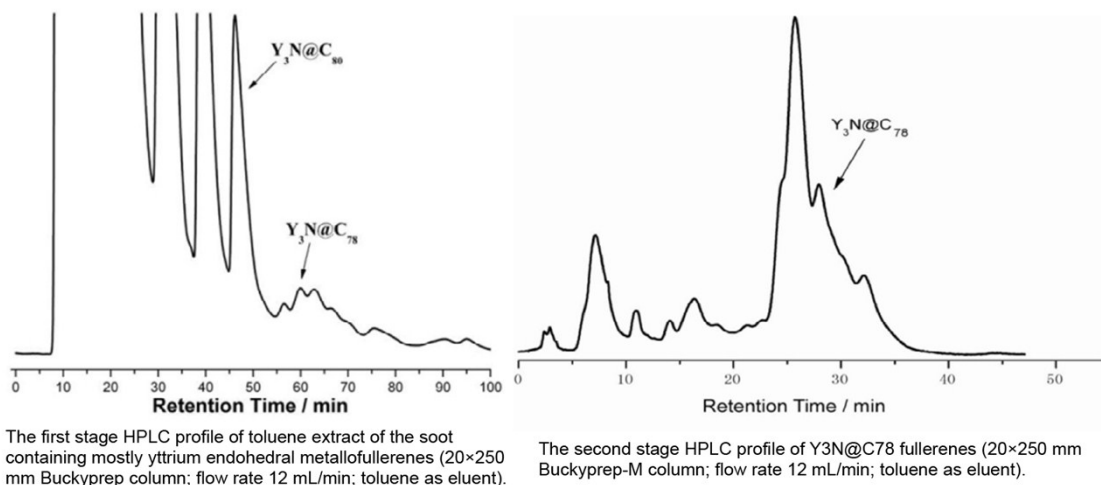
Y1: Y₂@C₇₉N
 Y2: Y₃N@{(I_h)}-C₈₀ + Y₃N@{(D_{5h})}-C₈₀
 Y3: Y₃N@{(39633)}-C₈₂
 Y4: Y₃N@{(51465)}-C₈₄
 Y5: Y₃N@{(IPR-19)}-C₈₆
 Y6: Y₃N@C₈₈
 Y7: Y₂C₉₄

Y₃N@{(I_h)}-C₈₀ + Y₃N@{(D_{5h})}-C₈₀ peak corresponds to the most abundant mixture of Y-based TNT EMFs, in agreement with ALAN predicted abundances. Also, relative abundances of C₈₂-C₈₆ Y₃N EMFs are correctly predicted by ALAN measures.

Nevertheless, Dorn and co-workers were not able to isolate and properly characterize the Y6 peak supposed to be Y₃N@{(IPR-35)}-C₈₀ (J. Am. Chem. Soc. 2009, 131, 11762), thus not ensuring its purity.

Figure S4. Quantitative HPLC chromatograms of the arc reactor carbon sample of a yttrium based TNT EMFs synthesis from J Nanoscale, 2011, 3, 4955.

From: Nanoscale, 2011, 3, 4955



From “Nanoscale, 2011, 3, 4955”:

“The sample was synthesized by the Kräschmer–Huffman arc discharging method and purified by two-stage high performance liquid chromatography (HPLC). Two complementary columns, i.e. Cosmosil Buckyprep and Buckyprep-M, were employed to isolate and purify the Y₃N@C₇₈. The Y₃N@C₇₈ was detected followed by Y₃N@C₈₀ on Buckyprep column, whereas the Sc₃N@C₇₈ has a shorter retention time than Sc₃N@C₈₀. Such abnormality has indicated how special this target molecule is.”

The first isolation and HPLC characterization of Y₃N@((22010)-C₇₈) EMF by Ma et al. (Nanoscale, 2011, 3, 4955) showed the particularities of this EMF, and the reasons why Dorn and coworkers were not able to purify by HPLC this compound (J. Am. Chem. Soc. 2009, 131, 11762).

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