Electronic Supplementary Material (ESI) for RSC Advances.

Self-induced organic guest packed in three dimensional architecture based on hetero-alkali metallic sulfonatothiacalix[4]arene

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Supplementary Information Comprises of

Experimental Section

Materials and instrumentations

All solvents were purchased from commercial sources, and used as received.*p*-^{t}Bu-thiacalix[4]arene was prepared according to our previously reported procedures.[S1] Fourier transform infrared (FT-IR) spectra were measured using Thermo Fisher Scientific Nicolet iS5 spectrophotometer (attenuated total reflection (ATR) method). NMR data were recorded on JEOL 600SSS ECA-600 instrument. Chemical shifts are quoted as parts per million (ppm) relative to tetrametylsilane ($CDCl_3$). Thermogravimetric analysis (TGA) was recorded on Thermoplus TG8120 (Rigaku Corp.) thermogravimetric analyzer under argon atmosphere. The temperature was raised at 10 °C/min. to 800 °C.Elemental analysis was performed using CE-440 elemental analyzer (System Engineering Inc)

References

(S1) (a) Y. Kondo, K. Endo, N. Iki, S. Miyano and F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, **2005**, *52*, 45; (b) Y. Kondo and F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, **2007**, *58*, 123. (c) T. Kimuro, M. Yamada, F. Hamada, *J. Incl. Phenom. Macrocycl. Chem.*, DOI: 10.1007/s10847.014.0435.1

Theoretical calculations

Spartan 10^{TM} software was used for the single-point energy calculations for the X-ray structure of **2 & 3**. The molecular frontier orbital energy calculations were carried out as Hatree-Fock calculations at the 6-31G* level.

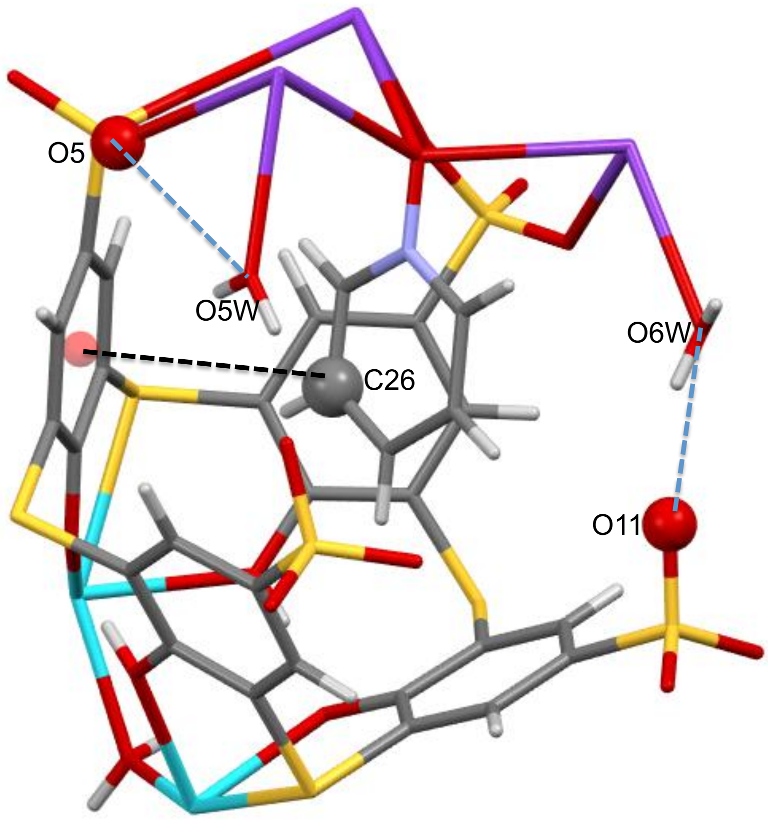

Fig. S1: Asymmetric unit **3** showing CH-π interactions between host and guest molecules (black dotted lines), intramolecular hydrogen bonding between sulfonate oxygens and water molecules (blue dotted lines). Each atom is depicted as follows: K = violet; Na = light blue; S = yellow; O = red; C = gray, H = white.

