Electronic Supplementary Material (ESI) for CrystEngComm.

Supramolecular Organic Frameworks of Cucurbit[n]uril-Based [2]Pseudorotaxanes in the Crystalline State

Supporting Information

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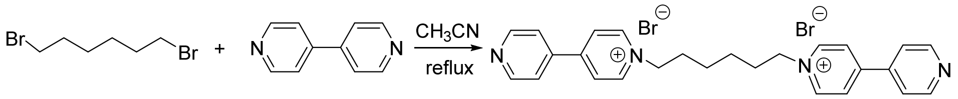
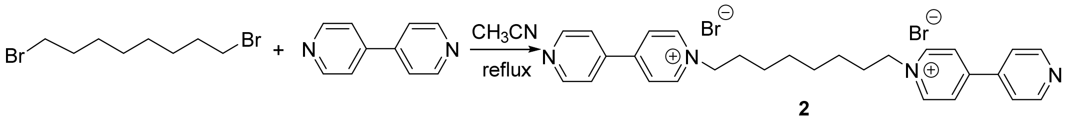
General Experimental Details. Starting materials were purchased from commercial suppliers were used without further purification. Compounds **1**,[1] **2**,[1] and **3**[2] were prepared according to the literature procedures. NMR spectra were measured on a spectrometers operating at 400 MHz for ^{1}H NMR spectra. Mass spectrometry was performed using a JEOL AccuTOF electrospray instrument (ESI). The isothermal titration calorimetry (ITC) experiments were performed on MicroCal iTC200. Thermal gravimetric analysis (TGA) experiments were performed on NETZSCH STA 449C Simultaneous Thermal Analyzer over the temperature 30–920 °C in a nitrogen-gas atmosphere. X-ray powder diffraction (XRD) experiments were recorded on Bruker D8 ADVAHCL.

Synthetic Procedures and Characterization Data.



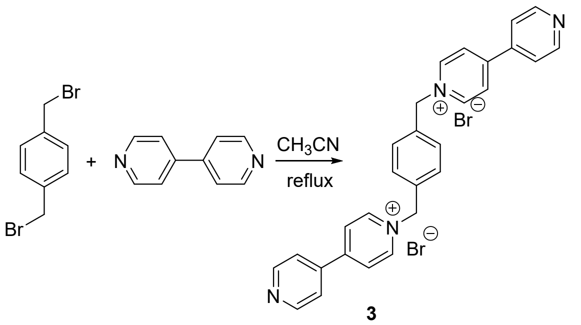
1

Compound 1. In a 100mL round flask, 4,4'-bipyridine (5.0 g, 32.0 mmol) was dissolved in CH_3CN (50 mL). 1,6-Dibromohexane (1.8 g, 8.3 mmol) in 20 mL of CH_3CN was added drop-wise the refluxing solution. The reaction mixture was maintained under reflux for a further 24 h. A precipitate produced was appeared and then filtered. The filter cake was washed with CH_3CN and then recrystallized from water to afford the product as a solid. The ^{1}H NMR matches that reported in the literature.[1]



2

Compound 2. In a 100mL round flask, 4,4'-bipyridine (5.0 g, 32.0 mmol) was dissolved in CH_3CN (50 mL). 1,8-Dibromooctane (2.26 g, 8.3 mmol) in 20 mL of CH_3CN was added drop-wise the refluxing solution. The reaction mixture was maintained under reflux for a further 24 h. A precipitate produced was appeared and then filtered. The filter cake was washed with CH_3CN and then recrystallized from water to afford the product as a solid. The ^{1}H NMR matches that reported in the literature.[1]



3

Compound 3. 4,4'-bipyridine (592 mg, 3.79 mmol) was dissolved in 10 mL of acetonitrile in a 50 mL round flask and the solution was brought to reflux. Next, *p*-bis-(bromo-methyl)benzene (100 mg, 0.38 mmol) was dissolved in 5 mL of acetonitrile. This solution was added to the bipyridine refluxing solution slowly. Then the mixture was refluxed for an additional 24 h. The precipitate formed was filtered and washed with acetonitrile (3 × 35 mL), and dried in high vacuum. The ^{1}H NMR matches that reported in the literature.[2]

References

1. Zhang, Z.; Zhang, Y.; Liu, Y. *J. Org. Chem.* **2011**, *76*, 4682-4685.
2. Geuder, W.; Hunig, S; Suchy, A. *Tetrahedron* **1986**, *42*, 1665-1677.

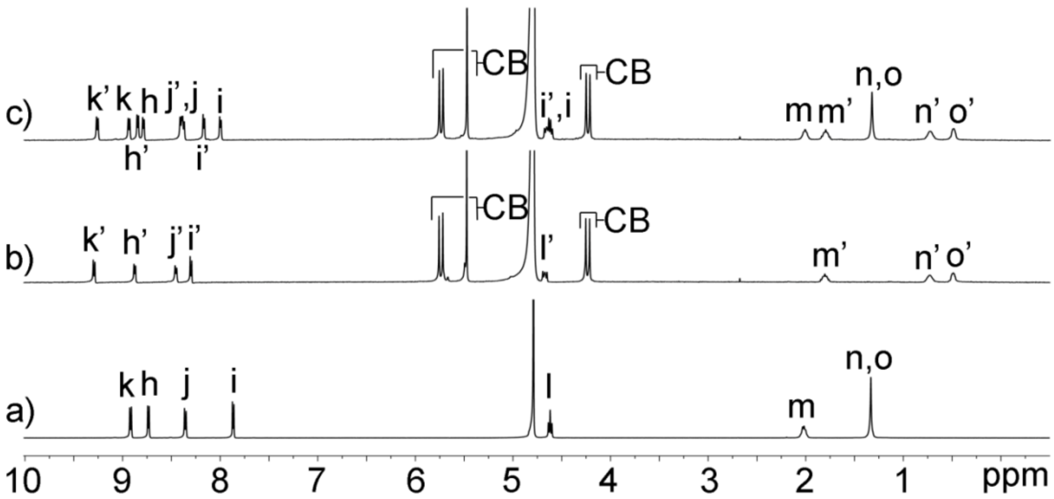


Figure S1. ^{1}H NMR spectra recorded (400 MHz, 298 K, D_2O) for: a) **2** (0.5 mM), b) pseudorotaxane CB[6]•**2** (0.5 mM), c) CB[6]•**2** (0.5 mM) and free **2** (0.5 mM). Here primed (') denote protons binding with CB[6].

