Journal Name

COMMUNICATION

Affinity modulation of photoresponsive hosts for fullerenes. Light-gated corannulene tweezers.

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Six azobenzene derivatives bearing polyaromatic fragments have been prepared and their reversible photoisomerization has been assessed. Corannulene-functionalized molecules have demonstrated excellent switchable hosting abilities towards fullerenes in which an interesting range of affinities has been found. The success of this design relies upon the reversible formation and destruction of tweezer-like structures.

The study of supramolecular chemistry is a hot topic in science since the end of last century[1] and a great development of a wide variety of concepts has been carried out in order to get a deep understanding of the assembly among molecular entities through weak and reversible interactions. One of such concepts consists of using molecular tweezers as hosts for recognizing a variety of molecules, in which fullerenes occupy an important position.[2] The main reason to achieve such an interaction relies upon a complementarity between curved fullerene and the receptor molecule, whose structure matches the surface of the guest. Several approaches have been carried out, being one of them the use of corannulene[3] due to its nonplanar structure, commonly known as buckybowl. Convex and concave faces have different electron density, allowing dipolar interactions and giving rise to interesting properties.[4]

Of particular interest are receptors that can modulate or even change totally their affinity by an external stimulus, such as light.[5] One of the most used photoresponsive moiety is azobenzene, which can be switched between both configurational isomers with a simple input of light.[6] Thus, several studies have been performed using this molecule in order to carry out considerably different work,[7] but none of them dealt with corannulene-fullerene interactions.[8] Herein, we present the first corannulene derivatives that contain azobenzene as tether resulting in photoresponsive tweezers. Along with these compounds, other planar polycyclic aromatic

hydrocarbons derivatives, such as phenanthrene and pyrene, have been prepared in the same way in order to complete the whole family and for comparison purposes (Figure 1).

The preparation of all azobenzene-containing PAHs followed two different routes depending on the location of pinacol boronate groups prior to Suzuki-Miyaura C-C coupling (see the Supporting Information for a more detailed discussion about the most preferable chosen route).

Compounds **4**, **5** and **6** were fully characterized by NMR, UV-Vis absorption spectra and mass spectra (see Supporting Information). Single crystals suitable for x-ray diffraction of phenanthrene compounds **4a**, **4b** and corannulene derivative **6b** were obtained, showing their structures in solid state, as depicted in Figure 2. Phenylene moieties and nitrogen atoms of the azobenzene are placed at the same plane in all compounds, whereas phenanthrene and corannulene substituents have a CH-C-C-CH dihedral angle of around 50 degrees respect to azobenzene; 50.4° (in **4a)**, 59.5° (in **4b**) and 47.21° (in **6b**). In *meta*-substituted molecules, both substituents are in an expected *trans* configuration to avoid
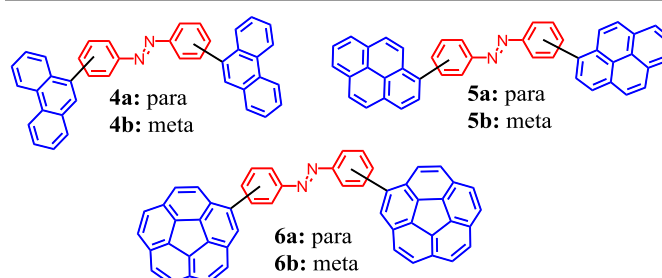

Figure 1. Six azobenzene derivatives prepared in this work.
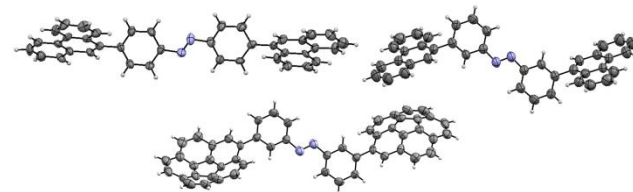

Figure 2. Crystal structures of **4a** and **4b** (top); and **6b** (bottom). Ellipsoids at 50% of probability

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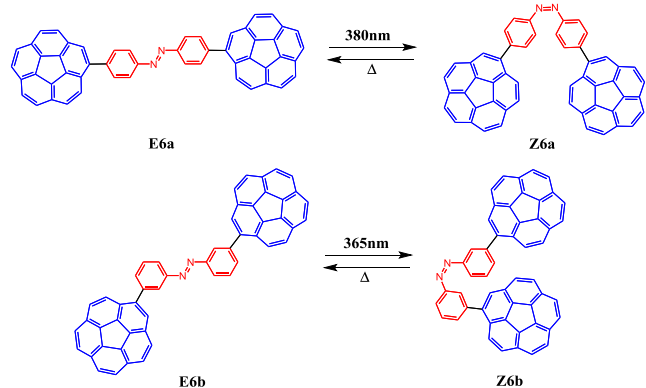
steric constraints of *cis* configuration.

