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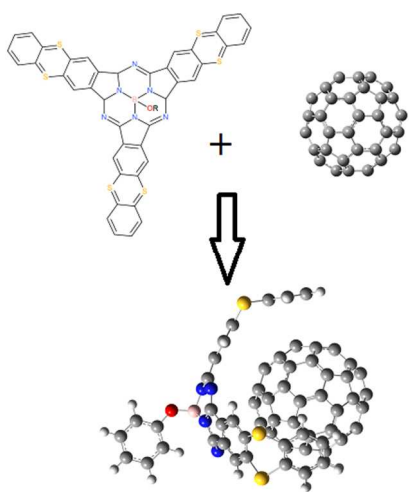
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One for the other! Functionalized at the peripheral region subphthalocyanines show a remarkable affinity towards C₆₀ and C₇₀

A comparative study on the performance of subphthalocyanines and corannulene derivatives as receptors for fullerenes

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Abstract

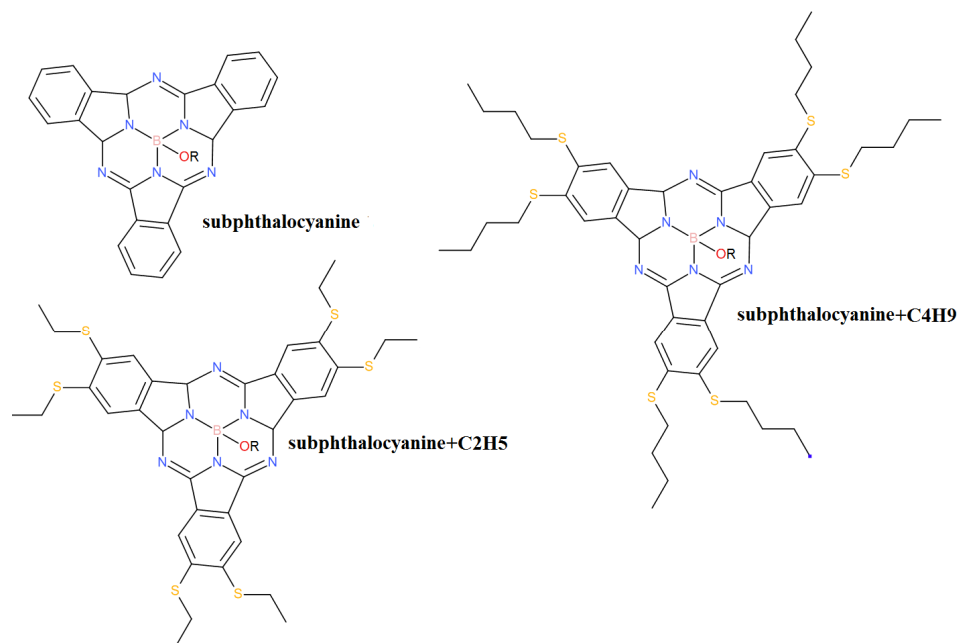
Herein, we have employed dispersion corrected density functional theory to study the performance of modified subphthalocyanines and dibenzo[a,g]corannulenes as fullerene receptors. Analysis of the interaction energies and structures of the catchers revealed that subphthalocyanines display excellent ball socket interactions with C₆₀ and C₇₀. However, dibenzo[a,g]corannulene showed an excellent fit only with C₇₀, as indicated by recent experimental results. The functionalization of subphthalocyanines with long thioalkyl chains, increases the interaction energies between receptors and fullerenes. Yet, the effect on the association constant is negligible, and in some cases it can be even harmful, because the long alkyl chains introduce large entropic penalties, which are translated in a small improvement of the free energy changes. We propose a new subphthalocyanine based receptor which bears three 1,4 dithino groups at the peripheral region. The new host has a strong affinity towards C₆₀ and C₇₀, as indicated by theoretical calculations, which showed a large change in free energy when the above mentioned modification is considered. In spite of the fact that long alkyl chains seem not to be useful in improving the binding affinity of several receptors, we have found that the addition of small ethyl chains onto dibenzo[a,g]corannulene increases the affinity of the bowl towards fullerenes. Nevertheless, new functional groups must be attached in places where the stacking interaction between host and guest is barely affected; otherwise the loss of π stacking should be compensated by the new functional groups.

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1. Introduction

Ball socket interactions¹ play a key role in the construction of metal-free fullerene receptors. In order to avoid the use of porphyrins²⁻⁶ to synthesize powerful fullerene traps, several curved π systems have been proposed. Among them, the well-known $C_{60}H_{28}$ buckycatcher is the most widely studied.⁷⁻¹⁵ In general, some sort of geodesic polyarene¹⁴⁻²² is employed to construct the receptor when porphyrins are not involved, even though exceptions are present such as azacalix pyrimidines²³ and the extended tetrathiafulvalene based receptors developed by Martin and coworkers.²⁴⁻²⁵ Recently, two new promising fullerene receptors have been proposed: a) those based on subphthalocyanines²⁶ and b) dibenzo[a,g]corannulene.²⁷ The investigation by Sanchez-Molina et al.²⁶ was centered on the interaction between C_{60}/C_{70} fullerenes and six concave-shaped subphthalocyanines. They considered bare and functionalized subphthalocyanines. The functional groups attached to them were fluorine, and thioalkyl chains. By means of Job's plots and titration experiments it was demonstrated the formation of supramolecular complexes with fullerenes, except in the case of perfluorinated subphthalocyanines. However, 1:1 complexes were detected for bare subphthalocyanines and 2:1 complexes were confirmed when thioalkyl groups were attached. The introduction of the latter functional groups induced negligible changes in the association constants and no appreciable trend was observed. For example, the K_{assoc} determined for the bare subphthalocyanine was similar to the one corresponding to the subphthalocyanine functionalized with six $SC_{16}H_{33}$ chains. Thus, even though the bare subphthalocyanine showed a good affinity towards fullerenes, the interaction could not be improved by modification of the peripheral region of the subphthalocyanine. All these findings strongly suggest that the core of the subphthalocyanine can be considered a good starting point for the development of new fullerene receptors. The second type of receptor recently proposed is based on corannulene. Filatov et al.²⁷ studied the structure in solution and condensed phase of the complexes formed by C_{60}/C_{70} and dibenzo[a,g]corannulene. The crystal structures evidenced marked differences between both fullerenes: a) only C_{70} interacted exclusively with the concave region of the bowl and b) the disorder found in