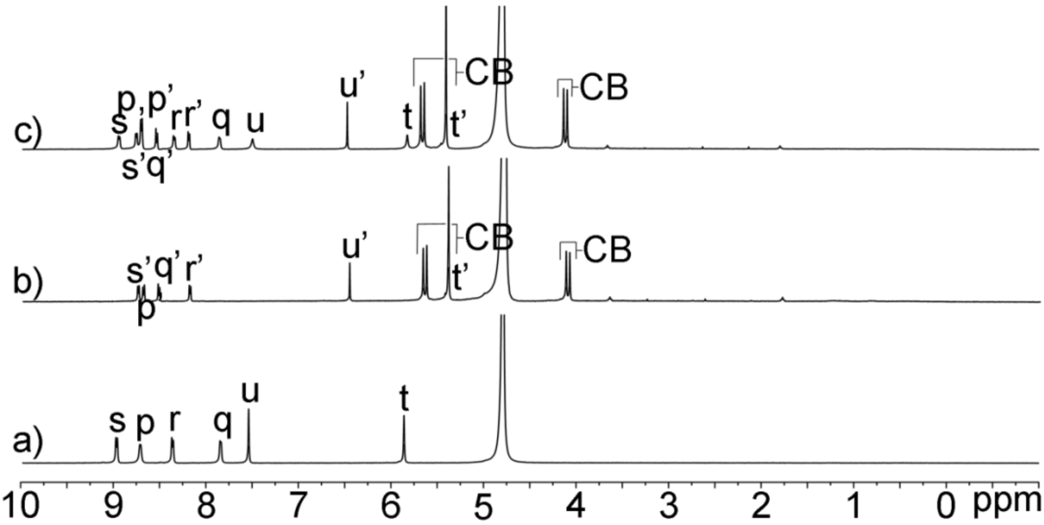


Figure S2. ^{1}H NMR spectra recorded (400 MHz, 298 K, D_2O) for: a) **3** (0.5 mM), b) pseudorotaxane CB[7]•**3** (0.5 mM), c) CB[7]•**3** (0.5 mM) and free **3** (0.5 mM). Here primed (') denote protons binding with CB[7].

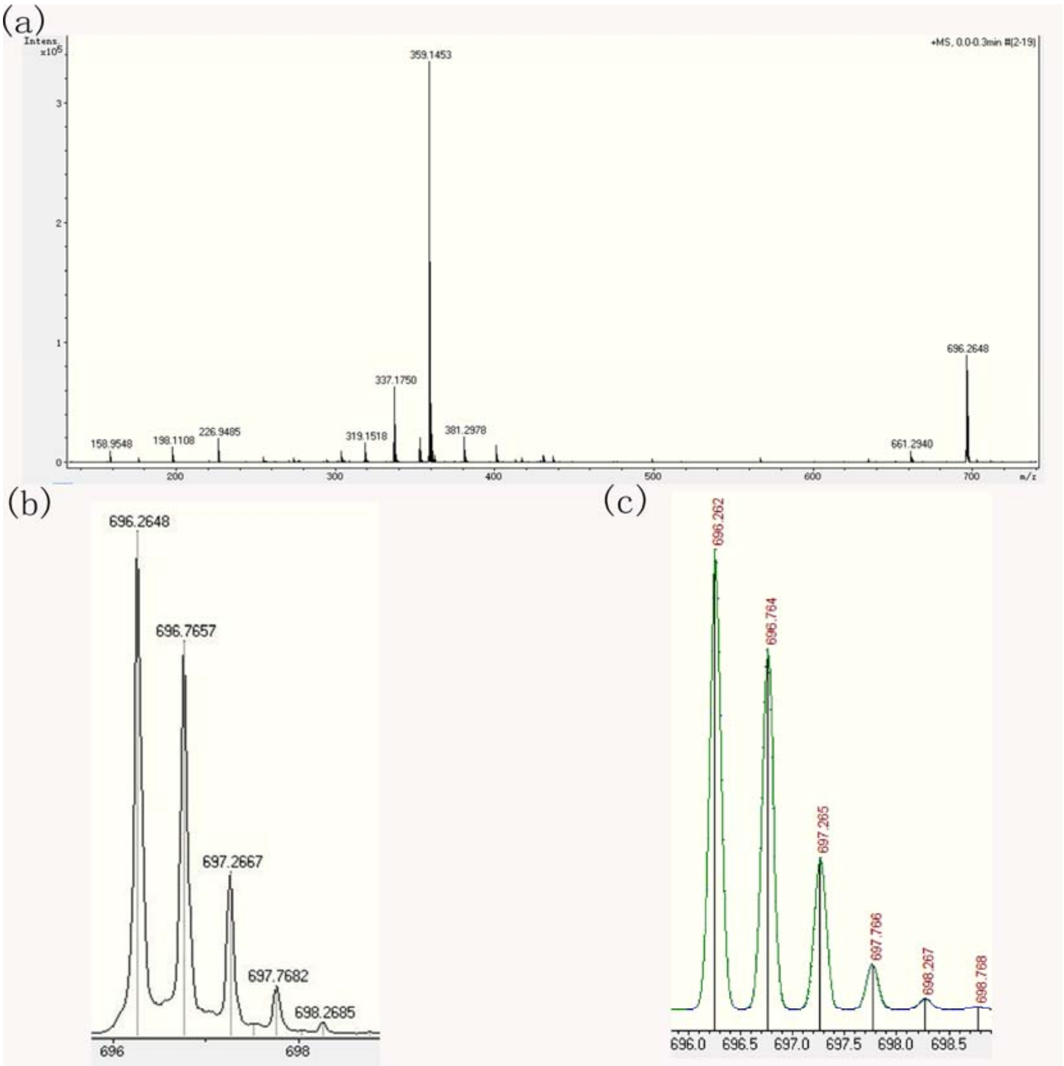


Figure S3. a) High-resolution ESI-MS spectrum for [2]pseudorotaxane [CB[6]•**1**]$^{2+}$; b) measured and c) simulated peaks. Expansions confirm the expect m/z spacing of 0.5 for the 2^{+} ion.

