Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Material

Advanced Buckyball Joints: Synthesis, Complex Formation and Computational simulations of Centrohexaindane-Extended Tribenzotriquinacene Receptors for C_{60} Fullerene.

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Determination of association constants by UV/vis spectroscopy

Complex stability constants were determined according to published literature procedures.[1] As an essential requirement for the use of optical absorption spectroscopy, a spectral change must occur as a consequence of complex formation. Spectral changes are detected and determined by a spectroscopic titration experiment. To a solution of the guest molecule (C_{60}) different aliquots of host **9** solutions are titrated. From the experimental absorption curve the absorption data corresponding to stock solutions of pure host or pure substrate, respectively, at equivalent concentrations are subtracted. Difference absorbance data (ΔA) thus obtained reflect the changes of absorbance due to formation of supramolecular complexes.

The first step in determining the stability constant is the identification of the number of (spectroscopically active) species in solution. The method of choice was in our case the continuous variation method. In this method, the sum of the total substrate and ligand concentrations held constant, whereas the mole fraction varies from zero to one. Plotting the absorbance difference (from the absorbance of each solution containing host and guest is substracted the absorbance that would have been observed in the absence of complexation), of a wavelength at which a large absorbance change is observed upon complexation, against the mole fraction of one component leads to the maximum in deviation x_{max}. With formula S1 the stoichiometric variables can be determined.

Formula S1

$$\frac{n}{m} = \frac{x_{max}}{1 - x_{max}}$$

For our reaction system, the result is the 1:1 host guest complex (Figure S1). Prior to the spectroscopic titration, absorption data from dilution series of host **9** solutions were examined for nonlinear effects.

[1] K. A. Connors, The Measurement of Molecular Complex Stability, Wiley, New York, **1987**, 141 – 202.

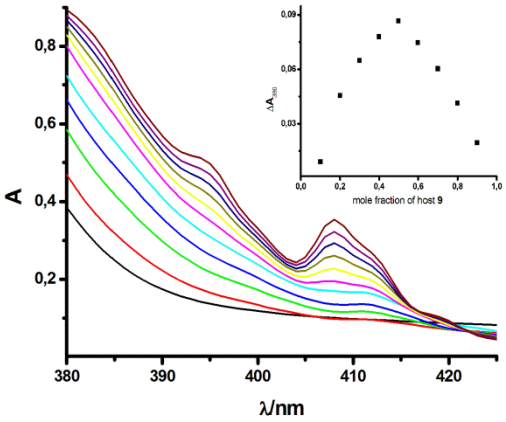

Fig. S1: Series of absorption spectra from host **9** and C_{60} at a concentration of 1.0×10^{-4} mol/l. From top to bottom drops the mole fraction of Fullerene C_{60} (1.0, 0.9, - , 0.1, 0). Inset: Continuous variation plot of C_{60} / host **9** at λ = 380 nm (**x** = conc. **9** / conc. C_{60}).

The **fitting formula S2 for a UV/vis titration series** is defined as follows:

Formula S2

$$\frac{\Delta A}{b} = \frac{K[S^\circ]\Delta\varepsilon_{SR}[R]}{1+K[R]}$$

where S° = starting concentration of the substrate (C_{60})

R = concentration of the host (**9**)

b = optical path length of the cuvette [cm]

$\Delta A = A^{\lambda}$ (reaction mixture) – (A^{λ}(host) + $A^{\lambda}(C_{60})$)

$\Delta\varepsilon_{SR} = \varepsilon_{SR} - \varepsilon_R - \varepsilon_S$

ε_{SR} = extinction coefficient of the 1:1 complex

ε_R = extinction coefficient of the host

ε_S = extinction coefficient of the substrate

K = stability constant of the 1:1 complex

Stock solutions of the following concentrations were employed:

Host **9** (10.0 mg/10.0 ml) in chloroform/carbon disulfide (1:1);

fullerene C_{60} (5.6 mg/50 ml) in chloroform/carbon disulfide (1:1).

1. Titration

To 1.0 mL of C_{60} stock solution and 1.5 mL of solvent 20 µl aliquots of host **9** stock solution were titrated in subsequent steps; 16 to realize a C_{60}/host ratio of 1:1.

