Electronic structure of positively and negatively charged fullerenes

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The most abundant fullerenes, C\textsubscript{60} and C\textsubscript{70}, and all the pure-carbon fullerenes larger than C\textsubscript{70} synthesized so far follow the isolated-pentagon rule (IPR)\cite{1-2}. Fullerenes containing adjacent pentagons (APs) are less stable due to the additional strain. Surprisingly, recent experiments have shown that a few endohedral fullerenes\cite{3}, for which IPR structures are possible, hence expected to be the most stable ones, are stabilized in non-IPR cages. These cages are either positively or negatively charged, depending on the character of electron acceptor or electron donor of the encapsulated species. It has been argued that this unexpected stability of charged non-IPR fullerenes is associated with electronic properties of the carbon cage, such as unusually large HOMO-LUMO gaps or bond resonance energies\cite{4,5}. These properties might be related to a reduction of strain induced by the encapsulated species, but the ultimate reasons remain unclear.

By performing density functional theory calculations\cite{6-8} on a large number of C\textsubscript{60} and C\textsubscript{70} derivatives with both IPR and non-IPR cages, we show that, apart from strain, the physical property that governs the relative stability of highly charged fullerenes is the charge distribution in the cage\cite{9}. This charge distribution is controlled by the number and location of two different structural motifs, one electrophilic (the pentalene motif, i.e., the pairs of APs,) and the other one electrophobic (the pyrene motifs). APs are the preferential sites to host additional electrons, either by adding explicitly those electrons or by making the AP bonds to react (or both). On the contrary, when one electron is removed from the fullerene cage, the resulting positive charge locates in the pyrene motifs, not in the pyrene bonds but in the more aromatic bonds surrounding the latter. Thus by playing with the number and position of pyrene bonds it is possible to generate non-IPR fullerenes with strongly non uniform positive charge distributions. We show that, when AP and pyrene motifs are uniformly distributed in the cage and well separated from each other, stabilization of non-IPR endohedral and exohedral fullerenes, as well as pure-carbon fullerene anions and cations, is more the rule than the exception. This suggests that non-IPR charged fullerenes might be even more common than IPR ones, which can be relevant to interpret recent experiments in which highly charged fullerenes are produced in collisions with ions or in storage rings.

References