

Electronic Supporting Information

Hetero-alkali metallic (Na, K) three-dimensional supramolecular assembly based on *p*- sulfonatocalix[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 K α radiation ($\lambda = 1.5406 \text{ \AA}$, 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 C₂₄H₁₀O₁₆S₈Na₂K₄ · 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, CH₃CH₂OH). Anal. Calcd. for C₂₄H₁₂O₁₆S₈Na₄ · C₂H₅OH (%): C, 32.83; H, 1.90; found (%): C, 32.71; H, 1.78.

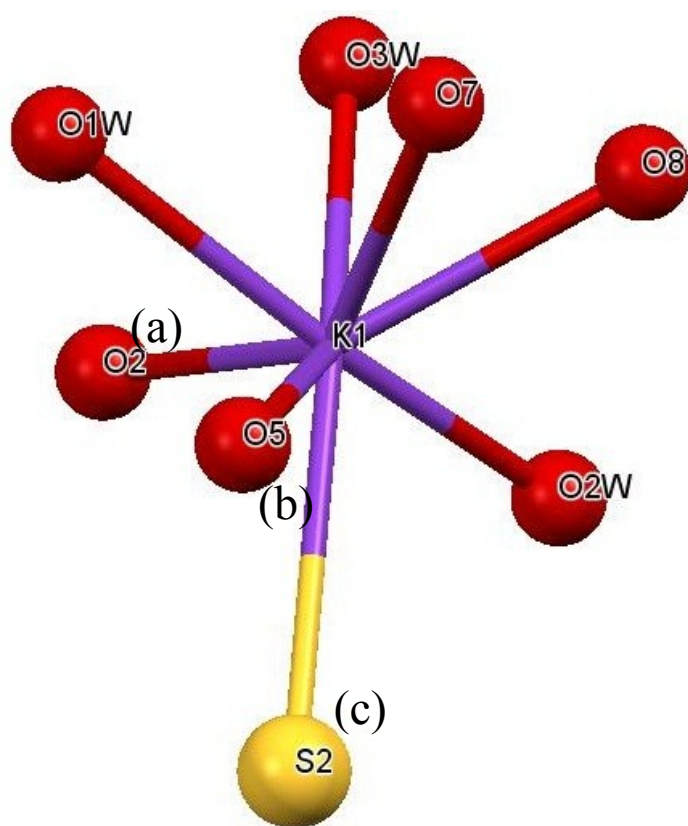


Fig. S1: Coordination environment of K1. It coordinated to three water molecules (O1W, O2W, O3W) three sulfonic acid oxygens (O2,^a O7, O8) of different **2** units, one phenolic oxygen (O5^b) and one bridged sulfur (S2^c). Symmetry elements: ^a, $x, y, -1+z$; ^b, $-x, 1-y, 1-z$; ^c, $-x, 1-y, 1-z$.

