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Nanosized Ball Joints Constructed from C_{60} and Tribenzotriquinacene Sockets: Synthesis, Component Self-Assembly and Structural Investigations

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Abstract: The formation of supramolecular host–guest complexes of fullerene (C_{60}) and two novel tribenzotriquinacene based hosts (**5a** and **5b**) was investigated in solution and in the solid state. Stability constants for 1:1 and 2:1 complexes were obtained from spectroscopic (UV/Vis, ^{1}H NMR) titration experiments. Association constants of $K_1 = (2908 \pm 360)\,\mathrm{L\,mol^{-1}}$ and $K_2 = (2076 \pm 300)\,\mathrm{L\,mol^{-1}}$ for C_{60}/**5a**, and $K_1 = (5608 \pm 220)\,\mathrm{L\,mol^{-1}}$ and $K_2 = (673 \pm 160)\,\mathrm{L\,mol^{-1}}$ for C_{60}/**5b** were obtained. Single crystal X-ray structural analysis of compound $C_{60}\subset$**5b**·3toluene revealed that a molecule of C_{60} was located at short van der Waals contact distances in the open pre-organised cavity of the rigid host. The supramolecular complex created resembles an engineered nanosized ball joint and represents the first member for a future nanomechanics construction kit.

Keywords: fullerenes · host–guest systems · nanostructures · supramolecular chemistry · tribenzotriquinacenes

Introduction

In the field of supramolecular chemistry the binding affinity of various host systems for fullerene (C_{60}) has been the subject of intense research.[1] Much attention has been devoted to the design of bowl-shaped host molecules, such as calix[*n*]arenes,[2] cyclodextrins,[3] cyclotriveratrylenes,[4] resorcarenes,[5] corannulenes[6] or similar macrocyclic molecules,[7] to provide optimal shape complementarity to the spherical C_{60} guest. Apart from fundamental aspects of C_{60} host–guest complex formation and stability, applications in the fields of separation science or molecular electronics have also been suggested.[8] However, no *realistic* technological concepts have been proposed to date that make use of C_{60} host–guest complexes as part of a kit of constructional elements for producing nanosized mechanical devices or machines. Progress in this direction in general is hampered by the fact that, until now, no commonly accepted technological standard exists for the design of molecular construction elements and interfaces (i.e., chemical functions) for their assembly. In this respect, the current situation of (chemical) nanotechnology resembles the technology from pre-industrial revolution, when small factories or workshops delivered unique masterpieces of custom-built products. In this paper we would like to propose a novel kind of supramolecular construction kit that targets simple mechanical devices, such as joints, bearings, hinges or gears. Any mechanical construction kit contains building blocks of rotating machine parts that we, and others,[9] would like to use as a basis for modified C_{60} fullerenes and carbon nanotubes. For static bearings and supporting parts of the machinery we are developing a novel family of rigid molecular building blocks that are based on tribenzotriquinacene moieties. Herein we describe the synthesis of nanosized ball joints constructed from C_{60}, and tribenzotriquinacene derivatives that constitute the socket. The components spontaneously self-assemble in solution. The thermodynamic stabilities of the complexes were investigated by means of spectroscopic titrations (UV/Vis and ^{1}H NMR). Structural details of the C_{60} host–guest complexes were obtained from single-crystal X-ray structural investigations that were compared to results from MM2 force field molecular mechanics calculations.

Results and Discussion

The design of new C_{60} hosts **5a** and **5b** was based on the tribenzotriquinacene moiety (Figure 1a),[10] which represents a

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains details of crystallographic data collection and analysis, and the determination of association constants by spectroscopic titrations.

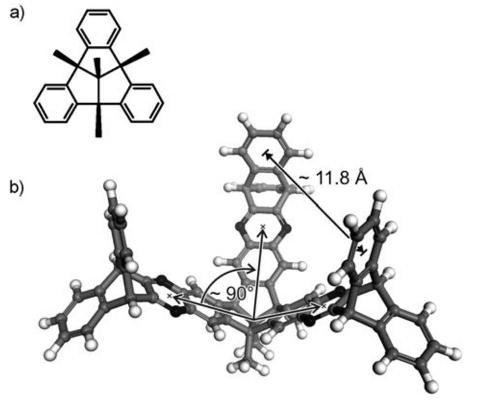
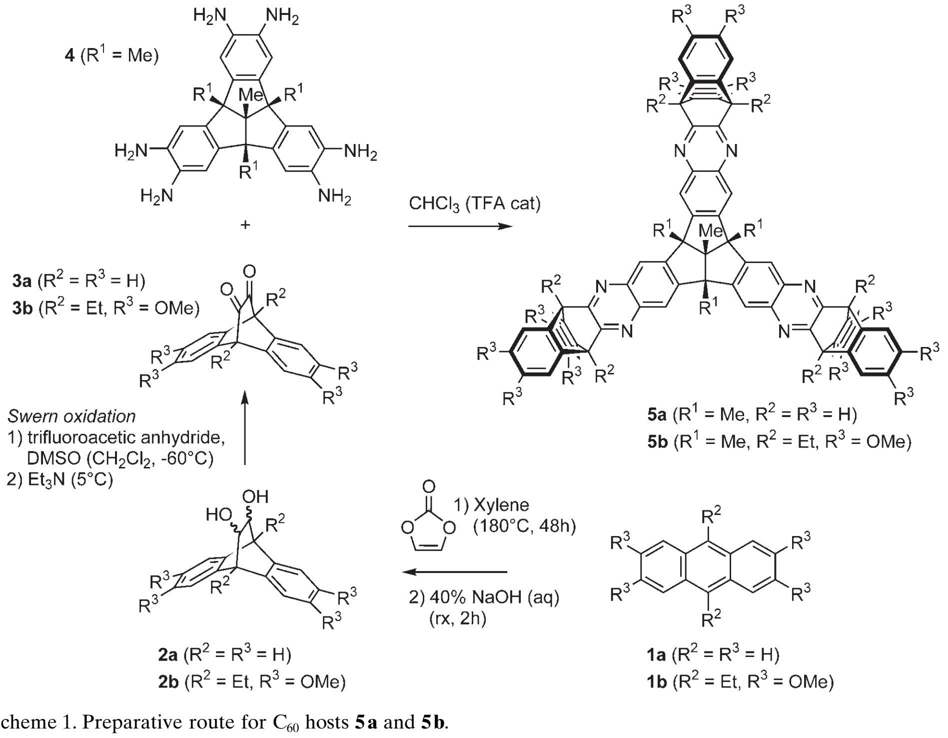


