Large fullerenes stabilized by encapsulation of metallic clusters†

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Structures are proposed for six endohedral metallofullerenes with large carbon cages (from C_{92} to C_{100}) on the basis of sizeable (LUMO−4)–(LUMO−3) gap and the formal transfer of six electrons to the cages.

Endohedral metallofullerenes (EMFs), *i.e.* fullerenes that contain metal clusters in their interior, have attracted special interest during past years due to their unique properties that are important for potential applications in biomedicine and nanomaterials sciences.[1–3] EMFs have been found containing one, two or three group 3 or lanthanide metal atoms inside the carbon cage. The carbon cages that encapsulate metal clusters in EMFs are usually structural isomers of the cages found for the corresponding empty-cage fullerenes. Frequently the cages do not fulfil the so-called isolated pentagon rule (IPR). A charge transfer from the metal cluster to the carbon cage when the cluster is incorporated into the fullerene explains the violation of the IPR.[1,3,4] A particular family of EMFs, the trimetallic nitride template (TNT) endohedral fullerenes, also known as Trimetasphere™ carbon nanomaterials (TMSs), has been extensively studied recently.[5–7] These cages encapsulate trimetallic nitride clusters such as Sc_3N, Y_3N, Er_3N, Gd_3N, *etc.* $M_3N@C_{80}$ compounds are the most abundant TMSs, in which the least stable icosahedral (I_h) IPR isomer of C_{80} is stabilized by the interaction with the TNT.[8]

Recently, a general rule for the stabilization of fullerene cages encapsulating TNT has been established using the density functional theory (DFT) methods.[9] This rule is based on the assumption that the bond between the metal cluster and the cage is markedly defined by the ionic model $M_3N^{6+}@C_k^{6-}$ (k = 68, 78, 80, *etc.*). Formally, a total of six electrons transfer from the three highest occupied orbitals of the TNT unit to the three low-lying unoccupied orbitals of the cage. The authors showed that the large HOMO–LUMO gap of the resulting EMFs, $Sc_3N@C_k$ (k = 68, 78, 80), which give them stability, could be estimated from the (LUMO−4)–(LUMO−3) gap found in their free cages assuming the aforementioned six-electron transfer. LUMO−n corresponds to the nth lowest unoccupied molecular orbital. LUMO−1 would contain the first two electrons after a reduction, LUMO−2 the next two electrons and so on. Hence, LUMO−3 and LUMO−4 of the empty cage would be the highest occupied and lowest unoccupied molecular orbitals, respectively, after a six-electron reduction of the cage. In particular, Campanera *et al.* found that the cages which are able to encapsulate TNTs show (LUMO−4)–(LUMO−3) gaps larger than 1 eV.[9] Moreover, based on this rule, they predicted that no IPR fullerene cages between C_{60} and C_{84} different from the already known would be capable of encapsulating TNTs. Indeed, the only TMS with a C_{84} cage characterized up to now, $Tb_3N@C_{84}$, is found to have a non-IPR structure.[10] Recently, Balch, Dorn and co-workers have also isolated and structurally characterized the TMSs $Tb_3N@C_{86}$ and $Tb_3N@C_{88}$, which are the largest cage structures that have been characterized by X-ray diffraction so far.[11] The cage isomers for these two large TMSs are found to fulfil the IPR. Larger cages (from C_{90} to C_{100}) are known to encapsulate TNTs or other metal clusters (Dy_n, n = 2, 3), but they have been produced in such low yields that cannot be isolated or whose structure cannot be characterized by X-ray diffraction.[12,13] Herein, we extend the prediction based on the (LUMO−4)–(LUMO−3) rule to IPR isomers up to C_{100} and propose carbon cages for novel EMFs.

We have computed the (LUMO−4)–(LUMO−3) gaps for the 1267 IPR structures from C_{60} to C_{100} (1 of C_{60}, C_{70}, C_{72} and C_{74}; 2 of C_{76}; 5 of C_{78}; 7 of C_{80}; 9 of C_{82}; 24 of C_{84}; 19 of C_{86}; 35 of C_{88}; 46 of C_{90}; 86 of C_{92}; 134 of C_{94}; 187 of C_{96}; 259 of C_{98}; and 450 of C_{100})[14] and some other non-IPR cages that are found to encapsulate metal clusters.‡ First we focus on the cages from C_{60} to C_{88} in order to test the predictive ability of the (LUMO−4)–(LUMO−3) rule. We have extended the work done by Campanera *et al.*[9] including the 19 C_{86} and 35 C_{88} IPR cages (Fig. 1). Six out of a total number of nine cages that encapsulate

