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Supporting information

Synthesis, spectral, and structural characterizations of imidazole oxalato molybdenum (IV/V/VI) complexes

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Experimental

Preparations of *trans*-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (1) and *trans*-$(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (2). $Na_2MoO_4·2H_2O$ (0.48 g, 2.0 mmol), $H_2ox·2H_2O$ (0.38 g, 3.0 mmol) and imidazole (68 mg, 1.0 mmol) were dissolved in 5 mL water. The mixture was kept stirring for 2 h and the pH value of the mixture was adjusted to 3.2 with dilute hydrochloric acid. The solution was transferred to a serum bottle and refluxed for 2 h. After cooling to room temperature, the solution was added with hydrazine hydrochloride (0.16 g, 1.5 mmol) to give a dark red solution (pH = 2.0) with constant stirring. The filtrate was evaporated at room temperature to give yellow crystals of **1** after one week. The crystals were collected and washed with water and ethanol. Yield: 0.48 g (78%). Anal. Found: C, 13.8; H, 2.2; N, 4.5. Calc. for $C_7H_{15}Mo_2N_2NaO_{17}$: C, 13.7; H, 2.5; N, 4.6. IR (KBr disk, cm^{-1}): 3148_{vs}, 2984_{vs}, 2859_{vs}, 1665_{vs}, 1586_s, 1409_{vs}, 1296_s, 1267_s, 1097_m, 1059_w, 1048_m, 973_{vs}, 901_m, 829_m, 795_s, 724_{vs}, 625_s, 534_m, 496_s, 440_w. Solution ^1H NMR (500 MHz, D_2O): δ_H (ppm) 8.68 (NC*H*NH), 7.48 (NC*H*CH); Solution ^{13}C NMR (500 MHz, D_2O): δ_C (ppm) 169.63 (*C*O_2), 136.06 (N*C*HNH), 121.57 (HN*C*HCH). The preparation of **2** was similar as that for **1** except that $Na_2MoO_4·2H_2O$ (0.48 g, 2.0 mmol) was replaced by $K_2MoO_4·5H_2O$ (0.66 g, 2.0 mmol) and the amount of imidazole was changed to 2.0 mmol. Yield: 0.38 g (62%). Anal. Found: C, 19.7; H, 2.1; N, 9.0. Calc. for $C_{10}H_{14}Mo_2N_4O_{14}$: C, 19.8; H, 2.3; N, 9.2. IR (KBr disk, cm^{-1}): 3149_{vs}, 2981_{vs}, 2859_{vs}, 1666_{vs}, 1586_s, 1409_{vs}, 1294_s, 1267_s, 1094_m, 1052_w, 971_{vs}, 899_s, 828_m, 785_s, 724_{vs}, 625_s, 534_m, 493_s, 442_w. Solution ^1H NMR (500 MHz, D_2O): δ_H (ppm) 8.69 (NC*H*NH), 7.47 (NC*H*CH); Solution ^{13}C NMR (500 MHz, D_2O): δ_C (ppm) 168.85 (*C*O_2), 136.10 (N*C*HNH), 121.64 (HN*C*HCH).

Preparation of $(Him)_4$[$Mo_8O_{26}(im)_2$] (8). $(NH_4)_6Mo_7O_{24}·4H_2O$ (2.47 g, 2.0 mmol) and imidazole (0.14 g, 2.0 mmol) were dissolved in 10 mL water. The mixture was kept stirring for 2 h and the pH value of the solution was adjusted to 4.7−5.0 by the addition of 2.0 M hydrochloric acid. The solution was transferred to a serum bottle and refluxed for 2 h. After cooling to room temperature, the solution was filtered. Slow evaporation at room temperature led to light blue crystals of **8** within one week. The crystals were collected and washed with 95% ethanol. Yield: 0.33 g (63%). Anal. Found: C, 13.5; H, 1.7; N, 10.6. Calc. for $C_{18}H_{28}Mo_8N_{12}O_{26}$: C, 13.5; H, 1.7; N, 10.5. IR (KBr disk, cm^{-1}): 3455_{vs}, 3136_{vs}, 3064_s, 2967_{vs}, 2856_{vs}, 2634_s, 1639_w, 1581_s, 1503_w, 1445_m, 1321_m, 1255_w, 1129_m, 1074_s, 942_s, 883_{vs}, 828_m, 760_m, 632_s, 562_m, 531_m, 482_w. Solution ^1H NMR (500 MHz, D_2O): δ_H (ppm) 8.69 (NC*H*NH), 7.47 (NC*H*CH); Solution ^{13}C NMR (500 MHz, D_2O): δ_C (ppm) 136.23 (N*C*HNH), 121.66 (HN*C*HCH).

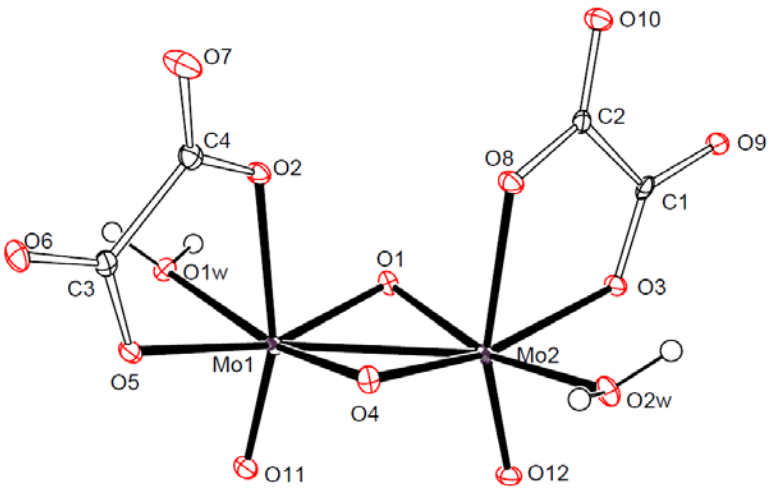

Figure S1. Anion structure of *trans*-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**).

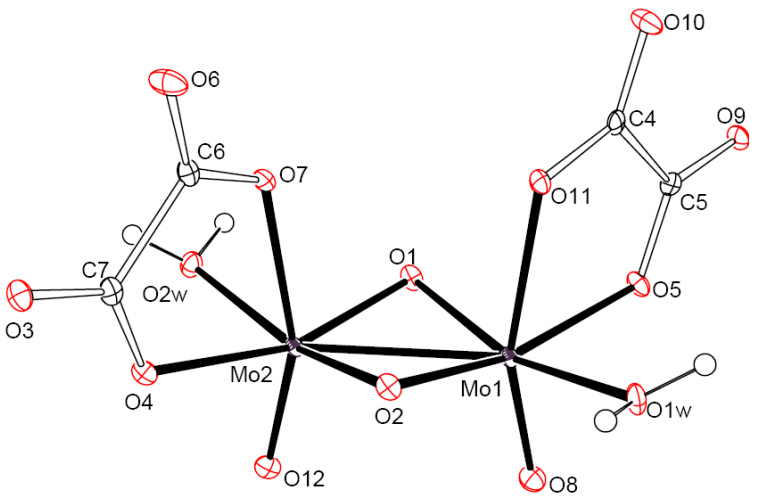

Figure S2. Anion structure of *trans*-$(Him)_2[Mo_2O_4(ox)_2(H_2O)_2]$ (**2**).

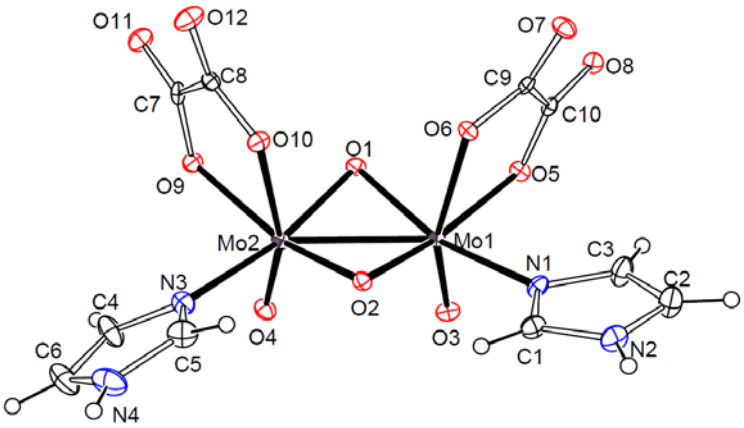

Figure S3 Anion structure of *cis*-$K_2[Mo_2O_4(ox)_2(im)_2]\cdot 3H_2O$ (**4**).

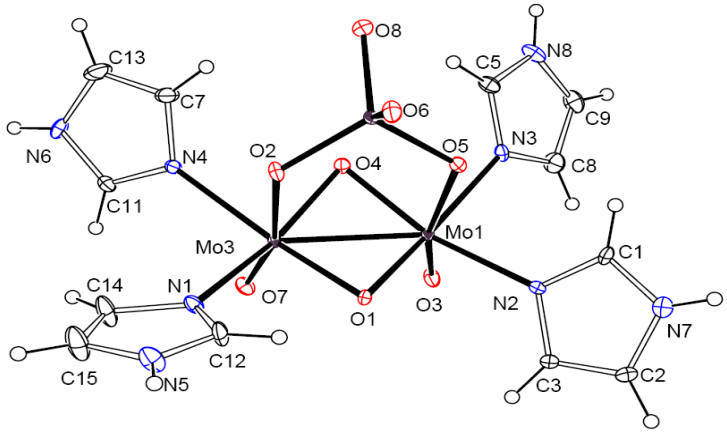

Figure S4 Anion structure of $[Mo_3O_8(im)_4]\cdot H_2O$ (**7**).