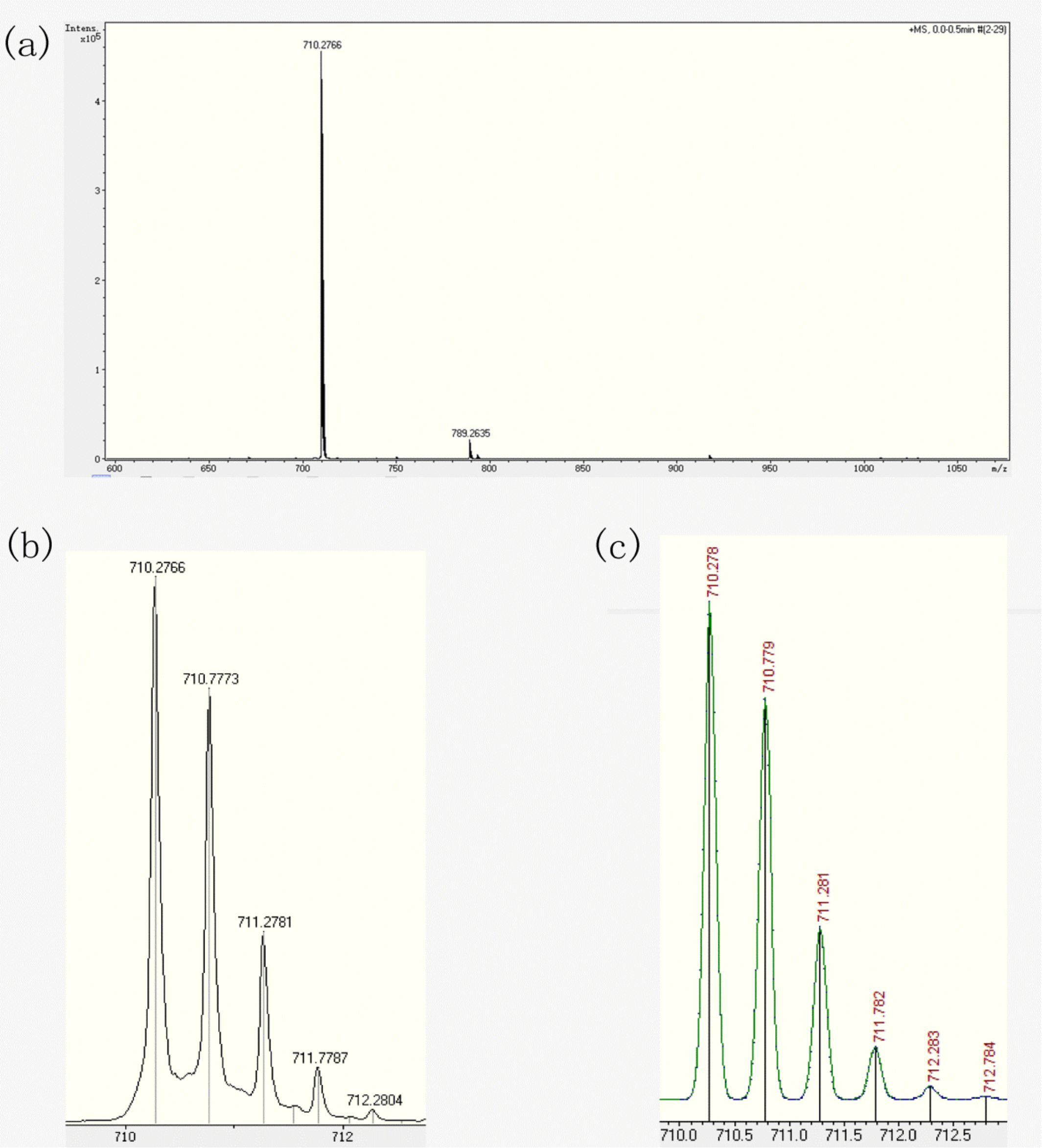


Figure S4. a) High-resolution ESI-MS spectrum for [2]pseudorotaxane [CB[6]•**2**]$^{2+}$; b) measured and c) simulated peaks. Expansions confirm the expect m/z spacing of 0.5 for the 2^{+} ion.