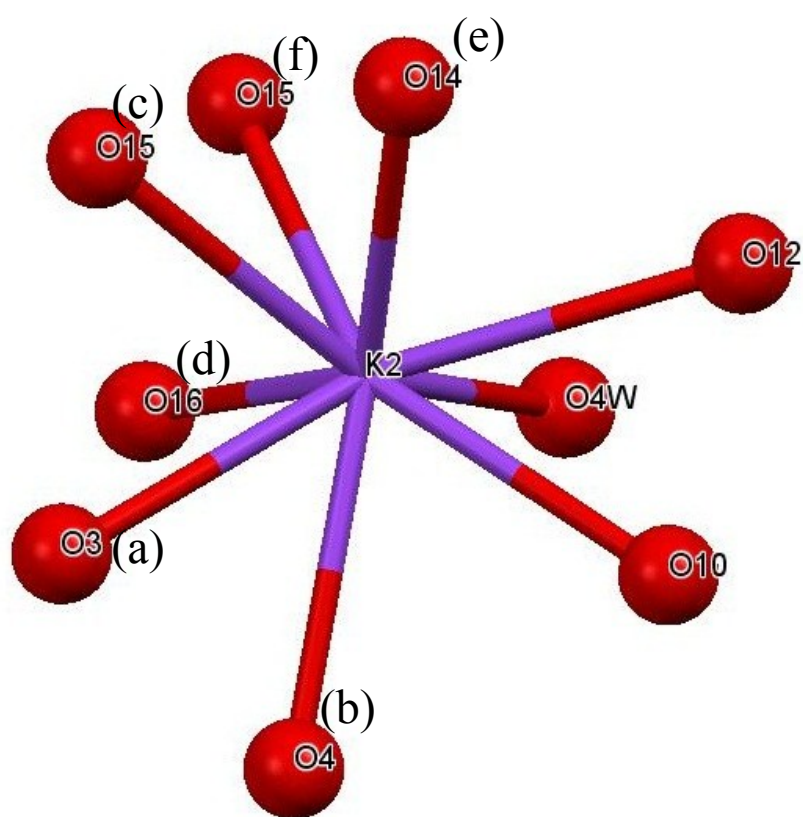


Fig. S2: Coordination environment of K2. It coordinated to one water molecule (O4W), eight sulfonic acid oxygens(O3,^a O4,^b O15,^c O16,^d O14,^e O15,^f O10, O12) of different 2 units.Symmetry elements: ^a, $-x, 2-y, 1-z$; ^b, $-x, 2-y, 1-z$; ^c, $x, y, -1+z$; ^d, $x, y, -1+z$; ^e, $1-x, 2-y, 1-z$; ^f, $1-x, 2-y, 1-z$.

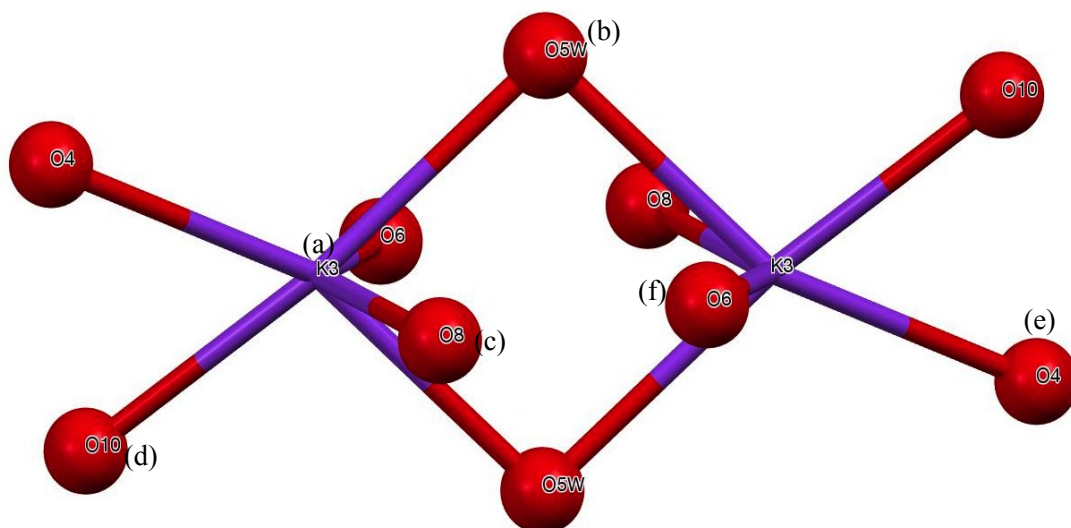


Fig. S3: (a) Coordination environment of K3. K3 and K3^a of different units connected to each other through bridged water molecule (O5W and O5W^b) and one K3 coordinated four sulfonic acid oxygens (O8, O10, O4, O6^f) of different 2 units. (b) bridge like coordination between two K3, O5W and O6W. Symmetry 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.

