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pH-Responsive mechanised nanoparticles gated by semirotaxanes

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General Methods: All reagents, including curcubit[6]uril, curcubit[8]uril, and 3-isocyanatopropyltriethoxysilane (3-ICPES) are commercially available and were used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 spectrometer at 25 °C. Chemical shifts were reported in parts per million (ppm) downfield from the Me₄Si resonance which was used as the internal standard when recording ¹H NMR spectra. Powder X-ray diffraction (XRD) measurements were carried out using a Panalytical X'Pert Pro powder diffractometer. The radiation source was copper ($K_{\alpha 1}$ and $K_{\alpha 2} = 1.5418 \text{ \AA}$). FT-IR spectra were recorded on a Perkin-Elmer FT-IR Paragon 500 spectrometer. Dynamic light scattering (DLS) was performed on a Beckman Coulter N4 Plus particle sizer, with a 633 nm HeNe excitation source. The controlled release profiles from the mechanized nanoparticles were obtained via luminescence spectroscopy using an Acton SpectraPro 2300i CCD. SEM images were collected on Hitachi S-3400N-II variable-pressure scanning electron microscope. Samples were sputter-coated with 7 nm Au/Pd to facilitate viewing by SEM.

Preparation of MCM-41: CTAB (1.00 g, 3.0 mmol) was added to deionized H₂O (240 mL). 2 M NaOH (3.5 mL) was added to the solution causing the pH to increase above 12 and inducing the complete dissolution of CTAB. The solution was heated to 80 °C while stirring to create a homogenous solution. Tetraethyl orthosilicate (TEOS, 5.0 mL, 23.0 mmol) was added to the solution dropwise over several min, resulting in the precipitation of the product. The reaction was allowed to go to completion over the course of 2 h. The solution was then filtered while hot using a fritted funnel, and the solid was washed with deionized H₂O and MeOH. The product was dried in an oven at 80 – 100 °C. The

resulting mass after reaction is approximately 2~3 g. The mesoporous structure was observed using XRD, and the size of the nanoparticles were determined using dynamic light scattering. Acidic MeOH was prepared by adding 12 M HCl (1.0 mL) to MeOH (100 mL) and mixing for 10 min. Acidic MeOH was slowly added to the MCM-41 nanoparticles. The nanoparticles were sonicated and then stirred continuously for 6 h at > 60 °C. The solution was filtered through a fritted funnel and washed with MeOH. Extraction was confirmed (Figure S1) by IR spectroscopy. Loss of the C–H stretching peaks verifies the removal of the surfactant. The structure of the MCM-41 nanoparticles post extraction was confirmed by XRD. The size of the nanoparticles was determined using dynamic light scattering (Table S1).

Table S1. Dynamic light scattering data for the MCM-41 nanoparticles.

	Mean (nm)	Standard Deviation (nm)
Run 1	455.2	217.0
Run 2	433.6	208.8
Run 3	427.9	203.2
Average	438.9	209.65

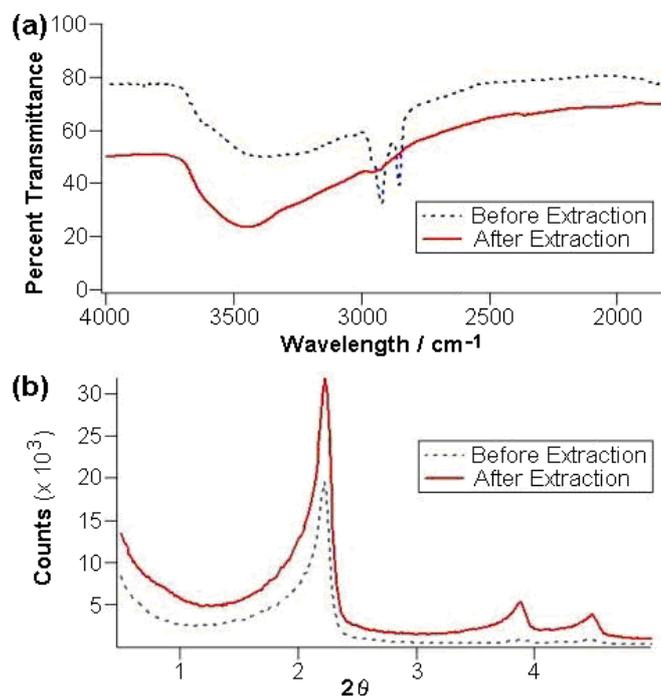


Figure S1. (a) The IR Spectra of the MCM-41 nanoparticles from KBr pellets before and after extraction. The loss of the C–H peak at $\sim 2900\text{ cm}^{-1}$ indicates the removal of the surfactant. (b) The XRD of the MCM-41 nanoparticles before and after extraction. The retention of the spectrum indicates that the meso-structure of the MCM-41 nanoparticles is maintained after the extraction.