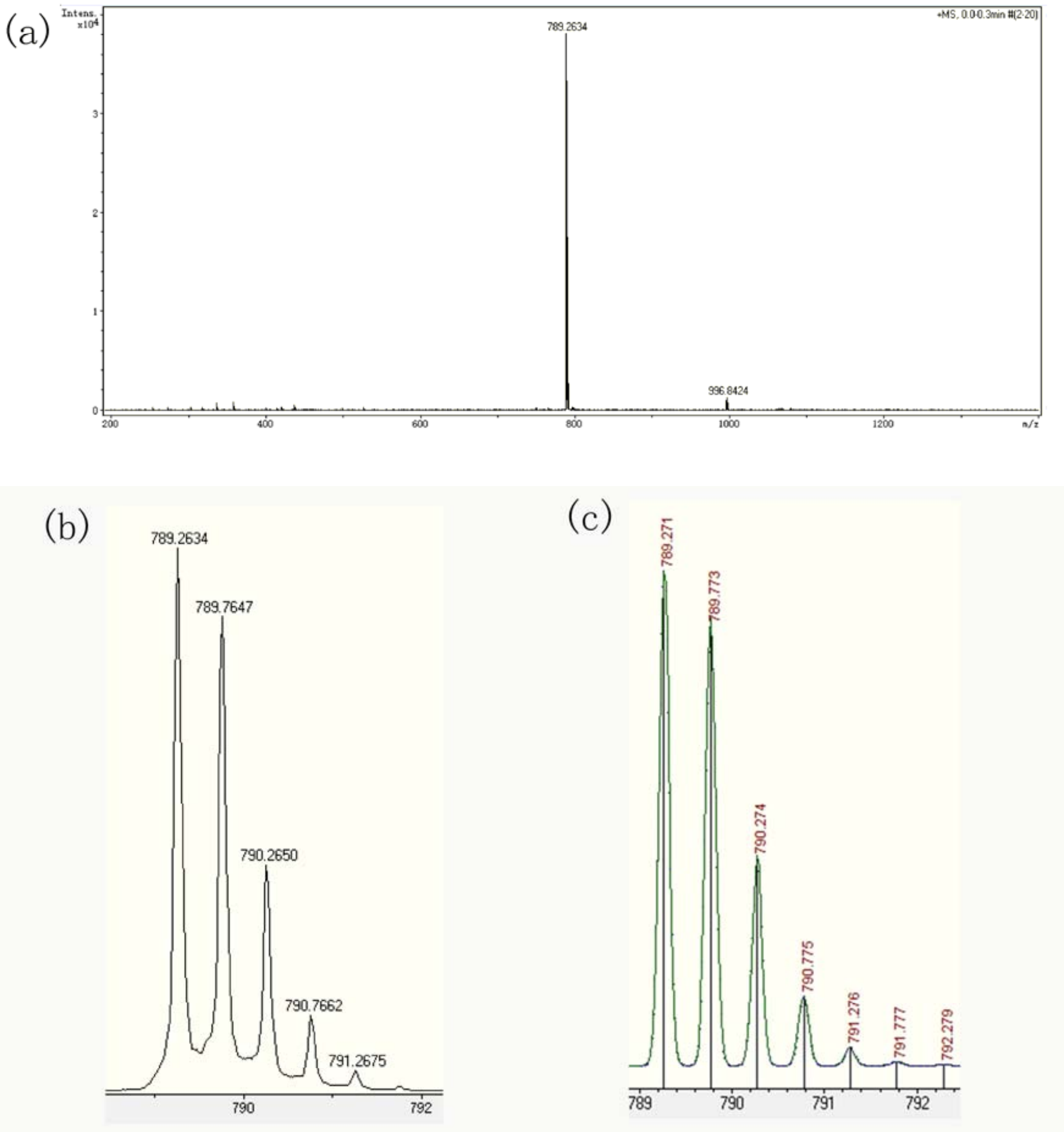


Figure S5. a) High-resolution ESI-MS spectrum for [2]pseudorotaxane [CB[7]•**3**]$^{2+}$; b) measured and c) simulated peaks. Expansions confirm the expect m/z spacing of 0.5 for the 2^+ ion.

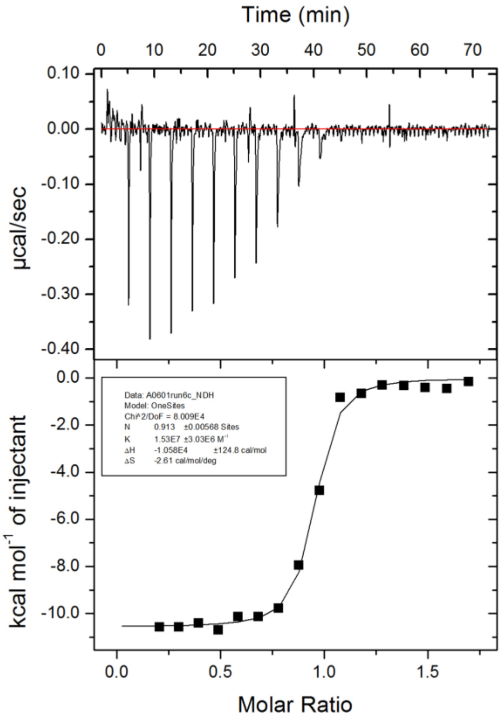


Figure S6. ITC titration data and fitting curves for CB[6] (0.02 mM) titrated by guest **1** (0.21 mM) in Tris buffer solution (10 mM, pH = 7.0) at 298 K. Top: raw ITC data for 17 sequential injection (2μL per injection) of the solution of **1** into the solution of CB[6]; bottom: net reaction heat obtained from the integration of the integration of the calorimetric traces.

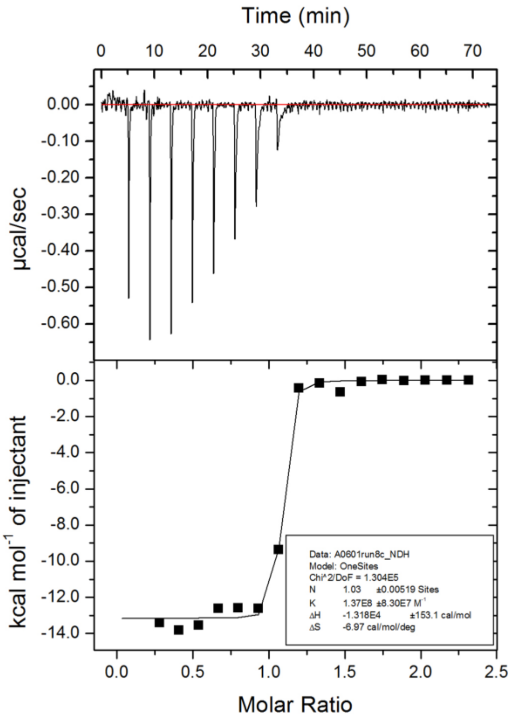


Figure S7. ITC titration data and fitting curves for CB[6] (0.02 mM) titrated by guest **2** (0.28 mM) in Tris buffer solution (10 mM, pH = 7.0) at 298 K. Top: raw ITC data for 17 sequential injection (2μL per injection) of the solution of **2** into the solution of CB[6]; bottom: net reaction heat obtained from the integration of the integration of the calorimetric traces.

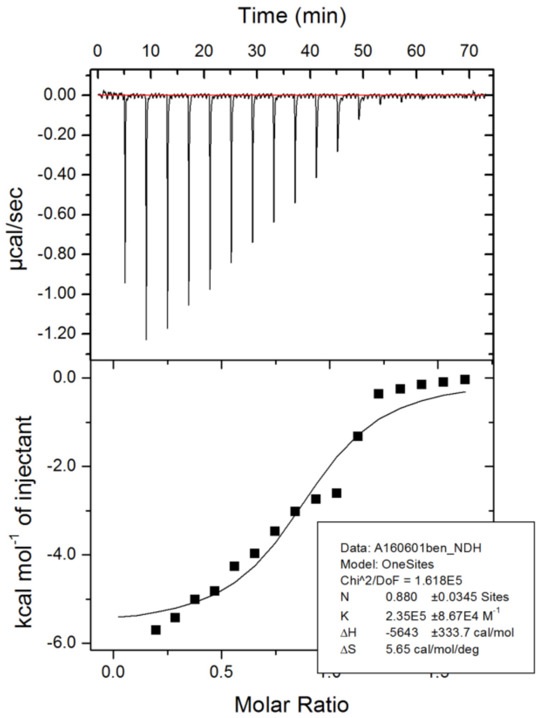


Figure S8. ITC titration data and fitting curves for CB[7] (0.11 mM) titrated by guest **3** (1.01 mM) in Tris buffer solution (10 mM, pH = 7.0) at 298 K. Top: raw ITC data for 17 sequential injection (2μL per injection) of the solution of **3** into the solution of CB[7]; bottom: net reaction heat obtained from the integration of the integration of the calorimetric traces.

