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Fullerene recognition with molecular tweezers made up of efficient buckybowls. A dispersion-corrected DFT study

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In 2007, Sygula and co-workers introduced a novel type of molecular tweezers with buckybowl pincers that have attracted a substantial interest of researchers due their ideal architecture for recognizing fullerenes by concave-convex π···π interactions (A. Sygula *et al. J. Am. Chem. Soc.* 2007, *129*, 3842). Although in recent years some modifications have been performed on these original molecular tweezers to improve the ability for catching fullerenes, very few improvements were achieved to date. For that reason, in the present work a series of molecular tweezers have been devised and their supramolecular complexes with C_{60} studied at the B97-D2/TZVP//SCC-DFTB-D and B97-D2/TZVP levels. Three different strategies have been tested: (1) changing the corannulene pincers by other buckybowls, (2) replacing the tetrabenzocyclooctatetraene tether by a buckybowl, (3) adding methyl groups on the molecular tweezers. According to the results, the three approaches are effective, in such a way that combination of the three strategies results in buckycatchers with complexation energies (with C_{60}) up to 2.6 times larger than that for the original buckycatcher, reaching almost -100 kcal/mol.

The B97-D2/TZVP//SCC-DFTB-D approach can be a rapid screening tool for testing new molecular tweezers. However, since this approach does not reproduce correctly the deformation energy and this energy represents an important contribution to the total complexation energy of complexes, then a subsequent higher-level re-optimization is compulsory to achieve reliable results (the full B97-D2/TZVP level is used herein). This re-optimization could be superfluous when quite rigid buckycatchers are studied.

Introduction

Nearly 30 years after their discovery, fullerenes, the third allotrope of carbon, still attract the attention of many researches worldwide due to their unique properties and their applications in a wide range of fields as material science or medicine.[1-3] Nowadays, one of the most active fields in fullerene chemistry is the search for molecular receptors capable to form stable associates with them. These receptors not only are useful for isolating fullerenes of the soot, but also for developing new materials for solar energy conversion, optoelectronics, catalysis and switching.[2,4,5]

Since dispersion forces are predominant in the stabilization of fullerene complexes, a key strategy to design new molecular receptors is to make use of concave-convex complementarity to maximize these forces. Nevertheless, the examples of concave fullerene receptors are relatively scarce given that curved molecules are not always an easy synthetic target due to their tensioned structures.[6] In this context, bowl-shaped polycyclic aromatic hydrocarbons, commonly known as buckybowls or fullerene fragments, seem very attractive because several buckybowls have been synthetized in the last years,[7-16] being their concave surface highly suitable for fitting to the convex surface of fullerenes through concave-convex "ball-and-socket" π···π interactions.[17]

The first strong evidence of π···π interactions between buckybowls and C_{60} was published in 2007 by Sygula and co-workers[17], with the synthesis of the molecular tweezers (a buckycatcher, $C_{60}H_{28}$) made up by two units of corannulene and a tetrabenzocyclooctatetraene tether (1a, Fig. 1). Thenceforth, the interest by concave-convex π···π interactions has revitalized and several studies have been performed.[18-30] The usefulness of molecular tweezers with buckybowls pincers could be very noticeable. So, Sygula and Collier envision future applications for buckycatchers as stationary phases in liquid chromatography for the separation of fullerenes or as buckycatcher-fullerene complexes in photovoltaic devices.[31] Moreover, some theoretical studies have already predicted potential applications for the host-guest complex 1a···C_{60}, such

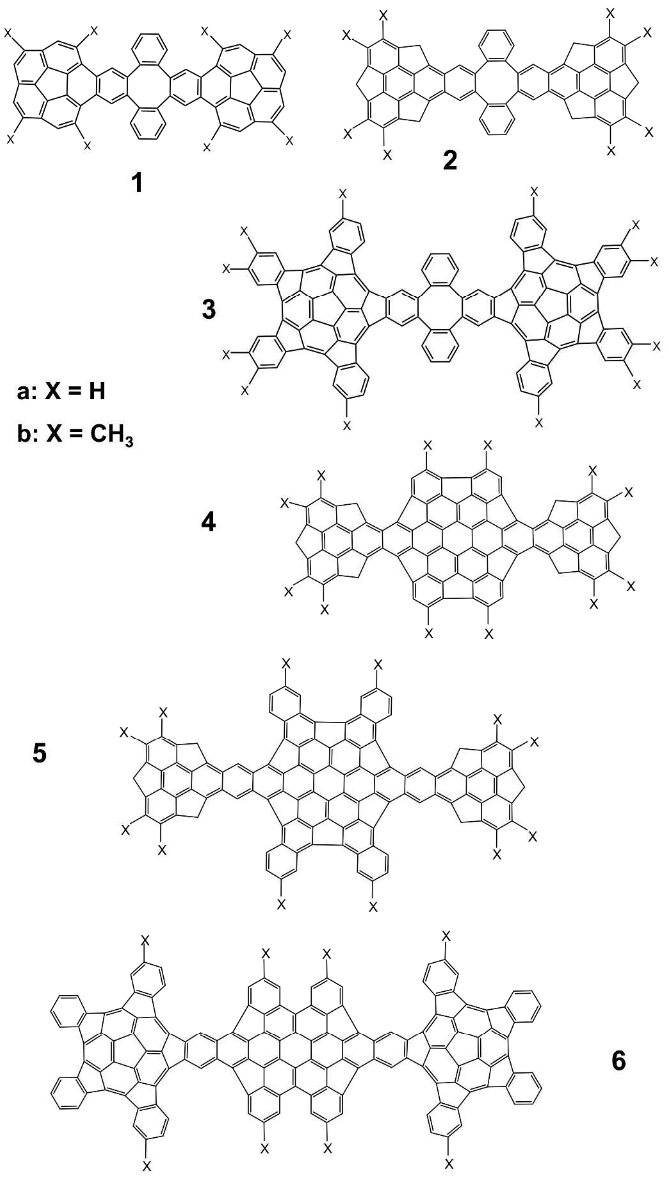


Fig. 1. Buckycatchers studied in this work. (1-6)a, X = H. (1-6)b, X = CH_3.