Attachment of 3-Aminopropyltriethoxysilane to Surface of MCM-41 Nanoparticles:

Extracted MCM-41 nanoparticles (100 mg) were added to dry PhMe (10 mL) and suspended as a result of stirring and sonication. 3-Aminopropyltriethoxysilane (25 μL , 0.1 μmol) was added to the mixture using a micropipette. The solution was placed under N_2 and heated under reflux overnight. The nanoparticles were removed from solution by filtration using a fritted funnel and washed with PhMe, THF, and MeOH, sequentially. The material was dried overnight under vacuum. The presence of amino groups was confirmed (Figure S2) by IR spectroscopy using the KBr pellet method.

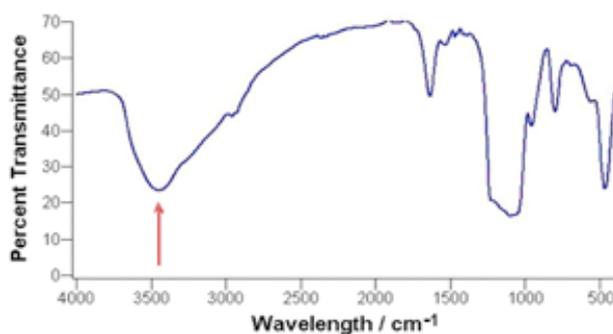


Figure S2. The IR Spectrum of the MCM-41 nanoparticles after extraction and subsequent modification using 3-aminopropyltriethoxysilane. The spectrum was generated using a KBr pellet. The growth of the peak at 3500 cm^{-1} is indicative of the presence of a primary amine group, which leads to the conclusion that the amine modification of the mesoporous glass has taken place.

Coupling Viologen Thread to Amino-Functionalized Mesoporous Silica

Nanoparticles: Viologen dicarboxylic acid ($100\ \mu\text{ mol}$) was added to nanoparticles (50 mg) in dry DMF under nitrogen. Then DCC ($50\ \mu\text{ mol}$) and a catalytic amount of DPTS and DMAP (10 mol % of each) were added. The nanoparticles were stirred and sonicated in solution to maximize dispersion. A sample of the mixture was centrifuged and washed with water and methanol successively, and the sample was dried over night under vacuum. The presence of amide and carboxylic acid groups was confirmed (Figure S3) by IR spectroscopy using the KBr pellet method.

Loading Nanoparticles with Rhodamine B: A Rhodamine B (0.48 g , 1 mM) solution (100 mL) was prepared using volumetric equipment, and an aliquot (10 mL , 1 mM) was added to the reaction flask containing nanoparticles (50 mg). The nanoparticles were