many co-crystallized fullerene products was absent for C_{70} . In solution, π - π adducts were not detected in solutions of solvents from which the crystals were grown. The different interactions that both fullerenes displayed with dibenzo[a,g]corannulene were attributed to the excellent match that exists between the bowl and C_{70} , when it is oriented along its long axis. Thus, dibenzo[a,g]corannulene exhibits good affinity for C_{70} and has an area that is close to that of the subphthalocyanines discussed above. These two traits make this compound an excellent structure to design new receptors. Since the beginning of the fullerene non covalent chemistry, theory has contributed to the characterization of the complexes formed by fullerenes and buckybowls as well as between buckybowls themselves.²⁸⁻³⁸ In this work, we continue our investigations for the search of new and improved fullerene receptors.^{14-15,28} By means of first principle calculations we have studied the interaction between fullerenes C_{60}/C_{70} and receptors that are derived from subphthalocyanines and dibenzo[a,g]corannulene. The structures of the hosts assayed are shown in Figures 1 and 2.



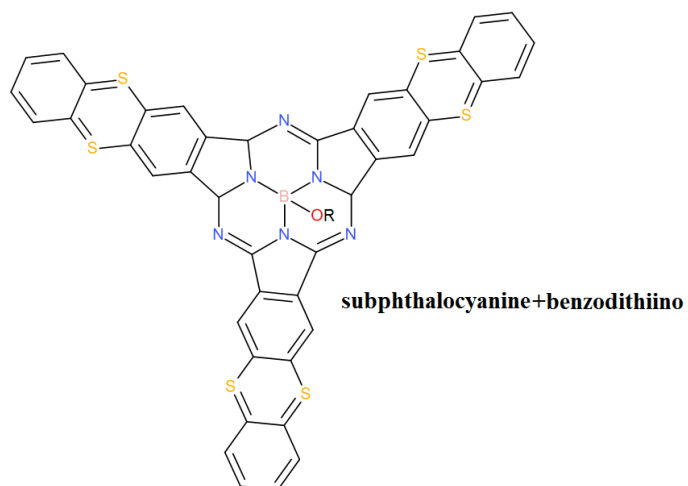


Figure 1. Subphthalocyanine based receptors.

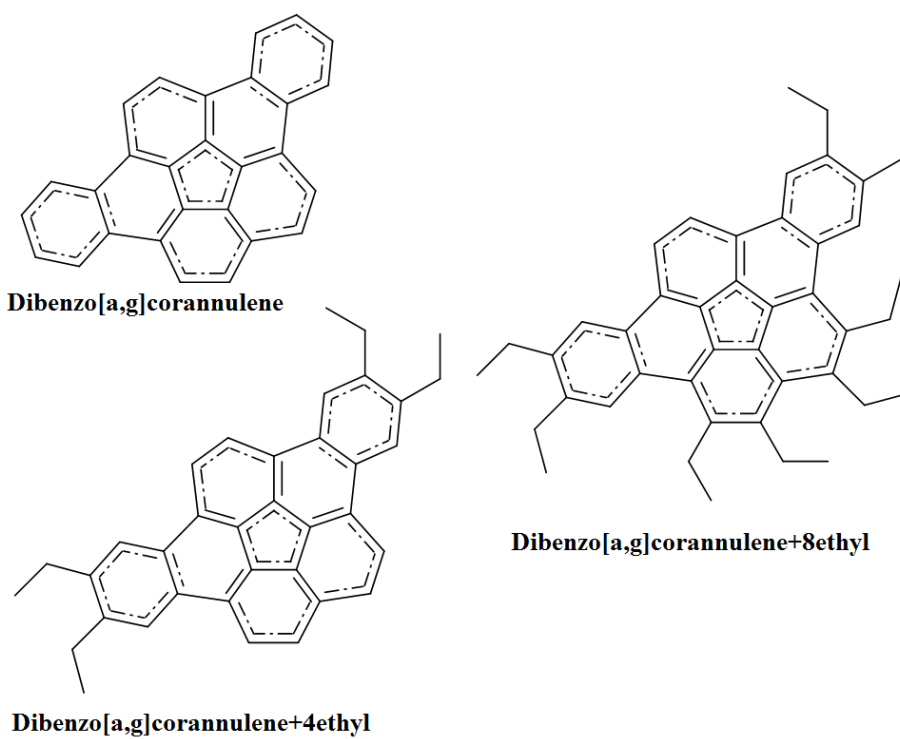


Figure 2. Dibenzo[a,g]corannulene based receptors.

