Supramolecular Chemistry

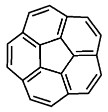
International Edition: DOI: 10.1002/anie.201505327
German Edition: DOI: 10.1002/ange.201505327

A 2:1 Receptor/C_{60} Complex as a Nanosized Universal Joint

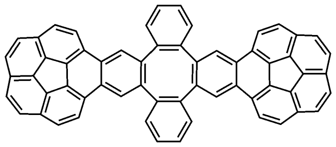
Michael Yanney, Frank R. Fronczek, and Andrzej Sygula**

Abstract: *Buckycatcher II, a $C_{51}H_{24}$ hydrocarbon with two corannulene pincers on a dibenzonorbornadiene tether, exhibits an affinity toward C_{60} in organic solvents that is dramatically higher than the original buckycatcher $C_{60}H_{28}$ and other corannulene-based molecular receptors for fullerenes. In addition to the formation of an usual 1:1 C_{60}@catcher inclusion complex, a trimeric C_{60}@(catcher)$_2$ assembly is detected in solutions and in the solid state. X-ray structure determination reveals a remarkable "universal joint" solvent-free crystal arrangement of the trimer, with a single fullerene cage wrapped by four corannulene subunits of two cooperating catcher receptors.*

Shape complementarity is a significant factor to consider in the design of supramolecular systems capable of undergoing self-organization.[1] In this context buckybowls, bowl-shaped polycyclic aromatic hydrocarbons,[2] appear to be suitable candidates to form "ball-and-socket" supramolecular assemblies with fullerenes owing to the complementarity of their concave and convex surfaces. Although such assemblies of the smallest buckybowl corannulene (**1**) with fullerene C_{60} (**2**) have been detected in the solid state[3a] and on metal surfaces,[3b] no evidence of significant association of the two has been observed in solutions.[4] Apparently, the usual solvation and entropy penalties associated with the formation of a supramolecular complex in solution are not overridden by the moderate dispersion-based binding energies of the fullerene@**1** complexes.

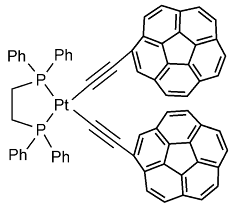


1

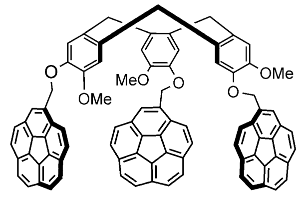


3

In 2007, we demonstrated that efficient molecular receptors for fullerenes can be constructed if at least two corannulene pincers are preorganized by a tether. Buckycatcher (**3**), which possesses two corannulene subunits linked to a tetrabenzocyclooctatetraene tether, formed stable 1:1 inclusion complexes with both C_{60} and C_{70} in toluene and in the solid state.[5,6] Recently, Alvarez et al prepared **4**, a receptor with two corannulene subunits connected to a platinum square planar complex, which binds C_{60} in solution with affinity comparable to that of **3**.[7,8] We tried to improve the fullerene affinities of the corannulene-based receptors by preparing **5**, which has three corannulene pincers placed on a cyclotriveratrylene tether. Disappointedly low association constants of **5** with both C_{60} and C_{70} (1500 ± 50 and 1180 ± 30 M^{-1}, respectively) underlined the importance of reduced conformational flexibility of the clips and preorganization of the corannulene pincers for the design of effective fullerene receptors.[9]



4



5

In pursuit of more efficient corannulene-based molecular tweezers for fullerenes, we turned our attention to norbornadiene tethers. Molecular modeling suggested that these tethers would preorganize corannulene pincers into receptors with potentially higher affinity for C_{60} than that of **3**. Herein, we report the synthesis and characterization of "buckycatcher II" (**6**, $C_{51}H_{24}$, Figure 1), which has two corannulene pincers preorganized on a dibenzonorbornadiene tether and exhibits significantly higher affinity toward C_{60} than **3**. Furthermore, a 2:1 trimeric complex exhibiting a remarkable "universal joint" assembly of two buckycatchers with the fullerene cage is detected in solution and was characterized by X-ray crystallography in the solid state.

