

**Thiacalix[4]arene–potassium assemblies:  
a supramolecular architecture based on coordination  
polymers and a dimeric structure based on triangular  
pyramidal arrangements**

**Manabu Yamada<sup>a</sup> and Fumio Hamada<sup>\*b</sup>**

*<sup>a</sup> Venture Business Laboratory, Akita University, Akita, 010-8502, Japan*

*<sup>b</sup> Department of Life Science, Faculty of Engineering and Resource Science, Akita University, Akita  
010-8502, Japan*

*\* Corresponding Author: hamada@ipc.akita-u.ac.jp; Fax: +81 18 837 0404. Tel: +81 18 889 2440.*

## **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 complexes **2** and **3**.

**Scheme S1** The thiacalixarene skeleton (A) and (B) diagrams in complex **2** showing the relevant atom labeling schemes.

**Scheme S2** The thiacalixarene skeleton diagram in complex **3** showing the relevant atom labeling scheme.

**Scheme S3** The thiacalixarene skeleton diagram of a quotation from Zeller and Radius' article showing the relevant atom labeling scheme.

**Table S1** Selected M-C distances and angles of alkali metal complexes of *p*-<sup>t</sup>Bu-thiacalix[4]arene and thiacalix[4]arene.

**Table S2** Crystal data and structure refinement for complexes **2** and **3**.

**Figure S1** Coordination environments of the potassium cations in complex **2**: (A) K $\cdots$ O coordination between the potassium cations and the thiacalixarene phenolic/phenoxide oxygen atoms, (B) K $\cdots$ S coordination between the potassium cations and the thiacalixarene sulfur linker atoms.

**Figure S2** Extended structure of complex **2** showing the supramolecular assembly by the inclusion the coordinated methanol molecules of the polymer into the thiacalixarene cavities of the adjacent polymer.

**Figure S3** Coordination environments of the potassium cations in the distorted triangular pyramidal arrangements of complex **3**: (A) K $\cdots$ O coordination between the potassium cations and the thiacalixarene phenolic/phenoxide oxygen atoms, (B) K $\cdots$ S coordination between the potassium cations and the thiacalixarene sulfur linker atoms.

**Figure S4** Extended structure of complex **3** showing the aggregation of the thiacalixarene aromatic rings and the solvated *n*-butanol molecules by intermolecular hydrophobic interactions.

**Figure S5** The ORTEP diagram of the asymmetric unit of complex **2** with thermal ellipsoids at 50% probability.

**Figure S6** The diagram of coordination environments in complex **2** showing the relevant atom labeling scheme.

**Figure S7** The ORTEP diagram of the asymmetric unit of complex **3** with thermal ellipsoids at 50% probability.

**Figure S8** The diagram of coordination environments in complex **3** showing the relevant atom labeling scheme.

## Experimental Section

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

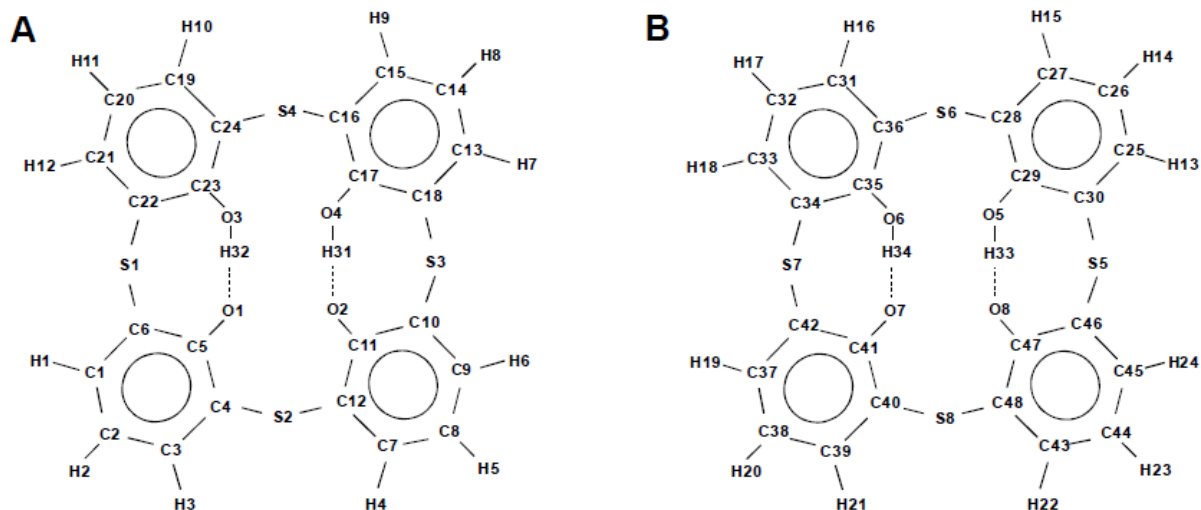
All reactions were carried out in nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium / benzophenone under nitrogen and stored over 4 Å activated molecular sieves. Methanol and *n*-butanol were commercially available and used as recrystallization solvent without further purification. *p*-H-thiacalix[4]arene (1·4H) was obtained by de *tert*-butylation reaction of *p*-*t*Bu-thiacalix[4]arene<sup>S1</sup> which was prepared according to our previously reported procedures<sup>S2</sup>. IR spectra were recorded with a Perkin-Elmer SPECTRUM 2000 spectrophotometer. <sup>1</sup>H NMR spectra were taken on a Bruker DPX 300, and measured using CD<sub>3</sub>OD as a solvent, unless otherwise noted.