Figure 1. a) Structure of tribenzotriquinacene. b) Ball-and-stick model of tribenzotriquinacene based host **5a**. (Displayed structural parameters are explained in the text.)

member of the centropolyindane family that was developed and investigated for many years by Kuck and co-workers.[11] Tribenzotriquinacenes are versatile building blocks in organic chemistry, yet their use in supramolecular science is largely unexplored.[12] The tricyclic core of the tribenzotriquinacene system has a remarkable feature, the three vectors that point from the central bridgehead carbon atom of the triquinacene system towards the centroids of the peripheral benzene rings span an almost perfect Cartesian coordinate system (Figure 1b). Thus, the tribenzotriquinacene forms a pre-organised flat cavity that can be deepened by attaching triptycene type organic groups to the benzene rings (Figure 1b and Scheme 1).



Scheme 1. Preparative route for C_{60} hosts **5a** and **5b**.

Condensation of hexaaminotribenzotriquinacene (**4**) with three equivalents of dibenzobicyclo[2.2.2]octane-2,3-dione (**3a**) leads to the formation of the novel supramolecular host **5a**, the structural model of which is shown in Figure 1b. Molecular mechanics calculations (MM2[13] force field) show that the benzene groups positioned at the perimeter of the open cavity of the host are almost parallel to the central C_3 symmetry axis. The centre-to-centre distances between the centroids of the benzene rings that point inwards amount to approximately 11.8 Å, which corresponds to a circular opening that has a diameter of 13.6 Å, or approximately 10.2 Å if twice the van der Waals radius of carbon (1.7 Å) is taken into account. Based on these calculations it can be safely predicted that the cavity of **5a** could easily accommodate a C_{60} guest molecule, the mean diameter of which is 10.0 Å (based on packing models obtained from a solid state structure of C_{60}).[14]

The two host molecules, **5a** and **5b**, were synthesised through a trifluoroacetic acid (TFA) catalysed condensation of **4**[15] with **3a** or **3b**, under conditions in which water was removed. Dione **3a** was prepared in three steps from anthracene (**1a**) and vinylene carbonate according to a literature procedure.[16] Derivative **3b** was synthesised from **1b**[17] by a similar procedure (Scheme 1). To summarise, a solution of **1b** and vinylene carbonate in xylene was heated for three days in an autoclave at 180 °C. Employing aqueous sodium hydroxide solution (40 %) to cleave the carbonate ester resulted in the formation of **2b**, which was subsequently converted into **3b** by Swern oxidation. The total yield over three reaction steps was 90 %. The ^{1}H NMR spectrum of **3b** shows only one singlet at $\delta = 6.99$ ppm for the aromatic protons and another singlet at $\delta = 3.93$ ppm that corresponds to the four methoxy groups. The ethyl groups correspond to a quartet and a triplet at $\delta = 2.65$ and 1.54 ppm, respectively. Total conversion of **4** was achieved by adding a twofold excess of the dione to the reaction mixture. The relatively poor yield of about 55 % is a result of some difficulties in separating the product from unreacted dione by preparative column chromatography. However, separation of products **5a** or **5b** from a mixture of partially substituted triquinacenes is more complicated and leads to even lower yields.

Host molecules **5a** or **5b** are C_{3v} symmetrical, therefore, their ^{1}H NMR spectra show only a few signals (see the Experimental Section). For **5a**, the six protons of the quinoxaline groups, the protons at bridgehead positions and the protons of the benzhydrylic methyl groups were singlets at $\delta = 7.97$, 5.51 and 1.81 ppm, respectively. Similar signal shifts were observed for **5b**.

