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Advanced buckyball joints: synthesis, complex formation and computational simulations of centrohexaindane-extended tribenzotriquinacene receptors for C_{60} fullerene†

Stefan Henne,[a] Björn Bredenkötter,[a] Abbas A. Dehghan Baghi,[b] Rochus Schmid[b] and Dirk Volkmer*[a]

The synthesis of a structurally optimized tribenzotriquinacene receptor **9** is described, which is extended by centrohexaindane moieties to give rise to a half-round concave ball bearing, with optimum shape complementarity towards C_{60} fullerene. Spectroscopic investigations reveal that this novel host forms a 1 : 1 host–guest complex with C_{60} with a complex stability constant of $K_1 = 14\,550 \pm 867\ M^{-1}$, which is considerably higher than those reported for structurally related tribenzotriquinacene hosts reported previously. Both the suppression for binding of a second receptor (*i.e.* formation of a 2 : 1 host–guest complex) as well as the increase of complex stability of the 1 : 1 complex can be rationalized in terms of multiple additive van der Waals and π–π interactions between C_{60} and the aromatic groups of the receptor, as revealed by DFT + D and force-field calculations. Combining results from spectroscopic and theoretical investigations leads to predictions in light of future receptor designs, which – apart from shape complementarity – will have to consider an optimized electronic match (*i.e.* partial charge transfer) between the receptor and the fullerene host.

Introduction

The construction of nano-sized motors and machines has gained considerable interest in the last decade.[2,3] C_{60} fullerene based devices are among the most intensively investigated systems owing to the fact that these almost spherical molecules might constitute a fundamental building block of future molecular mechanical devices.[4] Mankind made machinery rests on well-known construction principles such as shape-complementarity, and form- and friction-locking connections between modular components, which leads to basic mechanical parts such as ball bearings, toggle joints, gear units and so forth. The question arises as to how mechanically interlinked components of macroscopic machines might be scaled down to nano-sized dimensions, where quantum effects play the dominant role. The construction of a simple nano-sized ball joint might well be regarded as a test case for this rather fundamental issue: While C_{60} (and its derivatives) might serve the obvious purpose of the spherical ball head, the appropriate molecular design of a ball socket is less trivial than might be expected at first glance. Provided that the mounting of nano-sized devices has to rely on the principles of self-assembly, a supramolecular complex of 1 : 1 stoichiometry between C_{60} and its receptor R has to form from a thermally equilibrated (diluted) solution containing both components. Because complex formation is an equilibrium process, the stability constant of the $C_{60} \subset R$ complex should be maximized, in order to limit the fraction of (constantly) disassembling ball joints at the given experimental conditions. However, upon trying to optimize this single thermodynamic quantity, several issues occur from the experimentalists' point of view. First: the receptor design has to include an efficient means for suppressing the formation of C_{60} complexes with a stoichiometry different than 1 : 1. It is frequently found for instance, that concave-shaped receptors (*cf.* also Fig. 1) form highly stable $C_{60} \subset (R)_2$ complexes,[5] and thus starting from an equimolar mixture of fullerene and receptor will normally *not* result in a 1 : 1 complex (*i.e.* the nano-sized ball joint) being formed exclusively. Another potential pitfall might comprise the kinetic barrier that separates a loose contact pair of C_{60} and fullerene from the "correctly" assembled nanoball joint (in which C_{60} is located within the half-round cavity of the receptor). This activation barrier might well serve the purpose for assembling mechanically robust (*i.e.* interlocked) ball joints, which require "harsh" assembly conditions (*e.g.* elevated pressure or temperature) for the host–guest complex to form, thus mimicking the assembly process of their macroscopic counterparts. To the best of our knowledge, this possibility as yet has not been convincingly demonstrated for

[a]*Augsburg University, Institute of Physics, Chair of Solid State and Material Science, Universitaetsstrasse 1, D-86159 Augsburg, Germany. E-mail: dirk.volkmer@physik.uni-augsburg.de; Fax: (+49)821-598-5955; Tel: (+49)821-598-3006*
[b]*Ruhr University Bochum, Chair of Inorganic Chemistry 2, Organometallics and Materials Chemistry, Universitaetsstrasse 150, D-44780 Bochum, Germany. E-mail: rochus.schmid@rub.de; Fax: (+49)234-32-14174; Tel: (+49)234-32-24166*

