# Weak bonds between molecular tweezers and their guests

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It is proposed a molecular tweezer, which makes possible to design a scaffold structure, allowing to trap organic molecules, regardless of the size of the guest. Weak carbon-carbon and carbon-hydrogens interactions stabilized the compound. The analysis carried out with the Grimme's dispersion correction allow to quantify the weak interaction between the molecular tweezer and the guest. These assumptions were confirmed into the framework of quantum theory of atoms in molecules, due to the existence of bond critical points connecting carbon and hydrogen tweezer's atoms and carbon atom of the guest species. The density of states shows that it is possible to observe that the only contribution near the active regions is made by the guest species. The tweezer molecule is the perfect host for organic molecules, because there is no electronic interaction between them. The electronic properties of the guest species remains unchanged under the molecular tweezer interaction.

## 1. Introduction

Molecular tweezers [1–3] are organic systems (predominantly aromatic) that can be twisted in such a way that they adopt the shape of a claw. This generates a cavity, where it is possible propose a guest occupying the cavity, which is able to establish interactions with the host. Tweezers can take a number of forms, Fig. 1 presents some examples [4–6].

In Fig. 1, it is possible observe structures with aromatic rings at the ends. The aromatics rings at the end make possible that the π electron cloud could interact with different chemical entities, making these structures more viable for experimental designs [7,8].

Aromatic rings can form organometallic complexes by linking with metal atoms and this feature involves coordinated covalent bonds, which can also form very large arrangements by means of π-π stacking or even generate communications through space, as in nucleic acids [9]. However, most importantly, many of these cases correspond to supramolecular interactions that are able to produce different molecular complexes, suitable for a wide variety of applications [10].

It is important to emphasize the large relevance of this kind of molecules because molecular tweezers are receptors of other kind of molecules and this activity has been studied in experimental as well as theoretical works [1,11]. In particular the theoretical research can contribute in important manner because the development of new methods can help to explain the nature of weak bonds

[12] and the considerable influence of them in the supramolecular interactions which experiments the tweezers and their guests.

In this sense it is important to mention works as those of Martin [13], Denis [14] and Truhlar [15] which have theoretically studied the interaction of some tweezers and fullerenes, the study of Jacquemin [16,17] about the capture of aromatic molecules by means tweezers and the evaluation of the trapping power of these systems reported by Tkatchenko [18], all these works are important contributions to the study of weak interactions, but furthermore they contribute to design new chemical systems which can have utility in different fields of study which can be energy, pharmaceutical or catalysis.

Nanotubes are allotropes of carbon which can be considered as cylindrical arrangements of graphene sheets [19]. These can be either single or multiple walled and can present multiple diameters. The nature of the walls is closely related to the aromaticity of their single rings, i.e. the π-electrons are positioned to interact with other organic species.

The initial idea to form a complex between nanotubes and tweezers was published in 2008 [20,21]. This conceived a large diameter nanotube associated with pyrene-tetrathiafulvalene, and here the idea was to have a kind of staple to help with the immobilization of the nanotube.

The present work deals with a theoretical study about the interactions between molecular tweezers that work as a scaffold, and different guests such as chromium atoms or narrow nanotubes. There are different types of bonds, the nature of these bonds are discussed here

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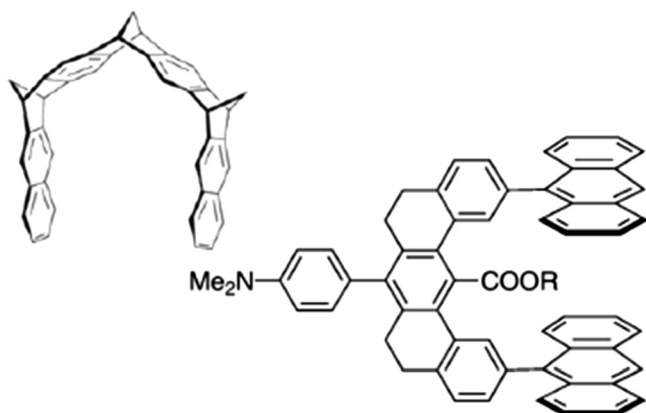*E-mail address:* salcevitch@gmail.com (R. Salcedo).

**Fig. 1.** Examples of molecular tweezers.

## 2. Methods

The optimization process of all designed species was carried out in two stages. Firstly, the computational chemistry software NWChem [24] was used to carried out a 10,000 stage Molecular Mechanic conformational search using Amber force field with the Amber parameter set [22,23], in order to achieve the global minimum, all NWChem default parameters were used. Secondly, as implemented in the Gaussian09 package [25] the highly parametrized functional meta-GGA of Truhlar and Zhao named M06-L [26,27] was used to optimize all geometries and in all calculations, the 6-31G** basis set was used for all atoms. A further comparison with the larger basis set 6-311G** was carried out for a chromium containing complex. The basis 6-31G** was used in order to save computational resources, giving comparable results to the larger basis set, details below.