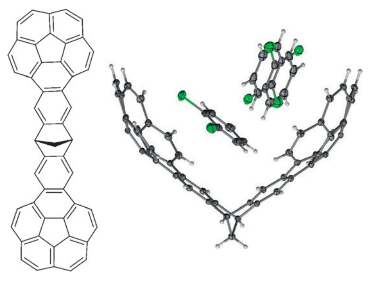
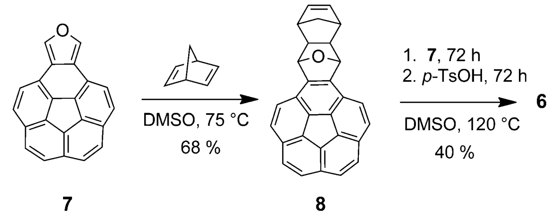


Figure 1. Buckycatcher II (6). Shown on the right is the crystal structure of the **6***1.5*o*-$C_6H_4Cl_2$ solvate, in which one of the solvating molecules is disordered.

---

[*] Dr. M. Yanney, Prof. A. Sygula
Department of Chemistry, Mississippi State University
Mississippi, MS 39762 (USA)
E-mail: yanneymichael@gmail.com
asygula@chemistry.msstate.edu
Dr. F. R. Fronczek
Department of Chemistry, Louisiana State University
Baton Rouge, LA 70803 (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505327.



Scheme 1. Synthesis of buckycatcher II (**6**).

Synthesis of **6** starts with isocorannulenofuran **7**, a versatile diene,[10] and bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene), which is employed as a dienophile in a stepwise Diels–Alder reaction (Scheme 1).[11] The monoadduct **8** is formed in good yield under relatively mild conditions. The second Diels–Alder cycloaddition of **8** to diene **7**, which leads to the mixture of stereoisomeric products, requires significantly harsher conditions. A double dehydration of the adducts catalyzed by *p*-TsOH produces **6** in a moderate yield of 40%.

Slow evaporation of *o*-dichlorobenzene (*o*DCB) solutions of **6** provided X-ray quality crystals, which revealed that buckycatcher II adopts a concave–concave conformation in the solvate (Figure 1).[12] Similarly to the more studied case of **3**,[13] the solvent molecules fill the cavity formed by the corannulene pincers in **6**. The size of this double-concave cleft defined by the distance between the centroids of the central five-membered rings in the pincers (R_c) in the solvate of **6** is 11.33 Å, which quite close to the analogous distance of 11.51 Å found in crystals of the C_{60}@**3** complex.[5] B97-D/TZVP calculations[11] find an "intrinsic" R_c value of 11.68 Å for the isolated concave–concave conformer of **6** (Table 1), thus indicating that the deformation penalties associated with the formation of an inclusion complex between buckycatcher II and fullerenes should be negligibly small. For comparison, the R_c value calculated at the same level of theory for the isolated buckycatcher **3** is slightly but significantly lower (10.23 Å), while in the inclusion complex C_{60}@**3**, it increases to 11.51–11.53 Å.[5,6a] Furthermore, molecular modeling reveals some flexibility of the norbornadiene-based tether in **6** since squeezing or stretching of the molecular clip resulting in a change in R_c by ± 1 Å from its minimum energy conformation increases the energy of isolated **6** by less than 0.5 kcal mol^{-1}. Clearly, preorganization of the corannulene clips in buckycatcher II offers potential for the inclusion of guest molecules like fullerenes.

Table 1: Comparison of the binding properties of Buckycatchers **3** and **6**.

