Octahedral molybdenum iodide clusters with pyrazole or pyrazolate ligands

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Powder X-ray diffraction analysis data

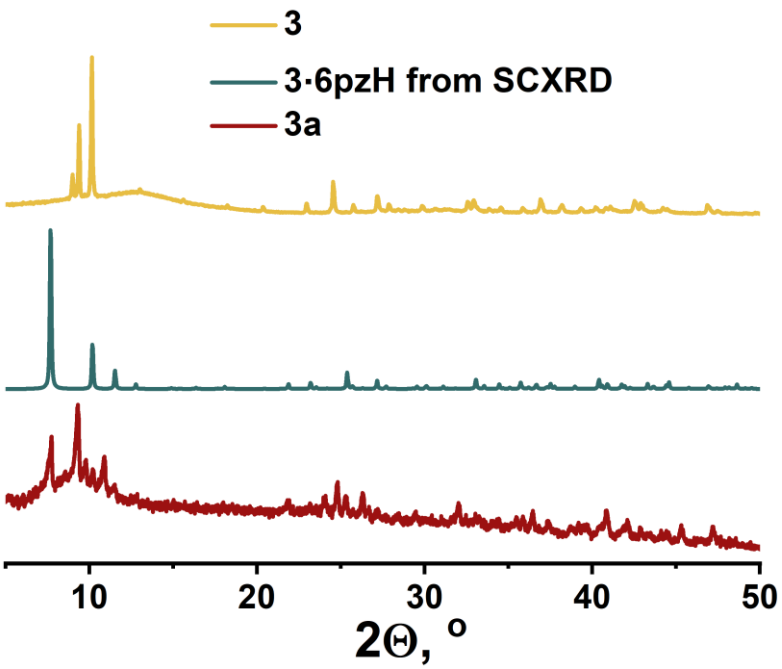

Figure S1. Powder X-ray diffraction patterns of **3** and **3a** in comparison with calculated one from the SCXRD data for **3·6pzH**.

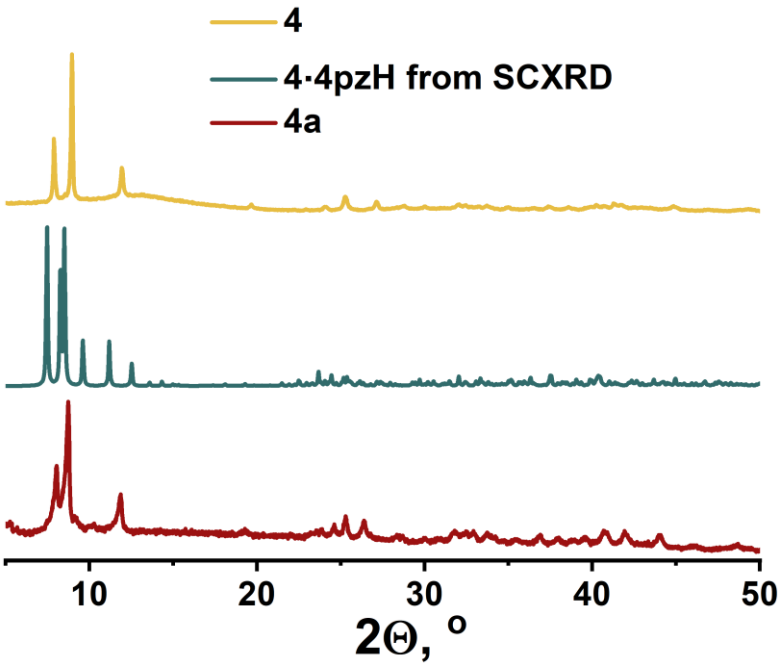

Figure S2. Powder X-ray diffraction patterns of **4** and **4a** in comparison with calculated one from the SCXRD data for **4·4pzH**.

Single-crystal X-ray diffraction data

Table S1. Selected crystallographic parameters of the single-crystal X-ray diffraction structural analysis for $K_2[Mo_6I_8(OH)_6]\cdot 13H_2O$ (**1·13H₂O**), $[Mo_6I_8(H_2O)_6](NO_3)_4\cdot 2H_2O$ (**2·2H₂O**), $[K_2[Mo_6I_8(pz)_6]\cdot 6pzH$ (**3·6pzH**), $[Mo_6I_8(pzH)_6](NO_3)_4\cdot 4pzH$ (**4·4pzH**) in comparison with literature data.

