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.
Thermal analysis was performed using a Al$_2$O$_3$ 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$_3$CN 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-FAn⁺) 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 \((m\text{-ClAni}^+)\) 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).