as two-photon absorption (TPA) active material at near IR wavelengths[32] that shows application in photodynamic cancer therapy (PDCT) and as a charge-transfer mediator for applications in nanoelectronic devices.[33] In addition, recent studies show that crystallization of supramolecular complexes made up buckycatcher 1a and endohedral nitrogen fullerene (N@C_{60}) provide a solid material with a columnar alignment of fullerene cages that can be candidates as qubits for quantum-information processing (QIP).[34]

Undoubtedly, the design and synthesis of buckycatchers with more ability and/or selectivity than 1a is a task of great interest. In order to obtain these buckycatchers, the classic approach would be a hard and expensive job that would include: selecting tethers and pincers to be potential candidates to maximize interactions with fullerenes, synthesizing several molecular tweezers, and then testing their recognition ability in solution and in the solid state. In this context, the utilization of computational models to design and identify synthetic targets with desired $\pi\cdots\pi$ interactions could be crucial for saving cost and time. In 2008, Zhao and Truhlar reported the first theoretical modification of traditional tweezers 1a. In that study, corannulene pincers were changed by a π-extended tetrathiafulvalene (TTF), in particular 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (TTFAQ, $C_{20}H_{10}S_4$).[29] Unfortunately, their results indicate that complexes between buckycatcher with TTFAQ pincers and fullerene C_{60} show an interaction energy smaller than that obtained for complex 1a$\cdots C_{60}$.

Recently, Yanney and Sygula[26] have synthesized a molecular clip made up three corannulene pincers and one cyclotriveratrylene (CTV) tether. Although the new clip consists of one more corannulene pincer than that of buckycatcher 1a, the results showed association constants lower than those reported for complexes of buckycatcher 1a with fullerenes C_{60} and C_{70}. According to these authors, the results could be due to the high conformational flexibility of this molecular clip; it not only results in the larger association entropy penalty in comparison with 1a, but also introduces the possible internally stacked conformers of the free clip competing with the formation of the fullerene inclusion complexes. In addition, a recent theoretical study pointed out that this molecular clip shows a very high deformation energy that is even larger than their complexation energy.[24]

Despite that most of modifications carried out on the buckycatcher 1a involve the change of the tether fragment of the tweezers,[21,26,31] to the best of our knowledge, no study has been attempted with a buckybowl working as tether. Furthermore, it is noteworthy that only one theoretical study has changed the corannulene pincers by a pentaindenocorannulene.[35]

In last years, our group has been devoted to the study of a series of concave-convex interactions between buckybowls and fullerenes in order to find the factors that maximize their interactions.[36-38] In particular, a buckybowl that shows an increase of interaction energy of about 11 kcal/mol regarding to buckycatcher 1a has been proposed.[38] So, the use (as tether or pincer fragment) of this kind of buckybowls could be very useful for designing new molecular tweezers.

In this context, the theoretical study of new molecular tweezers with different buckybowls used as pincers and/or tether could be very desirable. Therefore, the goal of this work is to carry out a detailed study of three different strategies that can give rise to more effective fullerene receptors: 1) changing the corannulene pincers by others buckybowls; (2) changing the tetrabenzocyclooctatetraene tether by a buckybowl; (3) introducing methyl substituents on the buckycatcher (since they favour emergence of C-H$\cdots\pi$ interactions contributing to the stability of the complexes as was shown[36]).

Computational details

First, complexes are optimized by the self-consistent charge density functional tight-binding method using an empirical correction to the dispersion (SCC-DFTB-D). The DFTB+ code is applied for this method together with mio-1-1 parameter set.[39-41] According to our previous work, SCC-DFTB-D method can be very useful to provide starting guesses for more accurate calculations of the largest π···π complexes.[38] Afterwards, a re-optimization is performed at the B97-D2/TZVP level using resolution of identity (RI) approximation implemented in TURBOMOLE 6.3.1 program suite.[42] The latter seems a good calculation level as explained in a recent work of us.[36] For the corannulene dimer (for which high quality QCISD(T) results are available[30]), B97 with the more recent dispersion corrections D3 and D3(BJ), led to slightly worse results (from a energetic point of view) than the D2 correction.[22] Anyway, some exploratory calculations suggest that the choice of the dispersion correction has a little effect on the conclusions of the study, given the high correlation between the results obtained by the different methods (Table S1, Supplementary Information).

Counterpoise corrections are applied to all reported interaction energies to avoid basis set superposition error (BSSE).[43] According to this method, the interaction energy of a system A···B is calculated according to:

$$E_{int} = E_{AB}^{AB}(AB) - \left(E_{A}^{AB}(AB) + E_{B}^{AB}(AB) \right)$$

where superscript refers to the geometry (that of the system AB) and the parenthesis indicates the basis set used (the full basis set of the system A···B). If, in addition, the energetic cost involved in the deformation of each monomer to adopt the geometry of the dimer is considered:

$$E_{def} = \left(E_{A}^{AB}(A) - E_{A}^{A}(A) \right) + \left(E_{B}^{AB}(B) - E_{B}^{B}(B) \right)$$

then, the full complexation energy is obtained as follows:

$$E_{complex} = E_{int} + E_{def}$$

According to our calculations (Table S2, Supplementary Information), the BSSE correction represents around a 10% of the interaction energy in all cases, with very small differences between complexes: it ranges from 9.7 to 10.8%.

