

Buckybowl Molecular Tweezers for Recognition of Fullerenes

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Buckybowl tweezers are a relatively young research area closely associated with the development of non-planar polycyclic aromatic systems and supramolecular chemistry. Since the appearance of the first prototypes in the early 2000s, the tweezers have undergone evolutionary changes. Nowadays they are able to effectively interact with fullerenes and the results opened up prospects for development in the field of sensing, nonlinear optics, and molecular switchers. In the

present study, examples of corannulene-based and other buckybowl tweezers for the recognition of C₆₀ and C₇₀ fullerenes were summarized and analyzed. The main structural components of the tweezers were also reviewed in detail and their role in the formation of complexes with fullerenes was evaluated. The revealed structural patterns should trigger the development of novel recognition systems and materials with a wide range of applications.

1. Introduction

The development of artificial receptors and sensors for efficient molecular recognition opens wide prospects for the design of molecular devices, ensembles, and materials with unique properties.^[1–4] They may be based on promising molecules that have already proved in the field of nanotechnology.^[5–8] Among them, special attention should be paid to all-carbon curved structures such as nanocones, nanotubes, and fullerenes, which have served as a driving force in many areas of science and technology.^[9,10] The detailed study of their properties has led to a large variety of applications: sensors,^[11–13] sorption materials,^[14] supports for metal catalysts,^[15] transistors,^[16] batteries,^[17,18] and perhaps the most well-known use in photovoltaics.^[19,20] Despite impressive progress in these areas, there are several challenges to further implementation. Such limitations include the difficulty in their synthesis and purification, which makes these molecules expensive.^[21] Moreover, often large all-carbon molecules have low solubility, which significantly complicates their handling.^[22,23]

In theory, separation and purification, solubility problems can be overcome by designing suitable molecular receptors.^[24,25] This approach will also provide interactions between components of molecular devices without covalent modification of the guest molecules.^[26] This is especially important for preserving the unique characteristics of pristine molecules. For example, covalent modification of fullerene C₆₀ leads to the removal of the degeneracy of its orbitals and changes its properties.^[27]

A quick view of the considered all-carbon structures reveals their similarities: 1) they are non-planar; 2) composed of sp²-hybridized carbon atoms; 3) possess a large extended π -system.^[5] Taking into account the properties of these structures, several strategies have been proposed for their molecular

recognition. For these purposes, the symmetric buckminsterfullerene molecule was used as a suitable spherical model. The first receptor for fullerene C₆₀ was designed using azacrownethers with lipophilic alkyl chains as early as 1992.^[28] Since then, the lipophilic cavity of various macrocycles such as cyclodextrins,^[29] calixarenes,^[30,31] cyclotrimeratrylenes^[32] has been used to bind and recognition of fullerenes. This strategy was based on utilizing the poor solubility of fullerenes and van der Waals interactions.^[33]

Another approach is the design non-cyclic hosts, like molecular tweezers to bind guest molecules by non-covalent interactions such as hydrogen bonds, coordination with metals, and the use of π - π interactions.^[34] An actively growing field is the development of molecular tweezers for the separation of all-carbon structures from carbon soot.^[35,36] For this purpose, quite widely used tweezers based on planar molecules such as porphyrin,^[37–39] pyrene.^[40,41] Here it is important to note the role of π - π interactions which is actively used in the fields of organic dyes,^[42] liquid crystals,^[43] organic semiconductors,^[44] and supramolecular chemistry for the recognition of organic substances.^[45–47] However, the planar structures are not adapted when complexing with non-planar, spherical fullerene structures, which leads to a decrease in binding constants.^[48] Therefore, the next research step towards effective molecular recognition was the use of bent π -, bowl-shaped systems. Here it is worth mentioning the successful synergy of macrocycles and curved aromatic systems: cycloparaphenylenes (CPP) which showed excellent complexation properties.^[49,50] While the evolution of molecular tweezers has been driven by the application of the supramolecular concept of 'ball in a socket' for fullerene recognition.^[51] From this point, buckybawls (curved-surface polycyclic aromatic hydrocarbons (PAHs)) represent a promising class of hydrocarbons whose concave surface perfectly corresponds to the convex surfaces of non-planar guests.^[52]

The subject of this review is to summarize the accumulated knowledge on buckybowl molecular tweezers for the recognition of fullerenes. The main structural components of tweezers and their properties essential for the design of effective guest-host complexes are discussed in details. The article is divided into sections according to the type and role of these structural components of molecular tweezers. For ease of comprehension, the data on the association constants of tweezers with fullerenes are summarized in the table. The revealed patterns can help in the design of novel supramolecular systems and materials.

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2. Non-Planar Polycyclic Aromatic Hydrocarbons

The curvature of bucky-bowls generates two surfaces: concave and convex, having different orbital structures and electron densities specifying their properties (Figure 1).^[53] Thus, the bowl-shaped structure induces a dipole moment in a perpendicular axis even in the absence of functional groups.^[52] This, in turn, leads to the solubility of buckyballs in various solvents, despite π interactions. The distortion of π -conjugation in buckybowls causes insufficient overlapping of p-orbitals and leads to an increase of s-orbital character in sp^2 hybridized carbon atoms compared to planar structures. This results in lower LUMO level, enhancement of acceptor properties, etc.^[54] As the local deformation index, often used is the pyramidalization angle of the individual carbon atom, defined as the p orbital axis vector (POAV).^[55] The angle between POAV and any of three σ -bonds (depicted as θ , and $\theta-90^\circ$) is often used to characterize deviation from planarity.^[56] This angle reflects not only structural features, but is also a valuable parameter for evaluating the reactivity and stability of a conjugated system with a nonplanar structure.^[57] The POAV angles for the structures considered in this paper are shown in Figure 1. For example, the POAV angle in fullerene C_{60} (11.6°) induces a large heat of formation $\Delta H_f^\circ = 9.1 \text{ kcal mol}^{-1}$ (per carbon atom), while in graphite this value is zero.^[58]

The simplest non-planar fragment of fullerene C_{60} is corannulene (Figure 1b), which was synthesized in 1966 long before the discovery of fullerene.^[59] However, the investigation of the properties of this amazing buckybowl, possessing C_{5v} symmetry, was abandoned, mainly by the 17-step synthesis to obtain substance in milligram scale. With the advent of the fullerene era interest in corannulene was revived after the invention of flashvacuum pyrolysis and three-step synthesis proposed by Scott in 1997.^[60,61] However, a synthetic procedure allowing the preparation of corannulene on a kilogram scale was proposed only in 2012 by Siegel.^[62] Significant progress in the study of the properties of corannulene and interactions with fullerenes was made in the group of Stuparu.^[63,64] For instance, nanoparticles and polymeric materials for noncovalent

