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COMMUNICATION

Enhanced Association for C₇₀ over C₆₀ with a Metal Complex with Corannulene Derivate Ligands

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The geometry imposed by the coordination sphere around the metal, together with the choice of the “arms” can be used advantageously to build corannulene-based molecular tweezers which show great affinities for C₆₀ and C₇₀, as revealed by NMR titration experiments, mass spectroscopy, DFT calculations and the single crystal X-ray structural analysis of compound C₆₀⊂1.

The design of molecular receptors has attracted the interest of the research community along the years. In particular, the syntheses of compounds that can form supramolecular aggregates by non-covalent interactions have been studied in detail.¹ In this regard, the most significant progress has been made in fullerene recognition.² Both size and shape are the main factors that determine the design of molecular architectures to be used to this purpose and thus cages, macrocycles or molecular tweezers are the most recurrent constructions.³

Fullerene receptors that bear heteroatoms or polar substituents are well known and, in these cases, it has been demonstrated that a high complementarity between host and guest leads to a maximization of the electrostatic interactions that play an important role in the association of fullerenes.^{2b} However, it is much more difficult to build purely carboaromatic fullerene receptors and, consequently, the number of examples that describe the formation of these supramolecular adducts is very limited. As far as we know, the onion type structures of the carbon nanorings,^{4,5} and the corannulene buckycatcher of Sygula et al.⁶ are the only examples described. On the other hand, aside from porphyrin derivatives, the use of metal complexes as receptors for fullerenes has been reported for the formation of several fullerene cages.⁷

In the current work, we describe a simple procedure to prepare molecular tweezers by attaching different polycyclic aromatic hydrocarbons (PAHs) in a *cis* arrangement to platinum square planar

complexes. It was expected that an angle close to 90° between the two PAH fragments would provide a suitable distance to bear a fullerene. Four different molecules (1-4) have been prepared in this way by attaching fragments with different shapes that, *a priori*, can interact strongly with a fullerene molecule. On one hand, corannulene fragment presents good complementarity with the external fullerene surface. On the other hand, helicene fragments are chiral nonplanar good π-donors PAHs species and can form charge-transfer complexes with appropriate π-acceptors.⁸ Finally, pyrene is a completely planar molecule and many of its derivatives have been widely used in supramolecular chemistry, mainly in studies of π-π interactions with different kinds of nanotubes.⁹ Thus, with all this in mind, these platinum compounds were evaluated as hosts for C₆₀ and C₇₀.

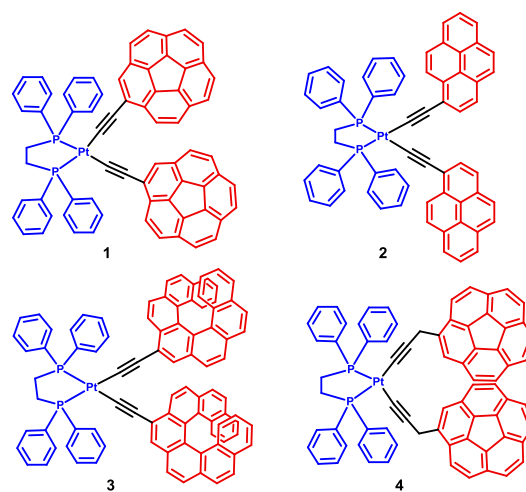


Fig 1. Square planar Platinum complexes used as molecular tweezers.

Synthesis of complexes 1-4 was carried out in a one pot procedure by the coupling of the corresponding trimethylsilyl

ethynylpolyaromatic derivative and $[\text{PtCl}_2(\text{dppe})]$ at room temperature in very good yields. The resulting complexes bear the well-known 1,2-bis(diphenylphosphino)ethane ligand (dppe), and the two remaining coordination positions are occupied by the two polyaromatic ethynyl units (Figure 1). All these new compounds are air stable and were characterized by analytical and spectroscopic methods (see supporting information for experimental details and spectroscopic data).