X-ray structural analysis: Single crystals of $C_{60}{\subset}C_{98}H_{96}N_6O_{12}{\cdot}3\,C_7H_8$ (=$C_{60}{\subset}$**5b**·3 toluene) were obtained from an equimolar solution of C_{60} and **5b** in toluene. Dark red crystals began to form after several days by slow evaporation of the solvent at room temperature. The compound crystallises in the orthorhombic crystal system, in space group *P*bca (no. 61) with lattice constants of $a = 26.4689(3)$, $b = 25.3726(3)$, and $c = 37.0319(5)$ Å. Attempts to grow single crystals of suitable quality for host–guest complexes of **5a** and C_{60} or complexes of **5b** and C_{60} in 2:1 stoichiometry have been unsuccessful to date. Some problems in refining the structure of $C_{60}{\subset}$**5b**·3 toluene arose from the fact that the toluene molecules occluded in the crystal lattice are largely disordered. Moreover, it was impossible to refine the atom positions of the C_{60} molecule without constraints because the electron density was largely dislocated in this region of the asymmetric unit, which we ascribe to multiple disorder of the almost spherical fullerene. As the relative positions of carbon atoms in a C_{60} moiety that contains no conformational degree of freedom are unambiguous, we refined this molecule as a rigid fragment for which the atomic positions were taken from literature.[18] Details of the crystallographic data collection and analysis are given in the Supporting Information. Figure 2a shows different graphical representations of host–guest complex $C_{60}{\subset}$**5b**, as determined by X-ray structure analysis. The packing of the complex in the crystal lattice is presented in Figure 2b.

The C_{60} guest is nested inside **5b**. Space-filling (CPK) representations of the complex indicate that the molecules are in close (non-bonding) contact with each other. This is further confirmed by calculating the distance between the centroid of C_{60} and the centroid of each benzene group positioned at the perimeter of the open cavity of the host (c.f., Figure 1b). The distances are identical to within 0.02 Å (average distance = 6.81 Å). As a general formulation we might loosely define the centre of **5b** as the geometric centroid of the peripheral benzene groups that point inwards. The centroid of C_{60} is then shifted outwards by 0.83 Å with respect to the midpoint of the host, which demonstrates that close contacts also exist between C_{60} and atoms belonging to the central tribenzotriquinacene moiety. As an empirical measure of the penetration depth of C_{60} in the cavity of **5b**, the distance between the centroid of C_{60} and the central bridgehead atom of the triquinacene moiety was determined. In the crystal structure, this distance is 8.308 Å, however, molecular mechanics geometry optimisation of isolated complexes (both at stoichiometries of 1:1 and 2:1) typically result in slightly smaller distances (deviation from the crystallographic value of up to 0.3 Å; c.f. Figure 7). As the force fields employed (MM2, MM3) are not stringently optimised for non-bonding intermolecular interactions, the deviation between the observed and calculated structures of the host–guest complexes are insignificant.

Host–guest complex formation of C_{60}: The experimental determination of precise complex stability constants for C_{60} host–guest complexes often faces the problem of limited solubility of reactants or complex(es) in common organic solvents.[19,20] To determine host–guest association constants for **5a** and **5b** by spectroscopic methods we had to use two different solvent systems. Host **5a** was sufficiently soluble in a solvent mixture of $CHCl_3$ and CS_2 (1:1), whereas host **5b** dissolved cleanly in toluene. As the experimentally accessible concentration regime, the spectroscopic method (which sets the detection limits for each molecular species) and the magnitude of the association constant(s) are correlated with each other,[21] the stability constants for C_{60} complexes of **5a** and **5b** were determined by UV/Vis and ^{1}H NMR spectroscopic techniques ($K_{max} = 10^5$ and 10^4 L mol^{-1}; $c_{min} = 10^{-5}$ and 10^{-4} mol L^{-1}, respectively).

To exclude experimental artefacts of non-specific complex formation,[22] such as non-linearity[23] or self-aggregation,[21,24] the validity of Lambert–Beer's law, that is, a linear dependence of absorbance from the concentration of the solute was tested for pure solutions of **5a** and **5b** in the appropriate concentration regime within the first set of experiments. Subsequently, a series of UV/Vis spectroscopic titration experiments were performed (Figures 3 and 4; only selected data sets are shown, full experimental details are provided in the Supporting Information).

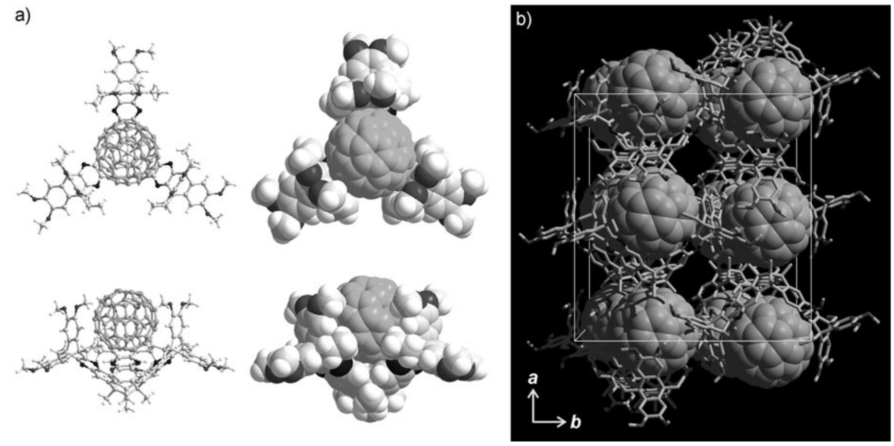


Figure 2. a) Ball-and-stick and space-filling representations of the host–guest complex of C_{60} with **5b** obtained from crystal data of $C_{60}{\subset}$**5b**·3 toluene. b) Packing diagram for $C_{60}{\subset}$**5b**·3 toluene. (For clarity the occluded toluene molecules are omitted, as well as all hydrogen atoms. Host molecules are drawn as stick models, whereas C_{60} molecules are displayed as space-filling models.)

