CHEMICAL COMMUNICATIONS

Pronounced pH effects on the kinetics of cucurbit[7]uril-based pseudorotaxane formation and dissociation

Angel E. Kaifer,[a,]*,Wei Li,[a] Serena Silvi,[b,]* and Vladimir Sindelar[c,]*

[a]*Center for Supramolecular Science and Department of Chemistry, University of Miami, Coral Gables, USA.* [b]*Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy.* [c]*Department of Chemistry, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic and Centre for Toxic Compounds in the Environment, Masaryk University, Kamenice 3, 625 00 Brno, Czech Republic.*

ELECTRONIC SUPPORTING INFORMATION

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Materials and Methods

The pH of the solutions was adjusted by addition of small aliquots of concentrated solutions of HCl and NaOH, and then measured with a pH-meter. The solutions of $\mathbf{1}^{2+}$ and **CB7** also contain NaCl 50 mM, which ensures that the concentration of Na^+ ions does not change significantly when adjusting the pH. Titration experiments were performed adding small aliquots of a concentrated solution of **CB7** (concentration ranging from 5×10^{-4} to 1×10^{-3} M) with a precision Hamilton syringe to a diluted solution of $\mathbf{1}^{2+}$ (concentration ranging from 1×10^{-5} to 5×10^{-5} M). The pH in the titration of Figure S3 was measured directly by means of a pH-meter.

Absorption spectra were recorded with Perkin Elmer Lambda45 and Lambda650 spectrophotometers, on air equilibrated H_2O NaCl 50 mM solutions at room temperature (ca. 298 K), with concentrations ranging from 9×10^{-6} to 1×10^{-3} mol L^{-1}. Solutions were examined in 1-cm spectrofluorimetric quartz cells. The experimental error on the wavelength values was estimated to be ±1 nm. Titration curves were fitted by means of the SPECFIT fitting program.
Reaction kinetic profiles were collected on air-equilibrated H_2O NaCl 50 mM solutions at 293 K with an Applied Photophysics SX 18-MV equipment. The standard flow tube used had an observation path length of 1.0 cm, and the driving ram for the mixing system was operated at the recommended pressure of 8.5 bar. Under these conditions the time required to fill the cell was 1.35 ms (based on a test reaction). As regards the stopped-flow traces, a baseline correction was applied to take into account the dependence of the instrument response on pressure. In all the experiments, the cell block and drive syringes were thermostated by using a circulating constant-temperature bath maintained at the required temperature. The data were fitted by means of the SPECFIT fitting program.

NMR spectra were recorded using a Bruker Avance 300 spectrometer operating at frequencies of 300.13 MHz (^{1}H) at 298 K. In typical experiment, to a 3.54 mM equimolar solution of guest **1** and **CB7** a NaOD was added to adjust pH to 10. Then the competitive guest **2** (7.24 mM) was added and the NMR spectra were recorded for several hours.

Spectroscopic Titrations

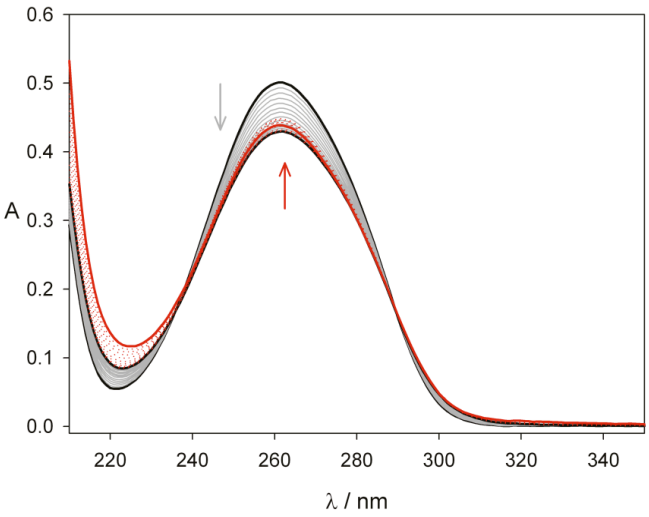

Figure S1. Absorption spectra of a 2.1×10^{-5} M solution of $\mathbf{1}^{2+}$ upon titration with **CB7** up to 1.5 equivalents (grey lines), and from 1.5 to 8 equivalents (red lines). H_2O, NaCl 50 mM, pH 4.

