The Supporting Information

Coordination of alkaline-earth metal ions in the inverted cucurbit[7]uril supramolecular assemblies formed in the presence of tetrachloride zincate and cadmiumcate

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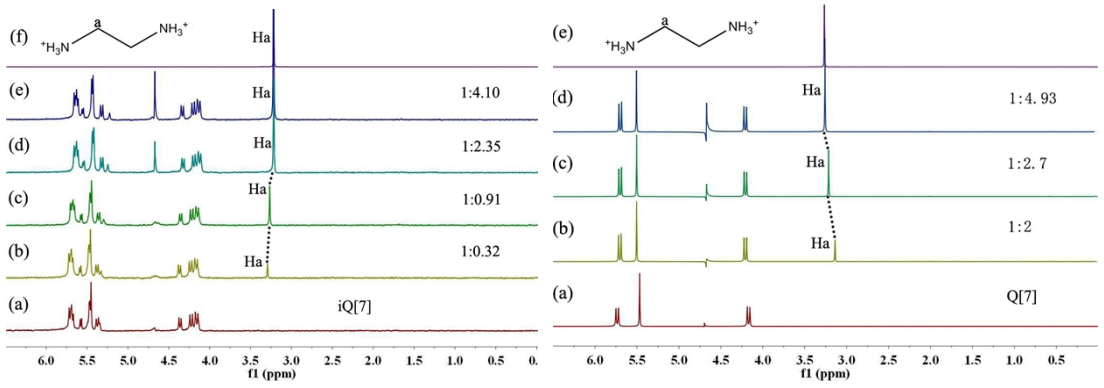
Experimental Section

Materials and methods: Six *α*,*ω*-alkyldiamanes ($H_2N(CH_2)_xNH_2$, x = 2, 4, 6, 8, 10, and 12) were purchased from Aldrich and used as supplied without further purification. *α*,*ω*-alkyldiammonium guests ($H_3N(CH_2)_xNH_3Cl_2$, x = 2, 4, 6, 8, 10, and 12; **1-6**) were prepared by protonation of the corresponding amines with concentrated HCl. *i*Q[7] was prepared according to a literature method,[1] and separated according to the method as we recently reported.[10]

Nuclear magnetic resonance measurements: All ^1H NMR spectra, including those for titration experiments, were recorded at 25°C on a VARIAN INOVA-400 spectrometer. D_2O was used as a field-frequency lock, and the observed chemical shifts are reported in parts per million (ppm) relative to an internal standard (TMS at 0.0 ppm).

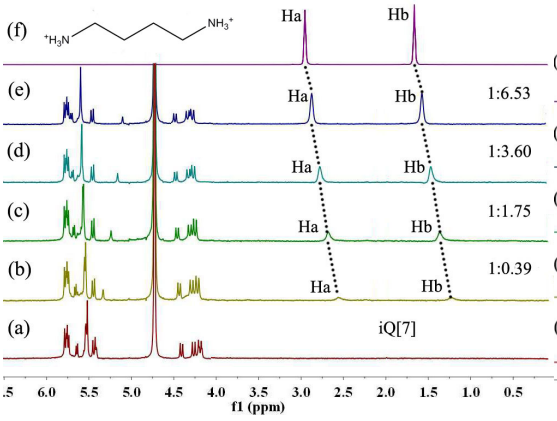
Isothermal titration calorimetry (ITC) experiments: The association constants and thermodynamic parameters for the inclusion complexation of aliphatic ammonium ions with *i*Q[7] were determined by titration calorimetry with a Nano ITC instrument (TA, USA). All solutions were prepared in purified water and degassed prior to titration experiments. An aqueous solution (0.1 mM) of *i*Q[7] was placed in the sample cell (1.3 mL). Solutions of guests **1-6** (1 mM) were added over a series of five 10 μL injections or 50 5 μL injections, and the change in enthalpy was recorded at T =

298.15 K. The heat of dilution was corrected for by injecting guest solutions into deionized water and subtracting the resulting data from the host-guest titrations. Computer simulations (curve fitting) were performed using the Nano ITC analyze software.



