Supramolecular Cations of *m*-halogenated-anilinium(Dibenzo[18]crown-6) in Keggin $[SMo_{12}O_{40}]^{2-}$ Polyoxometallates

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Supporting Information

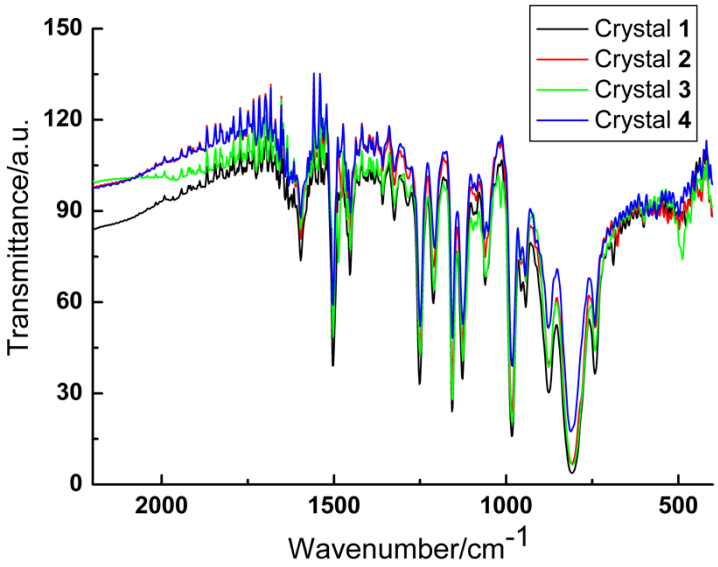

Fig. S1. The IR spectrum of crystal **1**, **2**, **3** and **4**.

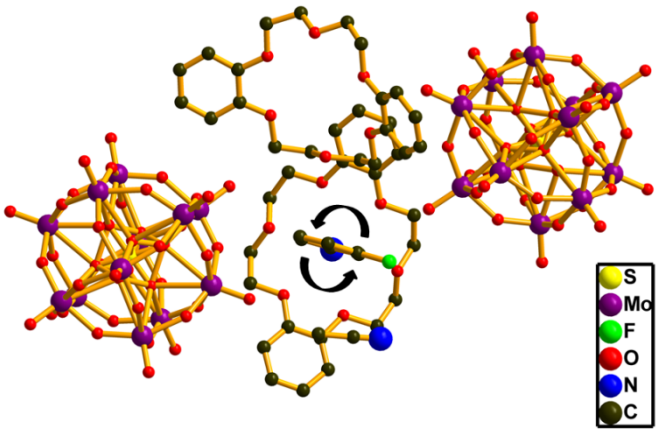

Fig. S2. Initial model structure for the potential energy calculations of crystal **1**, hydrogen atoms are omitted for clarity.