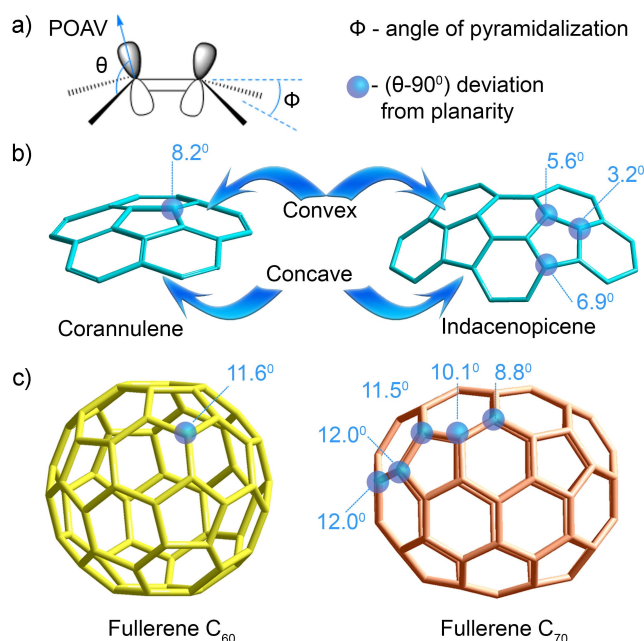


Figure 1. a) Schematic representation of p orbital axis vector (POAV). b) Convex and concave surfaces of corannulene and Indacenopicene c) POAV angles of fullerenes C_{60} and C_{70} .

encapsulation of fullerenes were developed on a base of corannulene moiety.^[65-67]

Another fundamental buckybowl, summanen (C_{3v} symmetry) was first synthesized in 2003 and became commercially available in 2017, but its price is still high.^[68]

The remaining challenging synthesis of other buckybowls, such as diindeno[1,2,3-c:4,5-c']p[1,2,3-c:4,5-c']picene does not allow extensive studies of their properties. Thus, at the moment only corannulene and its derivatives are intensively studied. Nevertheless, the discovery of new synthetic approaches and methods such as cyclodehydrofluorination,^[69,70] microfluidics^[71-73], mechanochemistry^[63,74] and others^[75] will help to access a wide range of novel buckybowls in sufficient quantities.

3. Buckybowl Molecular Tweezers

3.1. Molecular Tweezers

The term “molecular tweezers” was introduced by Whitlock in 1978 to describe a molecular receptor having two identical aromatic moieties linked by a rigid unit (spacer) capable of binding aromatic guests with the formation of a sandwich complex.^[76] It was found that the binding affinities of the molecular tweezers significantly exceed those of the individual aromatic components due to the cooperative nature.^[77] The pre-organization of the system also plays an essential role: the nature of the components, their geometric matching, and the rigidity of the structures.^[78] The structural potential of the molecular tweezers can be varied by two main parameters: 1) the chemical nature and structure of interaction sites (Fig-



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ure 2d) and 2) the structure of the spacer, which determines the relative location of recognition sites.^[34] It is hard to overestimate the role of the spacer: i) it prevents self-association of recognition sites, ii) orientates them (rigidly holds them in syn-conformation), iii) provides the necessary distance between components.

Molecular tweezers can be divided into several types based on the nature of the spacer: flexible spacer (Figure 2a), rigid spacer (Figure 2b,c), and stimuli-responsive spacer (Figure 2e).^[79] Molecular receptors of the first type do not occur in the systems under consideration, probably due to their low pre-organization and correspondingly small binding constants with fullerene. The second type of molecular receptors can be divided into rigid spacer (e.g. Klärner tweezers) and semi-rigid spacer (e.g. Zimmerman tweezers possible rotation of recognition sites around a single bond).^[34] The third type includes mainly molecular switchers, which are able to change the orientation of recognition sites by external stimulation.

3.2. Rigid Spacer

The first attempt to synthesize molecular tweezers for binding fullerenes was performed in the group of A.Sygula in 2003 (Figure 3).^[80] This non-planar pincer molecule, consisted of two corannulene moieties linked through a rigid barrelene tether spacer. Unfortunately, the association constants could not be determined since the binding energy of C_{60} to **1** was not strong enough to override the solvation/entropic and strain penalties of the host molecule.^[51] Here should be noted the following details of pristine corannulene: i) it has low bowl-to-bowl

inversion barriers (ca. 10 kcal/mol) allowing rapid interconversions of the conformers;^[60,81] ii) the association constant for complex corannulene with C_{60} is low in solution (estimated to be $\ll 1 \text{ M}^{-1}$, in PhCN).^[82] Therefore, special attention should be paid to the pre-organization of the system and optimal spacer geometry in particular in the design of corannulene-based hosts.

The topology and preorganization of the convex pincers on the receptor were adjusted in molecule **2** for efficient fullerene coordination.^[83] The X-ray crystal structure of the C_{60} @**2** inclusion complex (Figure 3a) showed that most of the corannulene atoms were located relative to C_{60} at a distance corresponding to van der Waals contacts. The results obtained by A. Sygula's group in 2008 on the complexation of the molecular tweezers provided the first experimental evidence regarding the importance of dispersion-based concave-convex interactions in the supramolecular chemistry of non-planar carbon structures. The C_{60} @**2** inclusion complex has become a model for testing computational methods used to describe relatively weak dispersive interactions.^[84–86] To obtain reliable thermodynamic data on the formation of 1:1 inclusion complexes of C_{60} and C_{70} fullerenes with tweezers **2**, ^1H NMR and isothermal titration calorimetry (ITC) experiments were carried out.^[87] The measurements were performed in different solvents and a temperature range of 30 K, and the association constants obtained by these methods were in good agreement. The formation of inclusion complexes was found to be mainly enthalpically driven. It is worth noting that the free energies of complex formation change linearly depending on the dielectric constant of the solvent, becoming 1.5–2 kcal mol⁻¹ less favorable in *o*-dichlorobenzene than in toluene, enthalpy, and