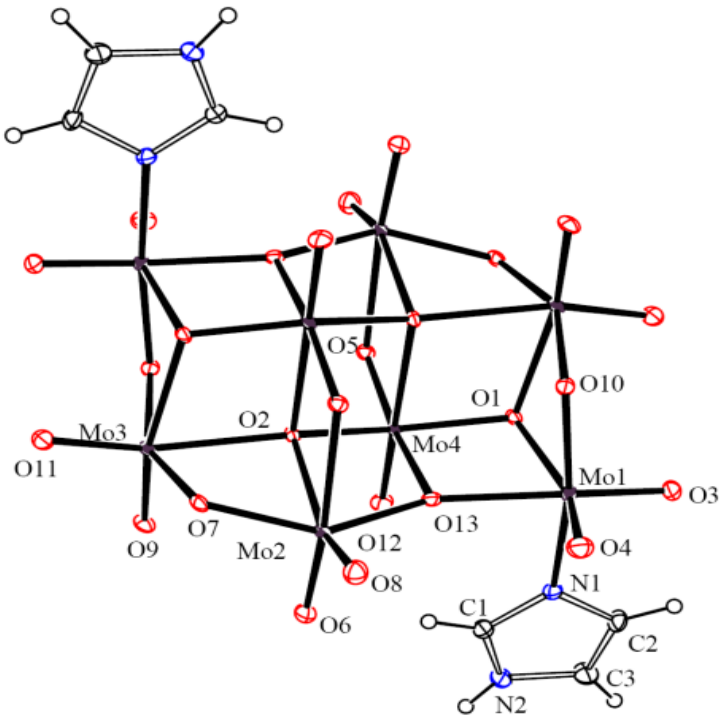

Figure S5. Anion structure of $(Him)_4[Mo_8O_{26}(im)_2]$ (**8**).

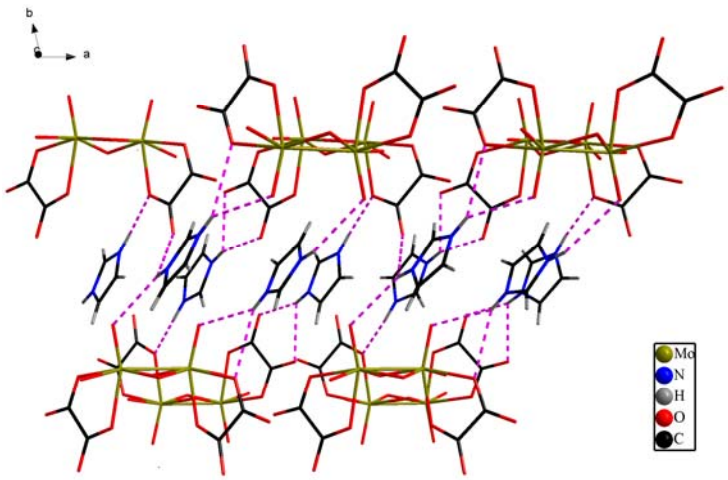

Figure S6. The 3D supramolecular are linked through hydrogen bonds in **2**. (Dotted line represents the possible hydrogen bonds)

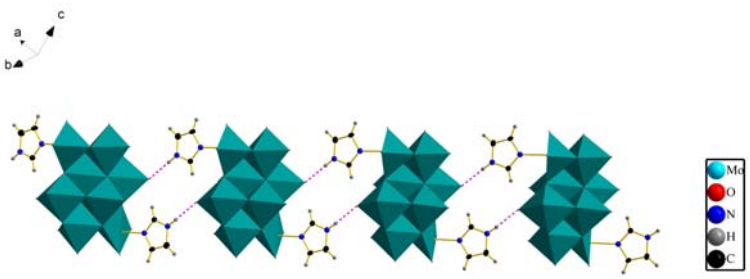

Figure S7. The 1D supramolecular chain of the discrete $[(im)_2Mo_8O_{26}]^{4-}$ clusters linked through hydrogen bonds in **8**. (Dotted line represents the possible hydrogen bonds)

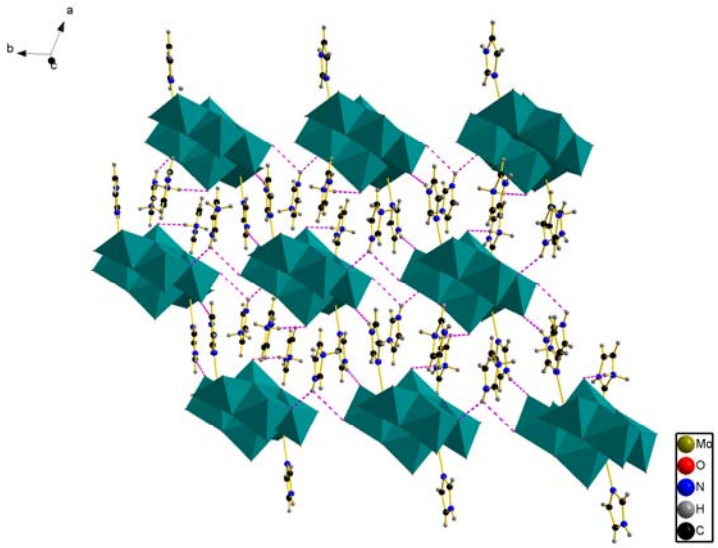

Figure S8. The 3D supramolecular is linked through hydrogen bonds in **8**. (Dotted line represents the possible hydrogen bonds)

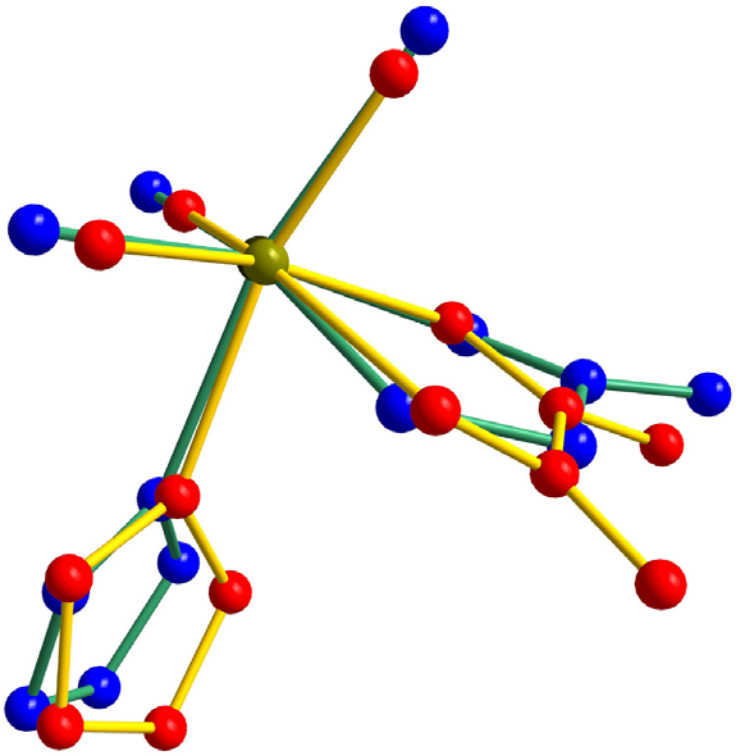

Figure S9. Comparisons of Mo-oxalato-im unit of *cis*-$Na_2[Mo_2O_4(ox)_2(im)_2]\cdot 4.5H_2O$ (**3**) with Mo-homocitrate-his of nitroganse. Yellow-red: Mo-oxalato-im unit of *cis*-$Na_2[Mo_2O_4(ox)_2(im)_2]\cdot 4.5H_2O$ (**3**); Green-blue: Mo-homocitrate-im unit.

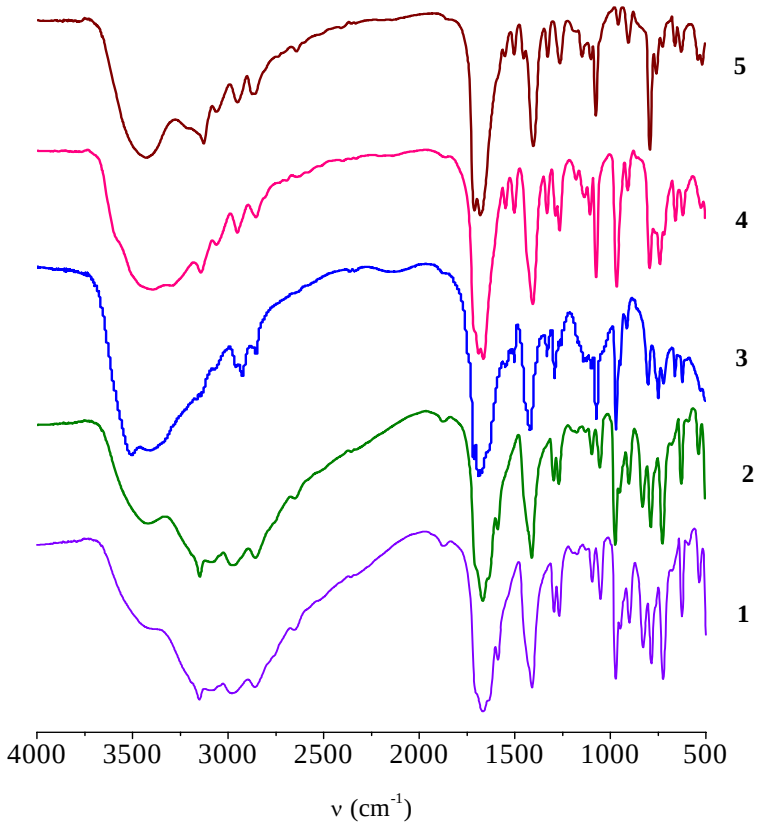

Figure S10. IR spectra of *trans*-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**), *trans*-$(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**), *cis*-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (**3**), *cis*-K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**), and K(Him)[$Mo_3O_4(ox)_3(im)_3$]·3H_2O (**5**).

