Electronic Supporting Information

Thiacalix[4]arene-rubidium assembly: supramolecular architecture based on alkali metal coordination and cation-π interactions

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Supporting Information Comprises:

Materials and Experimental Methods:

1. General procedures and the synthesis of *p*-H-thiacalix[4]arene (**1**·4H)

2. Crystal structure determination of complex **2**

Figure S1. Mol. A and Mol. B diagrams in complex **2** showing the relevant atom labelling schemes.

Figure S2. A comparison between Mol. A structural unit versus Mol. B structural unit in complex **2**.

Figure S3. Overall crystal structure in complex **2** showing alternately stacking of Layer A and Layer B viewed along the *bc* plane.

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Materials and Experimental Methods:

1. General procedures and the synthesis of *p*-H-thiacalix[4]arene (1·4H)

All reactions were carried out in nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium / benzophenone under nitrogen and stored over 4 Å activated molecular sieves. Methanol was commercially available and used as recrystallization solvent without further purification. *p*-H-thiacalix[4]arene (**1**·4H) was obtained by de *tert*-butylation reaction from *p*-^{t}Bu-thiacalix[4]arene[1] which was prepared according to our previously reported procedures[2]. IR spectra were recorded with a Perkin-Elmer SPECTRUM 2000 spectrophotometer. ^{1}H NMR spectra were taken on a Bruker DPX 300, and measured using tetramethylsilane as an internal standard and CH_3OD as a solvent, unless otherwise noted. Microanalyses were preformed at the microanalysis center of Tohoku University.

Supplementary References:

1. (a) Y. Higuchi, M. Narita, T. Niimi, N. Ogawa, F. Hamada, H. Kumagai, N. Iki, S. Miyano, C. Kabuto, *Tetrahedron*, 2000, **56**, 4659; (b) C. Kabuto, Y. Higuchi, T. Niimi, F. Hamada, N. Iki, N. Morohashi, S. Miyano, *J. Incl. Phenom. Macrocycl. Chem.*, 2002, **42**, 89; (c) O. Kasyan, D. Swierczynski, A. Drapailo, K. Suwinska, J. Lipkowski, V. Kalchenko, *Tetrahedron Lett.*, 2003, **44**, 7167.

2. (a) Y. Kondo, K. Endo, N. Iki, S. Miyano, F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, 2005, **52**, 45; (b) Y. Kondo and F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, 2007, **58**, 123.