2. Titration

To 2.0 mL of C_{60} stock solution 30 µl aliquots of host **9** stock solution were titrated in subsequent steps; 18 to realize a C_{60}/host ratio of 1:0.75.

3. Titration

To 2.0 mL of C_{60} stock solution 67 µl aliquots of host **9** stock solution were titrated in subsequent steps; 14 to realize a C_{60}/host ratio of 1:1.

Figures S2 - S4 show the UV/vis spectra of the titration of C_{60} with solutions of host **9**.

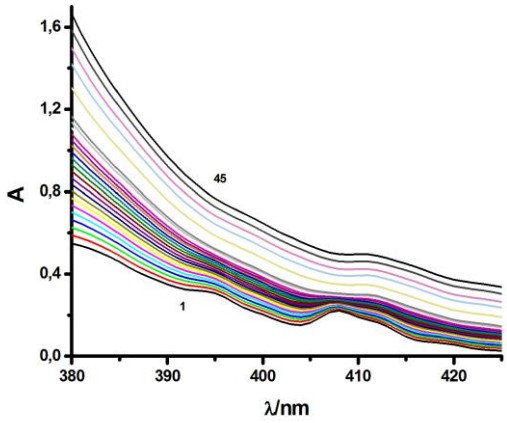

Fig. S2: First series of absorption spectra of C_{60} (0.62 x 10^{-4} mol/l) in the presence of **9** in $CS_2/CHCl_3$ (1:1). Concentration of host **9** increases from a 1:0 ratio (at the beginning, curve 1) to a final ratio of 1:2.5 (curve 44).

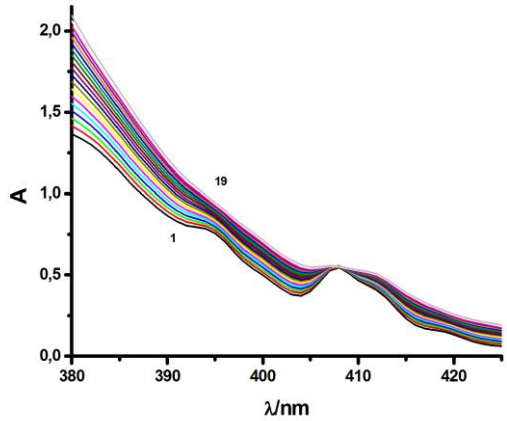

Fig. S3: Second series of absorption spectra of C_{60} (1.5 x 10^{-4} mol/l) in the presence of **9** in $CS_2/CHCl_3$ (1:1). Concentration of host **9** increases from a 1:0 ratio (at the beginning, curve 1) to a final ratio of 1:0.8 (curve 18).

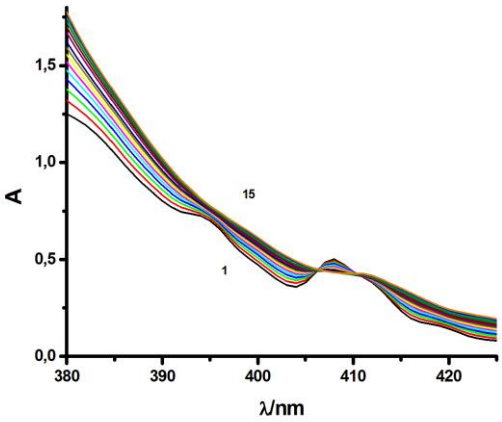

Fig. S4: Third series of absorption spectra of C_{60} (1.5 x 10^{-4} mol/l) in the presence of **9** in $CS_2/CHCl_3$ (1:1). Concentration of host **9** increases from a 1:0 ratio (at the beginning, curve 1) to a final ratio of 1:1 (curve 15).