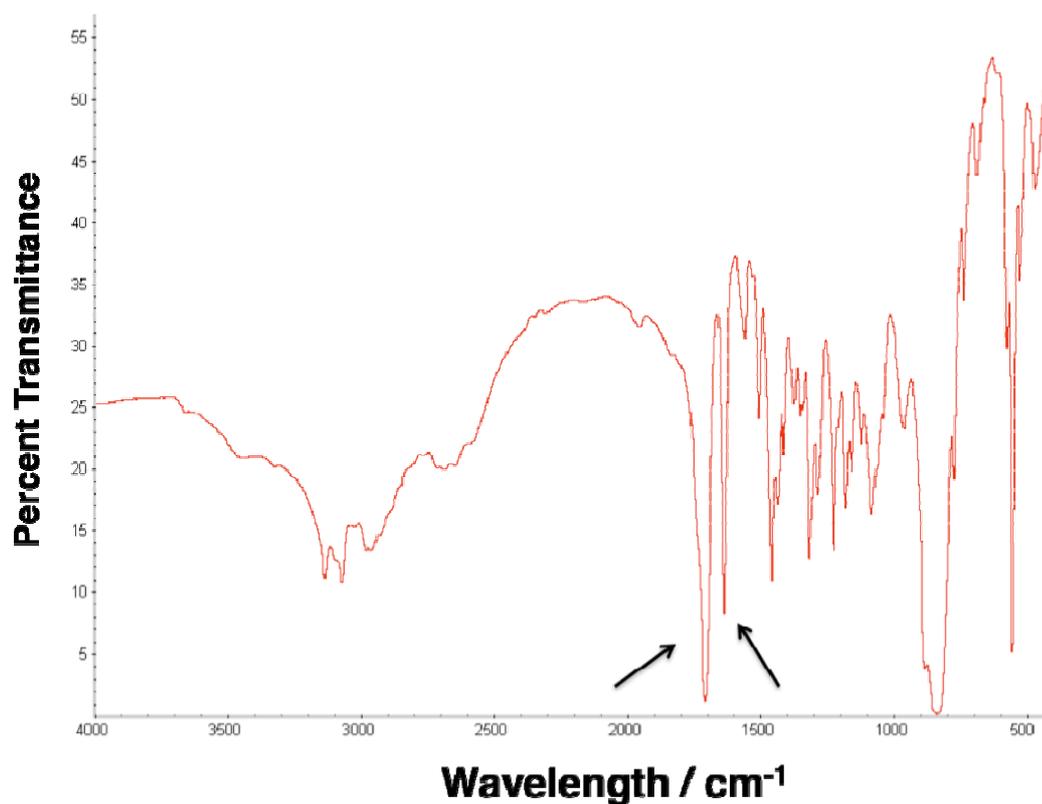


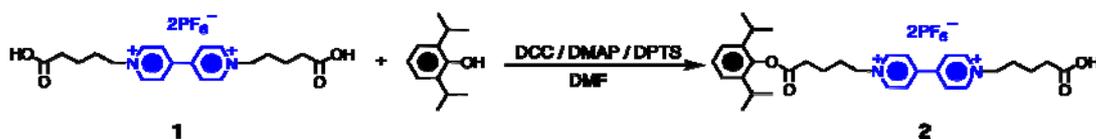
Figure S3. The IR Spectrum of the MCM-41 nanoparticles coupled with the viologen thread. The spectrum was generated using a KBr pellet. The peaks at 1700 and 1650 cm⁻¹ indicate the presence of carboxylic acid and amide carbonyls.

stirred and sonicated in solution to maximize dispersion, and the solution was then stirred overnight to allow Rhodamine B to diffuse into the nanopores.

Capping Nanoparticles with CB[6]: CB[6] (100 μ mol) was added to an aqueous solution containing the Rhodamine B-loaded nanoparticles (50 mg). The mixture was then stirred and sonicated. After complete solvation of **CB[6]**, the solution was left to stir

for > 12 h. The nanoparticles were separated from solution by centrifugation and were then washed with H₂O and MeOH. The product was separated from the washings by centrifugation, and the nanoparticles were subsequently dried under vacuum overnight for analysis. Further characterization of the mechanized nanoparticles was accomplished (Figure S4) by SEM.

Synthesis of Stoppered Viologen Thread 2



Viologen **1** (1.00 g, 1.54 mmol), 2,6-diisopropyl phenol (0.14 g, 0.77 mmol), DPTS, (18 mg, 0.077 mmol), and DMAP (9 mg, 0.077 mmol) were added to anhydrous DMF (20 mL), and the solution was evacuated and purged with nitrogen three times. A solution of DCC (0.35 g, 1.70 mmol) in DMF (5 mL) was then added via syringe, and the solution was stirred at room temperature for 16 h. The solution was then filtered through a pad of celite and washed with a minimal amount of DMF. The filtrate was evaporated and purified by reverse phase HPLC yielding 286 mg (23 %) of pure compound. ¹H NMR (500 MHz, D₂O): δ 9.14 (t, *J* = 4.5 Hz, 2H), 9.00 (t, *J* = 4.5 Hz, 2H), 8.54 (t, *J* = 4.5 Hz, 2H), 8.50 (t, *J* = 4.5 Hz, 2H), 7.31 (d, *J* = 6.0 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 2H), 4.77 (t, *J* = 6.0 Hz, 2H), 4.73 (t, *J* = 6.0 Hz, 2H), 2.88 – 2.81 (m, 4H), 2.44 (t, *J* = 6.0 Hz, 2H), 2.21 (t, *J* = 6.0 Hz, 2H), 2.10 (t, *J* = 6.0 Hz, 2H), 1.83 (t, *J* = 6.0 Hz, 2H), 1.65 (t, *J* = 6.0 Hz, 2H), 1.10 (d, *J* = 4.6 Hz, 2H); ¹³C NMR (500 MHz, D₂O): δ 177.9, 175.2, 160.0, 151.6, 150.0, 145.4, 144.4, 140.6, 127.5, 126.9, 125.0, 124.5, 71.5, 61.6, 60.3, 31.3, 30.0, 27.1, 22.8, 20.6, 20.5, 18.3.

