Electronic Supporting Information

Hetero-alkali metallic (Na, K) three-dimensional supramolecular assembly based on \( p \)-sulfonatothiacalix[4]arene

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Supporting Information Comprises of

Physical measurements and Characterization data of complex 4 & 5

Supplementary Fig. S1: Coordination environment of K1.
Supplementary Fig. S2: Coordination environment of K2.
Supplementary Fig. S3: Coordination environment of K3.
Supplementary Fig. S4: Coordination environment of K4.
Supplementary Fig. S5: Coordination environment of K5.
Supplementary Fig. S6: Thermogravimetric analysis of complex 5.
Supplementary Fig. S7: PXRD patterns of complex 5.
Physical measurements:
Fourier transform infrared (FT-IR) spectra were measured using Thermo Fisher Scientific Nicolet iS5 spectrophotometer (attenuated total reflection (ATR) method). MR data were recorded on JEOL 600SSS ECA-600 instrument. Chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane (CDCl₃). Melting points were determined by using Yanaco, MP-500P apparatus. Powder X-ray diffractions (PXRD) were collected with a Rigaku Ultima 1V diffractometer by using Cu Kα radiation (λ= 1.5406 Å, 40 kV, 40 mA) with a graphite monochromator at a step wise width of 0.02° 2theta and a scan speed 2.000°/min. Thermogravimetric analysis (TGA) was recorded on Thermoplus TG8120 (Rigaku Corp.) thermogravimetric analyzer under nitrogen atmosphere. The temperature was raised at 10 °C/min. to 800 °C. elemental analysis was performed using CE-440 elemental analyzer (System Engineering Inc)

Characterization of compound 5: m.p (°C): 231.8-232.1; IR (cm⁻¹): 3438.72 (OH), 3053.99 (Ar-CH), 1144.71 (S=O); ¹H-NMR (D₂O, DSS, ppm): 7.85 (8H, s, Ar). Anal. Calcd. for C₂₄H₁₀O₁₀S₄Na₂K₄: 5.5 H₂O (%): C, 25.91; H, 1.90; found (%): C, 25.61; H, 1.46.

Characterization of compound 4: m.p (°C): over 420 °C (dec), IR (cm⁻¹): 3327.98 (OH), 3051.55 (Ar-CH), 1151.39 (S=O); ¹H-NMR (D₂O, DSS, ppm): 8.04 (8H, s, Ar), 3.64 (q, 2H, CH₃CH₂OH), 3.36 (s, 1H, CH₃CH₂OH), 1.15 (t, 3H, CH₂CH₂OH). Anal. Calcd. for C₂₄H₁₂O₁₀S₄Na₄ C₂H₅OH (%): C, 32.83; H, 1.90; found (%): C, 32.71; H, 1.78.
Fig. S1: Coordination environment of K1. It coordinated to three water molecules (O1W, O2W, O3W) three sulfonic acid oxygens (O2, O7, O8) of different 2 units, one phenolic oxygen (O5) and one bridged sulfur (S2). Symmetry elements: a, x,y,-1+z; b, -x,1-y,1-z; c, -x,1-y,1-z.
Fig. S2: Coordination environment of K2. It coordinated to one water molecule (O4W), eight sulfonic acid oxygens (O3,\textsuperscript{a} O4,\textsuperscript{b} O15,\textsuperscript{c} O16,\textsuperscript{d} O14,\textsuperscript{e} O15,\textsuperscript{f} O10, O12) of different 2 units. Symmetry elements: \textsuperscript{a}, -x,2-y,1-z; \textsuperscript{b}, -x,2-y,1-z; \textsuperscript{c},x,y,1+z; \textsuperscript{d}, x,y,1+z; \textsuperscript{e},1-x,2-y,1-z; \textsuperscript{f}, 1-x,2-y,1-z.
Fig. S3: (a) Coordination environment of K3. K3 and K3\(^a\) of different units connected to each other through bridged water molecule (O5\(^b\) and O5\(^b\)) and one K3 coordinated four sulfonic acid oxygens(O8,\(^c\) O10,\(^d\) O4,\(^e\) O6) of different 2 units. (b) bridge like coordination between two K3, O5\(^b\) and O6\(^b\).Symmetry elements: \(^a\), -\(x,2\)-\(y,1\)-\(z\); \(^b\), -\(x,2\)-\(y,1\)-\(z\); \(^c\), -\(x,2\)-\(y,1\)-\(z\); \(^d\), -\(x,2\)-\(y,1\)-\(z\); \(^e\), -\(x,2\)-\(y,1\)-\(z\); \(^f\), -\(x,2\)-\(y,1\)-\(z\).
Fig. S4: Coordination environment of K4. It coordinated to two water molecules (O6W, O7W), six sulfonic acid oxygens (O6,\textsuperscript{a}O7, \textsuperscript{b}O11, \textsuperscript{c}O12, \textsuperscript{d}O11, O14) of different 2 units. Symmetry elements: \textsuperscript{a}, -x,2-y,1-z; \textsuperscript{b}, -x,2-y,1-z; \textsuperscript{c},1-x,2-y,1-z; \textsuperscript{d}, 1-x,2-y,1-z.
**Fig. S5:** Coordination environment of Na1, Na2. The two sodium atoms connected to each other through one bridged watermolecule (O1W) and each sodium coordinated to two phenolic oxygens (O1 & O13 to Na1, O5 & O9 to Na2), two sulfonic acid oxygens of different 2 units (O3^a& O15^b to Na1, O7^c& O12^d to Na2) and one bridged sulfur (S1 to Na1, S3 to Na2). Symmetry elements: \( a-x,1-y,2-z; b, 1-x,1-y,2-z; c, -x,1-y,1-z; d, 1-x,1-y,1-z. \)
Fig S6: Thermogravimetric Analysis of complex 5 recorded in the temperature range between 30 and 800°C at a heating rate 10°C/min.
Fig S7: (a) Calculated powder X-ray diffraction (PXRD) patterns from crystal structure of complex 5 (b) PXRD patterns of grinded crystals of complex 5 in oil.