Supplementary Information

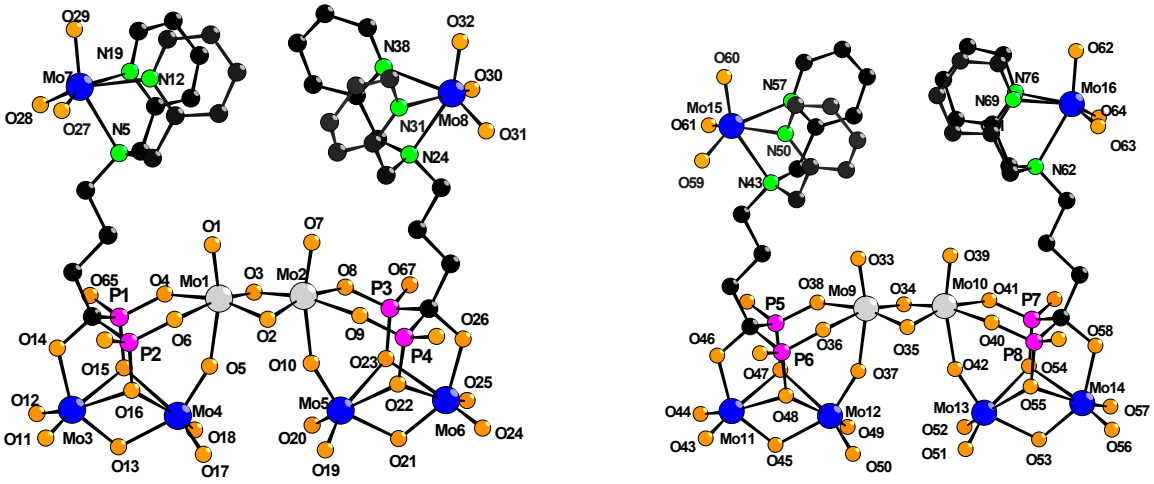


Figure S1. Ball and stick representation with partial atomic labeling scheme, selected bond distances (Å) and bond valence summations (BVS) for the two independent POMs in **$NH_4Mo_6(AlePy_2Mo)_2$**.

Mo1 O1 1.715(7) .
Mo1 O3 1.924(8) .
Mo1 O2 1.948(8) .
Mo1 O4 2.115(8) .
Mo1 O5 2.126(7) .
Mo1 O6 2.142(8) .
Mo1 Mo2 2.5630(14)
Σ(Mo1) = 4.5

Mo2 O7 1.700(7)
Mo2 O2 1.941(9)
Mo2 O3 1.957(9)
Mo2 O8 2.113(9)
Mo2 O9 2.124(8)
Mo2 O10 2.144(8)
Σ(Mo2) = 4.8

Mo3 O11 1.704(14)
Mo3 O12 1.723(14)
Mo3 O13 1.847(11)
Mo3 O14 1.986(10)
Mo3 O15 2.333(11)
Mo3 O16 2.361(11)
Mo3 Mo4 3.209(2)
Σ(Mo3) = 6.0

Mo4 O17 1.723(13)
Mo4 O18 1.747(12)
Mo4 O5 1.801(7)
Mo4 O13 2.018(11)
Mo4 O15 2.321(10)
Mo4 O16 2.392(11)
Σ(Mo4) = 5.9

Mo5 O19 1.704(14)
Mo5 O20 1.731(16)
Mo5 O10 1.772(8)
Mo5 O21 2.010(10)
Mo5 O22 2.348(11)
Mo5 O23 2.377(11)
Mo5 Mo6 3.210(2)
Σ(Mo5) = 6.1

Mo6 O24 1.684(17)
Mo6 O25 1.764(15)
Mo6 O21 1.839(10)
Mo6 O26 1.972(9)
Mo6 O23 2.318(13)
Mo6 O22 2.363(10)
Σ(Mo6) = 6.0

Mo7 O27 1.741(9)
Mo7 O29 1.746(7)
Mo7 O28 1.749(8)
Mo7 N12 2.294(9)
Mo7 N19 2.344(10)
Mo7 N5 2.360(8)
Σ(Mo7) = 6.0