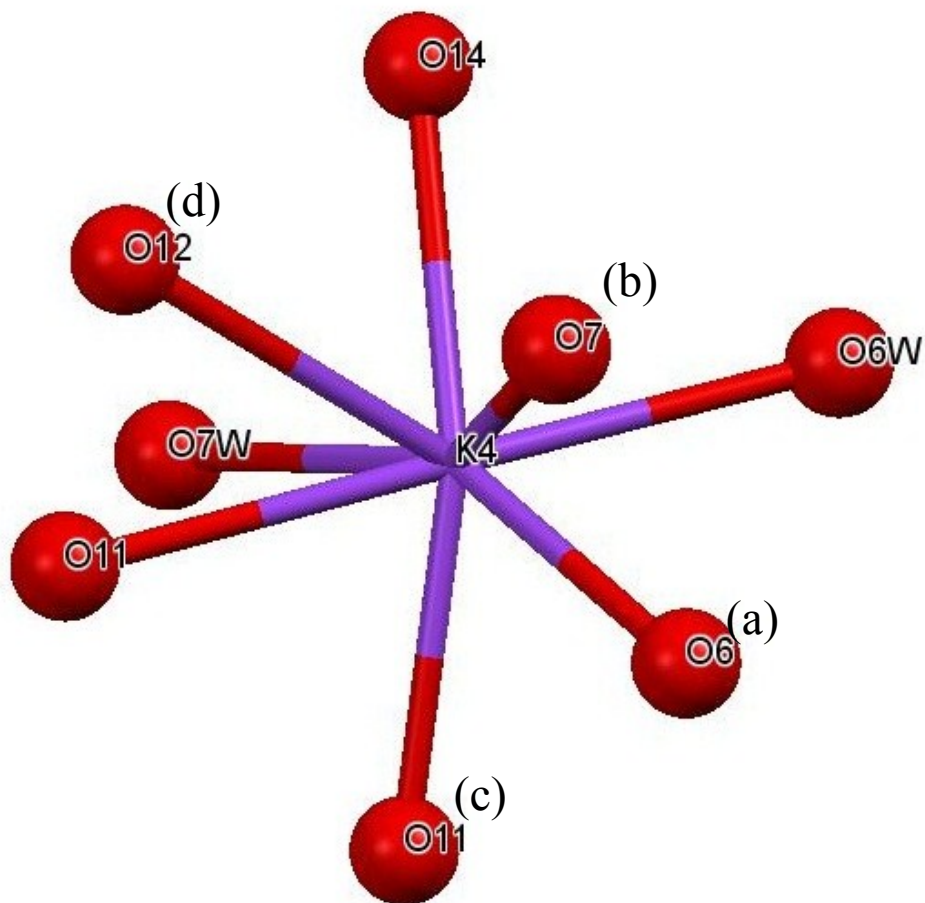


Fig. S4: Coordination environment of K4. It coordinated to two water molecules (O6W, O7W), six sulfonic acid oxygens (O6,^aO7, ^bO11,^c O12,^d O11, O14) of different 2 units. Symmetry elements: ^a, $-x, 2-y, 1-z$; ^b, $-x, 2-y, 1-z$; ^c, $1-x, 2-y, 1-z$; ^d, $1-x, 2-y, 1-z$.

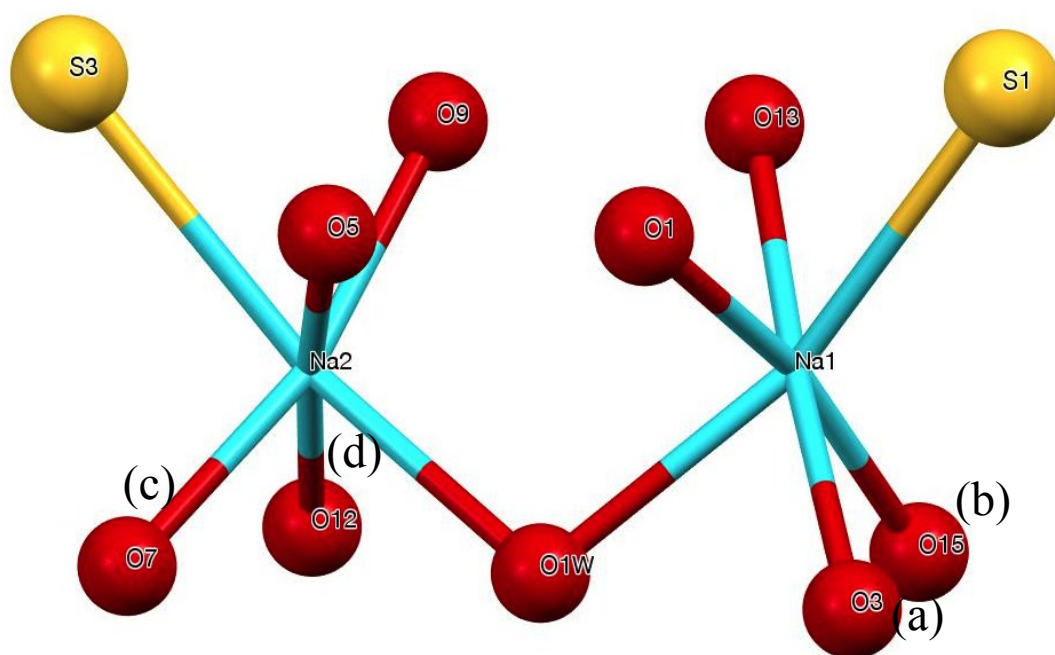


Fig. S5: Coordination environment of Na1, Na2. The two sodium atoms connected to each other through one bridged watermolecule (O1W) and each sodium coordinated to two phenolic oxygens (O1 & O13 to Na1, O5 & O9 to Na2), two sulfonic acid oxygens of different **2** units (O3^a & O15^b to Na1, O7^c & O12^d 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, $1-x, 1-y, 1-z$.

