Supplementary Material (ESI) for Chemical Communications

Molecular switch based on a cucurbit[6]uril containing bistable [3]rotaxane

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Electronic Supplementary Information

TABLE OF CONTENTS

GENERAL

All reagents and solvents were of the commercial reagent grade and used without further purification except where noted.

Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance DPX-400 MHz nuclear magnetic resonance spectrometer. In all cases, samples were dissolved in D_2O with DSS (3-(trimethyl silyl)-1-propanesulfonic acid), sodium salt as an external standard. Mass spectra were recorded in a reflection positive mode on a Bruker Reflex II MALDI-TOF MS spectrometer and the samples were measured in 2,4,6-Trihydroxyacetophenone (5% sol. in Methanol) as matrix. They were dissolved in H_2O (2mg/ml) , 1:1 mixed with the matrix and 0.5 µl of this mixture was add on the target.

SYNTHESIS AND CHARACTERIZATION OF [3]ROTAXANE

CB6 (342 mg, 0.342 mmol) was dissolved in 6 M HCl (5 mL) and the resulting solution was stirred for 30 min. Alkyne **1** (60 mg, 0.342 mmol) and subsequently azide **2** (60 mg, 0.171 mmol) were added under vigorous stirring at room temperature. The resulting solution was stirred at 25 °C for 48 h. The solvent was removed under reduced pressure to obtain a colorless film, which was redissolved in water (5 mL) and precipitated into acetone (50 ml). White precipitate was collected by filtration and redissolved in water; the solution was filtered through 0.45 µm membrane filtrate. Crystallization was carried out by diffusing acetone vapor into the filtrate. The crystals were collected by filtration and dried in a vacuum oven at rt for 12 h.

(430 mg, 95 %).

M.p.: > 300 °C.

Elemental Analysis for $C_{102}H_{136}Cl_4N_{58}O_{24}.22\ H_2O$

Calc.: C, 39.80; H, 6.06; N, 25.86; Found: C, 39.55; H, 5.86; N, 26.24.

IR (KBr, pellet, cm^{-1}): 3443 (m), 2927 (w), 2353 (vw), 1735 (vs), 1473 (vs).

^1H NMR (400 MHz, D_2O): δ 1.3–1.5 (m, 8H, f + g), 1.6 (s, 9H, *t*-butyl), 2.1 (m, 2H, e), 3.3 (t, 2H,$^3J_{HH}$ = 8.1 Hz, d), 3.8 (t, 2H, $^3J_{HH}$ = 6.3 Hz, a), 4.1 (s, 2H, c), 4.15 (t, 2H, b overlapped with CB6), 4.2 (d,12H, $^2J_{HH}$ = 15.6 Hz, CB6), 5.45 (s, 12H, CB6), 5.94 (dd, 12H, $^2J_{HH}$ = 15.6 Hz, CB6), 6.5 (s, 1H, t).

^{13}C NMR (100 MHz, D_2O): δ 25.2, 25.5, 28.7, 39.9, 41.8, 47.6, 49.1, 51.3 (CB6), 51.5 (CB6), 56.4, 58.6, 70.2 (CB6), 120.6 (triazole, = CH), 139.0 (triazole, = CR), 156.2 (CB6), 156.6 (CB6).

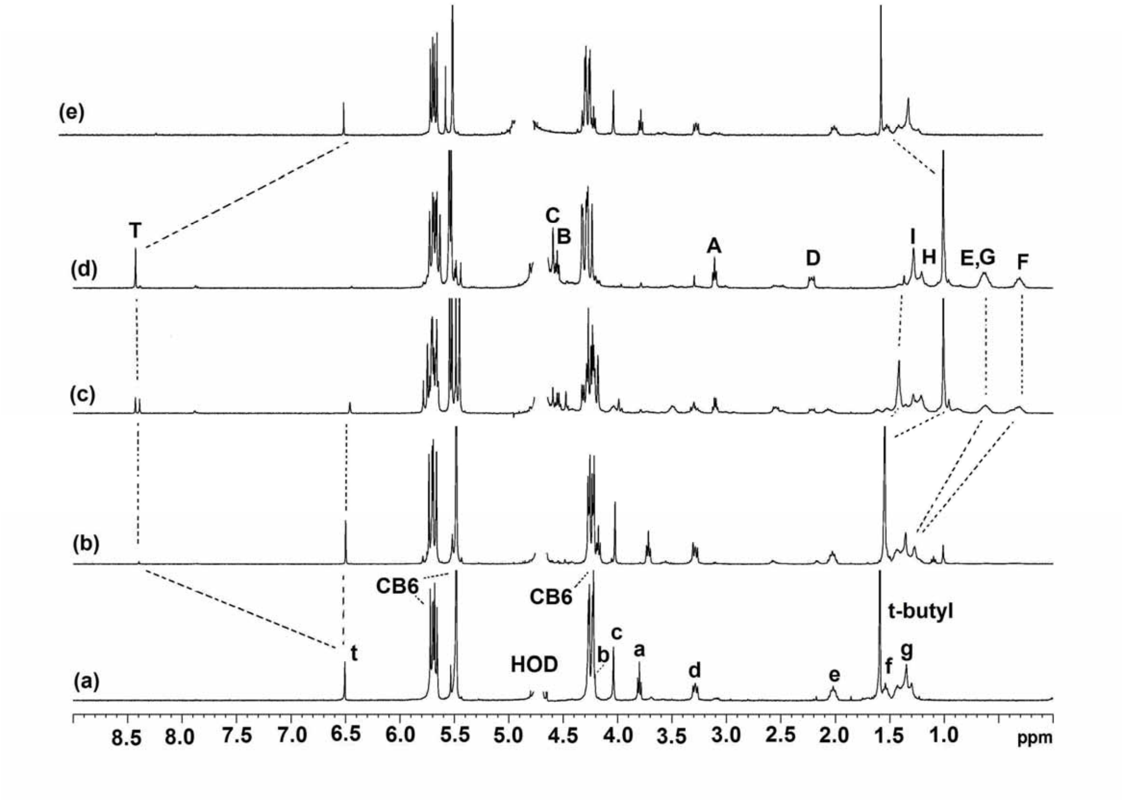

FIGURE S1: ^{1}H NMR (400 MHz, D_2O,25 °C) spectra of; before the addition of base or acid (a) State I, after the addition of (b) 1 equiv of NaOH, (c) 3 equiv of NaOH, (d) 5 equiv of NaOH, (e) after addition of excess HCl and heating the solution to 60 °C for 3 min. and cooling to rt.