Mo8 O30 1.704(8)
Mo8 O32 1.751(7)
Mo8 O31 1.753(7)
Mo8 N31 2.301(8)
Mo8 N38 2.306(8)
Mo8 N24 2.353(8)
Σ(Mo8) = 6.2

Mo9 O33 1.711(8)
Mo9 O34 1.921(8)
Mo9 O35 1.951(9)
Mo9 O36 2.120(8)
Mo9 O37 2.144(8)
Mo9 O38 2.155(8)
Mo9 Mo10 2.5606(14)
Σ(Mo9) = 4.8

Mo10 O39 1.708(7)
Mo10 O35 1.929(9)
Mo10 O34 1.947(8)
Mo10 O41 2.115(8)
Mo10 O40 2.120(9)
Mo10 O42 2.157(7)
Σ(Mo10) = 4.8

Mo11 O43 1.690(13)
Mo11 O44 1.714(14)
Mo11 O45 1.856(12)
Mo11 O46 1.970(9)
Mo11 O47 2.339(9)
Mo11 O48 2.348(10)

Σ(Mo11) = 6.1

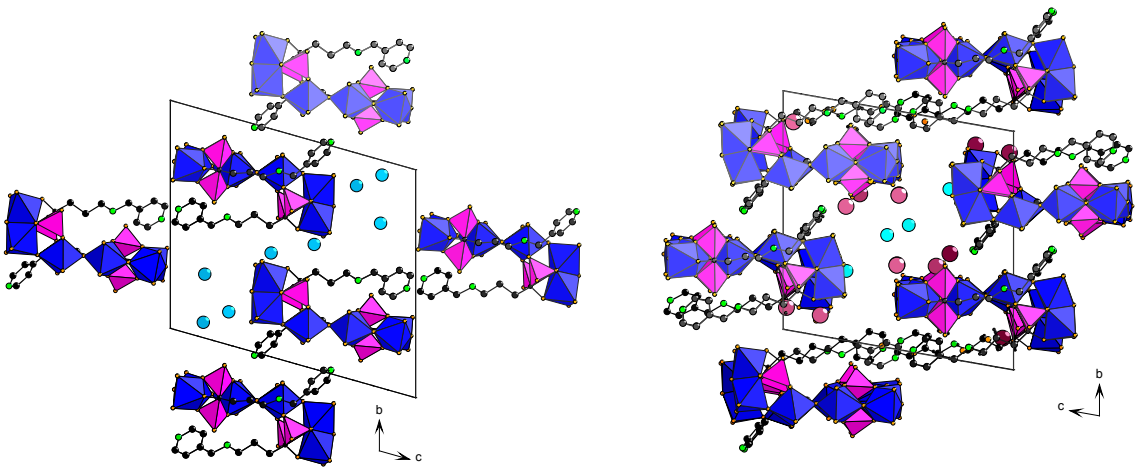
Mo12 O49 1.668(16)
Mo12 O50 1.747(13)
Mo12 O37 1.782(9)
Mo12 O45 2.024(11)
Mo12 O48 2.310(11)
Mo12 O47 2.364(10)
Σ(Mo12) = 6.2

Mo13 O51 1.706(13)
Mo13 O52 1.751(12)
Mo13 O42 1.763(7)
Mo13 O53 2.005(9)
Mo13 O54 2.333(9)
Mo13 O55 2.383(11)
Σ(Mo13) = 6.1

Mo14 O57 1.703(15)
Mo14 O56 1.740(13)
Mo14 O53 1.874(9)
Mo14 O58 1.970(9)
Mo14 O55 2.347(12)
Mo14 O54 2.380(8)
Σ(Mo14) = 5.8

Mo15 O61 1.732(9)
Mo15 O59 1.745(8)
Mo15 O60 1.747(8)
Mo15 N57 2.306(8)
Mo15 N50 2.348(10)
Mo15 N43 2.363(8)
Σ(Mo15) = 6.0