In order to perform the subsequent curve regression with the most accurate data, the particular wavelength at which the largest variations of absorbance occurred during titration was selected, owing to complex formation. For the non-linear curve regression we thus selected absorbance values at λ = 380 nm for host **9.**

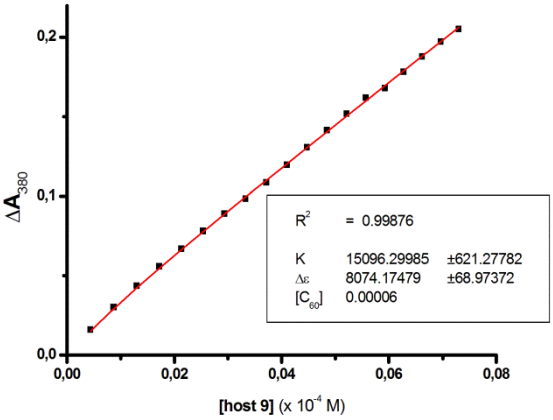

Fig. S5: Non-linear curve regression for the first titration of C_{60} (0.62 10^{-4} mol/l) with host **9**.

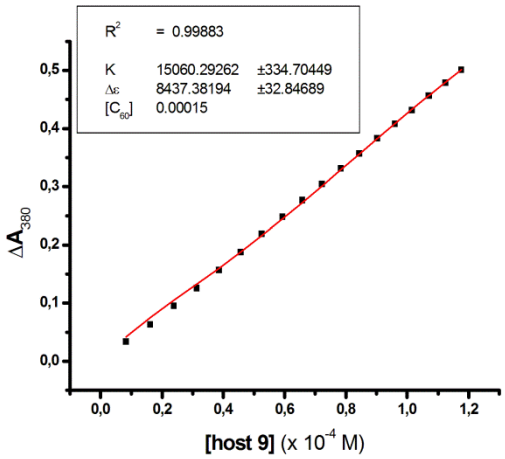

Fig. S6: Non-linear curve regression for the second titration of C_{60} (1.5 10^{-4} mol/l) with host **9**.

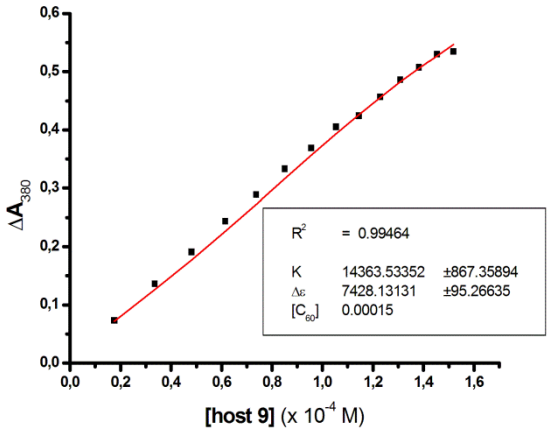

Fig. S7: Non-linear curve regression for the third titration of C_{60} (1.5 10^{-4} mol/l) with host **9**.

Fitting curves for the titration series are shown in Figures S5 - S7. Absorbance data were corrected by a concentration dependent dilution factor. The final association constants are averaged values for all three titrations. Numerical values are given in Table S1.

Table S1: Results of the non-linear curve regression for the titration of host **9**.

Titration	K (l/mol)	Δε (RS) (l/mol·cm)
1	15096	8074
2	15060	8437
3	14363	7428
average value	14550	7979
standard deviation	867	511
		ε_{380} (RS) 16732

The ^{1}H-NMR-spectra, the ^{13}C-NMR-spectra and the mass spectra of host **9** are represented in figure S8, S9 and S10 respectively.

