Electronic Supporting Information
Revisiting the Formation of Giant Molybdenum Blue Clusters

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Figure S1. Ball-and-stick representation of the mixed-valent Keplerate-type polyoxomolybdate 3, emphasizing the twelve slightly domed pentagonal {(Mo)Mo$_5$} building blocks (Mo in octahedral MoO$_6$ environments: dark blue spheres, Mo in pentagonal-bipyramidal MoO$_7$ environments: light blue spheres), where the Mo–(µ$_3$-O) bonds are shown as black lines, which are interlinked by thirty Mo(=O)(OH$_2$) groups (purple spheres). Also shown are two out of nine crystallographically located K$^+$ positions (large green spheres). Furthermore, sulfate groups coordinating to the {(Mo)Mo$_5$} building blocks from the interior of the cluster sphere are represented for an arbitrarily chosen configuration (one out of five evenly disordered S–O$_{term}$ vectors per {(Mo)Mo$_5$} group; S: yellow, S–O bonds; yellow). O: small red spheres, hydrogen positions not shown for clarity.
Figure S2. FT-IR spectra (KBr pellets) of molybdenum blue compounds: From bottom to top: (1) the spherical \{Mo_{102}\}-type Keplerate 3a; (2) the Na⁺ salt of 3; (3) the Na⁺ salt of the \{Mo_{368}\} cluster, 1a; (4) the Na⁺ salt of the \{Mo_{154}\} wheel-type polyanion, 2a.
Figure S3. TGA (top) and DTA (bottom) data for 3a. Crystalline samples were heated from 25 °C to 600 °C at a rate of 10 °C/min in an inert gas stream (N₂, 60 ml/min).