Photoisomerization (Scheme 1) was studied in toluene. UV-Vis absorption and ^{1}H-NMR spectra were recorded to check the process. Initially, all compounds show a E/Z ratio of around 80:20. After heating for 30 minutes at 80 °C, this ratio is shifted to 95:5. Irradiation with 365 nm at room temperature give rise to signals at higher field indicating the presence of Z isomer with different E/Z ratios (Figure S75). It's known that this wavelength is commonly used for switching azobeneze derivatives, but is not optimum for our corannulene and pyrene-substituted azobenzenes (**5** and **6**) whose $\pi \rightarrow \pi^*$ band appears at longer wavelengths for *para* substituted and shorter for *meta* substituted. Indeed, if irradiated at 380 nm, compounds **5a** and **6a** are more efficiently switched as it can be seen in the UV-Vis spectrum (Figures 3, S71 and S73) and, more explicitly, in their ^{1}H-NMR spectra (Figures 4 and S55-S58).

Once determined the structures of all compounds and the extent of photoisomerization, all compounds were subjected to preliminary supramolecular association tests in both photostationary states by recording ^{1}H-NMR spectra in toluene-d8. The addition of excess of C_{60} or C_{70} can produce chemical shift changes indicating supramolecular association event. As expected, compounds **4** gave no appreciable changes in chemical shift. Moreover, compounds **5** followed the same trend despite the ability of pyrene to establish strong association with polyaromatic architectures.[9] We expected, at least, a subtle interaction with the central part of C_{70} but that was not observed. On the other hand, corannulene-functionalized azobenzenes **6**, gave positive results. Regarding the case of **6a** we found a great explicit affinity modulation towards fullerenes.

Compound **E6a**, does not establish supramolecular association with C_{60} or C_{70} at all. ^{1}H-NMR spectra recorded after additions of fullerenes remained unchanged (Figures S88 and S89). As expected, its structure is not suitable to host the guest in a tweezer-like manner (Scheme 1, up left). However, **Z6a** (Scheme 1, up right) is capable of hosting fullerenes with estimated association constants (K_a) of $(2.6\pm0.3)\cdot10^3$ M^{-1} and $(2.5\pm0.3)\cdot10^3$ M^{-1} for C_{60} and C_{70}, respectively (Figures 5 and S90-S95); which are similar to those obtained for other
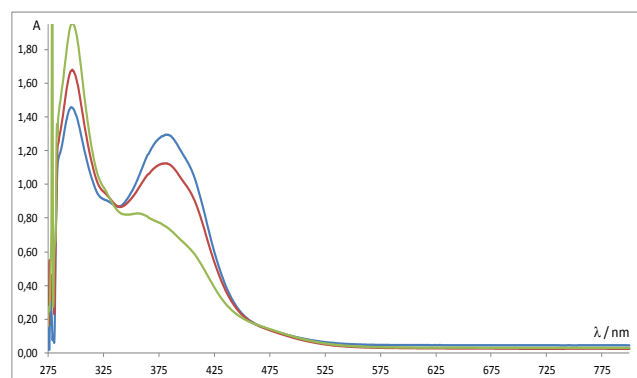
Figure 3. UV-Vis spectrum of **6a** in toluene (blue), after irradiation for 15 minutes at 365nm (red) and after irradiation for 15 minutes at 380nm (green).
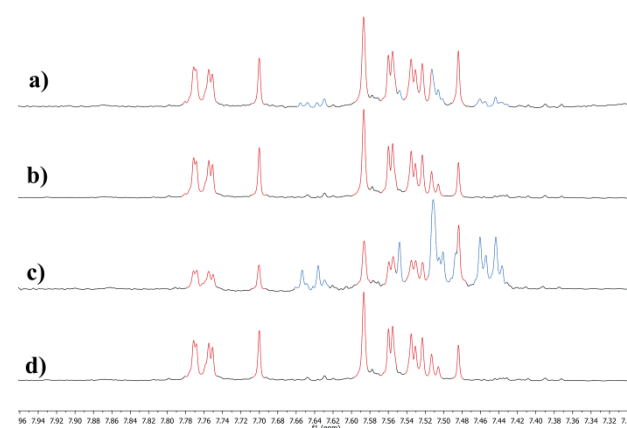
Figure 4. ^{1}H-NMR spectrum (500 MHz) of **6a** in toluene-d8. (a) Initial spectrum; (b) After heated at 80ºC for 15 minutes and cooled down to rt; (c) After irradiation at 380 nm for 30 minutes; (d) Thermal conversion to the initial state by heating the sample at 80 °C for other 15 minutes and cooled down to rt. Red color corresponds to E isomer, blue color to Z isomer.