	R_c[a]	R_c (*C_{60})[b]	BE[c]	K_1[d]	K_2[d]
3	10.23	11.53	41.8	2780 ± 80[e] 520 ± 20[f]	– –
6	11.68	11.48	42.5	85 000[e] 10 040 ± 1100[f]	5000[e] 1180 ± 640[f]

[a] Distance [Å] between the centroids of the five-membered rings of the corannulene pincers calculated at the B97-D/TZVP level. [b] R_c distances calculated for 1:1 C_{60}@buckycatcher inclusion complexes. [c] Calculated gas-phase binding energies [kcal mol^{-1}] of the C_{60} inclusion complexes (B97-D/QZVP*//B97-D/TZVP). [d] Microscopic association constants [see Eq. (1)]. [e] In [D$_8$]toluene (crude estimation for C_{60}@**6**). [f] In chlorobenzene-d_5.

Indeed, ^{1}H NMR titration experiments indicate the formation of inclusion complexes of C_{60} with **6** in both [D$_8$]toluene and chlorobenzene-d_5. The continuous variation plot based on the titration clearly shows that the association process goes beyond the usual 1:1 complex formation (Figure 2a). APPI-MS of the dilute mixtures of C_{60} and **6** in toluene or chlorobenzene show the presence of both 1:1 C_{60}@**6** ($C_{111}H_{24}^{\bullet+}$) and 1:2 C_{60}@**6**$_2$ ($C_{162}H_{48}^{\bullet+}$) complexes (Figure 2b,c), in contrast to **3**, for which no formation of the trimeric C_{60}@**3**$_2$ was detected by either NMR titrations or APPI-MS.[5,6]

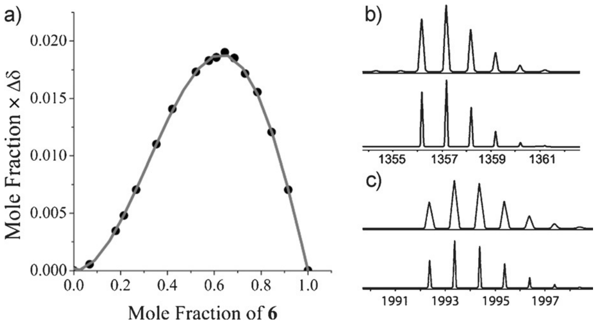


Figure 2. a) Job plot constructed from ^{1}H NMR titration data for one of the protons of **6** upon the addition of C_{60} (in PhCl-$_{d5}$). APPI-MS for 1:1 (b) and 1:2 (c) complexes of C_{60} with **6** are shown. The upper and lower traces show experimental and simulated MS spectra, respectively.

Non-linear fitting of the ^{1}H NMR titration results was therefore performed within the complexation model shown in Equation (1).

$$\mathbf{6} + C_{60} \overset{K_1}{\rightleftharpoons} C_{60}@\mathbf{6} \overset{K_2}{\rightleftharpoons} C_{60}@\mathbf{6}_2 \tag{1}$$

Toluene-d_8 titration provided only a very crude estimation of the association constants (Table 1), presumably owing to the limited solubility of the inclusion complexes in this solvent. More reliable determination of the association of **6** with C_{60} was achieved in deuterated chlorobenzene.[14] In both solvents, the K_1 values for C_{60}@**6** formation are more than an order of magnitude higher than for the analogous C_{60}@**3** complexation, thus indicating that the Gibbs free energy of the 1:1 complexation of C_{60} by **6** is ca. 1.4–2.0 kcal mol^{-1} more exergonic than with **3**. It is worth noting that the calculated gas-phase binding energies for the two 1:1 complexes differ by 0.7 kcal mol^{-1} in favor of **6** (Table 1). This perhaps fortuitous coincidence suggests that owing to the similar topologies and conformational flexibilities of the two buckycatchers, the solvation and entropy penalties associated with formation of an inclusion complex fare comparable in both cases and the difference in the binding affinities of the two molecular receptors is largely caused by the stronger binding energy of C_{60} with **6**. We therefore conclude that the increased affinity toward C_{60} exhibited by **6** compared to **3** results from subtle tuning of the topology of the tethers in the molecular receptors.