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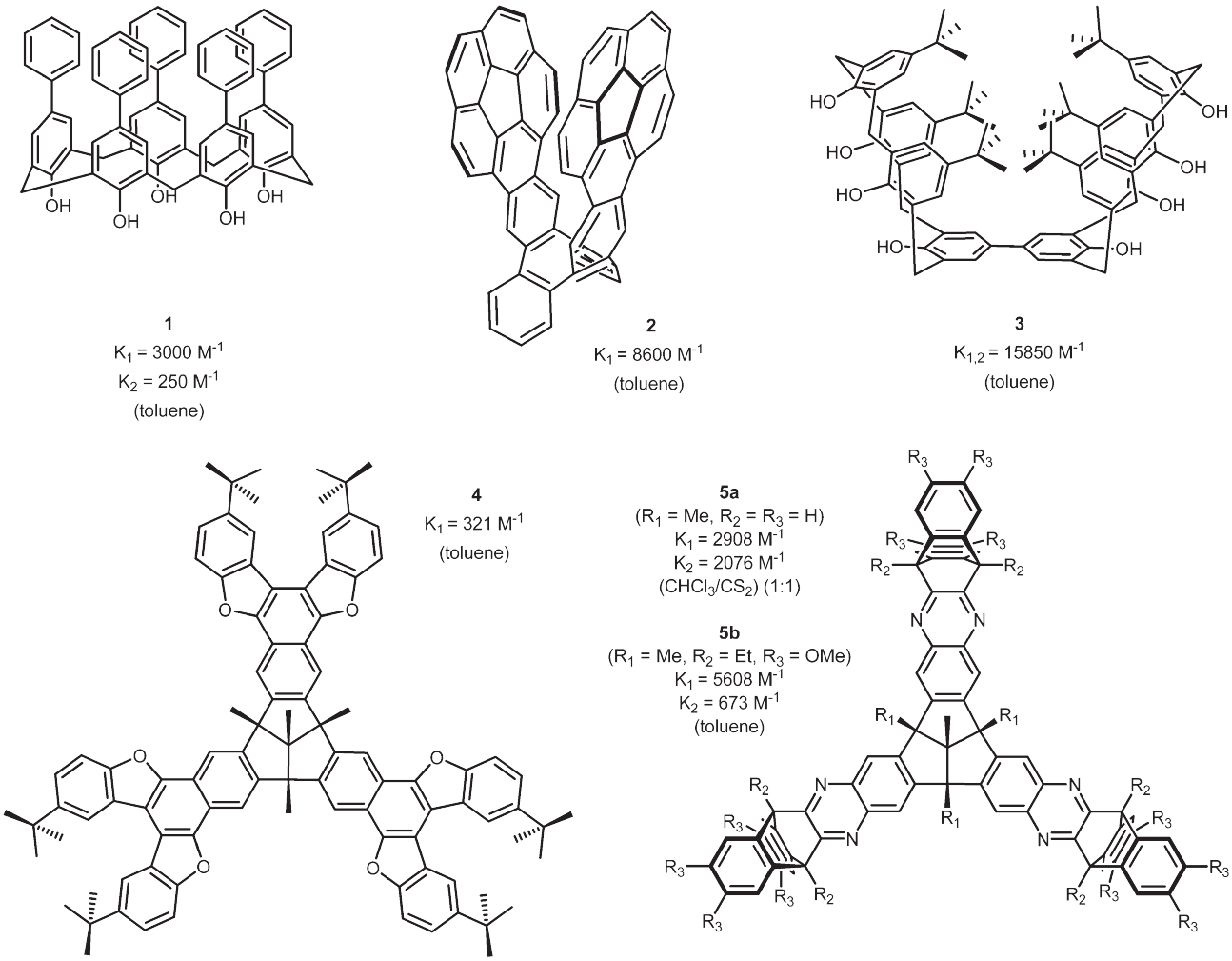


Fig. 1 Compilation of some types of host molecules that form strong van der Waals complexes with fullerene C_{60} and their individual association constants.

fullerene host–guest complexes. Another major obstacle concerns the problem of limited solubility of nanomachinery components, which leads to the fact that investigations of the assembly process have to be conducted in a good solvent, where the intermolecular interactions between solvent molecules and C_{60} (or receptor molecules, respectively) are energetically high and thus will compete with the favorable interactions between fullerene and its host.