Cluster	Mo–Mo distances, Å	Mo–I distances, Å	Mo–O distances, Å	Mo-N distances, Å	Ref
1·13H₂O	2.6536(5) – 2.6738(5)	2.7745(4) – 2.8147(4)	2.098(3) – 2.106(3)	–	This work
2·2H₂O	2.6469(7) – 2.6652(6)	2.7644(4) – 2.7852(4)	2.150(4) – 2.191(4)	–	This work
$[Mo_6I_8(H_2O)_2(OH)_4]\cdot 2H_2O$	2.6683(8)	2.7896(7) – 2.8092(6)	2.125(4)	–	[1]
$[Mo_6I_8(H_2O)_2(OH)_4]\cdot 12H_2O$	2.6623(5) – 2.6753(5)	2.7633(4) – 2.7923(4)	2.136(3)	–	[1]
$[Mo_6I_8(H_2O)_2(OH)_4]\cdot 14H_2O$	2.6533(3) – 2.6730(3)	2.7723(3) – 2.8195(3)	2.085(2) – 2.175(2)	–	[1]
$[Mo_6I_8(H_2O)_4(OH)_2](NO_3)_2\cdot 3H_2O$	2.6509(4) – 2.6751(4)	2.7599(4) – 2.8049(4)	2.113(2) – 2.189(3)	–	[2]
$[Mo_6I_8(H_2O)_4(OH)_2](OTs)_2\cdot 2H_2O$	2.647(1) – 2.662(1)	2.781(1) – 2.801(1)	2.053(7) – 2.175(8)	–	[2]
3·6pzH	2.6677(4) – 2.6808(4)	2.7687(4) – 2.7801(3)	–	2.186(3)	This work
4·4pzH	2.6757(3) – 2.6819(3)	2.7522(3) – 2.7782(3)	–	2.216(2) – 2.235(2)	This work
$(Bu_4N)_2[Mo_6I_8(trz)_6]$	2.6645(19) – 2.6973(19)	2.7479(19) – 2.7921(18)	–	2.158(13) – 2.210(14)	[3]
$Cs_{0.27}[Mo_6I_8(trz)I_5]_{0.27}\cdot$*cis*-$[Mo_6I_8(trz)_2I_4]_{0.73}$	2.665(10) – 2.688(8)	2.752(7) – 2.791(10)	–	2.21(2)	[4]
$(Bu_4N)_2[Mo_6I_8(N_3C_2(COOCH_3)_2)_6]$	2.6721(7) – 2.6794(6)	2.7588(6) – 2.7815(6)	–	2.183(5) – 2.220(4)	[5]
$(Bu_4N)_2[Mo_6I_8(N_4C\text{-}Ph)_6]$	2.6728(10) – 2.6856(9)	2.7588(8) – 2.7768(9)	–	2.230(8) – 2.238(9)	[6]

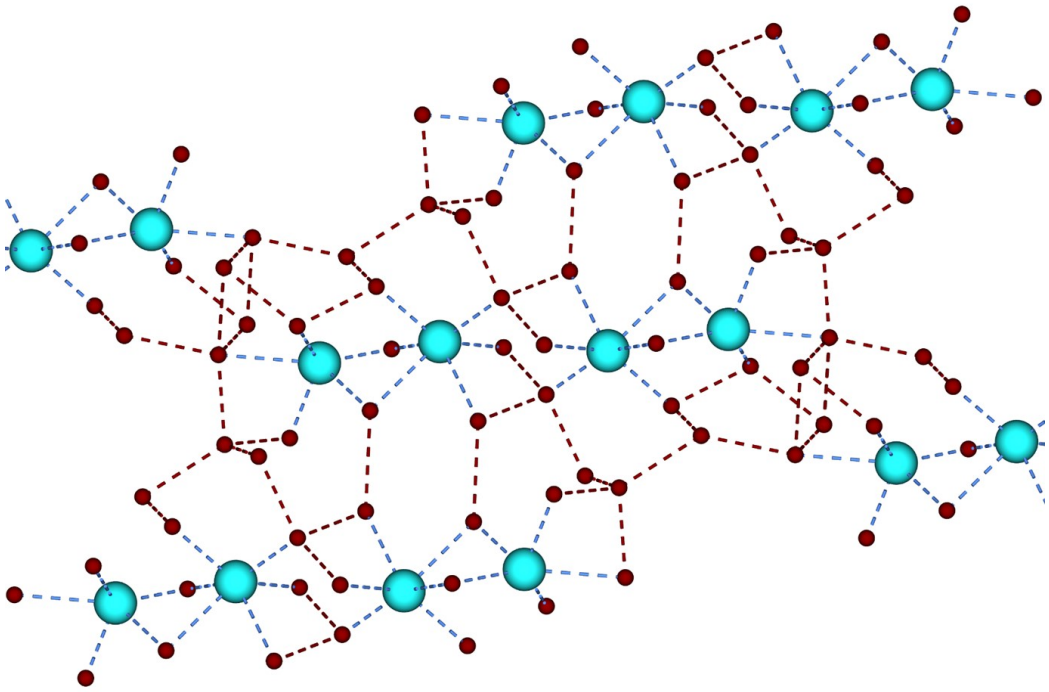

Figure S3. Packing of potassium cations in the layers in the crystal structure of **1·13H$_2$O**. Color code: O – red, K – cyan, O···O – dashed red, O···K – dashed blue.