bis-corannulene derivatives.[3b,d,f,h] This molecule forms 1:1 adducts with both fullerenes and no discrimination is observed since both constants are almost identical. In light of these results, an on-off behavior is suggested that can be carried out in several cycles making this compound a light-gated supramolecular tweezer.

Compound **E6b**, in contrast, shows a very different behavior (Scheme 1, bottom left). Supramolecular association is established with C_{60} and C_{70} having constants of $(5.0\pm0.1)\cdot10^2$ M^{-1} and $(8.3\pm0.1)\cdot10^2$ M^{-1} in toluene-d8, respectively (Figure 6 and S76-S81) corresponding to 1:1 stoichiometry according to Job plots. Switched form of that compound, **Z6b** (Scheme 1, bottom right), shows abilities to host fullerenes too. Association constants of **C_{60}@Z6b** and **C_{70}@Z6b** were estimated to be $(6.7\pm0.2)\cdot10^2$ M^{-1} and $(2.5\pm0.3)\cdot10^2$ M^{-1} (1:1 stoichiometry). The new structure has affected its ability to host fullerenes. Affinity for C_{60} is still moderate, although is slightly better than before. In the case of C_{70} we found a constant notably worse than that estimated for **E6b**. Its affinity has been decreased around 70%. We reasoned that the new structure of switched **6b** makes harder the approximation of C_{70} due to the lack of space and poor host preorganization (Figure S97). Due to the fact that **E6b** is not initially preorganized as host,

Scheme 1. Example of the switching process between corannulene-functionalized azobenzenes, depicting tweezer-like preorganization for **6a** upon conversion to Z isomer.
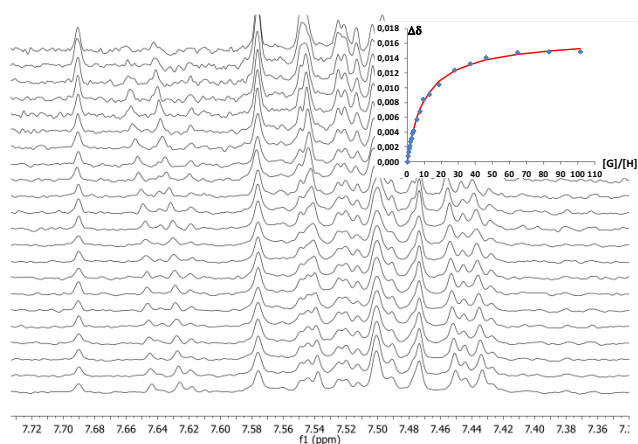
Figure 5. ^{1}H-NMR spectra (500MHz, toluene-d8) in the supramolecular titration of **Z6a** with C_{60}. Inset: Plot of changes in chemical shift against [G]/[H] where G is C_{60} and H is **Z6a**. Red line corresponds to the nonlinear fitting of $\Delta\delta$ for one proton to a 1:1 binding isotherm.
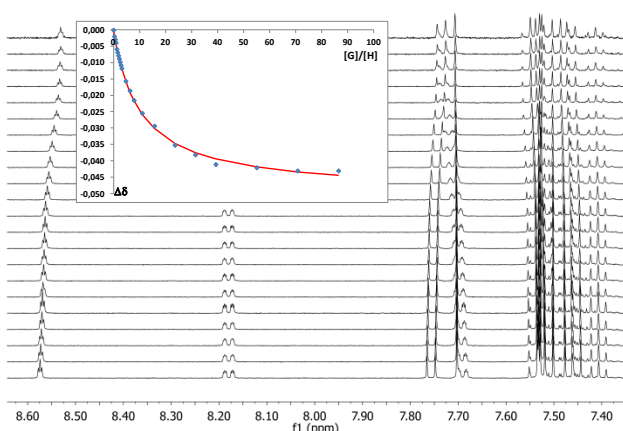

Figure 6. ^{1}H-NMR spectra (500MHz, toluene-d8) in the supramolecular titration of **E6b** with C_{60}. Inset: Plot of changes in chemical shift against [G]/[H] where G is C_{60} and H is **E6b**. Red line corresponds to the nonlinear fitting of $\Delta\delta$ for one proton to a 1:1 binding isotherm.

this compound must undergo a conformational twist from *trans* to *cis*, implying an additional deformation energy to be overcome before establishing the supramolecular association, eventually giving smaller K_a if compared to **Z6a**, but we did not expect a difference of one order of magnitude.