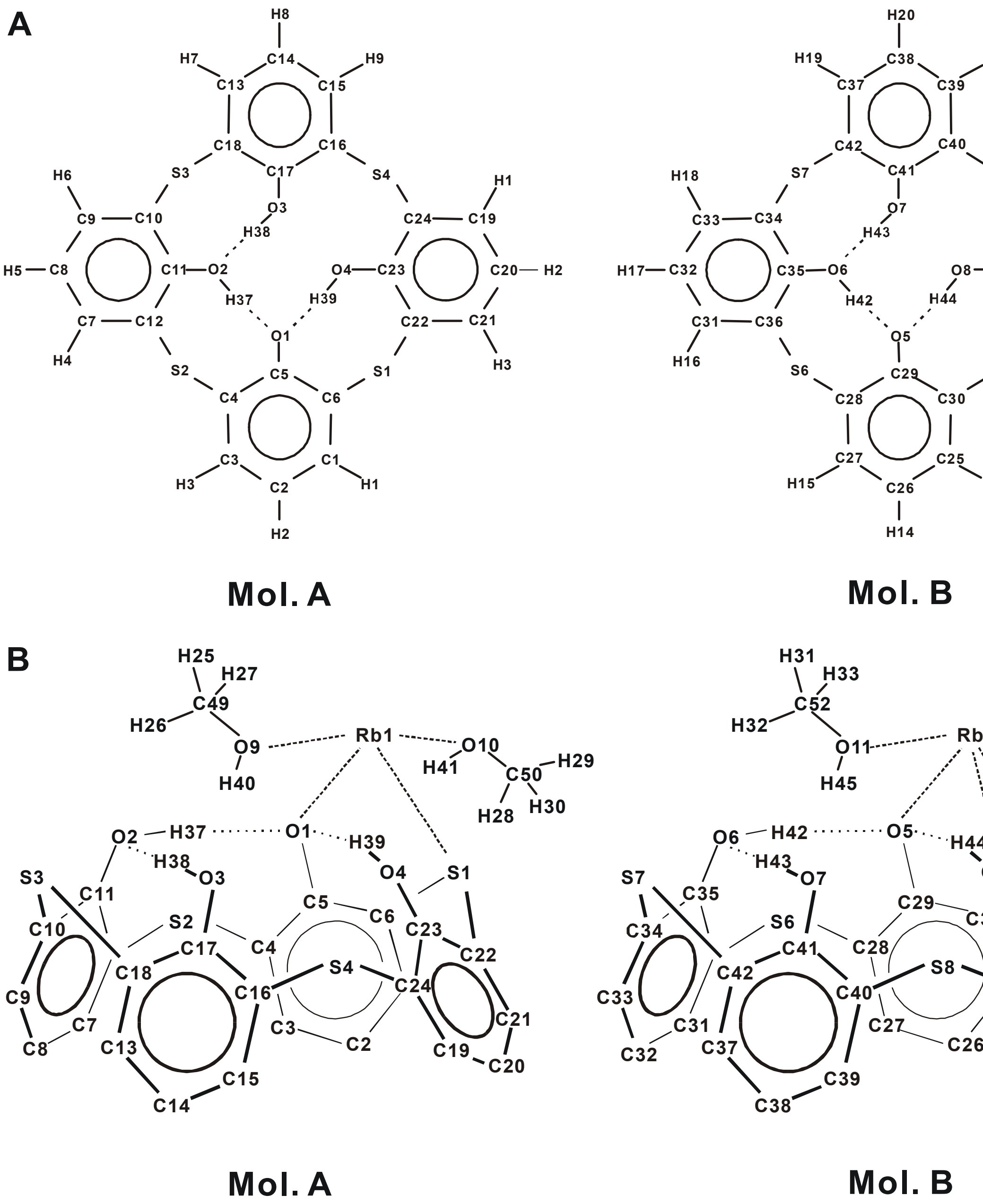
2. Crystal structure determination of complex 2

Single crystals of complex **2** decomposed rapidly from the mother liquor. The crystals containing mother liquor were drunk up with a pipette, which dropped in paraffin oil. The oil coated single crystals were picked up with on MicroMounts™, and the crystals were placed immediately in a cold nitrogen stream at −173ºC. X-ray diffraction data for complex **2** was collected on a Rigaku PAXIS RAPID imaging plate diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.71075 Å). Structures were solved by direct methods using SHELXS-97[3] and refined by full-matrix least-squares on F^2 using the SHELXL-97[4] program. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of aromatic rings and methyl group of the coordinated methanol molecules in complex **2** were calculated, and all hydrogen atoms of hydroxyl groups found from the residual density and refined with riding model.

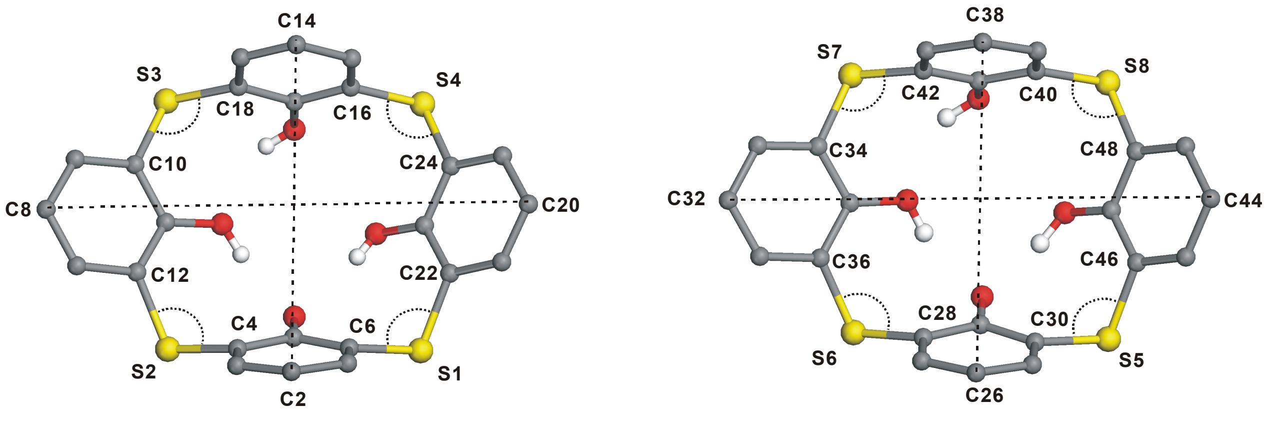
Supplementary References:

3. Sheldrick, G. M. *SHELXS-97* Program for solution of crystal structures, University of Göttingen, Germany, 1997.

4. Sheldrick, G. M. *SHELXL-97* Program for refinement of crystal structures, University of Göttingen, Germany, 1997.

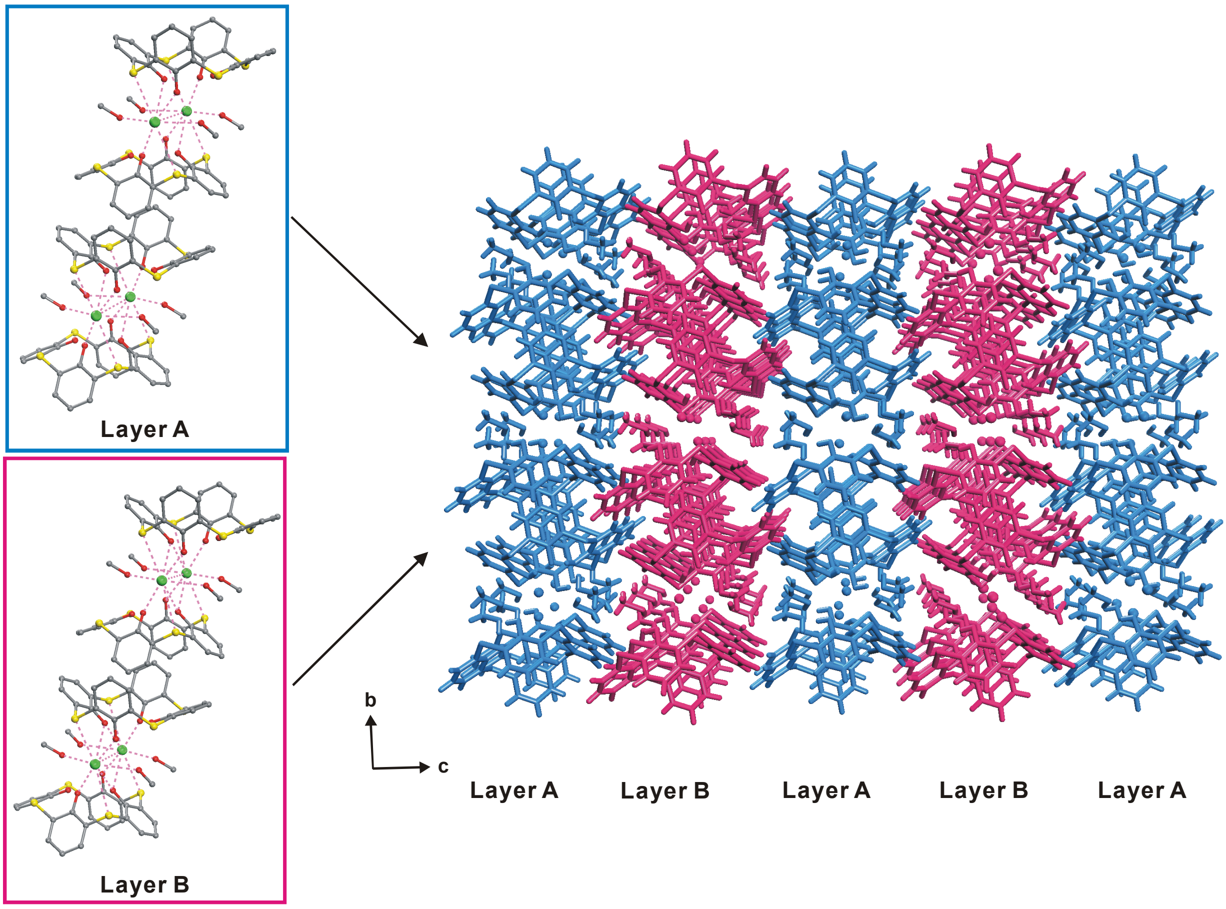


Supplementary Figure S1. Mol. A and Mol. B diagrams in complex **2** showing the relevant atom labeling schemes. (A) Top view and (B) Side view of Mol. A and Mol. Two 'pinched cone-like' conformations of Mol. A and Mol. B are stabilized by each of three intramolecular hydrogen bonds between one phenoxide and three phenolic groups in Mol. A or Mol. B. The hydrogen bonding distances in Mol. A: H(37)···O(1) 1.779 Å; H(39)···O(1) 1.897 Å; H(38)···O(2) 2.491 Å (corresponding O···O distances: O(1)···O(2) 2.543 Å; O(1)···O(3) 2.562 Å; O(2)···O(3) 2.943 Å). The hydrogen bonding distances in Mol. B: H(42)···O(5) 1.872 Å; H(44)···O(5) 1.691 Å; H(43)···O(6) 2.285 Å (corresponding O···O distances: O(5)···O(6) 2.639 Å; O(5)···O(7) 2.534 Å; O(6)···O(7) 2.858 Å).