Mo16 O63 1.744(7)
Mo16 O62 1.749(8)
Mo16 O64 1.759(7)
Mo16 N69 2.322(8)
Mo16 N76 2.322(8)
Mo16 N62 2.367(8)
Σ(Mo16) = 6.0



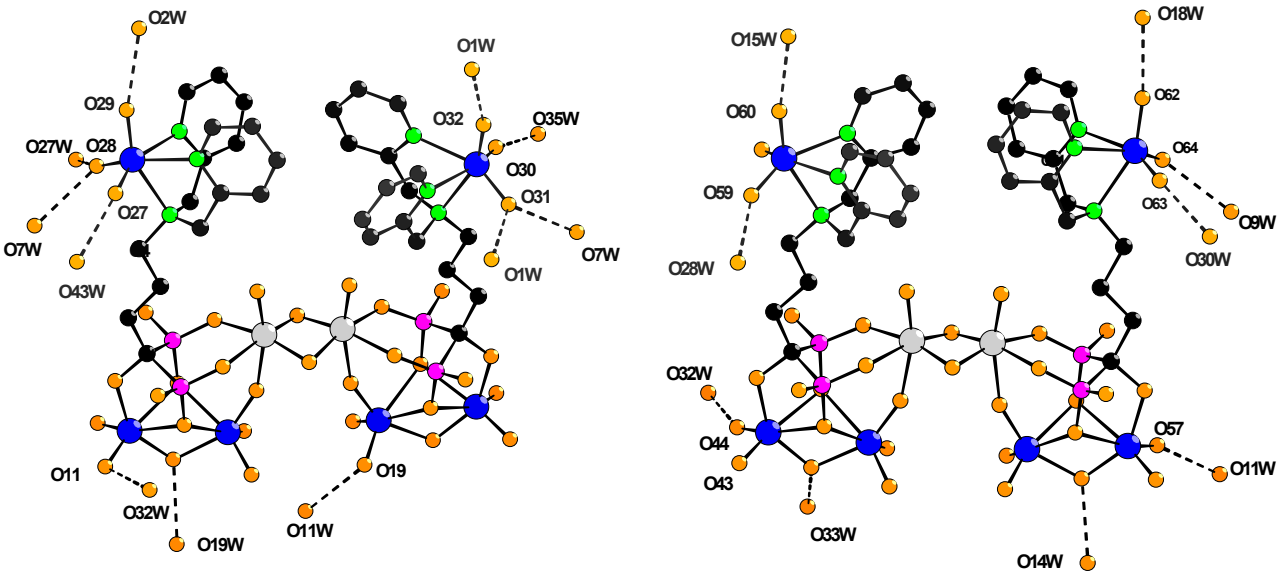
(a) (b)

Figure S2. Representation of the crystal packing in (a) **$NaMo_6(Ale\text{-}4Py)_2$** and (b) **$NaKMo_6(Ale\text{-}4Py)_2$**; 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.

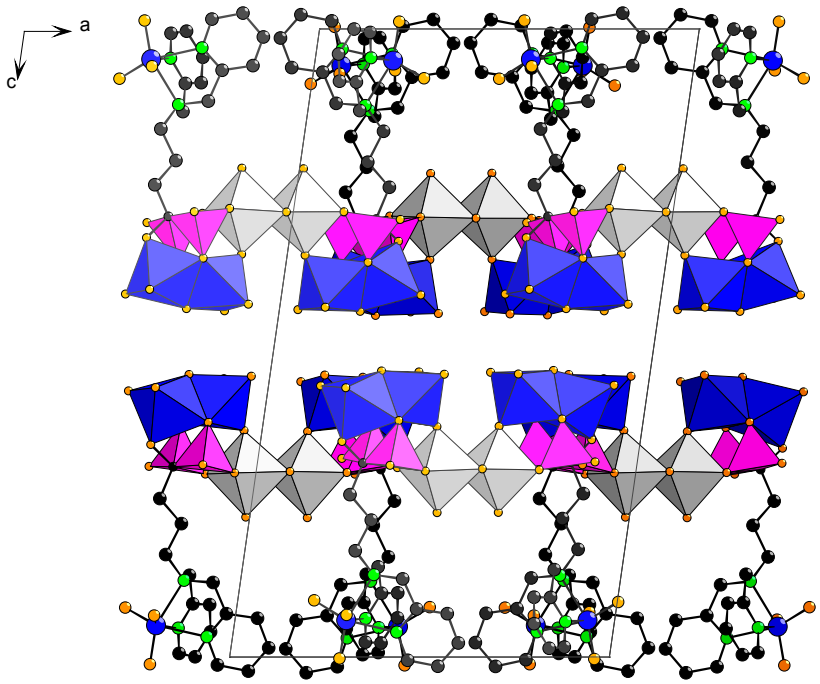
Table S1. Geometry of hydrogen-bonding interactions in **$NaMo_6(Ale\text{-}4Py)_2$** and **$NaKMo_6(Ale\text{-}4Py)_2$** for which N···O < 3.1 Å, associated to Figure 4.