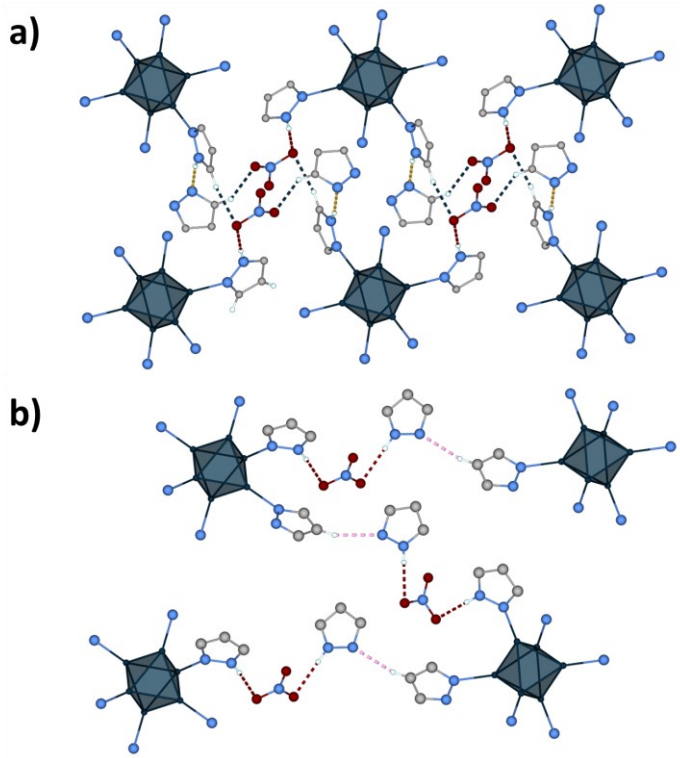

Figure S4. Packing in the crystal structure of **4·4pzH**: a) hydrogen bonds forming the layers, b) hydrogen bonds between layers. Color code: Mo – dark blue, N – light blue, O – red, C – gray, H – white, N···H-N – dashed yellow, O···H-N – dashed red, O···H-C – dashed blue, N···H-C – dashed pink.

Reactivity: ^{1}H NMR data

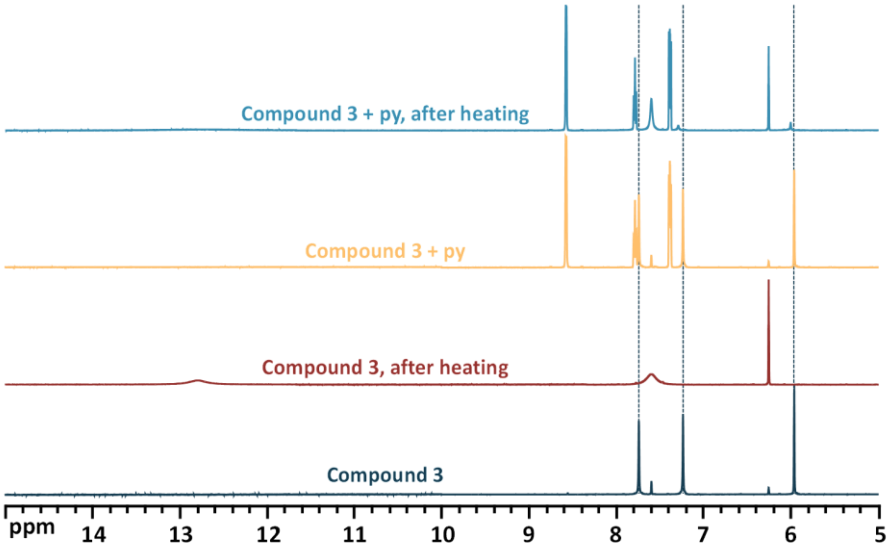

Figure S5. ^{1}H NMR spectra of compound **3** in DMSO-d_6 in presence of competing ligands (py = pyridine) and/or under heating at 100°C for 4 h.