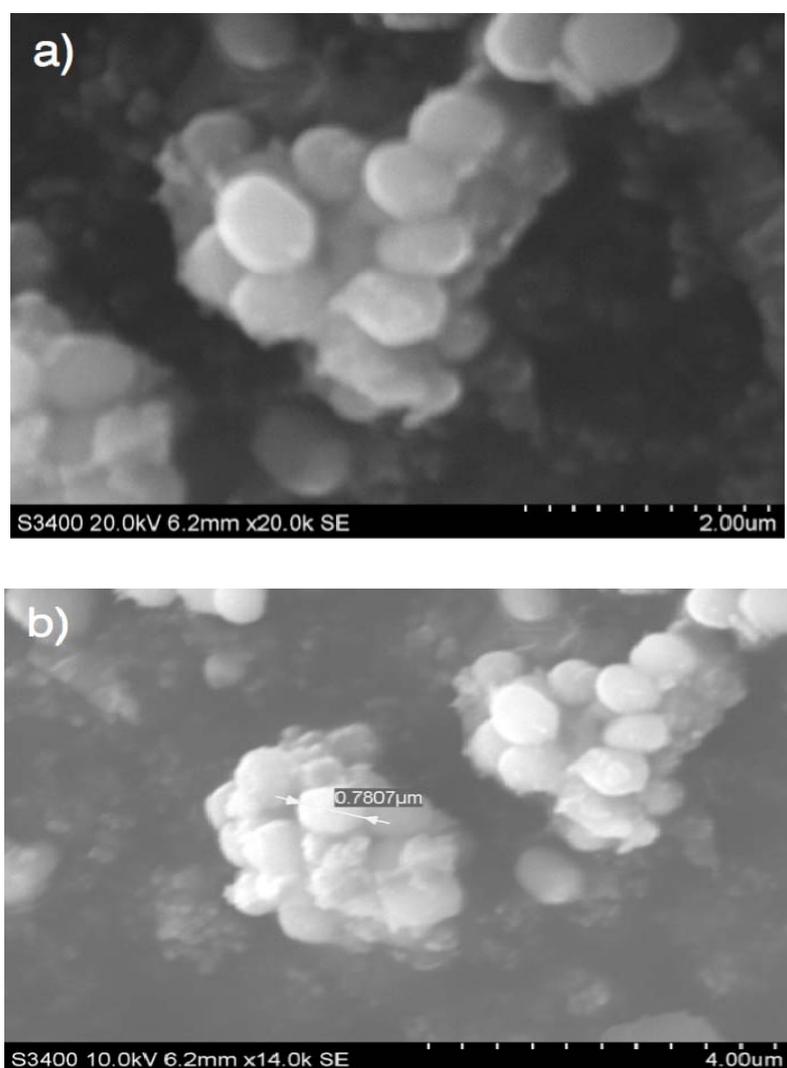


Figure S4. a) SEM image of viologen-functionalized mesoporous silica nanoparticles. b) SEM image showing the size of an individual nanoparticle.

Controlled Release Experiments. Luminescence spectroscopy was used to monitor the release of dye molecules as a function of time. The spectroscopic setup for the controlled release experiments is illustrated in Figure S5.