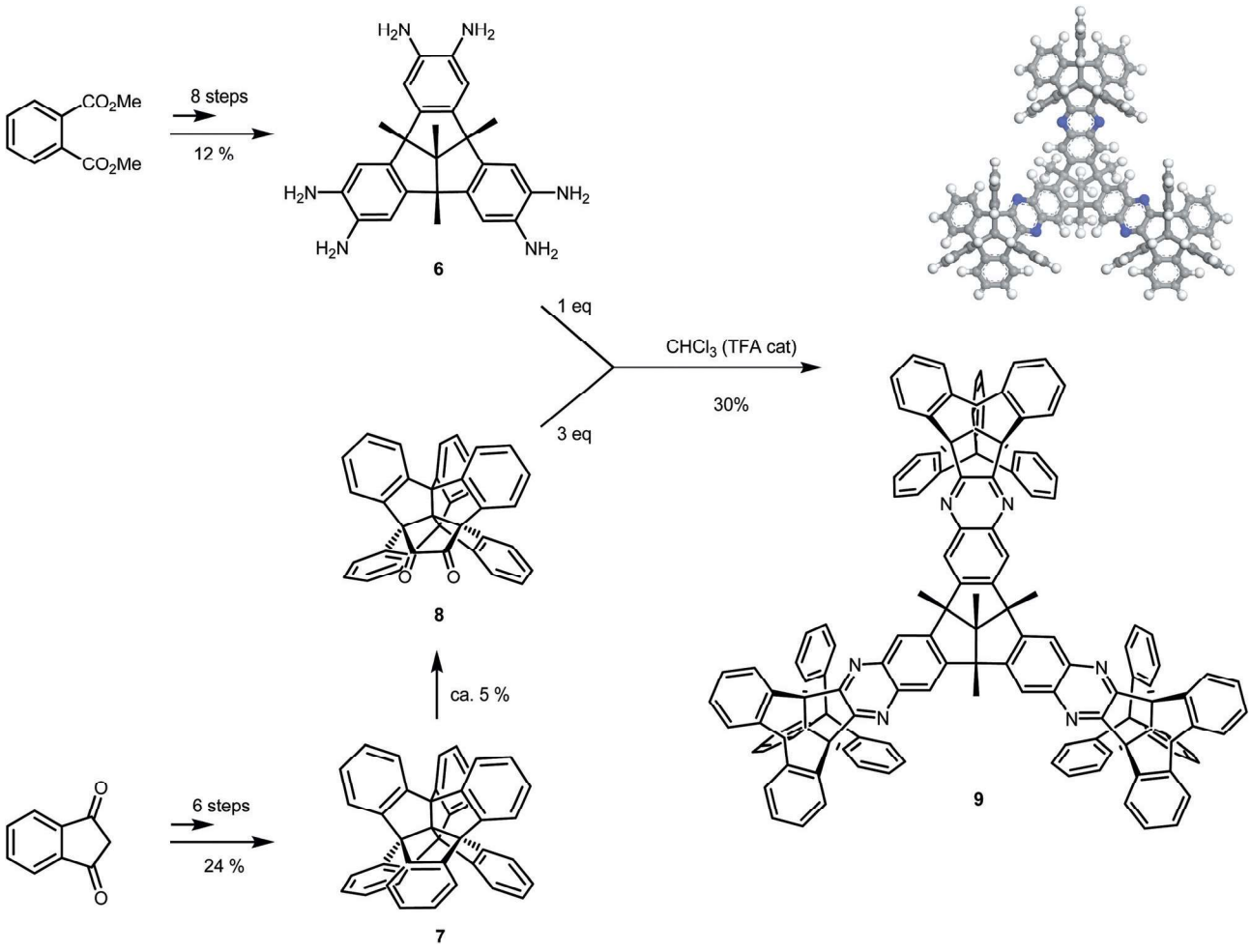
Concave receptor molecules such as calix[*n*]arenes,[6] cyclodextrines,[7] cyclotriveratrylenes,[8] resorcarenes,[9] corannulenes,[10] or similar macrocyclic molecules[11] have been used for the formation of C_{60} van der Waals complexes.[4a,12]

Fig. 1 summarizes some of the main types and includes calix[5]arene **1**,[4b] bi-corannulene **2**,[13] bi-calix[4]arene **3**[4c] and the tribenzotriquinacenes **4**[14] and **5a/b**.[1] The complex stoichiometry varies between 1 : 1 and 2 : 1 and the association constants range from 3×10^3 to 1.6×10^4 M^{-1}. (N.B.: **2** and **3** represent two covalently linked receptors, resulting in a 1 : 1 stoichiometry of their C_{60} complexes).

Taking these (and further limitations not mentioned here) into account, it becomes clear that the engineering of molecular C_{60} receptors constitutes an empirical development process, which starts from an appropriately designed receptor that provides an optimized shape complementary towards C_{60}.

In a previous study,[1] we presented a novel fullerene (C_{60}) host–guest system based on conformationally rigid tribenzotriquinacene derivatives constituting the ball bearing (Fig. 1, compounds **5a** and **5b**). Extending these studies we here present functional and theoretical investigations on a novel tribenzotriquinacene-based host, which has been optimized in terms of shape complementarity and its ability to form a 1 : 1 host–guest complex with C_{60}. The thermodynamic stability of the complex is determined by UV-vis spectroscopic titration experiments.

In order to reveal the structure and binding on an atomistic level and to elucidate the type of interaction between the spherical C_{60} guest and its concave host, we perform theoretical calculations at different levels, including a comparison to structurally related systems previously described.[1] Dispersion corrected DFT calculations were used to quantify any electrostatic interactions beyond the pure dispersive binding in these systems. In addition, they were used as a benchmark in order to validate the force field method.



Scheme 1 Preparative route for receptor **9**. Inset: Ball- and stick model of the final stage.

Results and discussion

Synthesis

The novel receptor **9** was synthesized through a trifluoroacetic acid (TFAA) catalysed condensation of hexaamino-tribenzotriquinacene **6**[15] with three equivalents of dione **8**[16] under conditions in which water was removed (Scheme 1). Hexaamine **6** was synthesized in 8 steps starting from dimethyl phthalate with an overall yield of 12%.[15,17] The second starting material dione **8** was prepared in 7 steps according to a literature procedure.[16,18] In detail, centrohexaindane **7** was synthesized in 6 steps with an overall yield of 24% starting from 1,3-indanedione. The limiting factor of this preparative route is the final oxidation step to get dione **8**. The yield of this step is less than 5%, rendering the synthesis of the final receptor **9** in terms of atom economy a challenging task (*e.g.* starting from 360 mg of centrohexaindane **7** will lead to approx. 15 mg dione **8** for the synthesis of which 1.03 g $RuCl_3$ and 250 ml CCl_4 are required). The final condensation to receptor **9** was achieved by using an excess (4 : 1) of dione **8** with respect to hexaamine **6** in the reaction mixture. The relatively poor yield of about 30% is a result of some difficulties in separating the product from unreacted dione by preparative column chromatography. However, separation of the product **9** from a mixture of partially substituted triquinacenes turned out to be more complicated and leads to even lower yields.