The visualization of non-covalent interactions is conducted using the NCIPLOT-3.0 program.[44,45] Graphic displays of concave-convex π···π interactions are obtained using the VMD 1.9.1 software.[46] NCI enables identification of non-covalent interactions and is based on the peaks that appear in the reduced density gradient (RDG) at low densities. When an RDG isosurface for a low value of RDG is plotted, the non-covalent regions clearly appear in the supramolecular complex. These interactions correspond to both favourable and unfavourable interactions. To differentiate between them, the sign of the second eigenvalue of the density Hessian times the density is colour-mapped onto the isosurface; bonding interactions can be identified by the negative sign. To save computation time, promolecular densities have been used, as was done previously with good results.[36]

Results and discussion

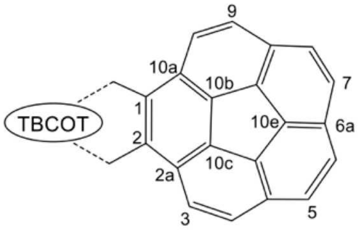
A series of molecular tweezers are devised (Fig. 1) and their supramolecular complexes with C_{60} are studied at the B97-D2/TZVP//SCC-DFTB-D and B97-D2/TZVP levels. C_{2v} symmetry is kept to save computation time. These tweezers are devised using three strategies in order to improve the ability of the buckycatcher designed by Sygula (1a).[17] First, the corannulene pincers are changed by other buckybowls: for sumanene in 2, and for an efficient buckybowl (studied in our previous work[38] in 3. Second, the tetrabenzocyclooctatetraene tether is changed by buckybowls, specifically bowl-shaped hexabenzocoronene derivatives (studied in our previous work;[38] with sumanene pincers (4 and 5) and with efficient buckybowl pincers (6). Finally, methyl substituents have been added on the buckycatcher structure to favour the development of C-H···π interactions: buckycatchers "b".

Analysis of B97-D2/TZVP//SCC-DFTB-D performance regarding to B97-D2/TZVP

Calculations at the B97-D2/TZVP level seem a reasonable choice for studying concave-convex π···π interactions.[20,28,30,47,48] Although this level is chosen in the present work, it is noteworthy that this level is still quite expensive for large complexes. For that reason, assessing the accuracy of "cheaper" procedures could be a very important task for future investigations involving even greater systems. In this context, B97-D2/TZVP//SCC-DFTB-D calculations seem a good alternative as screening tool for studying concave-convex π···π interactions, as observed in our previous study.[38] So, B97-D2/TZVP//SCC-DFTB-D calculations are performed to verify their usefulness.

First, the X-ray geometrical data for complex the 1a···C_{60} is compared with both theoretical (B97-D2/TZVP and SCC-DFTB-D) results. According to Table 1, SCC-DFTB-D calculations reproduce the experimental data reasonably well. In general, the calculated distances are slightly larger than the experimental data, with average deviation of 0.07 Å, due to more opened pincers that corresponds to an increase of aperture from 12.81 to 13.08 Å. Previously reported B97-D2/TZVP calculations behave oppositely, with distances slightly shorter than the experimental data, with average deviation of 0.08Å.[28] Thus, both theoretical methods seem to give rise to results of similar quality; in one case the error is excess and in another is shortage, regarding distances of Table 1. However, if only distances involving the central regions of the pincers (the central five-membered rings of the corannulene pincers that are more directly "catching" the fullerene) are taken into account, the B97-D2/TZVP results are much closer to the experimental,

Table 1. Distances (in Å) between the centroid of fullerene cage and the pincer carbon atoms of the buckycatcher in $1a\cdots C_{60}{}^{a}$. Tetrabenzocyclooctatetraene tether is represented as TBCOT.



	X-Ray^{b}	B97-D^{c}	SCC-DFTB-D
C1(C2)	6.77	6.68	6.78
C2a(C10a)	6.71	6.63	6.75
C3(C10)	6.73	6.65	6.76
C4(C9)	6.76	6.68	6.80
C4a(C8a)	6.77	6.69	6.84
C5(C8)	6.83	6.73	6.88
C6(C7)	6.85	6.74	6.90
C6a	6.80	6.71	6.87
C10b(C10c)	6.85	6.80	6.98
C10d(C10f)	6.88	6.82	7.02
C10e	6.90	6.84	7.04
$R_p{}^{d}$	12.81	12.80	13.08

[a] Distances averaged over C_{2v} symmetry-related carbon atoms of the corannulene subunits of 1a.

[b] Ref. 17

[c] Ref. 28

[d] Defined as the distance between carbon atoms C10e and C10e'.

Table 2. Inter-pincer distance for buckycatcher$\cdots C_{60}$ (R_{pc}) complex, inter-pincer distance for isolated buckycatchers (R_{pi}) and distances between the centroid of the C_{60} cage and the centroid of tether part of buckycatchers (R) (in Å). The calculations were performed at the B97-D2/TZVP level. SCC-DFTB-D results are given in parenthesis for comparison.