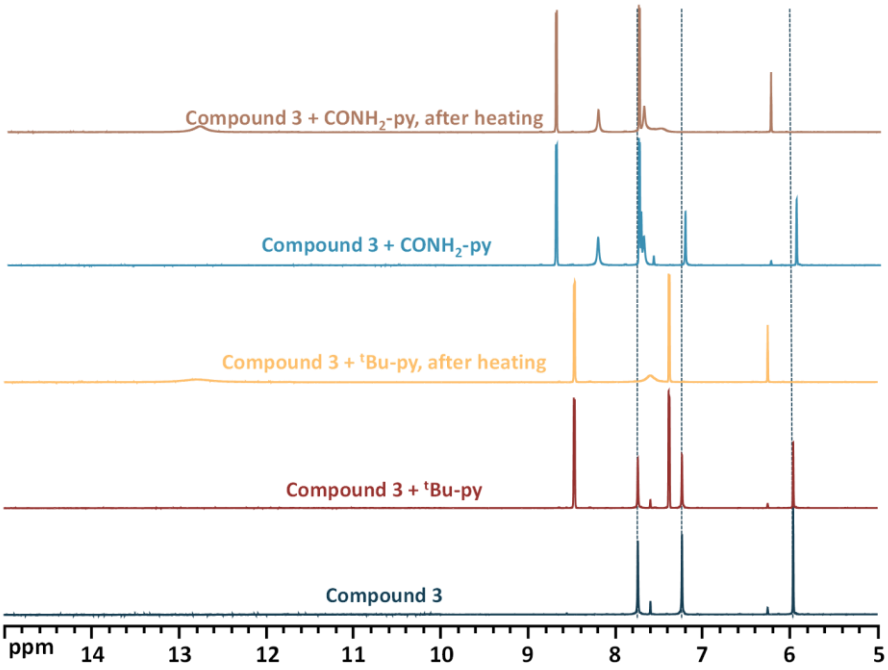

Figure S6. ^{1}H NMR spectra of compound **3** in DMSO-d_6 in presence of competing ligands (^{t}Bu-py = 4-tert-butylpyridine, $CONH_2$-py = isonicotinamide) and under heating at 100°C for 4 h.

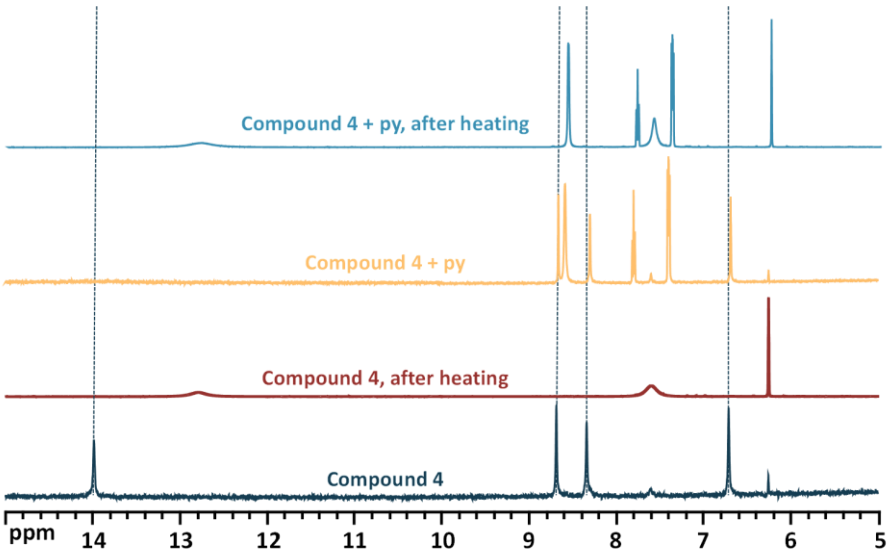

Figure S7. ^{1}H NMR spectra of compound **4** in DMSO-d_6 in presence of competing ligands (py = pyridine) and/or under heating at 100^{o}C for 4 h.

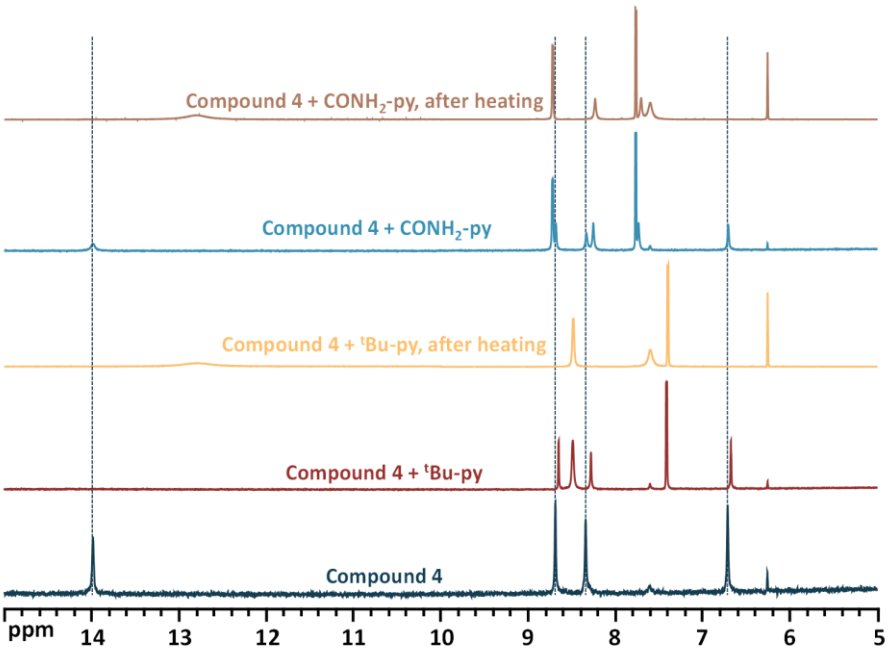

Figure S8. ^{1}H NMR spectra of compound **4** in DMSO-d_6 in presence of competing ligands (^{t}Bu-py = 4-tert-butylpyridine, $CONH_2$-py = isonicotinamide) and under heating at 100^{o}C for 4 h.

