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, ^1H NMR) titration experiments. Association constants of $K_1=(2908 \pm 360)$ L mol$^{-1}$ and $K_2=(2076 \pm 300)$ L mol$^{-1}$ for C_{60}/5a, and $K_1=(5608 \pm 220)$ L mol$^{-1}$ and $K_2=(673 \pm 160)$ L mol$^{-1}$ for C_{60}/5b were obtained. Single crystal X-ray structural analysis of compound C_{60}5b·3 toluene 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,$^4$ resorcarines,$^5$ coronulenes$^6$ 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
Condensation of hexaminotribenzotriquinacene (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[14] force field) show that the benzene groups positioned at the perimeter of the open cavity of the host are almost parallel to the central C₃ 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 C₆₀ guest molecule, the mean diameter of which is 10.0 Å (based on packing models obtained from a solid state structure of C₆₀)[15].

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 vinylen 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 vinylen 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 ¹H NMR spectrum of 3b shows only one singlet at δ = 6.99 ppm for the aromatic protons and another singlet at δ = 3.91 ppm that corresponds to the four methoxy groups. The ethyl groups correspond to a quartet and a triplet at δ = 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 C₃ᵥ symmetrical, therefore, their ¹H 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 3.79, 5.51 and 1.81 ppm, respectively. Similar signal shifts were observed for 5b.

**X-ray structural analysis**: Single crystals of CsN₂H₄N₃O₁₂·3C₆H₆ (CsN₂ = 5b·3-toluene) were obtained from an equimolar solution of Csₙ 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 Pnma (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 Csₙ or complexes of 5b and Csₙ in 2:1 stoichiometry have been unsuccessful to date. Some problems in refining the structure of Csₙ·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 Csₙ 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 Csₙ 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. Details of the crystallographic data collection and analysis are given in the Supporting Information. Figure 2a shows different graphical representations of host–guest complex Csₙ·5b, as determined by X-ray structure analysis. The packing of the complex in the crystal lattice is presented in Figure 2b.

The Csₙ 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 Csₙ and the centroid of each benzene group positioned at the perimeter of the open cavity of the host (cf., 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 Csₙ is then shifted outwards by 0.83 Å with respect to the midpoint of the host, which demonstrates that close contacts also exist between Csₙ and atoms belonging to the central tribenzotriquinacene moiety. As an empirical measure of the penetration depth of Csₙ in the cavity of 5b, the distance between the centroid of Csₙ 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; cf. 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 Csₙ**: The experimental determination of precise complex stability constants for Csₙ–host–guest complexes often faces the problem of limited solubility of reactants or complex(es) in common organic solvents. 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 CHCl₃ and CS₂ (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, the stability constants for Csₙ complexes of 5a and 5b were determined by UV/Vis and ¹H NMR spectroscopic techniques (Kₘₐₓ = 10¹² and 10¹⁷ L·mol⁻¹; ε₂ₐₕₚ = 10⁻⁸ and 10⁻⁹ mol·L⁻¹, respectively).

To exclude experimental artefacts of non-specific complex formation, such as non-linearity or self-aggregation, 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 3. UV/Vis absorption spectra of C₆₀ (2.22×10⁻⁴ mol L⁻¹) in the presence of 5a in chloroform/CS₂ (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 C₆₀ (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 C₆₀ (2.22×10⁻⁴ mol L⁻¹) with 5a. Absorbance values determined at λ = 435 nm: ΔA = Aₜₐ₉₀ – (Aₜₐ₉₀ + Aₐ₉₀).

Figure 6. Nonlinear curve regression for the results of the titration of C₆₀ (2.45×10⁻⁴ mol L⁻¹) with 5b. Absorbance values determined at λ = 450 nm: ΔA = Aₜₐ₉₀ – (Aₜₐ₉₀ + Aₐ₉₀).