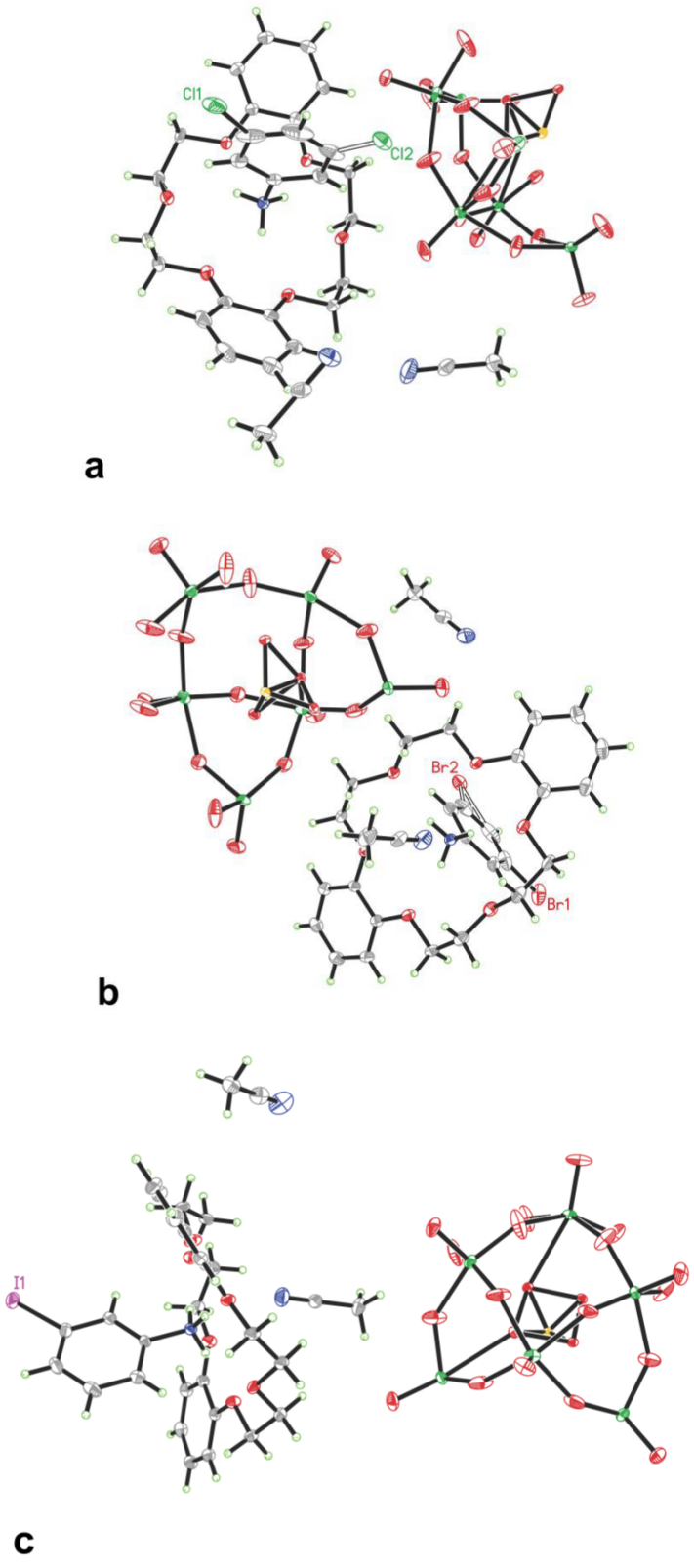

Fig. S3. ORTEP diagram of the asymmetric unit of crystals **2** (a), **3** (b) and **4** (c) with the atomic numbering scheme and 30% thermal ellipsoids

