**Supplementary Information**

*Figure S1.* Ball and stick representation with partial atomic labeling scheme, selected bond distances (Å) and bond valence summations (BVS) for the two independent POMs in \( \text{NH}_4\text{Mo}_6(\text{AlePy}_2\text{Mo})_2 \).

\[
\begin{align*}
\text{Mo1} & \quad \text{O1} \quad 1.715(7) & \quad \text{Mo5} & \quad \text{O12} \quad 1.690(13) & \quad \text{Mo10} & \quad \text{O48} \quad 2.348(10) \\
\text{Mo1} & \quad \text{O3} \quad 1.924(8) & \quad \text{Mo6} & \quad \text{O23} \quad 2.138(13) & \quad \Sigma(\text{Mo1}) = 4.5
\end{align*}
\]

\[
\begin{align*}
\text{Mo2} & \quad \text{O7} \quad 1.700(7) & \quad \Sigma(\text{Mo2}) = 4.8
\end{align*}
\]

\[
\begin{align*}
\text{Mo3} & \quad \text{O11} \quad 1.704(14) & \quad \Sigma(\text{Mo3}) = 6.0
\end{align*}
\]

\[
\begin{align*}
\text{Mo4} & \quad \text{O17} \quad 1.723(13) & \quad \Sigma(\text{Mo4}) = 5.9
\end{align*}
\]

\[
\begin{align*}
\text{Mo5} & \quad \text{O19} \quad 1.704(14) & \quad \Sigma(\text{Mo5}) = 6.1
\end{align*}
\]

\[
\begin{align*}
\text{Mo6} & \quad \text{O25} \quad 1.764(15) & \quad \Sigma(\text{Mo6}) = 6.0
\end{align*}
\]
**Figure S2.** Representation of the crystal packing in (a) \( \text{NaMo}_6(\text{Ale}-4\text{Py})_2 \) and (b) \( \text{NaKMo}_6(\text{Ale}-4\text{Py})_2 \); blue octahedra: Mo\(^{VI}\)O\(_6\), pink tetrahedra: PO\(_4\), orange spheres: O, black spheres: C, green spheres: N, cyan spheres: Na, plum spheres: K; hydrogen atoms have been omitted for clarity.

**Table S1.** Geometry of hydrogen-bonding interactions in \( \text{NaMo}_6(\text{Ale}-4\text{Py})_2 \) and \( \text{NaKMo}_6(\text{Ale}-4\text{Py})_2 \) for which N⋯O < 3.1 Å, associated to Figure 4.

<table>
<thead>
<tr>
<th>N-H⋯O</th>
<th>H⋯O (Å)</th>
<th>N⋯O (Å)</th>
<th>N-H⋯O (°)</th>
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</thead>
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<tr>
<td></td>
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<tr>
<td>N5-H5B⋯O5W</td>
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<tr>
<td>N34-H34⋯O40</td>
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<td>N46-H46⋯O6W</td>
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<td>N17-H17A⋯O13</td>
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<td>N22-H22⋯O21W</td>
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Figure S4. (a) Photographs of the powder of NaMo₆(Ale-4Py)₂ at different UV irradiation time (in min). (b) Evolution of the photo-generated absorption in NaMo₆(Ale-4Py)₂ after 0, 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 30, 60, 90, and 130 min of UV irradiation (λ_{ex} = 365 nm).

Figure S5. Evolution of the photoreduction degree (Y(t)) in (a) NaMo₆(Ale-4Py)₂ and (b) NaKMo₆(Ale-4Py)₂ with the UV irradiation time t. Y(t) is defined as 100×C₅⁺(t)/C₆⁺,r(0), with C₆⁺,r(0) the concentration of reducible Mo⁶⁺ cations at t = 0 i.e., at the time just before UV illumination, and C₅⁺(t) the concentration of photo-reduced Mo⁵⁺ ions at a given UV irradiation time t (for details of the photocoloration kinetics model, see reference 6 in the manuscript).
Table S2. Optical characteristics and coloration kinetic parameters of NaMo$_6$(Ale-4Py)$_2$ and NaKMo$_6$(Ale-4Py)$_2$ compared with those of Mo$_6$-Ale, i.e., the fastest photochromic members of the Mo$_6$(BP)$_2$ series (reference 19 in the article). The R$_{508}$(t) vs. t curve relative to the three materials are fitted as R$_{508}$(t) = a/(bt+1) + R$_{508}$(∞). R$_{508}$(∞) is the reflectivity value at the end of the photochromic process, that is at t = ∞. The a parameter is defined as a = R$_{508}$(0)-R$_{508}$(∞), i.e. the difference between the reflectivity values just before UV illumination (t = 0) and at t = ∞. The b parameter is defined as b = k$^c$×C$_{6+}$(0), where k$^c$ is the coloration rate constant, and C$_{6+}$(0) is the initial concentration of photo-reducible Mo$^{6+}$ centers per unit volume. The coloration kinetic half-life time (t$_{1/2}$) is defined as t$_{1/2}$ = b$^{-1}$. The coloration rate constant ratio k$_i$/k$_j$ is defined as k$_i$/k$_j$ = b$_ia_j$/b$_ja_i$.

<table>
<thead>
<tr>
<th></th>
<th>NaMo$_6$(Ale-4Py)$_2$</th>
<th>NaKMo$_6$(Ale-4Py)$_2$</th>
<th>Mo$_6$-Ale</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)$^a$</td>
<td>508</td>
<td>508</td>
<td>508</td>
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<tr>
<td>R$_{508}$(0)$^b$</td>
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<td>0.655</td>
<td>0.892</td>
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<td>a$^c$</td>
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<td>0.589</td>
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<td>b$^c$</td>
<td>2.682</td>
<td>2.731</td>
<td>0.348</td>
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<tr>
<td>R$_2$$^d$</td>
<td>0.995</td>
<td>0.998</td>
<td>0.997</td>
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<tr>
<td>t$_{1/2}$ (min)$^e$</td>
<td>0.37</td>
<td>0.37</td>
<td>2.87</td>
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<tr>
<td>k$^c$$_i$/k$^c$$(\text{Mo}_6$-Ale)$^f$</td>
<td>9.4</td>
<td>10.6</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$Photoinduced absorption band wavelength. $^b$ Reflectivity value before UV excitation (t = 0) at $\lambda_{\text{max}}$ = 508 nm. $^c$ Salient coloration kinetic parameters. $^d$ Regression coefficient for the R(t) vs. t plots. $^e$ Coloration kinetic half-life time (min). $^f$ Coloration rate constants ratio.