X-ray Structure determination. X-ray diffraction data collection of the compounds were performed using a Bruker SMART APEX II diffractometer at 150 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the SHELXL program.

The crystal of CB[6]•**1**: A mixture of CB[6] (1.0 mmol, 997 mg), guest **1** (1.0 mmol, 556 mg) and $NaNO_3$ (4.0 mmol, 588 mg) in water (500 mL) was heated at reflux until all the compounds were dissolved, and for another 12 h at room temperature. After that, the mixture was passed through a 0.45-μm filter into a 20 mL tube. Slow evaporation of this aqueous solution over the period of one week yielded colorless single crystals of CB[6]•**1**. $C_{62}H_{64}ClN_{30}O_{25,}$ M = 1664.88 g/mol, Tetragonal, *P*41212, a = 23.256(3) Å, b = 23.156(3) Å, c = 13.0810(16) Å, α = 90°, β = 90°, γ = 90°, V = 7014(2) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.54676 g·cm^{-3}, final R_1 = 0.0985 and wR_2 = 0.2363 (R_{int} = 0.0632) for 6223 independent reflections [I > 2σ(I)]. There are several alert level B induced by some disordered solvent molecules. CCDC 1483150 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request /cif.

The crystal of CB[6]•**2**: A mixture of CB[6] (1.0 mmol, 997 mg), guest 2 (1.0 mmol, 584 mg) and $NaNO_3$ (4.0 mmol, 588 mg) in water (500 mL) was heated at reflux until all the compounds were dissolved, and for another 12 h at room temperature. After that, the mixture was passed through a 0.45-μm filter into a 20 mL tube. Slow vapor diffusion of acetone into this aqueous solution over three weeks yielded colorless single crystals of CB[6]•**2**. $C_{100}H_{112}N_{56}O_{41}$, M = 2748.95 g/mol, Monoclinic, C2/m, a = 28.597(2) Å, b = 27.378(2) Å, c = 19.9414(15) Å, α = 90°, β = 124.639(1)°, γ = 90°, V = 12845.3(16) $Å^3$, Z=4, $\rho_{calcd.}$= 1.41795 g·cm^{-3}, final R_1=0.0801 and wR_2=0.2379 (R_{int}=0.0342) for 11485 independent reflections [I > 2σ(I)]. Hydrogen atoms were not added on the H_2O molecules, and the disordered

C46, C47 on flexible segment made the alert level B. A severely disordered solvent H_2O with 51 electrons were removed from the asymmetric unit by the SQUEEZE command, which could correspond with the removal of 19.3 molecules of H_2O per unit cell. CCDC 1483151 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request /cif.

The crystal of CB[7]•**3**: A mixture of CB[7] (1.0 mmol, 1163 mg), guest 3 (1.0 mmol, 576 mg) was dissolved in water (10 mL). Then the satured aqueous solution of KI was drop-wise to the mixture. After that, the mixture was passed through a 0.45-μm filter into a 20 mL tube. Slow evaporation of this aqueous solution over the period of three weeks yielded colorless single crystals of CB[7]•**3**. $C_{126}H_{142}Br_6N_{40}O_{28}$, M = 3144.25 g/mol, Monoclinic, P 2_1/c, a = 24.382(2) Å, b = 23.126(2) Å, c = 27.053(3) Å, α = 90°, β = 109.521(1)°, γ=90°, V = 14378(2) $Å^3$, Z = 4, $\rho_{\mathrm{calcd.}}$ = 1.43949 g·cm^{-3}, final R_1 = 0.0779 and wR_2 = 0.2163 (R_{int} = 0.0798) for 25488 independent reflections [I > 2σ(I)]. A severely disordered solvent H_2O with 82 electrons were removed from the asymmetric unit by the SQUEEZE command, which could correspond with the removal of 2.0 molecules of H_2O per formula unit. CCDC 1483223 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request /cif.

Table S1. Analysis of orthogonal *π-π* stacking model and parallel *π-π* stacking model between 4,4'-bipyridin-1-ium units in CSD.

parallel *π-π* stacking model	orthogonal *π-π* stacking model
DMDPCO, JACLAA, NOFDUH, NOFFAP, NOWDUY, PALGAL, PAQUCL, PARQCC, PARQUI02, QULBUU, SEQBEV, UCENAS, UCENIA, VISHEK, XAKGAS, YIBCER, BAYVAA, BAYVEE, AWADUY, HANTEX, HASKUJ, VERJEI, NIMJID, JODYUX, LUFDUM, HOWSOC, HOWSAO	HABJUP01, KATYIO, KEPXIM, NAWKEB, PUXBOZ, RABNOX, KOZDOU, TOGZIA, TOGZOG, NILHAT, NILGUM, GIHNIV

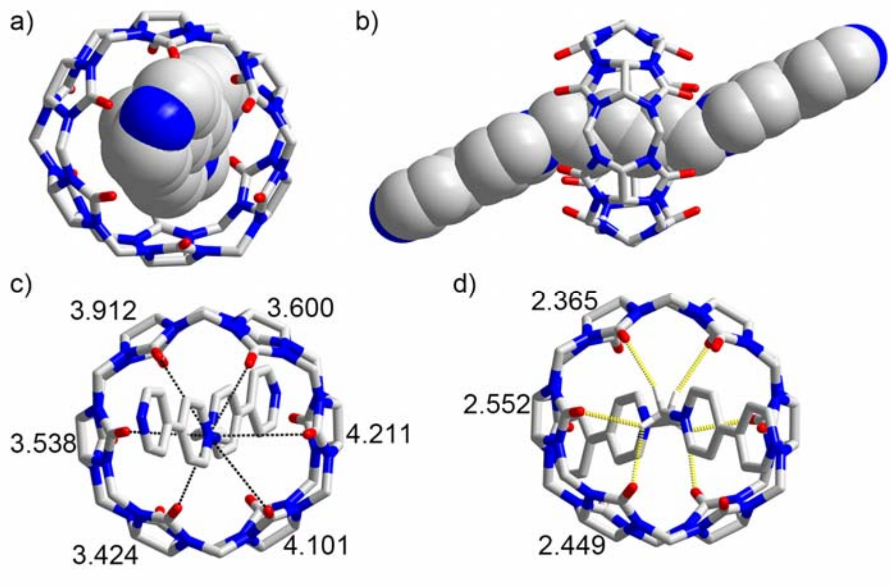


Figure S9. Representations of the X-ray crystal structures of: a) top view and b) side view of pseudorotaxanes CB[6]•**1**, c) N^+…O=C ion-dipole (black dotted line) and d) C–H…O interaction (yellow dotted line) distances (Å) in CB[6]•**1**. Color code: N, blue; O, red; C, gray. Hydrogen atoms and nitrate ions to balance the charge are omitted.

