Molybdenum complexes derived from 2-hydroxy-5-nitrobenzaldehyde and benzhydrazide as potential oxidation catalysts and semiconductors (Supporting Information)

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Table S1. Experimental and crystallographic data for complexes [MoO$_2$(L)(MeOH)] (**1**), [MoO$_2$(L)(H$_2$O)] (**2**) and [(MoO$_2$(L))$_2$(4,4-bpy)] (**3**).

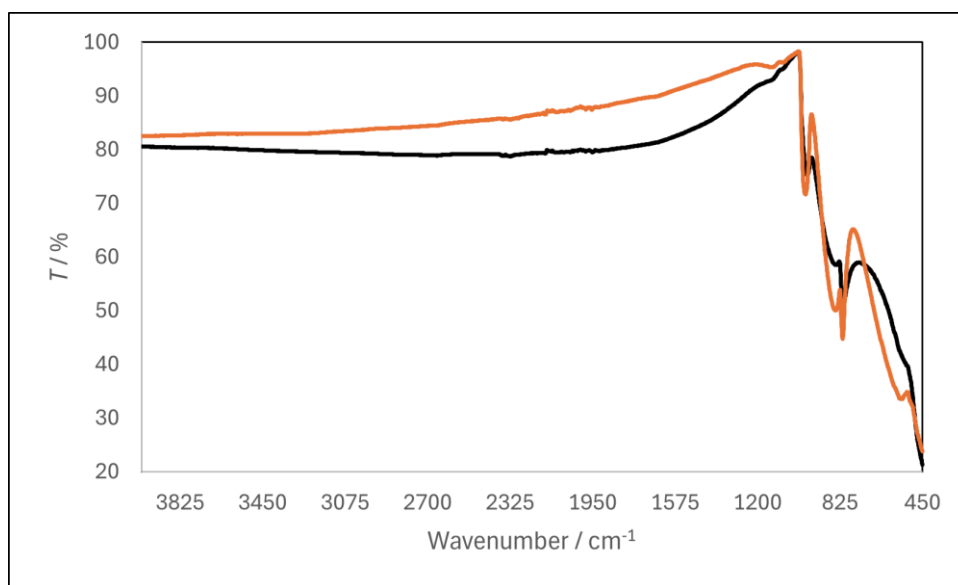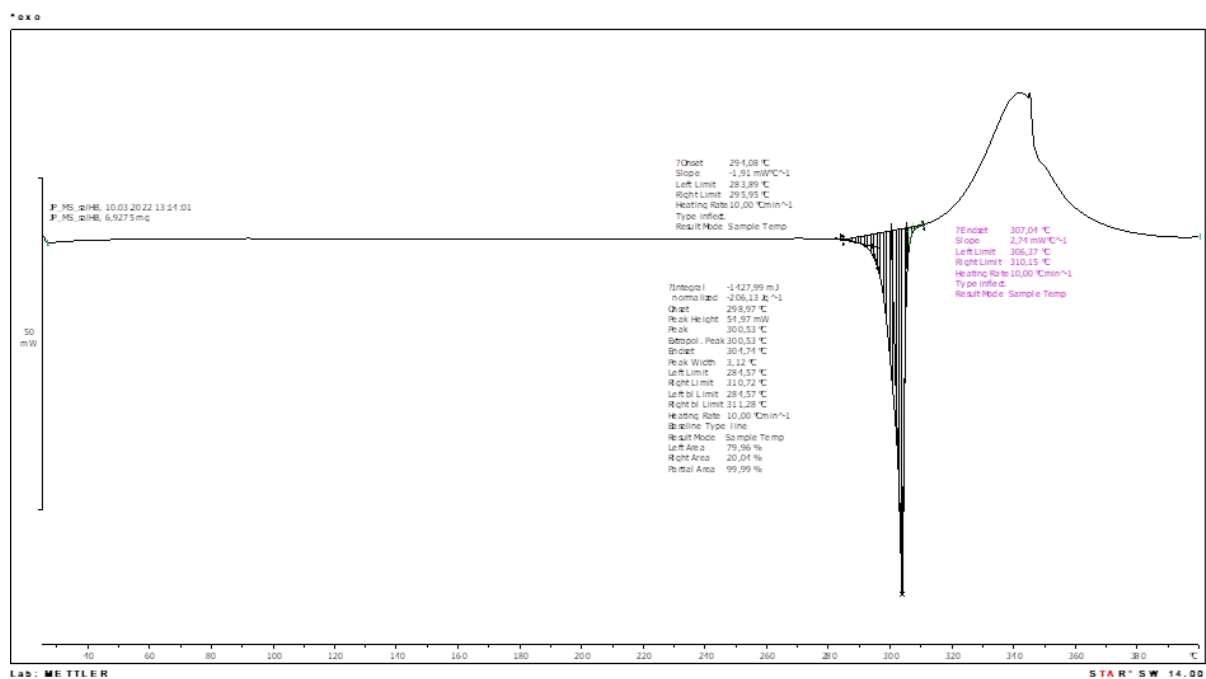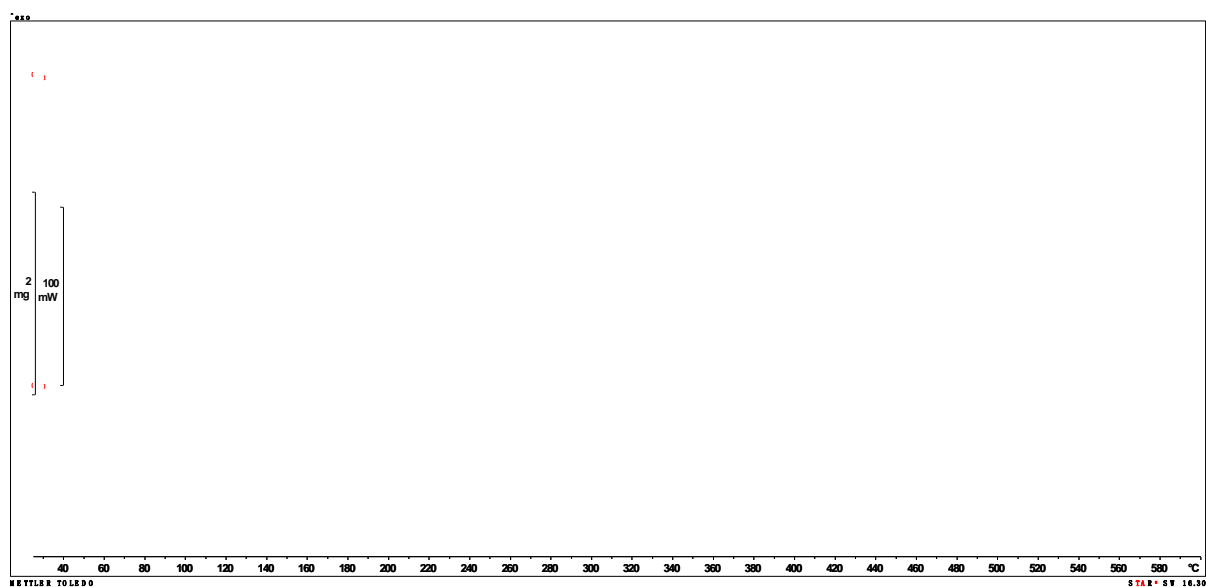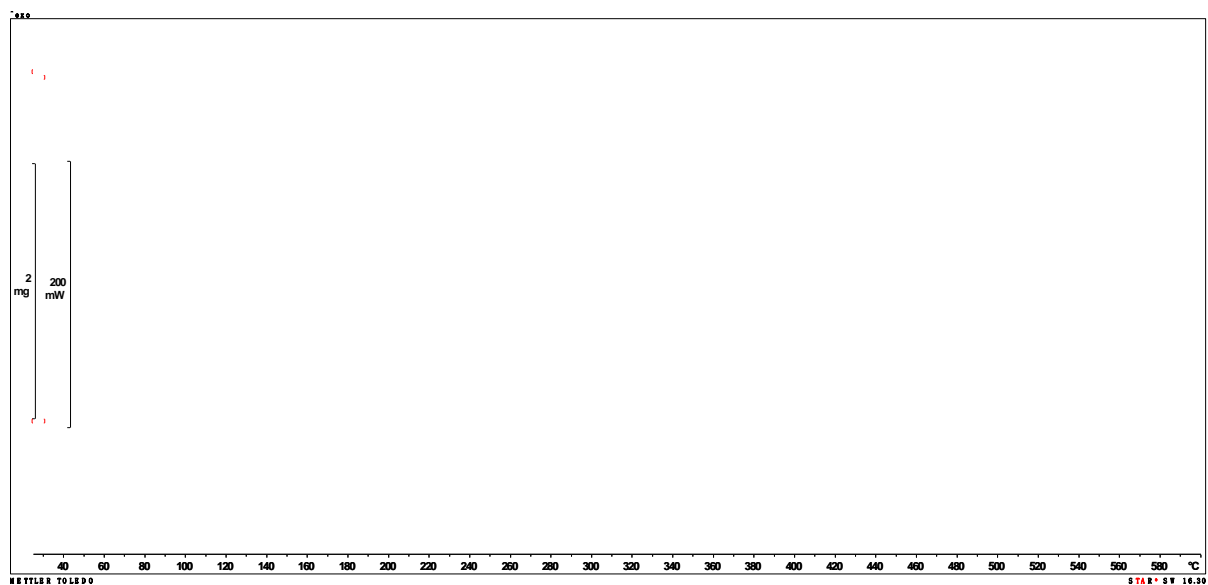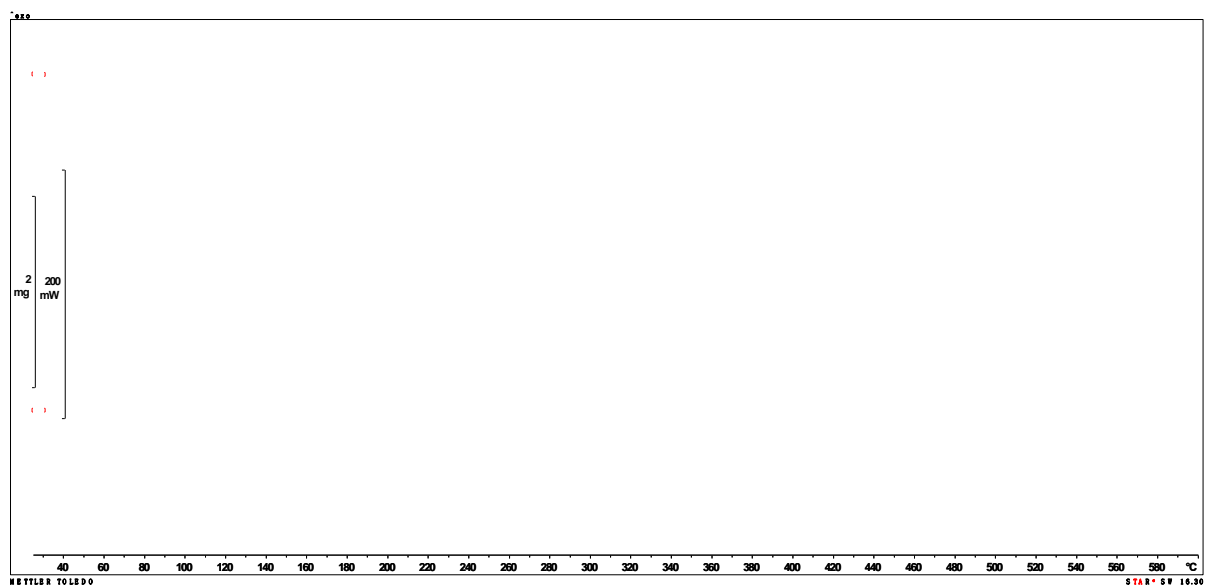| Identifier	[MoO$_2$(L)(MeOH)] (**1**)	[MoO$_2$(L)(H$_2$O)] (**2**)	[(MoO$_2$(L))$_2$(4,4-bpy)] (**3**)
Empirical formula	C$_{15}$H$_{13}$MoN$_3$O$_7$	C$_{14}$H$_{11}$MoN$_3$O$_7$	C$_{38}$H$_{26}$Mo$_2$N$_8$O$_{12}$