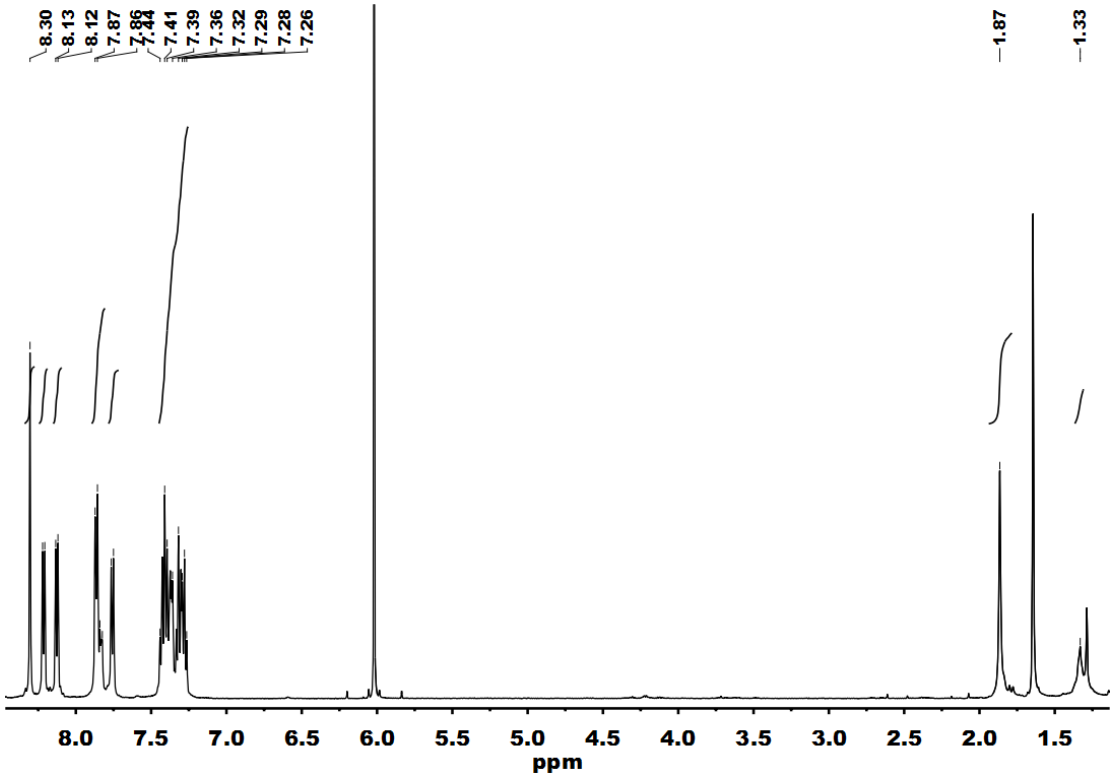

Fig. S8: ^{1}H NMR spectra (500 MHz, TCE, 300 K) of host **9**.