Table S2. Parameters from selected C–H…O interactions observed in CB[6]•**1**.

C–H…O Interactions	C…O distance(Å)	H…O distance(Å)	C–H…O angle(°)
C10–H11A…O2	3.189	2.449	132.91
C10–H11A…O4	3.292	2.552	133.10
C10–H11B…O6	3.309	2.366	164.38

Table S3. Parameters from N^+…O=C ion-dipole interactions observed in CB[6]•**1**.

N^+…O=C ion-dipole interactions	N^+…O distance(Å)	N^+…O=C angle(°)
N2…O1=C14	3.912	126.01
N2…O2=C18	3.600	142.26
N2…O3=C22	3.538	137.90
N2…O4=C24	4.211	128.44
N2…O5=C28	3.424	140.66
N2…O6=C30	4.101	125.96

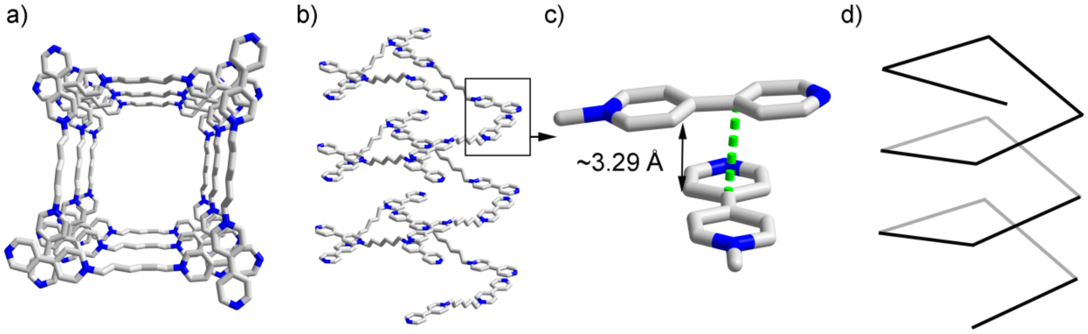


Figure S10. Representations of the X-ray crystal structures of: a) perspective view, b) side view, c) orthogonal π-π stacking, and d) topological view of square rotating staircase-like structures without CB[6] in the crystal structure of CB[6]•**1**. Color code: N, blue; O, red; C, gray. Hydrogen atoms and nitrate ions to balance the charge are omitted.

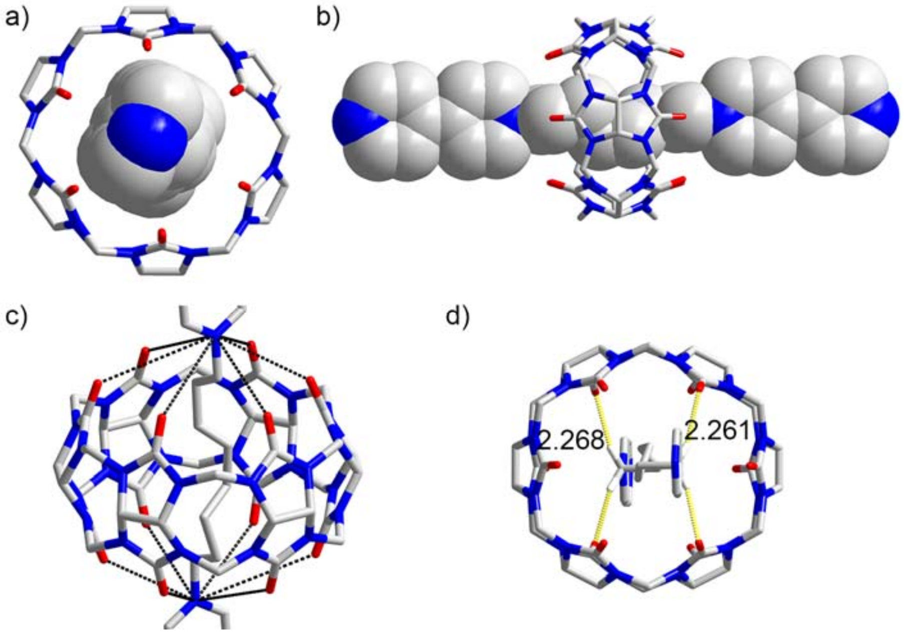


Figure S11. Representations of the X-ray crystal structures of: a) top view and b) side view of pseudorotaxanes CB[6]•**2**, c) N^+…O=C ion-dipole (black dotted line) and d) C–H…O interaction (yellow dotted line) distances (Å) in CB[6]•**2**. Color code: N, blue; O, red; C, gray. Hydrogen atoms and nitrate ions to balance the charge are omitted.

Table S4. Parameters from selected C–H…O interactions observed in CB[6]•**2**.

C–H…O Interactions	C…O distance(Å)	H…O distance(Å)	C–H…O angle(°)
C45–H45A…O3	3.172	2.268	154.59
C54–H54A…O6	3.183	2.261	158.43

Table S5. Parameters from N^+…O=C ion-dipole interactions observed in CB[6]•**2**.