	R_{pc}	R_{pi}	R
$1a\cdots C_{60}$	11.539 (11.736)	10.661 (9.872)	7.840 (7.988)
$1b\cdots C_{60}$	11.267 (11.447)	11.140 (10.962)	8.114(8.278)
$2a\cdots C_{60}$	11.983 (12.394)	10.360 (6.663)	7.382 (7.661)
$2b\cdots C_{60}$	12.030 (12.360)	9.270 (7.991)	7.340(7.689)
$3a\cdots C_{60}$	13.800 (14.055)	11.071 (10.800)	7.831 (7.920)
$3b\cdots C_{60}$	13.821 (14.032)	13.496 (11.893)	7.772 (7.997)
$4a\cdots C_{60}$	13.406 (13.910)	14.694 (15.424)	7.545 (7.782)
$4b\cdots C_{60}$	13.380 (13.852)	14.635 (15.441)	7.413 (7.700)
$5a\cdots C_{60}$	13.468 (14.159)	17.603 (17.712)	7.529 (7.702)
$5b\cdots C_{60}$	13.532 (14.150)	17.794 (17.843)	7.530 (7.656)
$6a\cdots C_{60}$	14.400 (14.692)	20.698 (20.759)	6.547 (6.740)
$6b\cdots C_{60}$	14.489 (14.714)	20.742 (20.797)	6.550 (6.760)

which clearly is manifested by an aperture of pincers practically equal to the experimental one (12.80 *vs.* 12.81 Å).

Table 2 shows three important geometrical parameters in order to obtain a more detailed evaluation of the performance of SCC-DFTB-D geometries regarding to B97-D2/TZVP ones. R_{pc} and R_{pi} are inter-pincer distances for buckycatcher$\cdots C_{60}$ complexes and for isolated buckycatchers, respectively. The inter-pincer distance is defined as the distance between the centroids of the buckybowl pincers, and R is defined as the distance between the centroid of the C_{60} cage and the centroid of tether (see Fig. 2).

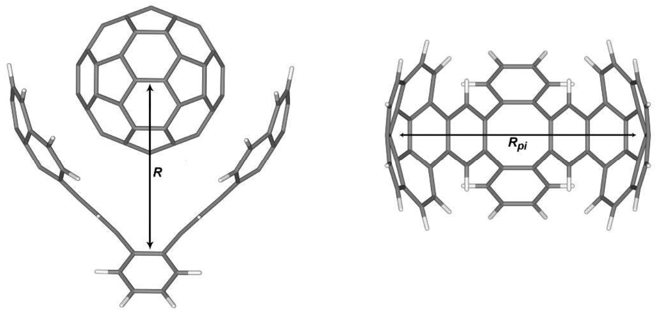


Fig. 2. R is defined as the distance between centroid of the C_{60} cage and the centroid of tether. The inter-pincer distance is defined as the distance between centroid of buckybowl pincers. R_{pi} is the inter-pincer distance for isolated buckycatchers.

If only R_{pc} and R are taken into account (*i.e.* parameters corresponding to complexes), the SCC-DFTB-D results could be considered rather acceptable, with differences with the B97-D2/TZVP results ranging from 0.18 to 0.69 Å and from 0.09 to 0.35 Å, for R_{pc} and R, respectively. In all cases SCC-DFTB-D distances are larger than B97-D2/TZVP ones. Thus, SCC-DFTB-D predicts complexes where the fullerene is less "embraced" by the tweezers: pincers are less closed and fullerene does not enter so much inside the catcher. As expected, differences between both methods are much larger for isolated buckycatchers because the tweezers bend more easily when not joined to the fullerene. Thus, buckycatchers with tetrabenzocyclooctatetraene tether (1, 2, and 3) show shorter R_{pi} distances obtained at the SCC-DFTB-D level than those obtained at B97-D2/TZVP level (especially in the case of 2a, where the difference is almost 3.7 Å). However, the opposite is true for buckycatchers with buckybowl tether (4, 5, and 6). In any case, it is worth mentioning that both calculation levels give rise to the same qualitative picture: buckycatchers with tetrabenzocyclooctatetraene tether open the pincers after complexation and buckycatchers with buckybowl tether close them.

As can be seen in Fig. 3, complexation energy obtained at the B97-D2/TZVP//SCC-DFTB-D level shows an acceptable correlation with that obtained at the B97-D2/TZVP level. The correlation is much better for the interaction energy (Fig. S1, Supplementary Information), since the discrepancy between both methods mainly comes from the deformation energy values (Table S3, Supplementary Information, includes the B97-D2/TZVP//SCC-DFTB-D data).

In summary, our results show that the B97-D2/TZVP//SCC-DFTB-D approach could be a fast screening tool for designing new molecular tweezers. So, reasonable geometries and interaction energies are obtained. However, the mediocre reproduction of deformation energies prevents getting very good complexation energies. The source of this weakness is the considerable difference in the inter-pincer distance, R_{pi}, of the isolated buckycatchers obtained with low and high level calculations. For more rigid monomers (where deformation is more irrelevant), the B97-D2/TZVP//SCC-DFTB-D approach leads to very good results, as happened in our previous work.[38]