In first place, we investigated the hosts studied experimentally: subphthalocyanine, subphthalocyanine+C₂H₉, subphthalocyanine+C₄H₉ and dibenzo[a,g]corannulene. On the other hand,

the receptors proposed are: subphthalocyanine-1+benzodithiino, dibenzo[a,g]corannulene+4ethyl and dibenzo[a,g]corannulene+8ethyl. Our work accounts for some interesting experimental observations like, why it was observed a small change of association constants upon thioalkyl chain extension,²⁶ and explains in detail the different behavior of C₆₀ and C₇₀ when interacting with dibenzo[a,g]corannulene.²⁷ In the second part of the work, we propose new receptors that were derived from subphthalocyanines and dibenzo[a,g]corannulene. We show that the peripheral region of the subphthalocyanine can be modified to improve its complexation capabilities. We expect that this work will encourage the synthesis of new fullerene receptors derived from subphthalocyanines or modified corannulenes.

2. Methods

The interaction between C₆₀/C₇₀ and the was studied following a similar methodology to the one successfully applied in our three recent works about fullerene traps.^{14,15-28} Briefly, we carried out M06-2X calculations³⁹ using Pople's 6-31G basis set.⁴⁰ In the particular case of the jellyfish-like subphthalocyanine receptors, which are functionalized with SC₂H₅ and SC₄H₉ chains, we extended the basis set to 6-31G*. The reason to do so is that polarization functions are necessary for sulfur containing compounds. However, it is important to remark that the result were very similar to those obtained using the smaller basis set. The ultrafine grid was utilized in all calculations and the structures were confirmed to be minima in the potential energy surface by the evaluation of analytic vibrational frequencies. No symmetry constrains were employed during the optimizations, and in all cases the fullerenes interacted with the concave region of the receptors because ball-socket interactions dominate the interaction. In the case of C₇₀ we always considered two cases: a) when the host interacts predominantly interacts with the polar region of C₇₀, dubbed as 1 and b) when the host interacts predominantly interacts with the equatorial region of C₇₀, dubbed as 2. Free energy changes were computed at 1 atm and 298 K. Interaction energies (IE) were computed using the structures of the isolated optimized monomers. We did not consider basis set superposition error because in our recent

works in the field we observed that the underestimation of dispersion interactions that affects the M06-2X functional is cancelled when the error is not taken into account.^{14-15,28} For example, the BSSE uncorrected M06-2X/6-31G interaction energies are very close to those obtained at the M06-2X/6-311G+BSSE level of theory.^{14-15,28} This finding is also supported by the recent investigation by Risthaus and Grimme¹² who also found that BSSE worsens the results provided by M06-2X (see Table S1 in the SI of ref 12). As a final argument supporting the methodology used here, we recall that for the corannulene dimer, that the interaction energy (IE) at the QCISD(T)/aug-cc-pVTZ+BSSE level is -15.5 kcal/mol,²⁹ a value which is only 0.4 kcal/mol larger than the M06-2X/6-31G estimation. For further details and justifications about the methodology selected we refer the reader to Section 3.1 of our recent work about fullerene receptors.¹⁴ All calculations were carried out using Gaussian 09.⁴¹

3. Results and Discussion

3.1 Complexes formed by subphthalocyanines: In Figure 3 we present the structures of the fullerene@subphthalocyanine based receptors which were recently studied experimentally.²⁶ The IE, deformation energies of the hosts, enthalpy, entropy and free energy changes, are listed in Table 1.