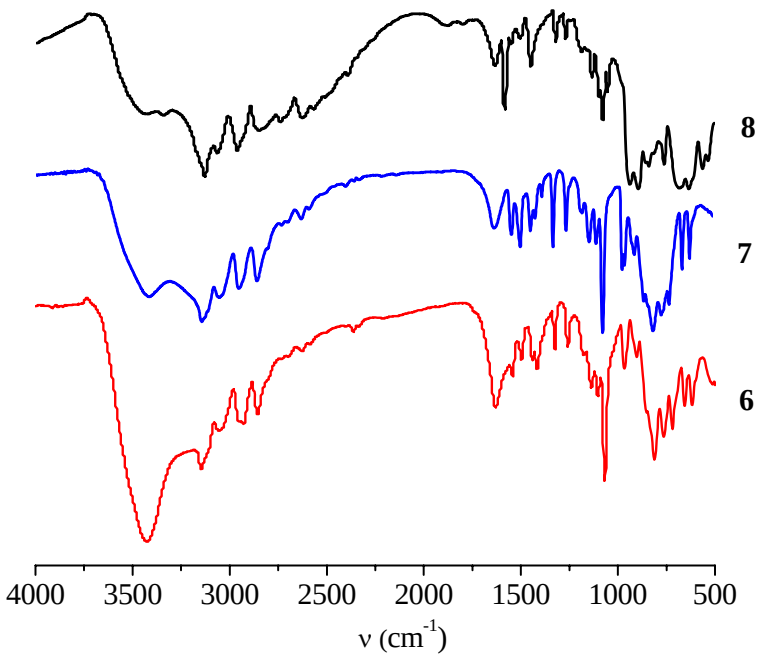

Figure S11. IR spectra of [$Mo_3O_8(im)_4$](im)·H_2O (**6**), [$Mo_3O_8(im)_4$]·H_2O (**7**), and $(Him)_4$[$Mo_8O_{26}(im)_2$] (**8**).

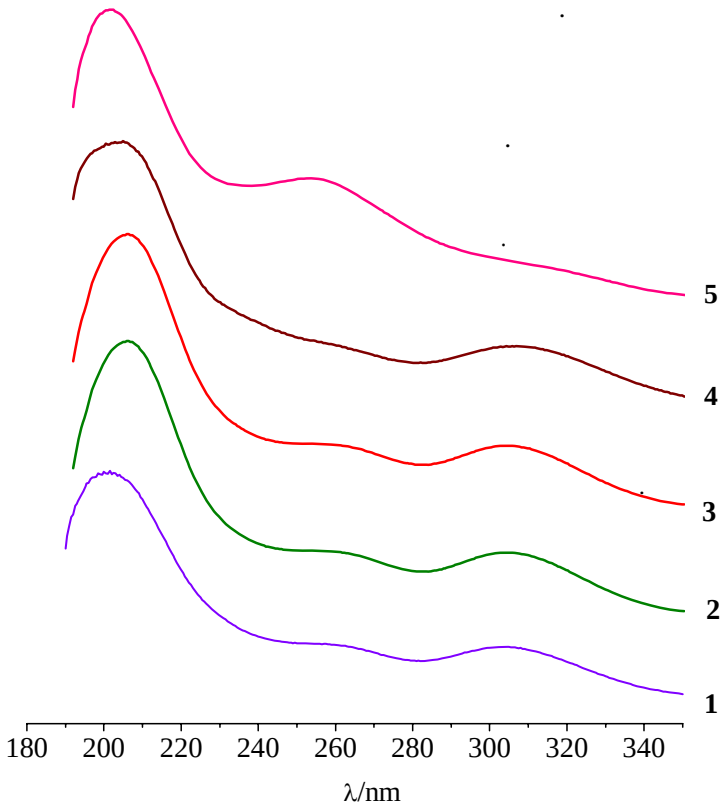

Figure S12. UV spectra of *trans*-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**), *trans*- $(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**), *cis*-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (**3**), *cis*-K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**), and K(Him)[$Mo_3O_4(ox)_3(im)_3$]·3H_2O (**5**).

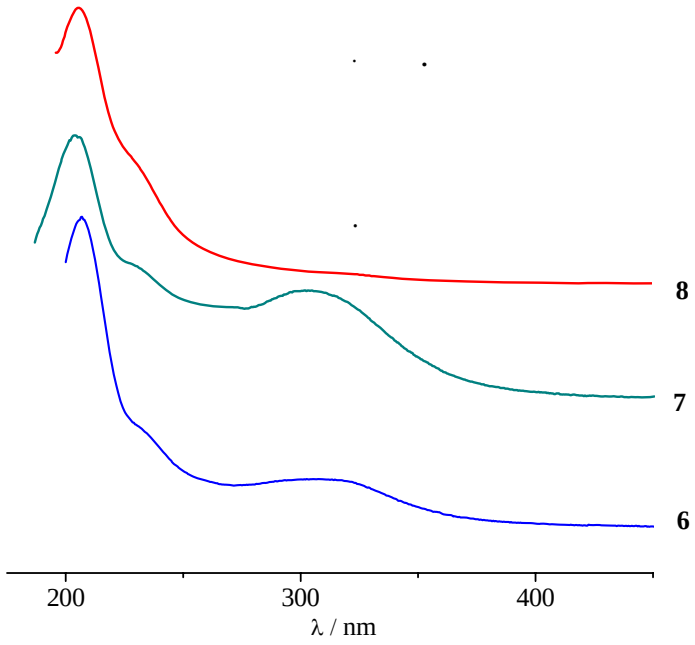

Figure S13. UV spectra of [$Mo_3O_8(im)_4$](im)·H_2O (**6**), [$Mo_3O_8(im)_4$]·H_2O (**7**), and $(Him)_4$[$Mo_8O_{26}(im)_2$] (**8**).

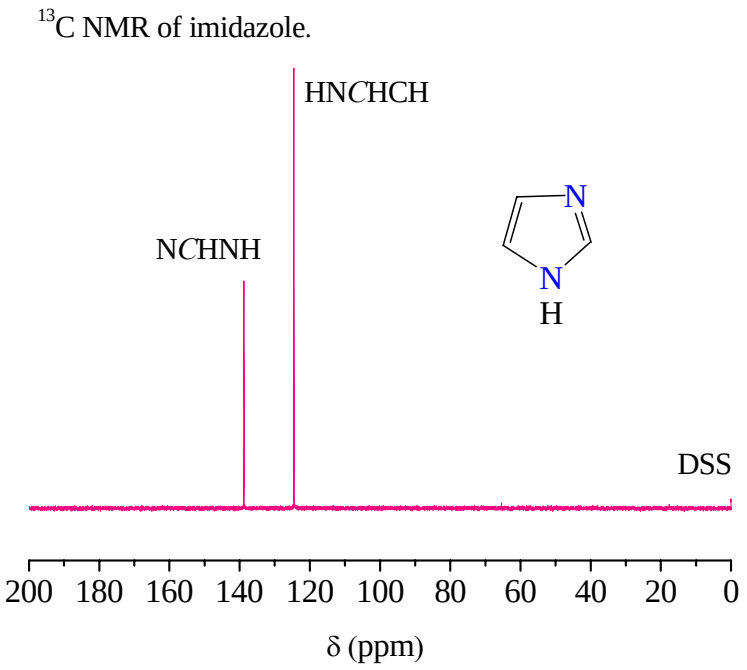

Figure S14. ^{13}C NMR spectrum of imidazole.

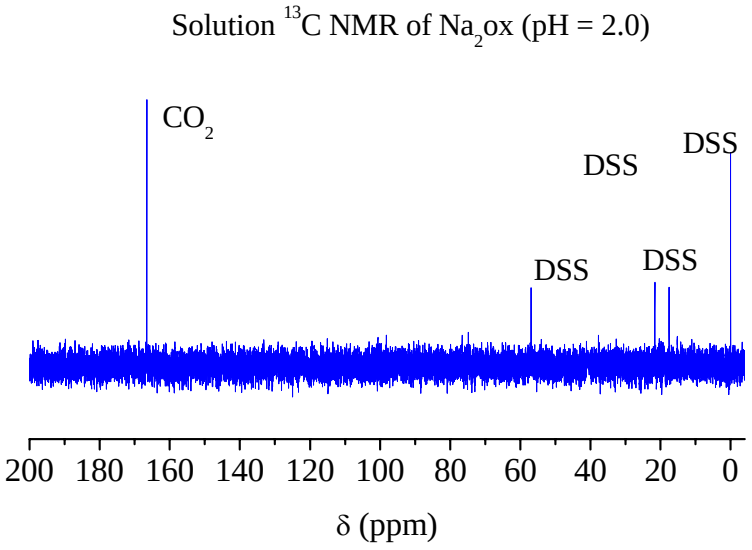

Figure S15. ^{13}C NMR spectrum of sodim oxalate.