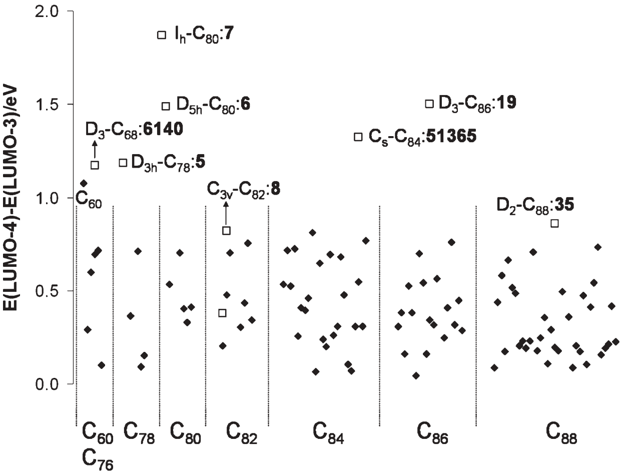

Fig. 1 The (LUMO−4)–(LUMO−3) gap for all the IPR isomers from C_{60} to C_{88} and also the non-IPR D_3-C_{68}:**6140** and C_s-C_{84}:**51365**. White squares represent the cages that are able to encapsulate TNT or M_2 clusters (where M is a group 3 or a lanthanide metal atom).

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† Electronic supplementary information (ESI) available: Optimized structures (*xyz* files), a Table displaying the (LUMO−4)–(LUMO−3) gaps and a Figure plotting the energy gap between the LUMO−4 and the arithmetic average of LUMO−1, LUMO−2 and LUMO−3 of the proposed candidates for large EMFs. See DOI: 10.1039/b709548a

TNT or M_2 units (where M is a group 3 or a lanthanide metal atom) show a (LUMO−4)–(LUMO−3) gap larger than 1 eV. The largest gap, 1.86 eV for I_h-C_{80}:**7**, corresponds to the most abundant TMSs, $M_3N@C_{80}$. The non-IPR structure C_s-C_{84}:**51365** and the IPR cage D_3-C_{86}:**17** that have been recently discovered to encapsulate Tb_3N are further evidences of the validity of this simple rule for TMSs. Two cages that encapsulate M_2 or TNT units, $Er_2@C_{82}$ isomer II and $Tb_3N@C_{88}$, have a (LUMO−4)–(LUMO−3) gap somewhat smaller than 1 eV, C_{3v}-C_{82}:**8** (0.82 eV) and D_2-C_{88}:**35** (0.86 eV). In both cases, however, these are the cages with the largest gap among all the C_{82} and C_{88} IPR structures, respectively (Fig. 1). Only the cage in $Er_2@C_{82}$ isomer I, C_s-C_{82}:**6**, with a (LUMO−4)–(LUMO−3) gap smaller than 0.5 eV do not satisfy the rule. It is not, however, the most abundant isomer of $Er_2@C_{82}$. Therefore, the proposed rule provides a straightforward manner of rationalizing why a particular cage encapsulates TNT or M_2 clusters for the most abundant EMF isomers from C_{68} to C_{88}. The (LUMO−4)–(LUMO−3) rule, however, does not consider the fact that low-lying unoccupied orbitals of the cage (*i.e.* LUMO−1 and LUMO−2) will confer an extra stabilization to the EMF. We have also incorporated the energies of the low-lying LUMO−1 and LUMO−2 orbitals computing the energy gap between the LUMO−4 and the arithmetic average of LUMO−1, LUMO−2 and LUMO−3. The gaps thus obtained become larger as compared to the original rule. All those cages with largest (LUMO−4)–(LUMO−3) gaps are also predicted to have now the largest gaps. The most important difference is that the two cages with a (LUMO−4)–(LUMO−3) gap slightly smaller than 1 eV, C_{3v}-C_{82}:**8** and D_2-C_{88}:**35**, are better discriminated with respect to the rest of the isomers in their respective C_n groups (see ESI†).