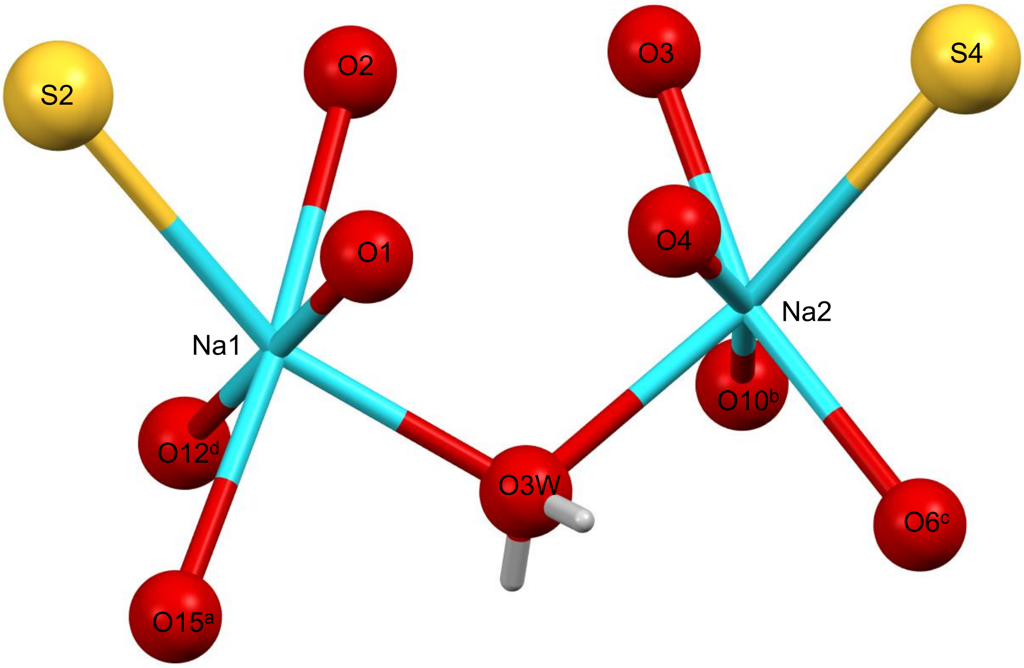

Fig. S2: Coordination environment of Na ions, Each Na coordinated to one bridged sulfur (S2 to Na1, S4 to Na2), two phenolic oxygens (O1 & O2 to Na1, O3 & O4 to Na2), two sulfonic oxygens (O15a & O12d to Na1, O10b & O6c to Na2). One water molecule (O3W) act as a bridge between two Na ions. Symmetry elements: ^{a}1-x, -1/2+y, 1/2-z; ^{b}2-x, 1/2+y, 1/2-z; ^{c}1-x, 1/2+y, 1/2-z; ^{d}2-x, -1/2+y, 1/2-z

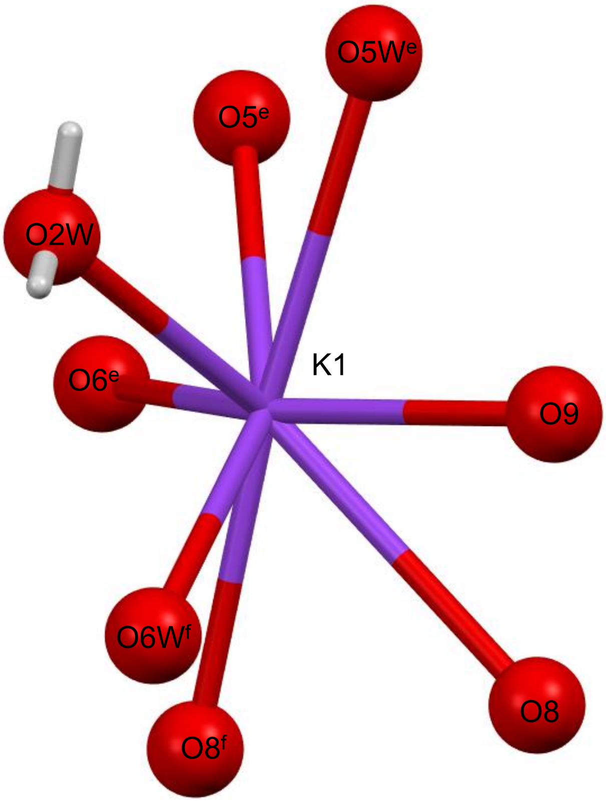

Fig. S3: Coordination environment of K1. It coordinated to three water molecules (O2W, O5W^{e}, O6W^{f}) and five sulfonate oxygens (O8, O9, O5^{e}, O6^{e}, O8^{f}). Symmetry elements: ^{e}1-x, -y, -z; ^{f}2-x, -y, -z