M_r	443.22	429.20	978.55
T/K	170(2)	169.98(10)	169.99(10)
Crystal system	triclinic, yellow needle	monoclinic, yellow plate	monoclinic, yellow plate
Space group	$P -1$	$P\,1\,2_1/c\,1$	$P\,1\,2_1/n\,1$
a/Å	7.9589(3)	10.8039(7)	13.1888(4)
b/Å	9.5589(3)	10.7689(6)	10.5504(3)
c/Å	10.5117(3)	13.5832(8)	14.1743(4)
α/°	83.639(2)	90	90
β/°	88.860(3)	108.087(7)	106.292(3)
γ/°	89.126(3)	90	90
V/Å^3	794.56(4)	1502.26(17)	1893.11(10)
Z	2	4	2
ρ_{calc}/g cm^{-3}	1.853	1.898	1.717
μ/mm^{-1}	7.200	7.592	6.092
$F(000)$	444	856	980
Crystal size/mm^3	0.08×0.03×0.03	0.08×0.05×0.004	0.3×0.08×0.02
Radiation			Cu Kα (λ = 1.54184Å)
2Θ range/°	8.466 to 155.052	8.61 to 154.716	8.096 to 155.81
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 9$, $-13 \le l \le 13$	$-13 \le h \le 12$, $-13 \le k \le 13$, $-16 \le l \le 15$	$-16 \le h \le 16$, $-13 \le k \le 13$, $-16 \le l \le 17$
Reflections collected	12446	10107	21369
Independent reflections	3268 [R_{int} = 3.58%, R_{sigma} = 4.08 %]	3007 [R_{int} = 6.13%, R_{sigma} = 6.47 %]	4006 [R_{int} = 6.9%, R_{sigma} = 10.16 %]
Data/restraints/parameters	3268/-/239	3007/-/227	4006/-/271
g_1, g_2 in w^a	0.0579, 1.3589	0.0531, 46.7310	0.1059, 0
Goodness–of–fit on F^2, S^b	1.079	1.057	1.048
Final R and wR^c values [$I \ge 2\sigma(I)$]	R_1 = 3.62%, wR_2 = 9.81%	R_1 = 8.67%, wR_2 = 21.35%	R_1 = 5.19%, wR_2 = 14.31%
Final R and wR^c values [all data]	R_1 = 3.86%, wR_2 = 9.98%	R_1 = 11.31%, wR_2 = 22.69%	R_1 = 5.71%, wR_2 = 15.02%
Largest diff. peak/hole / e Å^{-3}	1.076/–1.187	3.097/–1.384	0.873/–1.330