Luminesce in solution: ^{1}H NMR data

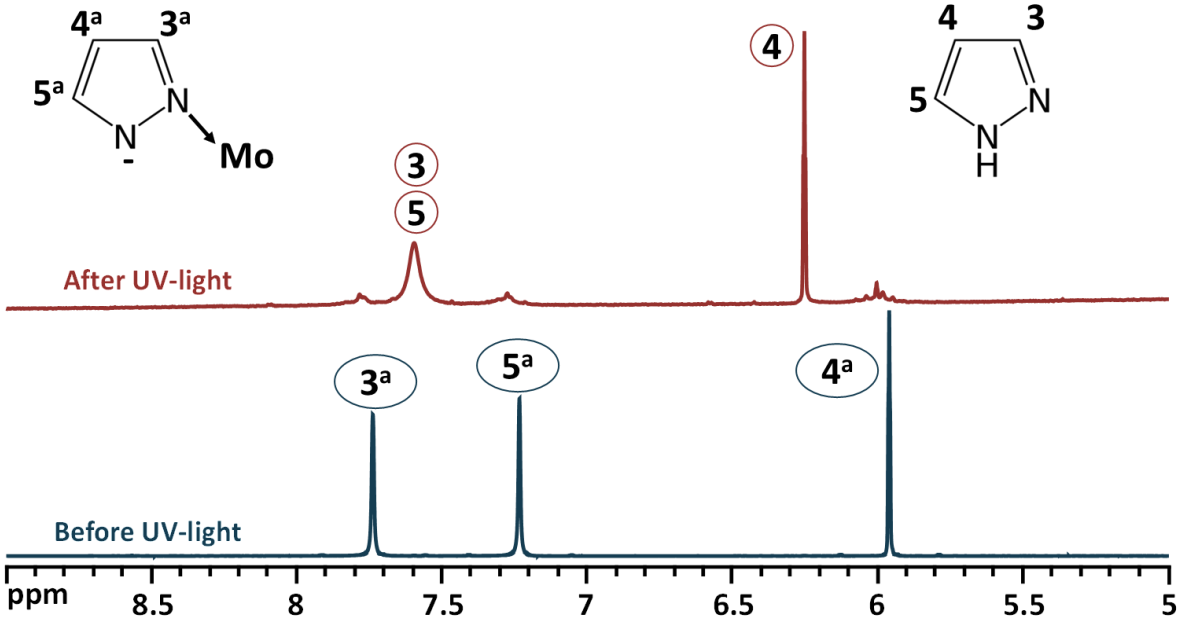

Figure S9. ^{1}H NMR spectra of DMSO-d_6 solution of compound **3** before and after UV irradiation (λ = 365 nm).

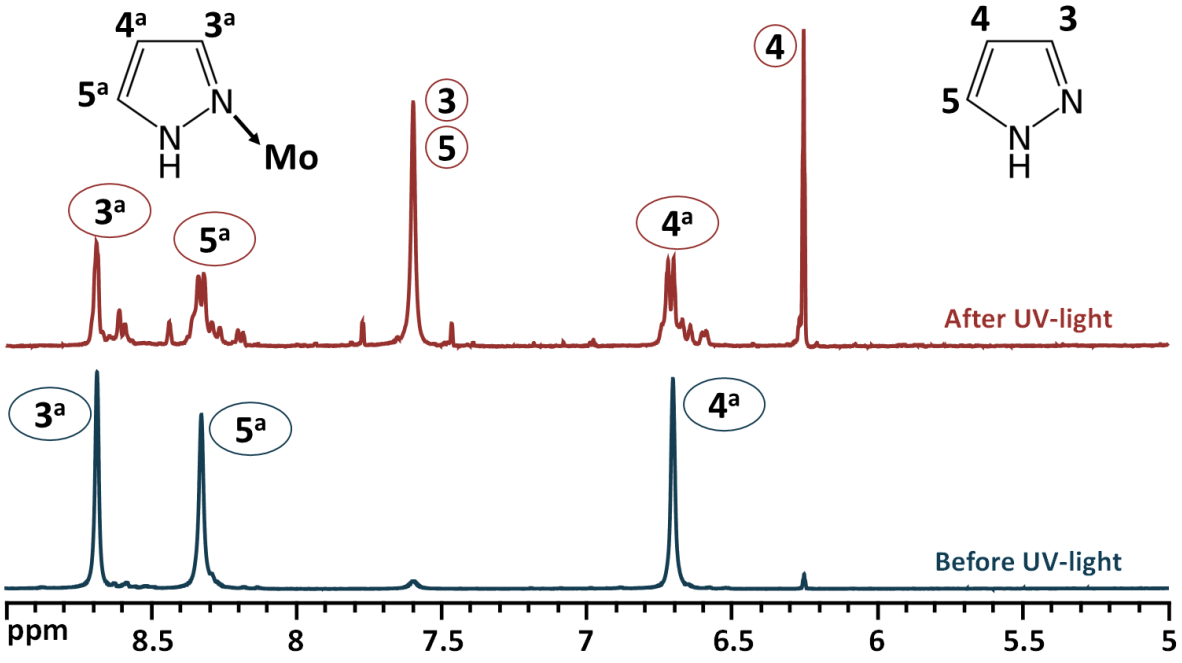

Figure S10. ^{1}H NMR spectra of DMSO-d_6 solution of compound **4** before and after UV irradiation (λ = 365 nm).