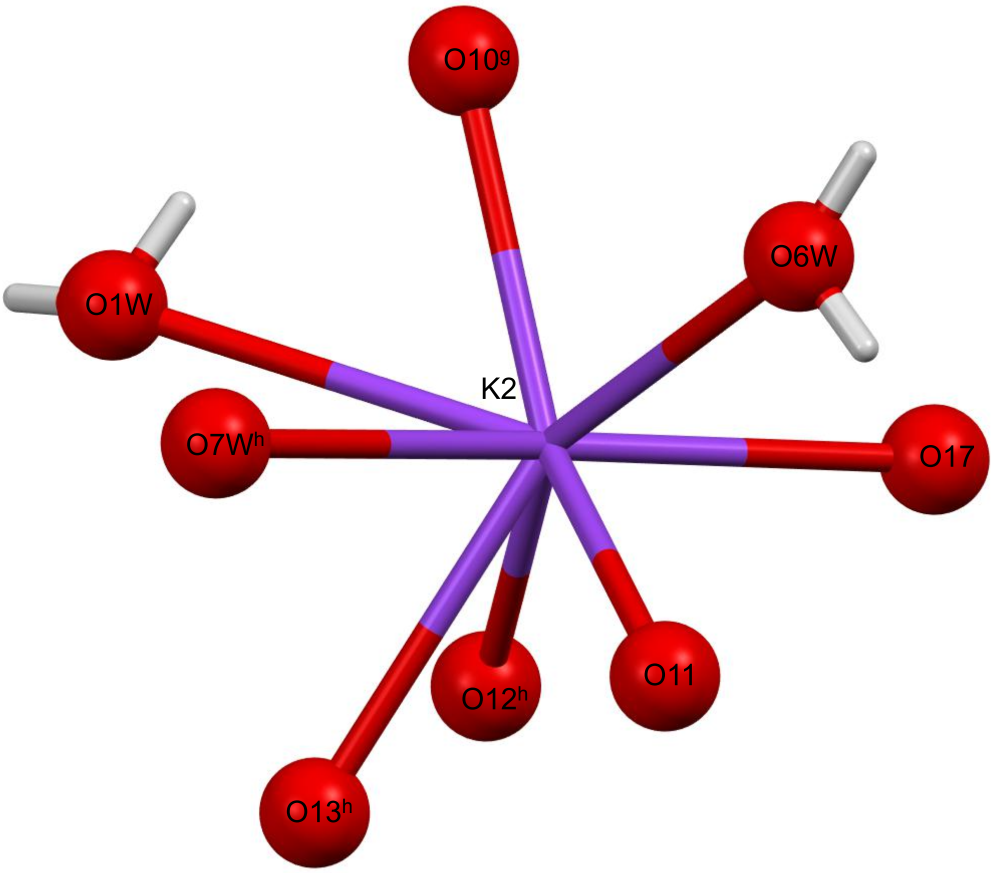

Fig. S4: Coordination environment of K2. It coordinated to three water molecules (O1W, O6W, O7W^{h}), Oxygen of PNO molecule (O17), four sulfonate oxygens (O11, O12^{h}, O13^{h}, O10^{g}). Symmetry elements: ^{g}2-x, -y, -z; ^{h}2-x, 1-y, -z