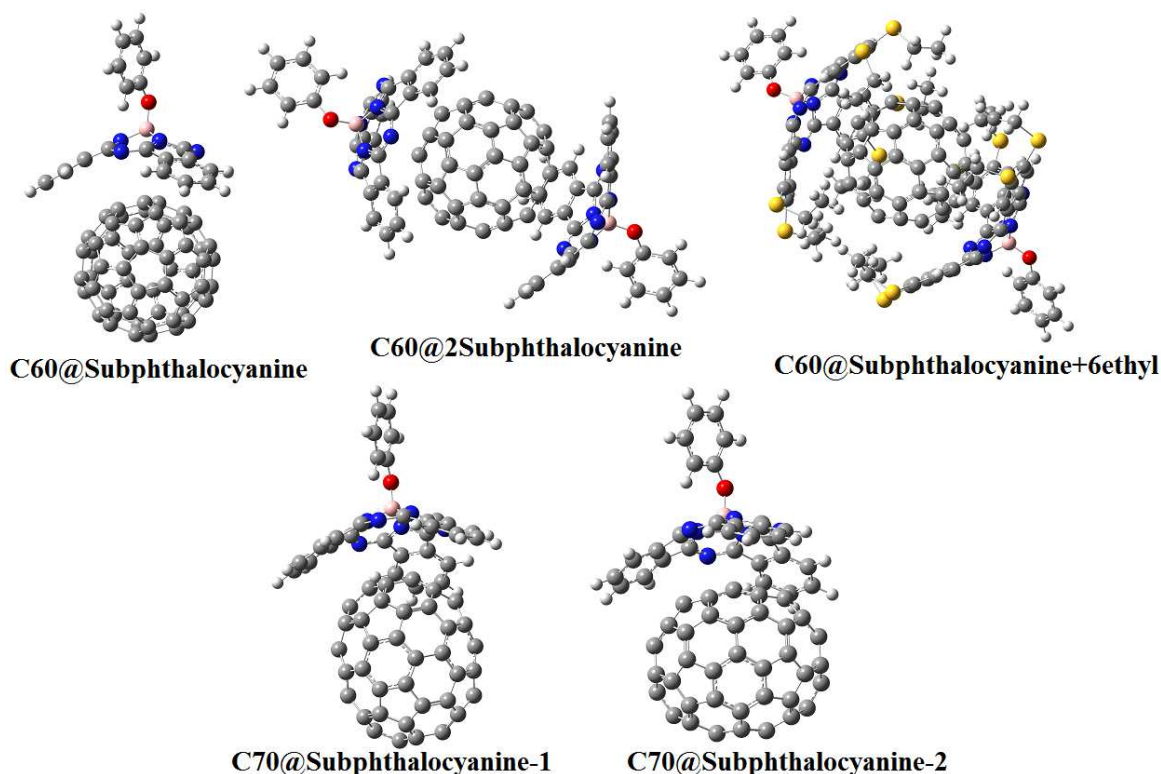


Figure 3. Optimized structures determined at the M06-2X/6-31G level of theory for the complexes formed by fullerene and subphthalocyanine based receptors recently studied experimentally.

Table 1. Gas phase complexation energies (kcal/mol) and free energy changes determined for C₆₀ and C₇₀, interacting with subphthalocyanine based hosts, at the M06-2X/6-31G level of theory.

	ΔE (6-31G)	$\Delta E(6-31G^*)$	ΔH_{298}°	T ΔS	$\Delta G_{298}^\circ(6-31G)$	Host Deformation
C ₆₀ @subphthalocyanine	-19.9		-19.5	15.1	-4.4	0.6
C ₆₀ @2subphthalocyanine	-38.8		-36.6	25.8	-10.8	0.7/0.8
C ₇₀ @subphthalocyanine-1 ^a	-19.3		-18.7	11.1	-7.6	0.8
C ₇₀ @subphthalocyanine-2 ^b	-20.7		-20.1	12.0	-8.1	0.5
C ₇₀ @2subphthalocyanine-1	-38.6		-36.9	24.9	-12.0	0.8/0.7
C ₇₀ @2subphthalocyanine-2	-41.8		-40.1	27.6	-12.5	0.7/0.3
C ₆₀ @2subphthalocyanine-SC ₂ H ₅	-57.4	-59.8	-56.0	39.6	-16.4	3.8/5.6
C ₆₀ @2subphthalocyanine-SC ₄ H ₉	-65.3		-63.4	44.8	-18.6	14.8/10.3
C ₆₀ @subphthalocyanine-dithiino	-33.8	-34.0	-31.9	17.9	-14.0	2.4
C ₆₀ @2subphthalocyanine-dithiino	-68.5		-65.4	34.9	-30.5	2.6/2.6
C ₇₀ @subphthalocyanine-dithiino-1	-33.6		-32.6	15.6	-17.0	2.8
C ₇₀ @subphthalocyanine-dithiino-2	-34.1		-32.8	15.0	-17.8	1.6
C ₇₀ @2subphthalocyanine-dithiino-1	-72.5		-69.4	36.4	-33.0	2.6/3.0
C ₇₀ @2subphthalocyanine-dithiino-2	-74.6		-71.5	36.5	-35.0	2.8/3.1

a- 1 indicate that the polar region of C₇₀ interacts with the host.

b- 2 indicate that the equatorial region of C₇₀, predominantly interacts with the host. For details see, Figs 3-5.

The ball-socket interactions which govern the capture of fullerenes by aromatic curved π systems depend on the contact area. In the case of the simplest subphthalocyanine selected, its IE with C₆₀ is -19.9 kcal/mol. This value is 4.8 kcal/mol larger than the IE computed for C₆₀@corannulene, at the same level of theory. As a result, the IE of the latter system is 76% of the IE computed for C₆₀@subphthalocyanine, a value which is in good agreement with the quotient of the areas of corannulene/subphthalocyanine (71%). Therefore, as we observed for the corannulene and pentaindenocorannulene homodimers, there is a satisfactory correlation between the contact area and the IE. This fact proves that there is an excellent fit between the shapes of C₆₀ and subphthalocyanine. The closest contact between C₆₀ and the subphthalocyanine is 3.20 Å with the five membered rings, whereas the six member rings show 3.3-3.7 Å far from the fullerene surface. In contrast with C₆₀, the

different structure of C_{70} enables two types of interactions with the subphthalocyanine: a) when the polar region of C_{70} is close to the subphthalocyanine, or b) the equatorial region is close to the receptor. The latter orientation of C_{70} exposes a larger area of the fullerene to the π clouds of the receptor and for this reason it may be anticipated to have a larger IE. In effect, the calculations indicated that the IE are -19.3 and -20.7 kcal/mol for cases a) and b), respectively. Although there changes with respect to C_{60} are not huge, the IE when the polar region is involved in the interaction is 0.6 kcal/mol smaller than in C_{60} @subphthalocyanine. Yet, when the equatorial region is exposed to the receptor the IE becomes larger than in C_{60} @subphthalocyanine. The reason for such enhancement again can be found in the larger area of the equatorial region of C_{70} as compared with that of the polar region. Analysis of the key structural parameters also supports this hypothesis. In effect, for configuration 1, as observed for C_{60} , the shortest distance between the monomers occurs for the atoms of the pentagonal rings of the subphthalocyanine. However, for configuration 2, the orientation along its long axis enables the shortest distances (3.1 Å) with the hexagonal rings and thus more contact area is available and stacking is enhanced with respect to configuration 1.