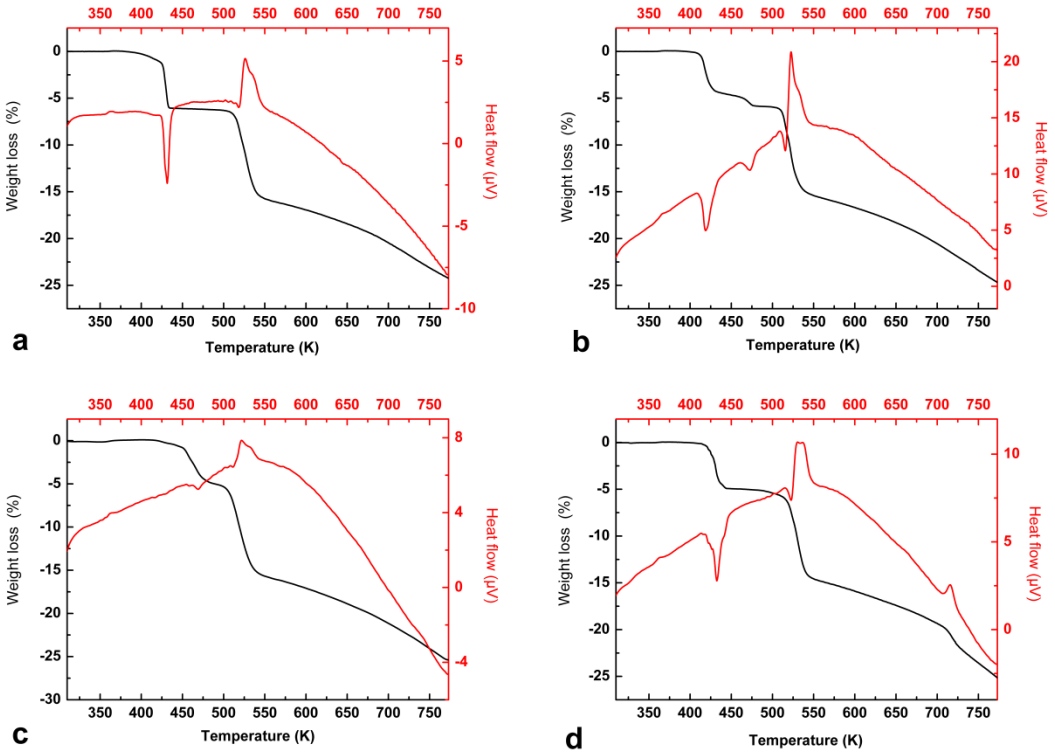

Fig. S4. The TG-DTA curve of compound **1** (a), **2** (b), **3** (c) and **4** (d).

Thermal analysis was performed using a Al_2O_3 reference in the temperature range from 303 to 773 K with a heating rate of 10 K min^{-1} under nitrogen atmospheric. Through the thermo-gravimetry measurement, this four compounds started to decompose at 423 K, and the existence of four CH_3CN in the compounds were lost at 433 K (**1**), 476 K (**2**), 500 K (**3**) and 493 K (**4**), which was confirmed by the weight loss of 5.9%, 5.7%, 5.3% and 5.1% respectively.

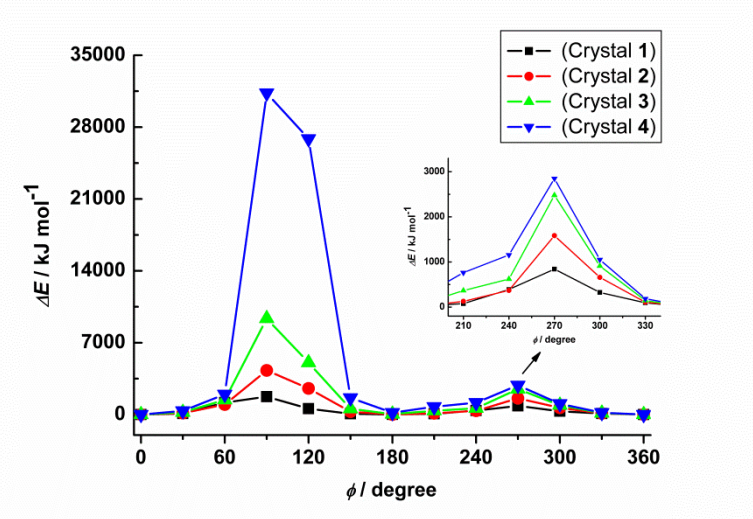

Fig. S5. Potential energy of (*m*-XAni^{+}) cations around the N(1)–C(21) bond. Relative energy (ΔE) vs. the rotation angle (ϕ) of crystal **1** (black line), **2** (red line), **3** (green line) and **4** (blue line).