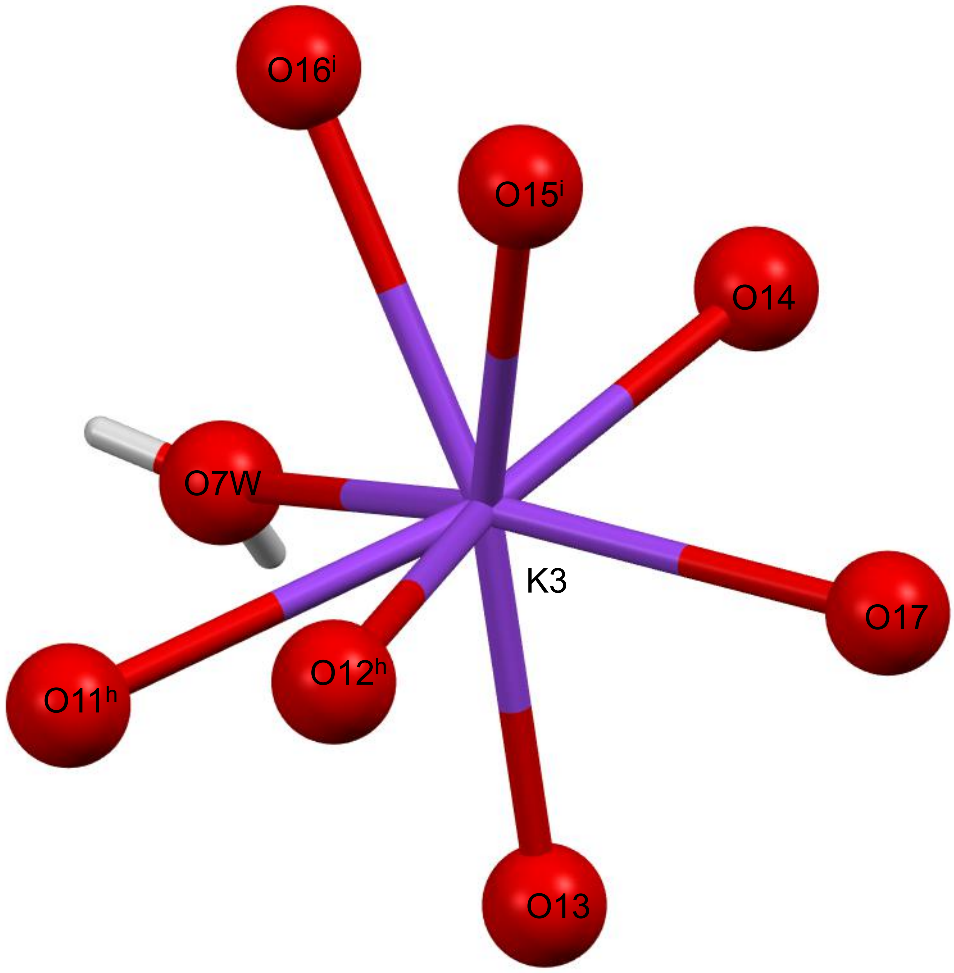

Fig. S5: Coordination environment of K3. It coordinated to one water molecule (O7W), Oxygen of PNO molecule (O17), Six sulfonate oxygens (O13, O14, O17, O11^{h}, O12^{h}, O15^{i}, O16^{i}). Symmetry elements: ^{h}2-x, 1-y, -z; ^{i}1-x, 1-y, -z.