### 2. Crystal structure determination of complex 2 and 3

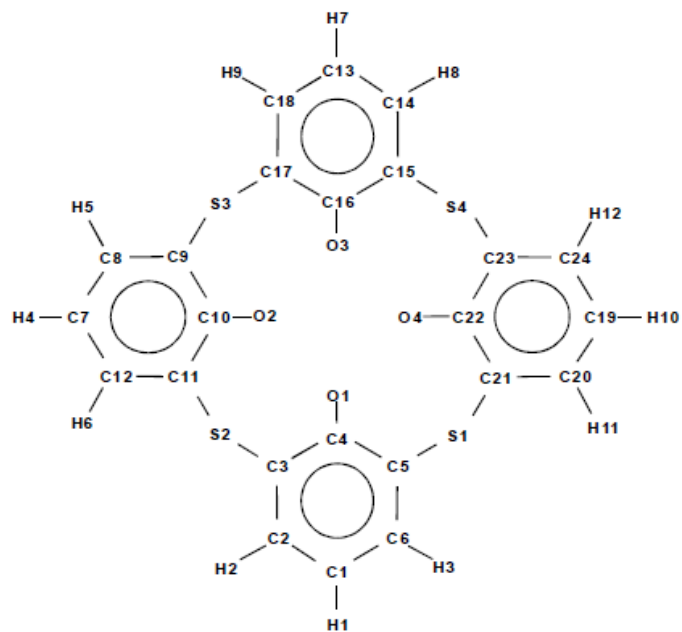
Single crystals of complexes **2** and **3** suitable for single-crystal X-ray diffraction studies were formed. The crystals containing mother liquid were drunk up with a pipette, which dropped in paraffin oil. Single crystals coated with the oil were picked up with on MicroMounts<sup>TM</sup>, and the crystals were placed immediately in a cold nitrogen stream at -100 or -153°C. X-ray diffraction data for complexes **2** and **3** were collected on a Rigaku PAXIS RAPID imaging plate diffractometer with a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å). Structures were solved by direct methods using SHELXS-97<sup>S3</sup> and refined by full-matrix least-squares on  $F^2$  using the SHELXL-97<sup>S4</sup> program.

## Supplementary References

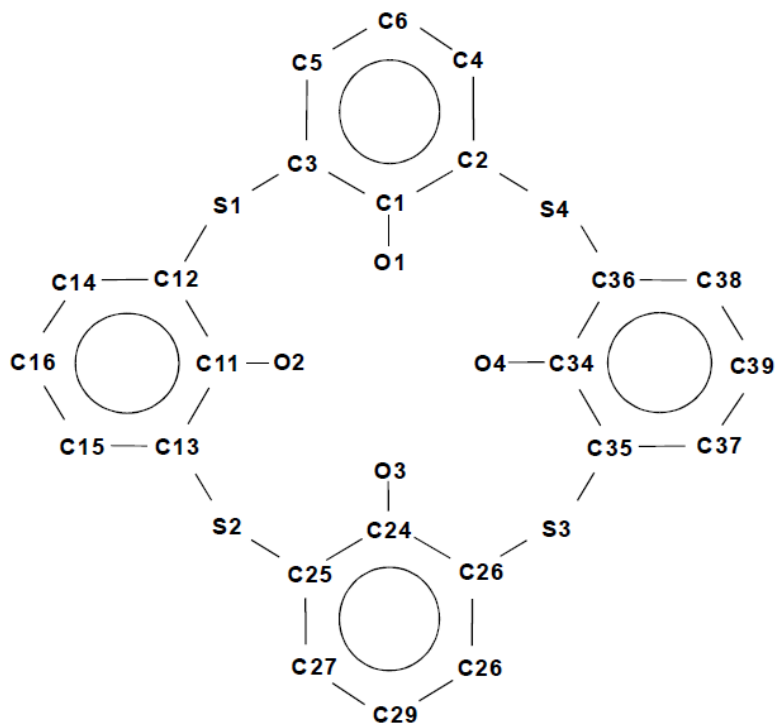
- S1. (a) Higuchi, Y.; Narita, M.; Niimi, T.; Ogawa, N.; Hamada, F.; Kumagai, H.; Iki, N.; Miyano, S.; Kabuto, C. *Tetrahedron* **2000**, *56*, 4659-4666. (b) Kabuto, C.; Higuchi, Y.; Niimi, T.; Hamada, F.; Iki, N.; Morohashi, N.; Miyano, S. *J. Incl. Phenom. Macrocycl. Chem.* **2002**, *42*, 89-98. (c) Kasyan, O.; Swierczynski, D.; Drapailo, A.; Suwinska, K.; Lipkowski, J.; Kalchenko, V. *Tetrahedron Lett.* **2003**, *44*, 7167-7170.
- S2. (a) Kondo, Y.; Endo, K.; Iki, N.; Miyano, S.; Hamada, F. *J. Incl. Phenom. Macrocycl. Chem.* **2005**, *52*, 45-49. (b) Kondo, Y.; Hamada, F. *J. Incl. Phenom. Macrocycl. Chem.* **2007**, *58*, 123-126.
- S3. Sheldrick, G. M. *SHELXS-97 Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
- S4. Sheldrick, G. M. *SHELXL-97 Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.