[a] $w = 1/[\sigma F_o{}^2 + (g_1 P)^2 + g_2 P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$

[b] $S = \{\Sigma[w(F_o{}^2 - F_c{}^2)2]/(N_r - N_p)\}^{1/2}$ where N_r = number of independent reflections, N_p = number of refined parameters.
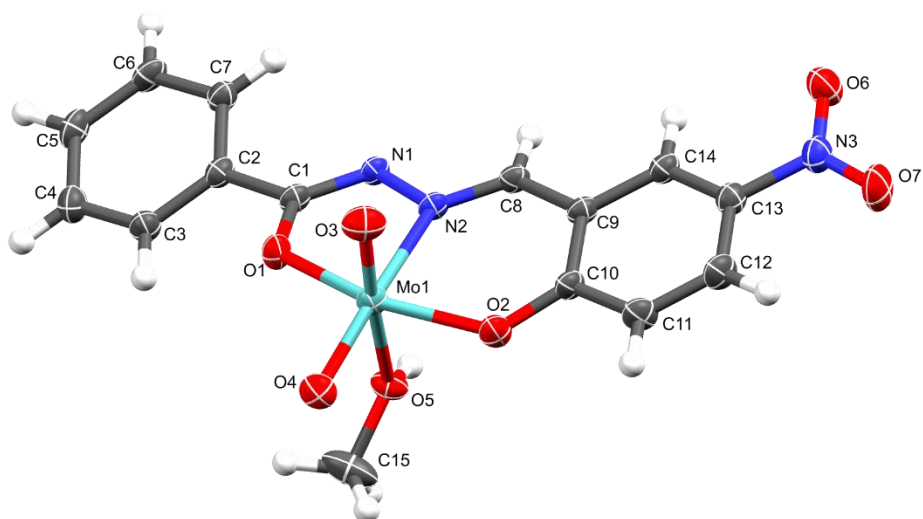
[c] $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$; $wR = \{\Sigma[w(F_o{}^2 - F_c{}^2)2]/\Sigma[w(F_o{}^2)2]\}^{1/2}$