The determined K_1/K_2 ratio is significantly higher than 4. This indicates negative cooperativity, which means that 1:1 complexation is favored over the formation of a 2:1 complex.[15] The overall affinity of **6** towards C_{60}, defined as $K_1 \times K_2$, is ca. $1.2 \times 10^7\,\text{M}^{-2}$, which by far exceeds the performance of the previously reported molecular clips with corannulene pincers.[5–7,9]

The trimeric C_{60}@$\mathbf{6}_2$ complex detected in solution by both ^{1}H NMR titration and APPI-MS, and by X-ray crystallography in the solid state further underlines the improved ability of **6** to include fullerene cages. We obtained X-ray quality crystals of this remarkable complex, in which the doubly-concave clefts of two molecules of **6** cooperatively cover most of the C_{60} surface (Figure 3).[16] The C_{60}@$\mathbf{6}_2$ complex, with C_{60} taken as a sphere, roughly approximates the idealized D_{2d} (tennis ball) symmetry, with the apical norbornadiene carbon atoms lying on the major S_4 axis. The C_{60} centroid lies near (0.16 Å from) the midpoint of this line. However, the bisecting planes of the two buckycatchers are not orthogonal but form a dihedral angle of 80.3°, thereby lowering the symmetry to more closely resemble D_2. Also, even though the C_{60} could conform to D_2 symmetry, it is oriented such that only one of three mutually orthogonal twofold axes is nearly normal to the major axis of the complex, thus further lowering the symmetry to the C_2 seen in the crystal. The C_{60} twofold axis most closely aligned with the major axis is tilted 10.3° from it. This arrangement allows a fully ordered crystal and 19 C···C close contacts in the range 3.17–3.40 Å between the corannulene pincers of each buckycatcher and the C_{60}. The R_c values for both symmetry-related catchers (11.45 Å) are very close to that found in the *o*-DCB solvate of **6**, as well as to the calculated value for the isolated **6** (Table 1). The B97-D/TZVP calculated R_c value for the isolated C_{60}@$\mathbf{6}_2$ trimer (11.42–11.50 Å) is also quite similar to that found in the crystal. The gas-phase calculated binding energy for the trimer is 85.2 kcal mol^{-1}, which is almost exactly a double the binding predicted for the 1:1 C_{60}@**6** complex. The fullerene cages in the crystal are arranged in a linear fashion with the closest intercentroid distance between two C_{60} molecules being 14.011 Å, while this distance is only 9.773 Å in C_{60}@**3**. C_{60}@$\mathbf{6}_2$ represents a rather uncommon packing pattern, with the fullerene completely encapsulated by two receptor molecules with no intimate contact with other carbon cages.[17,18] In contrast to the several reported structures of fullerene cocrystals, which demonstrate the critical nature of solvent molecules in the crystal packing of such assemblies,[19] no solvent molecules are incorporated into the crystal of C_{60}@$\mathbf{6}_2$. The topology of buckycatcher II results in the unprecedented crystal arrangement of four corannulene subunits interacting in a concave–convex fashion with a single fullerene cage in a trimeric C_{60}@$\mathbf{6}_2$ assembly.

