Electronic Supplementary Information (ESI)

Self-assembly of cucurbit[8]uril-based polypseudorotaxanes using host–guest interactions

Xin Xiao[a], Rui-Lian Lin, [b] Li-Mei Zheng,[c] Wen-Qi Sun[b], Zhu Tao[,a], Qian-Jiang Zhu[a], Sai-Feng Xue[a], Jing-Xin Liu*[,b]*

---

a X. Xiao, Z. Tao, Q.-J. Zhu, S.-F. Xue
Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, P. R. China
Fax: (+86) 8513620906
E-mail: gzutao@263.net

b R.-L. Lin, W.-Q. Sun, J.-X. Liu
College of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, P. R. China
E-mail: jxliu411@ahut.edu.cn

c L.-M. Zheng
College of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, P. R. China

Table of Contents

Part 1. General Information

Materials: 4,4'-trimethylene-dipiperdine, butyl bromide, 4,4'-bipyridine, hexyl bromide and solvents employed were used as supplied without further purification. The cucurbit[8]uril was synthesized according to literature methods.[1]

Methods: the ^{1}H NMR spectra were recorded at 20°C on a Varian INOVA-400 spectrometer. The C, H, and N microanalyses were carried out with a PE 240C elemental analyzer.

Part 2. Experimental Section

Synthesis:

Dihexyl-4,4'-bipyridinium (HV^{2+}): A mixture of 4,4'-bipyridine (1.0 equiv) and hexyl bromide (8 equiv) in CH_3CN was refluxed for 24 hours. The resulting precipitate was filtered, washed with hot chloroform to remove monoalkylated product and dried under vacuum. The end product was obtained in 75.9 % yield based on 4,4'-bipyridine.

1,3-Bis(4-butylpiperazin-1-ly)-propane (C_3PA^{2+}) dibromide: The guest was prepared by refluxing the mixture of 4,4'-trimethylene-dipiperdine (1.0 equiv), butyl bromide (2.5 equiv) and polyethylene glycol (0.02 equiv) for 5 hours. The resulting precipitate was filtered, and the residue was collected, washed with ether, and air dried. The end product was obtained in 69.3 % yield based on 4,4'-trimethylene-dipiperdine.

Inclusion complex Q[8]·HV^{2+}: Q[8] (0.27 g, 0.20 mmol) and guest HV^{2+} (0.097 g, 0.2 mmol) were dissolved in 3.0 M hydrochloric acid (25 mL). The mixture was heated at 80 °C for 30 min. After cooling to room temperature, the mixture was filtered. Slow evaporation of the filtrate over a period of a month provided colorless crystals. Anal. Calcd for Q[8]·HV^{2+}, $(C_{48}H_{48}N_{32}O_{16})\cdot(C_{22}H_{34}N_2)^{2+}\cdot(H_2O)_{34}\cdot 2Cl^-$: C, 35.94; H, 6.46; N, 20.36. Found: C, 36. 74; H, 6.52; N, 20.46.

Inclusion complex Q[8]·C_3PA^{2+}: C_3PA^{2+} guest (0.097 g, 0.20 mmol) was dissolved in H_2O (50 ml), and to this solution Q[8] (0.27 g, 0.20 mmol) was added. The mixture was stirred and heated at 80°C for 30 minutes and then filtered. Slow evaporation of the filtrate over a period of four weeks provided rod-shaped colorless crystals. Anal. Calcd for Q[8]·C_3PA^{2+}, $(C_{48}H_{48}N_{32}O_{16})\cdot(C_{21}H_{44}N_2)^{2+}\cdot(H_2O)_{18.5}\cdot 2Br^-$: C, 38.60; H, 6.06; N, 22.18. Found: C, 38.77; H, 5.95; N, 22.26.

Part 3. Crystallographic Information

Crystal structure Determination:

Single-crystal X-ray diffraction studies both inclusion complexes were performed on a computer-controlled Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were collected in ω and φ scan model at 173 K and 273 K, respectively. Absorption corrections were applied by using the multiscan program SADABS. Structural solution and full matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package,[2] respectively. All the non-hydrogen atoms were refined anisotropically. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom.

For the inclusion complex Q[8]·HV^{2+}, the SQUEEZE process in PLATON program was applied to remove the solvent waters and chloride anions because they could not be satisfactorily modeled.[3]

Details about the Squeezed Material are reported in a following loop.