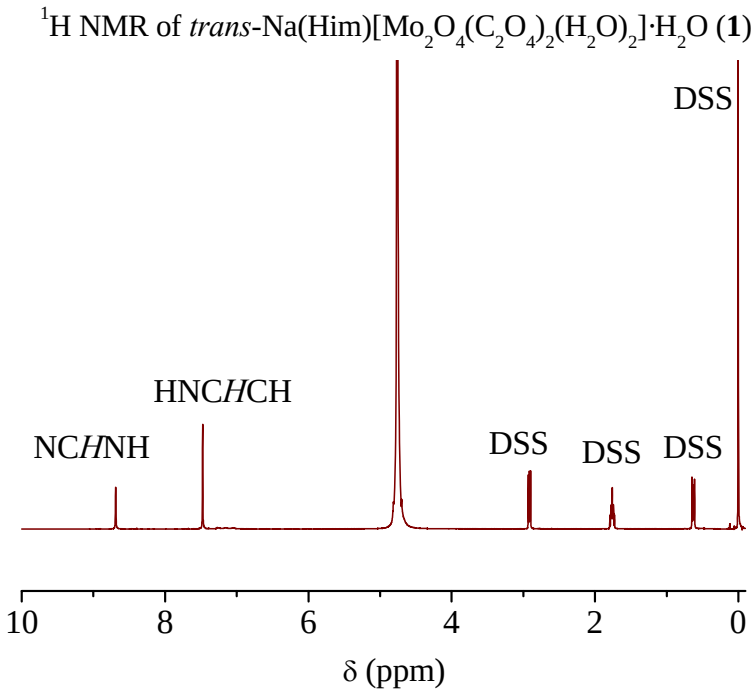

Figure S16. ^{1}H NMR spectrum of *trans*-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**).

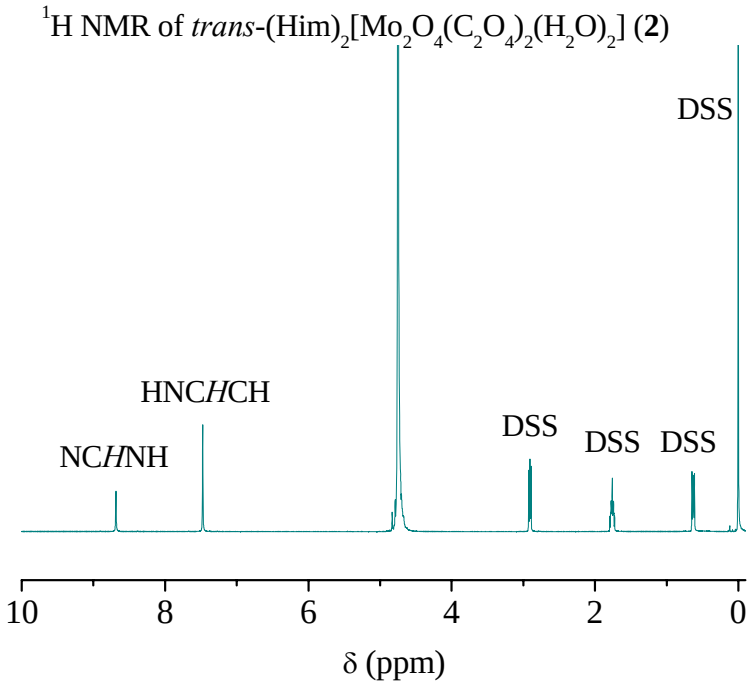

Figure S17. ^{1}H NMR spectrum of *trans*-$(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**).

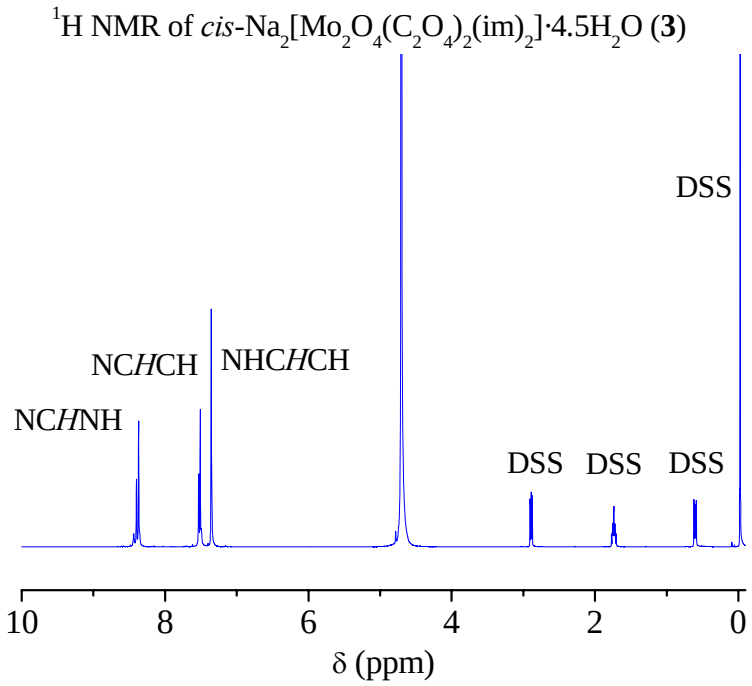

Figure S18. ^{1}H NMR spectrum of *cis*-$Na_2[Mo_2O_4(ox)_2(im)_2]\cdot 4.5H_2O$ (**3**).

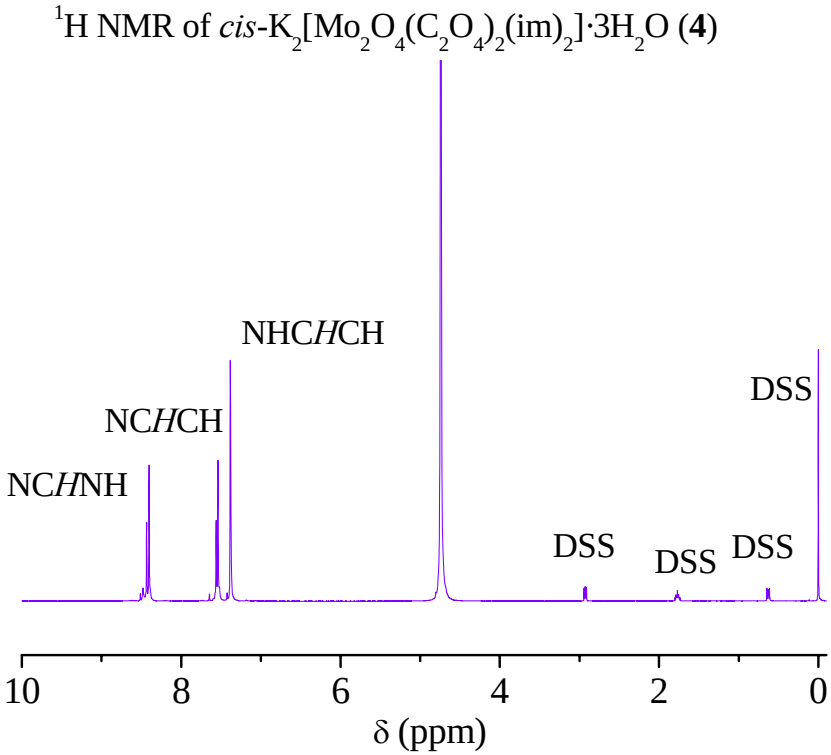

Figure S19. ^{1}H NMR spectrum of *cis*-$K_2[Mo_2O_4(ox)_2(im)_2]\cdot 3H_2O$ (**4**).

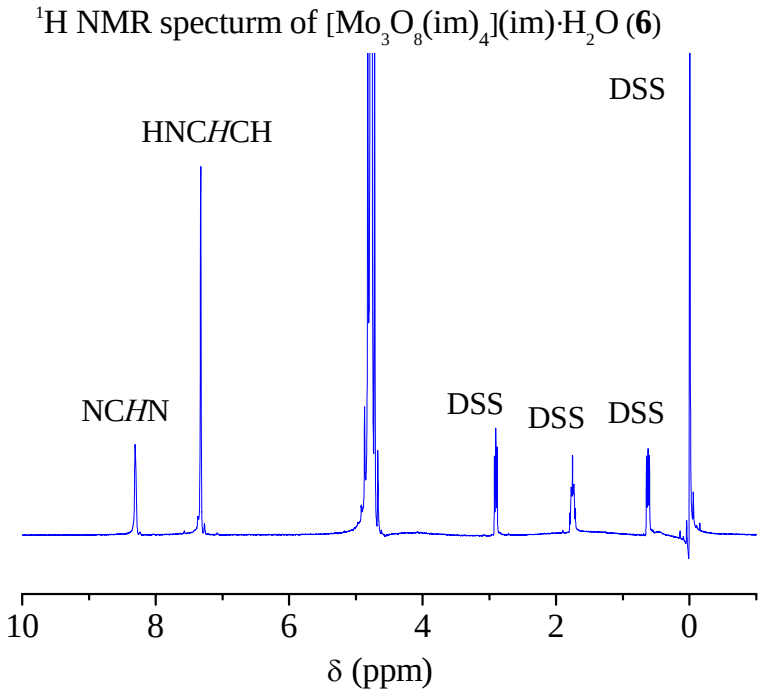

Figure S20. ^{1}H NMR spectrum of $[Mo_3O_8(im)_4](im)\cdot H_2O$ (**6**).