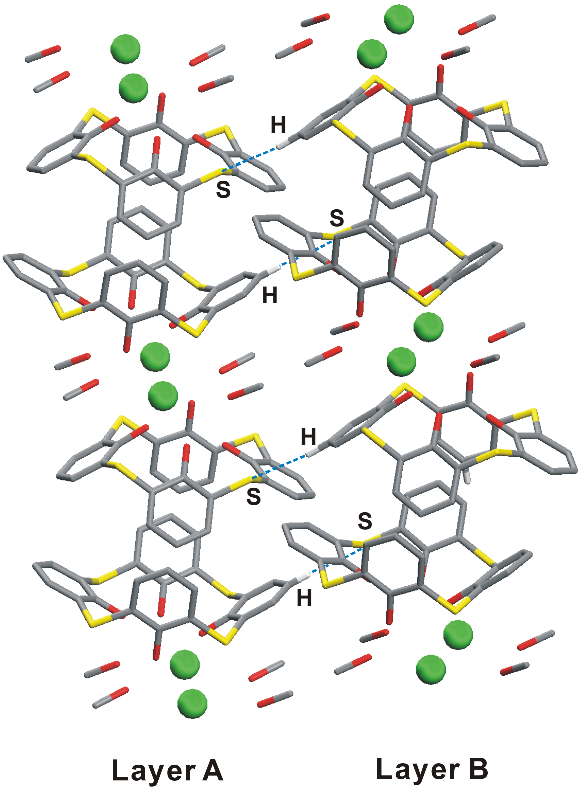


Mol. A **Mol. B**

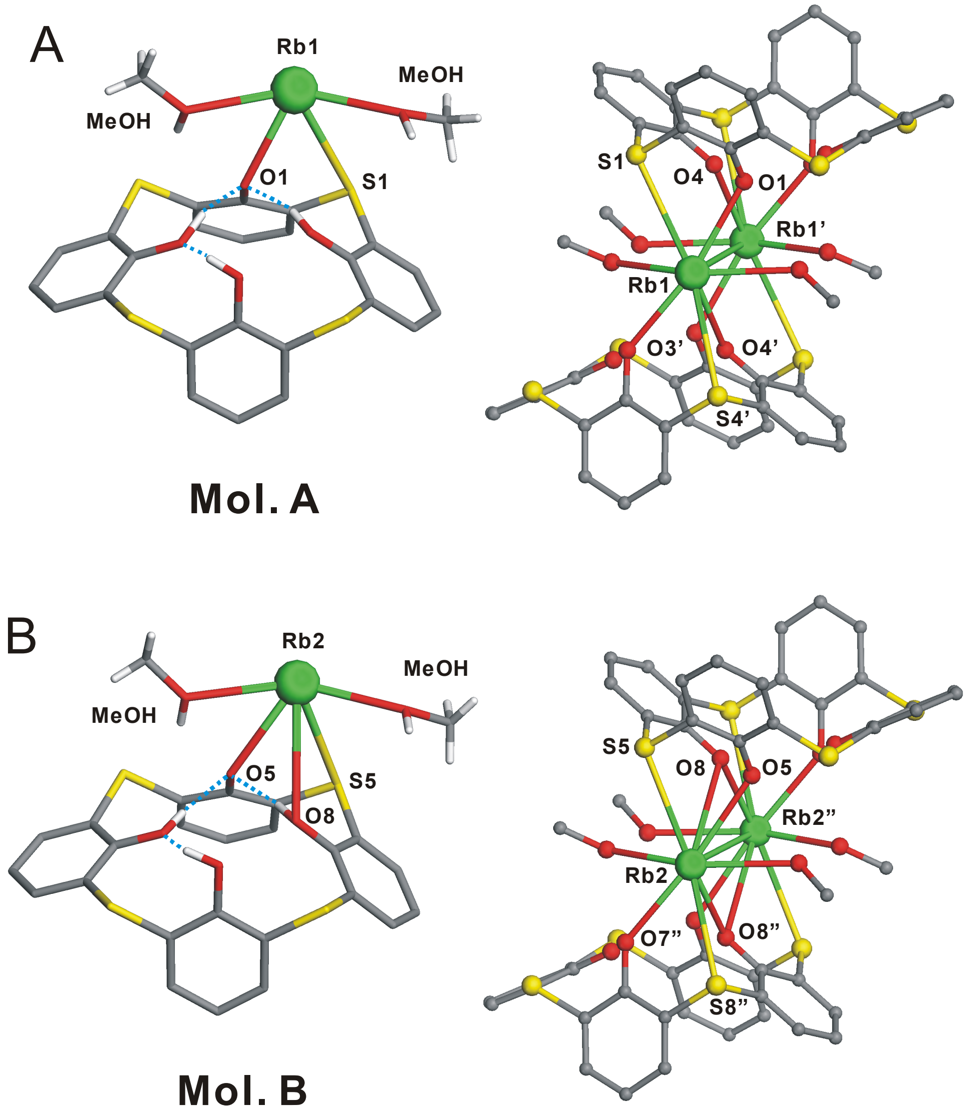
Supplementary Figure S2. A comparison between Mol. A structural unit versus Mol. B structural unit in complex **2**. Selected distances (Å): C(2)···C(14) 7.281, C(8)···C(20) 10.420, C(26)···C(38) 7.120, C(32)···C(44) 10.392, and selected bond angles (º): C(6)-S(1)-C(22) 105.21(13), C(4)-S(2)-C(12) 107.05(13), C(10)-S(3)-C(18) 109.91(13), C(16)-S4-C(24) 100.97(13), C(30)-S(5)-C(46) 103.98(13), C(28)-S(6)-C(36) 107.05(13), C(34)-S(7)-C(42) 104.31(13), C(40)-S(8)-C(48) 101.65(13).



Supplementary Figure S3. Overall crystal structure in complex **2** showing alternately stacking of Layer A and Layer B viewed along the *bc* plane.



Supplementary Figure S4. The extended structures in complex **2** showing hydrogen bonds between Layer A and Layer B (blue dotted lines). Most of hydrogen atoms are omitted for clarity.



Supplementary Figure S5. Large version of Fig. 2. (A) The asymmetric unit showing the coordination of Rb cation to one phenoxide oxygen and one sulfur linker of Mol. A, OH groups of two guest MeOH molecules. The three intramolecular hydrogen bonds are shown as blue dotted lines (left). The coordination environment of the formed dimer by Mol. A (right). (B) The asymmetric unit showing the coordination of Rb cation to two pendent phenoxide/phenolic oxygens and one bridging sulfur atom of Mol. B, OH groups of two guest MeOH molecules. The three intramolecular hydrogen bonds are shown as blue dotted lines (left). The coordination environment of the formed dimer by Mol. B (right).