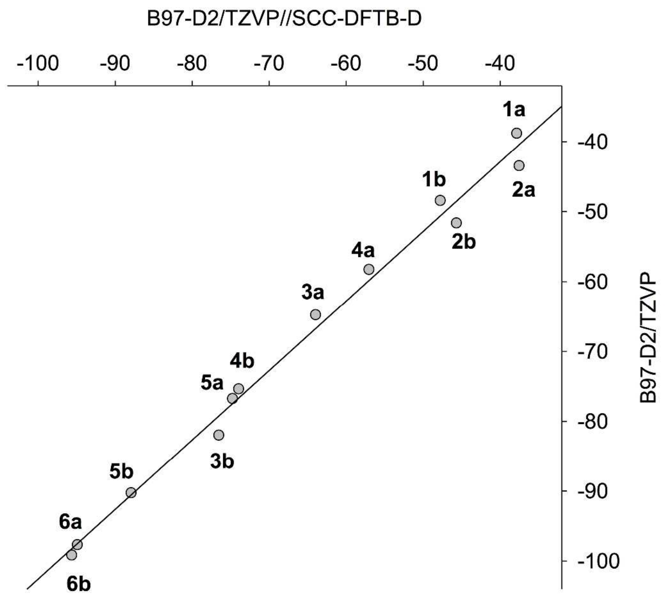


Fig. 3. B97-D2/TZVP//SCC-DFTB-D *vs.* B97-D2/TZVP complexation energy (in kcal/mol): $E_{complex}$ (B97-D2/TZVP) = 0.9948 × $E_{complex}$ (B97-D2/TZVP//SCC-DFTB-D) – 3.0762. R^2 = 0.991.

Table 3. Complexation energy ($E_{complex}$), deformation energy (E_{def}) in kcal/mol. Calculations are performed at the B97-D2/TZVP level. Percentage of deformation of buckycatcher is given in parenthesis.

	$E_{complex}$	E_{def}
1a···C_{60}	-38.80	1.12 (91%)
1b···C_{60}	-48.44	0.74 (87%)
2a···C_{60}	-43.48	3.78 (93%)
2b···C_{60}	-51.64	5.59 (96%)
3a···C_{60}	-64.76	8.10 (98%)
3b···C_{60}	-81.97	3.76 (91%)
4a···C_{60}	-58.26	5.57 (95%)
4b···C_{60}	-75.35	5.17 (91%)
5a···C_{60}	-76.74	0.79 (37%)
5b···C_{60}	-90.25	1.94 (80%)
6a···C_{60}	-97.67	6.05 (97%)
6b···C_{60}	-99.17	7.59 (97%)

However, for flexible monomers (such as tweezers) this approach can be used for a preliminary searching, but a re-optimization at the high level would be highly recommended. This is precisely what has been done in the present work, and results will be discussed below.

Improving the ability of buckycatcher $C_{60}H_{28}$ for catching C_{60}

As shown in Table 2, the inter-pincer distance value for the complex (R_{pc}) differs significantly from its isolated value (R_{pi}). Therefore, deformation energies are very important, as shown in Table 3. Deformation plus interaction energies give rise to complexation energies, also shown in this table. Regarding their corresponding interaction energies, deformation energies range from an almost insignificant 1% (for complex 5a···C_{60}) to an important 11% (for complex 3a···C_{60}). As expected, most of deformation (80-98%) corresponds to the buckycatcher, since fullerene is very rigid. The only exception to this trend is the complex 5a···C_{60} (37%) where deformation is very small, both for the buckycatcher and for the fullerene: 0.29 and 0.50 kcal/mol, respectively. In the complex with the largest deformation energy (3a···C_{60} with 8.10 kcal/mol) it almost entirely corresponds to the buckycatcher: 7.94 kcal/mol. As fully expected, there is some relationship between the magnitude of the deformation energy and the difference of aperture of the tweezers, before and after complexation, which is manifested by the difference between R_{pc} and R_{pi}. As commented above, this difference is positive in some cases (tweezers open after complexation) and negative in other cases (tweezers close after complexation). The former occurs for buckycatchers with tetrabenzocyclooctatetraene tether, and the latter for buckycatchers with buckybowl tether. In general, according to results of Tables 2 and 3, it seems that closure of tweezers is energetically an easier process than opening. For example, for complex 6a···C_{60} the deformation energy is 6.05 kcal/mol with a huge closure of 6.298 Å (R_{pc} - R_{pi} = -6.298 Å), whereas for complex 3a···C_{60} the deformation energy is 8.10 kcal/mol with a much smaller opening of 2.729 Å. The only exceptions to this trend are the complexes with buckycatchers 4a and 4b; in these cases a small closure (1.29, 1.26 Å) leads to a substantial deformation energy (5.6, 5.2 kcal/mol).

The first strategy employed herein in order to increase the catching ability of tweezers 1a has been to change the corannulene pincers by other buckybowls. Recently, our studies have shown that buckybowls with CH_2 groups[37] or *flaps*[38] can improve considerably the recognition of fullerenes. In this context, buckycatcher 2a includes two sumanene pincers with CH_2 groups, and buckycatcher 3a includes two efficient buckybowls (with *flaps*) as pincers. According to the results of Table 3, both options (especially the latter) lead to complexes with an important enhancement in their complexation energy, which rises from -38.80 to -43.48 and -64.76 kcal/mol, respectively. Thus, for complex 3a···C_{60} an extraordinary increase is obtained (67%), even though this complex exhibits the largest deformation penalty (the increase in interaction energy is 83%).

