



Supporting Information

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Flying Capsules: Mass Spectrometric Detection of Pyrogallarene and Resorcinarene Hexamers

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Experimental Details for the Mass Spectrometric Experiments

High resolution ESI mass spectra and MS/MS spectra were recorded on a Bruker APEX IV Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source equipped with an off-axis 70° spray needle. A mixture of chloroform : acetone = 2 : 1 served as the spray solvent. The solutions were 200 to 250 µM with respect to the concentration of the pyrogallarene and resorcinarenes. Analyte solutions were introduced into the ion source with a syringe pump (Cole-Parmer Instruments, Series 74900) at flow rates of ca. 3 - 4 µL/min. Ion transfer into the first of three differential pumping stages in the ion source occurred through a glass capillary with 0.5 mm inner diameter and nickel coatings at both ends. Ionization parameters were adjusted as follows: capillary voltage: -4.5 to -5.0 kV; endplate voltage: -4.0 to -4.5 kV; capexit voltage: +240 to +345 V; skimmer voltages: +5 to +17 V; temperature of drying gas: 50-100 °C. The flows of the drying (ca. 1 psi) and nebulizer gases (ca. 10 psi) were kept in a low range. Ion intensities are somewhat sensitive to the drying gas flow. At higher flow rates, the intensities decrease. The ions were accumulated in the instruments hexapole for 2.0 – 9.0 s. The ions are then introduced into the FT-ICR cell, which was operated at pressures below 10⁻¹⁰ mbar, and finally detected by a standard excitation and detection sequence. For each measurement 32 to 150 scans were averaged to improve the signal-to-noise ratio. In particular, the rather high capexit voltages and the quite long accumulation times in the hexapole point to quite a stable assembly which is not as easily destroyed during ionization as many other non-covalent species.

For infrared multiphoton dissociation (IRMPD) experiments, all parameters, in particular the hexapole accumulation time, were optimized for maximum intensities of the desired

parent ions. All isotopes of the ions of interest were isolated and irradiated with a CO₂ IR laser at a wavelength of 10.6 μm. The max. laser power of 25 W was attained to 95%. The reaction was monitored after different reaction times to monitor the fragmentation kinetics of the parent ions. In this experiment, it should be noted that the laser not only excites the parent ion, but also the fragment ions after their formation. This is different from a normal collisional excitation under single-collision conditions in a CID experiment.

Note on ionization conditions:

The ionization conditions reported above represent the optimum for maximum hexamer intensity and low abundances of larger and smaller clusters. In the main text, we refer to ionization conditions as soft or harsh which mainly means that different capexit voltages are used. By changing the capexit voltage, collisions with residual gas in the region behind the ion cell can be tuned to some extent. At lower capexit voltages (ca. +180 - 220 V, the so-called "softer conditions"), the abundance of smaller clusters such as pentamers and tetramers (all containing 7²⁺) becomes smaller, while the intensity of signals for larger clusters (heptamers and octamers) increases somewhat. At higher capexit voltages (ca. +350 - 380 V), signals for smaller clusters such as pentamers and tetramers increase in intensity. The hexamer remains the major signal.

Our explanation for this finding supports the assignment of a specific hexamer formation as follows: We interpret the larger clusters (hepta- and octamers) as unspecific aggregates in which one or two monomers are attached to the hexamer. The smaller clusters can be assigned to fragments of the hexamer (as evidenced by the MS/MS experiments reported in the article). Lower capexit voltages lead to softer collisions and thus the amount of surviving unspecific aggregates (larger clusters) is higher. Higher capexit voltages give rise to harsher collisions and destroy the unspecific aggregates. The fact that there exist optimum conditions, under which the hexamers form with high abundance accompanied by minimal contributions of both unspecific aggregates and fragments, is in agreement with a lower binding energy of the unspecifically bound monomers as compared to those incorporated in the hexamer structure.