N^+…O=C ion-dipole interactions	N^+…O distance(Å)	N^+…O=C angle(°)
N26…O2=C1	3.472	141.63
N26…O3=C7	3.663	140.56
N26…O5=C13	4.513	134.80
N26…O7=C20	4.957	133.26
N28…O1=C3	4.720	138.38
N28…O4=C9	4.391	133.37
N28…O6=C15	3.738	143.01
N28…O8=C19	3.666	141.95

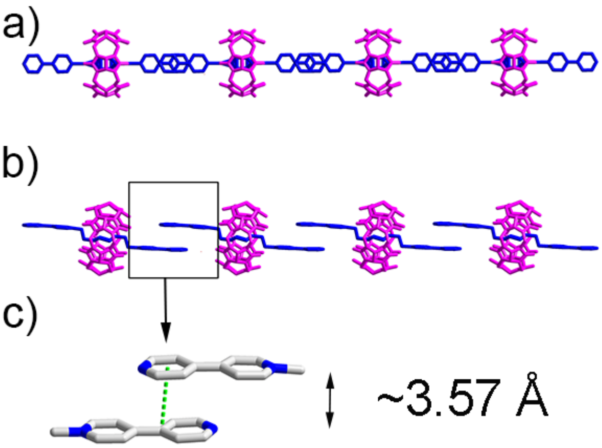


Figure S12. Representations of the X-ray crystal structures of: a) top view and b) side view of 1D linear polyrotaxane self-assembled from pseudorotaxanes CB[6]•**2**; c) parallel *π*-*π* stacking between CB[6]•**2**. Color code: N, blue; O, red; C, gray. Hydrogen atoms and nitrate ions to balance the charge are omitted.

Table S6. Parameters from selected C–H…O interactions observed between 1D linear polyrotaxane and CB[6].

C–H…O Interactions	C…O distance(Å)	H…O distance(Å)	C–H…O angle(°)
C39–H39…O10	2.978	2.361	123.65
C40–H40…O12	3.361	2.566	143.65
C43–H43…O12	3.138	2.422	133.92
C48–H48…O9	3.067	2.255	145.46
C49–H49…O11	3.276	2.366	165.75
C52–H52…O11	3.235	2.347	159.66

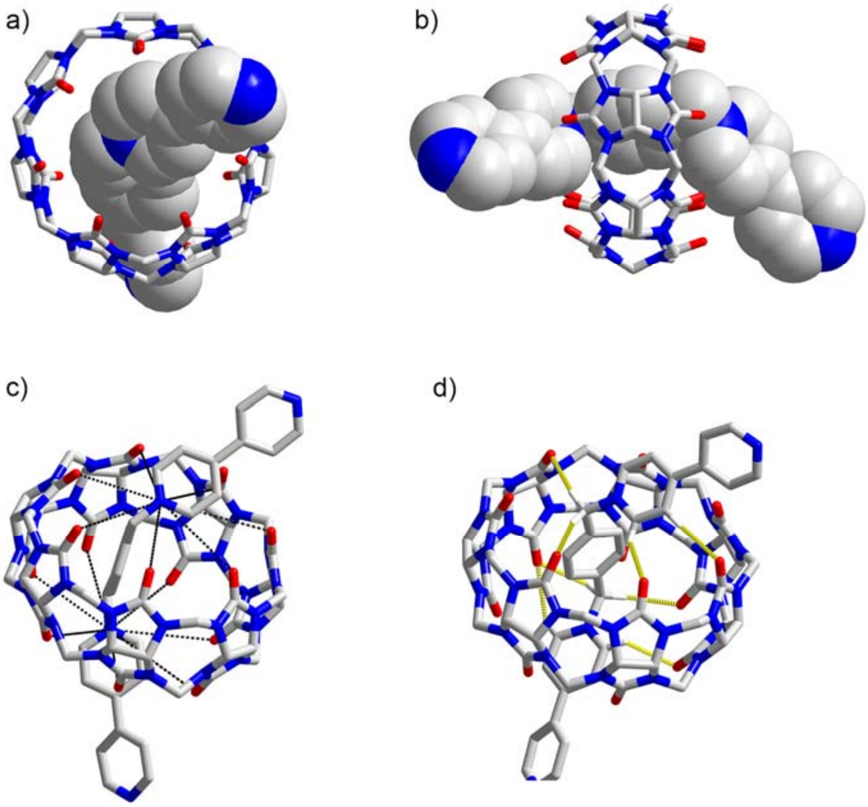


Figure S13. Representations of the X-ray crystal structures of: a) top view and b) side view of pseudorotaxanes CB[7]•**3**, c) N^+…O=C ion-dipole (black dotted line) and d) C–H…O interaction (yellow dotted line) distances (Å) in CB[7]•**3**. Color code: N, blue; O, red; C, gray. Hydrogen atoms and nitrate ions to balance the charge are omitted.

Table S7. Parameters from selected C–H…O interactions observed in CB[7]•**3**.

C–H…O Interactions	C…O distance(Å)	H…O distance(Å)	C–H…O angle(°)
C50–H50…O7	3.066	2.293	138.24
C51–H51…O6	3.230	2.467	137.20
C53–H53…O3	3.384	2.554	146.23
C54–H54A…O3	3.231	2.399	141.30
C54–H54A…O4	3.101	2.508	118.14
C54–H54B…O5	3.440	2.450	176.39
C60–H60A…O12	3.245	2.308	157.82
C60–H60B…O9	3.585	2.618	165.01
C65–H65…O14	3.138	2.494	134.83
C66–H66…O13	3.192	2.395	130.27

Table S8. Parameters from N^+…O=C ion-dipole interactions observed in CB[7]•**3**.

N^+…O=C ion-dipole interactions	N^+…O distance(Å)	N^+…O=C angle(°)
N31…O1=C32	4.631	115.55
N31…O2=C23	3.948	125.67
N31…O3=C20	3.764	124.87
N31…O4=C12	4.278	113.04
N31…O5=C7	4.117	128.58
N31…O6=C42	4.391	128.61
N31…O7=C37	4.995	115.41
N32…O8=C6	4.529	120.56
N32…O9=C30	4.118	128.73
N32…O10=C11	3.674	127.19
N32…O11=C26	4.436	115.93
N32…O12=C18	4.000	119.82
N32…O13=C38	4.387	131.63
N32…O14=C43	5.061	115.61

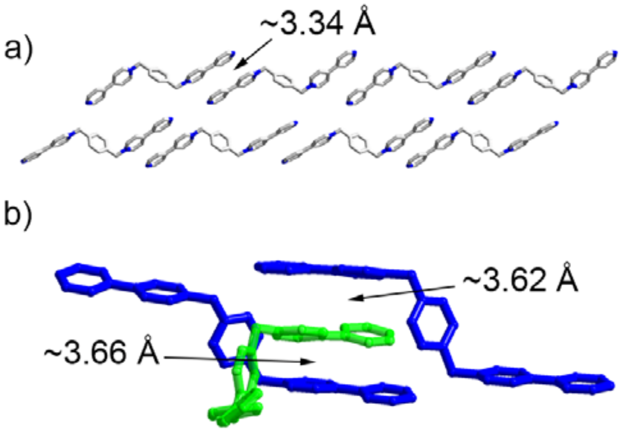


Figure S14. Representations of the X-ray crystal structures of: a) side view of 1D linear structure self-assembled from **3** by parallel *π-π* stacking; b) orthogonal *π-π* stacking between pyridinium units. Color code: N, blue; O, red; C, gray. Hydrogen atoms and bromide ions to balance the charge are omitted.