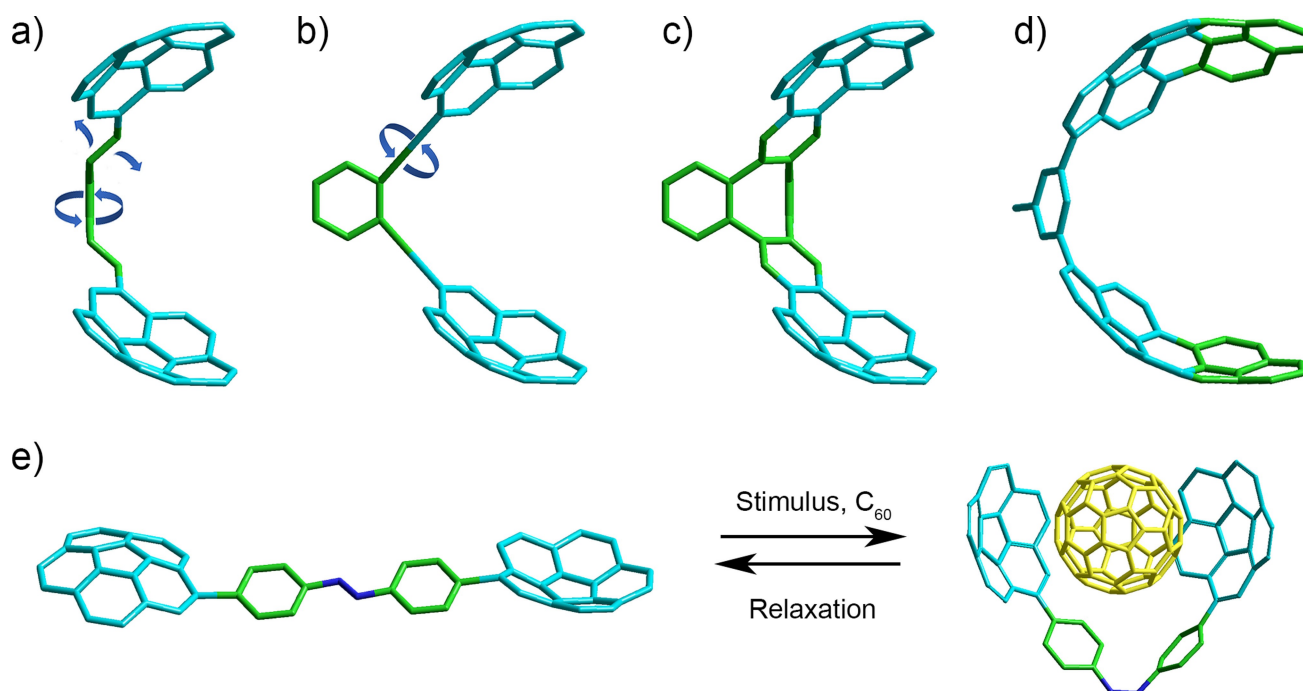


Figure 2. Types of molecular tweezers according to the spacer structure: a) flexible (multiple degrees of freedom), b) semi-rigid spacer (possible rotation of recognition sites around a single bond), c) “absolutely” rigid spacer, e) stimuli-responsive spacer; d) modification of binding sites. The green color indicates the corresponding molecular fragments.

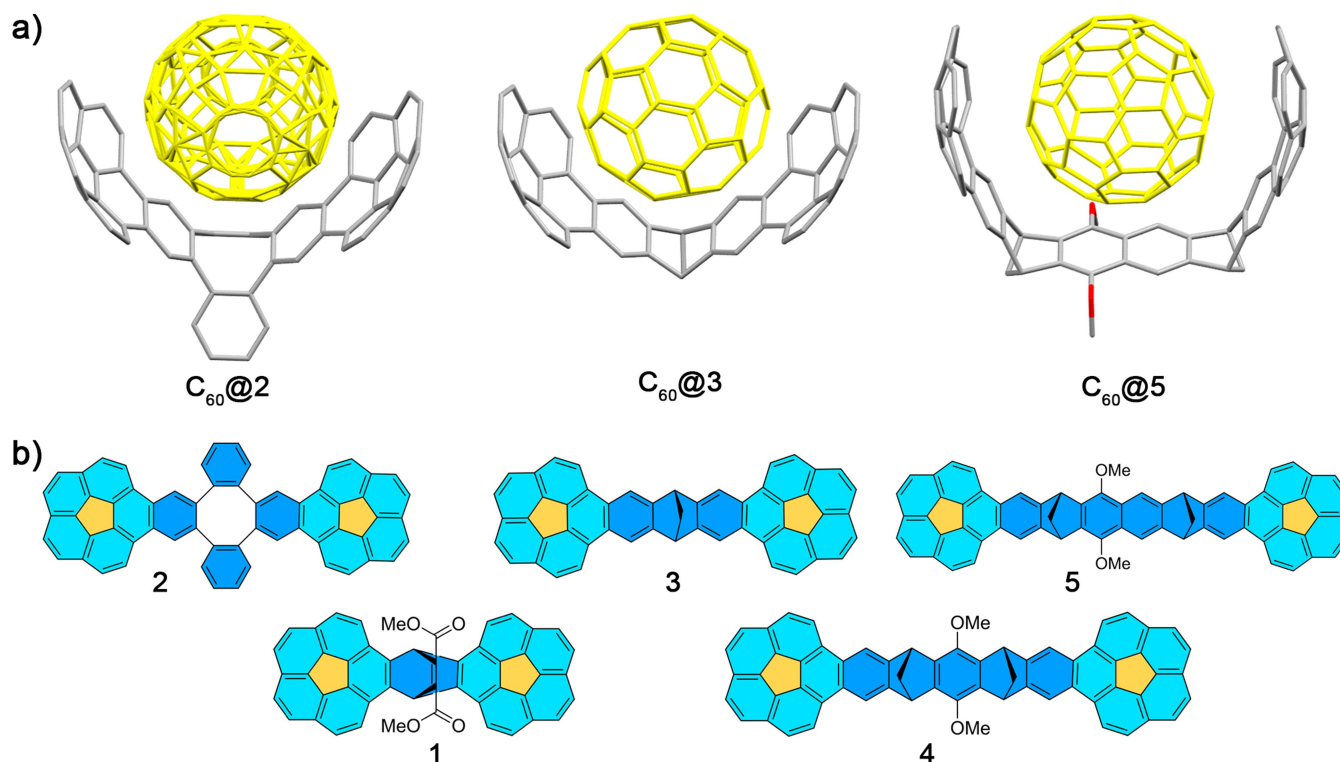


Figure 3. a) The X-ray crystal structures of the C₆₀@2, C₆₀@3 and C₆₀@5 inclusion complexes. b) Structures of the molecular tweezers 1–5.

entropy changes vary unpredictably while a high degree of compensation was observed. Complex formation becomes less favorable in solvents where the solubility of fullerene or tweezers is higher, presumably highlighting the importance of any desolvation penalty.^[87]

The change in the nature of the solvent significantly affects not only the association constant, but also the host selectivity. For example, according to ITC experiments, the C₇₀@2 association constant ranged from $K_a = (4.6 \pm 0.17) \times 10^3$ in toluene to $K_a = (2.0 \pm 0.1) \times 10^2$ in *o*-dichlorobenzene and becomes the same as for C₆₀@2 (Table 1).