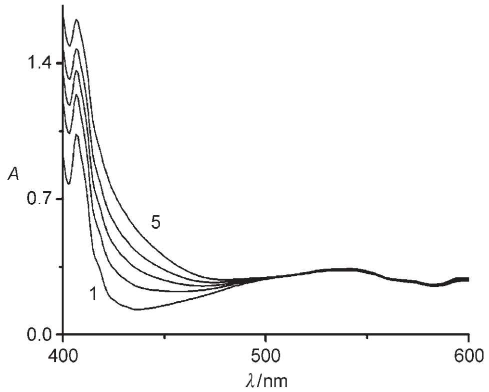


Figure 3. UV/Vis absorption spectra of C_{60} (2.22×10^{-4} mol L^{-1}) in the presence of **5a** in chloroform/CS_2 (1:1) at 295 K. Concentrations of **5a** are, from the bottom to the top (curves 1–5), 0, 1.23, 2.16, 3.08 and 4.32×10^{-4} mol L^{-1}, respectively.

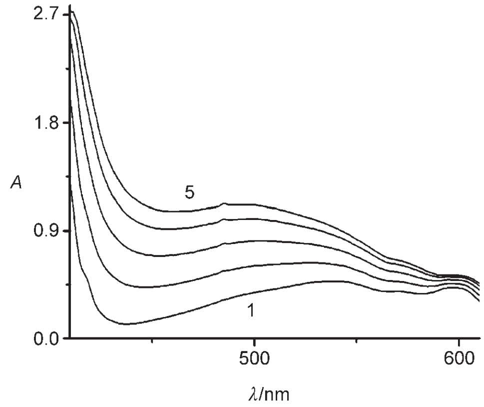


Figure 4. UV/Vis absorption spectra of C_{60} (2.45×10^{-4} mol L^{-1}) in the presence of **5b** in toluene at 295 K. Concentrations of **5b** are, from the bottom to the top (curves 1–5), 0, 0.90, 1.78, 2.63 and 3.46×10^{-4} mol L^{-1}, respectively.

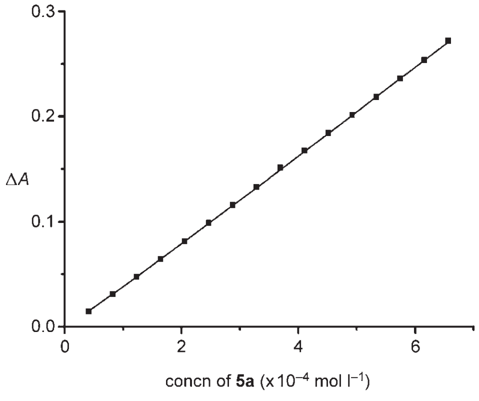


Figure 5. Nonlinear curve regression for the results of the titration experiment of C_{60} (2.22×10^{-4} mol L^{-1}) with **5a**. Absorbance values determined at $\lambda = 435$ nm; $\Delta A = A^{435}-(A^{435}_{C_{60}}+A^{435}_{\mathbf{5a}})$.

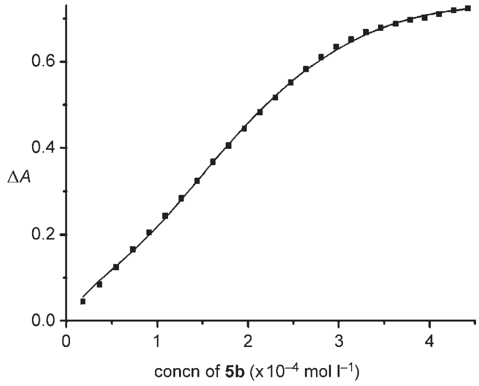


Figure 6. Nonlinear curve regression for the results of the titration of C_{60} (2.45×10^{-4} mol L^{-1}) with **5b**. Absorbance values determined at $\lambda =$ 450 nm; $\Delta A = A^{450}-(A^{450}_{C_{60}}+A^{450}_{\mathbf{5b}})$.

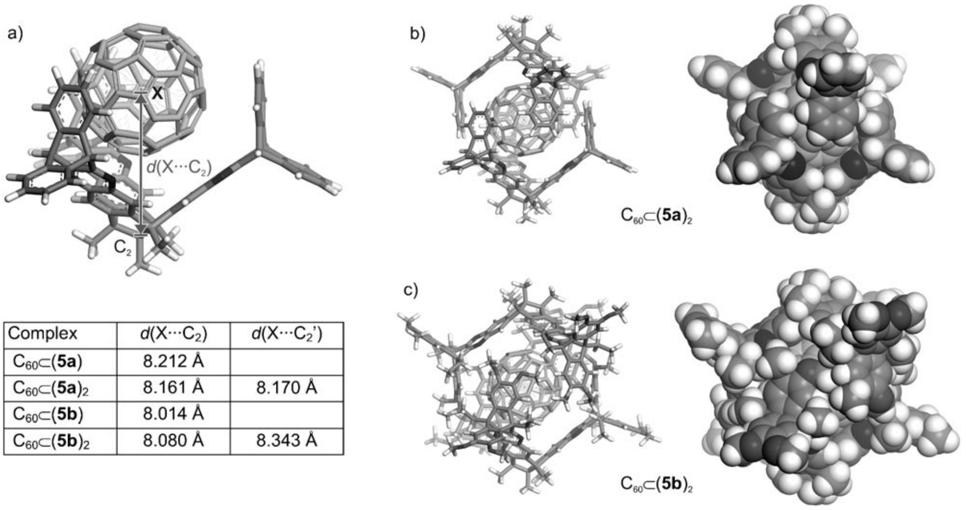
Plotting the change of absorbance (for a fixed wavelength) versus the concentration of the host (Figures 5 and 6), the relative ratios of components in the reaction mixtures were determined by the molar ratio method, which employs non-linear curve regression.[25] Complex formation involves four different components, the guest molecule (C_{60}), the host h (**5a** or **5b**), and the corresponding host–guest complexes $C_{60}{\subset}h$ and $C_{60}{\subset}h_2$, according to equilibria shown in Equation (1):