A

B



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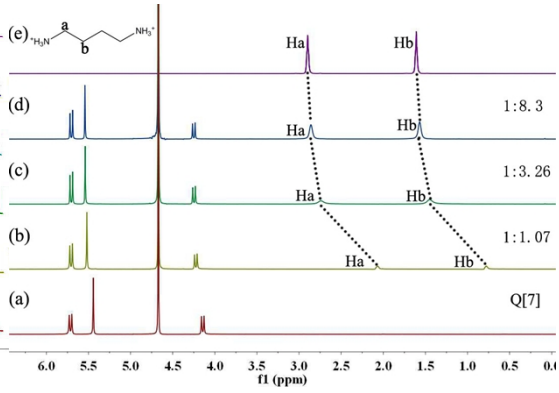

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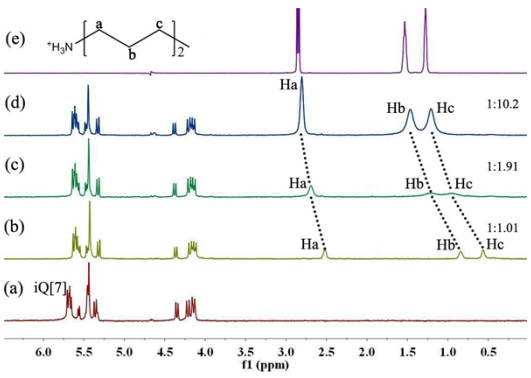

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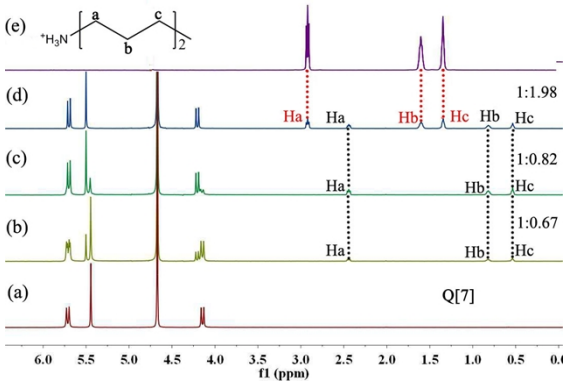

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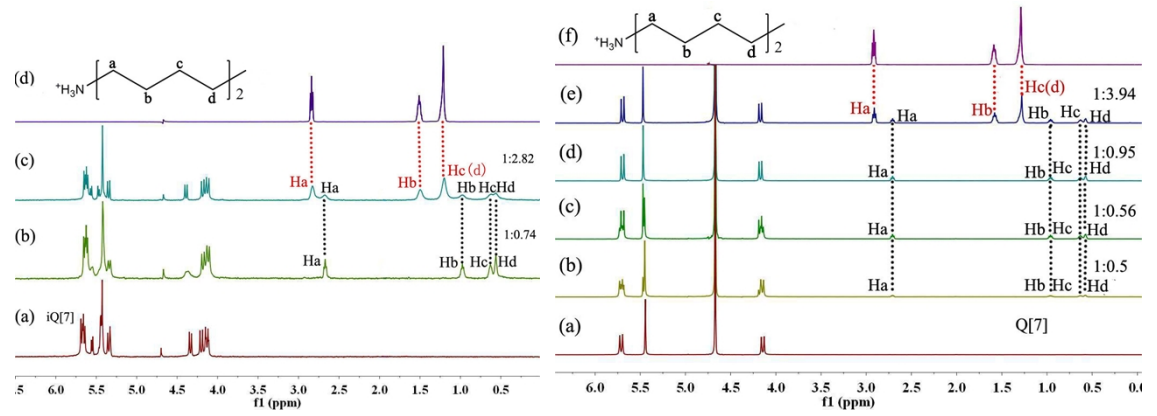
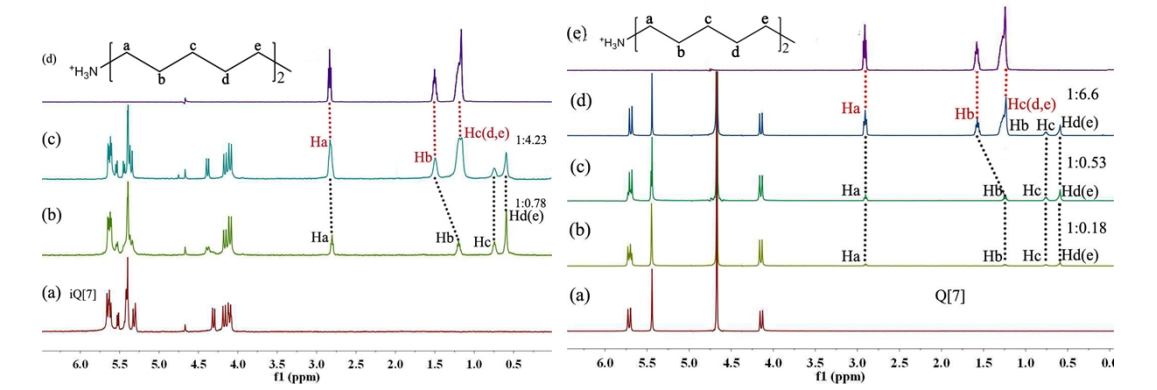