Table S2. Selected bond lengths in the crystal structures of [MoO$_2$(L)(MeOH)] (**1**), [MoO$_2$(L)(H$_2$O)] (**2**) and [(MoO$_2$(L))$_2$(4,4-bpy)] (**3**).
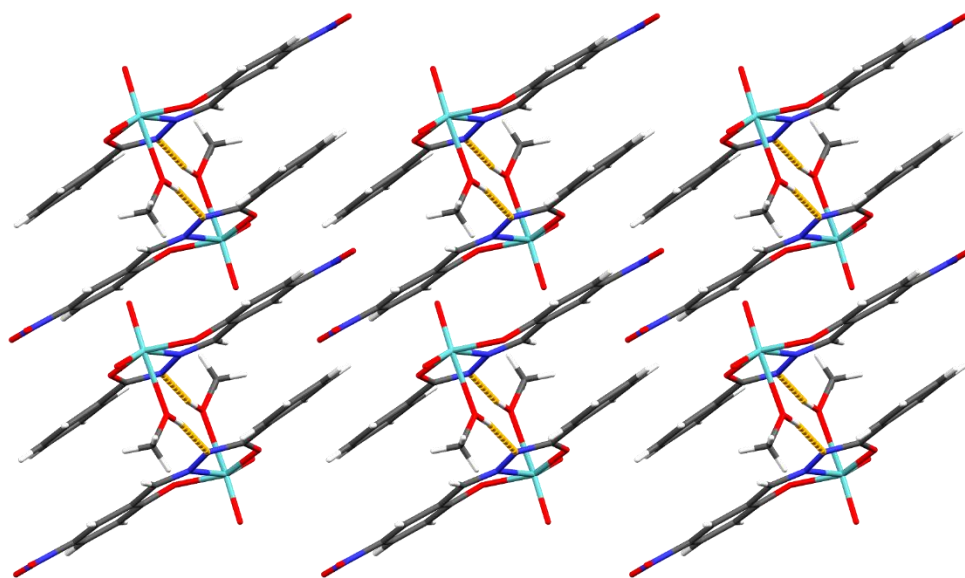
\[MoO$_2$(L)(MeOH)\] (**1**)					
Atoms	Bond length/Å	Atoms	Bond length/Å	Atoms	Bond length/Å
C2–C3	1.390(5)	C12–C13	1.392(5)	N1–N2	1.400(4)
C2–C7	1.396(4)	Mo1–N2	2.260(3)	O1–C1	1.312(4)
C3–C4	1.391(5)	Mo1–O1	2.007(2)	O2–C10	1.326(4)
C4–C5	1.385(5)	Mo1–O2	1.939(2)	O5–C15	1.423(6)
C9–C14	1.394(4)	Mo1–O3	1.696(3)	O6–N3	1.221(4)
C10–C11	1.409(5)	Mo1–O4	1.702(3)	O7–N3	1.223(4)
C11–C12	1.371(6)	Mo1–O5	2.309(2)		

\[MoO$_2$(L)(H$_2$O)\] (**2**)					
Atoms	Bond length/Å	Atoms	Bond length/Å	Atoms	Bond length/Å
C2–C7	1.382(17)	C13–C14	1.385(16)	N1–C1	1.271(16)
C3–C4	1.40(2)	Mo1–N2	2.234(10)	N1–N2	1.416(12)
C4–C5	1.37(2)	Mo1–O1	2.021(8)	O1–C1	1.316(14)
C5–C6	1.38(2)	Mo1–O2	1.940(10)	O2–C10	1.330(17)
C10–C11	1.411(17)	Mo1–O3	1.742(12)	O6–N3	1.233(14)
C11–C12	1.380(19)	Mo1–O4	1.690(11)	O7–N3	1.210(15)
C12–C13	1.375(17)	Mo1–O5	2.270(10)		