Based on the obtained findings and conclusions A.Sygula's group decided to develop Buckycatcher 3. They applied computer modeling to develop the molecular receptor 3 with two benzocorannulene pincers preorganized on a norbornadiene tether.^[88] The geometry of the pincers was optimized so that the distance between the centers of the central five-membered rings in the pincers both in solution and when complexed with C₆₀ was close to 11.5 Å, a distance that was found in the X-ray structure of C₆₀@2. Also, calculations indicated a more energetically favorable formation of the C₆₀@3 complex compared to C₆₀@2. The formation of complex 3 with C₆₀ was confirmed by NMR, mass spectroscopy, and X-ray analysis. An interesting point was that the stoichiometry of the complex was not described by the usual 1:1 stoichiometry as was the case for C₆₀@2. In contrast, the results indicated stepwise constants and associative patterns of 1:1 and 1:2. Using ¹H NMR titrations it was possible to accurately estimate the constants only in chlorobenzene-*d*₅, since they were too high in toluene-*d*₈. A grown X-ray crystal of the 1:2 C₆₀@3₂

confirmed the complex structure, in which the double-concave clefts of the two molecules 3 cooperatively cover most of the C₆₀ surface.

Some correlations between the structural features of molecular receptors and their complexation were found by analyzing molecules 4 and 5. Both molecules were designed using Klärner's tethers for strong preorganization of the corannulene pincers in a *syn* fashion, resulting in significant gas-phase binding energies with C₆₀ 33.6 and 50.0 kcal/mol, respectively.^[89] ¹H NMR titrations and Job plot analysis experiments indicated the formation of 1:1 stoichiometry associates for tweezers 4 and fullerenes C₆₀ and C₇₀. However, in toluene-*d*₈, the association constants were average and no selectivity between the binding of C₆₀ and C₇₀ fullerenes was observed. On the other hand, the larger molecular receptor 5 showed preferential binding to C₇₀, and affinity was high for both fullerenes with a 1:1 and 1:2 binding pattern. The X-ray structure of the C₆₀@5 complex (Figure 3a) revealed that the fullerenes were located in the center of the cleft of the receptor, interacting not only with the concave faces of both corannulene pincers but also with the naphthalene subunit of the tether. It should be noted that for molecule 5 the calculated host-deformation energy was negligible, indicating precise preorganization of the tweezers, making it an exceptional host with high affinity to fullerenes.

Considered type of molecular tweezers conceptually reflect the key-lock model. They have the highest rigidity and require the most careful optimization of the structure geometry. On the one hand, the structure of the rigid linker must be carefully designed otherwise mistakes may result in a complete loss in

Table 1. Comparison of measured K_a values for binding of C_{60} and C_{70} with the buckybowl molecular tweezers as obtained from titration experiments.

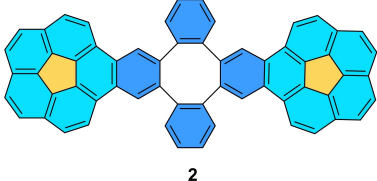
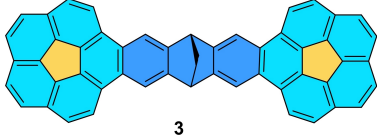
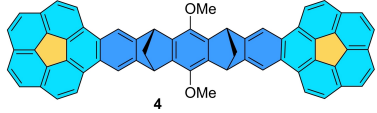
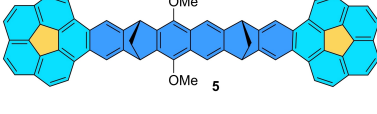
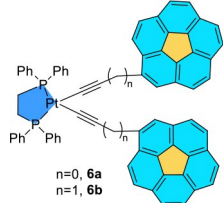
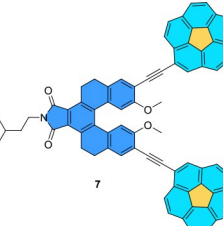
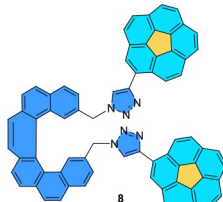
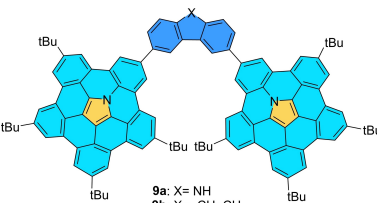
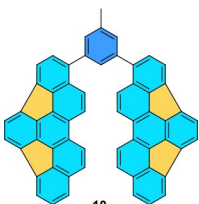
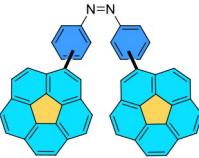
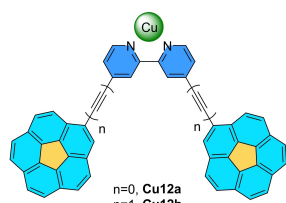
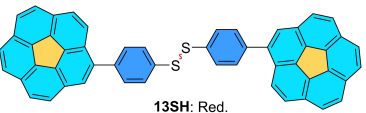
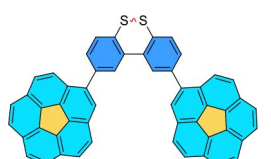
Structure	Method	Solvent	Association constants (M^{-1})		ref.
			C_{60}	C_{70}	
 2	1H NMR	Toluene- <i>d</i> 8	$(2.78 \pm 0.08) \times 10^3$	$(3.03 \pm 0.33) \times 10^3$	[87]
		Chlorobenzene- <i>d</i> 5	$(5.2 \pm 0.2) \times 10^2$	$(9.2 \pm 0.9) \times 10^2$	
	ITC	Toluene	$(3.2 \pm 0.15) \times 10^3$	$(4.6 \pm 0.17) \times 10^3$	
		Chlorobenzene	$(8.0 \pm 0.1) \times 10^2$	$(9.0 \pm 0.3) \times 10^2$	
 3	1H NMR	Toluene- <i>d</i> 8	K_1 Ca. 8.5×10^4 K_2 Ca. 5×10^3	n/a	[88]
	1H NMR	Chlorobenzene- <i>d</i> 5	K_1 $(1.004 \pm 0.11) \times 10^4$ K_2 $(1.1 \pm 0.64) \times 10^3$	n/a	
 4	1H NMR	Toluene- <i>d</i> 8	$(2.55 \pm 0.05) \times 10^3$	$(2.95 \pm 0.11) \times 10^3$	[89]
 5	1H NMR	Chlorobenzene- <i>d</i> 5	K_1 Ca. 5×10^4 K_2 Ca. 8×10^3	K_1 $(2.0 \pm 0.7) \times 10^5$ K_2 $(3.3 \pm 0.9) \times 10^4$	[89]
2015, A. Sygula					
 6a n=0, 6a n=1, 6b	1H NMR	Toluene- <i>d</i> 8	$(4.6 \pm 0.1) \times 10^3$	$(2.07 \pm 0.06) \times 10^4$	[90]
	1H NMR		n/d	n/d	
 7	Fluorescence	Toluene	$(2.79 \pm 0.18) \times 10^3$	$(6.42 \pm 0.26) \times 10^5$	[91]
 8	1H NMR	Toluene- <i>d</i> 8	$(2.55 \pm 0.14) \times 10^3$	n/a	[94]
 9a : X=NH 9b : X=-CH=CH-	UV-vis	Toluene	$(4.4 \pm 0.4) \times 10^7$	$(7.0 \pm 3.1) \times 10^8$	[48]
	UV-vis	<i>o</i> -DCB	$(3.0 \pm 0.3) \times 10^5$	n/a	
	UV-vis	Toluene	$(3.0 \pm 1.1) \times 10^8$	$(6.3 \pm 0.8) \times 10^7$	
	UV-vis	<i>o</i> -DCB	$(2.2 \pm 0.7) \times 10^6$	n/a	