Similar to the previously described receptors (Fig. 1, **5a** and **5b**) host **9** is C_{3v} symmetrical and, therefore, its ^{1}H NMR spectrum shows only relatively few signals (Fig. 2). The six protons of the quinoxaline groups and the twelve protons of the methylene groups at the tribenzotriquinacene moiety correspond to the singlets at δ = 8.30, 1.87 and 1.33 ppm, respectively. For the 24 *ortho* protons, which are found adjacent to the quinoxaline moiety, four doublets at δ = 8.21, 8.12, 7.86 and 7.76 ppm are observed. The signal of the remaining six *ortho* protons of the arenes (at orthogonal positions in relation to the quinoxaline fragment) overlaps with the doublet at δ = 7.86 ppm. The signal corresponding to all *meta* protons gives rise to the multiplet at δ = 7.44–7.26 ppm.

The ^{13}C NMR spectrum of host **9** likewise reflects the high symmetry of the compound (Fig. 2). To the 114 arene carbon atoms only seventeen and to the 23 aliphatic carbon atoms six resonance peaks correspond, respectively, among which the signal for the central methylene group is not detectable. Focused on the centrohexaindane moieties, the low number of signals shows that the greater the distance between the nucleus and the central carbon atom, the smaller the difference in the magnetic environment of the "*inward*" and "*outward*" oriented (in relation

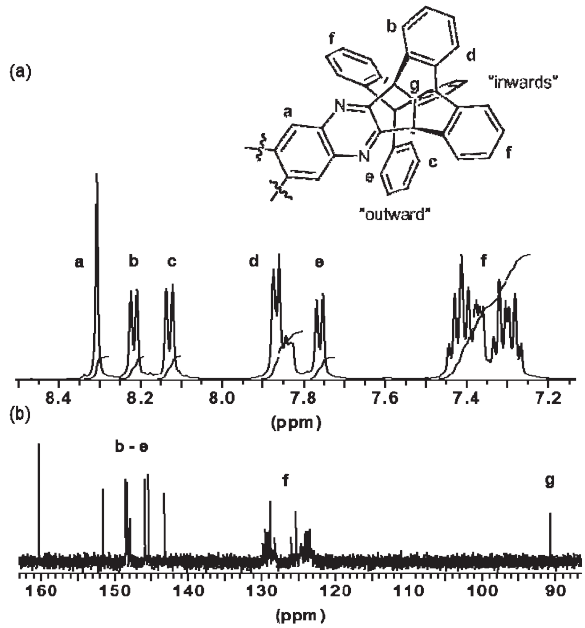


Fig. 2 ^{1}H NMR spectrum (400 MHz, TCE, 300 K) (a) and ^{13}C NMR spectrum (100 MHz, TCE, 300 K) (b) of the aromatic resonance region of host **9**.

to the cavity) arenes turns out to be. Comparing to dione **8**, the quaternary carbon atoms (from δ = 149 to 145 ppm) lead to three signals while for the more distant tertiary carbon atoms (from δ = 130 to 123 ppm) only one signal can be observed, in addition. The chemical shift of the three centred aliphatic carbon atoms corresponds to the signal at δ = 90.7 ppm and is comparable with the central carbon atom of the analogue centrohexaindane **7** (δ = 95.0 ppm; CD_2Cl_2).[18c]

Host–guest complex formation

The stoichiometry of the complex formed between host **9** and C_{60} and the host–guest association constant was determined by UV-vis titration experiments. All investigations were performed with a solvent mixture of $CHCl_3$ and CS_2 (1 : 1), which allowed us to compare results from this study with the corresponding values from our previous investigations.[1] Job plot investigations (method of continuous variation)[19] identify the expected 1 : 1 binding stoichiometry between host **9** and C_{60} (Fig. 3). This result is confirmed by a mass spectrometry investigation. Mass spectrometry provides a convenient means to elucidate the exact stoichiometry of the fullerene complex, based on the mass and isotopic composition of observed ionized fragments.

When 1 : 1 mixtures of host **9** and C_{60} are analyzed, beneath the empty host and guest, the mass isotope pattern relating to the 1 : 1 complex ([C_{60} ⊂ host **9** + H]$^+$ calcd m/z = 2528.7) at m/z = 2528.7 is detectable (Fig. 4). This result is consistent with the results of other groups,[20] related on mild ionization techniques, but is a somewhat unexpected result in light of the fact that the entropic driving force for dissociation in the gas phase is often too high for letting weakly bound van der Waals complexes to be directly observed in a mass spectrometer.[21] More importantly, no mass peaks corresponding to molecular aggregates of any other stoichiometry than 1 : 1 were found.