\[(MoO$_2$(L))$_2$(4,4-bpy)\] (**3**)					
Atoms	Bond length/Å	Atoms	Bond length/Å	Atoms	Bond length/Å
C9–C10	1.414(5)	Mo1–N4	2.395(3)	N4–C15	1.343(5)
C9–C14	1.392(6)	Mo1–O1	1.995(2)	N4–C19	1.339(5)
C10–C11	1.396(6)	Mo1–O2	1.950(3)	O1–C1	1.330(4)
C11–C12	1.374(6)	Mo1–O3	1.703(3)	O2–C10	1.336(5)
C12–C13	1.388(6)	Mo1–O4	1.704(2)	O5–N3	1.229(5)
C13–C14	1.367(6)	N1–C1	1.288(5)	O6–N3	1.225(6)
C15–C16	1.385(6)	N1–N2	1.397(5)		
C16–C17	1.398(5)	N2–C8	1.297(5)		
Mo1–N2	2.250(3)	N3–C13	1.466(6)		

Table S3. Hydrogen bond parameters in the crystal structures of prepared complexes [MoO$_2$(L)(MeOH)] (**1**), [MoO$_2$(L)(H$_2$O)] (**2**) and [(MoO$_2$(L))$_2$(4,4-bpy)] (**3**)..