TGA data and FTIR spectra

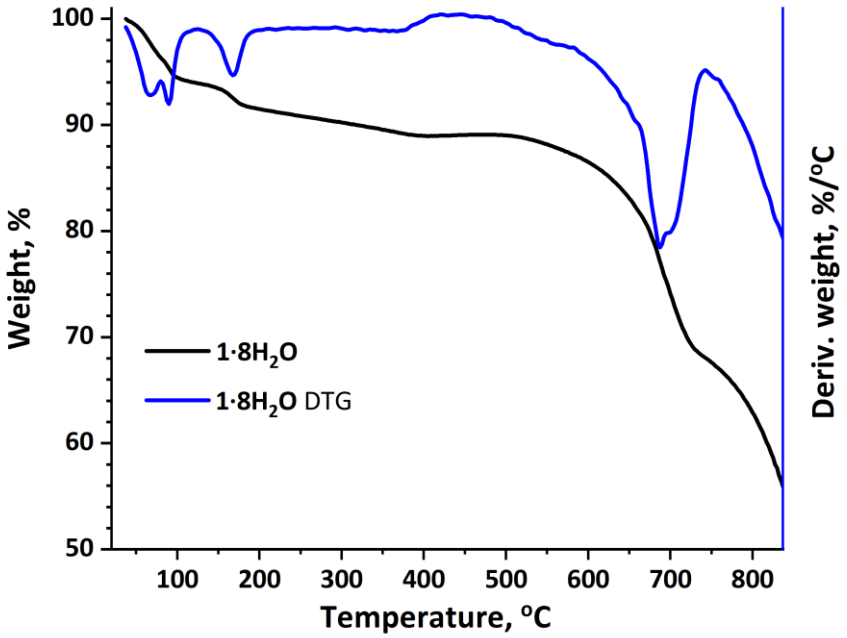

Figure S11. TG and DTG curves of **1·8H₂O**.

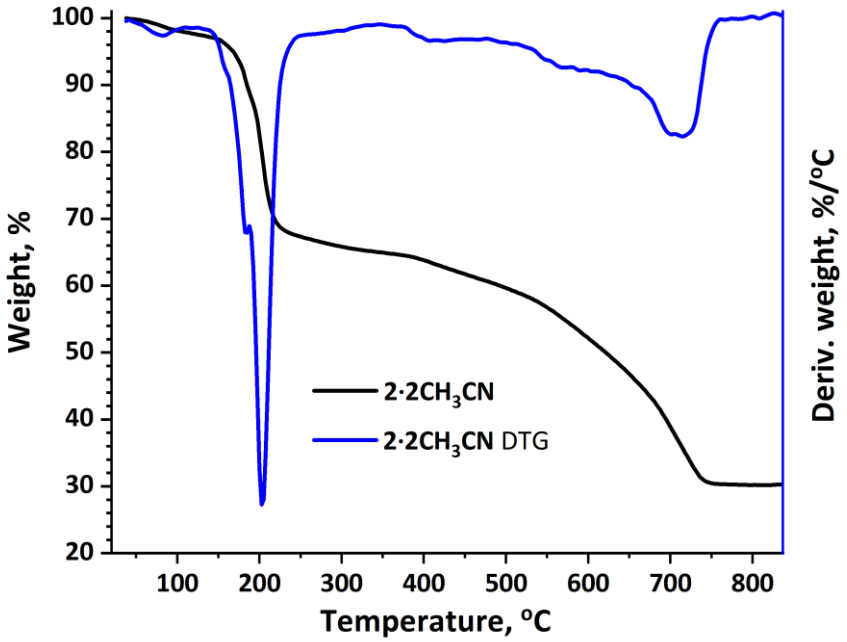

Figure S12. TG and DTG curves of **2·2CH₃CN**.