A recent study of Yanney and Sygula showed that a molecular clip with three corannulene pincers[26] is not better than the original tweezers 1a[17] with two pincers. However, molecular tweezers with three buckybowls, two as pincers and one as tether, could be a possible strategy worthy to be tested for the design of new fullerene receptors, especially using rigid pincers as Klärner's molecular tweezers.[49] Obviously, the main reason for designing buckycatchers using a buckybowl as tether is supported by the fact that its concave surface offers a natural advantage for interacting with the convex surface of fullerenes. This strategy was checked by means of three buckycatchers (4a, 5a and 6a). Bowl-shaped hexabenzocoronene derivatives are employed as tether because in our previous study they showed excellent ability for recognition of fullerenes.[38] If the behaviour of complex 4a···C_{60} is compared with that of 2a···C_{60}, a moderate increase in complexation energy (-14.78 kcal/mol, 34%) is observed, which is only due to introduction of a buckybowl as tether. However, the effect is much larger for

Table 4. B97 interaction energy and dispersion contribution of the complexes obtained at the B97-D2/TZVP level (kcal/mol).

	B97	*Disp*
1a···C_{60}	36.27	-76.19
1b···C_{60}	42.48	-91.66
2a···C_{60}	49.46	-96.72
2b···C_{60}	57.77	-115.00
3a···C_{60}	66.44	-139.30
3b···C_{60}	75.22	-160.95
4a···C_{60}	54.31	-118.14
4b···C_{60}	71.77	-152.29
5a···C_{60}	72.65	-150.18
5b···C_{60}	81.96	-174.15
6a···C_{60}	81.54	-185.26
6b···C_{60}	78.53	-185.29

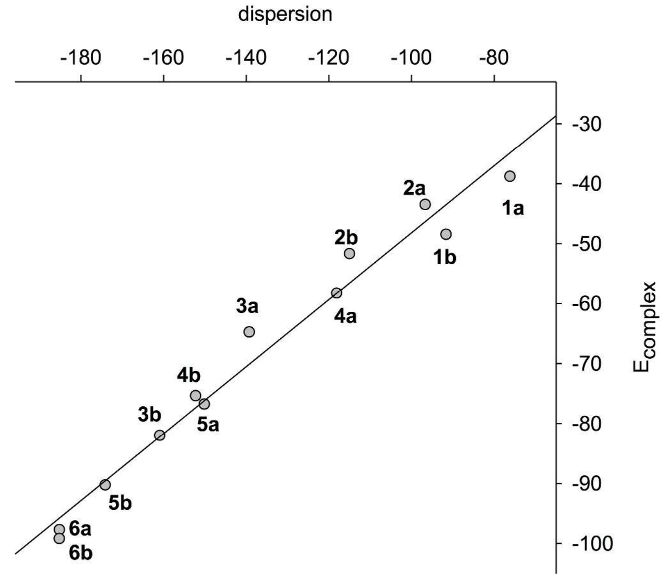


Fig. 4. Dispersion contribution *vs.* complexation energy (in kcal/mol): $E_{complex}$ = 0.5583 × E_{disp} + 7.6635. R^2 = 0.975.

buckycatcher 5a, with an increase of -33.26 kcal/mol (76%) relative to 2a. Thus, the hexabenzocoronene used as tether in 5a is much better than that used in 4a. This is not surprising considering the results of our previous work: the difference in behaviour of the two buckybowls was very large, which was attributed to the action of the *flaps* of the latter buckybowl.[38] Comparison of complexes 3a···C_{60} and 6a···C_{60} allows determining the behaviour of a third hexabenzocoronene (which is used in 6a) as tether. In this case the increase is -32.91 kcal/mol (51%), *i.e.* very similar in absolute terms to that obtained for the tether used in 5a.

As a summary of the results commented above, it can be concluded that the best pincers are those used in the buckycatchers 3a (and 6a). In the same way, the best tether is a bowl-shaped hexabenzocoronene. However, it is difficult to choose which one because those used in 5a and in 6a give rise to a similar enhancement of the complexation energy; that used in 5a leads to somewhat better results, but at the expense of a huge increase in size. Moreover, in our previous study, it was already showed that bowl-shaped hexabenzocoronene used in

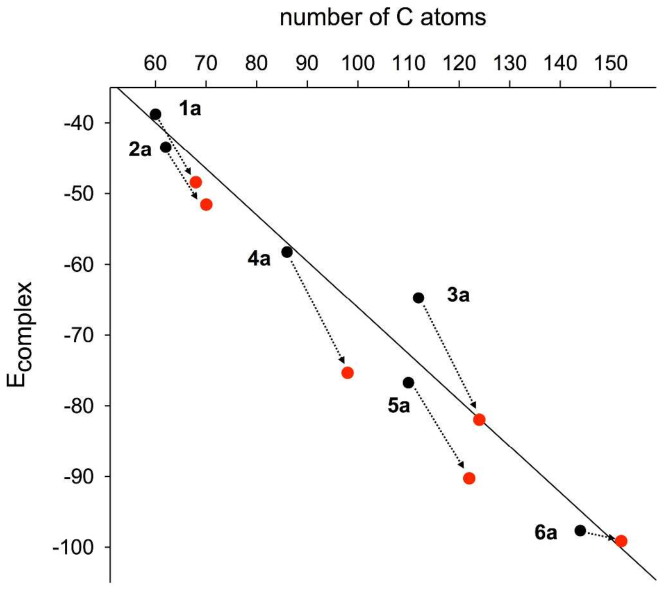


Fig. 5. Number of C atoms *vs.* complexation energy. $E_{complex}$ = -0.6533 × (number of C atoms) - 0.7815. R^2 = 0.951. Arrows point to methylated buckycatchers (1-6)b, red points.

6a as tether was a very efficient buckybowl.[38] For these reasons, the biggest buckycatcher devised in the present study is 6a, with the best pincers and a very efficient tether: an enhancement in complexation energy of -58.87 kcal/mol (152%) is obtained regarding the original tweezers 1a.