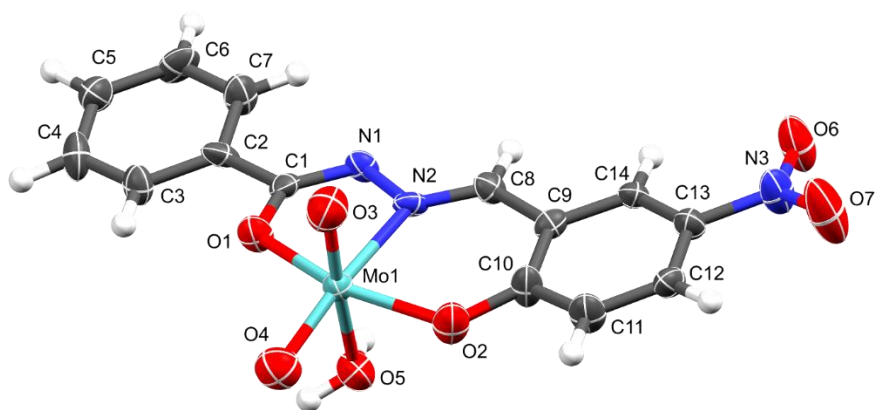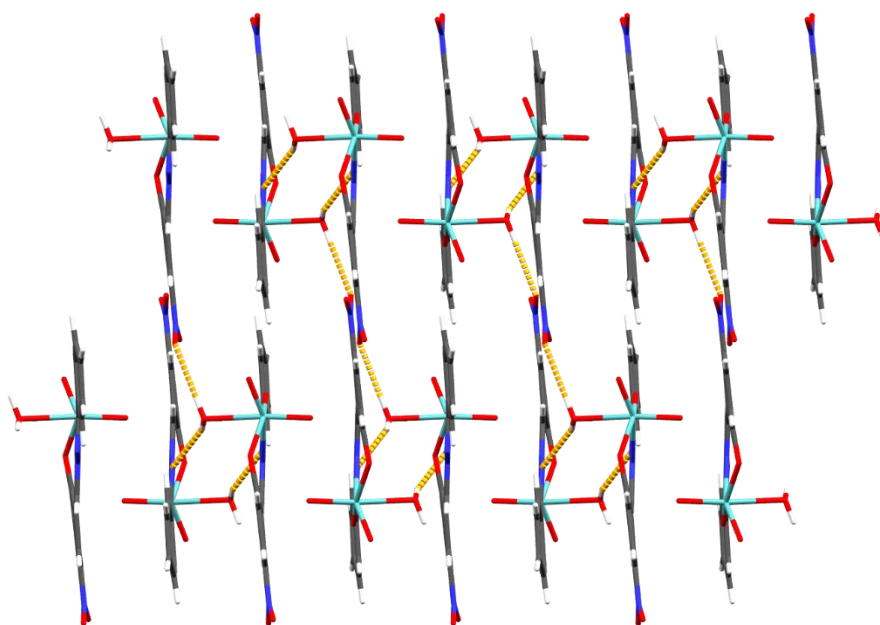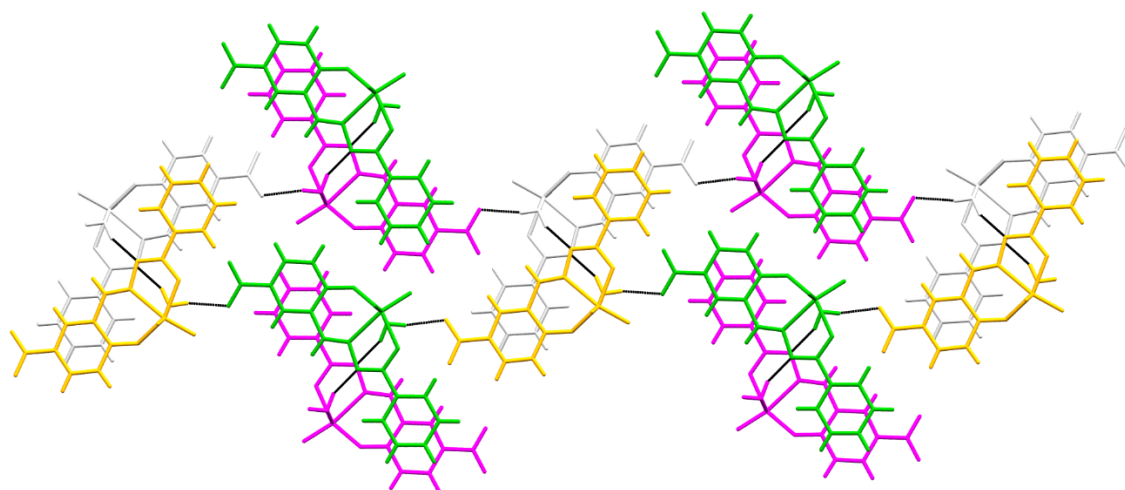| D–H···A	D-H	H···A	D···A	∠D–H···A	Symmetry code
\[MoO$_2$(L)(MeOH)\] (**1**)					
O5–H5···N1	0.82(5)	1.97(5)	2.779(4)	171(5)	1–x, 1–y, 2–z
C8–H8···O3	0.95	2.52	3.170(4)	126	–x, 1–y, 2–z
\[MoO$_2$(L)(H$_2$O)\] (**2**)					
O5–H5A···N1	0.88	2.15	2.904(14)	143	1–x, 1–y, 1–z
O5–H5B···O6	0.88	2.11	2.971(15)	168	–1+x, 1/2–y, –1/2+z
C4–H4···O4	0.95	2.36	3.208(18)	149	–x, 1–y, 1–z
C7–H7···O3	0.95	2.59	3.431(18)	148	1–x, 1/2+y, 3/2–z
C8–H8···O7	0.95	2.59	3.402(18)	144	2–x, 1/2+y, 3/2–z
C12–H12···O6	0.95	2.51	3.439(16)	167	2–x, –1/2+y, 3/2–z
C14–H14···O7	0.95	2.26	3.152(16)	157	2–x, 1/2+y, 3/2–z
\[(MoO$_2$(L))$_2$(4,4-bpy)\] (**3**)					
C8–H8···O3	0.95	2.53	3.159(5)	124	1–x, 1–y, 1–z
C12–H12···O5	0.95	2.30	3.171(5)	153	3/2–x, 1/2+y, 1/2–z
C14–H14···O3	0.95	2.55	3.245(5)	130	1–x, 1–y, 1–z

(a)

(b)