Table 1. continued					
Structure	Method	Solvent	Association constants (M^{-1})		ref.
			C_{60}	C_{70}	
	1H NMR	<i>o</i> -DCB- <i>d</i> ₄	$(1.50 \pm 0.10) \times 10^2$	$(1.08 \pm 0.01) \times 10^3$	[99]
	1H NMR 11a (<i>E,Z</i>)	Toluene- <i>d</i> ₈	(<i>E</i>)-n/d (<i>Z</i>) $(2.6 \pm 0.3) \times 10^3$	(<i>E</i>)-n/d (<i>Z</i>) $(2.5 \pm 0.3) \times 10^3$	[103]
para-, 11aZ meta-, 11bZ	1H NMR 11b (<i>E,Z</i>)	Toluene- <i>d</i> ₈	(<i>E</i>) $(5.0 \pm 0.1) \times 10^2$ (<i>Z</i>) $(6.7 \pm 0.2) \times 10^2$	(<i>E</i>) $(8.3 \pm 0.1) \times 10^2$ (<i>Z</i>) $(2.5 \pm 0.3) \times 10^2$	
	1H NMR (Cu12a)	CD_2Cl_2	$(2.00 \pm 0.01) \times 10^3$	$(4.99 \pm 0.01) \times 10^4$	[102]
n=0, Cu12a n=1, Cu12b	1H NMR (Cu12b)	CD_2Cl_2	$(1.15 \pm 0.01) \times 10^3$	$(2.11 \pm 0.01) \times 10^4$	
	1H NMR 13SH: Red.	Toluene- <i>d</i> ₈	n/d	n/d	[104]
13SS: Ox.	1H NMR 13SS: Ox.	Toluene- <i>d</i> ₈	$(1.87 \pm 0.03) \times 10^2$	$(7.24 \pm 0.17) \times 10^2$	
	1H NMR 14SH: Red.	Toluene- <i>d</i> ₈	$(1.90 \pm 0.02) \times 10^3$	$(2.03 \pm 0.01) \times 10^3$	[104]
14SS: Ox.	1H NMR 14SS: Ox.	Toluene- <i>d</i> ₈	$(3.93 \pm 0.04) \times 10^2$	$(4.65 \pm 0.07) \times 10^2$	

binding and recognition. On the other hand, optimally chosen geometries maximize host preorganization, minimize the cost of conformational selection, and ultimately lead to a significant increase in binding constants and selectivity.

However, synthetic difficulties impose significant limitations on the structural variation of these tweezers. Alternatively, a semi-rigid linker can be used as synthetically more accessible and the system will reflect the "induced-fit" guest-host recognition model.

3.3. Semi-Rigid Spacer

Thus, a conceptually different approach to the design of molecular tweezers – the use of a coordination sphere around the metal was reported by Alvarez et al.^[90] The tweezers **6a,b** consisted of the 1,2-bis(diphenylphosphino)ethane ligands, and the two remaining coordination positions of platinum were occupied by the two corannulene ethynyl units (Figure 4a). Their complexation with fullerenes was studied by 1H NMR

titration. For compound **6b** the interaction with fullerenes was not significant, which did not allow to obtain reliable association constants. This is explained by the fact that the introduction of a methylene group between the acetylidene and corannulene molecules increases their flexibility and prevents effective guest-host interaction. In contrast, tweezers **6a** showed good affinity to fullerenes C_{60} and C_{70} with a 1:1 binding model. The X-ray structure of the $C_{60}@6a$ (1:1) inclusion complex revealed that the distance between the C_{60} cage and the inner surface of the corannulene units is about 3.6 Å, which roughly corresponds to the convex-concave interactions in curved π -materials such as multi-walled carbon nanotubes.^[50] It should be noted that the association constant of **6a** with C_{70} was approximately 5 times larger than for $C_{60}@6a$. This behavior was explained by more favorable dispersion interaction and less Pauli repulsion between the electron charge densities of C_{70} and molecular tweezers **6a**.