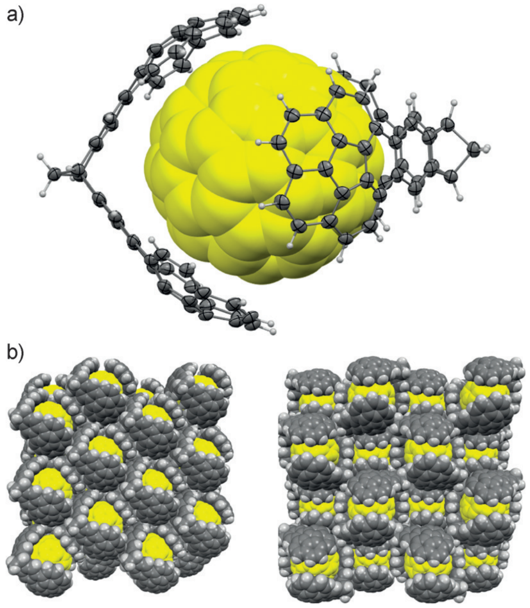


Figure 3. a) Ortep representation of the crystal arrangement in C_{60}@$\mathbf{6}_2$. b) Crystal packing pattern of the trimeric complex, with C_{60} viewed along the crystallographic axes *a* (left) and *c* (right).

The molecular arrangement in the 2:1 complex resembles a universal joint in which two perpendicularly oriented hinges of **6** are connected by a fullerene ball (cross shaft). While rigorous computational studies are in progress, preliminary screening of the flexibility of the complex by the rigid-body approach with a B97-D/6-31G* computational model indicates the conformational behavior expected for a universal joint.[11] Bending of the assembly by an α value of up to 40° (i.e., rotation of one of the hinges in its *Cs* plane of symmetry while keeping the remaining two components frozen; Figure 4) is a low-energy process compared to the calculated dissociation energy of the trimer. On the other hand, rotation of one of the hinges along the C_2 symmetry axis, defined by the two apical norbornadiene carbon atoms (as well as the fullerene centroid), significantly increases the total energy of the assembly for rotation angles δ exceeding 20° because of the steric hindrance of the rim hydrogen atoms of the clips.[11] This hindrance would potentially allow the transmission of rotary motion from one of the hinges to the other.

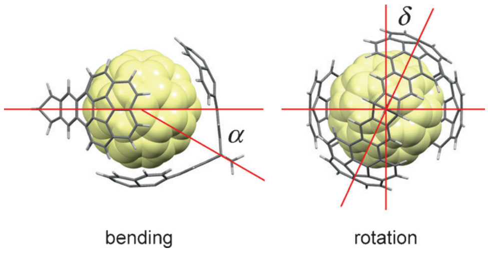


Figure 4. Bending (α) and rotation (δ) angles in the C_{60}@$\mathbf{6}_2$ complex.

In conclusion, we have demonstrated that fine tuning of the tether of a bis-corannulene molecular receptor significantly increases its ability to bind C_{60} by concave–convex π–π stacking of the curved carbon networks. The increased affinity of buckycatcher II for fullerenes results in the formation of a remarkable trimeric C_{60}@$\mathbf{6}_2$ complex, with the fullerene cage tightly wrapped by the four corannulene subunits of the two cooperating molecular receptors and no solvent molecules incorporated into the crystal. The supramolecular assembly in the crystal state exhibits a "universal joint" pattern and computational screening of its conformational behavior shows the expected flexibility for bending of the joint and only limited freedom of rotation around one of its hinges. The custom design of molecular receptors like **6** opens up new possibilities for creating robust supramolecular assemblies with potential applications in material sciences and nanotechnology.

Acknowledgements

Financial support of this work from the Office of Basic Energy Sciences, Office of Science, US Department of Energy through grant DE-FG02-04ER15514 is gratefully acknowledged by A.S.

Keywords: fullerenes · inclusion compounds · molecular receptors · pincer ligands · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 11153–11156
Angew. Chem. **2015**, *127*, 11305–11308

---

[1] J. L. Atwood, J. W. Steed, *Encyclopedia of Supramolecular Chemistry*, *Vols. 1–2*, Marcel Dekker, New York, **2004**.