Once the predictive capability of the rule has been tested, we now apply it to the IPR cages from C_{90} to C_{100}. Several EMFs with such large cages already exist, but their structures have not been solved yet. Dorn and Balch have produced and isolated one isomer of $Tb_2@C_{90}$, $Tb_2@C_{92}$ and two isomers of $Tb_2@C_{94}$.[15] Dunsch and Yang have also isolated Dy_3N and Dy_2-based EMFs with large carbon cages: $Dy_3N@C_n$, with n up to 88 and two isomers of $Dy_2@C_{94}$, one of $Dy_2@C_{100}$ and one of $Dy_3@C_{98}$.[12,13] We here propose IPR cages for those large EMFs that encapsulate TNT or M_2 units provided that the charge transfer from the cluster to the cage is large enough to consider a formal six-electron transfer, as occurs for smaller cages.[8,9] No clear candidate appears for the C_{90} group because there is not any IPR cage with a (LUMO−4)–(LUMO−3) gap larger than 1 eV (Fig. 2). Our candidate for the C_{92} group is T-C_{92}:**86** with a gap larger than 1.5 eV (Fig. 2), one of the largest gaps obtained so far. For C_{94}, the largest gap (1.18 eV) corresponds to the C_2-C_{94}:**121** isomer. Two candidates with very similar gaps, D_2-C_{96}:**186** (1.17 eV) and D_{6d}-C_{96}:**187** (1.16 eV), are proposed for C_{96}. For C_{98}, the D_3-C_{98}:**215** is the isomer with the largest gap (1.27 eV). Finally, for C_{100} we find again an isomer with a gap larger than 1.5 eV, D_5-C_{100}:**450**. The structures of the proposed cages for novel EMFs along with their (LUMO−4)–(LUMO−3) gaps are shown in Fig. 3.

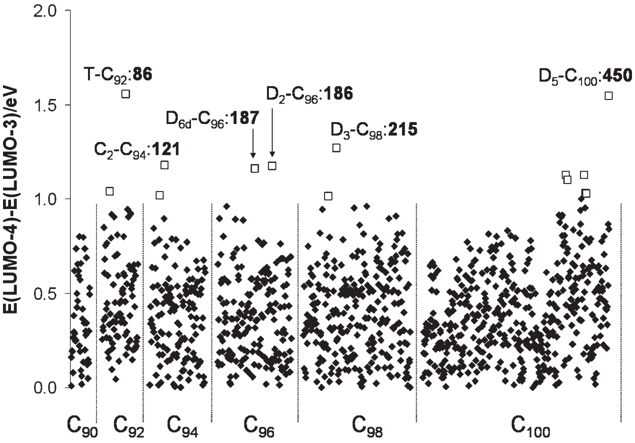
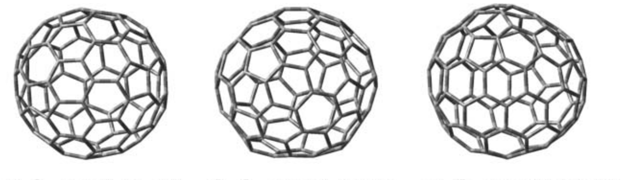
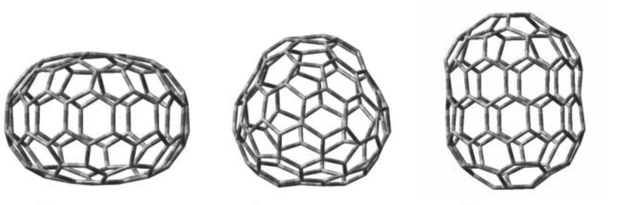


Fig. 2 The (LUMO−4)–(LUMO−3) gap for all the IPR isomers from C_{90} to C_{100}. White squares represent the carbon cages that will be able to encapsulate TNT or M_2 clusters (where M is a group 3 or a lanthanide metal atom).



T-C_{92}:**86** (1.55 eV) C_2-C_{94}:**121** (1.18 eV) D_2-C_{96}:**186** (1.17 eV)



D_{6d}-C_{96}:**187** (1.16 eV) D_3-C_{98}:**215** (1.27 eV) D_5-C_{100}:**450** (1.54 eV)

Fig. 3 Structures of the proposed candidates for large cage EMFs and their (LUMO−4)–(LUMO−3) gaps (in parenthesis).

Besides the large (LUMO−4)–(LUMO−3) gap, D_5-C_{100}:**450** shows other characteristics that make it a major candidate for encapsulating a TNT unit. Its geometry and its electronic structure are very similar to those of D_{5h}-C_{80}:**6** and I_h-C_{80}:**7**, the two isomers that encapsulate TNT units among the seven IPR cages of C_{80}. The geometry of D_5-C_{100}:**450** can be seen as the joining of the two moieties that constitute D_{5h}-C_{80}:**6** or I_h-C_{80}:**7** with an extra row of 20 C atoms in the middle (Fig. 4). So, instead of a row formed by 10 hexagons as occurs in the C_{80} isomers, a total of 20 hexagons in two rows are present. Notice the similarity with the C_{60}/C_{70} pair, which differs in 10 C atoms in the equatorial zone. The electronic structure is also equivalent: the electronic states for the empty cages are triplets in the three cases and the sequence of HOMO and LUMOs for each system is nearly identical (Fig. 4). Furthermore, the energy difference between our candidate and the lowest energy isomer for the empty cage, D_2-C_{100}:**449**, is only around 1 eV. This energy difference seems to be attainable given that the difference between the most stable isomer for C_{84}, D_{2d}-C_{84}:**23**, and the only non-IPR cage that encapsulates a Tb_3N unit, C_s-C_{84}:**51365**, is as much as 2.6 eV. Therefore, we propose D_5-C_{100}:**450** as the most probable cage for encapsulating a TNT unit. Calculations performed for the model system $La_3N@C_{100}$ show that isomer **450** is more stable than isomer **449** by more than 1 eV. In both isomers the TNT unit is planar even thought the