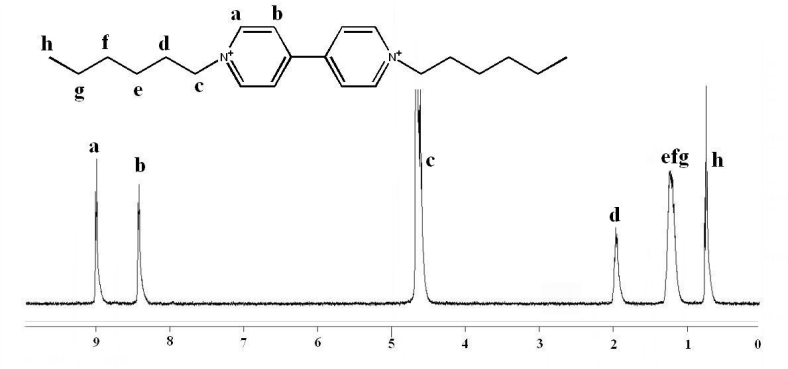
```
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1   -0.008   -0.005   -0.011   7978      3095 '34(H2O)2Cl^-^ '
    2   0.473    0.092    0.055      8         1 ' '
    3   0.973    0.592    0.055      8         1 ' '
    4   0.250    0.156    0.064      7         0 ' '
```

5	0.750	0.656	0.064	7	0 ' '
6	0.027	0.592	0.445	8	0 ' '
7	0.527	0.092	0.445	8	0 ' '
8	0.250	0.656	0.436	7	0 ' '
9	0.750	0.156	0.436	7	0 ' '
10	0.473	0.908	0.555	8	1 ' '
11	0.973	0.408	0.555	8	1 ' '
12	0.250	0.844	0.564	7	0 ' '
13	0.750	0.344	0.564	7	0 ' '
14	0.027	0.408	0.945	9	0 ' '
15	0.527	0.908	0.945	9	0 ' '
16	0.250	0.344	0.936	7	0 ' '
17	0.750	0.844	0.936	7	0 ' '

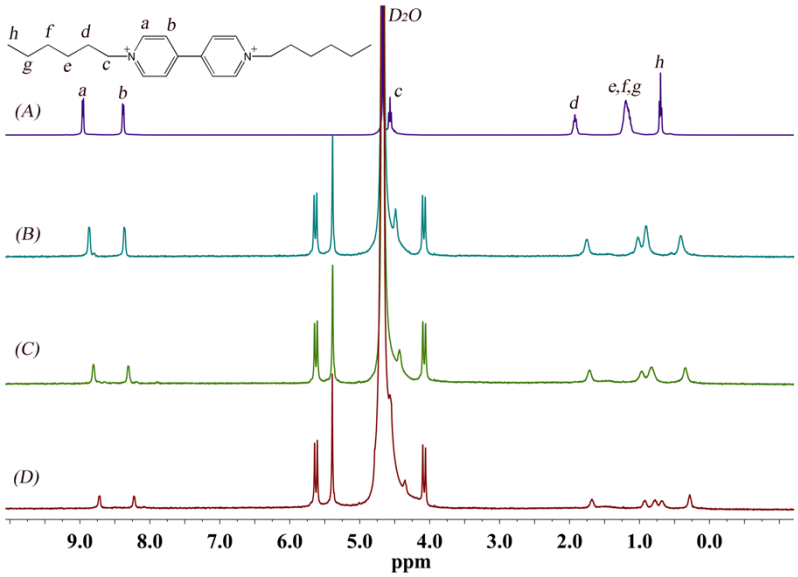
_platon_squeeze_details

CCDC 1018028 and 1018029 contain the supplementary crystallographic data for inclusion complexes Q[8]·HV^{2+} and Q[8]·C_3PA^{2+}. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