Finally, the third strategy for improving fullerene recognition could be the addition of methyl substituents on the buckycatchers, because according to previous theoretical studies the alkylation of buckybowls seems a promising method to the synthesis of better new fullerene receptors.[24,36,37] Addition of alkyl groups increases dispersion as well as the number of hydrogen atoms that can interact with fullerenes through CH···π interactions. As shown in Table 3, the addition of methyl groups on buckycatchers leads to a considerable increase in the complexation energy values, that can be greater than 17 kcal/mol (for 3a and 4a). The smallest effect takes place precisely on the best buckycatcher: only 1.5 kcal/mol, (6a *vs.* 6b).

In summary, all devised tweezers behave as better receptor of C_{60} than the original one designed by Sygula (1a).[17] The best results correspond to buckycatcher 6b, where the three above commented strategies are combined. Thus, complexation energy 2.6 times larger than that for the original 1a is obtained (from -38.80 to -99.17 kcal/mol, an increase of -60.37 kcal/mol, a 156%).

In order to analyse in more detail the balance of energy contributions to the stability of the complexes, the interaction energy is decomposed according to a simple method. So, the two contributions of the model employed are taken into account; that is, the pure B97 interaction energy and the empirical dispersion contribution to the interaction energy. As it can be seen from Table 4, dispersion is mainly responsible for the attraction of all the complexes evaluated. Furthermore, an

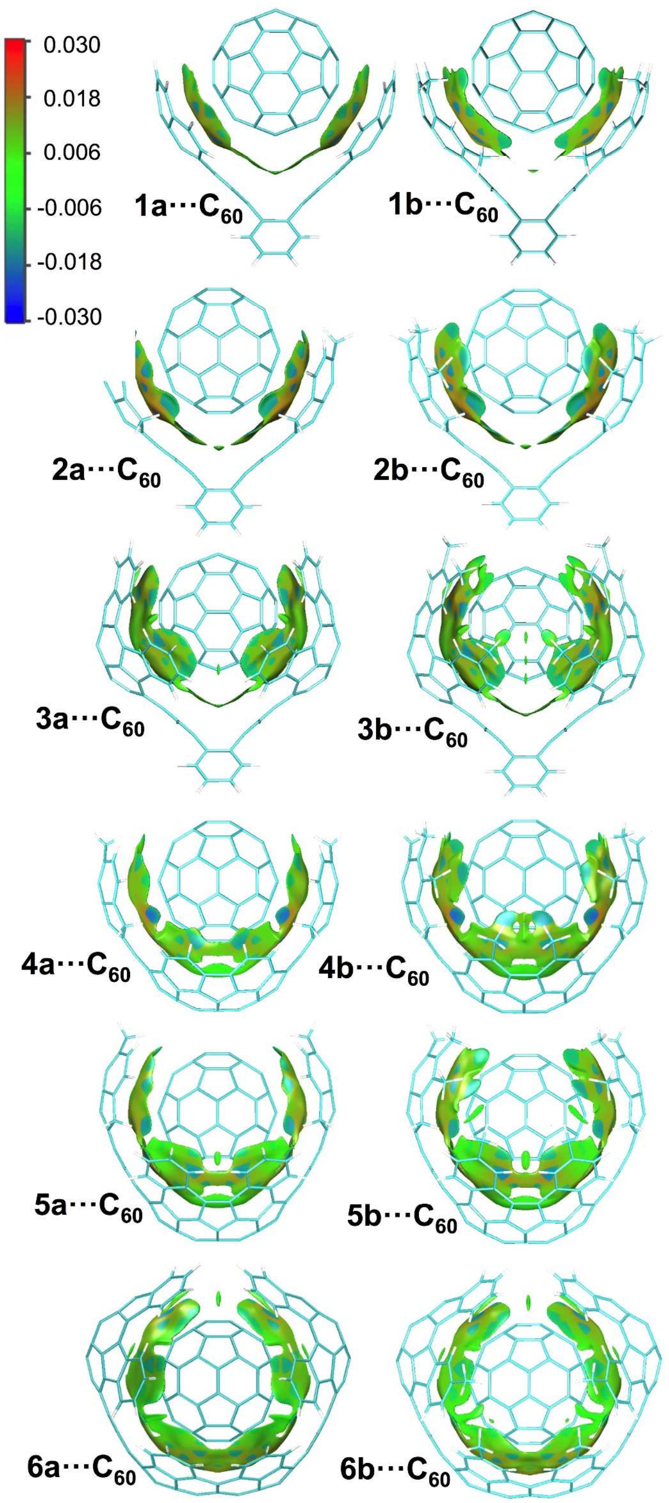


Fig. 6. Front views of the NCIPLOT gradient isosurface (0.35 a.u.). The surfaces are colour-mapped onto a blue-green-red scale according to the strength and type (attractive or repulsive) of interaction. Blue indicates strong attractive interactions, green indicates weak vdW interactions, and red indicates strong non-bonded overlap.

excellent relationship between the dispersion contribution and the total complexation energy can be clearly visualized in Fig. 4, with a very good correlation (R^2=0.975).