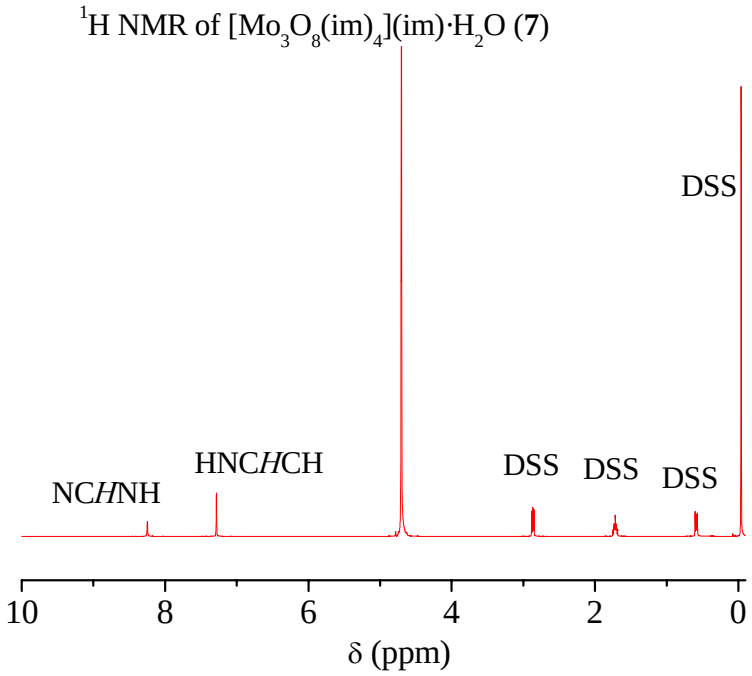

Figure S21. ^{1}H NMR spectrum of $[Mo_3O_8(im)_4]\cdot H_2O$ (**7**).

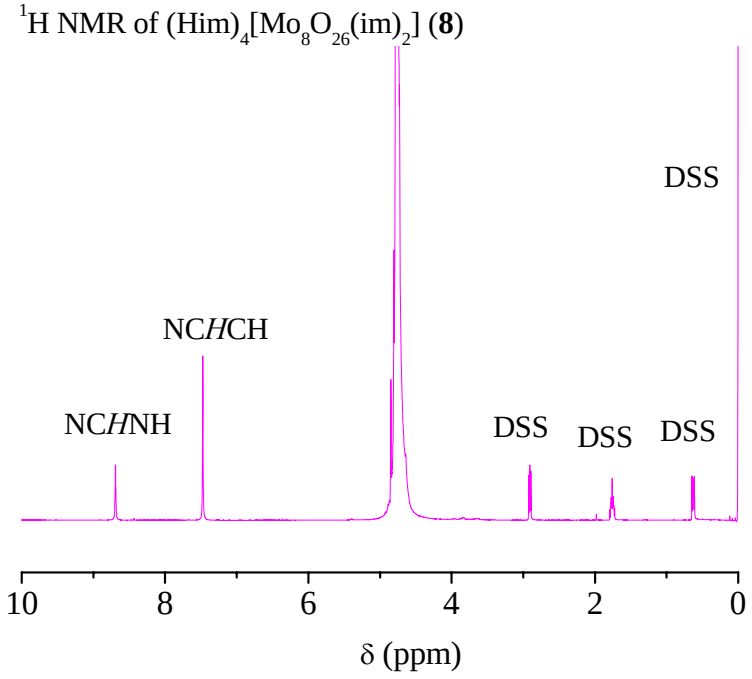

Figure S22. ^{1}H NMR spectrum of (Him)$_4$[Mo$_8$O$_{26}$(im)$_2$] (**8**).

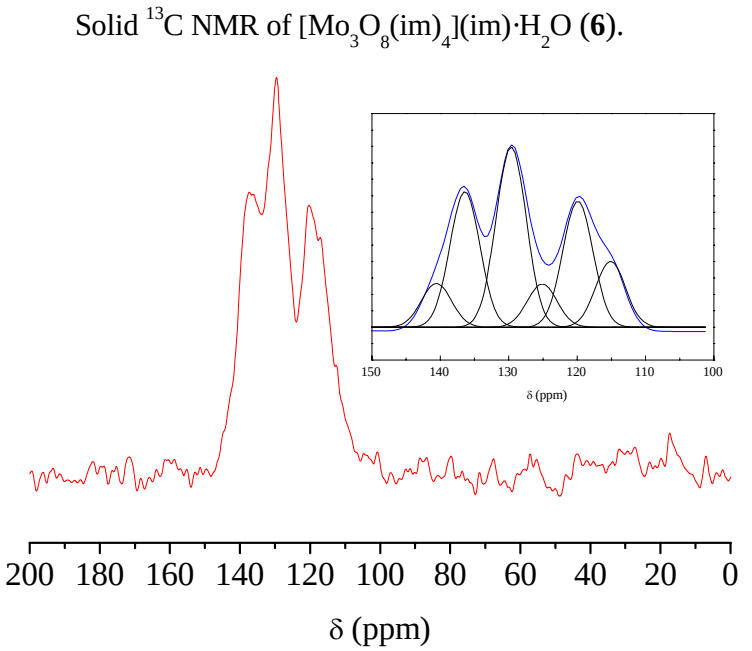

Figure S23. Solid ^{13}C NMR spectrum of of [Mo$_3$O$_8$(im)$_4$](im)·H$_2$O (**6**).

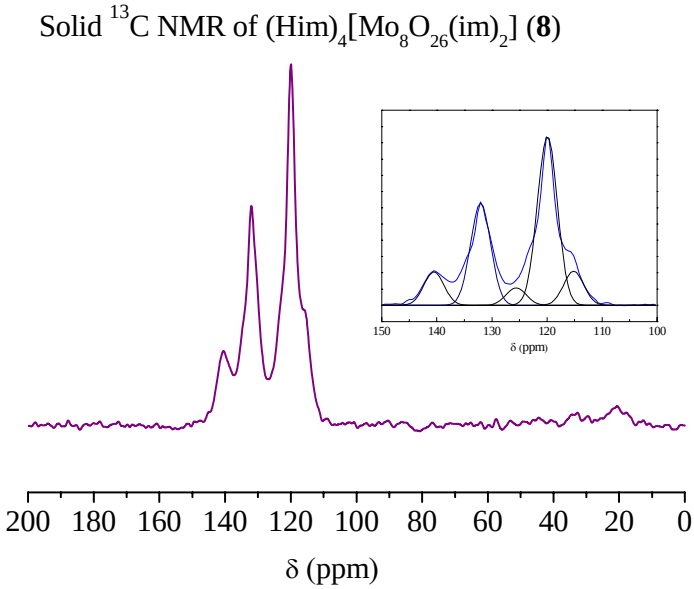

Figure S24. Solid ^{13}C NMR spectrum of $(Him)_4[Mo_8O_{26}(im)_2]$ (**8**).

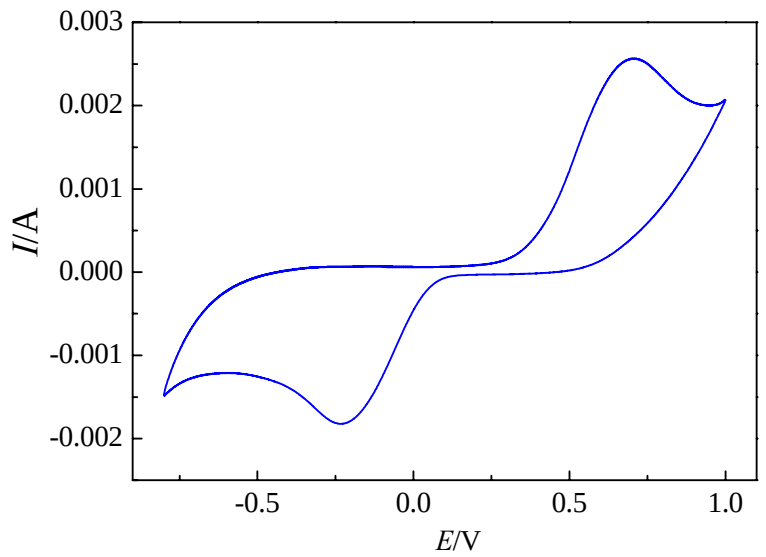

Figure S25. Cyclic voltammogram of *trans*-$(Him)_2[Mo_2O_4(ox)_2(H_2O)_2]$ (**2**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