Taking advantage of the suitable arrangement of the two corannulene units in the molecular tweezers **1**, we decided to study its binding to fullerenes. The first evidence to support the formation of supramolecular association was found by means of MALDI-TOF MS experiments. The spectrum of a 1:1 mixture of **1** and C_{60} , showed peaks at m/z 1859.4 and 1860.4, corresponding to $[\text{C}_{60}\text{C}\mathbf{1}]^+$ and $[\text{C}_{60}\text{C}\mathbf{1}\text{-H}]^+$ and when C_{70} is used, peaks at m/z 1979.0 and 1980.0 were observed, due in this case to $[\text{C}_{70}\text{C}\mathbf{1}]^+$ and $[\text{C}_{70}\text{C}\mathbf{1}\text{-H}]^+$ ions (see Supporting Information).

The association of **1** and fullerenes in solution was also investigated by ^1H NMR titration (400 MHz, 298K) in toluene- d_8 . Although toluene may lead to underestimated association constants due to host and fullerene solvation, it is the most commonly used solvent for corannulene derivatives, and we decided to use it for a better comparison with published work.

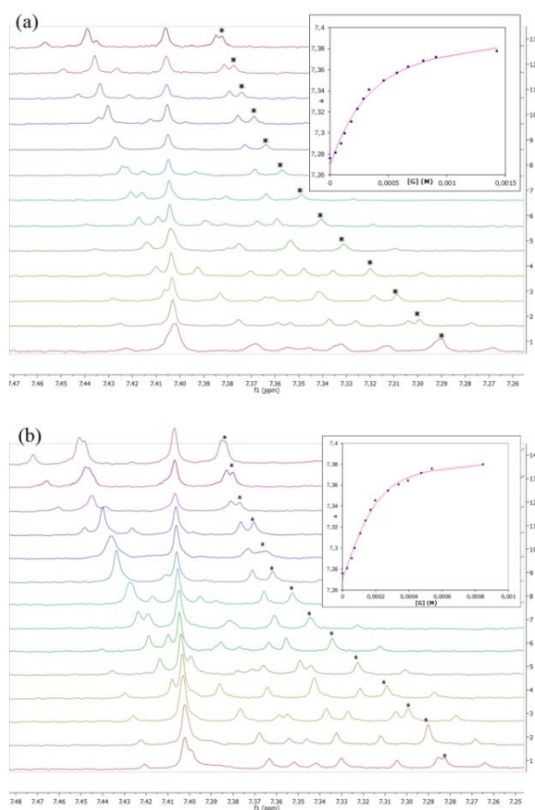


Fig. 2. Selected ^1H NMR spectra (400 MHz, 298K, toluene- d_8) of **1** upon addition of C_{60} (a) or C_{70} (b) showing the shielding of corannulene protons. Nonlinear curve regression for the results of the titration for proton labelled.

Gradual addition of fullerene to a solution of **1** in toluene- d_8 caused a corresponding change in the chemical shifts of all corannulene protons, while the signals of the dppe ligand remained

unchanged. Figure 2 shows NMR shift spectral changes for selected protons of corannulene in receptor **1** upon addition of C_{60} or C_{70} . Job plots supported the 1:1 stoichiometry of the complexation in both cases (see Figure S22 in the Supporting Information). The association constants (K_{assoc}) determined for complexes $\text{C}_{60}\text{C}\mathbf{1}$ and $\text{C}_{70}\text{C}\mathbf{1}$ gave values of $4600 \pm 100 \text{ M}^{-1}$ and $20700 \pm 600 \text{ M}^{-1}$, respectively, thus showing a notable increase of about four times in the binding constant value for the fullerene C_{70} when compared with C_{60} . This behavior differs markedly from that of the corannulene derivative synthesized by Sygula et al. for which both association constants are similar.^{6b} This interaction was also confirmed by variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (see Figure S25 in the Supporting Information). It is worth noticing that UV-vis titration studies have been tried in PhCl at 298K, although host-guest charge transfer bands have been observed, obscuring the much weaker affected bands and preventing the estimation of an association constant by this technique.

Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution of a (1:1) mixture of compound **1** and C_{60} (Figure 3). The molecular structure obtained reveals that C_{60} is embraced by the two corannulene units, showing unequivocally the inclusion of fullerene into the concave cavity formed. The depth of penetration of the C_{60} into one of the corannulene fragments is 6.92 \AA , measured from the centroid of the C_{60} to the centroid of the corannulene five-membered ring, and 6.90 \AA to the other corannulene. The average distance between the C_{60} cage and the inner surface of the corannulene units in **1** is roughly estimated to be 3.6 \AA , which is similar to the interlinear distance in multiwalled carbon nanotubes.

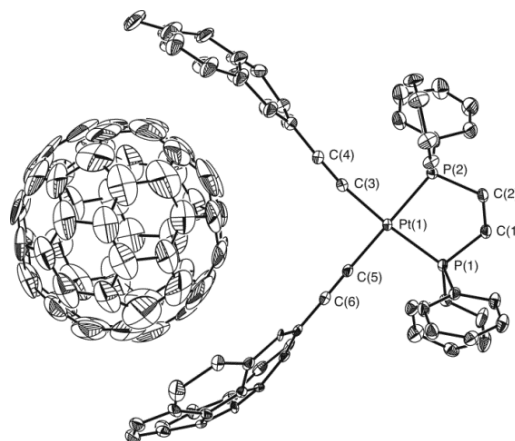


Fig. 3. X-ray crystal structure of $\text{C}_{60}\text{C}\mathbf{1}$. Minor components of one corannulene and one phenyl ring, hydrogen atoms and toluene solvent molecules are omitted for clarity.

In order to add additional information to experimental data, we performed DFT calculations at BLYP-D3/TZP level of theory for the supramolecular adducts of receptor **1** with C_{60} and C_{70} . These results support several empirical facts. The binding energy of the optimized structure for the adduct with C_{70} (using the more stable conformation, $\mathbf{1}\text{C}_{70}(\text{a})$, see Figure S29 in the Supporting Information) is lower than that of the complex $\mathbf{1}\text{C}_{60}$ by 1.5 kcal/mol . The larger stability of the C_{70} adduct is in agreement with the empirical data and supports the ratio 4:1 in the K_{assoc} values

discussed above. We additionally conducted an energy decomposition analysis for 1C_{60} and $1\text{C}_{70}(\text{a})$ in order to shed some light on the larger stability of the latter complex. The results (see Table S3 in the Supporting Information) show that the main contributor to the binding energy is the dispersion forces (E_{DISP}) whereas electrostatic forces (E_{ES}) and charge transfer/orbital interaction (E_{ORB}) are hardly significant. This behavior has been observed previously in another purely carboaromatic fragment, corannulene derivative $\text{C}_{60}\text{H}_{28}$.^{6c} The theoretical results suggest that the reason why $1\text{C}_{70}(\text{a})$ has a larger binding energy than 1C_{60} is twofold: a more favorable dispersion interaction in the former and a smaller Pauli repulsion between the C_{70} and the catcher electronic charge densities. The energy required to deform the fragments from their equilibrium geometries is very similar in both complexes and contributes merely 0.1 kcal/mol to the final relative energy.

To elucidate the importance of the complementarity in the concave-convex surface to the binding of fullerenes, we also studied the complexation with fullerenes in the complexes **2** and **3**, which contain pyrene or helicene acetylide pincers, respectively. As we stated above, helicenes are nonplanar polyaromatic compounds, as corannulene, and pyrene is a completely planar molecule that has been extensively proven as a good fragment for π - π interactions.⁹ In both cases, we have performed ^1H NMR studies of association with C_{60} in toluene- d_8 showing that the proton signals remain unchanged upon addition of fullerenes and therefore evidencing no significant formation of supramolecular associations.

Another factor that can influence the interactions between fullerenes and corannulenes is the degrees of freedom of the molecule acting as receptor. If the flexibility of the molecular tweezers arms is increased too much, the corannulene moieties can interact between them competing in fact with the fullerene and, consequently, lowering the association constant. Having that in mind, we designed a different compound with one methylene group between the acetylide and corannulene moieties (**4**, Figure 1). The presence of an extra methylene allows an increase in the distance between the corannulene pincers and more flexibility, therefore, potentially leading to a more efficient association. The ^1H NMR titration studies of **4** with C_{60} showed a variation in some corannulene protons, but the changes were too small for the measurement of a reliable association constant. It is assumed therefore that the association between **4** and C_{60} is barely significant. DFT calculations were again performed for this adduct, but no equilibrium structure was found. Additionally, it is worth pointing out that during the course of the optimization we observed a relatively large deformation of the acetylide groups. This would suggest that the catcher geometry has to deform significantly in order to maximize the interaction between corannulene and C_{60} . Although the theoretical calculations do not provide a conclusive answer, they are in agreement with the experimental observations that an extra methylene does not yield a more efficient association in this case. This behavior could be justified by considering a plausible intramolecular interaction between the two corannulene pincers in the molecular clip **4**.