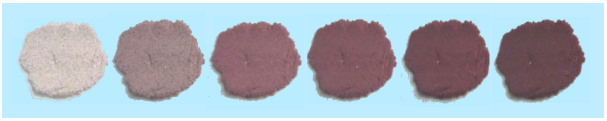
N-H···O	H···O (Å)	N···O (Å)	N-H···O (°)
	$NaMo_6(Ale\text{-}4Py)_2$		
N5-H5B···O5W	1.800	2.765	164.92
N5-H5A···O19	1.925	2.825	169.33
N10-H10···O14	1.899	2.764	167.41
N17-H17B···O7W	1.751	2.618	158.43
N17-H17A···O13	1.815	2.761	158.50
N22-H22···O4W	1.873	2.674	150.43
	$NaKMo_6(Ale\text{-}4Py)_2$		
N29-H29A-O7W	2.171	2.961	144.97
N29-H29B···O46	1.969	2.844	160.48
N34-H34···O40	1.832	2.704	170.44
N41-H41B···O1W	2.355	3.208	156.41
N41-H41A···O41	1.963	2.848	163.93
N46-H46···O6W	1.862	2.688	155.68
N5-H5B···O13W	1.952	2.801	154.70
N5-H5A···O18	1.968	2.808	152.66
N10-H10···O14	1.837	2.704	167.83
N17-H17B···O5W	1.917	2.729	147.63
N17-H17A···O13	1.949	2.792	153.37
N22-H22···O21W	1.861	2.695	157.18

(a)


O2W
O29
O27W
O28
O27
O7W
O43W
O1W
O32
O35W
O30
O31
O7W
O1W
O11
O32W
O19W
O19
O11W
O15W
O60
O59
O28W
O32W
O44
O43
O33W
O18W
O62
O64
O63
O9W
O30W
O57
O11W
O14W

(b)


a
c



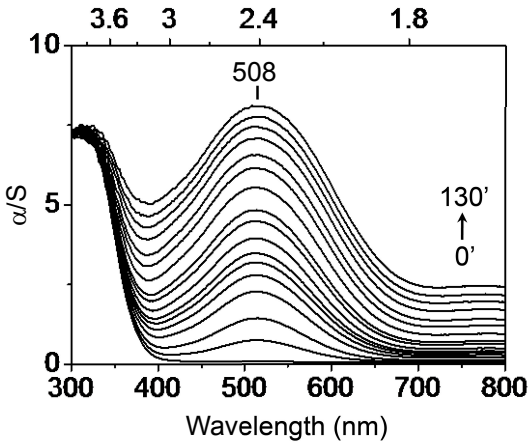


Figure S4. (a) Photographs of the powder of **$NaMo_6(Ale\text{-}4Py)_2$** at different UV irradiation time (in min). (b) Evolution of the photo-generated absorption in **$NaMo_6(Ale\text{-}4Py)_2$** after 0, 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 30, 60, 90, and 130 min of UV irradiation (λ_{ex} = 365 nm).