**Supplementary Scheme S1** The thiocalixarene skeleton (A) and (B) diagrams in complex **2** showing the relevant atom labeling schemes. The hydrogen bonding distances in the dimers: H(32)⋯O(1) 1.631 Å; H(31)⋯O(2) 1.636 Å; H(34)⋯O(7) 1.701 Å; H(33)⋯O(8) 1.656 Å (corresponding O⋯O distances: O(1)⋯O(4) 2.447 Å; O(2)⋯O(3) 2.455 Å; O(5)⋯O(8) 2.459 Å; O(6)⋯O(7) 2.455 Å).



**Supplementary Scheme S2** The thiacalixarene skeleton diagram in complex **3** showing the relevant atom labeling scheme.



**Supplementary Scheme S3** The thiacalixarene skeleton diagram of a quotation from Zeller and Radius' article showing the relevant atom labeling scheme. Hydrogen atoms and 'Bu-groups have been omitted for clarity.



**Supplementary Table S1** Selected M-C distances and angles of alkali metal complexes of *p*-<sup>t</sup>Bu-thiacalix[4]arene and thiacalix[4]arene.

Compound	M-ArC (Å)		Selected angle(°)		Ref.
	interior	exterior	interior	exterior	
<i>p</i> - <sup>t</sup> BuTC4A·Na·Py	2.731-4.505	2.825-5.168	O1-O3-C29: 96.97 <sup>b</sup> O3-O1-C6: 110.71 <sup>b</sup>	O2-O4-C39: 129.40 <sup>b</sup> O4-O2-C16: 132.67 <sup>b</sup>	S5
<i>p</i> - <sup>t</sup> BuTC4A·K·Py	3.087-3.482 <sup>a</sup>	3.009-5.123	O1-O3-C29: 82.30 <sup>b</sup> O3-O1-C6: 87.42 <sup>b</sup>	O2-O4-C42: 135.54 <sup>b</sup> O4-O2-C16: 138.31 <sup>b</sup>	S5
Complex <b>3</b>	3.039-3.295 <sup>a</sup>	3.017-5.142	O1-O3-C13: 84.06 O3-O1-C1: 83.67	O2-O4-C19: 135.62 O4-O2-C7: 138.14	<sup>c</sup>

<sup>a</sup>  $\eta^6$  coordination distances for cation- $\pi$  interactions.

<sup>b</sup> The relevant atom labeling is carried a quotation from Zeller and Radius' article<sup>S5</sup>, and the relevant atom labeling scheme is shown in Scheme S3.

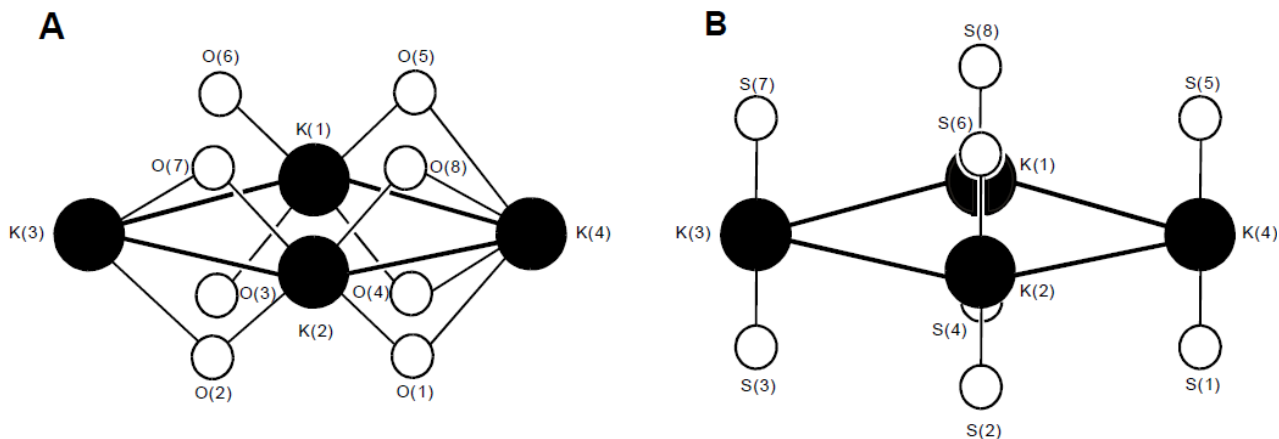
<sup>c</sup> This work.