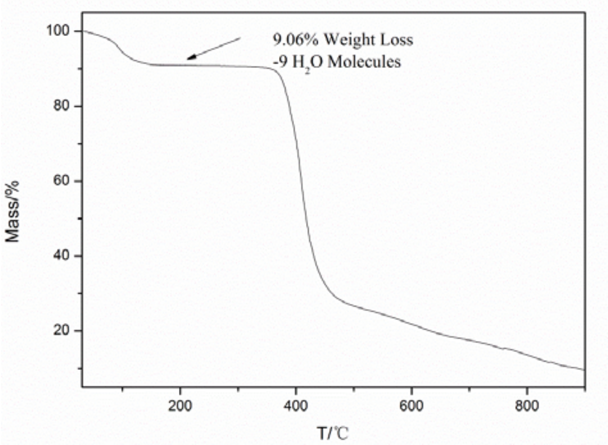


Figure S15. Thermal gravimetric analysis (TGA) curve for the crystal of CB[6]•**1**. Water crystallization is volatilized from room temperature to about 143℃ and organic ligand decomposed rapidly only after 355℃

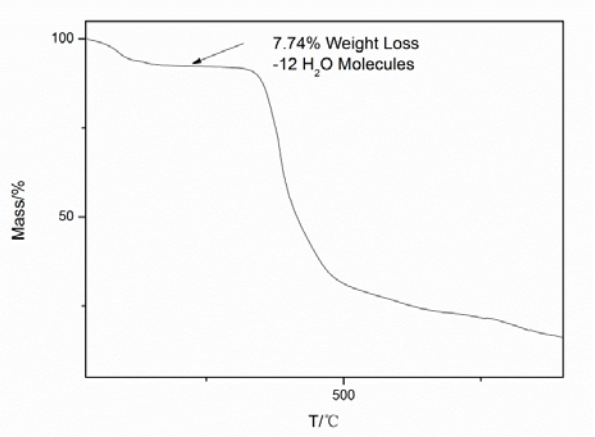


Figure S16. Thermal gravimetric analysis (TGA) curve for the crystal of CB[6]•**2**. Water crystallization is volatilized from room temperature to about 210℃ and organic ligand decomposed rapidly only after 332℃.

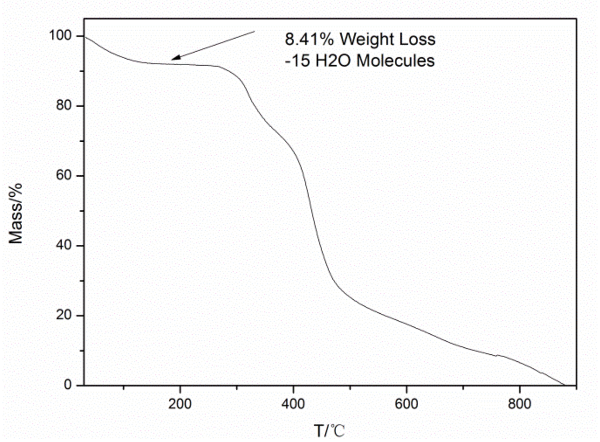


Figure S17. Thermal gravimetric analysis (TGA) curve for the crystal of CB[7]•**3**. Water crystallization is volatilized from room temperature to about 136℃ and organic ligand decomposed rapidly only after 276℃.

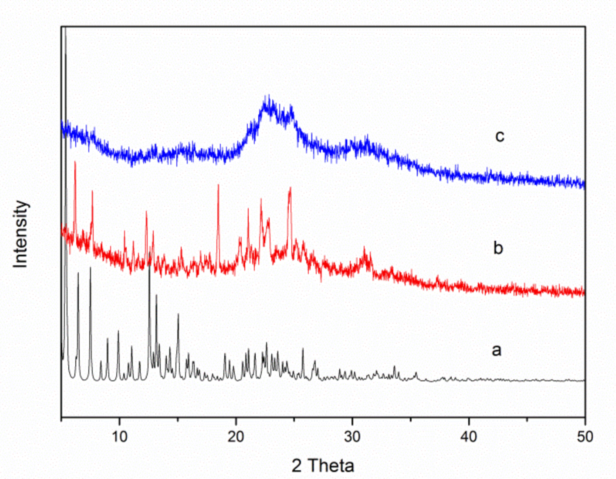


Figure S18. X-ray powder diffraction patterns for: a) simulated, b) as-synthesized, and c) activated CB[6]•**2.**

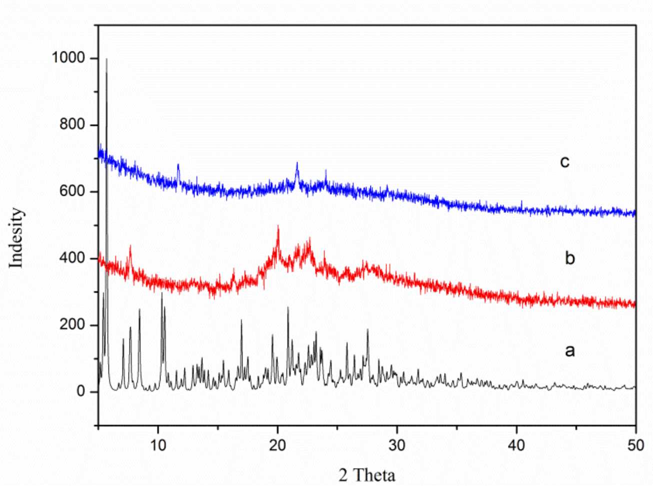


Figure S19. X-ray powder diffraction patterns for: a) simulated, b) as-synthesized, and c) activated CB[7]•**3.**