G H



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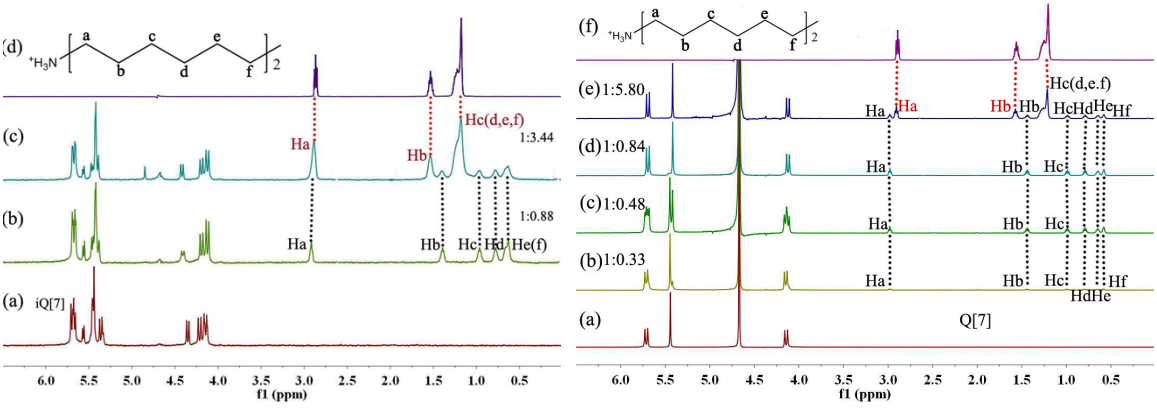
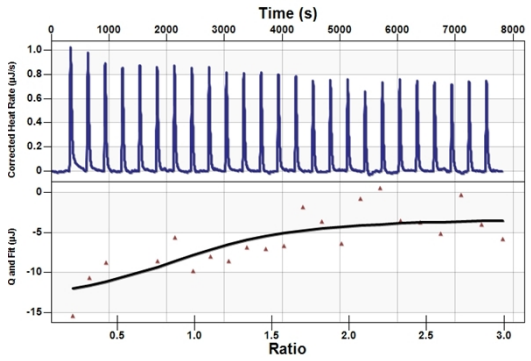


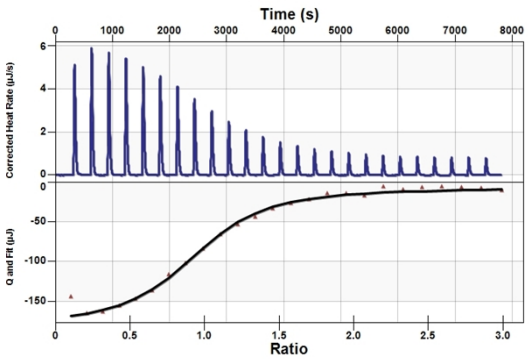
J L

Figure S1 titration ^{1}H NMR spectra (left) for *i*Q[7]-guest (**1**-**6**) respectively, (right) for Q[7]-guest (**1**-**6**) respectively.