### Supplementary Reference

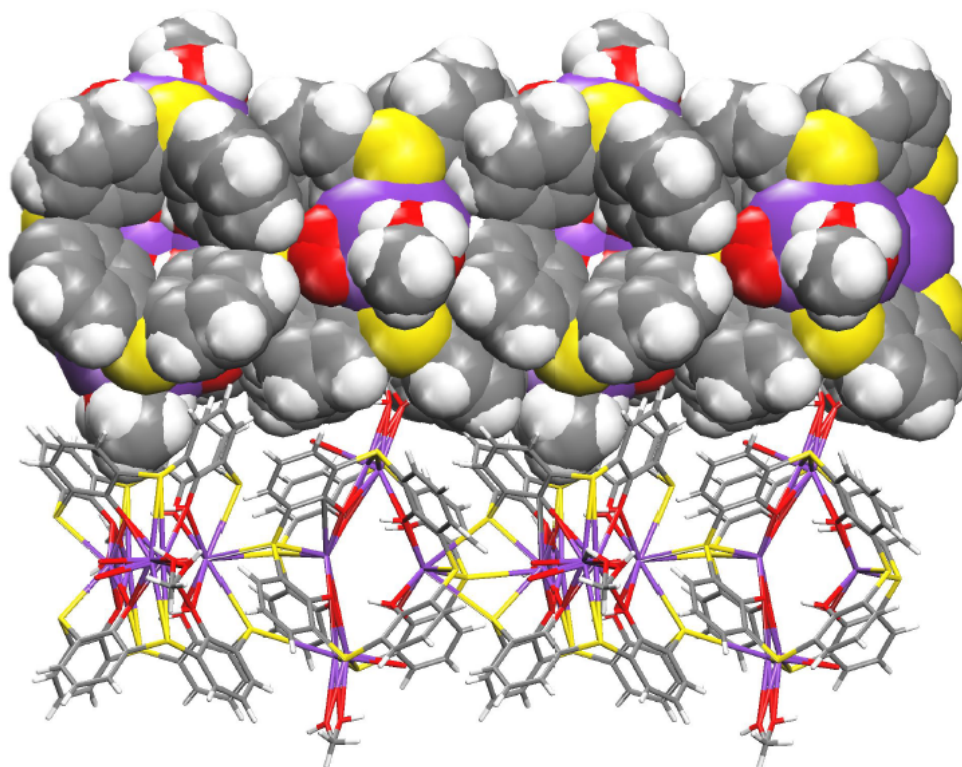
S5. J. Zeller and U. Radius, *Inorg. Chem.*, 2006, **45**, 9487-9492.