In order to test the methodology selected we computed the IE of C_{70} @subphthalocyanine-1 at the M06-2X/6-311+G*+BSSE level of theory. We found that at the latter level, the IE is 17.0 kcal/mol. This value is 2.3 kcal/mol below our previous estimation, and thus confirms our hypothesis about the good performance of the methodology selected.

The particular shape of the subphthalocyanine facilitates the formation of complexes with fullerenes in which not one but two molecules interact with the guest, as indicated by experiment.²⁶ For the complex C_{60} @2subphthalocyanine the IE is -38.8 kcal/mol. This value is only 1 kcal/mol smaller than twice the IE calculated above for C_{60} @subphthalocyanine, so the interactions appear to be additive. This scenario is confirmed when C_{70} is complexed by two receptor molecules. Indeed, the IE of the two optimized C_{70} @2subphthalocyanine supramolecular complexes are -38.6 and -41.7 kcal/mol, for C_{70} @2subphthalocyanine-1 and C_{70} @2subphthalocyanine-2, respectively. As observed

for the 1:1 complexes, when the equatorial region of C_{70} is close to the receptor, the IE becomes larger. In general, the IE computed for both fullerenes are similar, hence distinction between C_{60} and C_{70} will be difficult.

In addition to the bare subphthalocyanine studied above, the experimental work by Sanchez-Molina et al.²⁶ also investigated the complexation ability of hexaalkylthio-substituted subphthalocyanines. In terms of binding energy, the presence of six SC_2H_5 and SC_4H_9 chains increases the IE with C_{60} . In this context, the computed IE for the 2:1 complexes are -57.4 and -65.3 kcal/mol, respectively. These two IE are -18.6 and -26.5 kcal/mol larger than the IE calculated for $C_{60}@2$ subphthalocyanine. In contrast, the free energy changes are modestly increased by 5.6 and 7.8 kcal/mol for SC_2H_5 and SC_4H_9 , respectively. This finding is in good agreement with the results obtained from titration experiments monitored by UV/VIS spectroscopy which indicated that the binding constants were barely affected by functionalization.²⁶ Indeed, the K_{eq} determined for the bare subphthalocyanine, subphthalocyanine-(SC_2H_5)₆ and subphthalocyanine-(SC_4H_9)₆ are 2.1E4, 2.1E4 and 1.9E M⁻¹, respectively.²⁶ The lack of improvement in the association constants by the incorporation of long alkyl chains is not surprising if the TΔS terms and deformation energies presented in Table 1 are analyzed. In effect, in our recent work about functionalized corannulenes, we found that long chains significantly reduce the complexation free energies.¹⁴ Moreover, in several cases they can even reduce the IE, as in the receptor isolated form the long alkyl chains adopt conformations which are very different from those adopted in the supramolecular complex. Thus, a large amount of energy is required to bring the receptor from its most stable conformation to the one found in the host-guest system.

In order to increase the complexation capabilities of subphthalocyanines we envisioned that the functionalization of the subphthalocyanines should be performed with groups which present a lower number of degrees of freedoms than the long alkyl chains discussed above. Bearing in mind the work by Georghiou et al.¹⁷ about sulfide linked flaps, and our recent study of said type of receptors,¹⁴ we

attached to the benzene rings of the subphthalocyanine, six sulfur atoms connected by orthophenylene rings (two to each branch of the subphthalocyanine), which, as correctly pointed out by Georghiou et al.¹⁷ reduce the steric impedance occurring in thioalkyl groups. We note that in a recent work, Sanchez-Lozano et al.⁴² showed that subphthalocyanine receptor very similar to the one studied herein, is able to capture anions in solvents with a large dielectric constant. The structures of the complexes formed by the receptors proposed in this work are shown in Figure 4 and the IE and ΔG°_{298} can be found in Table 1.