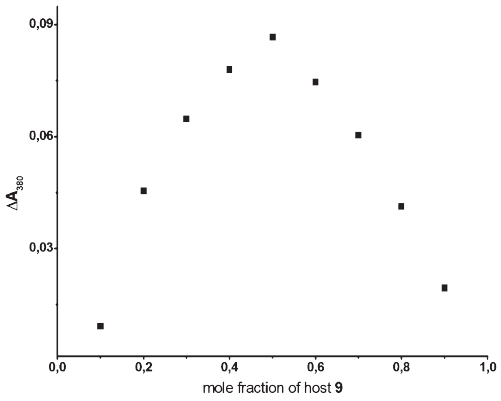


Fig. 3 Job plot showing the 1 : 1 stoichiometry of host **9** *vs.* C_{60} in solution ($CHCl_3$: CS_2 (1 : 1) at 0.1 mM). Absorbance values determined at λ = 380 nm.

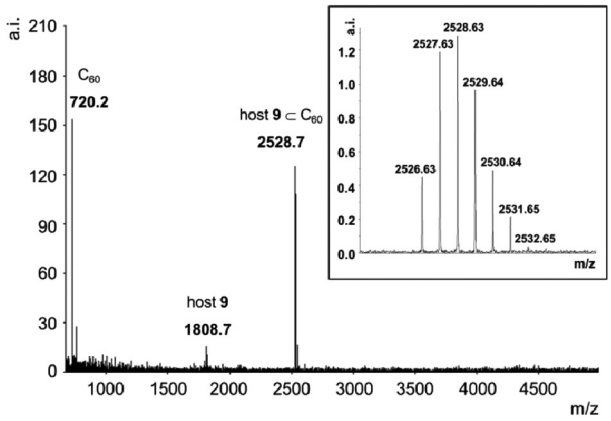


Fig. 4 Mass spectrum (MALDI-TOF) of host **9** and C_{60}; Inset: Found isotopic pattern for ($C_{197}H_{79}N_6$) m/z = 2529 [C_{60} ⊂ **9** + H]$^+$ (high resolution mass spectrum).

The quantitative association constant was determined by the Benesi–Hildebrand method and by the procedure outlined by Connors,[22] to give the value of K_1 = (14 550 ± 867 M^{-1}). This is an average value of non-linear curve regressions that were performed within three independent UV-vis titration experiments. In a typical experiment, 0.07 equivalent portions of host **9** were added to a constant concentration of C_{60} (0.63 × 10^{-4} M). Upon the addition of C_{60}, an increase from about 395 nm toward lower wavelengths and a decrease in intensity of the band at λ_{408} was observed (Fig. 5).

Above the molar ratio of 1 : 1 the steady deviation in absorption remains almost static. Apparently, this observation confirms the absence of a 2 : 1 complex, in addition to our previous findings. The very high value of about 1.5 × 10^4 M^{-1} for the association constant with C_{60} is the highest ever reported for the class of tribenzotriquinacenes. Compared to the first generation host **5a** (K_1 = 2908 ± 360 M^{-1}) and calix[5]arene **1** (K_1 = 3000 ± 200 M^{-1}) the stability constant is about five times higher. For comparison: host molecule **2**, which features two covalently-linked corannulene subunits leading to strong concave–convex π–π interactions with enclosed C_{60}, displays a K_1 = 8600 ± 500 M^{-1}. In fact, the C_{60} association constant of **9** comes pretty

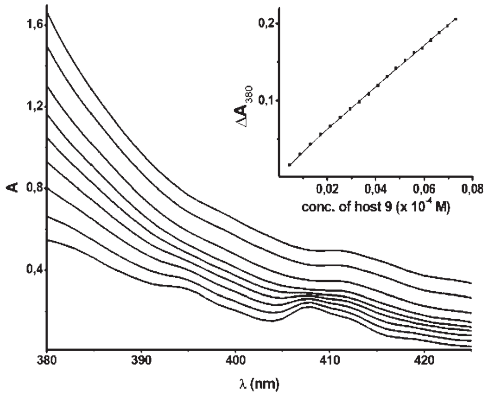


Fig. 5 UV-vis absorbance spectra of C_{60} (0.63×10^{-4} M) in the presence of host **9** in chloroform–CS_2 (1 : 1) at 295 K. Concentrations of **9** are, from bottom to top (curves 1–9), 0, 1.29, 2.93, 4.47, 5.92, 7.29, 8.91, 11.8 and 14.4×10^{-5} M. Inset: Nonlinear curve regression for the absorbance values determined at $\lambda = 380$ nm.