**Supplementary Table S2** Crystal data and structure refinement for complexes **2** and **3**.

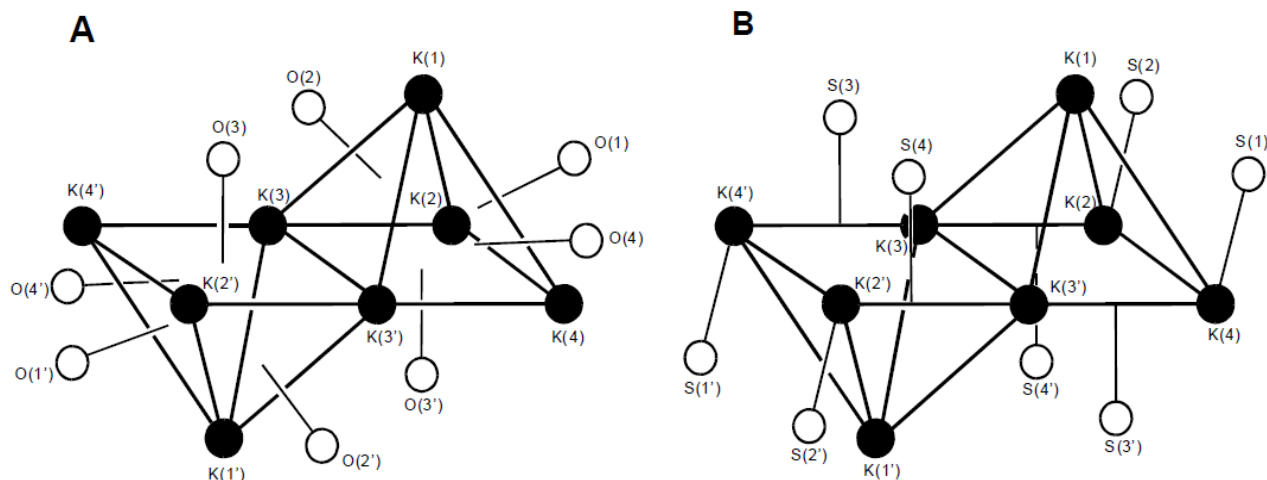
Complex	<b>2</b>	<b>3</b>
Empirical formula	C <sub>100</sub> H <sub>72</sub> O <sub>23</sub> S <sub>16</sub> K <sub>8</sub>	C <sub>72</sub> H <sub>84</sub> O <sub>14</sub> S <sub>8</sub> K <sub>8</sub>
Formula weight	2467.50	1742.71
Temperature/K	173.1	120.1
Crystal system	monoclinic	monoclinic
Space group	Cc	P2 <sub>1</sub> /n
<i>a</i> / Å	22.2021(10)	12.7148(6)
<i>b</i> / Å	19.4371(9)	13.1573(5)
<i>c</i> / Å	15.8554(6)	23.5690(12)
$\beta$ / °	130.5960(9)	98.1440(17)
<i>V</i> / Å <sup>3</sup>	5195.5(4)	3903.2(3)
<i>Z</i>	2	2
<i>D</i> <sub>calcd</sub> / g cm <sup>-3</sup>	1.577	1.483
$\mu$ / mm <sup>-1</sup>	0.726	0.717
<i>F</i> (000)	2528	1816
Reflection collected	24329	37384
Independent reflections ( <i>R</i> <sub>int</sub> )	11157 (0.0375)	8930 (0.040)
Data / parameters	11157 / 665	8930 / 455
Goodness-of-fit	1.379	1.047
<i>R</i> and <i>wR</i> for <i>I</i> > 2 $\sigma$ ( <i>I</i> )	0.0552, 0.1577	0.0559, 0.1884
CCDC Number	790086	790085