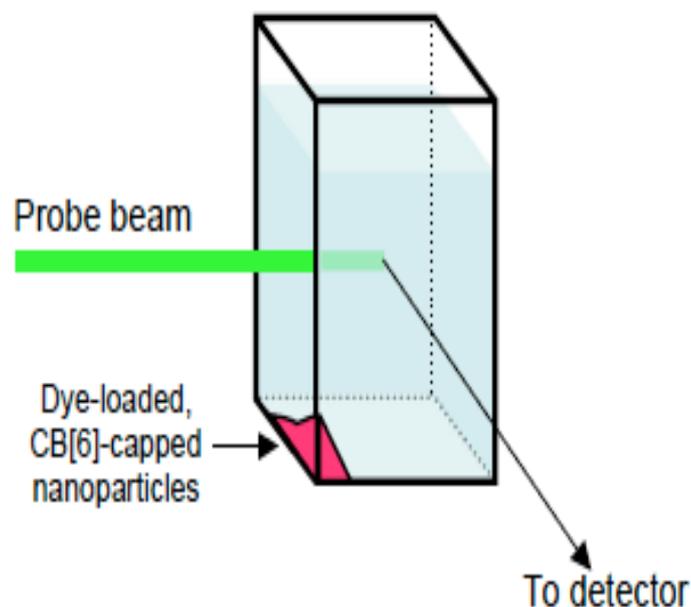


Figure S5. Spectroscopic setup for the controlled release experiments for the [2]pseudorotaxane ($1 \subset \text{CB}[6]$).

Dye-loaded, **CB[6]**-capped nanoparticles (5 mg) were placed in the corner of a cuvette ($\ell = 1$ cm), and deionized H_2O (2 mL) was added. A 10 mW, 530 nm probe beam, directed into the liquid, was used to excite the dissolved dye molecules. The release profiles were obtained by plotting the luminescence intensity at the emission maximum (~ 575 nm) as a function of time. The emission intensity of the dye was relatively constant prior to acid addition. Adjustment to pH 4, upon the addition of acetic acid, resulted (Figure S6) in a gradual increase in luminescence intensity, corresponding to the pseudorotaxane dethreading, and the consequent release of dye molecules.

Absorption: In order to determine how much dye was released during an experiment, the absorption spectrum of the dye dissolved in aqueous solution was recorded before and after the release process. A sample was prepared as usual for controlled release experiments: dye-loaded, CB6-capped silica nanoparticles, (5 mg) were placed in the corner of a cuvette ($\ell = 1$ cm), and DI H₂O (2 mL) was added. At this point, an absorbance spectrum of the solution on top of the particles was recorded using a Cary 300 (Varian) spectrophotometer maintained at 25.0 ± 0.2 °C by the flow of a Haake NB 22 thermostat. Then the controlled release experiment was carried out and the absorbance of the solution on top of the particles was re-measured until it stabilizes.