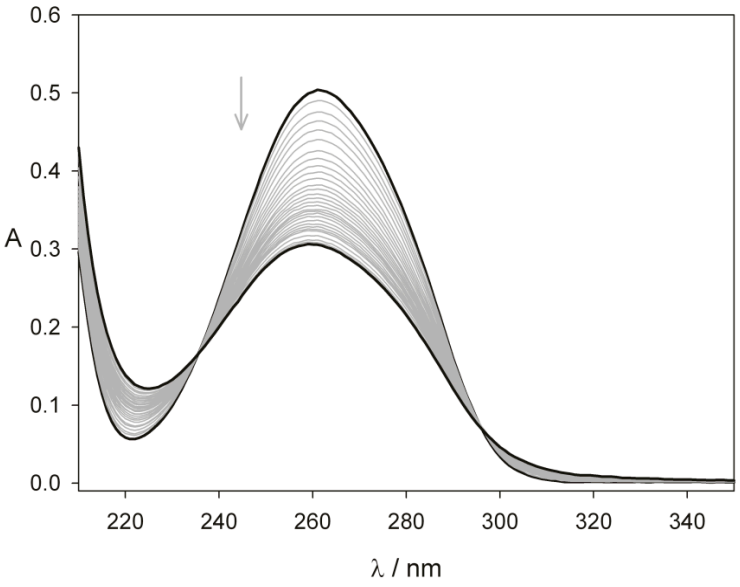

Figure S2. Absorption spectra of a 2.1× 10^{-5} M solution of $\mathbf{1}^{2+}$ upon titration with **CB7**. H_2O, NaCl 50 mM, pH 7.

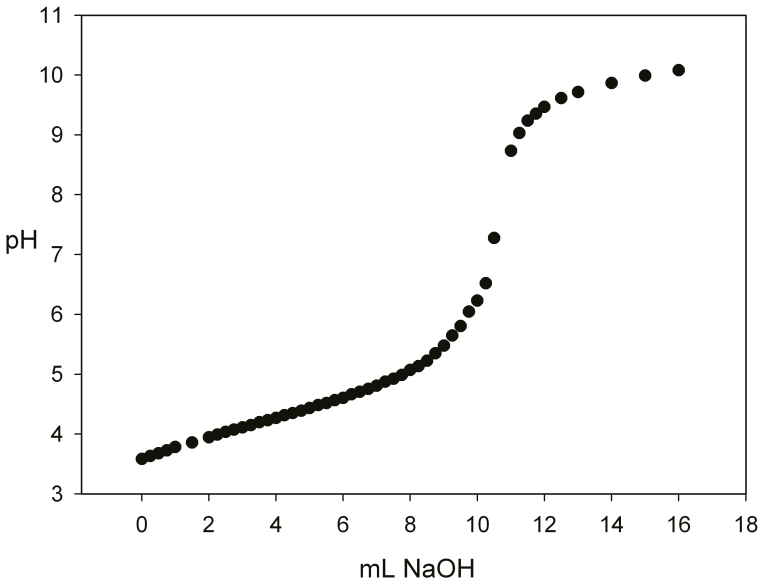

Figure S3. pH titration of 5 mL of a 1×10^{-3} M solution of $\mathbf{1}^{2+}$ with a 1×10^{-3} M solution of NaOH.