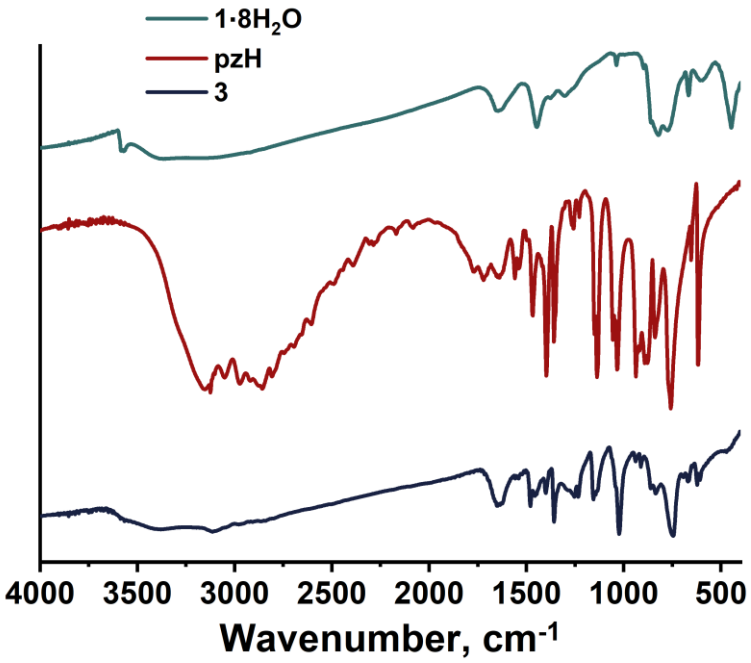

Figure S13. FTIR spectrum of **3** in comparison with pyrazole and **1·8H$_2$O**.

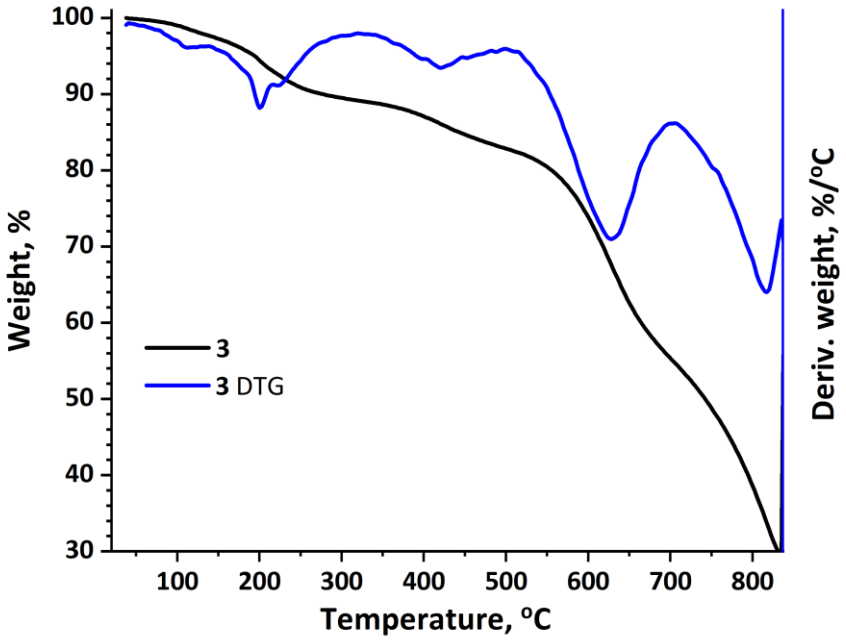

Figure S14. TG and DTG curves of **3**.

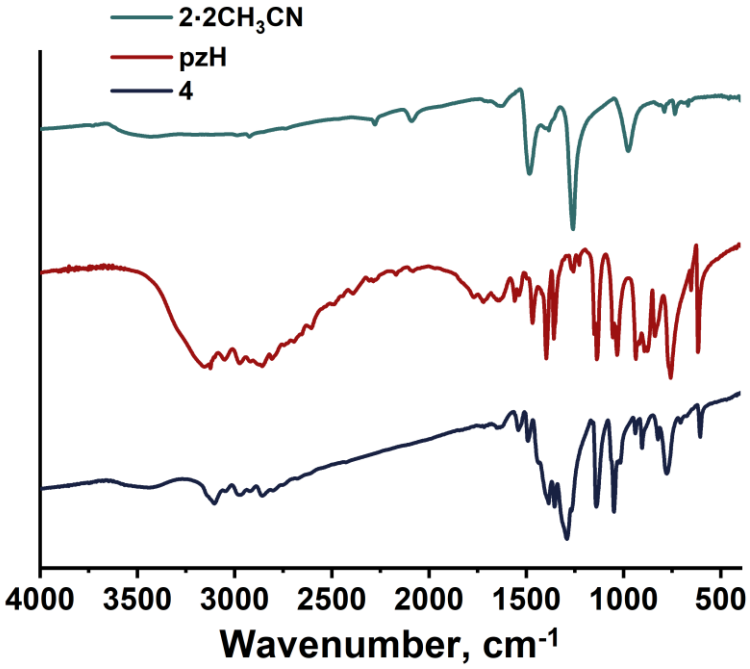

Figure S15. FTIR spectrum of **4** in comparison with pyrazole and **2·2CH$_3$CN**.