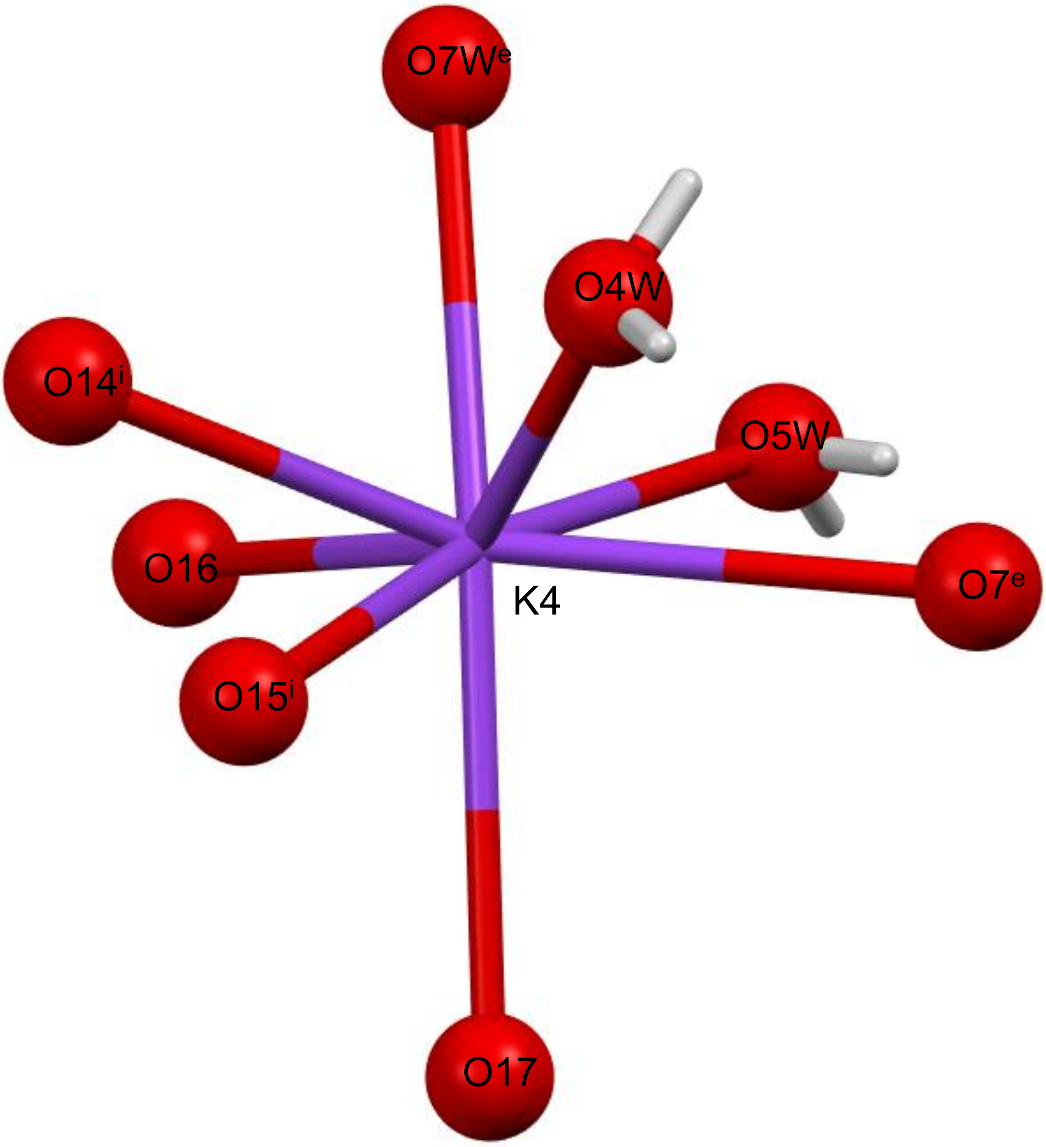

Fig. S6: Coordination environment of K4. It coordinated to three water molecules (O4W, O5W, O7W^{e}), Oxygen of PNO molecule (O17), four sulfonate oxygens (O16, O7^{e}, O14^{i}, O15^{i}).

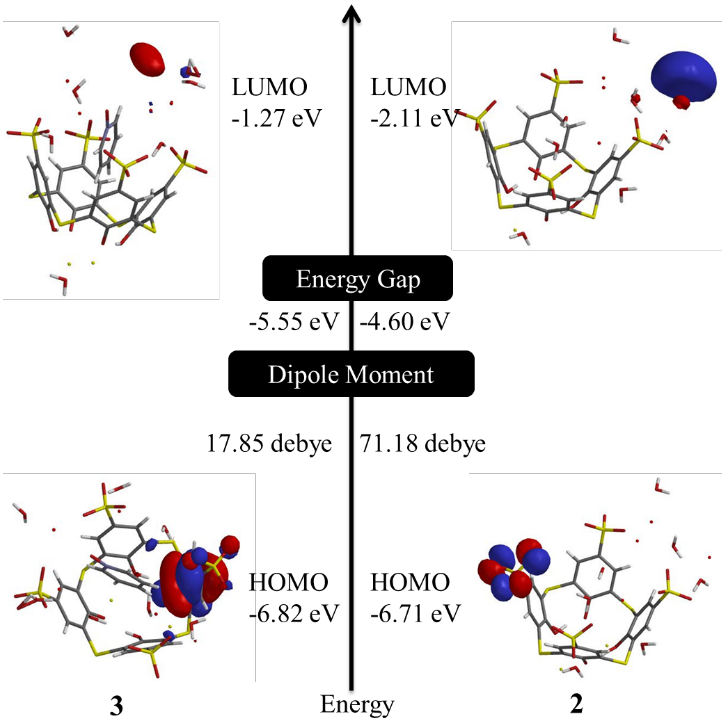

Fig S7: Dipole moment and energy gap of frontier orbitals of **3** and **2**.