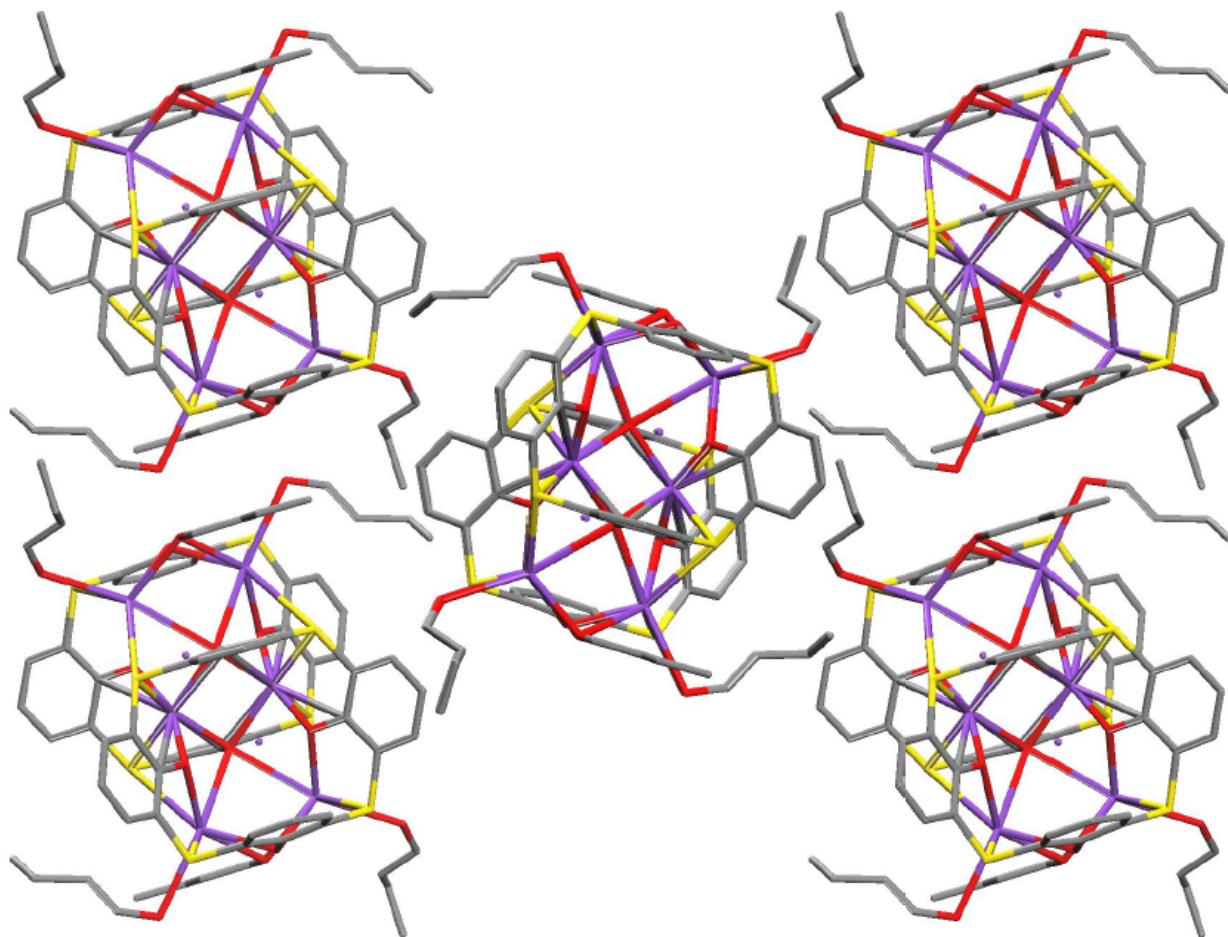
**Supplementary Figure S1** Coordination environments of the potassium cations in complex **2**: (A) K...O coordination between the potassium cations and the thiocalixarene phenolic/phenoxide oxygen atoms, (B) K...S coordination between the potassium cations and the thiocalixarene sulfur linker atoms. Selected bond lengths (Å) and angles (deg): K(1)···O(3) 2.718(4); K(1)···O(4) 2.710(6); K(1)···O(5) 2.748(4); K(1)···O(6) 2.712(5); K(2)···O(1) 2.438(4); K(2)···O(2) 2.414(4); K(2)···O(7) 2.426(4); K(2)···O(8) 2.389(4); K(3A)···O(2) 2.768(4); K(3A)···O(7) 2.770(4); K(3A)···O(9) 2.751(15); K(3B)···O(2) 2.746(6); K(3B)···O(7) 2.759(6); K(4A)···O(1) 2.812(4); K(4A)···O(8) 2.846(4); K(4B)···O(1) 2.764(6); K(4B)···O(8) 2.824(6); K(1)···S(4) 3.1975(16); K(1)···S(8) 3.2286(16); K(2)···S(2) 2.832(2); K(2)···S(6) 2.857(2); K(3A)···S(3) 3.283(2); K(3A)···S(7) 3.296(2); K(3B)···S(3) 3.231(5); K(3B)···S(7) 3.252(5); K(4A)···S(5) 3.219(3); K(4A)···S(1) 3.274(2); K(4B)···S(1) 3.272(5); K(4B)···S(5) 3.249(5); S(4)-K(1)-S(8) 125.15(5); S(2)-K(2)-S(6) 89.11(7); S(3)-K(3A)-S(7) 154.86(14); S(3)-K(3B)-S(7) 164.1(2); S(5)-K(4A)-S(1) 163.69(10); S(5)-K(4B)-S(1) 160.5(3).



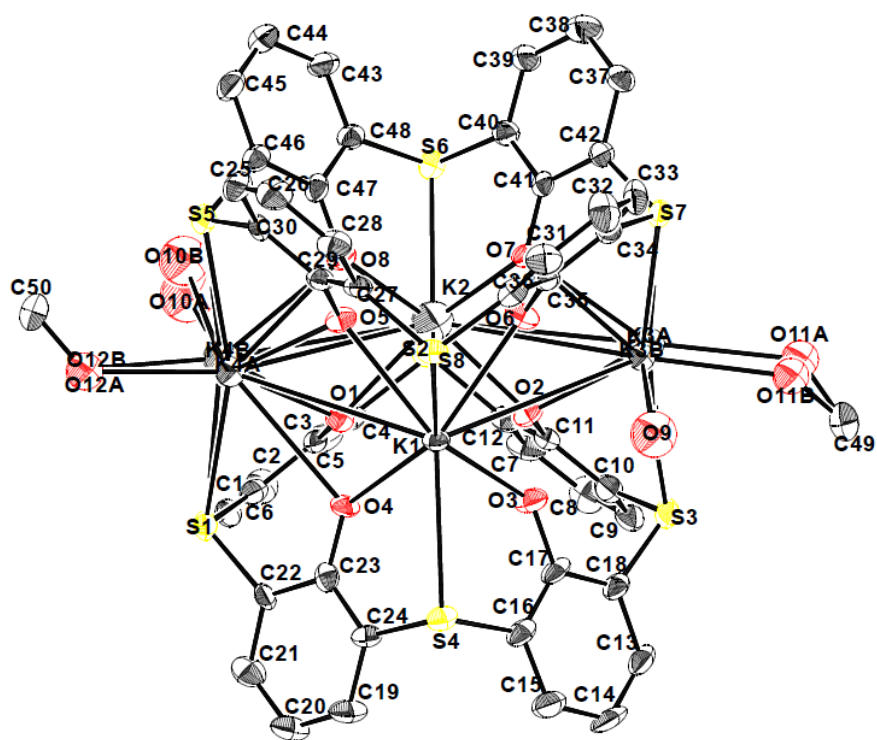
**Supplementary Figure S2** Extended structure of complex **2** showing the supramolecular assembly by the inclusion the coordinated methanol molecules of the polymer into the thiocalixarene cavities of the adjacent polymer (Stick and space-filling representation).