were determined by the molar ratio method, which employs non-linear curve regression.²⁹ Complex formation involves four different components, the guest molecule (C₆₀), the host h (5a or 5b), and the corresponding host–guest complexes C₆₀:h and C₆₀:h₂, according to equilibria shown in Equation (1):

h + C₆₀ ⇌ K₁ C₆₀:h
b + C₆₀ ⇌ K₂ C₆₀:h₂

which means that K₁=[C₆₀:h]/[h][C₆₀] and K₂=[C₆₀:h₂]/[C₆₀:h][h] have to be taken into account for the determination of association constants. The K₁/K₂ 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 C₆₀ and 5a (Figure 5) indicates a K₁/K₂ ratio close to unity, whereas the constantly diminishing slope for the C₆₀ and 5b (Figure 6) indicates a K₁/K₂ ratio that is much greater than one, that is, K₁ should be much larger than K₂. Quantitative values of K₁ and K₂ were determined by the Benesi–Hildebrand method and by the procedure outlined by Connors,²⁴ to give values of K₁=(2908±360) L mol⁻¹ and K₂=(2076±300) L mol⁻¹ for C₆₀/5a, and K₁=(5608±220) L mol⁻¹ and K₂=(673±160) L mol⁻¹ for C₆₀/5b, 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 K₁ and K₂ were independently verified by determining the association constants through ¹H NMR spectroscopy titration experiments. For this purpose the ¹H 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 K₁=(2531±750) L mol⁻¹ and K₂=(1819±860) L mol⁻¹ for host 5a, and K₁=(5328±580) L mol⁻¹ and K₂=(1376±260) L mol⁻¹ for complex formation of 5b and C₆₀. A nota-
bable 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$_{60}$C(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$_{60}$C(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, $d(X-C_2)$ = 8.16 Å and $d(X-C_2')$ = 8.17 Å). This should be compared to the corresponding values from the fully converged structure of C$_{60}$C(5b)$_2$ ($d(X-C_2)$ = 8.08 Å and $d(X-C_2')$ = 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.)

Another remarkable aspect is the fact that the association constant, $K_2$, 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.

**Conclusion**

The formation of complexes of C$_{60}$ with macrocyclic hosts, porphyrins, curved-faced triptycenes, and other molecules 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 ($K = 1.4 \times 10^9$ M$^{-1}$). 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 cyclotrimeratylene ($K = 4.8 \times 10^3$ M$^{-1}$) and a biphenyl linked bi-5,5'-p-tert-butylcalix[4]arene ($K = 1.6 \times 10^4$ M$^{-1}$). However, in both cases the fullerene guest becomes completely enclosed by a single host. For simpler hemispherical hosts, such as calix[n]arenes, resorcarennes, cyclotrimeratylene or substituted coronulenes, smaller association constants ranging from $10^2$ to $3.5 \times 10^3$ M$^{-1}$ were reported.

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$_{60}$C(5b) ($K_2 \approx 6 \times 10^4$ M$^{-1}$). This value is considerably higher than representa-
Experimental Section

General: Melting points were recorded by using BUCHI Melting Point B-540 apparatus and are uncorrected. IR spectra were recorded by using a Bruker FT-IR IFS 113v spectrometer at KBr pellets. UV/Vis spectra were recorded by using a J&K 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 DPPH-135 method. CI mass spectra were recorded by using a Finnigan MAT, SSQ 7000 mass spectrometer equipped with a single-stage quadrupole pole 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 Nd:YAG laser (357 nm), pulsed ion extraction (PFE) and HIMAS-detector. An acceleration voltage of 20 kV was used with a 2,5-dihydroxybenzene acid matrix. TL was performed by using silica gel (Kieselgel 60 F254 plates on aluminium foil purchased from Merck).

Column chromatography was performed 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 Cambridge Soft 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-tetramethyl-9,10-dihydro-9,10-ethanoanthracene-11,12-die-11-di-cyclo-