Kinetic Experiments

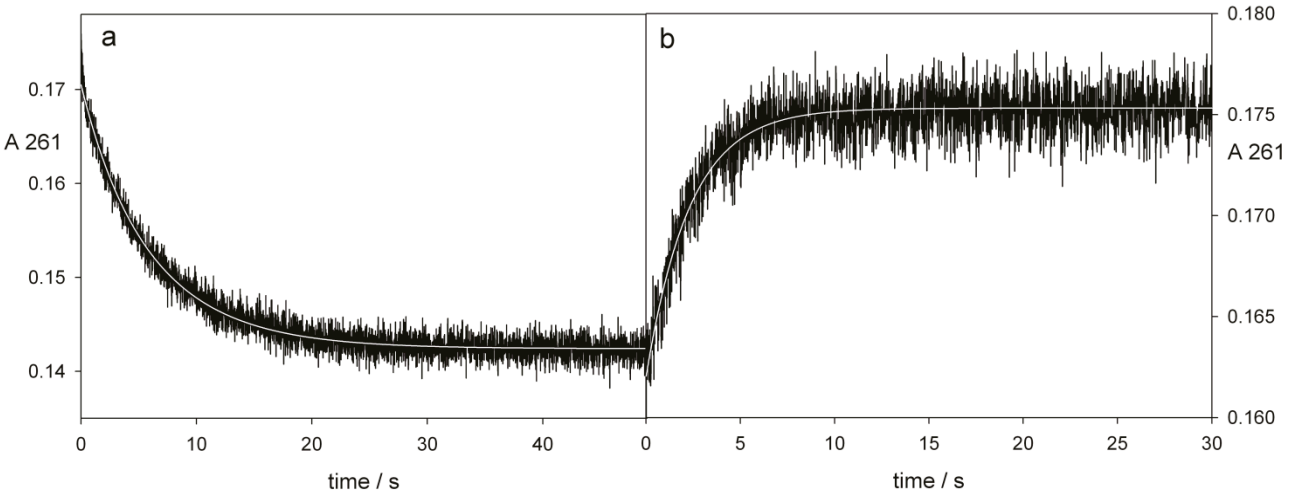

Figure S4. Stopped-flow kinetic traces, recorded at 293 K at pH 2, for the absorbance change at 261 nm obtained upon mixing a) $\mathbf{1}^{2+}$ and **CB7** (concentration after mixing 9×10^{-6} M) and b) **CB7•1**$^{2+}$ (9×10^{-6} M) and 4.5 equivalents of $\mathbf{2}^{+}$ (H_2O, NaCl 50 mM, path length=1.0 cm). Black lines= experimental data, white lines=fitting.

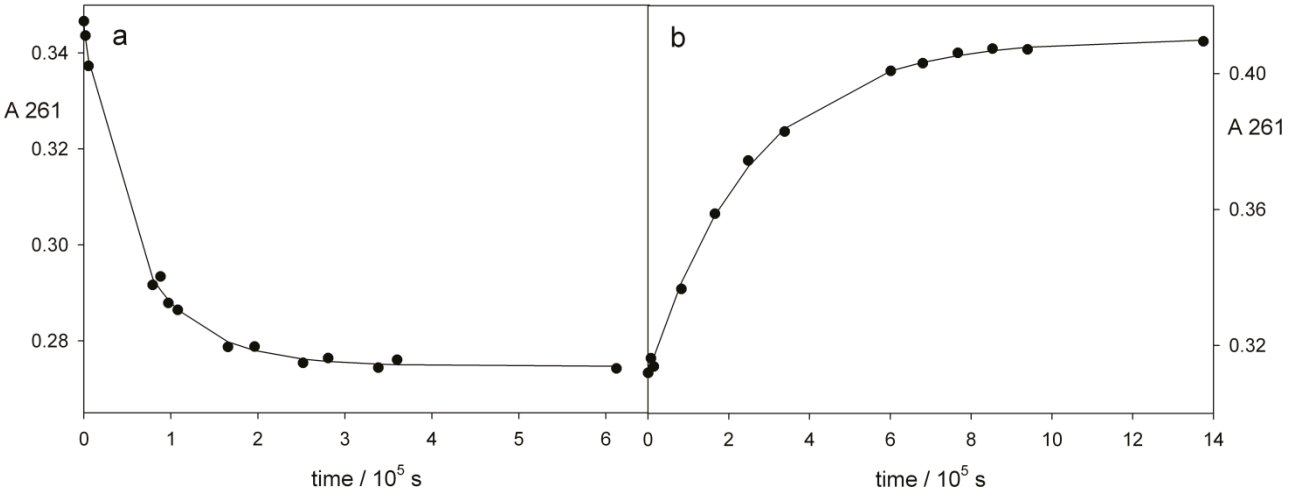

Figure S5. Kinetic traces at pH 11 for the absorbance change at 261 nm obtained upon mixing a) $\mathbf{1}^{2+}$ and **CB7** (concentration after mixing 1.8×10^{-5} M) and b) **CB7•1**$^{2+}$ (1.8×10^{-6} M) and 4.5 equivalents of $\mathbf{2}^{+}$ (H_2O, NaCl 50 mM, path length=1.0 cm). Black circles= experimental data, black lines=fitting.

Simulations

Threading and dethreading kinetic measurements could be simulated by means of the SPECFIT fitting program. For the threading process the followong simplified model was used:

Reaction	Rate constant
a + b > c	k1=1.4 × 10^6 (measured value)
a + d > c	k2=0.6 (measured value)
b > d	k3 = 2 × 10^8
d > b	k4 = 1 × 10^7

where
a=CB7
b=an axle with at least one -COOH
c= the pseudorotaxane
d=an axle with at least one -COO^-
k3 and k4 represent the rate constants of the proton exchange: this process is likely to be very fast. The values have been chosen in order to have a ratio of 20 between -COO^- and COOH units (reasonable at pH 6).