$$\begin{aligned} &h+C_{60} \underset{}{\overset{K_1}{\rightleftharpoons}} C_{60}\subset h \\ &h+C_{60}\subset h \underset{}{\overset{K_2}{\rightleftharpoons}} C_{60}\subset h_2 \end{aligned} \tag{1}$$

which means that $K_1=[C_{60}{\subset}h]/[h][C_{60}]$ and $K_2=[C_{60}{\subset}h_2]/[C_{60}{\subset}h][h]$ have to be taken into account for the determination of association constants. The K_1/K_2 ratio can be directly estimated from experimental curves that correlate the changes of absorbance at a fixed wavelength and the stoichiometric ratio of the compounds (Figures 5 and 6). An almost constant slope for the system that involves C_{60} and **5a** (Figure 5) indicates a K_1/K_2 ratio close to unity, whereas the constantly diminishing slope for the C_{60} and **5b** (Figure 6) indicates a K_1/K_2 ratio that is much greater than one, that is, K_1 should be much larger than K_2. Quantitative values of K_1 and K_2 were determined by the Benesi–Hildebrand method and by the procedure outlined by Connors,[26] to give values of $K_1=(2908\pm360)$ L mol^{-1} and $K_2=(2076\pm300)$ L mol^{-1} for C_{60}/**5a**, and $K_1=(5608\pm220)$ L mol^{-1} and $K_2=(673\pm160)$ L mol^{-1} for C_{60}/**5b**, respectively. These are averaged results of non-linear curve regressions that were performed within three independent UV/Vis titration experiments for each host–guest system.

The values of K_1 and K_2 were independently verified by determining the association constants through ^{1}H NMR spectroscopy titration experiments. For this purpose the ^{1}H NMR spectroscopy chemical shifts of four signals for **5a** and two signals for **5b** were plotted against the concentration of the host and individual association constants were fitted by non-linear curve regression to give values of $K_1=(2531\pm750)$ L mol^{-1} and $K_2=(1819\pm860)$ L mol^{-1} for host **5a**, and $K_1=(5328\pm580)$ L mol^{-1} and $K_2=(1376\pm260)$ L mol^{-1} for complex formation of **5b** and C_{60}. A notable difference between the individual association constants K_1 (1:1 complex) and K_2 (2:1 complex) for **5b** are gathered from UV/Vis as well as from ^{1}H NMR spectroscopy titration experiments, therefore, a systematic experimental error might be ruled out.

Molecular mechanics calculations (MM2 force field) indicate that the much lower complex stability of $C_{60}\subset$(**5b**)$_2$ (compared with its counterpart **5a**) could arise from steric repulsion between the R^2 and R^3 substituents (Scheme 1) from adjacent host molecules in a 2:1 complex. Whereas two molecules of **5a** ($R^2 = R^3 = H$) fit tightly around the encapsulated C_{60} guest, the methoxy (R^3) and bridgehead ethyl substituents (R^2) of **5b** repel each other. Indeed, based on MM2 force field geometry optimisations of the 1:1 and 2:1 complexes investigated in this work, the fully converged structure of $C_{60}\subset$(**5a**)$_2$ shows a highly symmetrical arrangement of the molecules of **5a** with almost equal distances between the centroid of C_{60} and the central bridgehead atom of the triquinacene moieties (Figure 7, $d(X\cdots C_2) = 8.16$ Å and $d(X\cdots C_2') = 8.17$ Å). This should be compared to the corresponding values from the fully converged structure of $C_{60}\subset$(**5b**)$_2$ ($d(X\cdots C_2) = 8.08$ Å and $d(X\cdots C_2') = 8.34$ Å), which shows that deep penetration of C_{60} into **5b** is only possible for 1:1 stoichiometry, whereas the association of a second molecule of **5b** is much weaker. (Similar structural data were obtained from MM3 force field geometry optimisations.)



Complex	$d(X\cdots C_2)$	$d(X\cdots C_2')$
$C_{60}\subset$(**5a**)	8.212 Å	
$C_{60}\subset$(**5a**)$_2$	8.161 Å	8.170 Å
$C_{60}\subset$(**5b**)	8.014 Å	
$C_{60}\subset$(**5b**)$_2$	8.080 Å	8.343 Å

Figure 7. Stick representations for host–guest complexes of C_{60} with **5a** or **5b** obtained from MM2 force field geometry optimisations. a) Structural model of $C_{60}\subset$**5a** in which the distance between the centroid of C_{60} and the central atom (C_2) of the tribenzotriquinacene moiety represents a measure for the penetration depth of C_{60}. b) and c) Stick and space-filling representations of the 2:1 complexes of **5a** and **5b**,which highlight the tight arrangement of hosts and the encapsulated fullerene.