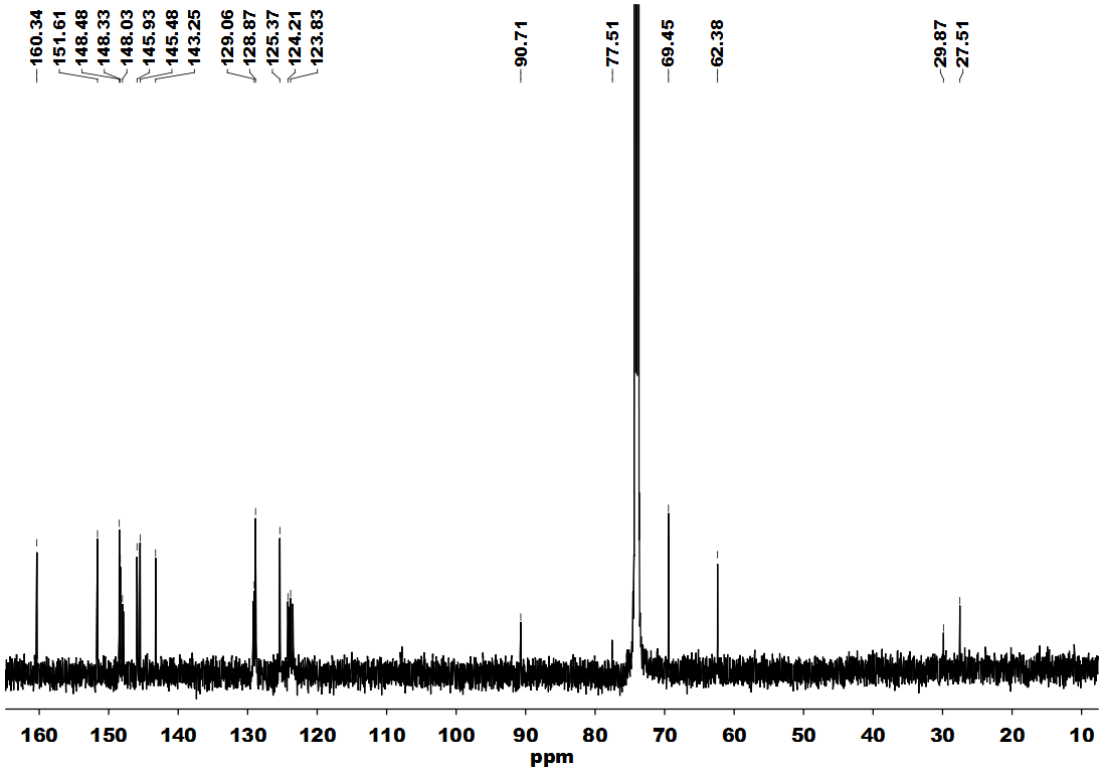

Fig. S9: ^{13}C NMR spectra (500 MHz, TCE, 300 K) of host **9**.

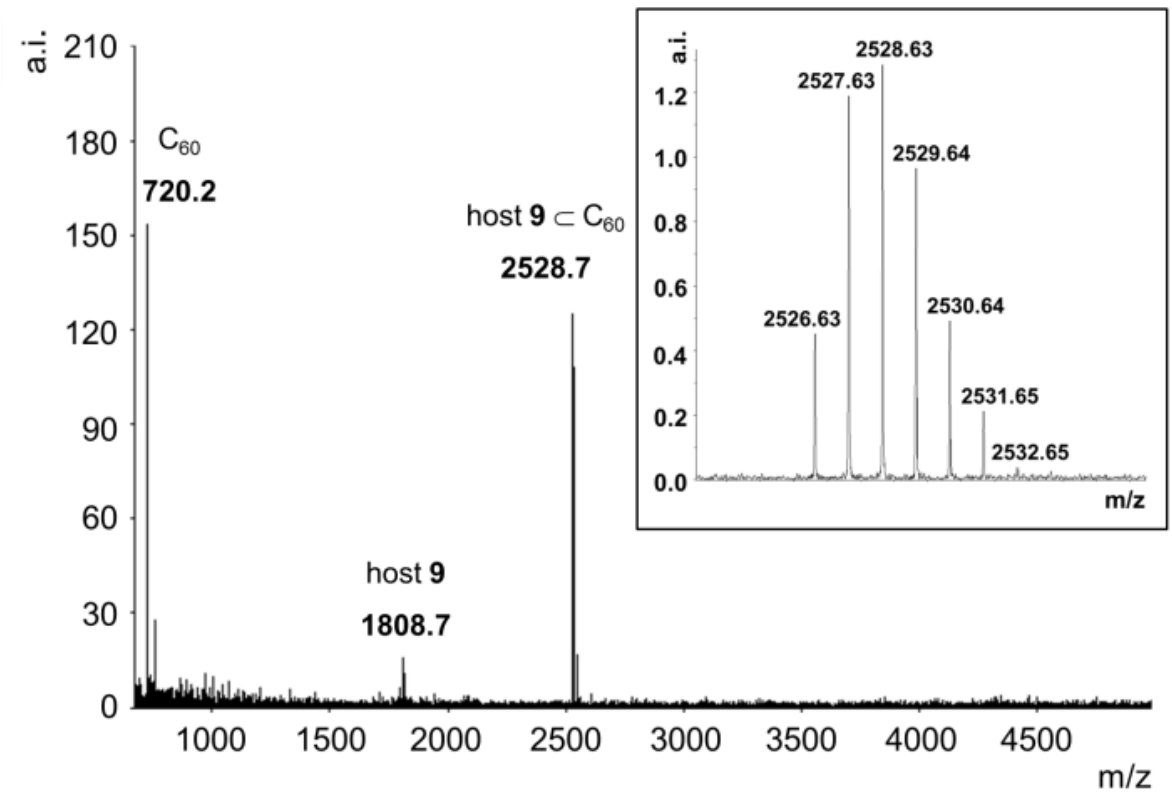

Fig. S10: Mass spectra (MALDI-TOF) of host **9** and C_{60}; Inset: Found isotopic pattern for ($C_{197}H_{79}N_6$) *m/z* = 2529 [host **9** ⊂ C_{60}+H]$^+$ (High resolution mass spectra)).