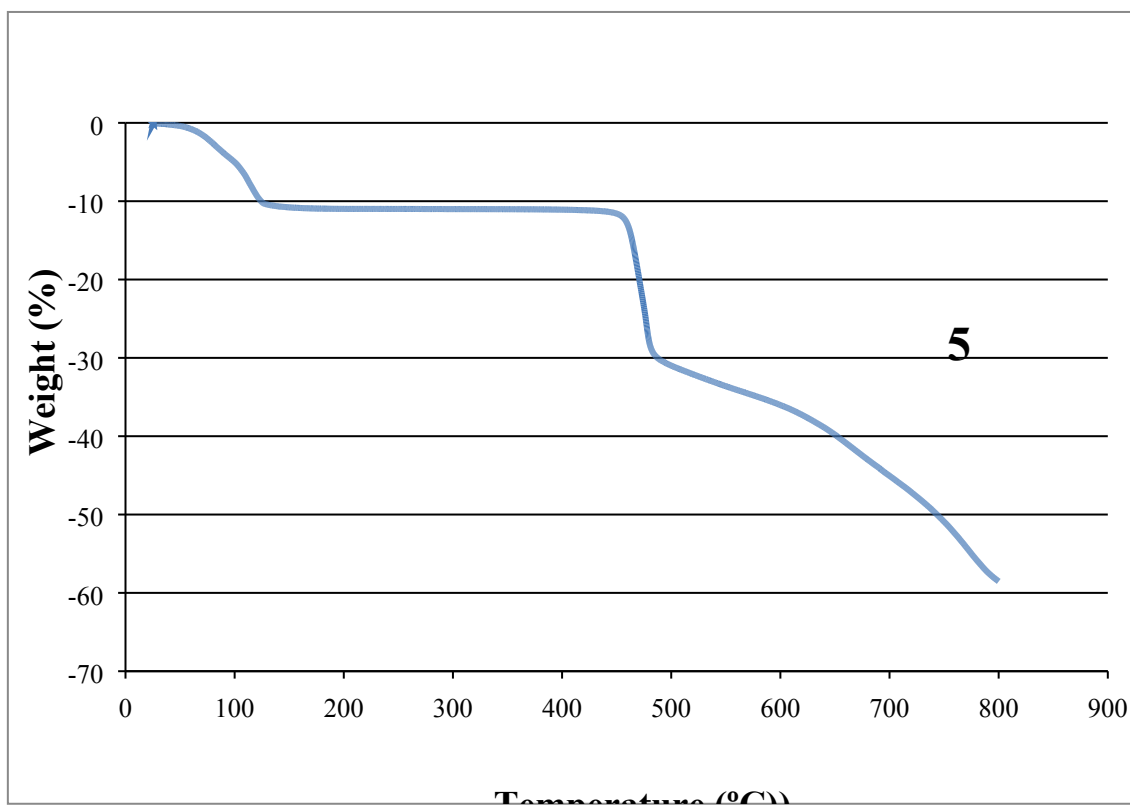


Fig S6: Thermogravimetric Analysis of complex **5** recorded in the temperature range between 30 and 800°C at a heating rate 10°C /min.

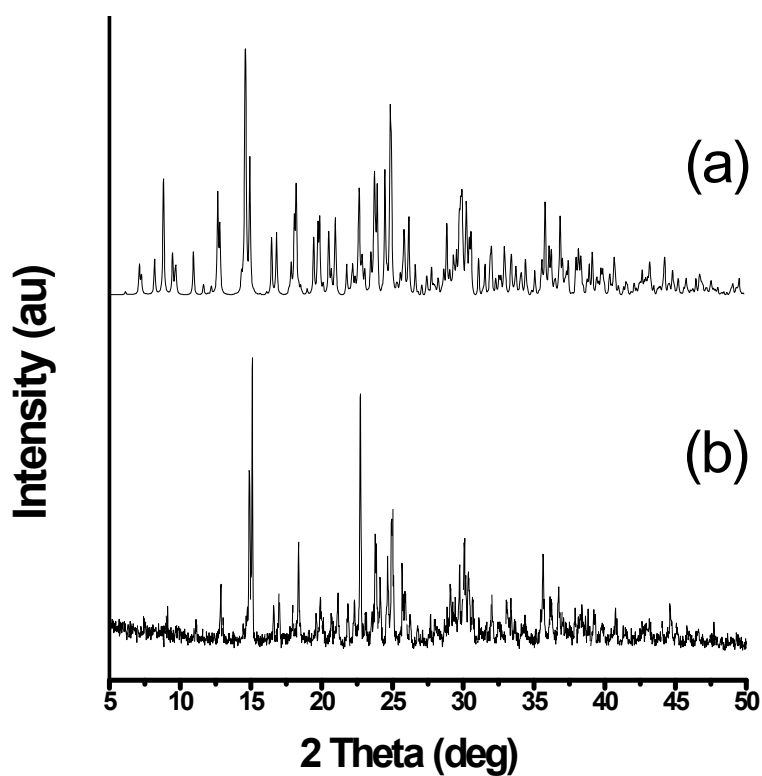


Fig S7: (a) Calculated powder X-ray diffraction (PXRD) patterns from crystal structure of complex **5** (b) PXRD patterns of grinded crystals of complex **5** in oil.