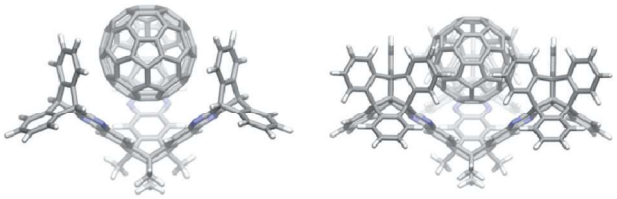


Fig. 6 Force field optimized structures of the 1 : 1 fullerene complexes of hosts **5a** (left) and **9** (right).

close to that reported for bi-calix[4]arene receptor **3** ($K_{1,2} = 1.6 \times 10^4 \pm 360$ M^{-1}), taking into account, however, that in the latter case the enclosed fullerene guest is clamped by two juxtaposed and covalently fixed half-shells. It should be noted that the absolute values of the association constants reported here are not strictly comparable to those reported by other groups, unless titration experiments are performed within the same solvent (mixture).[23]

Since fullerene titration experiments for **9** were performed under similar conditions (solvent, temperature) as reported previously for the smaller host **5a**, a 5 times higher association constant of **9** reflects nicely the larger free energy of binding for fullerene molecules, confirming the general validity of the improved host design.

Theoretical investigations

Theoretical calculations were performed for atomistic models of the 1 : 1 fullerene complexes of hosts **5a** and **9** (Fig. 6), employing dispersion corrected density functional theory (DFT) calculations on the B97-D/TZVPP level as suggested by Grimme.[24] Even upon exploiting symmetry, the size of these systems was too large to allow for wave function correlation based methods like spin-component scaled MP2.[25] In Table 1 the results of the quantum mechanics calculations are summarized. For **5a** we computed a gas phase binding energy of −185 kJ mol^{-1}, which comprises a purely repulsive (+142 kJ mol^{-1}) DFT energy,

Table 1 Binding energies and distance computed on the B97-D/TZVPP level for 1 : 1 fullerene complexes of hosts **5a** and **9**

	$C_{60} \subset$ **5a** (1 : 1)	$C_{60} \subset$ **9** (1 : 1)
DFT-D binding energy [kJ mol^{-1}]	−185	−248
DFT binding energy [kJ mol^{-1}]	142	205
Dispersion contribution [kJ mol^{-1}]	−327	−449
d_{COM} [Å]	8.09	8.17

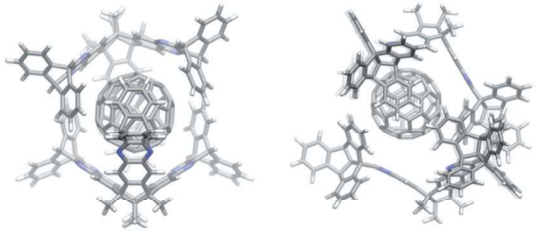


Fig. 7 Force field optimized structures of the 1 : 2 fullerene complexes of host **5a** (left) and **9** (right).

which is fully compensated by the dispersion correction of −327 kJ mol^{-1}.

Thus, the interaction is solely due to dispersive interactions. In accord with that we find a negligible charge transfer from the host to the C_{60} upon binding. For this we analyzed atomic point charges computed *via* the Natural Population Method.[26] The total charge on the C_{60} guest molecule deviated by less than 0.01 from zero. Individual atomic charges on carbon centers of the enclosed C_{60} also deviated only slightly from the values of the free C_{60} molecule, indicating a negligible polarization owing to complex formation. Therefore, energetic contributions by electrostatic interactions or charge transfer stabilization between the fullerene and the receptors can be safely ruled out. Accordingly, it should be permissible to ignore Columbic interactions in the force field calculations, as described below.

Based on these results we have used the MM3 force field by Allinger *et al.*,[27] which is known to yield accurate conformational energies for molecular systems, to investigate fullerene host–guest complexes including the larger and less symmetric 1 : 2 complexes (Fig. 7). This molecular mechanics approach also serves as a basis for future molecular dynamics simulations including explicit solvent molecules, which are completely out of reach for quantum mechanical electronic structure methods.

The MM3 force field was slightly modified in order to recover the proper bond length variations in the C_{60} molecule. With this model the complex formation between C_{60} and **5a** or **9** was investigated. Starting from different initial geometries no steric barrier was observed upon reaching the energetically optimized minimum structure of the complexes. Embedding the C_{60} molecule within the concave receptors leads to only tiny deformations of the host's structure. All results are summarized in Table 2. For the smaller **5a** a binding energy of −157 kJ mol^{-1} is predicted, which is in reasonable accord to the B97-D result. Note that the dispersion corrections in B97-D are usually very small and represent only a minor correction. Here, however, it represents the major contribution to the overall binding. In principle, both B97-D and MM3 use a parameterized dispersion potential of the form $E_{disp} = -C/r^6$ with just different

Table 2 Force field computed energies and properties of the 1 : 1 and 1 : 2 complexes of hosts **5a** and **9**