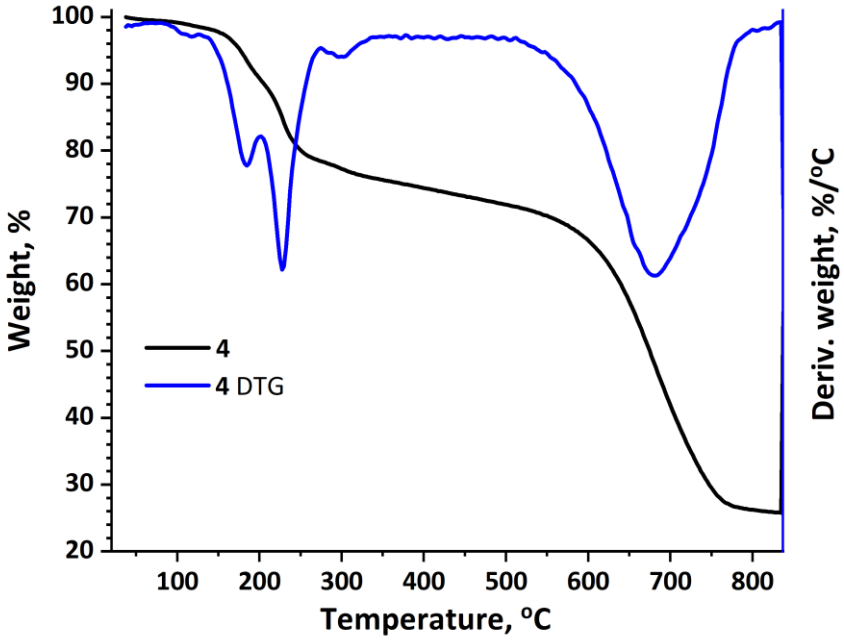

Figure S16. TG and DTG curves of **4**.

Crystal structure data

Table S2. Selected crystallographic parameters of the single-crystal X-ray diffraction structural analysis for $K_2[Mo_6I_8(OH)_6]\cdot 13H_2O$ (**1·13H₂O**), $[Mo_6I_8(H_2O)_6](NO_3)_4\cdot 2H_2O$ (**2·2H₂O**), $K_2[Mo_6I_8(pz)_6]\cdot 6pzH$ (**3·6pzH**), $[Mo_6I_8(pzH)_6](NO_3)_4\cdot 4pzH$ (**4·4pzH**).

Compound	**1·13H₂O**	**2·2H₂O**	**3·6pzH**	**4·4pzH**
CCDC	2363823	2363821	2363822	2363824
Empirical formula	$H_{32}I_8K_2Mo_6O_{19}$	$H_{16}I_8Mo_6N_4O_{20}$	$C_{36}H_{42}I_8K_2Mo_6N_{24}$	$C_{30}H_{40}I_8Mo_6N_{24}O_{12}$
Formula weight	2005.29	1983.01	2479.97	2519.70
Temperature, K	220	150	150	150
Crystal system	Triclinic	Triclinic	Trigonal	Monoclinic
Space group	$P\ \bar{1}$	$P\ \bar{1}$	$R\ \bar{3}$	$P\ 2_1/n$
a, Å	9.6328(4)	10.5953(2)	17.3571(3)	11.0559(3)
b, Å	11.7341(5)	10.7947(2)	17.3571(3)	11.5527(3)
c, Å	15.9020(7)	15.9552(3)	17.8314(6)	24.1189(6)
α, °	88.590(2)	90.1550(10)	90	90
β, °	86.932(2)	90.6780(10)	90	101.3400(10)
γ, °	88.658(2)	117.1390(10)	120	90
V, Å^3	1793.88(13)	1623.75(5)	4652.3(2)	3020.46(14)
Z	2	2	3	2
ρ_{calc}, g/cm^3	3.712	4.056	2.656	2.770
μ, mm^{-1}	9.207	9.925	5.343	5.368
F (000)	1796	1760	3420	2320
Crystal size	0.07 × 0.08 × 0.03	0.24 × 0.18 × 0.16	0.08 × 0.07 × 0.03	0.20 × 0.14 × 0.09
Θ range for data collection, °	2.135 to 31.547	1.276 to 27.604	2.347 to 28.288	2.215 to 34.355
Index ranges	$-14 \le h \le 14$ $-17 \le k \le 17$ $-23 \le l \le 23$	$-13 \le h \le 13$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-20 \le h \le 23$ $-23 \le k \le 22$ $-23 \le l \le 23$	$-17 \le h \le 17$ $-18 \le k \le 18$ $-33 \le l \le 38$
Reflections collected	40283	13976	18111	69472
Independent reflections	11877 [R_{int} = 0.0322]	7429 [R_{int} = 0.0411]	2572 [R_{int} = 0.0369]	12673 [R_{int} = 0.0496]
Data/restraints/parameters	11877/0/317	7429/15/353	2572/0/125	12673/18/375
Goodness-of-fit on F^2	1.036	1.080	1.088	1.068
R_1 / wR_2(I > 2σ(I))	0.0279/0.0655	0.0333/0.0817	0.0223/0.0448	0.0306/0.0586
R_1 / wR_1 (all data)	0.0363/0.0681	0.0369/0.0836	0.0325/0.0467	0.0505/0.0617
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^{-3})	2.546/–2.540	1.448/–1.745	0.571/–0.532	1.377/–1.271

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