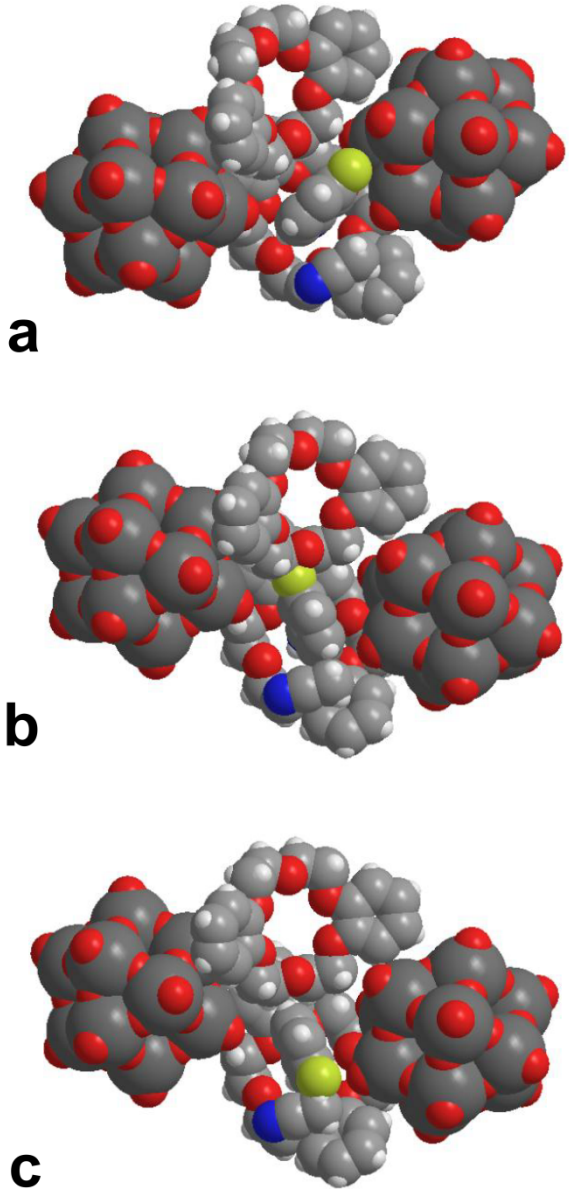

Fig. S6. The model structure of crystal **1** when the (*m*-FAni^{+}) cations around the N(1)–C(21) bond rotating 0° (a), 90° (b) and 270° (c).

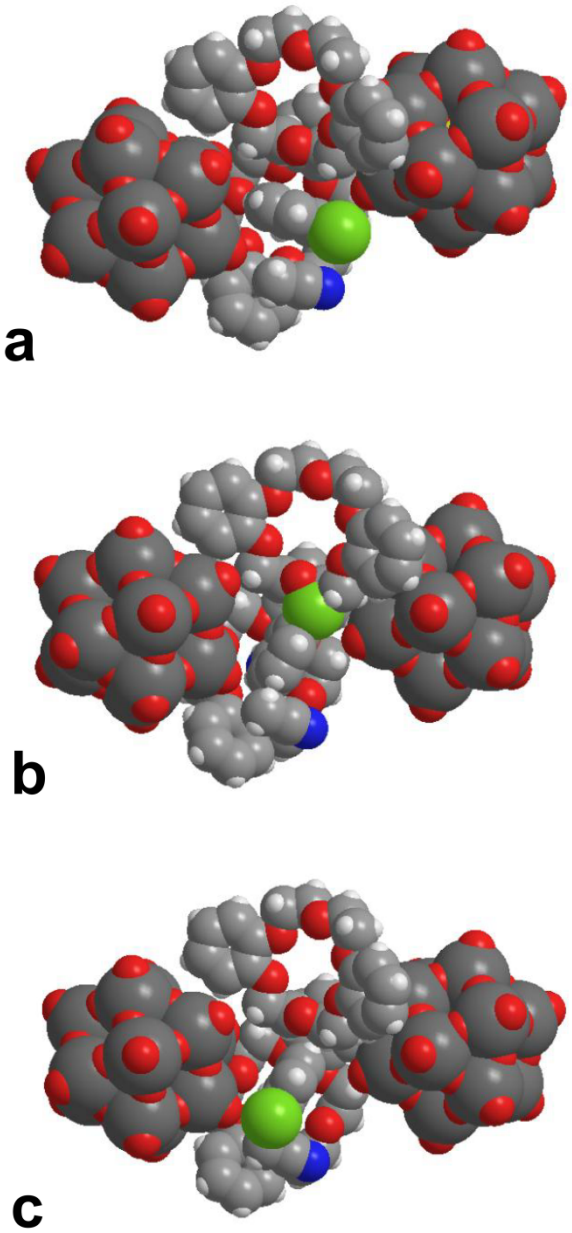

Fig. S7. The model structure of crystal **2** when the (*m*-ClAni$^+$) cations around the N(1)–C(21) bond rotating 0° (a), 90° (b) and 270° (c).