Grimme's empirical dispersion corrections [28] (D3) were used for calculate the energy due to weak interactions (London dispersion forces) between molecular tweezer and hosted species. That scheme has been used satisfactorily since its original formulation to quantify the dissociation energies in van der Waals complexes as a "bucky ball catcher" hosting a fullerene $C_{60}$.

Those calculations were carried out using the DFT-D3 stand alone code provided by Grimme [28], which provides the correction to the total electronic energy (calculated at the DFT level M06-L/6-31G**) in addition to separate intra and intermolecular weak interactions. The M06-L functionals is claimed to capture "medium-range" interactions [29], meanwhile our Grimme analysis consider part of the large distance interactions. With the combination of both methods, it is enough to have a quantitative analysis of the interaction between the hosted species and the molecular tweezer.

In comparison to experimental measures obtained for several organic van der Waals complexes, dispersion-corrected methods have proven to improve the results obtained with uncorrected functionals [30] including highly parametrized functionals as the family M06 [31]. Overall, include a correction to the energy as the proposed by Grimme is necessary to study complexes which involve weak interactions, apart from the DFT functional chosen.

The convergence threshold used in the present paper are the threshold default given in the Gaussian09 package; scf convergencia criteria is $10^{-8}$ a.u.; and RMS force criterion is $10^{-4}$ a.u.

The density of states of the total system (TDOS) has been calculated using the MULTIWFN computational package [32]. In order to achieve the TDOS for isolated systems, the TDOS is extrapolated with a Gaussian function $G(x)$:

$$G(x) = \frac{1}{c\sqrt{2\pi}} e^{\frac{x^2}{2c^2}},$$

In which $c = \frac{d}{2\sqrt{2\ln 3}}$, $d$ is an adjustable parameter which represent the full width at half maximum. The Fermi energy is determined as the middle point of the band gap $E_F = \frac{(E_{LUMO} - E_{HOMO})}{2}$. It is also shown the contribution in the density of states of each compound (Tweezer and Nanotube/Nanotori) of the whole system, which is called as the partial density of states (PDOS). The PDOS for the fragment $A$ is calculated as

$$PDOS_A(E) = \sum_i \Xi_{i,A} G(E - \varepsilon_i),$$

where $\Xi_{i,A}$ is the composition of the fragment A in the orbital i. The composition of the fragment A is estimate with Mulliken charge analysis. To estimate the DOS is necessary to include the option "pop = full" in the optimization input, in specific in the G09 input.

## 3. Results and discussion

### 3.1. Molecular tweezer metallocene

In Fig. 2a, it is shown the empty tweezer molecule (molecule **1**). In Fig. 2b, it is shown the tweezer molecule with an anthracene complex as guest, this structure is entitled as molecule **2**. In Fig. 2c, it is shown the tweezer molecule with an anthracene π complex and four chromium atoms as guest.

The election of chromium as the guest of the tweezer has its source in the nature of the bis-dibenzene-chromium compound [33] in which two benzene rings can interact with a chromium atom in oxidation state 0, therefore the resultant species can be studied considering it as a large example of a metallocene, the inclusion of other transition metals will be the theme of a future research work. The structure can be studied including four or six metal atoms which can interact with the aromatic rings of the tweezer and also with those of the anthracene guest, however the species containing six atoms shows large difficult to optimize, perhaps the regions is so crowded in electronic traffic, however the species containing four was easily optimized and this was the cornerstone of this part of the study. Therefore the whole compound shows a charge of 0. Respect the multiplicity, several other calculations were performed looking for stable large multiplicity states because in particular chromium exhibits the tendency to delocalize several electrons, however no other multiplicity state reach stable configuration.

The molecule **1** belongs to a $C_2$ point group symmetry; the average distance between arms is 8 Å. The hollow molecular tweezer (molecule **1**) shows three electron rich regions; the lateral bridge; and the both arms of the molecular tweezer. This behavior can be appreciated in the schemes of the frontier molecular orbitals (MO's) shown in Fig. 3. The size and shape of the three main regions suggest that there exist limited or null communication between them. Likewise, the energy gap (HOMO-LUMO gap) between these functions is 5.36 eV or 123.28 kcal/mol, placing this species in the category of insulator. According with previously mentioned, the communication should be established by the formation of inclusion complexes, In addition to the possibility of adjust the energy gap.

The formation of this type of inclusion complex has been suggested previously [1,5]. Molecule **2** is an example where an anthracene molecule is placed in the cleft between both arms, reaching the minimum energy structure. The included anthracene species is not localized at a completely symmetric position with respect to the arms of the tweezer (see Fig. 4), therefore the distances between the corresponding carbon atoms vary around an average