Significantly improved selectivity of complexation with C_{70} over C_{60} was achieved by tweezers **7** developed in Chen's group.^[91] The flexible tetrahydro[5]helicene imide linker enabled

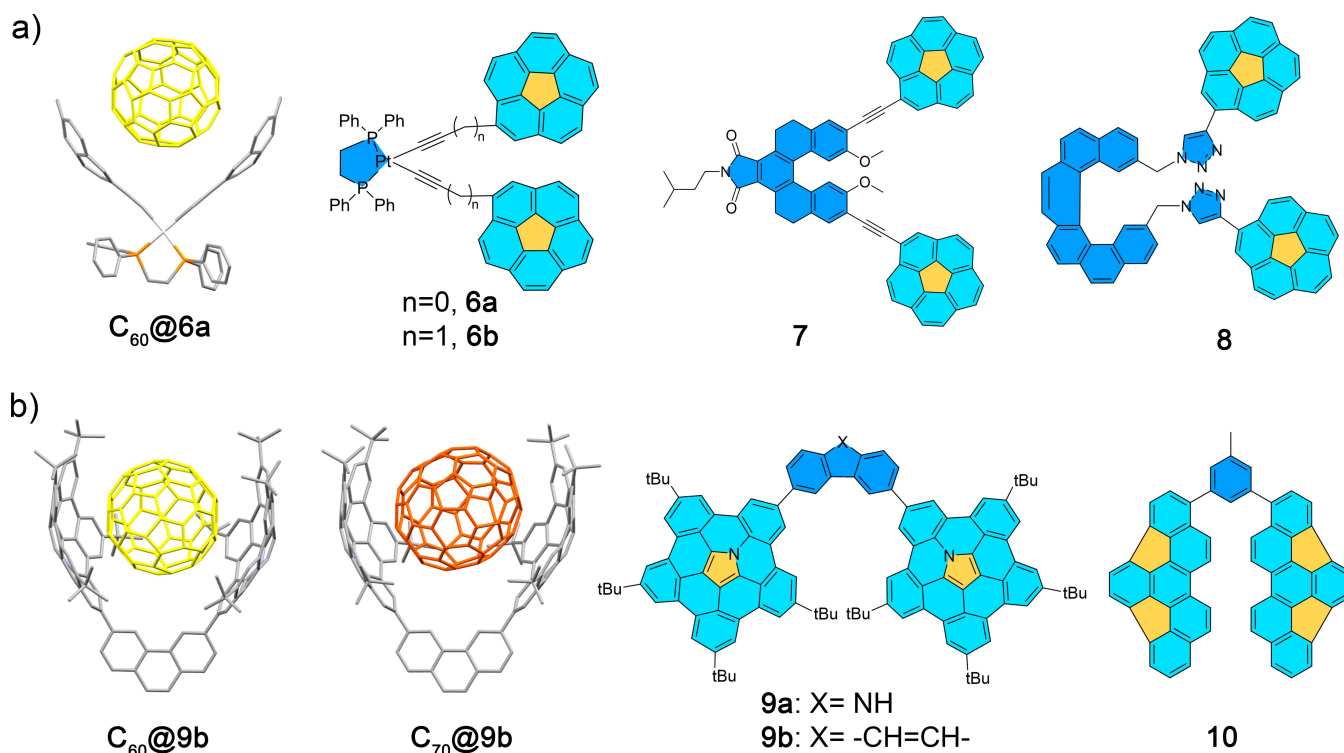


Figure 4. Buckybowl molecular tweezers and their X-ray structures: a) molecules with semi-rigid spacer; b) molecules with modification of binding sites.

form-adaptation of receptor **7** for efficient complexation with the oval fullerene C_{70} . The presence of the imide chromophore allowed the use of UV-vis and fluorescence spectroscopy to investigate the **7** binding properties. The addition of the fullerenes to a solution of receptor **7** caused an increase in absorbance and the quenching of fluorescence, with color changes that could be seen with the naked eye. Fluorescence titrations resulted in a $K_a C_{70}/K_a C_{60}$ value higher than 230/1. The 1:1 binding model was confirmed by Job's plot analysis. The authors did not give information regarding binding constants obtained from NMR titration, but provide the spin-spin (T_2) relaxation times of the complexes. The 1H T_2 values for **7** decreased significantly upon the addition of 1 equivalent of C_{70} , indicating reduced molecular mobility due to the formation of non-covalent interactions. The $C_{60}@7$ and $C_{70}@7$ structures attracted the attention of researchers in the field of charge transfer complexes and nonlinear optics.^[92] It was found that larger fullerene C_{70} contributed to increased intermolecular interaction and charge transfer, thereby increasing the first hyperpolarizability of the charge transfer complexes.

Copper-catalyzed azide-alkyne cycloaddition is an efficient synthetic route that can be used to obtain, in particular, corannulene-rich compounds and materials. Triazole-linked corannulene derivatives were described by Stuparu, while tweezers **8** based on their chiral hexahelicene skeleton were obtained in the Alvarez group (Figure 4a).^[93,94] Optimization of geometry **8** revealed that the most stable structure corresponds to the arrangement of both corannulene subunits in a concave-concave position. Thus, host **8** is already preorganized and can accommodate C_{60} by slightly opening the tweezers. Compound

8 showed an average association constant with fullerene C_{60} in toluene (Table 1) and due to its chirality can theoretically be applied for enantioselective molecular recognition.

The structural variation of the linkers described in this section has improved the selectivity of the tweezers towards C_{70} binding. It also opened the way to the development of chiral and fluorescent sensors.

3.4. Non-Corannulene Buckybowl Tweezers

To achieve efficient binding with fullerenes, not only the linker but also the receptor bowls can be modified. In this case, the electron-donating properties of the receptor should be improved to achieve better interaction with the electron acceptor convex surface of fullerenes. For this purpose, one can introduce electron-donating substituents, extend the π -surface, or introduce heteroatoms into the bowl structure. Following this strategy, the Nozaki and Shinokubo groups independently synthesized pyrrolic-nitrogen-embedded azabuckybowl, which showed a large binding constant with C_{60} ($(6.2 \pm 0.4) \times 10^5$ in toluene).^[95,96] Then, via cross-coupling of 2-borylated azabuckybowl and 3,6-dibromocarbazole or 3,6-diiodophenanthrene units, the tweezers **9a** and **9b** were synthesized (Figure 4b).^[48] UV-vis absorption and emission titrations with fullerenes in toluene revealed a binding pattern 1:1 with extremely high associating constants for both tweezers (Table 1). Furthermore, compound **9a** preferentially bound C_{60} , while compound **9b** had a higher affinity towards C_{70} . The stability of the $C_{60}@9b$ complex was so high in DCM, that it allowed its purification by