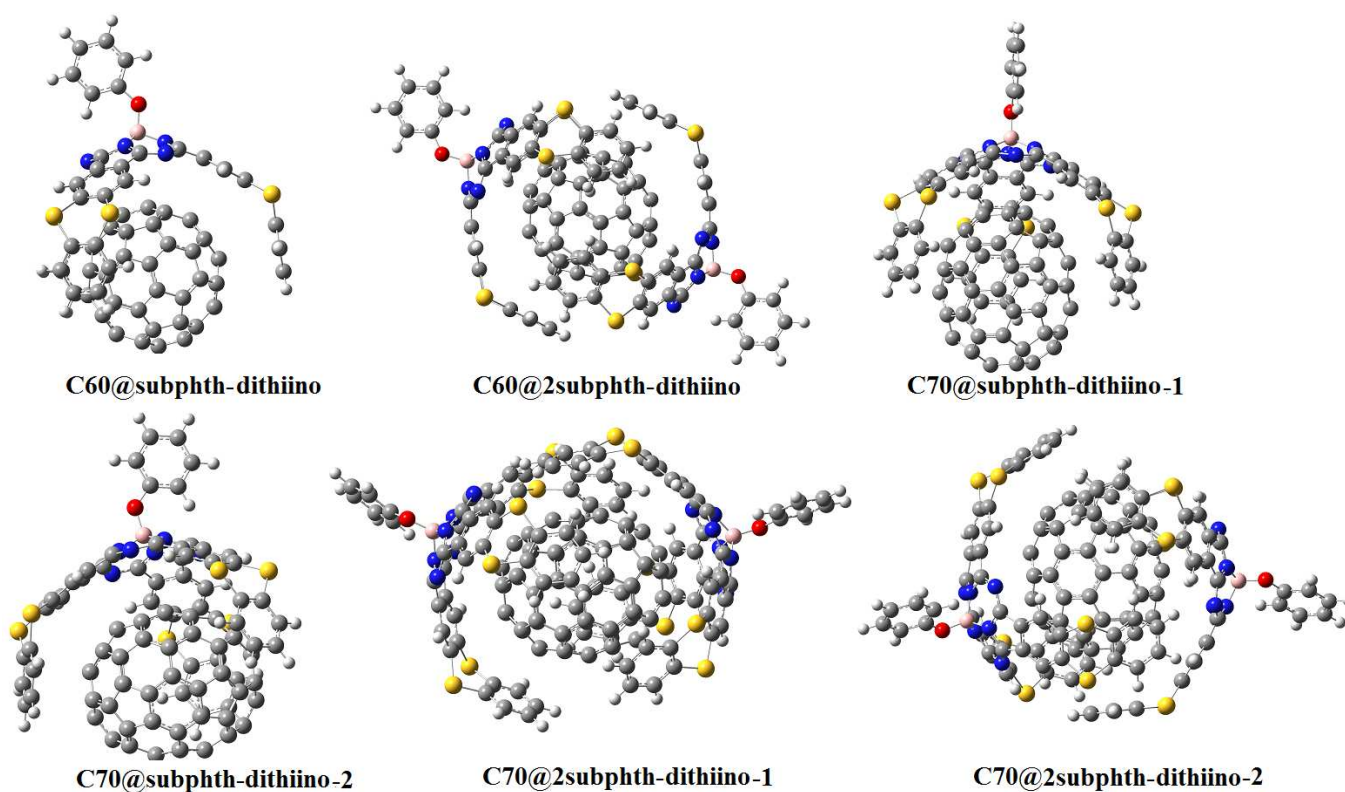


Figure 4. Optimized structures determined at the M06-2X/6-31G level of theory for the complexes formed by fullerenes and subphthalocyanine based receptors proposed in this work.

In all cases it can be appreciated that both the IE and ΔG°_{298} are significantly increased by the introduction of three 1,4-benzodithiino groups. In the case of C_{60} , the IE determined for $C_{60}@2\text{subphthalocyanine-SBz}$ is -33.8 kcal/mol. This IE is 13.9 kcal/mol larger than the one determined for $C_{60}@subphthalocyanine$. As for the free energy change, the modified receptor exhibits

a ΔG°_{298} which is 9.6 kcal/mol larger, a fact that should be translated into a dramatic change of the association constant, taking into account the exponential relationship existing between the association constant and the free energy. If a 2:1 complexation is now considered, the changes are even more noticeable since the IE is -68.5 kcal/mol and the $\Delta G^{\circ}_{298} = -30.5$ kcal/mol. This free energy change is more than twice the value determined for the 1:1 complex, so we can expect a strong association between the proposed modified subphthalocyanines and the fullerenes. For the sake of completeness, we also assayed the interaction between C_{70} and the new receptors. In line with the results observed for C_{60} , a striking increase of IE and ΔG°_{298} takes place when the 1,4-benzodithiino groups are introduced. For the 1:1 complexes, the IE increase by 14.3 and 13.4 kcal/mol, for orientations 1 and 2, respectively. Thus, when the polar region of C_{70} interacts with the receptor, a larger enhancement of the IE occurs. Yet, the IE determined when the polar region interacts with the receptor is not as large as the IE of the conformation which prioritizes the stacking interaction with the equatorial region. More significant changes were observed for 2:1 complexes were considered. Indeed, the largest IE was -74.6 kcal/mol which corresponds to an almost dimeric capsule sequestration of the receptor.