Another remarkable aspect is the fact that the association constant, K_1, for the 1:1 complex of the electron-rich host **5b** and C_{60} is twice as large as that for **5a**. One possible explanation for this effect could be that the electron-releasing methoxy substituents of **5b** lead to a partial charge transfer from the host onto the electron-accepting C_{60} molecule. However, as mentioned previously, the absolute values of the association constants determined for both host–guest systems in this work are not strictly comparable because the titration experiments had to be performed in different solvents owing to solubility problems. Thus, solvent specific effects could be also responsible for this observation.[27]

Conclusion

The formation of complexes of C_{60} with macrocyclic hosts, porphyrins,[28] curved-faced triptycenes,[29] and other molecules,[30] has been studied in some detail. One of the highest association constants was that reported for a complex of C_{60} and a zinc-containing porphyrin ($K = 1.4\times10^6$ M^{-1}),[28c,a] the unusually high complex stability is attributed to strong non-specific π–π interactions between the electron-rich porphyrin and the fullerene. Host–guest systems based on receptors that are designed to provide optimal shape complementarity to the fullerene hosts typically show much lower stability constants. Favourable design strategies for increasing fullerene binding affinities of the hosts include making the binding pockets deeper or the introduction of highly polarisable substituents and/or electron-rich aromatic rings. The largest association constants reported for fullerene complexes of half-bowl-shaped hosts are those of an *N*-methylpyrrole substituted cyclotriveratrylene ($K = 4.8\times10^5$ M^{-1})[4b] and a biphenyl linked bi-5,5′-*p*-*tert*-butylcalix[4]arene ($K = 1.6\times10^4$ M^{-1}).[2z] However, in both cases the fullerene guest becomes completely enclosed by a single host. For simpler hemispherical hosts, such as calix[*n*]arenes, resorcarenes, cyclotriveratrylenes or substituted corannulenes, smaller association constants ranging from 10^2 to 3.5×10^3 M^{-1} were reported.[2g,v,x,z,4g,5d,e,6a]

In this work we have presented a novel C_{60} host system based on conformationally inflexible and highly rigid tribenzotriquinacene moieties. X-ray structural investigations and molecular modelling studies show that host molecules, such as **5a** or **5b**, provide excellent structural pre-organisation that is suitable for binding C_{60}. This statement is corroborated by the experimental complex stability constants, the highest value of which was determined for $C_{60}\subset$**5b** ($K_1 \approx 6\times10^3$ M^{-1}). This value is considerably higher than representative association constants typically found for other half-bowl-shaped hosts, which can maximise their non-covalent interactions with C_{60} through induced fit owing to some conformational flexibility.

By combining tribenzotriquinacene hosts with suitably functionalised fullerenes, components of a nanomechanical construction kit, such as joints, rotors, ratchets or gear systems, might become available in the near future. Backbone functionalisation at the R^1 positions (Scheme 1) of tribenzotriquinacene provides a means of attaching these components to the surface of a metal, a metal oxide or a polymer. Investigations in this direction are currently underway in our laboratory.

Experimental Section

General: Melting points were recorded by using Büchi Melting Point B-540 apparatus and are uncorrected. IR spectra were recorded by using a Bruker FTIR IFS 113v spectrometer as KBr pellets. UV/Vis spectra were recorded by using a J&M TIDAS instrument. NMR spectra were recorded by using Bruker DRX 500 or Bruker Avance 400 spectrometers. Data are given in ppm with spectra referenced to the residual solvent peak. The degree of substitution of carbon atoms was determined by the DEPT-135 method. CI mass spectra were recorded by using a Finnigan MAT, SSQ 7000 mass spectrometer equipped with a single-stage-quadrupole system. Intensities are given relative to the base peak. MALDI-TOF mass spectra were recorded by using a Bruker Daltonics REFLEX III instrument equipped with an N_2 laser (337 nm), pulsed ion extraction (PIE) and HIMAS-detector. An acceleration voltage of 20 kV was used with a 2,5-dihydroxybenzoic acid matrix. TLC was perfomed by using silica gel (Kieselgel F_{254}) plates on aluminium foil purchased from Merck. Column chromatography was perfomed by using silica gel (Kieselgel 60, 0.063–0.200 mm) obtained from Merck. All solvents were purified by distillation before use and dried according to standard procedures when necessary.

Molecular mechanics calculations were performed by using CambridgeSoft Chem3D Ultra V10 (MM2 force field) or Tinker V4.2 (MM3 force field). Visualisation of the results was occasionally performed within the Visualizer module of Accelrys Materials Studio V4.0.