	$C_{60} \subset$ **5a** (1 : 1)	$C_{60} \subset$ **9** (1 : 1)	$C_{60} \subset$ **5a** (1 : 2)	$C_{60} \subset$ **9** (1 : 2)
E_{form}(FF) [kJ mol^{-1}]	−157	−226	−363	−409
d_{COM} [Å]	8.07	8.12	8.05/8.05	8.26/10.06
SAS change upon binding [Å^2]	−542	−576	−1450	−1464
E_{form}(solv) [kJ mol^{-1}]	118	126	316	319
E_{form} [kJ mol^{-1}]	−39	−100	−47	−90

parameterizations for *C*. It is well known that force field parameters, adjusted to bulk properties[27] give somewhat smaller dispersive energies, since three body terms are implicitly included.[28] Noteworthy, the distance between the center of mass (COM) of the C_{60} and the central "bottom" sp^3-carbon atom of the host (referred to as d_{COM}) is 8.07 Å on the MM3 level, which is virtually identical to the 8.09 Å computed on the B97-D level. Interestingly, the strain energy needed to deform host **5a** into the shape to accommodate C_{60} is only 1 kJ mol^{-1}, which demonstrates how perfectly the geometry of the hosts fit to the shape and the diameter of C_{60}. In case of the extended host **9**, a substantially higher binding energy of −226 kJ mol^{-1} is found, even though the d_{COM} is with 8.12 Å, a bit larger. Also, a larger but still negligible deformation energy of 4.2 kJ mol^{-1} is computed. Thus, a 50% increase of the binding energy in the gas phase is predicted for **9** in agreement with the higher value of the experimentally determined association constant. It should be noted, however, that experimental values are gleaned from solution studies and a large part of the dispersive interaction in the gas phase will be compensated by a loss of solute–solvent interactions. In order to estimate this effect, we determined the loss of solvent accessible surface area (SAS) during the binding of the guest molecule. Note that due to the absence of strong electrostatic interactions the major contribution to the change in the solvation energy is due to dispersive interactions, which are roughly proportional to the change in the accessible surface area. With this method we find a SAS for the bare C_{60} of 553 Å^2. With an experimentally determined solvation energy of 120 kJ mol^{-1} for C_{60} in toluene[29] we can estimate a solvation contribution of about 0.218 kJ mol^{-1} Å^2. By assuming the stabilization upon solvation to be roughly independent of the molecule we can estimate a total energy of complex formation E_{form} = E_{form}(FF) + E_{form}(solv) as the sum of the gas phase binding energy of the complex computed by the force field and the change in solvent stabilization energy. In Table 2 the loss in surface area for both receptors is actually close to the C_{60} total area, indicating that about half the guest surface is "covered" by the receptor. In addition, the loss of exposed surface area – and consequently the solvent destabilization – is somewhat larger for **9** as compared to the smaller **5a**. However, overall this is more than compensated by the larger gas phase binding energy resulting in a E_{form} of only −39 kJ mol^{-1} for host **5a**, whereas a three times larger value of −100 kJ mol^{-1} is found for **9**.

As already mentioned in the introduction, an important aspect in the design of the new receptor, besides the improved binding, was to suppress the unwanted formation of the 2 : 1 complex with two receptors embracing the C_{60} molecule. We optimized this case for both receptors. The resulting global minimum structures are shown in Fig. 7. It is quite obvious that two receptors of **5a** are able to encapsulate the fullerene guest molecule in an optimal fashion, basically by covering the second half of the exposed surface area. In this case both receptors have the identical distance d_{COM} to the C_{60} COM and the gas phase binding energy E_{form}(FF) is −363 kJ mol^{-1}, more than twice as high as for a single receptor. This increase is due to the additional dispersive interactions between the two receptors. Again, the loss of accessible surface area leads to a reduction of this value in solution. However, with −47 kJ mol^{-1} the formation of the 1 : 2 complex is still stabilized with respect to the 1 : 1 complex. In other words, the binding of a further receptor **5a** to the 1 : 1 complex is exothermic with about −8 kJ mol^{-1}. In contrast to that, the larger **9** does not allow such a perfect fit of a second receptor. In Fig. 7 it becomes immediately apparent that the second host binds at a certain offset, leading to a different and larger d_{COM}. Consequently E_{form}(FF) in the gas phase is less than twice the value for the 1 : 1 complex and the overall binding energy is −90 kJ mol^{-1}, lower than that of the 1 : 1 complex. In accord with our experimental results, the receptor **9** forms only the 1 : 1 complex.

Despite the approximate treatment of the solvation contribution, we believe that this picture represents the qualitative trends in a proper way. Based on our force field customized for the host guest system we are currently developing a scheme to compute the binding energies by a potential of mean force approach in the presence of an explicit solvent model.

Conclusions

In summary, we have successfully synthesized and characterized the tribenzotriquinacene-derived C_{60} host **9**, which represents a largely improved fullerene receptor design. We show that this host leads exclusively to the formation of 1 : 1 complexes with C_{60}. The resulting huge K_1 value of 14 550 M^{-1} for the association constant of $C_{60} \subset$ **9** confirms our predictions concerning the optimized shape complementarity between the receptor **9** and its C_{60} guest as a result of an increasing number of aromatic rings appropriately positioned at the upper rim of the half-spherical shaped receptor **9**. These qualitative predictions are corroborated by quantitative molecular modelling studies, which show that the increase of the association constant of $C_{60} \subset$ **9** if compared to the simpler $C_{60} \subset$ **5a** are mainly due to an increase of dispersive interactions between the aromatic moieties of the host and C_{60}. Most importantly, the functionalized upper rim of host **9** prevents the formation of a 1 : 2 complex (*i.e.* $C_{60} \subset$ (**9**)$_2$) efficiently and thus the model system presented here can well be regarded as a fully functional, self-assembling nano-sized counterpart to a mechanically interlocked ball joint.