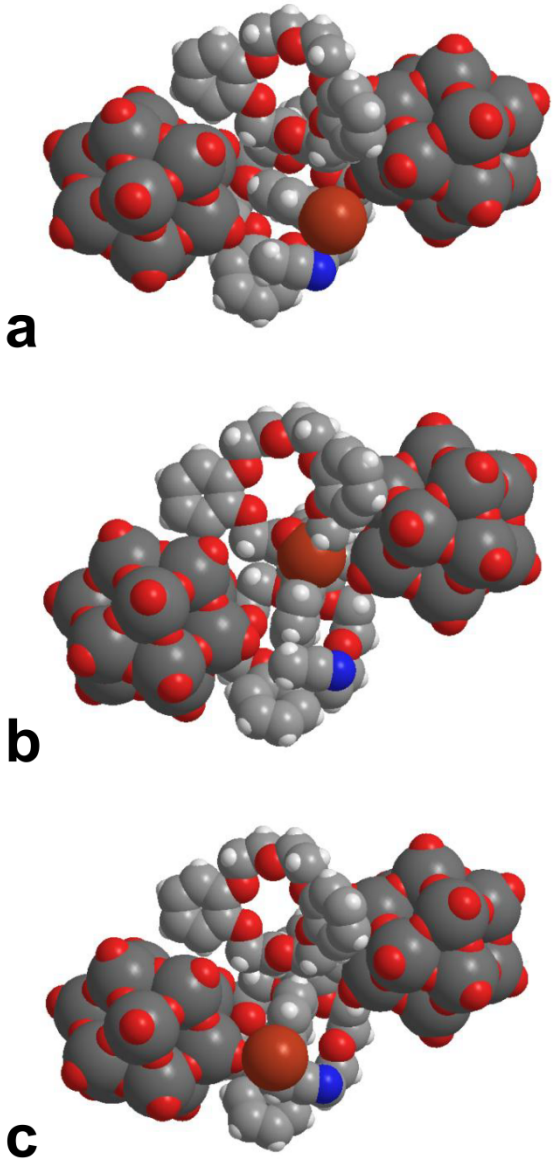

Fig. S8. The model structure of crystal **3** when the (*m*-BrAni$^+$) cations around the N(1)–C(21) bond rotating 0° (a), 90° (b) and 270° (c).

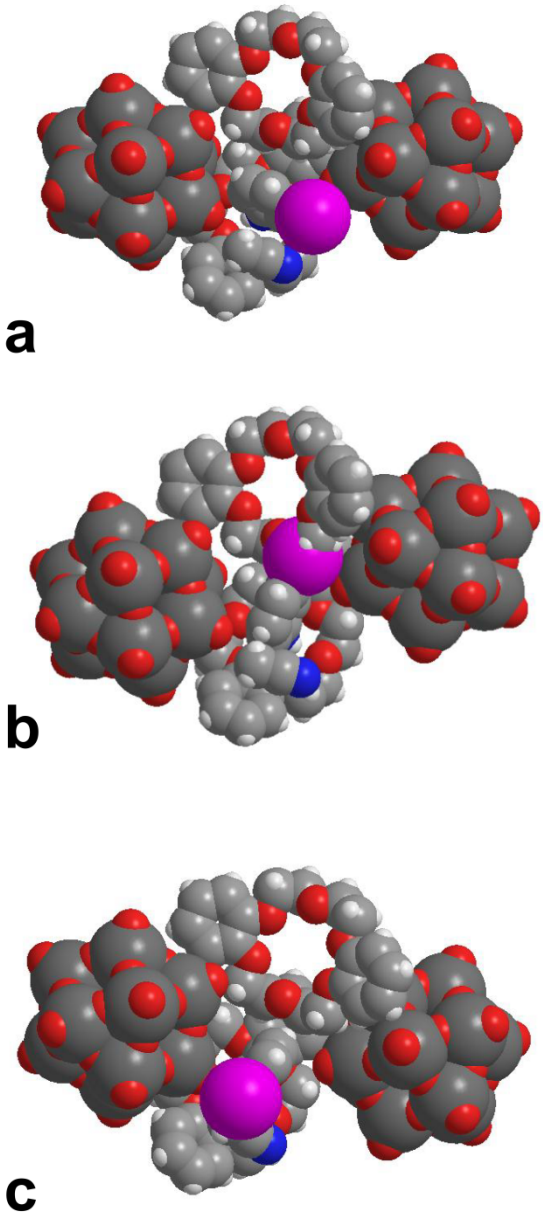

Fig. S9. The model structure of crystal **4** when the (*m*-IAni^{+}) cations around the N(1)–C(21) bond rotating 0° (a), 90° (b) and 270° (c).