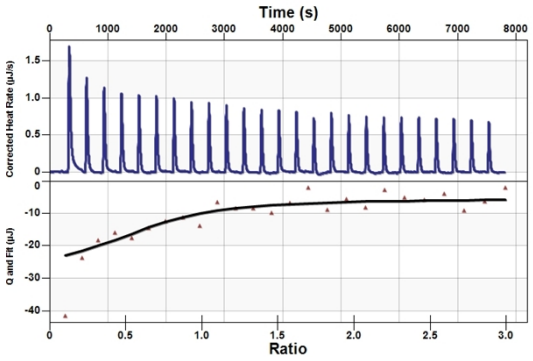
iQ[7]-1



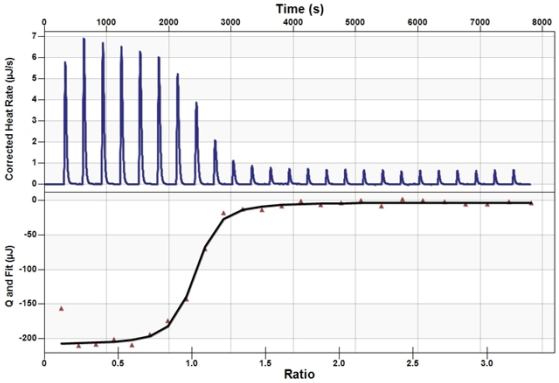
Q[7]-1



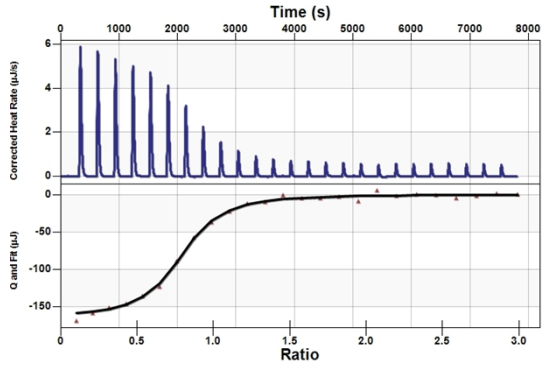
iQ[7]-2



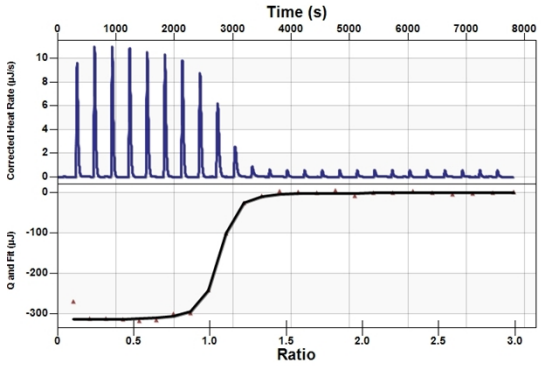
Q[7]-2



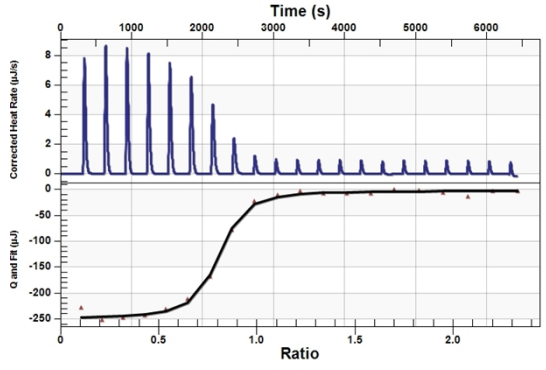
iQ[7]-3



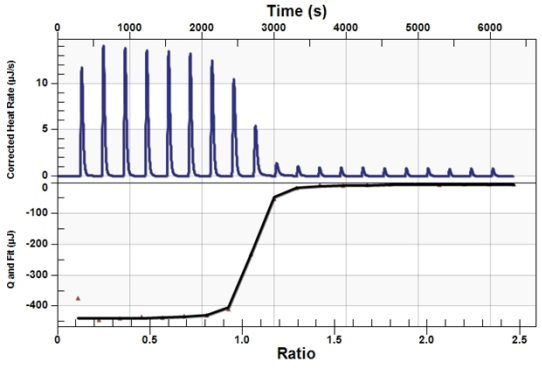
Q[7]-3