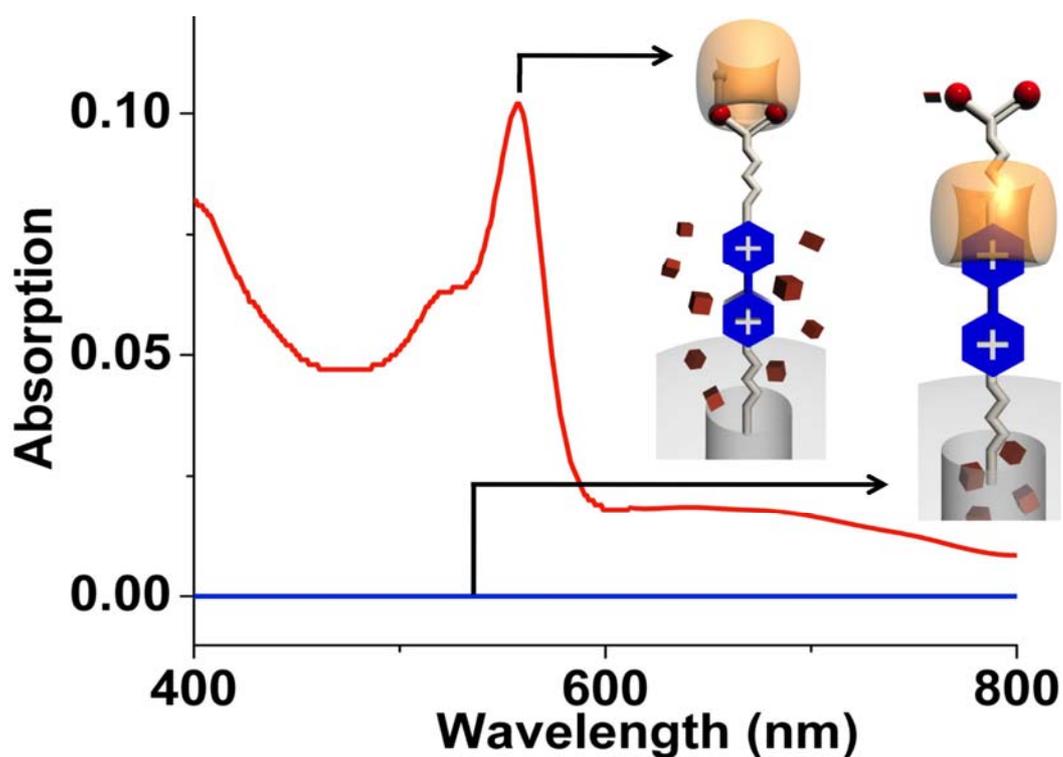


Figure S6. The absorption spectrum of RhB released from **1** \subset **CB[6]** before (blue) and after (red) the pH-activated release process.

The absorbance of the solution (Figure S7) prior to release is almost zero, but is significantly increased after acid activation. Using Beer's Law, it can be calculated that for 5 mg of particles, 1.4 μ mol of dye molecules is released.

NMR Expansion of Figure 1

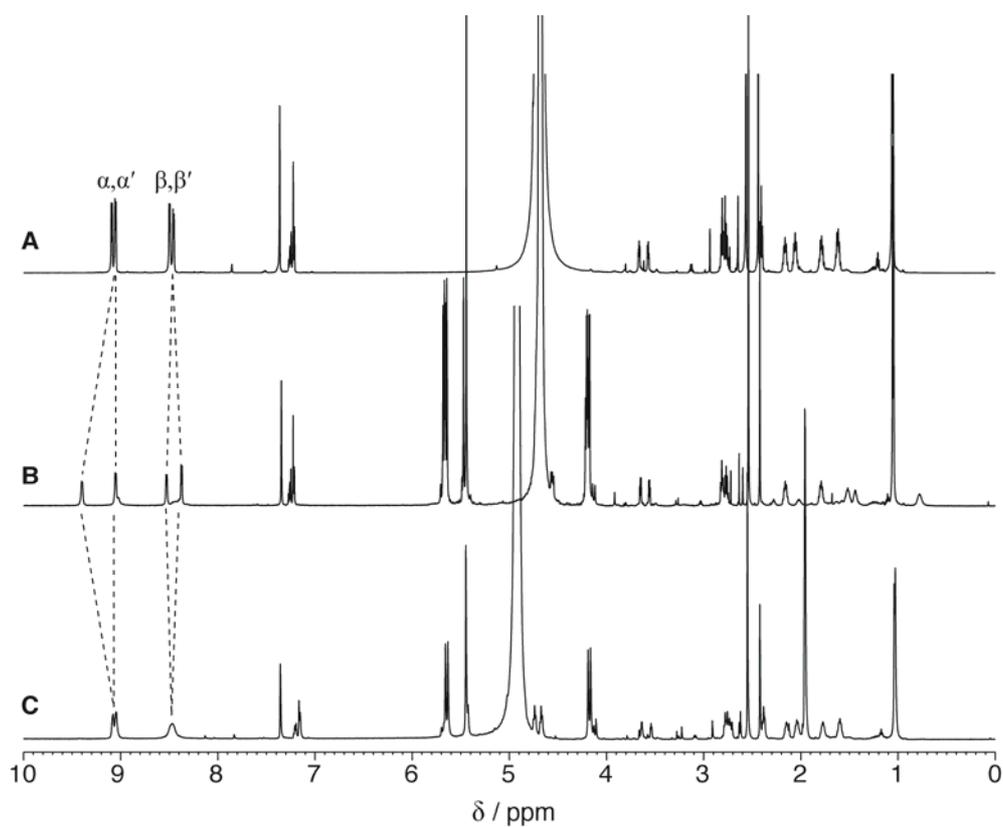


Figure S7. Expansion of Figure 1, Full ¹H NMR Spectrum (600 MHz, 10 mM phosphate D₂O, 298K) of (a) thread **2**·2PF₆ (b) in the presence of 1.0 equiv of CB[6] and (c) after the addition of CD₃CO₂D (pH 4)