Figure S9. (a) Molecular structure of [MoO$_2$(L)(MeOH)] (**1**). Atoms are shown as thermal ellipsoid with 50% probability level. The asymmetric unit contains one whole molecule of the complex. (b) Packing of mononuclear complexes [MoO$_2$(L)(MeOH)] (**1**) in the crystal structure. The molecules form supramolecular $R_2^2(10)$ homodimers formed by methanol O–H···N1 imido hydrogen bonds. No other significant interactions between the dimers are observed.
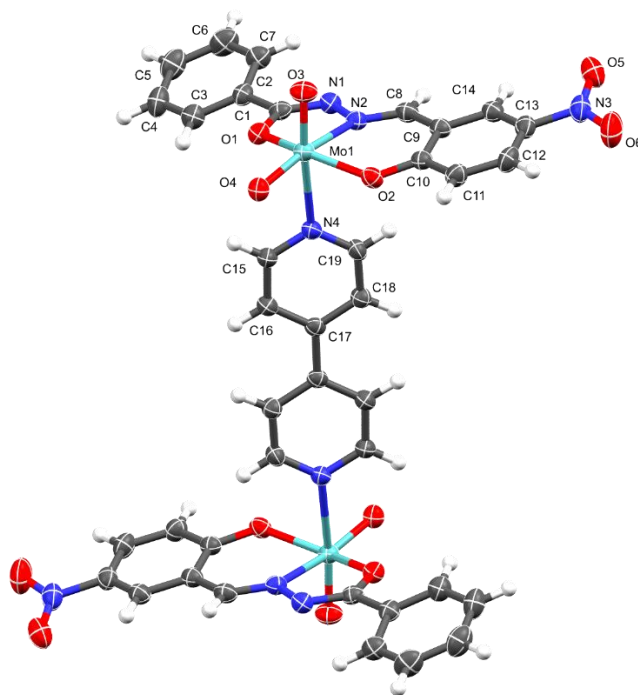
(a)

(b)

(c)

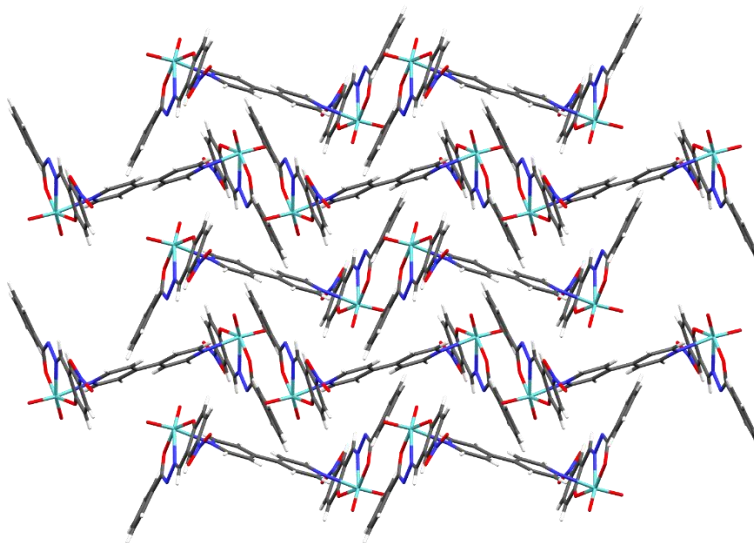Figure S10. (a) Molecular structure of [MoO$_2$(L)(H$_2$O)] (2). Atoms are shown as thermal ellipsoid with a 50% probability level. The asymmetric unit contains one whole molecule of the complex. (b) Packing of mononuclear complexes [MoO$_2$(L)(H$_2$O)] (2) in the crystal structure. The molecules form supramolecular $C_4^4(26)$ chains spanning through water O–H⋯O6(nitro) hydrogen bonds and water O–H⋯N1 imido hydrogen bond. The latter enables the formation of supramolecular homodimers connected via hydrogen bonds with nitro moiety. (c) Packing of mononuclear complexes 2 in the crystal structure. Molecules are colored by symmetry operation, showing the formation of supramolecular dimers bridged by O–H⋯O6(nitro) hydrogen bonds.

(a)

(b)

Figure S11. (a) Molecular structure of [(MoO$_2$(L))$_2$(4,4-bpy)] (**3**). Atoms are shown as thermal ellipsoid with a 50% probability level. The asymmetric unit contains the upper half of the shown molecule only (center of inversion is situated at the midpoint of 4,4'-bpy C–C bond). (b) Packing of dinuclear complexes [(MoO$_2$(L))$_2$(4,4-bpy)] (**3**) in the crystal structure. The molecules do not form any significant intermolecular interactions due to the lack of hydrogen bond donors.