As shown in Table 4 and Fig. 4, the increase of complexation energy is directly related to the increase of dispersion energy. It could be argued that this latter increase might be simply caused by the increase of the size of the buckycatcher. For that reason, it could be interesting to know the efficiency of a buckycatcher relative to its size. In this context, although the number of carbon atoms of a compound is not a very reliable measure of its size, it is an easy-to-use parameter closely related to the size of that compound. Fig. 5 shows a rather good correlation between the number of C atoms of the buckycatcher an its complexation energy with C_{60} (R^2 = 0.951, the linear regression is done with the unmethylated buckycatchers, 1-6a). However, the most important thing is detecting the deviations of the linear behaviour looking for the most efficient receptors; that is to say, the best receptors that produce large complexation energies without a large increase of size. In this respect, and taking into account the unmethylated buckycatchers, 1-6a, it seems clear that buckycatchers 5a and 6a are efficient fullerene receptors with larger complexation energy than predicted by their size. It is worth noting that the original tweezers, 1a, shows a mediocre efficiency, only beaten (in the bad sense) by 3a. When methyl groups are added to the buckycatcher (compounds 1-6b, red circles in Fig. 5) the efficiency undergoes an important increase, except for compound 6 where suffers a slight decrease, which is due to the above commented small effect of methylation (only 1.5 kcal/mol in complexation energy) that takes place for 6a. According to Fig. 5 the best efficiency corresponds to buckycatchers 4b and 5b (both with added methyl groups). On the contrary, methylation of the best buckycatcher (in absolute terms), 6a, is not worthwhile.

Finally, a non-covalent interactions (NCI) analysis has also been performed in order to obtain more information about $\pi\cdots\pi$ interactions. The visualization of $\pi\cdots\pi$ interactions between the two monomers in the real space is drawn using VMD software[46] with an isosurface of 0.35 a.u. and scale running from -0.030 (min) to 0.030 (max); blue, green and red indicate strongly attractive, weak and strongly repulsive interactions, respectively. Fig. 6 shows front view of the NCI plots (more detailed views are available in the Supplementary Information Fig. S2). As shown in Fig. 5, all modifications proposed herein display an enhancement of the C_{60} recognition regarding to the buckycatcher 1a: both weak and strongly attractive interactions grow substantially. The change of the tetrabenzocyclooctatetraene tether by a bowl-shaped hexabenzocoronone is especially evident, since the former seems to play a small role in the fullerene recognition. It is also patent that the best pincers are those used in the buckycatcher 3a (and 6a). Fig. 6 also displays clearly the effect of adding methyl groups on the buckycatchers: the C-H$\cdots\pi$ contacts are readily observable by the emergence of new regions on the RDG surface of strong attractive character (blue). In this context, as expected (according to complexation energies of Table 3) the smallest effect is observed for buckycatcher 6b. Fig. 6 allows understanding this small effect: in the complex 6b$\cdots C_{60}$ methyl groups of pincers are very far from fullerene; the same applies largely to methyl groups on the tether (only for complex 4b$\cdots$C$_{60}$ the effect of methyl groups placed on the tether is important).

Conclusions

Our results show that the B97-D2/TZVP//SCC-DFTB-D approach could be a rapid screening tool for designing of new molecular tweezers. In this way, this methodology leads to reasonable results for buckycatcher$\cdots$C$_{60}$ complexes, both for the geometry and the energetic values. Its main failure is the deficient description of the deformation energy, since considerable deviations in inter-pincer distance of the isolated buckycatchers are found. As shown in our previous results,[38] the B97-D2/TZVP//SCC-DFTB-D results can be of high quality when the receptor has a quite rigid structure; this is not the case of tweezers, and thus only can be used as starting point for a higher level re-optimization. Since for tweezers the deformation energy represents an important contribution to the total complexation energy, a re-optimization at the full B97-D2/TZVP level is performed herein.

To improve the ability for fullerene recognition of the original buckycatcher designed by Sygula *et al.*,[17] three different strategies are tried. The first one is to change the corannulene pincers by other buckybowls. The results show an important improvement when sumanene and, especially an efficient buckybowl, are used as pincers. The second strategy consists on replacing the tether part of the tweezers by a buckybowl. For this purpose, a bowl-shaped hexabenzocoronene is employed and good results are also obtained. Finally, methyl substituents have been added on the buckycatcher structure to favour the development of C-H$\cdots\pi$ contacts: as with the other two strategies, the improvements achieved are outstanding.

Combination of the three above commented strategies leads to several enhanced buckycatchers, with complexation energies for the complex buckycatcher$\cdots$C$_{60}$ up to 2.6 times larger than that for the original buckycatcher (from -38.80 to -99.17 kcal/mol, an increase of -60.37 kcal/mol, a 156%).

Dispersion plays a crucial role on the interaction in all the complexes: it is responsible for the binding in them and shows an excellent correlation with the complexation energies. As expected, the increase on dispersion energy shows a fairly good correlation with the increase on bowl size. However, there are several deviations that mark differences in efficiency between the different buckycatchers. Thus, the best buckycatcher in absolute terms (6b) possesses only a mediocre efficiency, clearly overtaken by its unmethylated precursor, 6a. Only for this case the methylation is not worthwhile, since for the remaining cases it does have an important effect both in absolute terms and in relation to efficiency.

In summary, according to our results, and taking into account a balance between the absolute "catching" ability and the efficiency, the best tweezers could be 6a, 4b, and 5b. The first one is a strong fullerene receptor with a considerable efficiency. The two second ones, having a rather moderate size, possess a considerable ability as fullerene receptor that leads to a high efficiency. In any case, all three clearly overtake the features of the original buckycatcher 1a as fullerene receptors. Another issue is to know whether these receptors are easy to synthesize or not. Anyway, the theoretical contribution presented herein leads to the fact that the tweezers synthesized by Sygula *et al*.[17] have much room for improvement. Some possible strategies for achieving this improvement are the three ones analysed here, which represent promising possibilities.

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