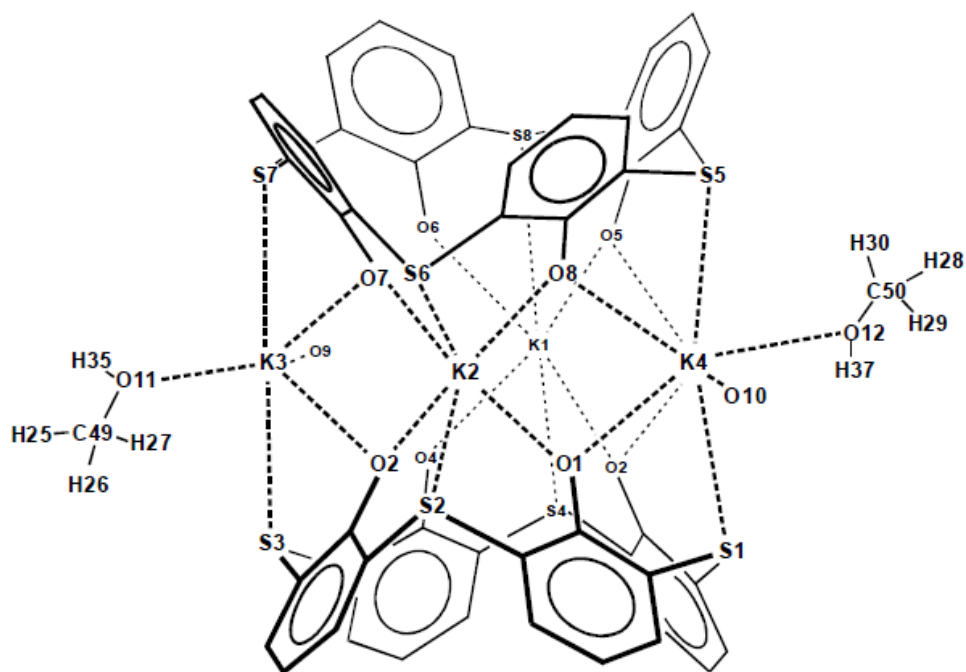
**Supplementary Figure S3** Coordination environments of the potassium cations in the distorted triangular pyramidal arrangements of complex **3**: (A) K $\cdots$ O coordination between the potassium cations and the thiocalixarene phenolic/phenoxide oxygen atoms, (B) K $\cdots$ S coordination between the potassium cations and the thiocalixarene sulfur linker atoms. Symmetry transformations used to generate equivalent atoms:  $x, -x+1, -y+2, -z$ . Selected bond lengths ( $\text{\AA}$ ) and angles (deg): K(1) $\cdots$ O(2) 2.689(2); K(1) $\cdots$ O(4) 2.670(2); K(2) $\cdots$ S(2) 3.1479(11); K(2) $\cdots$ S(4') 3.3381(11); K(2) $\cdots$ O(1) 2.673(2); K(2) $\cdots$ O(2) 2.748(2); K(2) $\cdots$ O(3') 2.823(2); K(3) $\cdots$ S(3) 2.9830(14); K(3) $\cdots$ S(4') 2.9377(16); K(3) $\cdots$ O(2) 2.330(2); K(3) $\cdots$ O(3) 2.394(2); K(3) $\cdots$ O(3') 2.441(2); K(3) $\cdots$ O(4') 2.327(2); K(4) $\cdots$ S(1) 3.1478(13); K(4) $\cdots$ S(3') 3.3168(11); K(4) $\cdots$ O(1) 2.755(2); K(4) $\cdots$ O(3') 2.971(2); K(4) $\cdots$ O(4) 2.676(2); K(3)-K(2)-K(4) 88.07(2); K(3')-K(3)-K(4') 96.84(4); K(2)-K(4)-K(3') 84.12(2)



**Supplementary Figure S4** Extended structure of complex **3** showing the aggregation of the thiacalixarene aromatic rings and the solvated *n*-butanol molecules by intermolecular hydrophobic interactions.