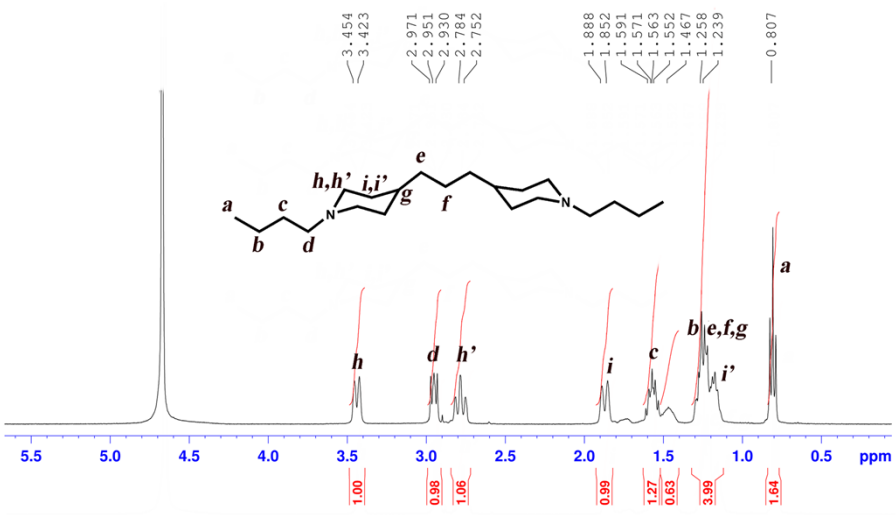
Part 4. Copies of ^{1}H-NMR Spectra



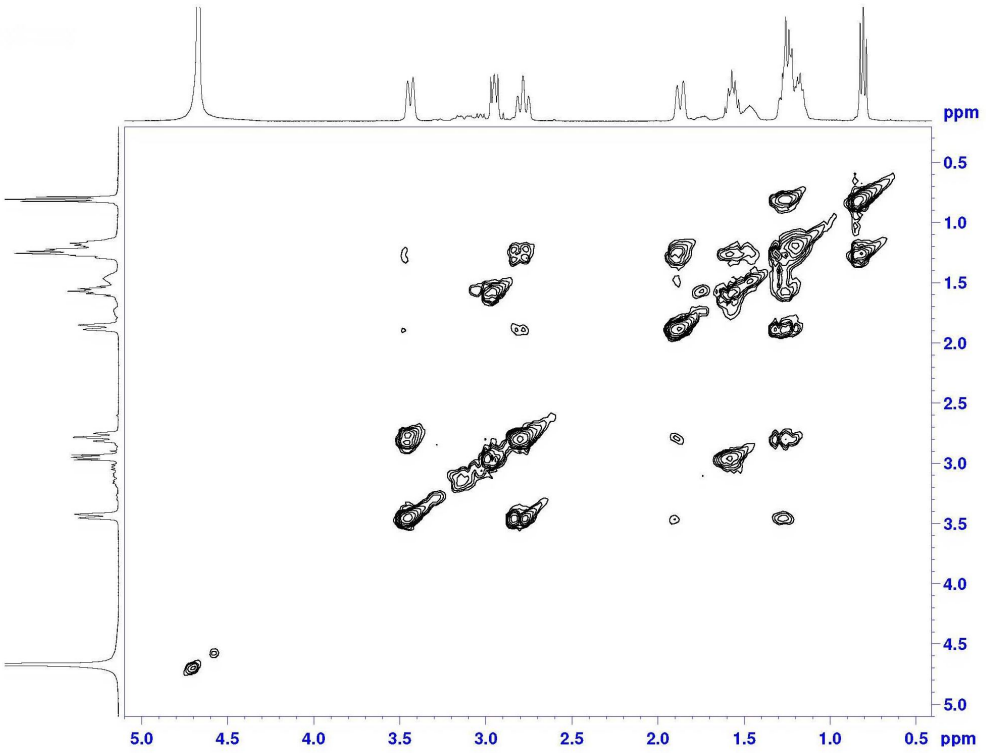
S1 ^{1}H NMR of HV^{2+}



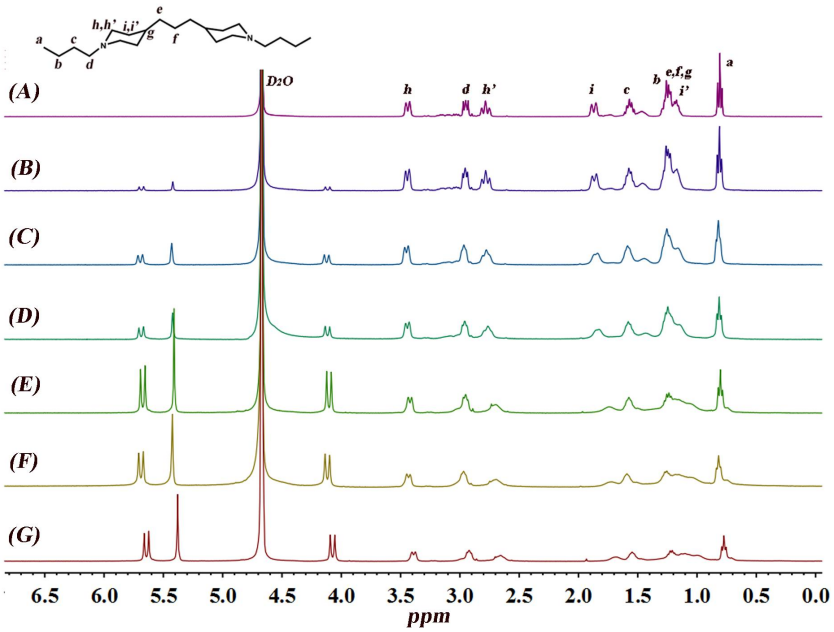
S2 ^{1}H NMR spectra of HV^{2+} in the absence *(A)* and presence of more and more Q[8] *(B-D)*



S3 ^{1}H NMR of C_3PA^{2+}



S4 2D-COSY spectrum of C_3PA^{2+}



S5 ^{1}H NMR spectra of C_3PA^{2+} in the absence *(A)* and presence of more and more Q[8] *(B-G)*

Part 5. References

1 a) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc*. **2000**, *122*, 540; b) A. I. Day, A. P. Arnold, Method for synthesis cucurbiturils, WO 0068232, **2000**, 8; c) A. Day, A. P. Arnold, R. J. Blanch, B. J. Snushall, *Org. Chem*. **2001**, *66*, 8094.

2 a) G. M. Sheldrick, SHELXS-97, *Program for X-ray Crystal Structure Determination*; University of Göttingen, Germany, 1997; b) G. M. Sheldrick, SHELXL-97, *Program for X-ray Crystal Structure Refinement*; University of Göttingen, Germany, 1997; c) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112–122.

3 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.