[2] For the recent reviews see: a) A. Sygula, *Eur. J. Org. Chem.* **2011**, 1611; b) T.-Y. Wu, J. S. Siegel, *Chem. Rev.* **2006**, *106*, 4843; c) V. M. Tsefrikas, L. T. Scott, *Chem. Rev.* **2006**, *106*, 4868; d) A. Sygula, P. W. Rabideau in *Carbon Rich Compounds* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, p. 529.

[3] a) L. N. Dawe, T. A. AlHujran, H.-A. Tran, J. I. Mercer, E. A. Jackson, L. T. Scott, P. E. Georghiou, *Chem. Commun.* **2012**, *48*, 5563; b) W. Xiao, D. Passerone, P. Ruffieux, K. Ait-Mansour, O. Groning, E. Tosatti, J. S. Siegel, R. Fasel, *J. Am. Chem. Soc.* **2008**, *130*, 4767.

[4] Very recently, a low association constant of $19\,\mathrm{M}^{-1}$ was determined for the cationic endohedral complex $\mathrm{Li}^+@\mathrm{C}_{60}@$**2** in PhCN at RT, while K_{ass} for formation of the pristine $\mathrm{C}_{60}@$**2** complex under the same conditions was estimated to be $\ll 1\,\mathrm{M}^{-1}$. M. Yamada, K. Okhubo, M. Shionoya, S. Fukuzumi, *J. Am. Chem. Soc.* **2014**, *136*, 13240.

[5] A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842.

[6] a) C. Mück-Lichtenfeld, S. Grimme, L. Kobryn, A. Sygula, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7091; b) V. H. Le, M. Yanney, M. McGuire, A. Sygula, E. A. Lewis, *J. Phys. Chem. B* **2014**, *118*, 11956.

[7] C. M. Álvarez, L. A. Garcia-Eskudero, R. Garcia-Rodrĭguez, J. M. Martĭn-Álvarez, D. Miguel, V. M. Rayón, *Dalton Trans.* **2014**, *43*, 15693.

[8] Surprisingly, despite the high degree of conformational flexibility of **4**, a significantly higher affinity towards C_{70} was reported.[7]

[9] M. Yanney, A. Sygula, *Tetrahedron Lett.* **2013**, *54*, 2604.

[10] A. Sygula, R. Sygula, P. W. Rabideau, *Org. Lett.* **2006**, *8*, 5909.

[11] See the Supporting Information.

[12] Crystallographic data, X-ray experimental conditions and structure refinement details are given in Table S1 in the Supporting Information.[11] CCDC 1405182 (*o*-DCB solvate of **6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[13] A. Sygula, M. Yanney, W. P. Henry, F. R. Fronczek, A. V. Zabula, M. A. Petrukhina, *Cryst. Growth Des.* **2014**, *14*, 2633.

[14] As demonstrated earlier, the higher solubility of fullerenes and the molecular receptors in PhCl compared to toluene causes a significant reduction in the association constants determined in the former solvent, presumably owing to the increased solvation penalties.[6b]

[15] K. A. Connors in *Comprehensive Supramolecular Chemistry*, *Vol. 3* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. McNicol, F. Vögtle), Pergamon, Oxford, **1996**, p. 205.

[16] Crystallographic data, X-ray experimental conditions and structure refinement details are given in Table S2 in the Supporting Information.[11] CCDC 1405183 ($\mathrm{C}_{60}@$**6**$_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[17] See M. Makha, A. Purich, C. L. Raston, A. N. Sobolev, *Eur. J. Inorg. Chem.* **2006**, 507, and references therein.

[18] K. B. Ghiassi, S. Y. Chen, P. Prinz, A. de Meijere, M. M. Olmstead, A. L. Balch, *Cryst. Growth Des.* **2014**, *14*, 4005 and references therein.

[19] Recent examples: K. B. Ghiassi, J. Wescott, S. Y. Chen, A. L. Balch, M. M. Olmstead, *Cryst. Growth Des.* **2015**, *15*, 2480.

Received: June 10, 2015
Revised: July 13, 2015