Experimental

General

Melting points (uncorrected): OptiMelt, MPA 100 apparatus. Infrared (IR) spectra: Bruker FTIR IFS 113v spectrometer; KBr pellets. NMR spectroscopy: Bruker DRX 500 or Bruker Avance

400; data given as ppm; *J* values are given in Hz; spectra referenced to the residual solvent peak; the degree of substitution of C atoms was determined by the APT-DEPT method. MALDI-TOF mass spectra: Bruker, Daltonics REFLEX III. N_2-laser (337 nm), pulsed ion extraction (PIE), HIMAS-detector, acceleration voltage 20 kV, matrix: DHB. Thin layer chromatography: silica gel (Kieselgel F_{254}) on Al foils (Merck). Gravity column chromatography: silica gel (Kieselgel 60, ∅ = 0.063–0.200 mm, Merck). All solvents were purified by distillation before use and dried according standard procedures.

Receptor (9)

Under argon, a catalytic amount of trifluoroacetic acid was added to a solution of 21 mg (49 µmol) of 4b,8b,12b,12d-tetramethyl-2,3,6,7,10,11-hexaamino-4b,8b,12b,12d-tetrahydrodibenzo[2,3 : 4,5]pentaleno[1,6-*ab*]indene **6** and 100 mg (170 µmol) of 13,14-dioxo-13*H*,14*H*-4b,12b[1′,2′]:8b,14a[1″,2″]-dibenzodiben[*a*,*f*]-benzo[2,3]pentaleno[l,6-*cd*]pentalene **8** in 50 mL chloroform and 20 mL ethanol and the mixture was subsequently refluxed for 60 h under water separation. The solvent was removed and the residue was purified by column chromatography (chloroform–cyclohexane 1 : 1) to get 23 mg (13 µmol, 30%) of host **9** as a colorless powder; mp > 400 °C; UV-vis: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$–CS_2 (1 : 1)), 380 (3856), 450 (819), 600 (373); IR: $\tilde{\nu}_{max}$ (KBr)/cm^{-1}, 3425s (NH), 3061w (CH), 3021w (CH), 2923vs (CH), 2852s (CH), 2356w (conj. CN), 1628w (CN), 1468vs (CH), 1383s (CH), 751vs (CC); ^{1}H NMR: δ_H (400 MHz, TCE-d_2) 8.30 (6 H, s, Ph_a), 8.21 (6 H, d, ^3J 7.32 Hz, Ph_b), 8.12 (6 H, d, ^3J 7.32 Hz, 6 Ph_c), 7.86 (6 H, d, ^3J 7.53 Hz, Ph_d), 7.86–7.84 (6 H, m, $Ph_{ortho,\ ortogonal}$), 7.76 (6 H, d, ^3J 7.53 Hz, Ph_e), 7.44–7.26 (30 H, m, Ph_{metha}), 1.87 (9 H, s, $Me_{benzylic}$), 1.33 (3 H, s, $Me_{centric}$); ^{13}C NMR: δ_C (100 MHz, $CDCl_3$) = 160.3 (q), 151.6 (q), 148.4 (q), 148.3 (q), 148.0 (q), 147.9 (q), 145.9 (q), 145.4 (q), 143.2 (q), 129.2 (t), 125.1 (t), 129.0 (t), 128.8 (t), 125.3 (t), 124.2 (t), 124.0 (t), 123.8 (t), 123.4 (t), 90.7 (q), 77.5 (q), 69.4 (q), 62.5 (q), 29.8 (q), 27.5 (p) ppm, one primary carbon atom cannot be detected; MS (MALDI-TOF): *m*/*z* calc. for ($C_{137}H_{78}N_6$): 1808; found: *m*/*z* 1809 $[M + H]^+$.

Calculation details

All force field calculations were performed using the 4.2 version of the TINKER package[30] using the MM3 force field.[27] The parameterization of the atom type "2" (aromatic sp^2 carbon) was modified in order to reproduce the bonding pattern of C_{60}. Note that in MM3 bond dipoles are used instead of atomic point charges. No bond dipoles were used for C_{60} resulting in a pure van der Waals type bonding as suggested by the DFT calculations. The Solvent Accessible Surface (SAS) areas have been determined using the SPACEFILL program of the TINKER package using a probe radius of 1.4 Å and the force fields standard van der Waals radii. A listing of force field parameters in the TINKER file format can be received upon request.

All DFT calculations were performed using the TURBOMOLE package.[31] All structures were fully optimized starting from the force field computed structures in the highest possible symmetry. The TZVPP basis set[32] was used for all atoms together with the B97-D functional as reparameterized by Grimme[24] including an atom pairwise dispersion correction. Atomic charges have been derived *via* the Natural Population Analysis.[26]

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