Conclusions

In summary, we have designed a handy platform to build molecular tweezers with different polycyclic aromatic

hydrocarbons (PAHs) at the end of a rigid acetylide group. The coordination geometry about the metal center is shown to be optimal to form supramolecular host-guest complexes with fullerenes for the corannulene derivative **1** as manifested in the single crystal X-ray structural analysis of compound $\text{C}_{60}\text{C}1$. As far as we know, this compound is the corannulene derivative with the highest association constant for C_{70} ($K_{\text{assoc.}} = 20700 \pm 600$ in toluene- d_8) and one of the best binders for C_{60} ($K_{\text{assoc.}} = 4600 \pm 100$ in toluene- d_8). The difference between these two $K_{\text{assoc.}}$ (4:1), shows that compound **1** presents a surprisingly high selectivity, preferring C_{70} over C_{60} . In contrast, the increase in the degrees of freedom and the lack of complementarity have been shown to be critical factors to impede this association as revealed by the studies of complexation with fullerenes in compounds **2**, **3** and **4**.

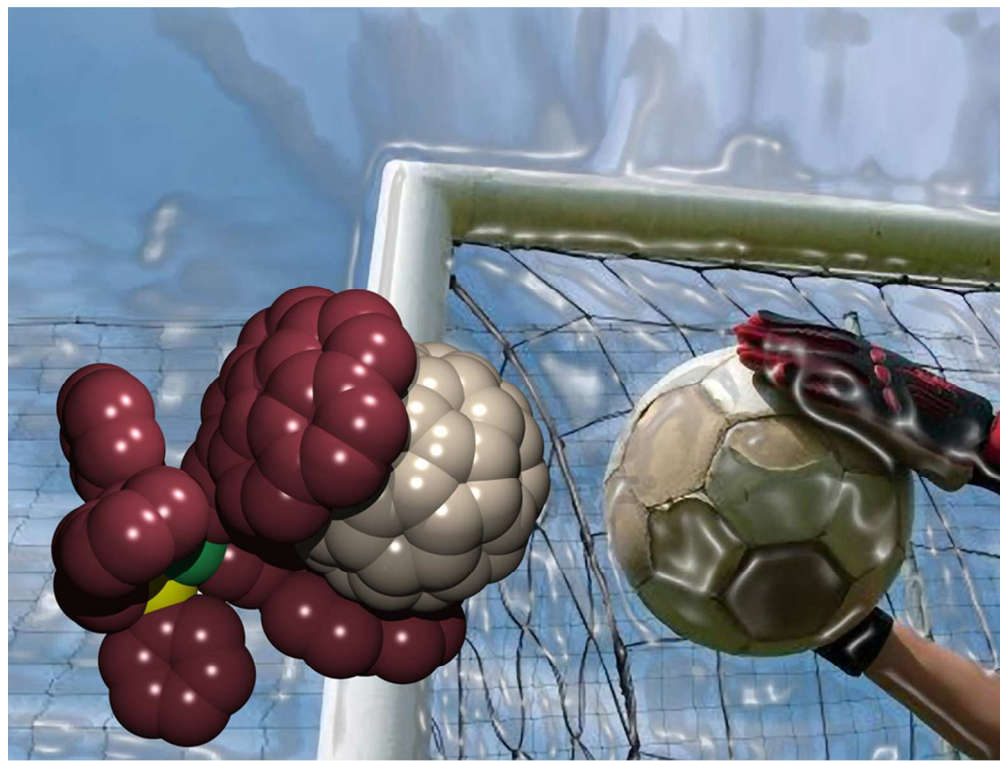
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