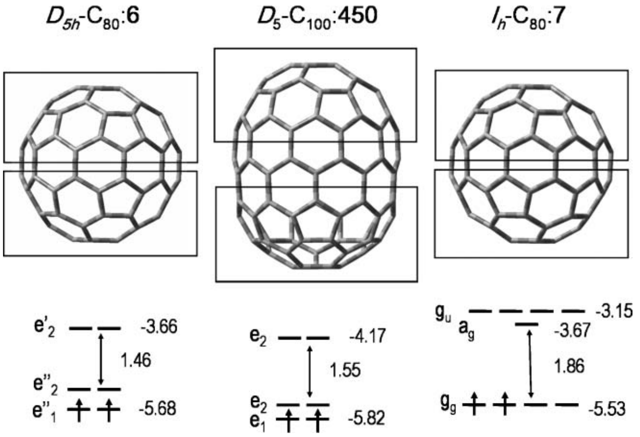


Fig. 4 Comparison of geometries and electronic structures (energy, in eV, and symmetry of HOMO and LUMOs) of *D_5*-C$_{100}$:**450**, *I_h*-C$_{80}$:**7** and *D_{5h}*-C$_{80}$:**6**.

large size of La atoms. Although a more exhaustive search for different orientations of TNT unit inside the cage should be done these preliminary results are in good agreement with our predictions. Alternatively, Dunsch and Yang have proposed the six most stable C_{100} cages, none of them matching our candidate, as the most probable isomers for encapsulating the Dy_2 unit. These authors assumed that for large cages like C_{100} the charge transfer between the metal unit and the fullerene cage should not be very large as it seems to occur for $Sc_2@C_{84}$ where the Sc_2 unit is thought to be encaged in the most stable *D_{2d}*-C$_{84}$:**23** isomer.[16,17] Calculations done for $Y_2@C_{100}$ as model for $Dy_2@C_{100}$ (Y has similar electronegativity and size as Dy) show that a formal six-electrons transfer exists and that $Y_2@C_{100}$:**450** is much more stable (more than 2 eV) than $Y_2@C_{100}$:**449**.[18]

In summary, we have extended the application of the general rule for the stabilization of TMSs proposed by Campanera *et al.* to IPR carbon cages of dimensions up to C_{100}. This empirical rule, based on the formal transfer of six electrons from the cluster to the carbon cage, is able to predict the most abundant cage isomer for all the TMSs known to date. Some EMFs with M_2 clusters, however, seem to escape this simple rule. We have proposed six large carbon cages (from C_{92} to C_{100}) with sizeable (LUMO−4)–(LUMO−3) gaps and achievable energies as candidates for encapsulating TNT units or M_2 clusters on condition that the formal six-electron transfer is accomplished. In particular, we propose the *D_5*-C$_{100}$:**450** isomer as the most likely cage to encapsulate TNT according to its unique structural and electronic features. It is important to keep in mind that this simple rule is intended for qualitative trends. The use, for example, of other density functionals (*i.e.* those that include the exact exchange) will provide different values for the gaps, but the same qualitative information. Moreover, from this rule, we cannot not exclude that non-IPR fullerenes could encapsulate TNT units or that other less stable species could be detected in the future.

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Notes and references

‡ The calculations were carried out by using DFT methodology with the ADF 2004 program.[19,20] The exchange–correlation functionals of Becke[21] and Perdew[22] were used. Relativistic corrections were included by means of the ZORA formalism. Triple-ζ polarization basis sets were employed to describe the valence electrons of C. The calculations for the $M_2@C_n$ systems have been done with the TURBOMOLE code (V5-8) using the hybrid B3LYP functional and TZP or DZP basis sets for M or C atoms, respectively.[23] The geometries of all fullerene cages have been extracted from the Fullerene Structure Library created by Mitsuho Yoshida.[24] Single-point calculations were performed for all empty cages except for *D_3*-C$_{68}$:**6140**, *C_s*-C$_{84}$:**51365** which were fully optimized. Initially, all the cages have been computed as closed-shell electronic structure systems. The small number of cages whose electronic structure has not been converged as a singlet state has been recomputed as open-shell triplets.

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