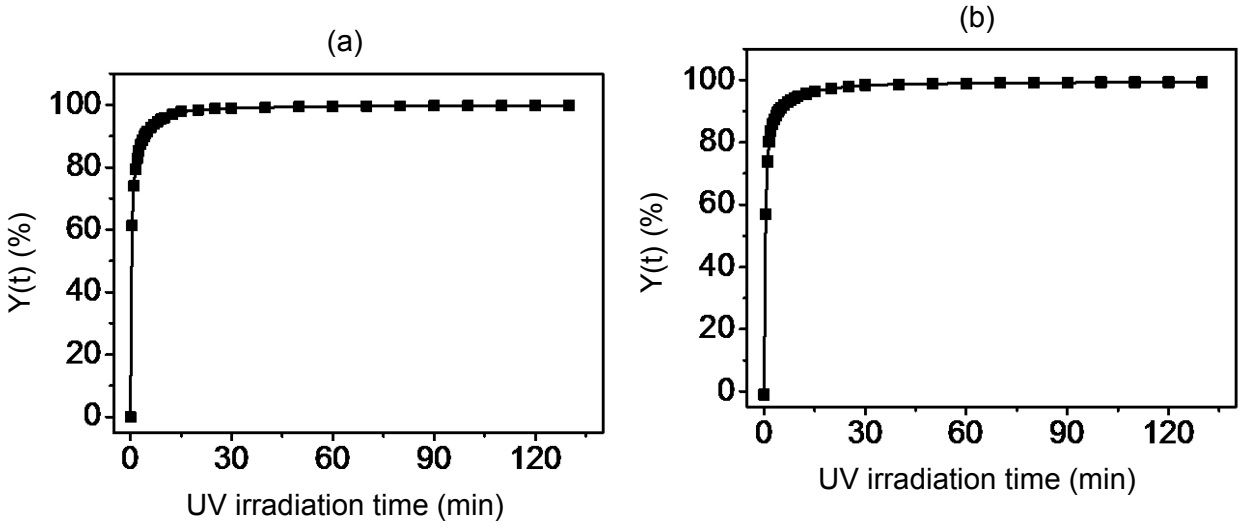


Figure S5. Evolution of the photoreduction degree (Y(t)) in (a) **$NaMo_6(Ale\text{-}4Py)_2$** and (b) **$NaKMo_6(Ale\text{-}4Py)_2$** with the UV irradiation time *t*. Y(t) is defined as $100\times C_{5+}(t)/C_{6+,r}(0)$, with $C_{6+,r}(0)$ the concentration of reducible Mo^{6+} cations at $t = 0$ i.e., at the time just before UV illumination, and $C_{5+}(t)$ the concentration of photo-reduced Mo^{5+} 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 **$NaMo_6(Ale\text{-}4Py)_2$** and **$NaKMo_6(Ale\text{-}4Py)_2$** 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 $R^{508}(t) = a/(bt+1) + R^{508}(\infty)$. $R^{508}(\infty)$ is the reflectivity value at the end of the photochromic process, that is at $t = \infty$. The a parameter is defined as $a = R^{508}(0)-R^{508}(\infty)$, i.e. the difference between the reflectivity values just before UV illumination (t = 0) and at $t = \infty$. The b parameter is defined as $b = k^c \times C_{6+,r}(0)$, where k^c is the coloration rate constant, and $C_{6+,r}(0)$ 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 $k_i/k_j = b_j a_i/b_i a_j$.

	$NaMo_6(Ale\text{-}4Py)_2$	**$NaKMo_6(Ale\text{-}4Py)_2$**	**Mo_6-Ale**
λ_{max} (nm)[a]	508	508	508
$R^{508}(0)$[b]	0.730	0.655	0.892
a[c]	0.655	0.589	0.799
b[c]	2.682	2.731	0.348
R^2 [d]	0.995	0.998	0.997
$t_{1/2}$ (min)[e]	0.37	0.37	2.87
$k^c(j)/k^c(_{Mo6\text{-}Ale})$[f]	9.4	10.6	1

[a]Photoinduced absorption band wavelength. [b] Reflectivity value before UV excitation (t = 0) at λ_{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.