2,3,6,7-tetramethoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-*cis*-diol (2b): A suspension of 9,10-diethyl-2,3,6,7-tetramethoxyanthracene **1b**[17] (3.3 g, 9.0 mmol) and vinylene carbonate (6.5 g, 72.1 mmol) in dry xylene (20 mL) was heated in an autoclave at 180 °C for three days. The solvent was evaporated, the brownish residue was recrystallised from toluene, filtered by suction and dried in vacuo. Subsequently the resulting solid was heated under reflux for 2 h in 40 % aqueous NaOH (60 mL). The resulting solid was filtered by suction, washed with water and dried in vacuo to yield **2b** (3.4 g, 8.1 mmol, 91 %). M.p. 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.94$ (s, 2H; H_{arom}), 6.93 (s, 2H; H_{arom}), 4.02 (d, $^3J(H,H)=3.52$ Hz, 2H), 3.89 (s, 6H; H_{OMe}), 3.88 (s, 6H; H_{OMe}), 2.66–2.44 (m, 4H; $H_{\mathbf{CH_2}CH_3}$), 1.97 (brs, 2H; H_{OH}), 1.46 ppm (t, $^3J(H,H)=7.32$ Hz, 6H; $H_{CH_2\mathbf{CH_3}}$,); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=147.1$, 135.6, 135.3, 108.5, 108.4, 68.5, 56.3, 56.2, 49.3, 20.6, 9.0 ppm; IR (KBr): $\tilde{\nu}=3524$, 3374, 2933, 2830, 1610, 1494, 1463, 1401, 1272, 1161, 1050, 993, 782 cm^{-1}; MS (CI): *m/z* (%): 415 (94) $[M+H]^+$, 397 (100) $[(M+H)-H_2O]^+$, 354 (76) $[M-C_2H_5O_2]^+$; elemental analysis calcd (%) for $C_{24}H_{30}O_6$: C 69.54, H 7.30; found: C 69.38, H 7.27.

2,3,6,7-tetramethoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dione (3b): Trifluoroacetic acid anhydride (2.4 mL, 16.4 mmol) was added at −78 °C to a mixture of dry DMSO (1.4 mL, 19.8 mmol) and dry CH_2Cl_2 (90 mL) under argon and the resulting solution was stirred for 10 min. A solution of **2b** (2.4 g, 5.7 mmol) in CH_2Cl_2/DMSO (2:1, 45 mL) was added within 15 min and the mixture was stirred for a further 60 min at −78 °C. Triethylamine (5.4 mL, 38.7 mmol) was added slowly, the reaction mixture was allowed to warm to 5 °C and subsequently poured into 2 M aqueous HCl (200 mL). When the evolution of gas had stopped, the two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (6×). The combined organic layers were washed with water (6×) and dried with sodium sulfate. The solvent was evaporated and the residue was recrystallised from *n*-pentane to yield **3b** as an orange powder (2.3 g, 5.6 mmol, 99 %). M.p. 202–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.99$ (s, 4H; H_{arom}), 3.93 (s, 12H; H_{OMe}), 2.65 (q, $^3J(H,H)=7.32$ Hz, 4H; $H_{\mathit{CH_2}CH_3}$), 1.54 ppm (t, $^3J(H,H)=7.32$ Hz, 6H; $H_{CH_2\mathit{CH_3}}$); ^{13}C NMR (100 MHz, $CDCl_3$,): $\delta=185.6$, 149.6, 108.1, 58.4, 56.2, 55.7, 18.2, 9.4 ppm; IR (KBr): $\tilde{\nu}=3433$, 3088, 2999, 2935, 2853, 2831, 1724, 1574, 1494, 1457, 1403, 1258, 1168, 1043, 858 cm^{-1}; MS (CI): *m/z* (%): 439 (64) $[M+C_2H_5]^+$, 411 (100) $[M+H]^+$, 383 (6) $[M-C_2H_3]^+$; elemental analysis calcd (%) for $C_{24}H_{26}O_6$: C 70.23, H 6.38; found: C 70.43, H 6.38.

13b,27b,41b,41d-Tetramethyl-13b,27b,41b,41d-tetrahydro(1″,4″-diaza-9″,10″-dihydro-9″,10″-*o*-benzoanthraceno)[2″,3″:5′,6′]indeno[1′,2′,3′:3,4]-(6′,11′-diaza-5′,12′-dihydro-5′,12′[1″,2″]benzonaphthaceno)[8′,9′:5,6]-pentaleno[1,2-*k*](6′,11′-diaza-5′,12′-dihydro-5′,12′[1″,2″benzonaphthacene) (5a): A catalytic amount of TFA (0.1 mL) was added under argon to a solution of **4**[15] (140 mg, 328 μmol) and **3a**[16] (480 mg, 1.97 mmol) in chloroform (100 mL) and the mixture was subsequently heated at reflux for 60 h under conditions in which water was removed. The solvent was evaporated and the residue was purified by column chromatography (gradient: methanol/chloroform 10:1 to 1:1) to yield **5a** as a yellow powder (192 mg, 188 μmol, 58 %). M.p. >410 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.97$ (s, 6H; H_{arom}), 7.54–7.39 (m, 12H; H_{arom}), 7.15–6.97 (m, 12H; H_{arom}), 5.51 (s, 6H), 1.81 (s, 9H; H_{CH_3}), 1.42 ppm (s, 3H; H_{CH_3}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=156.6$ (q), 151.2 (q), 142.0 (q), 141.7 (q), 139.4 (q), 126.6 (t), 126.4 (t), 124.9 (t), 124.7 (t), 122.1 (t), 70.7 (q), 62.4 (q), 55.2 (t), 26.8 ppm (p), one primary carbon atom could not be detected; IR (KBr): $\tilde{\nu}=3412$, 3019, 2968, 2924, 2854, 1740, 1626, 1489, 1458, 1374, 1301, 1147, 896, 732 cm^{-1}; MS (MALDI-TOF): *m/z*: 1021 $[M+H]^+$; elemental analysis calcd (%) for $C_{74}H_{48}N_6{\cdot}3CH_3OH$: C 82.77, H 5.41, N 7.52; found: C 83.06, H 5.87, N 7.07.