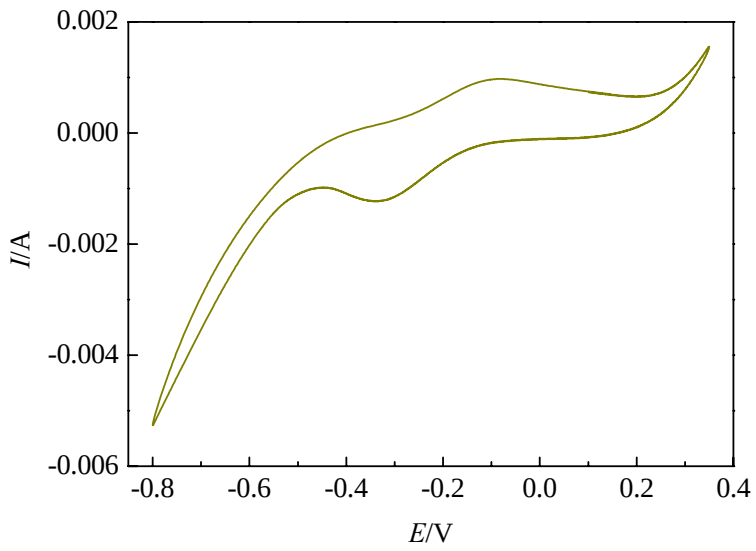

Figure S26. Cyclic voltammogram of *cis*-$K_2[Mo_2O_4(ox)_2(im)_2]\cdot 3H_2O$ (**4**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

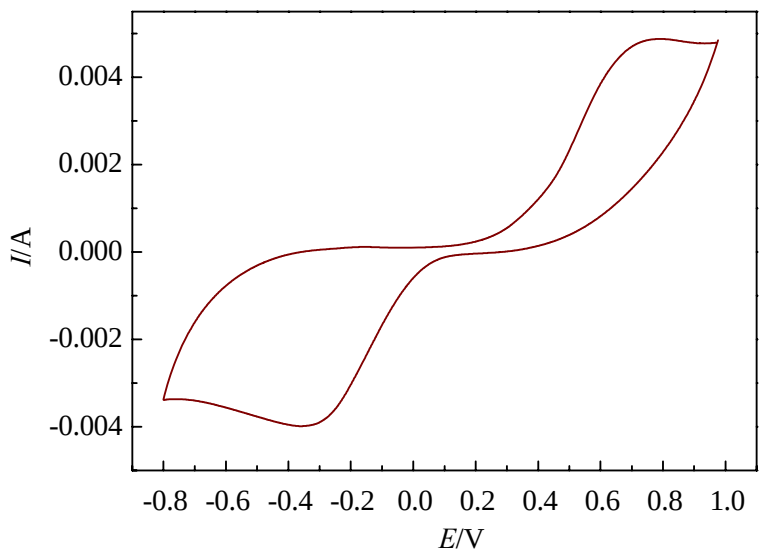

Figure S27. Cyclic voltammogram of K(Him)[$Mo_3O_4(ox)_3(im)_3$]·3H_2O (**5**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

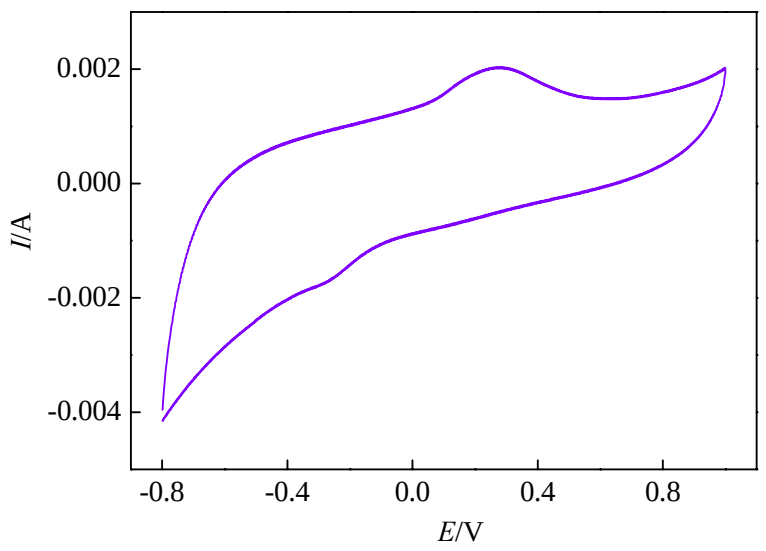

Figure S28. Cyclic voltammogram of [$Mo_3O_8(im)_4$](im)·H_2O (**6**) versus an Hg/Hg_2Cl_2 reference electrode in 1 mol/L Na_2SO_4 at a scan rate of 100 mV s^{-1}.

Table S1. Crystal data and structural refinements for **1**, **2** and **8**.

Compounds	**1**	**2**	**8**
Chemical formula	$C_7H_{15}Mo_2N_2NaO_{17}$	$C_{10}H_{14}Mo_2N_4O_{14}$	$C_{18}H_{28}Mo_8N_{12}O_{26}$
Formula mass	614.08	606.13	1596.04
Crystal system	triclinic	triclinic	triclinic
a/Å	8.6765(2)	8.8559(4)	9.3045(3)
b/Å	9.5675(3)	9.3464(4)	10.5573(5)
c/Å	11.8913(4)	11.5089(5)	12.4212(4)
α/°	100.703(3)	95.999(4)	106.644(4)
β/°	100.708(2)	96.930(4)	103.017(3)
γ/°	102.734(3)	103.116(5)	109.367(4)
Unit cell volume/Å^3	919.24(5)	912.36(8)	1031.34(7)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temperature (K)	173	173	173
Z	1	2	1
No. of reflections measured	7001	8976	12699
No. of independent reflections	3919	3916	4446
R_{int}	0.0323	0.0388	0.0420
Final R_1 values ($I > 2\sigma(I)$)	0.0340	0.0386	0.0489
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0677	0.1053	0.0985
Final R_1 values (all data)	0.0450	0.0546	0.0602
Final $wR(F^2)$ values (all data)	0.0721	0.1436	0.1030
Goodness of fit on F^2	1.029	1.097	1.058

Table S2. Selected bond distances (Å) for *trans*-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**), *trans*-(Him)$_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**), *cis*-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (3), *cis*- K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**), K(Him)[$Mo_3O_4(ox)_3(im)_3$]·3H_2O (**5**), [$Mo_3O_8(im)_4$](im)·H_2O (**6**), [$Mo_3O_8(im)_4$]·H_2O (**7**), and (Him)$_4$[$Mo_8O_{26}(im)_2$] (**8**).

trans-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**)			
Mo1–O11	1.679(3)	Mo2–O12	1.685(2)
Mo1–O1	1.927(2)	Mo2–O4	1.928(2)
Mo1–O4	1.941(3)	Mo2–O1	1.948(3)
Mo1–O5	2.111(2)	Mo2–O2w	2.130(3)
Mo1–O1w	2.145(3)	Mo2–O3	2.132(2)
Mo1–O2	2.210(2)	Mo2–O8	2.182(3)
Mo1–Mo2	2.5568(4)		

trans-(Him)$_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**)			
Mo1–O8	1.671(4)	Mo2–O12	1.678(4)
Mo1–O2	1.929(4)	Mo2–O1	1.928(4)
Mo1–O1	1.951(4)	Mo2–O2	1.940(4)
Mo1–O5	2.132(4)	Mo2–O4	2.133(4)
Mo1–O1w	2.152(4)	Mo2–O2w	2.160(4)
Mo1–O11	2.218(4)	Mo2–O7	2.177(4)
Mo1–Mo2	2.5547(6)		

cis-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (**3**)			
Mo1–O6	1.678(2)	Mo2–O11	1.685(2)
Mo1–O1	1.923(3)	Mo2–O1	1.927(2)
Mo1–O2	1.952(2)	Mo2–O2	1.949(3)
Mo1–O7	2.143(2)	Mo2–O5	2.121(2)
Mo1–N3	2.188(3)	Mo2–N1	2.183(3)
Mo1–O9	2.207(2)	Mo2–O4	2.225(2)
Mo1–Mo2	2.5597(5)		

cis-K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**)			
Mo1–O3	1.681(3)	Mo2–O4	1.682(3)
Mo1–O2	1.939(2)	Mo2–O2	1.929(3)
Mo1–O1	1.943(3)	Mo2–O1	1.949(3)
Mo1–O5	2.118(3)	Mo2–O9	2.123(3)
Mo1–N1	2.187(3)	Mo2–N3	2.186(3)
Mo1–O6	2.215(3)	Mo2–O10	2.221(3)
Mo1–Mo2	2.5482(5)		

$K(Him)[Mo_3O_4(ox)_3(im)_3]\cdot 3H_2O$ (**5**)			
Mo1–O3	1.900(4)	Mo2–O7	2.107(5)
Mo1–O2	1.909(4)	Mo2–O4	2.112(4)
Mo1–O1	2.026(4)	Mo2–N1	2.177(6)
Mo1–O6	2.093(4)	Mo2–Mo3	2.4931(8)
Mo1–O8	2.113(4)	Mo3–O3	1.915(4)
Mo1–N3	2.190(6)	Mo3–O5	1.918(4)
Mo1–Mo2	2.4921(8)	Mo3–O1	2.041(4)
Mo1–Mo3	2.4966(7)	Mo3–O11	2.099(4)
Mo2–O5	1.900(4)	Mo3–O9	2.110(4)
Mo2–O2	1.916(4)	Mo3–N5	2.185(5)
Mo2–O1	2.022(4)		