For the dethreading process the following simplified model was used:

Reaction	Rate constant
a > b + c	k1=0.46 (measured value)
d > b + c	k2=3.9 × 10^{-6} (measured value)
a > d	k3 = 2 × 10^8
d > a	k4 = 1 × 10^7

where
a=pseudorotaxane with at least one -COOH
b=CB7
c= free axle
d=pseudorotaxane with at least one –COO^-

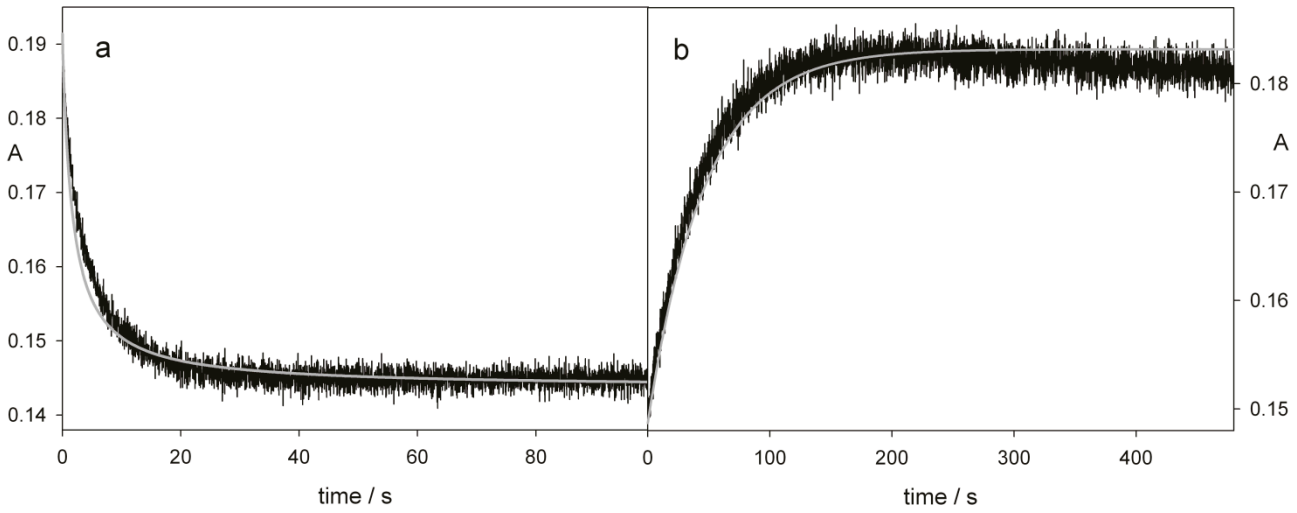

Figure S6. Simulation of the kinetic traces at pH 6 for the threading (a) and unthreading (b) processes (grey lines). The black lines are the stopped-flow kinetic traces, recorded at 293 K at pH 6, for the absorbance change at 261 nm obtained upon mixing a) $\mathbf{1}^{2+}$ and **CB7** (concentration after mixing 9×10^{-6} M) and b) **CB7•1**$^{2+}$ (9×10^{-6} M) and 4.5 equivalents of $\mathbf{2}^{+}$ (H_2O, NaCl 50 mM, path length=1.0 cm).

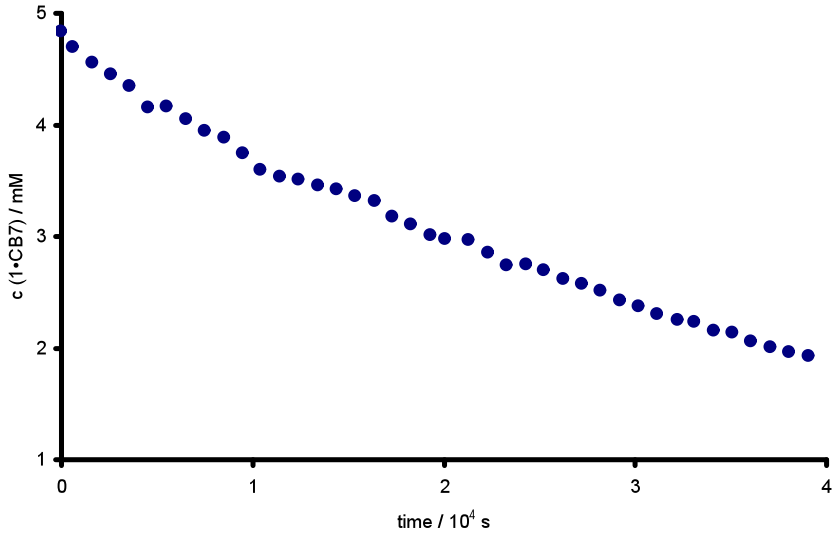

Figure S7. Kinetic traces at pD 10 for the integration of signal α* in ^{1}H NMR spectra obtained upon mixing of **CB7•1**$^{2+}$ (4.83 mM) and 2 equivalents of $\mathbf{2}^{+}$ (D_2O / NaOD).