4,5,9,10,18,19,23,24,32,33,37,38-Dodecamethoxy-2,7,16,21,30,35-hexaethyl-13b,27b,41b, 41d-tetramethyl-13b,27b,41b,41d-tetrahydro(1″,4″-diaza-9″,10″-dihydro-9″,10″-*o*-benzoanthraceno)[2″,3″:5′,6′]indeno[1′,2′,3′:3,4]-(6′,11′-diaza-5′,12′-dihydro-5′,12′1″,2″]benzonaphthaceno)[8′,9′:5,6]-pentaleno[1′,2′*k*](6′,11′-diaza-5′,12′-dihydro-5′,12′-[1″,2″]benzonaphthacene) (5b): A solution of **3b** (807 mg, 2 mmol), **4**[15] (140 mg, 328 μmol), and a catalytic amount of TFA (0.1 mL) in chloroform (150 mL) were heated at reflux for 60 h under argon and conditions in which water was removed. The solvent was evaporated and the residue was purified by column chromatography (ethyl acetate/chloroform 1:1) to yield **5b** as an orange powder (280 mg, 180 μmol, 55 %). $R_f=0.25$; m.p. 326–327 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.97$ (s, 6H; H_{arom}), 7.13 (s, 6H; H_{arom}), 7.00 (s, 6H; H_{arom}), 3.89 (s, 18H; H_{OMe}), 3.78 (s, 18H; H_{OMe}), 3.12–2.98 (m, 12H; $H_{C\mathbf{H_2}CH_3}$), 1.83 (t, $^3J(H,H)=7.08$ Hz, 18H; $H_{CH_2C\mathbf{H_3}}$), 1.81 (s, 9H; H_{CH_3}), 1.41 ppm (s, 3H; H_{CH_3}); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta=158.7$ (q), 150.7 (q), 146.8 (q), 146.7 (q), 139.0 (q), 138.9 (q), 138.5 (q), 122.3 (t), 108.6 (t), 108.5 (t), 70.9 (q), 62.3 (q), 56.2 (p), 56.1 (p), 53.7 (q), 27.3 (p), 20.1 (s), 10.8 ppm (p), one primary carbon atom could not be detected; IR (KBr): $\tilde{\nu}=3431$, 2929, 1735, 1609, 1575, 1484, 1402, 1378, 1275, 1166, 1046, 781, 758 cm^{-1}; MS: (MALDI-TOF): *m/z*: 1549 $[M+H]^+$; elemental analysis calcd (%) for $C_{98}H_{96}N_6O_{12}$: C 75.95, H 6.24, N 5.42; found: C 76.09, H 6.57, N 5.07.

Single crystals of $C_{60}{\subset}C_{98}H_{96}N_6O_{12}{\cdot}3C_7H_8$ (=$C_{60}{\subset}$**5b**·3 toluene) were obtained from an equimolar solution of C_{60} and **5b** in toluene. Dark red crystals were obtained by slow evaporation of the solvent at room temperature.

Crystallographic data

*$C_{60}{\subset}$**5b**·3 toluene*: X-ray crystal structure analysis for $C_{60}{\subset}$**5b**·3 toluene: formula $C_{179}H_{120}N_6O_{12}$; $M=2546$ g mol^{-1}; red crystal; 0.25×0.10×0.06 mm; orthorhombic; space group *P*bca (no. 61); $a=26.4689(3)$, $b=25.3726(3)$, $c=37.0319(5)$ Å; $V=24870.1(5)$ Å^3; $\rho_{calcd}=1.362$ g cm^{-3}; $\mu=0.671$ mm^{-1}; empirical absorption correction ($0.850\leq T\leq0.961$); $Z=8$; $Cu_{K\alpha}$ radiation ($\lambda=1.54178$ Å); $T=223$ K; ω and ϕ scans; 1306480 reflections collected (*h*, *k*, *l*); $[(\sin\theta)/\lambda]=0.62$ Å^{-1}; 21728 independent

($R_{\mathrm{int}}=0.108$) and 9662 observed reflections [$I \geq 2\sigma(I)$]; 1460 refined parameters; $R=0.144$; $wR_2=0.445$; maximum residual electron density $=0.86(-0.46)\,\mathrm{e\,Å^{-3}}$; hydrogen atoms calculated and refined as riding atoms.

The data set was collected by using an Enraf-Nonius CAD4 and a Nonius Kappa CCD diffractometer. COLLECT[31] was used for data collection, Denzo-SMN[32] was used for data reduction, Denzo[33] was used for absorption correction, SHELXS-97[34] was used for structure solution, SHELXL-97[35] was used for structure refinement and Diamond V3.1[36] was used to obtain the molecular graphics.

Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited at the Cambridge Data Centre. CCDC-656443 contains the supplementary crystallographic data for $C_{60}\subset$**5b**·3toluene. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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