$[Mo_3O_8(im)_4](im)\cdot H_2O$ (**6**)			
Mo1–O1	1.953(4)	Mo2–O6	1.742(4)
Mo1–N2	2.204(5)	Mo2–O8	1.739(4)
Mo1–O3	1.684(4)	Mo3–O1	1.949(4)
Mo1–O4	1.949(4)	Mo3–O2	2.175(4)
Mo1–O5	2.204(4)	Mo3–O4	1.935(4)
Mo1–N3	2.201(5)	Mo3–O7	1.678(4)
Mo2–O2	1.787(4)	Mo3–N1	2.200(5)
Mo2–O5	1.790(4)	Mo3–N4	2.200(4)
Mo1–Mo3	2.5731(6)		

$[Mo_3O_8(im)_4]\cdot H_2O$ (**7**)			
Mo1–O3	1.677(4)	Mo2–O5	1.789(4)
Mo1–O1	1.952(3)	Mo2–O2	1.790(4)
Mo1–O4	1.955(4)	Mo3–O7	1.683(4)
Mo1–N2	2.178(5)	Mo3–O4	1.946(3)
Mo1–O5	2.206(4)	Mo3–O1	1.955(4)
Mo1–N3	2.219(4)	Mo3–O2	2.185(4)
Mo1–Mo3	2.5731(6)	Mo3–N1	2.195(4)
Mo2–O8	1.730(4)	Mo3–N4	2.219(5)
Mo2–O6	1.753(4)		

$(Him)_4[Mo_8O_{26}(im)_2]$ (**8**)			
Mo1–O1	2.323(5)	Mo3–O2	2.240(4)
Mo1–O3	1.710(5)	Mo3–O7	1.940(5)
Mo1–O4	1.696(5)	Mo3–O9	1.717(4)

Mo1–O10	1.921(5)	Mo3–O11	1.692(5)
Mo1–O13	2.086(5)	Mo3–O1a	2.272(5)
Mo1–N1	2.218(6)	Mo3–O10a	1.954(5)
Mo2–O2	2.284 (5)	Mo4–O1	1.895(5)
Mo2–O6	1.718(5)	Mo4–O2	1.923(5)
Mo2–O7	1.920(5)	Mo4–O5	1.747(5)
Mo2–O8	1.696(5)	Mo4–O12	1.895(5)
Mo2–O13	1.935(5)	Mo4–O13	2.178(6)
Mo2–O5a	2.341(5)	Mo4–O2a	2.424(5)

Symmetric transformation: a $-x + 2, -y + 1, -z + 1$

Table S3. Comparisons of bond valence units for **1**–**8**.

trans-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**)						
Bond	Mo1–O11	Mo1–O1	Mo1–O4	Mo1–O5	Mo1–O1w	Mo1–O2
Bond distance	1.679(3)	1.927(2)	1.941(3)	2.111(2)	2.145(3)	2.210(2)
Valence unit	1.712	0.876	0.843	0.533	0.486	0.408
Mo1				4.858		
Bond	Mo2–O12	Mo2–O4	Mo2–O1	Mo2–O2w	Mo2–O3	Mo2–O8
Bond distance	1.685(2)	1.928(2)	1.948(3)	2.130(3)	2.132(2)	2.182(3)
Valence unit	1.685	0.874	0.828	0.506	0.503	0.440
Mo2				4.836		

trans-$(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**)						
Bond	Mo1–O8	Mo1–O2	Mo1–O1	Mo1–O5	Mo1–O1w	Mo1–O11
Bond distance	1.671(4)	1.929(4)	1.951(4)	2.132(4)	2.152(4)	2.218(4)
Valence unit	1.750	0.871	0.821	0.503	0.477	0.399
Mo1				4.821		
Bond	Mo2–O12	Mo2–O1	Mo2–O2	Mo2–O4	Mo2–O2w	Mo2–O7
Bond distance	1.678(4)	1.928(4)	1.940(4)	2.133(4)	2.160(4)	2.177(4)
Valence unit	1.717	0.874	0.846	0.502	0.467	0.446
Mo2				4.852		

cis-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (**3**)						
Bond	Mo1–O6	Mo1–O1	Mo1–O2	Mo1–O7	Mo1–N3	Mo1–O9
Bond distance	1.678(2)	1.923(3)	1.952(2)	2.143(2)	2.188(3)	2.207(2)
Valence unit	1.717	0.885	0.819	0.489	0.635	0.411
Mo1				4.956		
Bond	Mo2–O11	Mo2–O1	Mo2–O2	Mo2–O5	Mo2–N1	Mo2–O4
Bond distance	1.685(2)	1.927(2)	1.949(3)	2.121(2)	2.183(3)	2.225(2)
Valence unit	1.685	0.876	0.825	0.519	0.644	0.391
Mo2				4.940		

cis-K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**)						
Bond	Mo1–O3	Mo1–O2	Mo1–O1	Mo1–O5	Mo1–N1	Mo1–O6
Bond distance	1.681(3)	1.939(2)	1.943(3)	2.118(3)	2.187(3)	2.215(3)
Valence unit	1.703	0.848	0.839	0.523	0.637	0.402
Mo1				4.952		
Bond	Mo2–O4	Mo2–O2	Mo2–O1	Mo2–O9	Mo2–N3	Mo2–O10
Bond distance	1.682(3)	1.929(3)	1.949(3)	2.123(3)	2.186(3)	2.221(3)
Valence unit	1.698	0.871	0.825	0.516	0.638	0.396
Mo2				4.944		

$K(Him)[Mo_3O_4(ox)_3(im)_3]\cdot 3H_2O$ (**5**)						
Bond	Mo1–O3	Mo1–O2	Mo1–O1	Mo1–O6	Mo1–O8	Mo1–N3
Bond distance	1.900(4)	1.909(4)	2.026(4)	2.093(4)	2.113(4)	2.190(6)
Valence unit	0.888	0.687	0.632	0.527	0.499	0.592
Mo1			4.005			
Bond	Mo2–O5	Mo2–O2	Mo2–O1	Mo2–O7	Mo2–O4	Mo2–N1
Bond distance	1.900(4)	1.916(4)	2.022(4)	2.107(5)	2.112(4)	2.177(6)
Valence unit	0.888	0.850	0.638	0.507	0.501	0.613
Mo2			3.997			
Bond	Mo3–O3	Mo3–O5	Mo3–O1	Mo3–O11	Mo3–O9	Mo3–N5
Bond distance	1.915(4)	1.918(4)	2.041(4)	2.099(4)	2.110(4)	2.185(5)
Valence unit	0.853	0.846	0.607	0.519	0.503	0.600
Mo3			3.928			

$[Mo_3O_8(im)_4](im)\cdot H_2O$ (**6**)						
Bond	Mo1–O1	Mo1–N2	Mo1–O3	Mo1–O4	Mo1–O5	Mo1–N3
Bond distance	1.953(4)	2.204(5)	1.684(4)	1.949(4)	2.204(4)	2.201(5)
Valence unit	0.817	0.608	1.689	0.825	0.414	0.613
Mo1			4.966			
Bond	Mo2–O2	Mo2–O5	Mo2–O6	Mo2–O8		
Bond distance	1.787(4)	1.790(4)	1.742(4)	1.739(4)		
Valence unit	1.383	1.372	1.562	1.575		
Mo2			5.892			
Bond	Mo3–O1	Mo3–O2	Mo3–O4	Mo3–O7	Mo3–N1	Mo3–N4
Bond distance	1.949(4)	2.175(4)	1.935(4)	1.678(4)	2.200(5)	2.200(4)
Valence unit	0.825	0.448	0.857	1.717	0.615	0.615
Mo3			5.077			

$[Mo_3O_8(im)_4]\cdot H_2O$ (**7**)						
Bond	Mo1–O3	Mo1–O1	Mo1–O4	Mo1–N2	Mo1–O5	Mo1–N3
Bond distance	1.677(4)	1.952(5)	1.955(4)	2.178(5)	2.206(4)	2.219(4)
Valence unit	1.722	0.819	0.812	0.652	0.412	0.584
Mo1			5.001			
Bond	Mo2–O8	Mo2–O6	Mo2–O5	Mo2–O2		
Bond distance	1.730(4)	1.753(4)	1.789(4)	1.790(4)		
Valence unit	1.613	1.516	1.376	1.372		
Mo2			5.877			
Bond	Mo3–O7	Mo3–O4	Mo3–O1	Mo3–O2	Mo3–N1	Mo3–N4
Bond distance	1.683(4)	1.946(3)	1.955(4)	2.185(4)	2.195(4)	2.219(5)
Valence unit	1.694	0.832	0.812	0.436	0.623	0.584
Mo3			4.981			

$(Him)_4[Mo_8O_{26}(im)_2]$ (**8**)						
Bond	Mo1–O1	Mo1–O3	Mo1–O4	Mo1–O10	Mo1–O13	Mo1–N1
Bond distance	2.323(5)	1.710(5)	1.696(5)	1.921(5)	2.086(5)	2.218(6)
Valence unit	0.325	1.698	1.775	0.960	0.615	0.620
Mo1			5.994			
Bond	Mo2–O2	Mo2–O6	Mo2–O7	Mo2–O8	Mo2–O13	Mo2–O5a
Bond distance	2.284 (5)	1.718(5)	1.920(5)	1.696(5)	1.935(5)	2.341(5)
Valence unit	0.360	1.667	0.965	1.770	0.927	0.309
Mo2			5.998			
Bond	Mo3–O2	Mo3–O7	Mo3–O9	Mo3–O11	Mo3–O1a	Mo3–O10a
Bond distance	2.240(4)	1.940(5)	1.717(4)	1.692(5)	2.272(5)	1.954(5)
Valence unit	0.407	0.916	1.669	1.789	0.374	0.881
Mo3			6.034			
Bond	Mo4–O1	Mo4–O2	Mo4–O5	Mo4–O12	Mo4–O13	Mo4–O2a
Bond distance	1.895(5)	1.923(5)	1.747(5)	1.895(5)	2.178(6)	2.424(5)
Valence unit	1.034	0.958	1.541	1.754	0.479	0.248
Mo4			6.014			

Symmetric transformation: a $-x + 2, -y + 1, -z + 1$

Table S4. Selected hydrogen-bonding geometric data (Å, °) in **1**–**8**.