column chromatography on silica gel. The formation of 1:1 complexes in solution has also been confirmed by two-dimensional diffusion-ordered NMR (DOSY) spectroscopy. The increase in diffusion coefficient values with the addition of fullerenes indicates that Stokes-Einstein radii (r) of tweezers **9a** and **9b** were reduced due to the folding of azabuckybowl pincers upon complexation. The cavity of **9a** was more suitable for C_{70} than for C_{60} , resulting in a higher diffusion coefficient value. The X-ray structures of complexes **9a** and **9b** showed the location of the guests inside the cavity. The distances between the azabuckybowl units and fullerenes corresponded to the sum of the van der Waals radii of carbon atoms, which indicated π - π interactions. The angle between the center of the fullerene and the centers of the azabuckybowls is also important. The narrower angle in case C_{70} @**9b** (136.91°) compared to C_{60} @**9b** (143.35°) indicates that the host covers a smaller convex surface of the fullerene, providing a larger volume of the complex and decreasing in binding constant. This observation was consistent with a larger diffusion coefficient C_{70} @**9b** compared to C_{60} @**9b**. The complexes **9a** and **9b** with fullerenes are good examples of supramolecular D-A-D (donor-acceptor-donor) assemblies that are capable of generating quadrupolar characteristics due to intermolecular charge transfer, which should enhance the two-photon absorption (TPA) cross-section.^[97] The performed experiments showed that TPA properties of these molecular tweezers can be modulated upon binding with fullerenes. Therefore, these compounds can help in the development of new concepts for nonlinear optics and two-photon absorption materials.^[98]

Another modification approach involves an extension of the bowl's π -surface. A heteroatom-free buckybowl tweezers **10** was designed on a base of indacenoprene moieties with a tolyl linker.^[99] The indacenoprene molecule consists of six six-membered and two five-membered rings and has a depth of 0.925 Å, which is larger compared to corannulene (0.875 Å) (Figure 1b).^[100] The 4-bromo-13,16-difluorobenzo[s]picene precursor was synthesized by alumina-mediated cyclodehydrofluorination and attached to the tolyl tether via Suzuki cross-coupling reaction (Figure 4b). Theoretical calculations revealed energetically favorable hosting of fullerenes inside the tweezers cavity. ^1H NMR titrations confirmed the complex formation in a 1:1 ratio with fullerenes C_{60} and C_{70} . Although the NMR titrations were carried out in highly solvating *o*-dichlorobenzene, it is worth noting that the preferential binding catcher with fullerene C_{70} compared to C_{60} was maintained, the binding constants differed by an order of magnitude. Another interesting point was the unusual shift of the proton signal corresponding to the tolyl linker facing towards the fullerene upon complexation. Given the information on the spherical aromaticity of fullerenes, the different shift of this signal for fullerenes C_{60} and C_{70} becomes clear. Hence the tweezers **10** demonstrated the fundamental possibility of creating sensors for spherical aromaticity.

Despite the fact that obtaining non-corannulene recognition elements often involves challenging synthesis, it is worthwhile because opens a way to novel structures with unique properties. One direction of modification is to increase

the buckybowl-fullerene affinity by introducing electron-donating substituents. But even here one should be careful since non-selective high affinity makes it impossible to construct the molecular machines discussed below.

3.5. Molecular Machines. Switchable Molecular Tweezers

Design of molecular devices, logic gates is an intensive developing direction of supramolecular chemistry.^[101] The central unit of their architecture is a molecular switcher, which can operate upon external stimuli such as light-irradiation, heat, chemical stimulus, etc. In molecular tweezers, the linker can be utilized as a switcher to dynamically control of the guest binding. At the same time, well-functioning systems should meet the following criteria: i) high stability of the coordination complexes, ii) well-defined ON/OFF behavior (dramatic change in the affinity of the host in different states), and iii) complete reversibility of the systems.^[102]

The first light-responsive corannulene tweezers were synthesized in the M. Alvarez group.^[103] Corannulene units were introduced into the para- and meta- positions of azobenzene linker (compounds **11a** and **11b** respectively) and could reversibly switch under the UV irradiation (*Z*) and relax upon heating (*E*) (Figure 5a,b). Compound **11aE** did not demonstrate any significant interaction with fullerenes during ^1H NMR

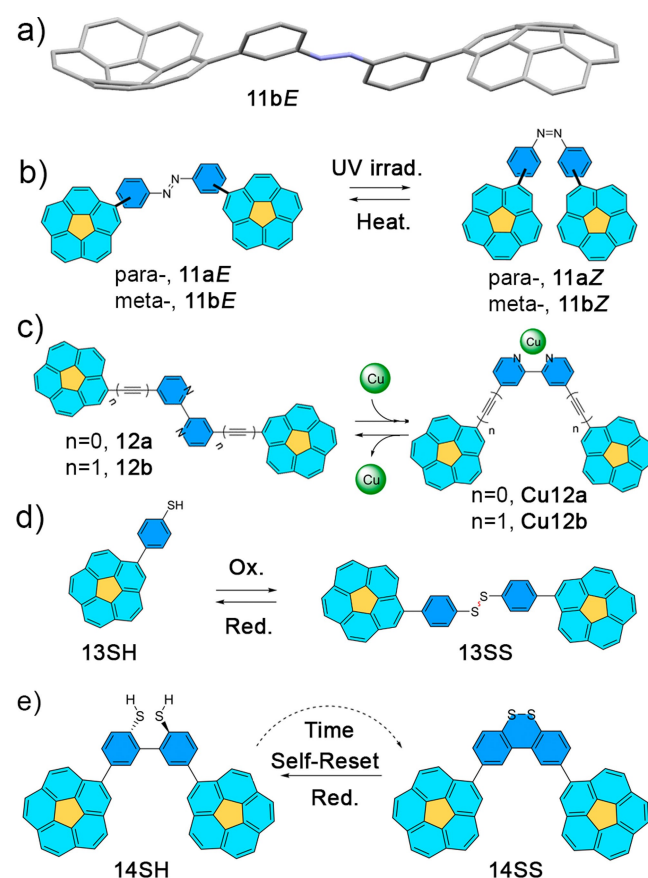


Figure 5. a) X-ray structure of **11bE**. Stimuli-responsive reactions for molecular tweezers: b) **11a,b**; c) **12a,b**; d) **13**; e) **14**.

titration, while **11aZ** showed significant improvement in binding and similar association constants for both fullerenes (Table 1). This complex 1:1 had on-off behavior and could be repeated for several cycles was proposed as a light-gated supramolecular tweezers. On the contrary, compound **11bE** already had a significant affinity for fullerenes, and after irradiation, the association constants changed in opposite directions: slightly increasing for C_{60} and decreasing for C_{70} . This striking difference in behavior was explained by the lack of space for the complexation of C_{70} and the weak preorganization of the host **11b** compared to **11a**.

