Chapter 8
Conclusions

The main achievements attained in the current manuscript are outlined as follows:

1. Cycloaddition reactions to carbon nanostructures

The nucleophilic (2+1) Bingel-Hirsch addition of dimethyl bromomalonate to the endohedral metallofullerene La@C_{2v}C_{82} was studied in detail in the current thesis. The formation of one fulleroid at bond 19 emerges as the kinetically and thermodynamically most favorable Bingel-Hirsch adduct in agreement with the experimental evidence; even though the fulleroid at bond 11 is in direct competition. On the other hand, experiments also report the formation of four singly-bonded derivatives; two of them, the ones with the highest yields, are assigned to carbon atoms C2 and C23. These positions generate the most thermodynamically stable intermediates associated to kinetically hampered cyclopropanation reactions; thus leading to the accumulation of these chemical species. Based on the thermodynamic stability, the other two singly bonded derivatives can be formed on C7, C11, C13, C18, C19, and C21; therefore, the Bingel-Hirsch addition to La@C_{2v}C_{82} is not regioselective and the formation of at least ten products can be expected, even under relatively mild reaction conditions.

Cycloaditions of benzyne to different carbon nanostructures is also another case study. The achieved goal is the elucidation of the chemoselectivity [(2+2) vs (4+2) additions] and regioselectivity ([5,6] vs [6,6] in fullerenes or parallel vs oblique addition in zig-zag single-walled carbon nanotubes) of the reactions. Reaction mechanisms for the benzyne cycloaddition to carbon nanostructures were quantum-chemically formulated, wherein the formation of a singly-bonded biradical intermediate determines the course of the reactions. These results demonstrate that the (2+2) benzyne cycloaddition to a [6,6] bond of C_{60} is the most thermodynamically and kinetically favored reaction pathway in excellent agreement with experimental observations, yet the attack on a [5,6] bond kinetically competes with the attack on a [6,6] bond. Therefore, a [5,6]-cycloaddition product can be also observed as suggested by indirect experimental evidence. Moreover, for the (2+2) benzyne cycloaddition to the endohedral metallofullerenes X_3N@C_{80} (X = Sc, Y), both [5,6] and [6,6] attacks also compete each other.\[^{443}\] In contrast, the most thermodynamically and kinetically preferred reaction pathway in zig-zag single-walled carbon nanotubes is the (4+2) benzyne cycloaddition; even though, in the case of armchair single-walled carbon nanotubes, the cycloaddition depends upon the diameter. However, in both cases of carbon nanotubes, it is
Conclusions

generally observed that the energy barrier increases and the exothermicity of the reaction decreases as the diameter of the nanostructure increases. As a final remark, changes in chemoselectivity and regioselectivity can be explained in terms of structural strain and interaction between reactants as determined by the activation strain model, wherein reaction pathways involving less or negligible structural deformation shall be favored.

To sum up, the chemo- and regioselectivity of the (2+1), (2+2), and (4+2) cycloadditions to (endohedral)fullerenes and carbon nanotubes have been determined in detail so as to provide a systematic understanding of the chemical functionalization of carbon nanostructures. As a result, the outcomes of the current thesis are guidelines in the characterization, prediction, and even design of innovative cycloadducts of carbon nanostructures.

2. Reactions catalyzed by transition metals involving fullerene C$_{60}$

The analysis of reactions involving C$_{60}$ and catalysts based on transition metals performed in this thesis is twofold: one encompasses the quantum-chemical development of the reaction mechanism that leads to the formation of an arylated hydrofullerene with the aim of rationalizing experimental observations; and the other provides the in silico synthesis of catalysts including C$_{60}$ for the metathesis of olefins.

In the first study, it is formulated a Suzuki-Miyaura-like reaction mechanism of the hydroarylation of C$_{60}$ with organoboron compounds catalyzed by a rhodium complex in the presence of water. The rate-determining step is described as the coordination of water to the PhC$_{60}$Rh(cod) complex to provide the hydrogen atom for the formation of the phenyl(hydro)[60]fullerene and the OH group to recover the catalyst. Therefore, the unknown role of water is consistently explained in this study, which turns out to be essential for the success of the reaction, thus discarding the steric hindrance as a key factor as previously suggested.

In the second study, it was developed a quantum-chemical exploration of the potential energy surface of the metathesis of ethylene catalyzed by complexes based on ruthenium as the metallic center and N-heterocyclic carbenes containing C$_{60}$. Three catalysts were discussed; complexes B and C bear a C$_{60}$ annulated in the backbone of the NHC ligand. Despite the thermodynamic stability among the three complexes A, B, and C is similar, complex B shows the lowest energy barriers for olefin metathesis, thus demonstrating that the inclusion of C$_{60}$ increases the catalytic power. Indeed, steric hindrance of B is similar to A in spite of the relatively large-sized fullerene structure. The activation strain model shows better reactant interactions for species of B, and this latter also has more electrophilicity. All these attributes certainly indicate a better performance of C$_{60}$-based catalysts for olefin metathesis.
3. Fullerene-based dye-sensitized solar cells

The investigation of electron transfer phenomena in the triphenylamine-$\text{C}_{60}$ donor-acceptor conjugate is included in this manuscript in order to better comprehend the photovoltaics behind fullerene-based solar cells. This is accomplished by the description of electronic transitions in triphenylamine-$\text{C}_{60}$ and the evaluation of electron transfer parameters of photoinduced charge transfer reactions occurring at the donor-acceptor interface. In the case of electronic transitions, an exciton characterized by a partial charge separation is described with the intention of explaining how the rate of charge transfer reactions varies. In this regard, the population of excitons with partial charge transfer character produce faster charge transfer reactions, and vice versa, which resembles experimental results. It is also observed that a closer distance between the donor-acceptor fragments promotes the formation of an exciton with partial charge separation. Therefore, highly efficient dye-sensitized solar cells can be engineered by avoiding the population of these excitons, which turns out in slower charge recombination reactions due to the formation of longer-lived charge transfer states.

In the case of the evaluation of the rate of charge transfer reactions, the estimations of the external reorganization energy and the energy of a solvated charge transfer state are key factors to reach reliable, consistent values of rate constants. Moreover, the importance of the solvent effects lies in the fact that the polarity of the solvent determines the charge transfer events; that is to say, nonpolar solvents cause lack of charge transfer activity due to they cannot stabilize the formation of a charge transfer state. In contrast, more polar solvents stabilize charge transfer states and, as a consequence, they are longer-lived and the charge recombination reaction is delayed. Accordingly, the stabilization of charge transfer states is reflected in higher-efficient dye-sensitized solar cells.

In general, the description, forecasting, and even design of functionalized carbon nanostructures with interesting physical and chemical properties, as well as potential applications in the construction of photovoltaic devices, are faced and proved through the current thesis.