Therefore, we conducted computational calculations and optimized its geometry in *trans* conformation from the structure observed in single crystal (see Supporting Information for the theoretical model followed). Thus, the rotation of N=N-C=CH dihedral angle was calculated in toluene and a maximum at 5.67 kcal/mol was obtained, low enough to be easily reachable at room temperature (Figure S98), because it is not hampered by other intramolecular associations (corannulene-corannulene intramolecular π stacking, for instance). Then, we minimized the structure of the adduct **C_{60}@E6b** at the same level of theory (Figure 7). The cavity formed by both corannulene subunits is suitable to host a fullerene, but CH hydrogens of azobenzenes pointing towards substituents seem to interfere guest approximation and the adduct is formed out of the ideal azobenzene line, forcing both corannulenes to adopt a bent conformation, and, consequently, diminishing the affinity.
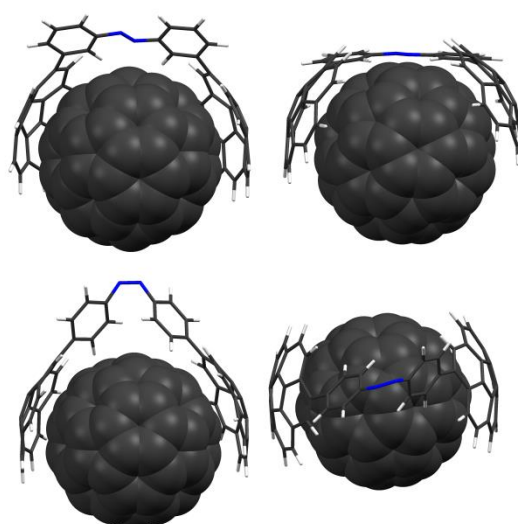

Figure 7. Optimized geometry of **C_{60}@E6b** (up) and **C_{60}@Z6a** (bottom).

An interaction energy between C_{60} and host molecule of -37.1 kcal/mol was obtained after taking into account basis set superposition error (see Supporting Information regarding how this calculation is done). That energy is very similar to those calculated for other corannulene derivatives.[10]

The geometry of **C_{60}@Z6a** adduct was also optimized (Figure 6) at the same level of theory giving rise to an expected geometry showing a very good complementarity between fullerene and host molecule. In this case, the adduct is formed in the ideal azobenzene line having both corannulene subunits almost perpendicular to it and parallel between them. This fact, along with the better preorganized structure could be the reasons of its better affinity. Interestingly, the calculated interaction energy is -34.9 kcal/mol.; this means 2.2 kcal/mol less than that calculated for **C_{60}@E6b**. This unexpected slight decrease encouraged us to map the interactions between host and guest. Non-covalent interactions[11] were analyzed in both optimized models revealing a more attractive interaction in **C_{60}@E6b** in which the isosurface almost covers half of fullerene surface, whereas in **C_{60}@Z6a**, it substantially lies at corannulene fragments (Figure 8). It seems that azobenzene tether contributes to interaction energy while C_{60} is close to it, but this contribution disappears when moves away.

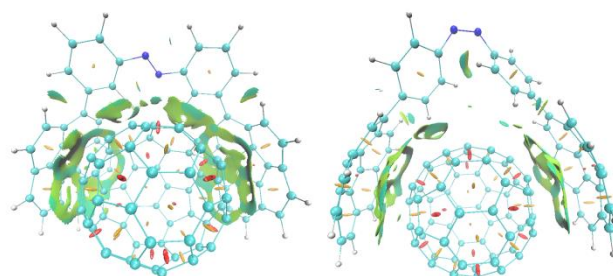**Figure 8.** Gradient isosurfaces (s=0.3 a.u.) of **C_{60}@E6b** (left) and **C_{60}@Z6a** (right). The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ. Red indicates repulsion, while green means weak attraction.

The effect of additional stabilization by the fragment connecting corannulene subunits has been pointed out by Sygula and cooworkers.[3i,j]

In summary, we have described six new azobenzene derivatives bearing polycyclic aromatic fragments assessed their ability to modulate their affinities towards fullerenes. One of this compounds, **6a**, has demonstrated to be an effective on/off light-gated molecular tweezer.

Acknowledgements

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