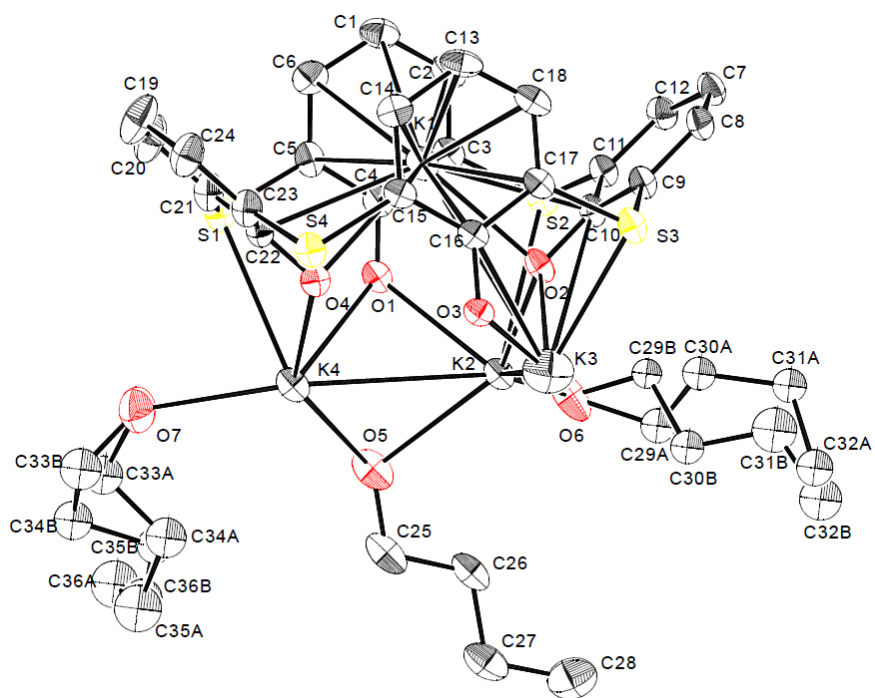


**Supplementary Figure S5** The ORTEP diagram of the asymmetric unit of complex **2** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

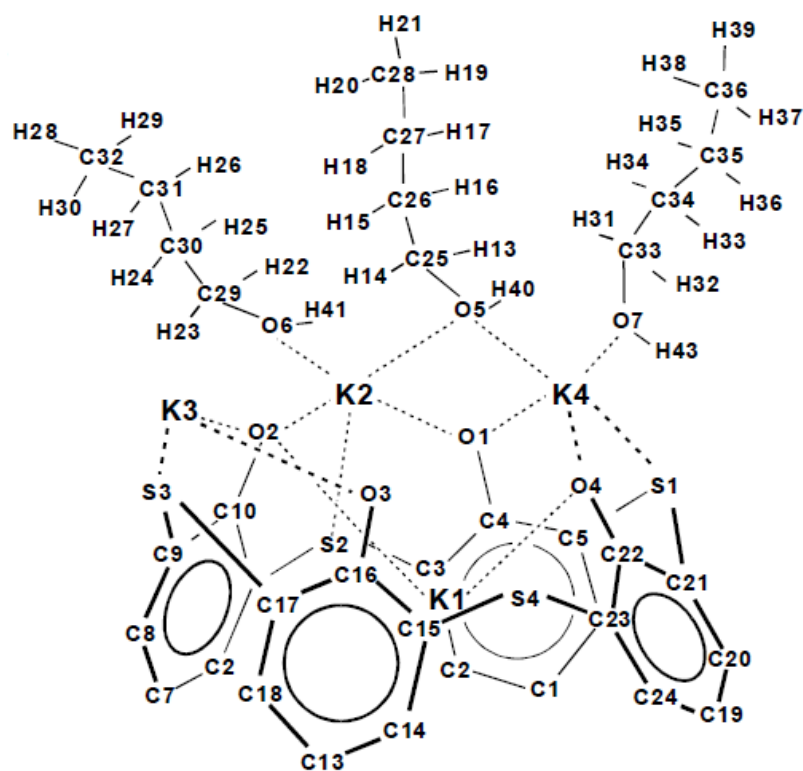


**Supplementary Figure S6** The diagram of coordination environments in complex **2** showing the relevant atom labeling scheme.





**Supplementary Figure S7** The ORTEP diagram of the asymmetric unit of complex **3** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.



**Supplementary Figure S8** The diagram of coordination environments in complex **3** showing the relevant atom labeling scheme.