iQ[7]-4



Q[7]-4



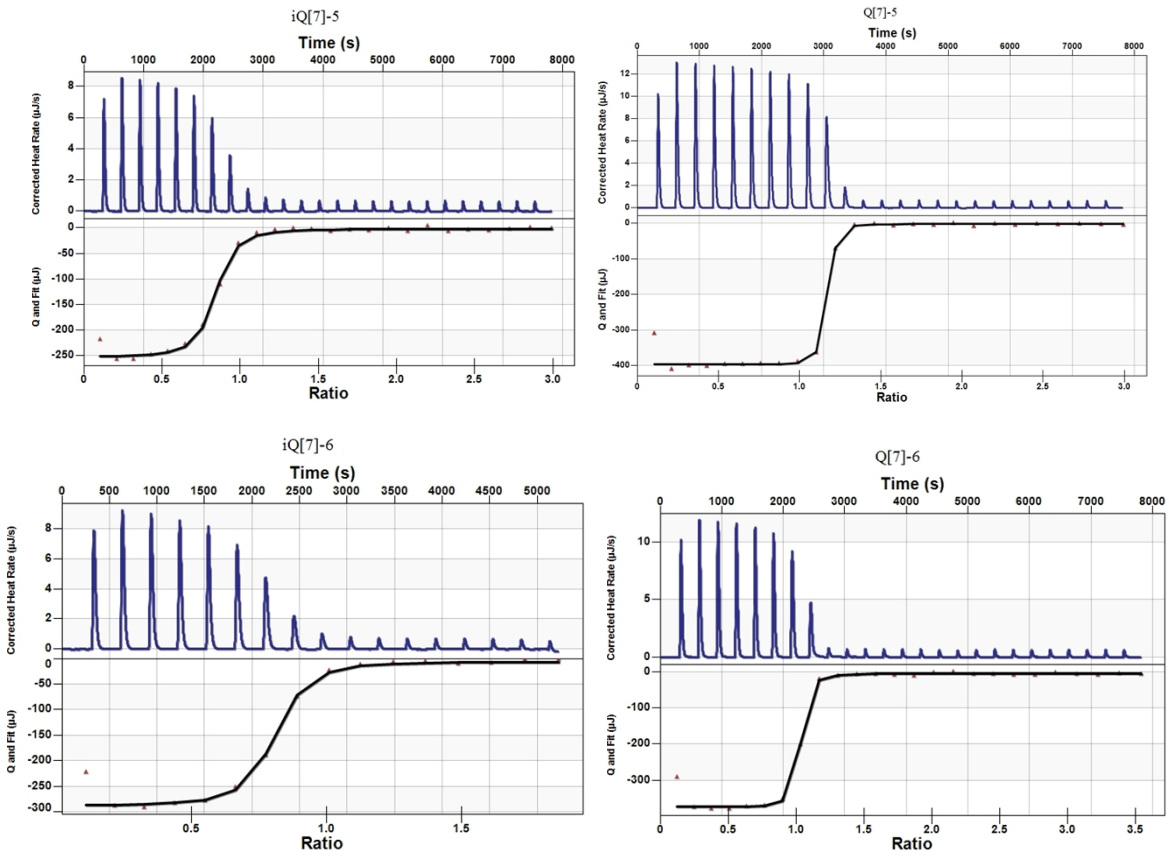
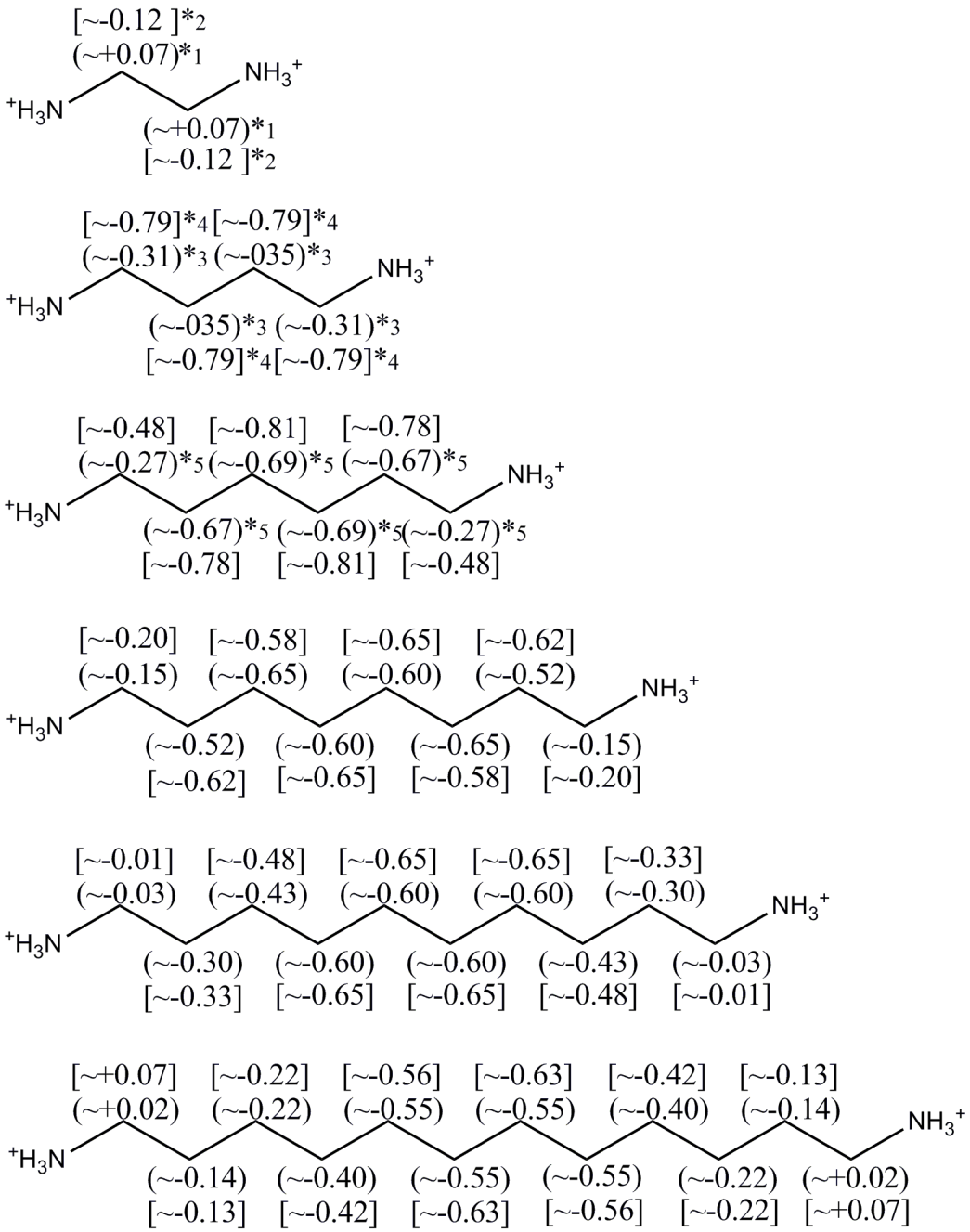


Figure S2 Isothermal titration calorimetry profiles of *i*Q[7] (left) and Q[7] (right) with six diamines respectively at 293.15 K.



*1 iQ[7]:**1**=1:0.32

*2 Q[7]: **1**=1:2

*3 iQ[7]:**2**=1:0.39

*4 Q[7]: **2**=1:1

*5 iQ[7]: **3**=1:1

Figure S3. Structures of *α*,*ω*-alkyldiammonium guests ($H_3N(CH_2)_xNH_3Cl_2$, x = 2, 4, 6, 8, 10, and 12 named **1**-**6**) and relative chemical shifts (Δδ, ppm) upon complexation with *i*Q[7] (round brackets) and Q[7] (square brackets) from ^{1}H NMR spectra.