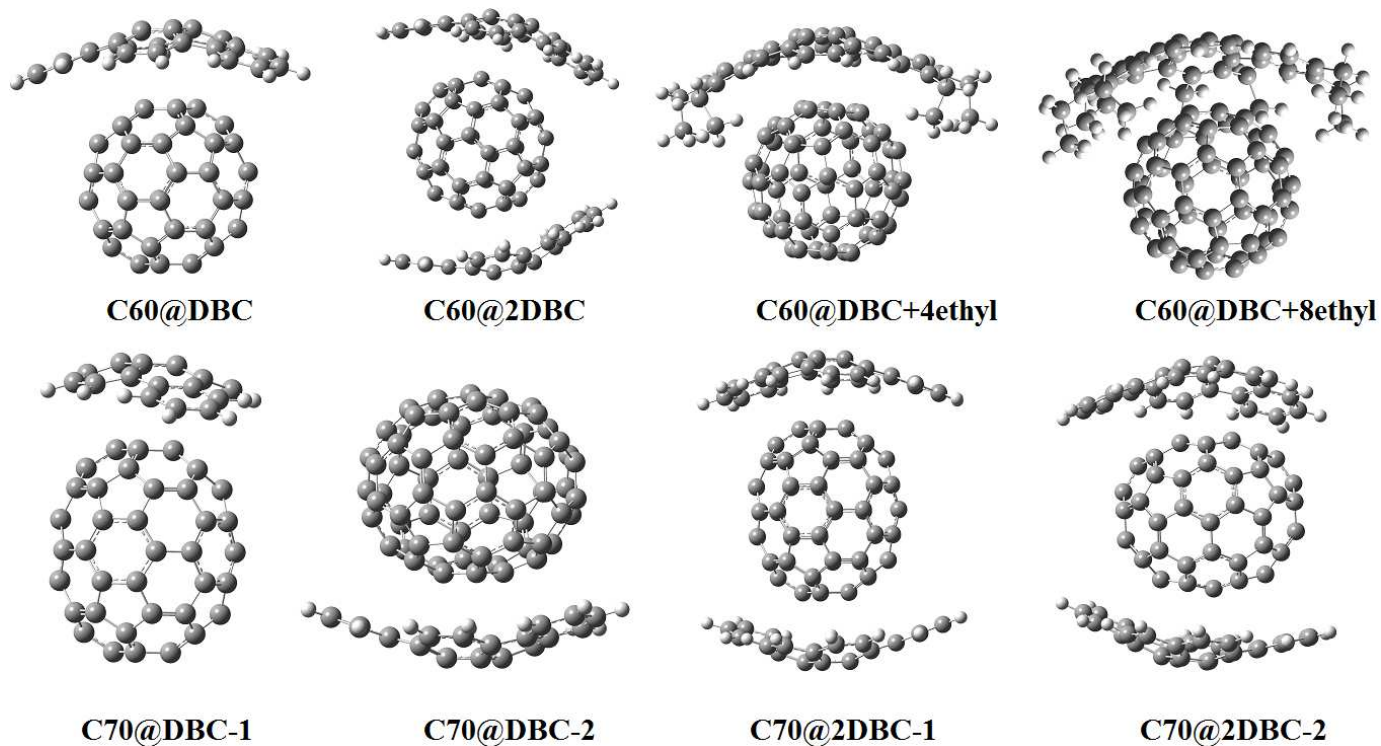
3.2 Complexes formed by dibenzocorannulenes: the second type of receptors modeled in this work were inspired in the recent investigation about dibenzo[a,g]corannulenes by Filatov et al.²⁷ The IE, deformation energies of the hosts, enthalpy, entropy and free energy changes, are presented in Table 2 and the structures in Figure 5. The IE determined for $C_{60}@dibenzo[a,g]corannulene$ is -17.1 kcal/mol, a value that is 2 kcal/mol larger than the IE computed for corannulene, at the same level of theory. For this complex, there is not a good correlation between the IE and the molecular areas. The quotient of the IE is $15/17.1 = 0.88$, whereas the quotient of the areas is 0.75. Thus, the IE $C_{60}@dibenzo[a,g]corannulene$ is not as high as one would expect from the larger surface of dibenzo[a,g]corannulene. The reason for such deviation is that even though the bowl has a larger area, it lacks the proper curvature to exhibit an optimal fit with C_{60} . This finding is in nice agreement with the observations made by Filatov et al.²⁷, which indicated that C_{60} and dibenzo[a,g]corannulene

Table 2. Gas phase complexation energies (kcal/mol) and free energy changes determined for C₆₀ and C₇₀, interacting with dibenzo[a,g]corannulene based hosts, at the M06-2X/6-31G level of theory.

	ΔE (6-31G)	ΔH°_{298}	T ΔS	ΔG°_{298}	Host Deformation
C ₆₀ @dibenzo[a,g]corannulene	-17.1	-16.1	11.9	-4.2	0.5
C ₆₀ @2dibenzo[a,g]corannulene	-34.1	-32.0	24.1	-7.9	0.4/0.5
C ₇₀ @dibenzo[a,g]corannulene-1	-17.0	-15.9	11.0	-4.9	0.4
C ₇₀ @dibenzo[a,g]corannulene-2	-19.5	-18.5	11.6	-6.9	0.4
C ₇₀ @2dibenzo[a,g]corannulene-1	-33.8	-31.6	20.1	-11.5	0.4/0.4
C ₇₀ @2dibenzo[a,g]corannulene-2	-38.2	-36.0	27.5	-8.5	0.5/0.4
C ₆₀ @dibenzo[a,g]corannulene+4ethyl	-22.4	-21.5	14.5	-7.0	2.2
C ₆₀ @dibenzo[a,g]corannulene+8ethyl	-24.2	-23.1	15.3	-7.8	5.0
C ₇₀ @dibenzo[a,g]corannulene+4ethyl-2	-25.9	-25.0	14.3	-10.7	1.3
C ₇₀ @dibenzo[a,g]corannulene+8ethyl-1	-22.4	-21.2	13.8	-7.4	2.1
C ₇₀ @dibenzo[a,g]corannulene+8ethyl-2	-24.0	-22.7	14.7	-8.0	5.6

a- 1 indicate that the polar region of C₇₀ interacts with the host.

b- 2 indicate that the equatorial region of C₇₀, predominantly interacts with the host. For details see, Figs 3-5.