Efficient metal-triggered ON/OFF molecular tweezers **12a** and **12b** were synthesized via Suzuki-Miyaura and Sonogashira C–C cross-coupling reactions under microwave irradiation using 4,4'-dibromo-2,2'-bipyridine and either bromocorannulene or 1-ethynylcorannulene respectively (Figure 5c).^[102] Tweezers **12a** and **12b** prefer the *anti*-conformation, whereas after the addition of $[Cu(NCMe)_4]BF_4$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe), complexes **Cu12a** and **Cu12b** were formed, adopting the *syn* conformation. This process is reversible and the addition of 1 equiv. of dppe to the **Cu12a** or **Cu12b** complexes released the **12a** or **12b** compounds and a more stable homoleptic complex $[Cu(dppe)_2]BF_4$ was formed as a byproduct, which remains in solution. The host-guest studies were carried out in deuterated DCM for stability reasons since in common aromatic solvents (such as toluene, *o*-DCB) Cu(I) complexes showed evidence of decoordination after 10 minutes, while in DCM they were stable for several weeks. For compounds **12a** and **12b**, which prefer the *anti*-conformation, no interaction with fullerenes was observed and the chemical shifts did not change, which indicated that the system was in the off state. The addition of Cu(I) imposed *syn* conformation, turning ON the system, which caused the formation of stable 1:1 complexes $C_{60/70}@Cu12a/b$ with fullerenes. Moreover, the association constants with C_{70} were an order of magnitude higher than with C_{60} for both tweezers, which is in accordance with the data for previously described corannulene-based molecular tweezers.^[90,91] It is worth noting that **Cu12b**, which had a longer ethynyl spacer, was only slightly inferior to **Cu12a** in recognition properties. Therefore, one can conclude that this system demonstrates a delicate balance between moderate flexibility, which reduces entropy, and rigidity of the system (size complementarity).

Inspired by nature Alvarez et al. designed two redox-based molecular machines capable of modulating their affinity towards fullerenes through disulfide bond formation (Figure 5d,e).^[104] The main structural element of those tweezers was para-corannulyl-thiophenol, which can be controlled and reversibly oxidized to form intra- and intermolecular S–S bonds. While monomer **13SH**, despite its slight electron donation nature, did not show any binding to fullerenes, its dimer **13SS** obtained after oxidation and formation of S–S bonds, demonstrated a certain affinity for these guests (Table 1). The binding constants were below average and there was almost no preference between C_{60} and C_{70} , which was associated with the large rotational freedom in this structure. For better preorganization, the host structure was modified by the addition of C–C

bond in tweezers **14**. As a result, the dihedral angle was expected to be (θ) between 70° and 90° a, with a torsional barrier high enough to limit the conformational population to a few geometries, leading to an increase in binding constants by almost an order of magnitude. Oxidation into the corresponding disulfide **14SS** led to a complete blocking of conformational freedom and structural rigidity but had a negative effect on the binding constants with fullerenes due to the non-optimal geometry of the complexes. An interesting point is that **14** tweezers have a self-resetting behavior. When exposed in the open air **14SH** is gradually oxidized by atmospheric oxygen leading to the compound **14SS**, which can then be converted back to **14SH** by an external stimulus (Figure 5e).

Although the described examples imperfect with a number of drawbacks, they demonstrate the fundamental possibility to construct molecular machines based on bucky-bowl tweezers. The selectivity and association constants of these molecules are inferior to the tweezers discussed in other sections, nevertheless, they fulfill the basic criteria of molecular switches. Thus, they provide a foundation for the development and further modification of promising molecular devices.

4. Summary and Outlook

The scientific fields related to the study of bowl-shaped π -conjugated systems are extremely rich and interesting. Their development directly correlates with the creation of novel supramolecular systems on their basis. Since the first attempts at molecular tweezers based on bucky bowls in the early 2000s, these systems have undergone an evolutionary development that has resulted in a conceptual diversity of the structures. Prototype systems capable for C_{70} recognition, spherical aromaticity sensors, fluorescence sensors, charge transfer systems, molecular machines, etc. have been developed. However, to date, examples of real-world applications of buckybowl tweezers are still lacking. It is also worth noting that most of the existing systems were obtained by varying the linker and using corannulene as the recognition site. This circumstance is due to the availability of the latter and the challenging synthesis of other bowl-shaped molecules. However, the development of synthetic methods in the near future promises to open access to a wide range of new non-planar structures.

The binding properties of the buckybowl tweezers are summarized in Table 1. In reviewing the table, the following points should be noted: i) in the series of solvents DCM > toluene > chlorobenzene > *o*-DCB, the binding constants of tweezers with fullerenes can decrease by several orders of magnitude, and the selectivity of binding between C_{60} and C_{70} can disappear due to solvation penalty.^[87] ii) The values of association constants obtained by UV-vis and fluorescence spectroscopy should be considered with caution. Spectra of the host and fullerenes may overlap, leading to an internal filter effect, as well as processes such as dynamic quenching of fluorescence may lead to overestimation of binding constants.^[105]

In conclusion, several factors responsible for successful guest-host interaction in the bucky bowl systems can be emphasized: i) The optimally chosen geometry of the complex should maximize the π -concave-to- π -convex interaction surface of the host and guest surfaces via van der Waals and π - π interactions. ii) The large size of the guest-host interaction surface is currently the main factor responsible for the preferential binding of C_{70} over C_{60} . iii) The more rigid the host structure, the better its preorganization, and the higher the binding constants with fullerenes. (However, concepts such as guest-induced conformation and molecular switches should not be overlooked). iv) Electron-rich aromatics are more preferable for the formation of complexes with fullerenes. v) The inclusion of heteroatoms such as nitrogen in the structure of recognition units can significantly increase binding constants.

Further development of systems based on bucky bowls should lead to breakthroughs in related fields of knowledge such as sensorics, nonlinear optics, creation of intelligent systems and materials.

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Conflict of Interests

The author declare no conflict of interest.

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