(2b): A suspension of 9,10-dichloro-2,3,7-tetramethylanthracene 1b[5] (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, 8.11 mmol, 96%). M.p. 137–139°C; 1H NMR (400 MHz, CDCl3): δ = 6.94 (s, 2H, H9); 6.93 (s, 2H, H10); 4.02 (d, 2J(H,H) = 3.5 Hz, 2H, 2H13); 3.89 (s, 6H, H12); 3.86 (s, 6H, H11a); 2.66–2.44 (m, 4H, H11b–13); 1.97 (brs, 2H12); 1.46 ppm (t, 2J(H,H) = 7.32 Hz, 6H, 2H14); 1.35 ppm (t, 2J(H,H) = 7.32 Hz, 6H, 2H14a); 1.01 ppm (s, 1H, H15); 0.50 ppm (s, 1H, H15a); 0.29 ppm (s, 1H, H15b). 13C NMR (100 MHz, CDCl3): δ = -147.1, 135.6, 135.3, 108.5, 108.2, 68.5, 56.3, 56.2, 49.3, 20.6, 9.9 ppm; IR (KBr): ν = 3294, 3274, 2933, 2830, 1610, 1494, 1463, 1401, 1277, 1161, 1050, 991, 782 cm⁻¹; MS (EI): m/z (%): 415 (94) [M+H]+, 397 (100) [M+H]+, H2O]+, 354 (76) [M-C2H5OH]+; elemental analysis calculated (%) for C24H18O4: C 74.9, H 5.4. Found: C 74.9, H 5.7. 3.10.3.5.7-tetramethyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dio-3: A solution of 2b (807 mg, 2 mmol), 42d[5] (40 mg, 328 μmol), and a catalytic amount of TFA (0.1 mL) in chloroform (150 mL) were heated at reflux for 20 h under argon 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%). M.p. 122–123°C; 1H NMR (400 MHz, CDCl3): δ = 7.97 (s, 6H, H1a); 7.31 (d, 2J(H,H) = 7.8 Hz, 6H, H1b–13); 7.17 (s, 1H, H14); 7.03 ppm (s, 1H, H15); 4.57 ppm (s, 1H, H15a); 2.86 ppm (s, 1H, H15b). 13C NMR (100 MHz, CDCl3): δ = 138.6, 138.4, 138.2, 138.1, 137.9, 137.4, 136.2, 134.9, 134.7, 130.5, 129.8, 126.8, 126.3, 125.8, 125.7, 124.4, 124.0, 123.7, 122.1 ppm (s, 1H, H15); 114.2 ppm (s, 1H, H15a); 108.5 ppm (s, 1H, H15b). 13C NMR (100 MHz, CDCl3): δ = 158.7 (q), 150.7 (q), 146.8 (q), 146.7 (q), 139.0 (q), 138.9 (q), 138.3 (q), 122.3 (t), 108.5 (t), 108.3 (t), 70.9 (q), 62.3 (q), 56.2 (q), 56.1 (q), 56.0 (q), 27.3 (q), 20.1 (q), 10.8 ppm (q), one primary carbon atom could not be detected; IR (KBr): ν = 3431, 2929, 1735, 1605, 1575, 1484, 1402, 1378, 1275, 1166, 1045, 781, 758 cm⁻¹; MS (MALDI-TOF): m/z: 1549 [M+H]+; elemental analysis calculated (%) for C13H18N4O2: C 75.9, H 6.4, N 5.2. Found: C 75.6, H 6.7, N 5.0.

Single crystals of C67H48N4O2.3CH3Cl were obtained from an equimolar solution of C6 and 5b in toluene. Dark red crystals were obtained from an equimolar solution of C6 and 5b in toluene.

Crystallographic data

C67H48N4O2.3CH3Cl: X-ray crystal structure analysis for C67H48N4O2.3CH3Cl. formulas C67H48N4O2.3CH3Cl: M = 2546 g/mol; red crystal, 0.25 × 0.25 × 0.06 mm; orthorhombic; space group Pbcn (no. 61); a = 25.468(4), b = 25.3726(5), c = 37.0319(5) Å, V = 24870.1(5) Å³, ρcalcd = 1.362 g/cm³, μ = 0.671 mm⁻¹; empirical absorption correction (0.850 ≤ θ ≤ 0.961); Z = 8; Cuvac, radiation (λ = 1.54178 Å); T = 223 K; ω and φ scans; 130648 reflections collected (h, k, l); [sin(θ)/λ] = 0.62 Å⁻¹; 2172 independent
Acknowledgements

The authors are grateful to Prof. Dr. Gerhard Erker and to Dr. Roland Fröhlich (Westälsische Wilhelms-Universität Münster, Institute of Organometallic Chemistry & Catalysis) for providing X-ray crystallographic data of compound C_{62}H_{58}S_5I_3. This work was supported by the German Research Foundation (DFG, A9 Project of the Collaborative Research Centre 569 “Hierarchic Structure Formation and Function of Organic-Inorganic Nano Systems”, Ulm University).