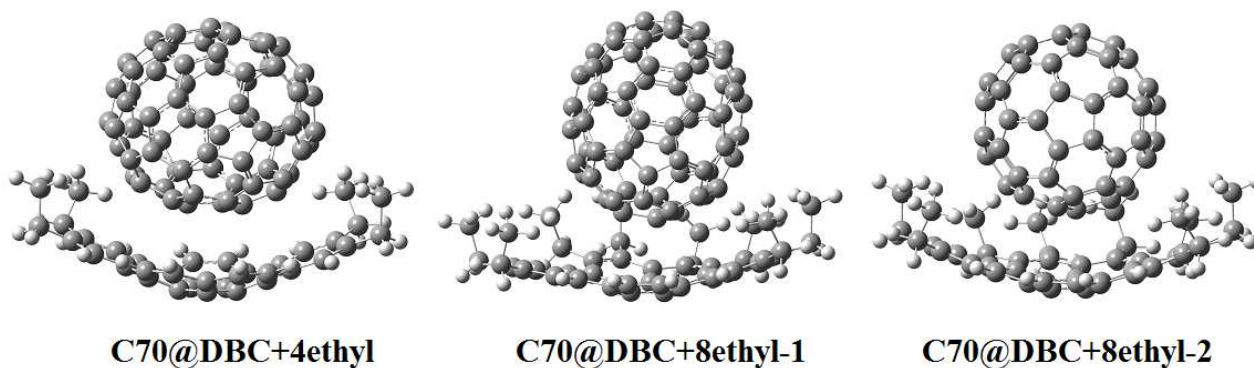


Figure 5. Optimized structures determined at the M06-2X/6-31G level, for the complexes formed by C_{60}/C_{70} fullerenes and dibenzo[a,g]corannulene based receptors.

showed a 1:1 ratio of fullerene:receptor and no differentiation between the concave and convex side of the receptor was observed. A different behavior was observed when the equatorial region of C_{70} interacted with the bowl. In this case, the IE value was -19.5 kcal/mol and the quotient of this figure with that computed for $C_{70}@corannulene$ was 0.77, essentially the same as the quotient of the areas calculated above. Consequently, when the curvatures of the fullerene and the bowl exhibit a good fit an excellent correlation between area and IE is obtained. Analysis of the bond distances also supports this hypothesis. In effect, the carbon atoms of the peripheral benzene rings of the receptor are 0.2-0.3 Å closer to C_{70} when this fullerene interacts with its equatorial region. A final confirmation of this statement is given by the IE determined for C_{70} , when the polar region of this fullerene interacts with dibenzo[a,g]corannulene employing its polar region. The IE is -17.0 kcal/mol, similar to that computed for C_{60} . The crystal structure of $C_{70}@dibenzo[a,g]corannulene$ showed that two bowls interact with the fullerene exclusively using their concave side. This prompted us to study the 2:1 complexes. In general the IE are twice the values computed for the 1:1 complexes. For C_{70} the highest IE with two bowl molecules is -38.2 kcal/mol, about 4.1 kcal/mol larger than the value corresponding to C_{60} .

In order to increase the IE we resorted to the functionalization of the rim of dibenzo[a,g]corannulene. We attached four and eight ethyl groups. The reason for selecting such short

groups is that they cannot interact via CH- π interactions with the bowl, but they can do so with the fullerenes. Also, since they are not too long the entropic effects would not be so harmful for the free energy change. Indeed, we observed that methylation of the $C_{60}H_{28}$ buckycatcher is effective in increasing the affinity of the host towards C_{60} .¹⁴ In this case, the introduction of four and eight methyl groups have a good impact on the IE since they are increased by 5.3 and 7.1 kcal/mol, respectively. However, the effect on the ΔG°_{298} is only significant when 4 ethyl groups are introduced producing an increase of 2.8 kcal/mol. We note that at the M06-2X/6-311+G*+BSSE level of theory IE computed for $C_{60}@dibenzo[a,g]corannulene+4ethyl$ is 2.5 kcal/mol smaller than the M06-2X/6-31G result, again confirming the good behavior of the methodology selected. The introduction of eight groups increases ΔG°_{298} by 3.6 kcal/mol. In the case of C_{70} an opposite behaviour is observed: the introduction of eight ethyl groups is less effective than four. The reason is that eight groups prevent the excellent fit observed when C_{70} is oriented along its long axis over the bowl. The free energy change determined for $C_{70}@dibenzo[a,g]corannulene+4ethyl$ is -10.7 kcal/mol. This value is 3.8 kcal/mol larger than the value determined for the bare bowl. Then, functionalization of the bowl should be performed in such a way that it does not disrupt the stacking interaction between host and guest, unless the functional groups are able to compensate the loss of stacking and at the same time, avoiding the introduction of undesired conformational and entropic side effects.

4. Conclusions

By means of first principle calculations we have performed a comparative study of the interaction between fullerenes and two types of receptors derived from subphthalocyanines and corannulene. The following are considered to be the most important findings of the investigation:

1- Analysis of the IE and areas of the receptors revealed that subphthalocyanines display excellent ball socket interactions with C_{60} and C_{70} . However, dibenzo[a,g]corannulene showed an excellent fit only with C_{70} , as indicated by recent experimental results.

2- The introduction of long thioalkyl chains in the rim of the subphthalocyanines increases the IE between receptors and fullerenes. Yet, the effect on the association constant is negligible, and in some cases it can be even harmful, because the long alkyl chains introduce large entropic penalties. Thus, the gain in IE caused by the thioalkyl chains is cancelled by the entropic penalties and the reaction free energy experiences a small variation. These findings explain why the association constants determined for the functionalized subphthalocyanines and fullerenes showed small variations upon chain enlargement.

3- We propose that the introduction of three 1,4 dithino groups at the peripheral region of the subphthalocyanine can improve its affinity towards C_{60} and C_{70} . This is supported by theoretical calculations which showed a large change in free energy (10 kcal/mol) when the above mentioned modification is effected.

4- Although long alkyl chains seem not to be useful to improve the binding affinity of several receptors, we have found that the addition of small ethyl chains onto dibenzo[a,g]corannulene increases the affinity of the bowl towards fullerenes. Nevertheless, new functional groups must be attached in places where the stacking interaction between host and guest is barely affected, otherwise the loss of π stacking should be compensated by the new functional groups.

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