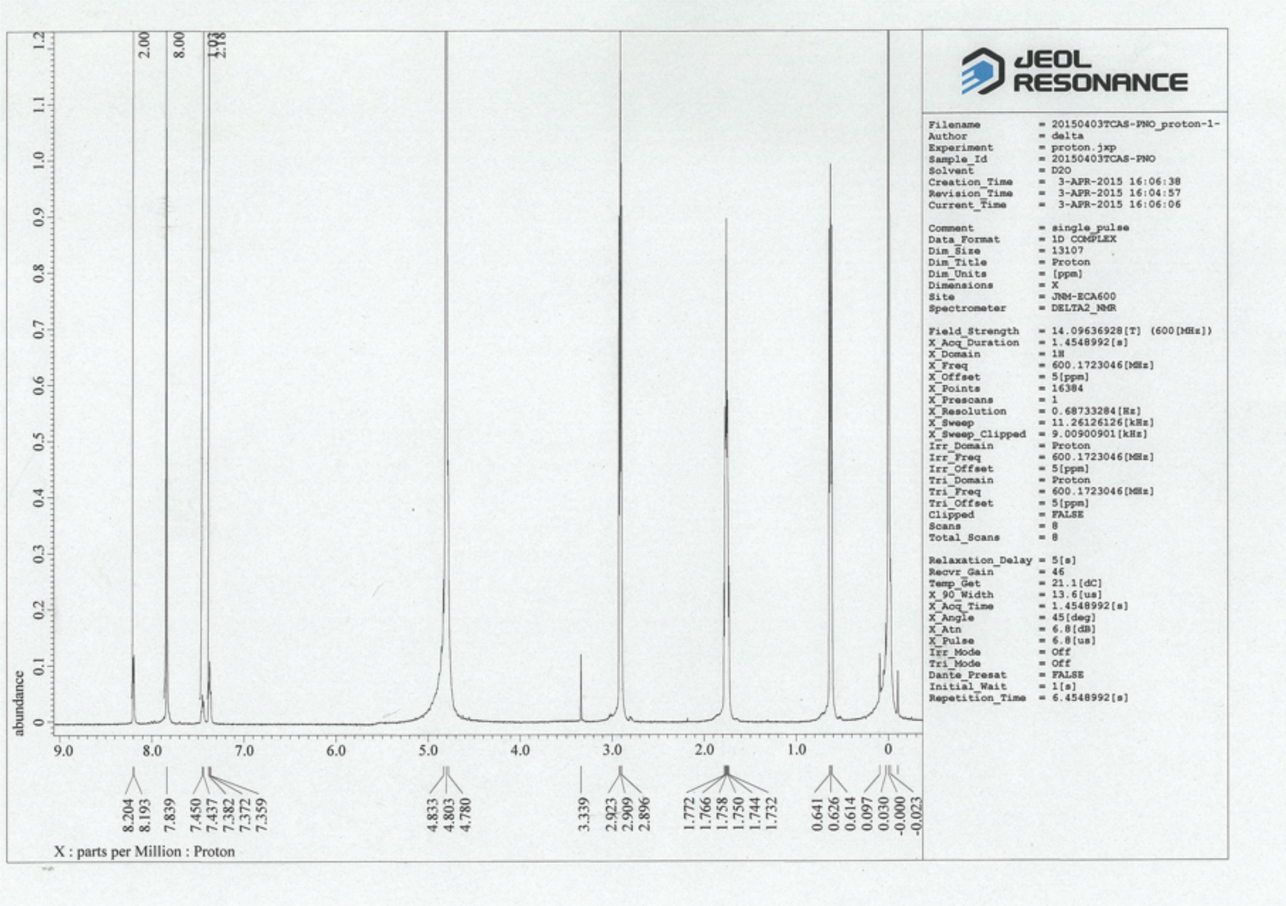

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Fig. S8: ^{1}H-NMR spectrum of **3**