D – H···A	*d* (D–A)	*d* (D···H)	*d* (A···H)	∠(DHA)
*trans-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**)*				
O1W–H1W1···O9a	2.597	0.848	1.766	166.22
O1W–H1W2··· O1b	2.621	0.842	1.802	163.56
O2W–H2W1··· O4c	2.696	0.845	1.860	169.95
O2W–H2W2 ···O6d	2.654	0.846	1.811	174.12
N1–H1A ···O7e	2.746	0.860	1.929	158.03
N1–H1A··· O6e	3.148	0.860	2.605	122.12
N2–H2A ···O4Wf	2.766	0.860	1.944	159.31
O3W–H3W2 ···O2f	2.899	0.846	2.075	164.43
O5W–H5W1 ···O12g	2.895	0.771	2.126	175.07
O5W–H5W2 ···O7f	2.734	0.963	1.779	170.52
*trans-$(Him)_2[Mo_2O_4(ox)_2(H_2O)_2]$ (**2**)*				
N1–H1A···O7	2.788	0.860	1.975	157.29
N2–H2A···O10a	2.780	0.860	1.958	159.61
N2–H2A···O9a	2.962	0.860	2.454	118.44
N3–H3A···O12b	3.230	0.860	2.454	147.47
N3–H3A···O4b	3.401	0.860	2.650	146.61
N4–H4A···O8c	3.343	0.860	2.622	142.13
O2W–H2W2···O1e	2.696	0.851	1.856	168.95
O2W–H2W1···O9f	2.662	0.850	1.828	166.51
O1W–H1W1 ···O3g	2.707	0.856	1.902	155.98
O1W–H1W2···O2c	2.686	0.861	1.843	165.66
*cis-$Na_2[Mo_2O_4(ox)_2(im)_2]$·4.5$H_2O$ (**3**)*				
N2–H2A···O9a	2.907	0.860	2.253	132.82
N2–H2A···O4b	2.861	0.860	2.316	121.46
N4–H4A···O2Wc	2.861	0.860	2.014	168.07
N4–H4A···O6e	3.028	0.860	2.544	116.62
*cis-$K_2[Mo_2O_4(ox)_2(im)_2]$·3H_2O (**4**)*				
N2–H2A···O1a	2.769	0.860	1.942	161.15
N4–H4A···O3b	2.827	0.860	2.034	153.02
*K(Him)[$Mo_3O_4(ox)_3(im)_3$]·3H_2O (**5**)*				
N2–H2A···O15a	2.808	0.860	1.993	157.65
N2–H2A···O12a	3.000	0.860	2.458	121.61
N4–H4A··· O10b	2.750	0.860	1.892	176.14
N6–H6A ···O13c	2.766	0.860	1.909	174.37
N7–H7B ···O3Wd	2.591	0.860	1.742	168.69
N8–H8B ···O2W'e	2.648	0.860	1.911	142.82
N8–H8B···O15f	3.006	0.860	2.411	126.76

*[Mo_3O_8(im)$_4$](im)·H_2O (**6**)*				
N5–H5A···O6a	2.959	0.860	2.178	150.89
N5–H5A···O6b	3.066	0.860	2.588	116.17
N6–H6B···O8c	2.785	0.860	1.929	173.02
N8–H8B···O1d	2.769	0.860	1.977	152.45
*[Mo_3O_8(im)$_4$]·H_2O (**7**)*				
N5–H5A···O4a	2.710	0.860	1.858	170.57
N7–H7B···O1W	2.766	0.860	1.908	175.13
N8–H8B···O6b	2.819	0.860	1.993	160.84
N6–H6B···O3c	2.825	0.860	2.168	133.01
N6–H6B···O8d	2.960	0.860	2.277	136.34
*(Him)$_4$[Mo_8O_{26}(im)$_2$] (**8**)*				
N2–H2A···O6a	2.825	0.860	1.987	164.56
N5–H5A···O7	2.719	0.860	1.956	147.25
N5–H5A···O8b	3.147	0.860	2.636	119.29
N4–H4B···O3c	3.194	0.900	2.296	175.80
N6–H6···N1b	3.345	0.900	2.537	149.76

Symmtric transformations: compound **1**, *a*: $x + 1, y, z$; *b*: $-x + 1, -y + 4, -z - 1$; *c*: $-x + 1, -y + 4, -z$; *d*: $x - 1, y, z$; *e*: $-x + 1, -y + 3, -z$; *f*: $-x, -y + 3, -z - 1$; *g*: $-x, -y + 4, -z - 1$; compound **2**, *a*: $-x, -y - 1, -z + 1$; *b*: $x - 1, y - 1, z$; *c*: $-x + 1, -y, -z + 2$; *d*: $-x + 1, -y, -z + 1$; *e*: $x + 1, y, z$; f: $x - 1, y, z$; compound **3**: *a*: $-x + 1/2, -y + 1/2, -z + 1$; *b*: $-x + 1/2, -y + 1/2, -z + 1$; *c*: $x + 1/2, -y - 1/2, z + 1/2$; *d*: $-x + 1/2, y - 1/2, -z + 1/2$; compound **4**: *a*: $x + 1, y, z$; *b*: $x, y, z–1$; compound **5**: *a*: $x - 1, y + 1, z$; *b*: $-x, -y + 1, -z + 3$; *c*: $-x, -y + 2, -z + 2$; *d*: $-x, -y + 1, -z + 2$; e: $x, y, z–1$; compound **6**: *a*: $x, y + 1, z$; *b*: $-x + 1, -y - 1, -z$; *c*: $x - 1, y, z$; *d*: $x, y - 1, z$; compound **7**: *a*：$x + 1, y, z$；*b*：$x - 1, y, z$；*c*：$-x, y - 1/2, -z$；*d*：$x, y, z - 1$；compound **8**: *a*: $-x + 1, -y, -z + 1$; *b*: $-x + 2, -y, -z + 1$; *c*: $-x + 1, -y + 1, -z + 1$.

Table S5. UV spectral data (in nm) of 1 − 8.

Compounds	Charge transfer	Mo−Mo
trans-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**)	201, 262	306
trans-$(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**)	204, 261	304
cis-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (**3**)	205, 264	305
cis-K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**)	203, 265	307
K(Him)[$Mo_3O_4(ox)_3(im)_3$]·3H_2O (**5**)	200	254
[$Mo_3O_8(im)_4$](im)·H_2O (**6**)	207, 232	318
[$Mo_3O_8(im)_4$]·H_2O (**7**)	207, 231	308
$(Him)_4$[$Mo_8O_{26}(im)_2$] (**8**)	210, 232	

Table S6. Solution ^{1}H NMR spectral data (in ppm) of **1**–**4**, **6**–**8**.

Compounds	NC*H*NH	NC*H*CH/NHC*H*CH
trans-Na(Him)[$Mo_2O_4(ox)_2(H_2O)_2$]·H_2O (**1**)	8.68	7.48
trans- $(Him)_2$[$Mo_2O_4(ox)_2(H_2O)_2$] (**2**)	8.69	7.47
cis-Na_2[$Mo_2O_4(ox)_2(im)_2$]·4.5H_2O (**3**)	8.38	7.50, 7.35
cis-K_2[$Mo_2O_4(ox)_2(im)_2$]·3H_2O (**4**)	8.43	7.56, 7.38
[$Mo_3O_8(im)_4$](im)·H_2O (**6**)	8.31	7.34
[$Mo_3O_8(im)_4$]·H_2O (**7**)	8.25	7.29
$(Him)_4$[$Mo_8O_{26}(im)_2$] (**8**)	8.69	7.47

Table S7. Electrochemical data for compounds **2**, **4**, **5** and **6**.

Compounds	E_{pc}/V	E_{pa}/V	$E_{1/2}$/V	ΔE_p/V
2	−0.228	0.704	0.238	0.932
4	−0.326	−0.099	0.113	0.227
5	−0.238	0.268	0.015	0.506
6	−0.343	0.719	0.188	1.062

The half-wave potentials $E_{1/2}$ are defined as $(E_{pc}+ E_{pa})/2$, and the peak separations ΔE_p are presented as $E_{pa}-E_{pc}$. E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively.