

## SUPPORTING INFORMATION for:

# Triazolyl, Imidazolyl and Carboxylic Acid Moieties in the Design of Molybdenum Trioxide Hybrids: Photophysical and Catalytic Behavior

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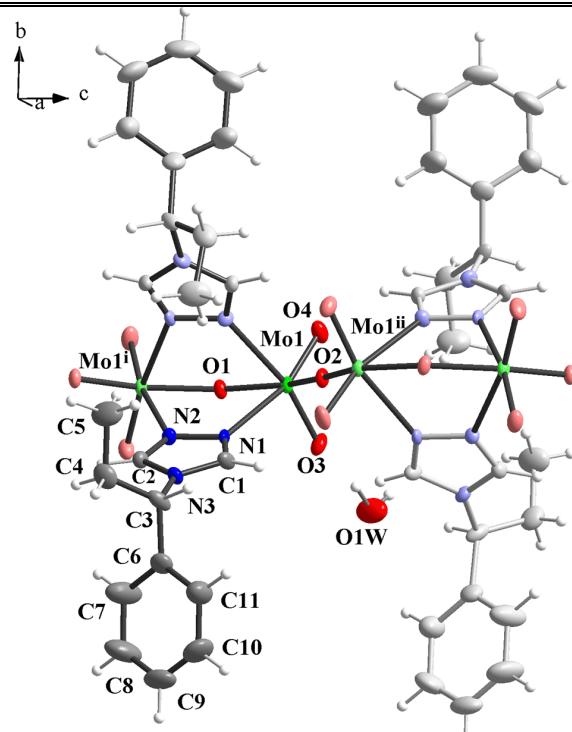
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**Table S1.** Crystal data for  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**),  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot0.5\text{H}_2\text{O}$  (**2a**),  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot\text{H}_2\text{O}$  (**2b**) and  $[\text{Mo}_8\text{O}_{25}(\text{trhis})_2(\text{Htrhis})_2]\cdot2\text{H}_2\text{O}$  (**3**)

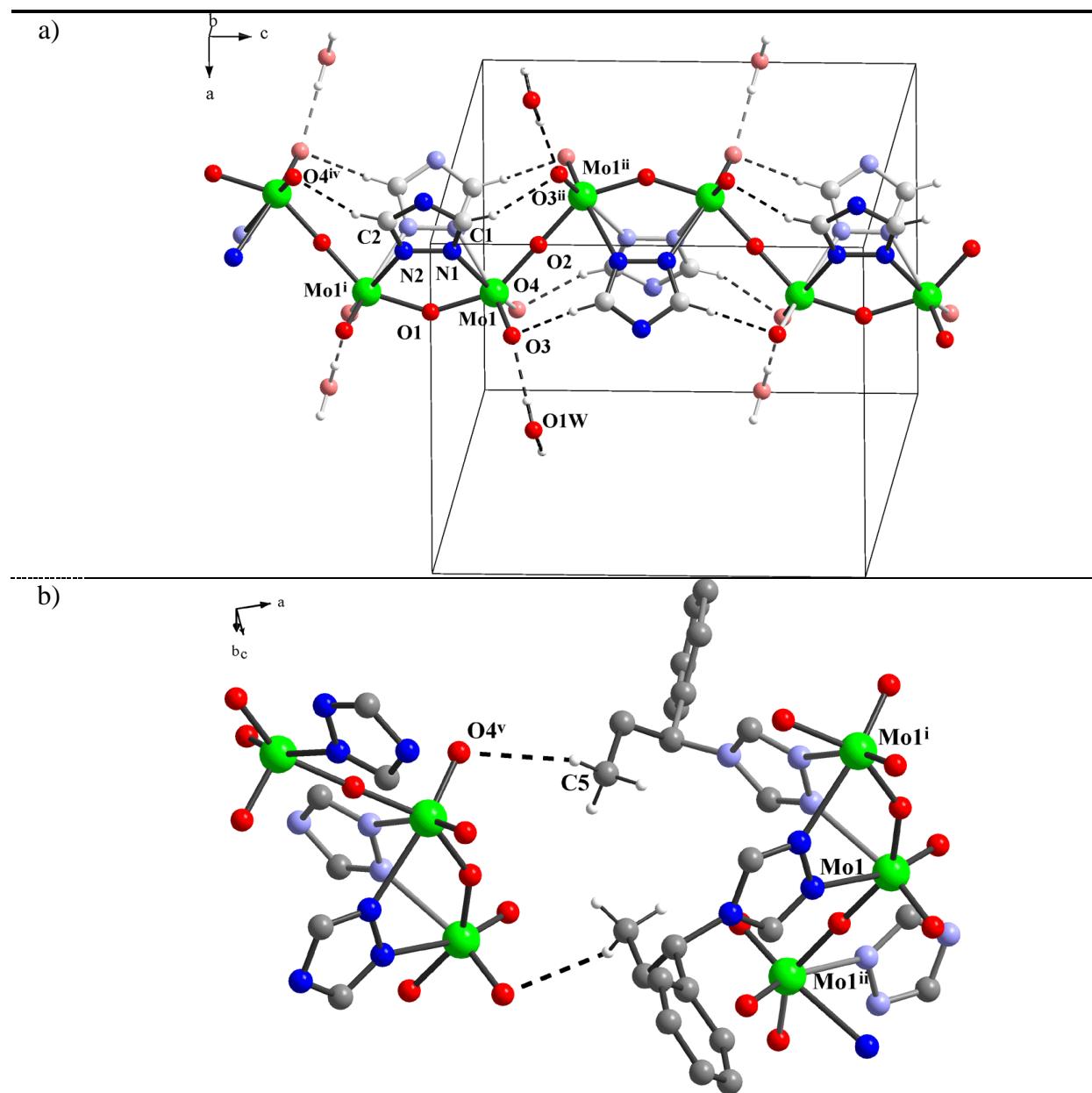
	<b>1</b>	<b>2a</b>	<b>2b</b>	<b>3</b>
Formula	$\text{C}_{22}\text{H}_{28}\text{Mo}_2\text{N}_6\text{O}_7$	$\text{C}_{18}\text{H}_{15}\text{Mo}_4\text{N}_6\text{O}_{16.5}$	$\text{C}_{18}\text{H}_{16}\text{Mo}_4\text{N}_6\text{O}_{17}$	$\text{C}_{32}\text{H}_{42}\text{Mo}_8\text{N}_{20}\text{O}_{35}$
<i>T</i> , K	213	213	213	213
<i>M</i>	680.38	963.12	972.13	2034.38
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group, <i>Z</i>	$C222_1, 4$	$P2_1, 2$	$P\bar{1}, 2$	$P2_1/c, 2$
<i>a</i> / Å	9.6544(5)	9.9831(5)	7.2937(5)	14.3760(9)
<i>b</i> / Å	23.0267(9)	13.6626(6)	14.4673(11)	9.1515(4)
<i>c</i> / Å	12.3254(4)	10.1235(5)	14.8484(11)	21.3642(14)
$\alpha/^\circ$	90	90	117.124(8)	90
$\beta/^\circ$	90	90.926(6)	92.334(7)	103.188(7)
$\gamma/^\circ$	90	90	99.015(8)	90
<i>U</i> / Å <sup>3</sup>	2740.0(2)	1380.62(11)	1366.0(2)	2736.6(3)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.966	1.864	1.887	1.895
$D_v/\text{g cm}^{-3}$	1.649	2.317	2.363	2.469
$\theta_{\max}/^\circ$	27.9	27.5	27.9	28.0
Meas/ Unique reflns	10348/ 3247	11600/ 5627	12768/ 6479	23148/ 6547
<i>R</i> <sub>int</sub>	0.027	0.017	0.045	0.029
Parameters refined	169	415	406	430
<i>R</i> 1 [ $I > 2\sigma(I)$ ]	0.022	0.014	0.029	0.020
<i>wR</i> 2 [all data]	0.050	0.031	0.060	0.047
Goof on <i>F</i> <sup>2</sup>	0.928	0.921	0.819	0.921
Flack <i>x</i> parameter	0.00(7)	-0.031(19)	-	-
Max, min peak/ e Å <sup>-3</sup>	1.77, -0.26	0.44, -0.31	0.98, -1.67	1.59, -0.52



**Figure S1.** Crystal structure and labeling scheme for  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**). Ellipsoids are shown at the 50% probability level. Symmetry codes: (i)  $x, -y, -z$ ; (ii)  $-x, y, -z+1/2$ .

**Table S2.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1**.

[Mo <sub>2</sub> O <sub>6</sub> ( <i>trethbz</i> ) <sub>2</sub> ]·H <sub>2</sub> O ( <b>1</b> ), symmetry codes: (i) $x, -y, -z$ ; (ii) $-x, y, -z+1/2$ .			
Mo1—O4	1.700 (4)	Mo1—O2	1.9065 (2)
Mo1—O3	1.723 (4)	Mo1—N2i	2.387 (5)
Mo1—O1	1.9030 (6)	Mo1—N1	2.401 (5)
O4—Mo1—O3	104.78 (12)	O4—Mo1—N1	162.8 (2)
O4—Mo1—O1	100.01 (15)	O3—Mo1—N1	92.40 (19)
O3—Mo1—O1	98.53 (16)	N1—N2—Mo1i	119.9 (4)
O4—Mo1—O2	98.9 (2)	O1—Mo1—N1	75.80 (13)
O3—Mo1—O2	99.9 (2)	O2—Mo1—N1	78.96 (19)
O1—Mo1—O2	149.20 (5)	N2i—Mo1—N1	73.72 (6)
O4—Mo1—N2i	89.1 (2)	N2—N1—Mo1	116.2 (4)
O3—Mo1—N2i	165.7 (2)	Mo1i—O1—Mo1	144.87 (10)
O1—Mo1—N2i	74.90 (13)	Mo1—O2—Mo1ii	178.0 (5)
O2—Mo1—N2i	81.33 (18)		

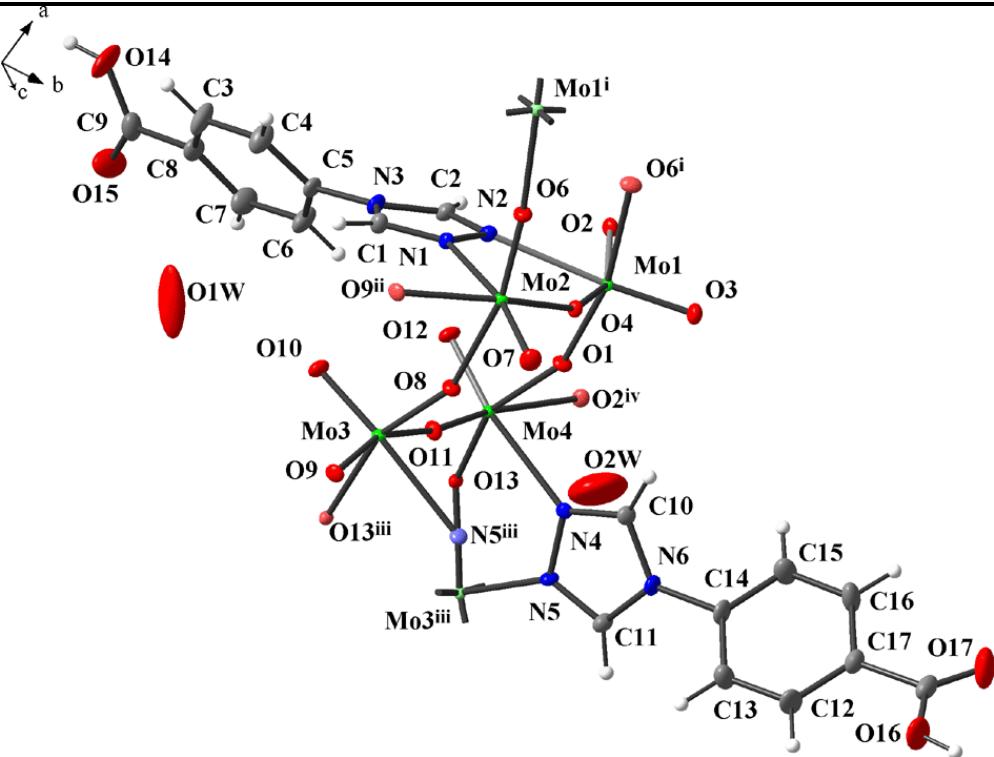


**Figure S2.** Illustration of the hydrogen-bonding interactions in the crystal structure of  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**). Symmetry codes: (i)  $x, -y, -z$ ; (ii)  $-x, y, -z+1/2$ ; (iii)  $-x+1, y, -z+1/2$ ; (iv)  $-x, -y, z-1/2$ ; (v)  $x-1, -y, -z$ .

**Table S3.** Hydrogen bonding scheme in the crystal structure of **1** ( $\text{\AA}$ ,  $^\circ$ ).<sup>S1, S2</sup>

$D\text{-H}\cdots A$	$H\cdots A$	$D\cdots A$	$D\text{-H}\cdots A$
O(1W)-H(1O) ..O(3)iii	1.96	2.8582	172
C(1)-H(1) ..O(3)ii	2.30	3.0815	140
C(2)-H(2) ..O(4)iv	2.19	3.0175	147
C(5)-H(5A) ..O(4)v	2.55	3.3113	136

symmetry codes: (i)  $x, -y, -z$ ; (ii)  $-x, y, -z+1/2$ ; (iii)  $-x+1, y, -z+1/2$ ; (iv)  $-x, -y, z-1/2$ ; (v)  $x-1, -y, -z$ .



**Figure S3.** Crystal structure and labeling scheme for  $[Mo_4O_{12}(trC_6H_4CO_2H)_2]\cdot 0.5H_2O$  (**2a**). Ellipsoids are shown at the 50% probability level. Symmetry codes: (i)  $-x+1, y, -z$ ; (ii)  $-x, y, -z$ ; (iii)  $-x, y, -z+1$ ; (iv)  $-x+1, y, -z+1$ .

**Table S4.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **2a**.

$[Mo_4O_{12}(trC_6H_4CO_2H)_2]\cdot 0.5H_2O$  (**2a**), symmetry codes: (i)  $-x+1, y, -z$ ; (ii)  $-x, y, -z$ ; (iii)  $-x, y, -z+1$ ; (iv)  $-x+1, y, -z+1$ .

Mo1—O3	1.6949 (18)	Mo3—O10	1.6945 (19)
Mo1—O2	1.7819 (17)	Mo3—O8	1.7560 (19)
Mo1—O1	1.7990 (19)	Mo3—O9	1.8266 (16)
Mo1—O4	2.0172 (18)	Mo3—O11	2.0668 (16)
Mo1—O6i	2.1486 (19)	Mo3—O13iii	2.087 (2)
Mo1—N2	2.361 (2)	Mo3—N5iii	2.362 (2)
Mo2—O7	1.692 (2)	Mo4—O12	1.697 (2)
Mo2—O6	1.7447 (18)	Mo4—O11	1.7708 (16)
Mo2—O4	1.8562 (18)	Mo4—O13	1.822 (2)
Mo2—O9ii	1.9818 (17)	Mo4—O1	2.0407 (19)
Mo2—O8	2.164 (2)	Mo4—O2iv	2.0861 (16)
Mo2—N1	2.372 (2)	Mo4—N4	2.362 (2)

**Table S4.** continued

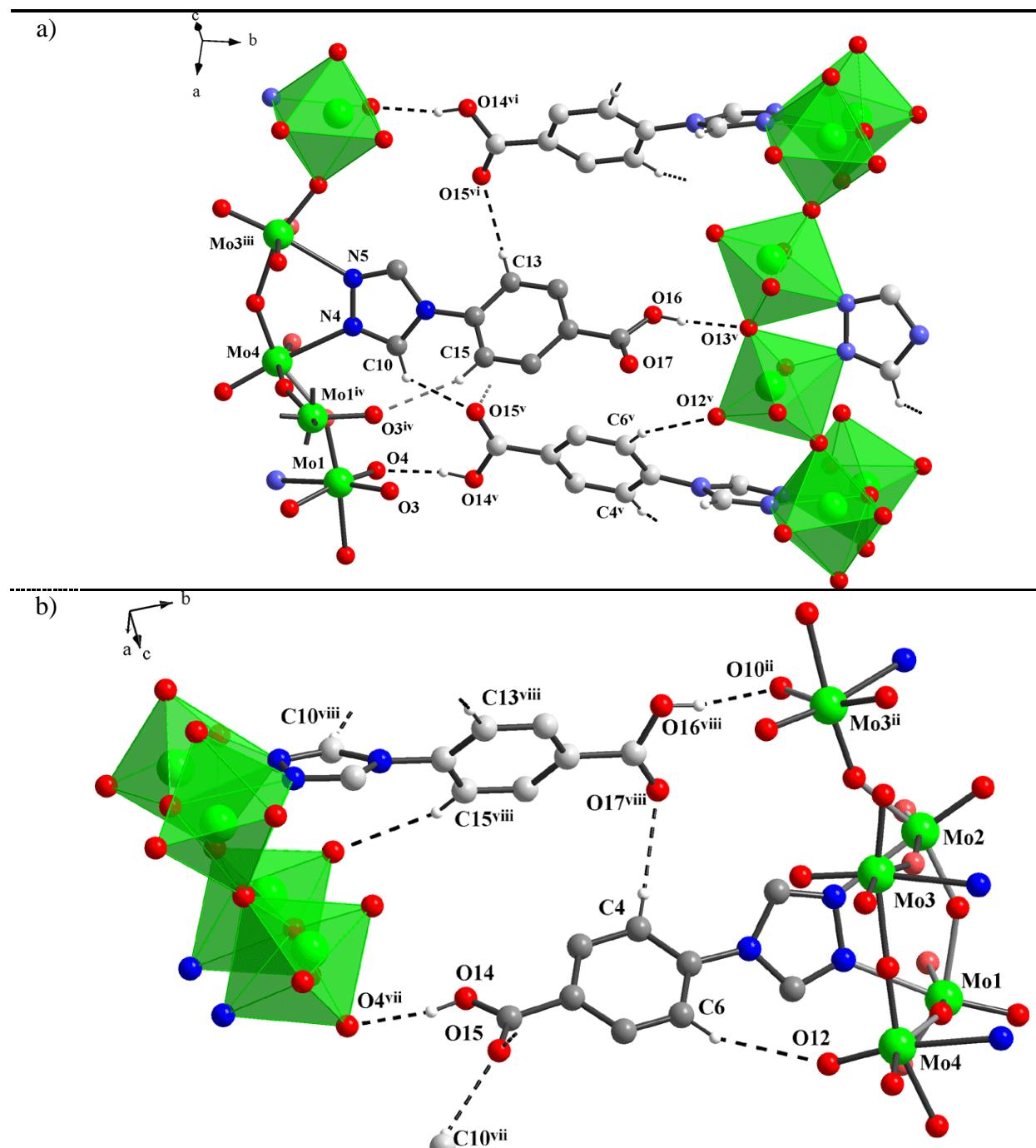
O3—Mo1—O2	104.45 (8)	O8—Mo3—O11	89.64 (8)
O3—Mo1—O1	102.43 (9)	O9—Mo3—O11	160.11 (8)
O2—Mo1—O1	99.89 (8)	O10—Mo3—O13iii	94.97 (9)
O3—Mo1—O4	95.30 (8)	O8—Mo3—O13iii	157.68 (9)
O2—Mo1—O4	153.55 (8)	O9—Mo3—O13iii	87.02 (8)
O1—Mo1—O4	92.69 (8)	O11—Mo3—O13iii	78.34 (7)
O3—Mo1—O6i	91.25 (9)	O10—Mo3—N5iii	169.32 (9)
O2—Mo1—O6i	84.38 (8)	O8—Mo3—N5iii	82.97 (9)
O1—Mo1—O6i	164.02 (8)	O9—Mo3—N5iii	84.36 (8)
O4—Mo1—O6i	77.69 (7)	O11—Mo3—N5iii	79.19 (8)
O3—Mo1—N2	168.99 (9)	O13iii—Mo3—N5iii	76.38 (8)
O2—Mo1—N2	81.40 (8)	O12—Mo4—O11	102.79 (10)
O1—Mo1—N2	85.46 (8)	O12—Mo4—O13	101.41 (9)
O4—Mo1—N2	76.48 (7)	O11—Mo4—O13	100.08 (8)
O6i—Mo1—N2	79.94 (8)	O12—Mo4—O1	99.42 (9)
O7—Mo2—O6	103.76 (10)	O11—Mo4—O1	87.86 (8)
O7—Mo2—O4	100.33 (9)	O13—Mo4—O1	155.40 (8)
O6—Mo2—O4	100.41 (8)	O12—Mo4—O2iv	91.53 (9)
O7—Mo2—O9ii	99.34 (8)	O11—Mo4—O2iv	161.32 (8)
O6—Mo2—O9ii	92.85 (8)	O13—Mo4—O2iv	88.57 (8)
O4—Mo2—O9ii	152.85 (8)	O1—Mo4—O2iv	77.90 (7)
O7—Mo2—O8	90.34 (9)	O12—Mo4—N4	168.54 (8)
O6—Mo2—O8	164.38 (9)	O11—Mo4—N4	88.12 (8)
O4—Mo2—O8	83.32 (8)	O13—Mo4—N4	79.80 (8)
O9ii—Mo2—O8	78.03 (7)	O1—Mo4—N4	77.21 (8)
O7—Mo2—N1	166.11 (9)	O2iv—Mo4—N4	77.07 (7)
O6—Mo2—N1	89.91 (9)	Mo1—O1—Mo4	151.43 (11)
O4—Mo2—N1	79.20 (8)	Mo1—O2—Mo4iv	158.03 (11)
O9ii—Mo2—N1	77.22 (7)	Mo2—O4—Mo1	145.44 (11)

<b>Table S4.</b> continued			
O8—Mo2—N1	75.80 (7)	Mo2—O6—Mo1i	173.10 (11)
O10—Mo3—O8	104.49 (10)	Mo3—O8—Mo2	154.95 (11)
O10—Mo3—O9	101.65 (9)	Mo3—O9—Mo2ii	151.10 (11)
O8—Mo3—O9	99.42 (8)	Mo4—O11—Mo3	168.74 (11)
O10—Mo3—O11	93.04 (9)	Mo4—O13—Mo3iii	143.92 (10)

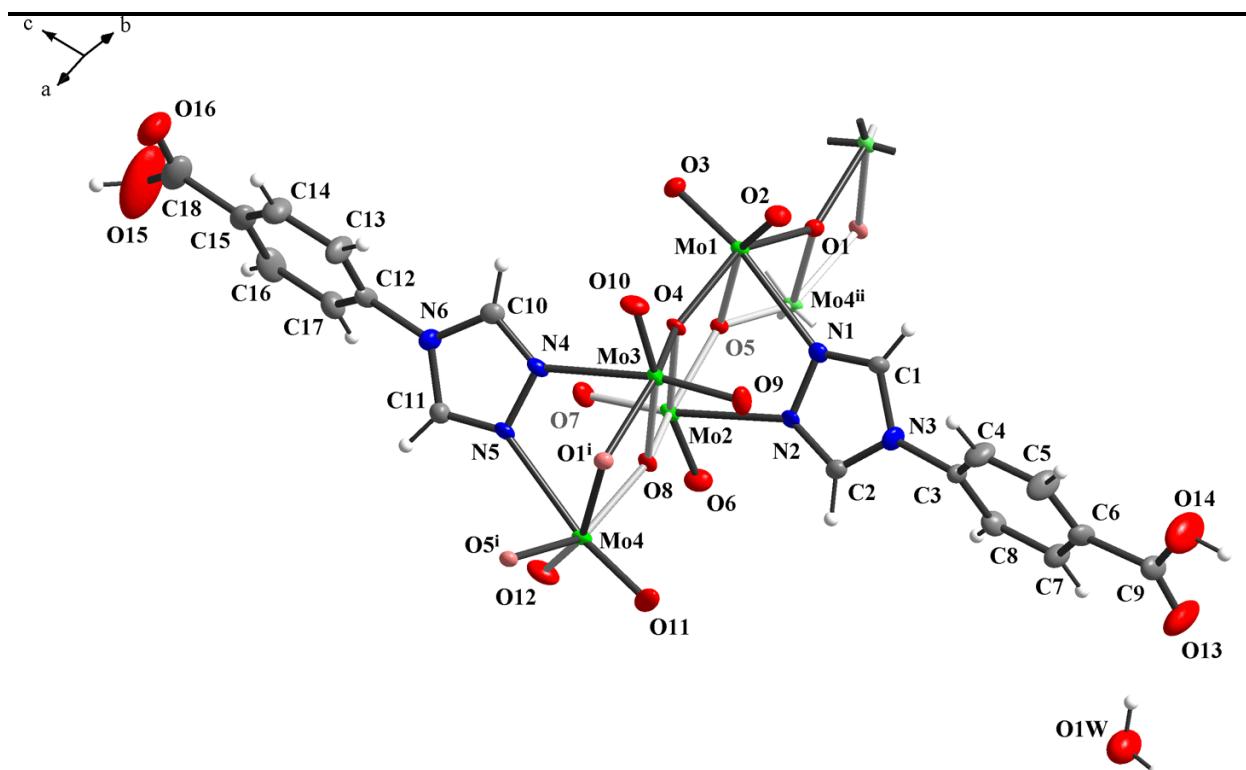
**Table S5.** Hydrogen bonding scheme in the crystal structure of **2a** ( $\text{\AA}$ ,  $^\circ$ ).<sup>S1, S2</sup>

D-H···A	H···A	D···A	D-H···A
O(14)-H(1O) ..O(4)vii	1.86	2.7080	177
O(16)-H(2O) ..O(13)v	1.86	2.7058	174
C(4)-H(4) ..O(17)viii	2.45	3.3726	168
C(6)-H(6) ..O(12)	2.50	3.3862	157
C(10)-H(10) ..O(15)v	2.40	3.1214	133
C(13)-H(13) ..O(15)vi	2.41	3.3333	168
C(15)-H(15) ..O(3)iv	2.49	3.3709	156

symmetry codes: (i)  $-x+1, y, -z$ ; (ii)  $-x, y, -z$ ; (iii)  $-x, y, -z+1$ ; (iv)  $-x+1, y, -z+1$ ; (v)  $x, y+1, z$ ; (vi)  $-x, y+1, -z$ ; (vii)  $x, y-1, z$ ; (viii)  $x, y-1, z-1$ .



**Figure S4.** Illustration of the hydrogen-bonding interactions in the crystal structure of  $[Mo_4O_{12}(trC_6H_4CO_2H)_2]\cdot 0.5H_2O$  (**2a**). Symmetry codes: (i)  $-x+1, y, -z$ ; (ii)  $-x, y, -z$ ; (iii)  $-x, y, -z+1$ ; (iv)  $-x+1, y, -z+1$ ; (v)  $x, y+1, z$ ; (vi)  $-x, y+1, -z$ ; (vii)  $x, y-1, z$ ; (viii)  $x, y-1, z-1$ .



**Figure S5.** Crystal structure and labeling scheme for  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot\text{H}_2\text{O}$  (**2b**). Ellipsoids are shown at the 50% probability level. Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $x-1, y, z$ .

**Table S6.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **2b**.

$[\text{Mo}_2\text{O}_6(\text{trPhCO}_2\text{H})]\cdot0.5\text{H}_2\text{O}$  (**2b**), symmetry codes: (i)  $x+1, y, z$ ; (ii)  $x-1, y, z$ .

Mo1—O3	1.689 (3)	Mo3—O9	1.699 (3)
Mo1—O2	1.694 (3)	Mo3—O4	1.960 (3)
Mo1—O1	1.963 (3)	Mo3—O1i	1.969 (3)
Mo1—O4	1.965 (3)	Mo3—O8	2.285 (3)
Mo1—O5	2.269 (3)	Mo3—N4	2.345 (4)
Mo1—N1	2.410 (4)	Mo4—O12	1.689 (3)
Mo2—O6	1.692 (3)	Mo4—O11	1.699 (3)
Mo2—O7	1.696 (3)	Mo4—O5i	1.952 (3)
Mo2—O8	1.960 (3)	Mo4—O8	1.956 (3)
Mo2—O5	1.969 (3)	Mo4—O1i	2.271 (3)
Mo2—O4	2.267 (3)	Mo4—N5	2.432 (4)
Mo2—N2	2.395 (4)	O1—Mo4ii	2.271 (3)

**Table S6.** continued

Mo3—O10	1.690 (3)	O5—Mo4ii	1.952 (3)
		O1—Mo3ii	1.969 (3)
O3—Mo1—O2	105.10 (16)	O10—Mo3—O8	160.76 (14)
O3—Mo1—O1	100.88 (15)	O9—Mo3—O8	94.90 (15)
O2—Mo1—O1	102.97 (16)	O4—Mo3—O8	72.75 (11)
O3—Mo1—O4	98.57 (15)	O1i—Mo3—O8	73.19 (12)
O2—Mo1—O4	102.72 (15)	O10—Mo3—N4	87.39 (15)
O1—Mo1—O4	142.25 (12)	O9—Mo3—N4	167.95 (16)
O3—Mo1—O5	96.20 (13)	O4—Mo3—N4	79.45 (13)
O2—Mo1—O5	158.69 (13)	O1i—Mo3—N4	75.55 (13)
O1—Mo1—O5	73.08 (12)	O8—Mo3—N4	73.56 (12)
O4—Mo1—O5	72.90 (13)	O12—Mo4—O11	103.61 (18)
O3—Mo1—N1	168.95 (15)	O12—Mo4—O5i	102.34 (16)
O2—Mo1—N1	84.98 (14)	O11—Mo4—O5i	100.65 (15)
O1—Mo1—N1	80.84 (13)	O12—Mo4—O8	103.65 (16)
O4—Mo1—N1	74.37 (13)	O11—Mo4—O8	97.07 (15)
O5—Mo1—N1	73.74 (11)	O5i—Mo4—O8	143.92 (12)
O6—Mo2—O7	103.93 (17)	O12—Mo4—O1i	159.84 (15)
O6—Mo2—O8	103.61 (15)	O11—Mo4—O1i	96.55 (15)
O7—Mo2—O8	99.42 (15)	O5i—Mo4—O1i	73.21 (12)
O6—Mo2—O5	102.45 (16)	O8—Mo4—O1i	73.74 (13)
O7—Mo2—O5	99.01 (15)	O12—Mo4—N5	86.57 (15)
O8—Mo2—O5	143.19 (12)	O11—Mo4—N5	168.58 (16)
O6—Mo2—O4	157.91 (15)	O5i—Mo4—N5	81.87 (13)
O7—Mo2—O4	98.14 (14)	O8—Mo4—N5	75.19 (13)
O8—Mo2—O4	73.17 (12)	O1i—Mo4—N5	73.39 (12)
O5—Mo2—O4	72.87 (12)	Mo1—O1—Mo3ii	139.35 (16)
O6—Mo2—N2	84.71 (16)	Mo1—O1—Mo4ii	106.62 (14)

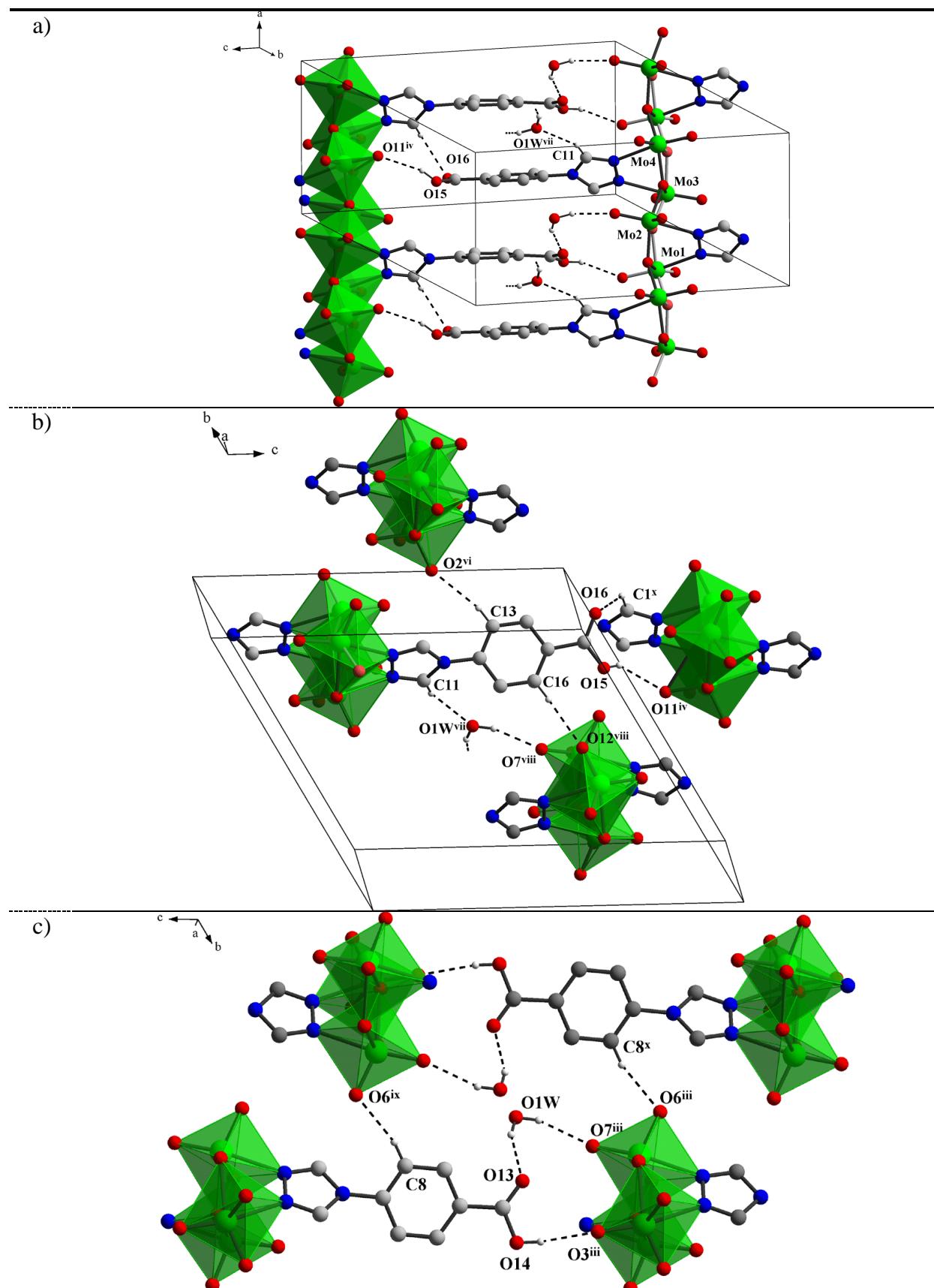
**Table S6.** continued

O7—Mo2—N2	171.05 (16)	Mo3ii—O1—Mo4ii	105.93 (14)
O8—Mo2—N2	80.47 (13)	Mo3—O4—Mo1	138.00 (16)
O5—Mo2—N2	76.53 (13)	Mo3—O4—Mo2	107.36 (13)
O4—Mo2—N2	73.20 (12)	Mo1—O4—Mo2	106.57 (14)
O10—Mo3—O9	104.27 (17)	Mo4ii—O5—Mo2	138.18 (16)
O10—Mo3—O4	101.60 (15)	Mo4ii—O5—Mo1	107.08 (13)
O9—Mo3—O4	100.76 (15)	Mo2—O5—Mo1	106.33 (14)
O10—Mo3—O1i	105.12 (16)	Mo4—O8—Mo2	139.16 (17)
O9—Mo3—O1i	98.08 (15)	Mo4—O8—Mo3	105.88 (14)
O4—Mo3—O1i	142.16 (12)	Mo2—O8—Mo3	106.70 (13)

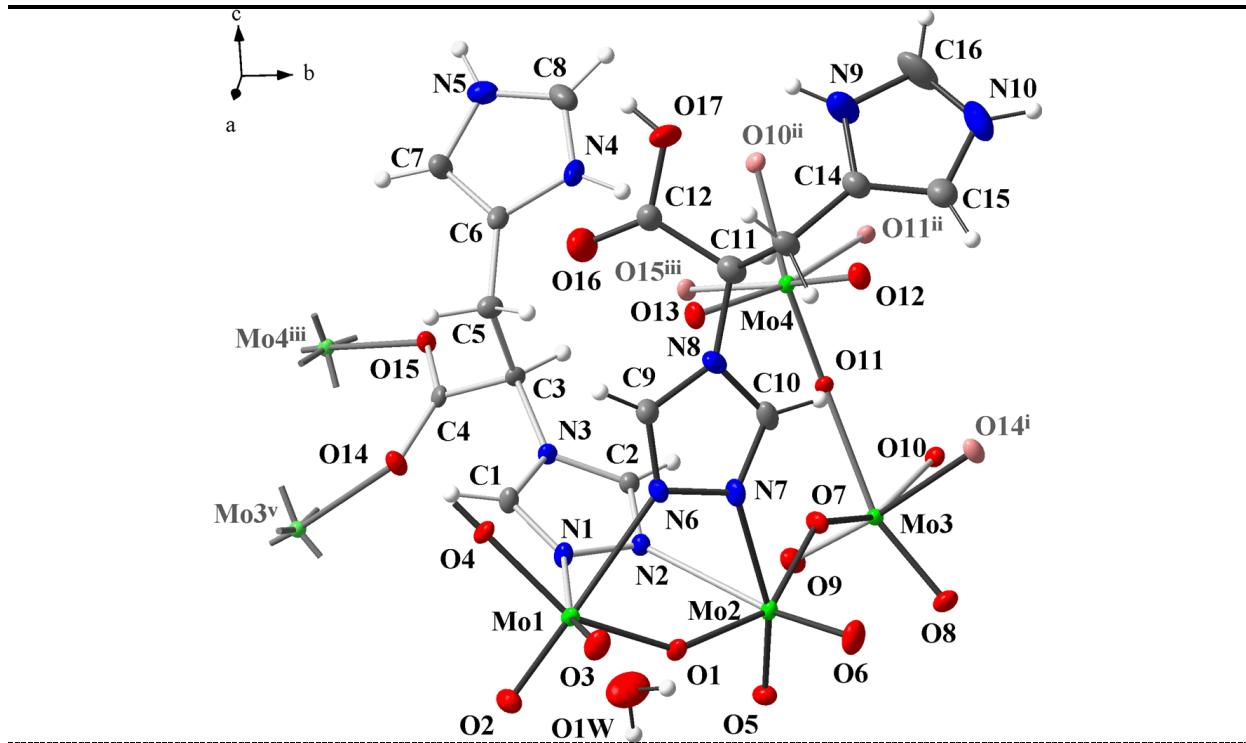
**Table S7.** Hydrogen bonding scheme in the crystal structure of **2b** (Å, °).<sup>S1, S2</sup>

D-H···A	H···A	D···A	D-H···A
O1W-H1WA ..O7iii	2.12	2.9202	156
O1W-H1WB ..O13	2.01	2.8083	156
O14-H14A ..O3iii	2.17	2.9503	153
O15-H15A ..O11iv	2.50	3.1142	130
C1-H1 ..O16v	2.43	3.0487	123
C10-H10 ..O10vi	2.48	3.3376	151
C11-H11 ..O1Wvii	2.43	3.2998	154
C13-H13 ..O2vi	2.40	3.3248	166
C16-H16 ..O12viii	2.43	3.3271	161
C8-H8 ..O6ix	2.37	3.2490	155

symmetry codes: (i)  $x+1, y, z$ ; (ii)  $x-1, y, z$ ; (iii)  $x, y, z-1$ , (iv)  $x, y, z+1$ , (v)  $x-1, y, z-1$ , (vi)  $-x+1, -y+2, -z+1$ , (vii)  $-x+1, -y+1, -z$ , (viii)  $-x+1, -y+1, -z+1$ , (ix)  $-x, -y+1, -z$ .



**Figure S6.** Illustration of the hydrogen-bonding interactions in the crystal structure of  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot\text{H}_2\text{O}$  (**2b**). Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $x-1, y, z$ ; (iii)  $x, y, z-1$ ; (iv)  $x, y, z+1$ ; (v)  $x-1, y, z-1$ ; (vi)  $-x+1, -y+2, -z+1$ ; (vii)  $-x+1, -y+1, -z$ ; (viii)  $-x+1, -y+1, -z+1$ ; (ix)  $-x, -y+1, -z$ ; (x)  $x+1, y, z+1$ .



**Figure S7.** Crystal structure and labeling scheme for  $[Mo_8O_{25}(trhis-2H)_2(trhis-H)_2] \cdot 2H_2O$  (**3**). Ellipsoids are shown at the 50% probability level. Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $x, y-1, z$ .

**Table S8.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **3**.

$[Mo_8O_{25}(trhis-2H)_2(trhis-H)_2] \cdot 2H_2O$  (**3**), symmetry codes: (i)  $x, y+1, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $x, y-1, z$ .

Mo1—O2	1.7090 (18)	Mo3—O9	1.7098 (18)
Mo1—O3	1.7113 (17)	Mo3—O8	1.7113 (16)
Mo1—O4	1.9092 (2)	Mo3—O7	1.9456 (16)
Mo1—O1	1.9213 (16)	Mo3—O10	1.9555 (15)
Mo1—N6	2.3956 (19)	Mo3—O11	2.1928 (15)
Mo1—N1	2.3963 (19)	Mo3—O14i	2.2798 (17)
Mo2—O6	1.7010 (18)	Mo4—O12	1.7116 (17)
Mo2—O5	1.7590 (16)	Mo4—O13	1.7204 (16)
Mo2—O7	1.8658 (15)	Mo4—O11	1.8975 (15)
Mo2—O1	1.9029 (16)	Mo4—O10ii	1.9604 (15)
Mo2—N7	2.309 (2)	Mo4—O11ii	2.1852 (15)
Mo2—N2	2.431 (2)	Mo4—O15iii	2.4122 (16)

<b>Table S8.</b> continued			
O2—Mo1—O3	104.15 (9)	O9—Mo3—O10	98.62 (8)
O2—Mo1—O4	101.08 (6)	O8—Mo3—O10	96.10 (7)
O3—Mo1—O4	100.45 (6)	O7—Mo3—O10	153.65 (6)
O2—Mo1—O1	97.94 (8)	O9—Mo3—O11	95.46 (7)
O3—Mo1—O1	97.22 (8)	O8—Mo3—O11	160.83 (7)
O4—Mo1—O1	149.90 (4)	O7—Mo3—O11	83.28 (6)
O2—Mo1—N6	163.23 (8)	O10—Mo3—O11	73.79 (6)
O3—Mo1—N6	91.91 (8)	O9—Mo3—O14i	174.03 (8)
O4—Mo1—N6	80.33 (5)	O8—Mo3—O14i	82.68 (7)
O1—Mo1—N6	74.89 (7)	O7—Mo3—O14i	79.27 (7)
O2—Mo1—N1	89.23 (8)	O10—Mo3—O14i	84.08 (6)
O3—Mo1—N1	165.67 (8)	O11—Mo3—O14i	80.12 (6)
O4—Mo1—N1	81.62 (5)	O12—Mo4—O13	102.26 (8)
O1—Mo1—N1	75.50 (7)	O12—Mo4—O11	102.22 (8)
N6—Mo1—N1	74.37 (7)	O13—Mo4—O11	104.52 (7)
O6—Mo2—N7	92.18 (8)	O12—Mo4—O10ii	99.71 (7)
O5—Mo2—N7	163.69 (8)	O13—Mo4—O10ii	96.54 (7)
O7—Mo2—N7	80.20 (7)	O11—Mo4—O10ii	145.37 (6)
O1—Mo2—N7	76.08 (7)	O12—Mo4—O11ii	99.05 (7)
O6—Mo2—N2	164.70 (8)	O13—Mo4—O11ii	157.86 (7)
O5—Mo2—N2	91.49 (7)	O11—Mo4—O11ii	76.45 (6)
O7—Mo2—N2	79.13 (7)	O10ii—Mo4—O11ii	73.87 (6)
O1—Mo2—N2	74.59 (7)	O12—Mo4—O15iii	177.51 (6)
N7—Mo2—N2	72.73 (7)	O13—Mo4—O15iii	79.47 (7)
O7—Mo2—O1	148.73 (7)	O11—Mo4—O15iii	78.97 (6)
O6—Mo2—O5	103.34 (9)	O10ii—Mo4—O15iii	78.25 (6)
O6—Mo2—O7	101.24 (8)	O11ii—Mo4—O15iii	79.05 (6)
O5—Mo2—O7	101.27 (7)	Mo2—O1—Mo1	144.26 (8)
O6—Mo2—O1	99.75 (8)	Mo1—O4—Mo1iv	180.0

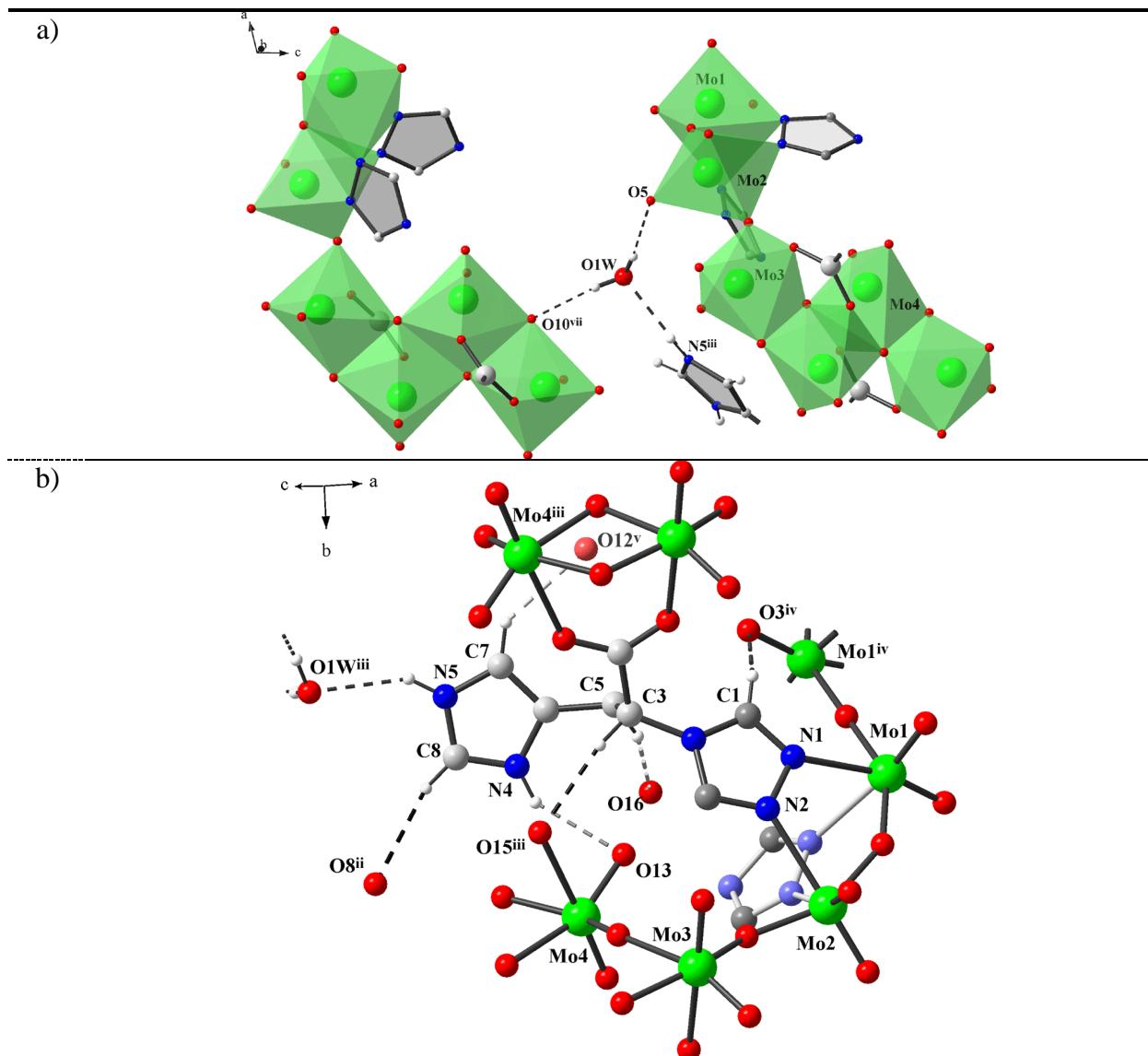
**Table S8.** continued

O5—Mo2—O1	96.10 (7)	Mo2—O7—Mo3	135.12 (9)
O9—Mo3—O8	102.25 (8)	Mo3—O10—Mo4ii	114.62 (8)
O9—Mo3—O7	96.29 (8)	Mo4—O11—Mo4ii	103.55 (6)
O8—Mo3—O7	101.82 (8)	Mo4—O11—Mo3	151.26 (8)
		Mo4ii—O11—Mo3	97.66 (6)

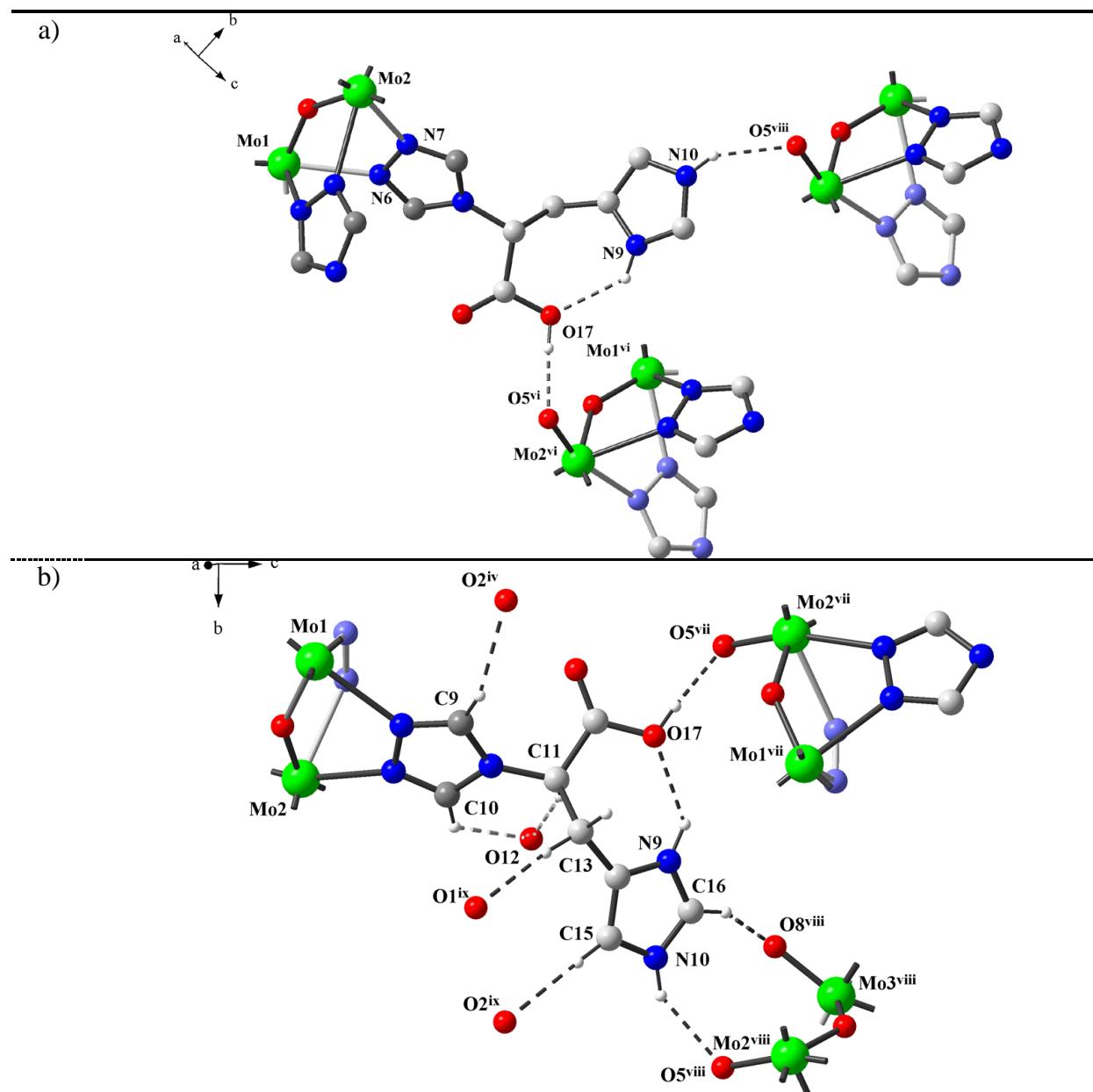
**Table S9.** Hydrogen bonding scheme in the crystal structure of **3** (Å, °).<sup>S1, S2</sup>

D-H…A	H…A	D…A	D-H…A
O1W-H1W ..O5	2.19	3.0378	175
O1W-H2W ..O10vii	2.03	2.8732	173
N4-H4 ..O10ii	2.17	2.8318	132
N4-H4 ..O13	2.31	3.0418	142
N5-H5 ..O1Wiii	2.15	2.9015	144
N9-H9 ..O17	2.13	2.7995	133
N10-H10 ..O5viii	2.08	2.8466	146
O17-H17A ..O5vi	1.80	2.6511	176
C1-H1 ..O3iv	2.28	3.0601	140
C3-H3 ..O15iii	2.28	3.2390	164
C5-H5B ..O16	2.55	3.4145	147
C7-H7 ..O12v	2.34	3.1209	140
C8-H8 ..O8ii	2.43	3.2597	147
C9-H9A ..O2iv	2.25	3.1121	152
C10-H10A ..O12	2.53	3.2344	132
C11-H11 ..O12	2.37	3.3164	160
C13-H13B ..O1ix	2.36	3.3259	168
C15-H15 ..O2ix	2.48	3.4015	168
C16-H16 ..O8viii	2.14	3.0030	152

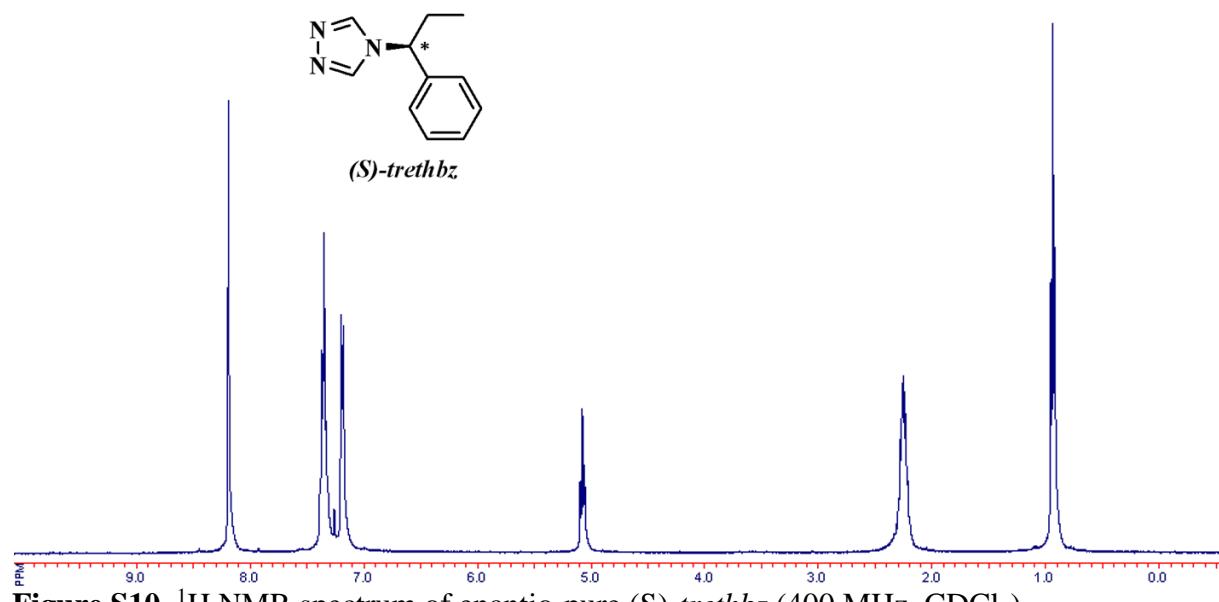
symmetry codes: : (i)  $x, y+1, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $x, y-1, z$ ; (vi)  $x, -y+1/2, z+1/2$ ; (vii)  $-x, y-1/2, -z+1/2$ ; (viii)  $x, -y+3/2, z+1/2$ ; (ix)  $-x+1, -y+1, -z+1$ .



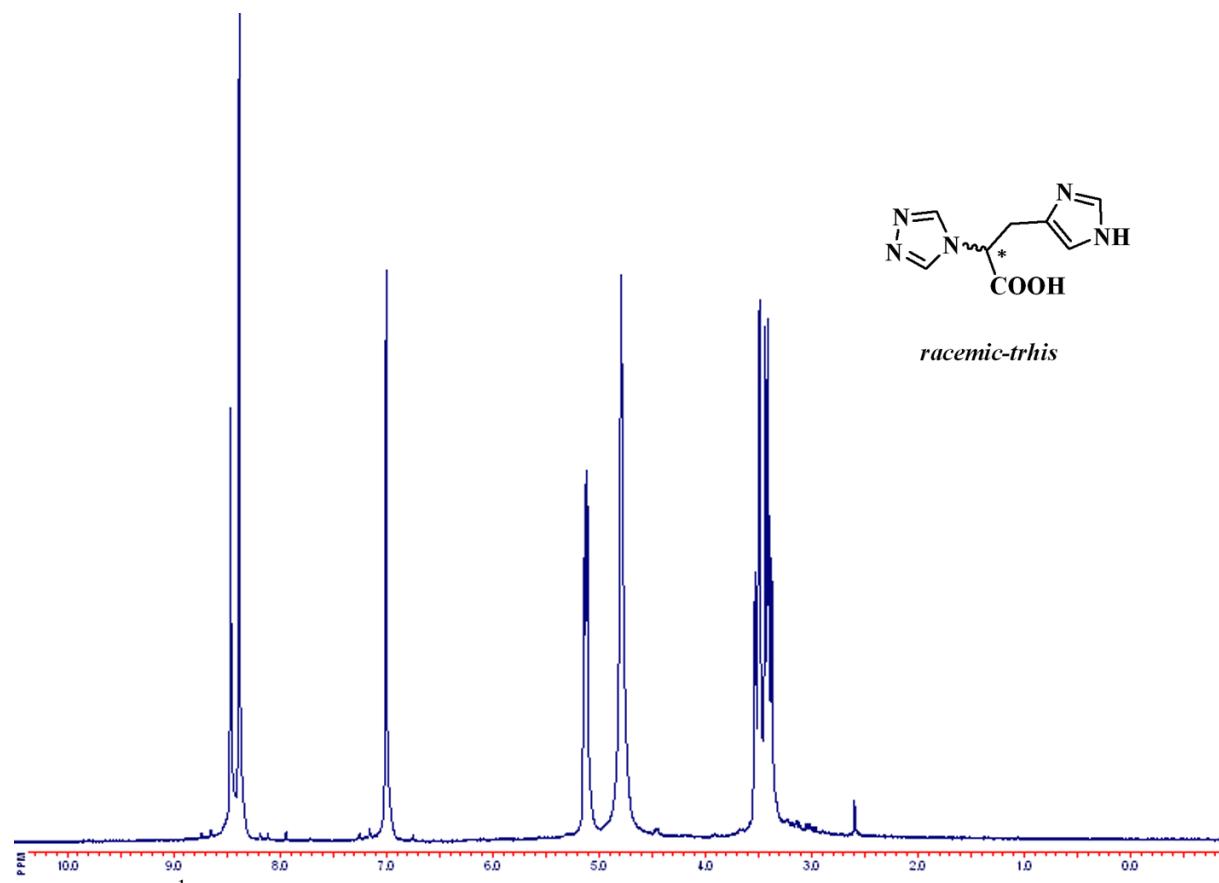
**Figure S8.** Illustration of the hydrogen-bonding interactions in the crystal structure of  $[\text{Mo}_8\text{O}_{25}(\text{trhis}-2\text{H})_2(\text{trhis}-\text{H})_2]\cdot 2\text{H}_2\text{O}$  (**3**). Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $x, y-1, z$ ; (vi)  $x, -y+1/2, z+1/2$ ; (vii)  $-x, y-1/2, -z+1/2$ ; (viii)  $x, -y+3/2, z+1/2$ ; (ix)  $-x+1, -y+1, -z+1$ .



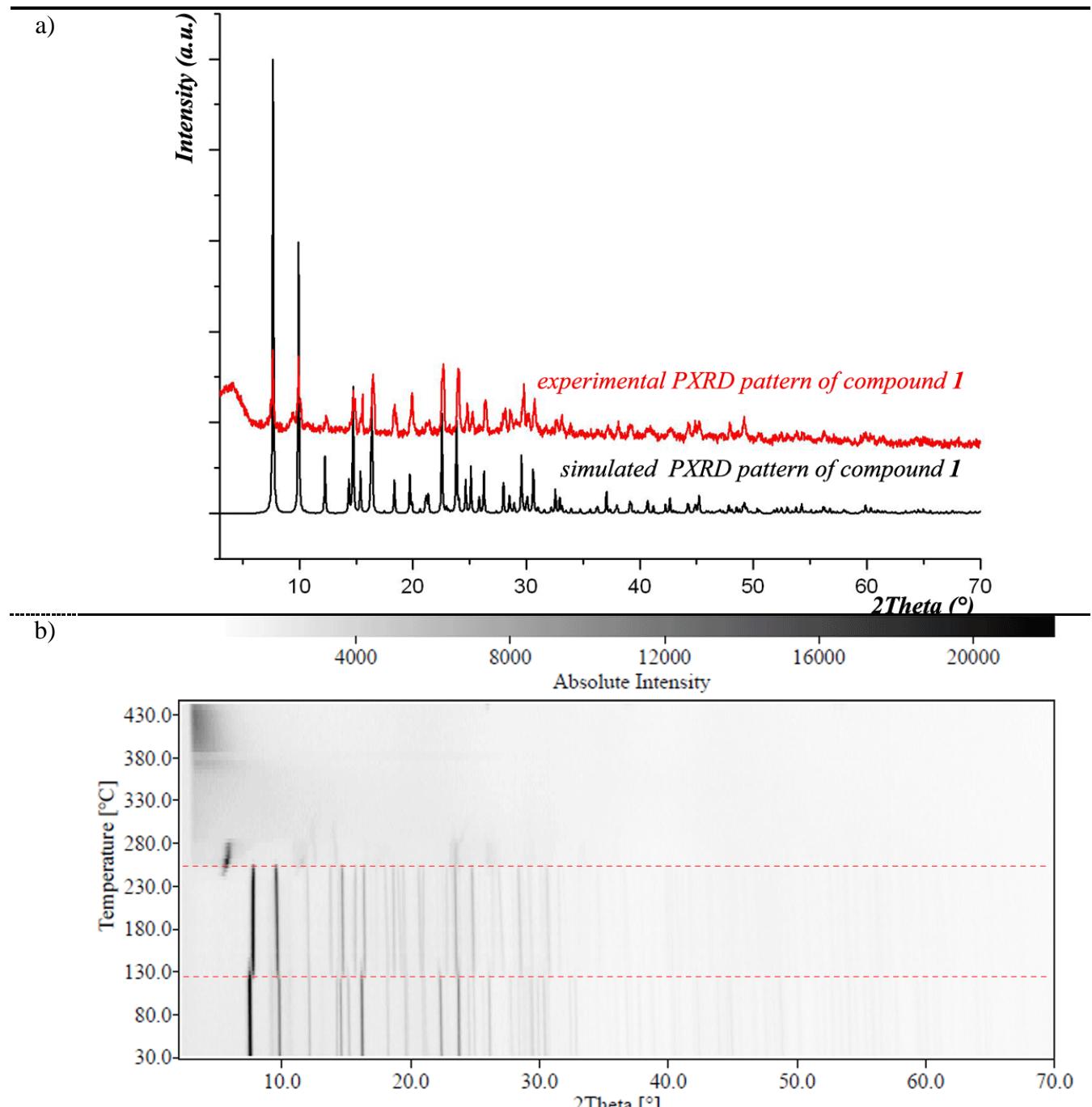
**Figure S9.** Illustration of the hydrogen-bonding interactions in the crystal structure of  $[Mo_8O_{25}(trhis-2H)_2(trhis-H)_2] \cdot 2H_2O$  (**3**). Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $x, y-1, z$ ; (vi)  $x, -y+1/2, z+1/2$ ; (vii)  $-x, y-1/2, -z+1/2$ ; (viii)  $x, -y+3/2, z+1/2$ ; (ix)  $-x+1, -y+1, -z+1$ .



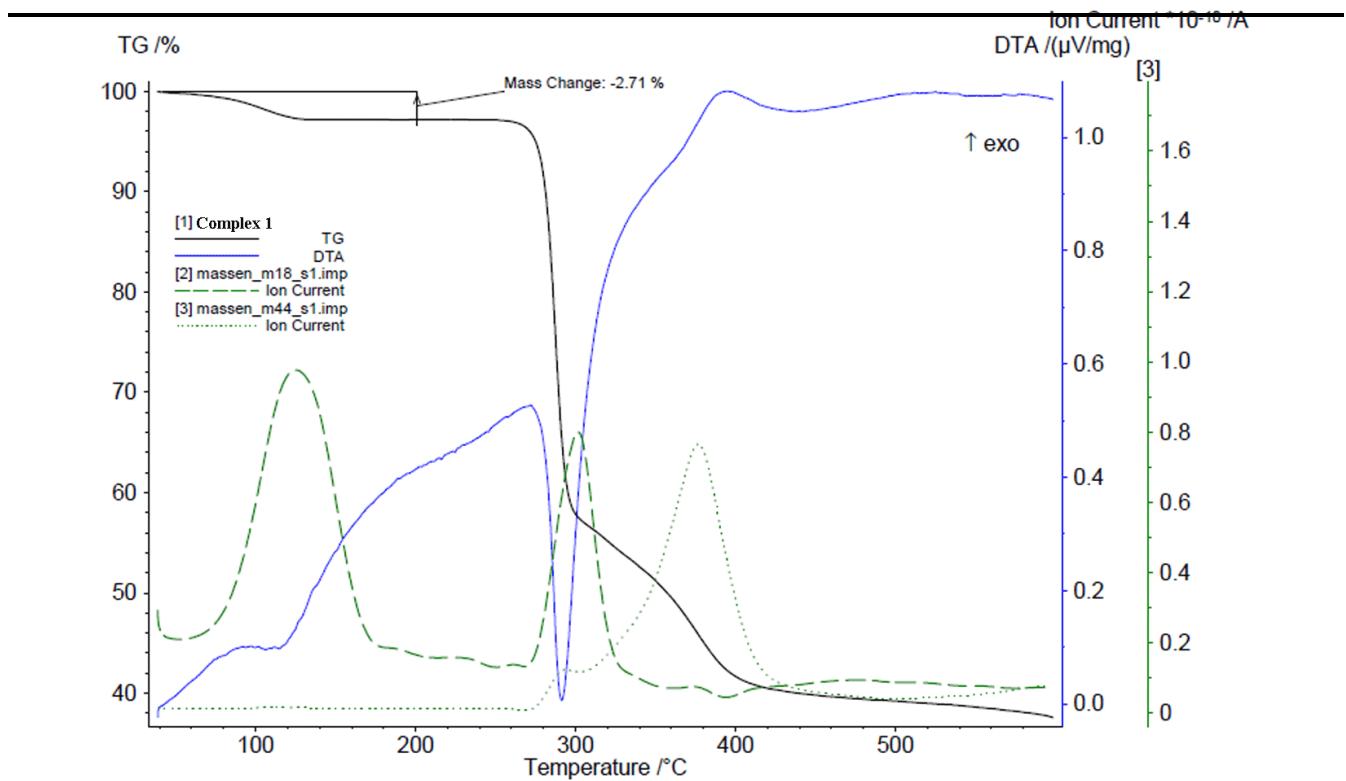
**Figure S10.**  $^1\text{H}$  NMR spectrum of enantio-pure (*S*)-*trethbz* (400 MHz,  $\text{CDCl}_3$ ).



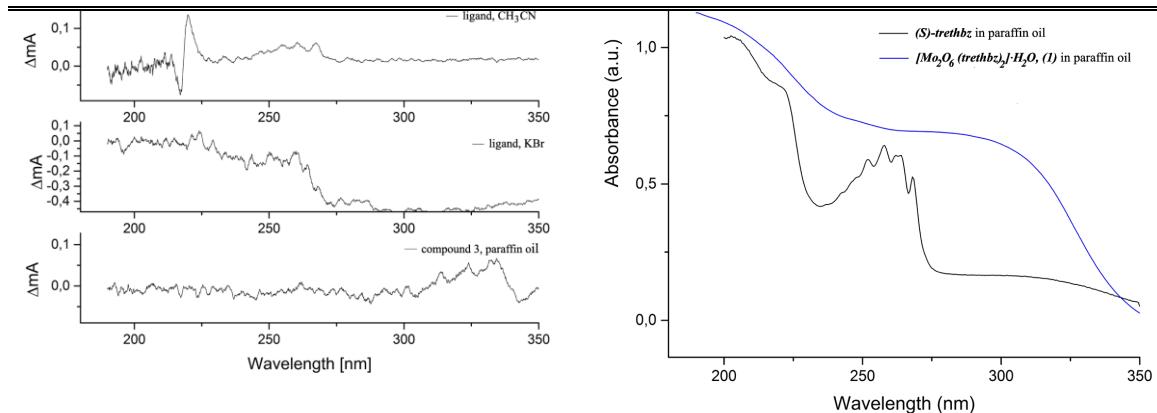
**Figure S11.**  $^1\text{H}$  NMR spectrum of racemic-*trhis* (400 MHz,  $\text{dmso-d}_6$ ).



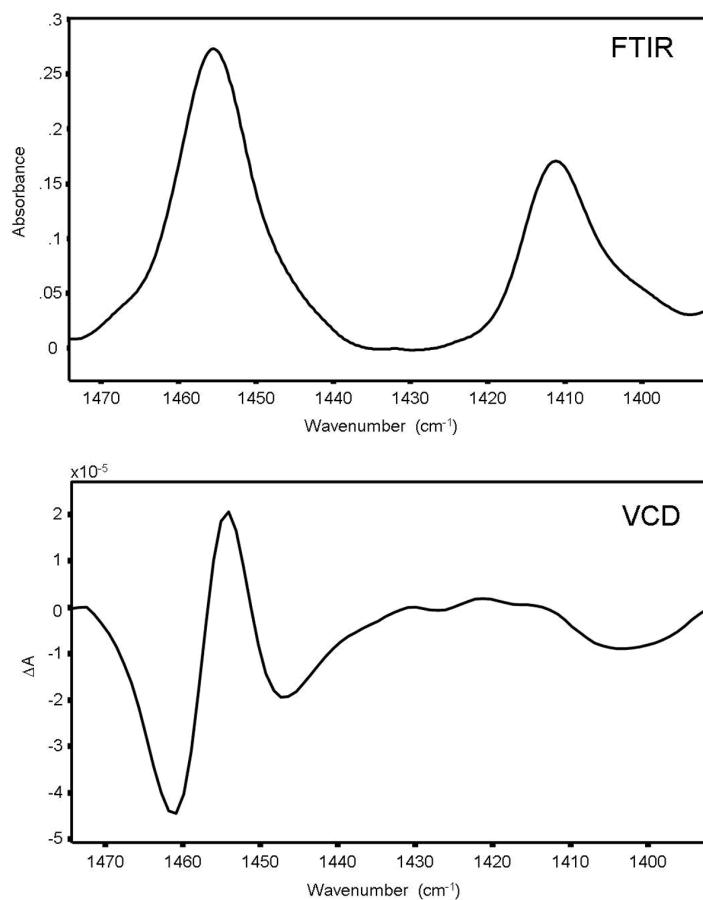
**Figure S12.** a) The PXRD patterns (observed and simulated) and b) 2D thermo-PXRD patterns (Cu-K $\alpha$  radiation,  $2\theta = 5$ – $70^\circ$ ) for compound  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**).



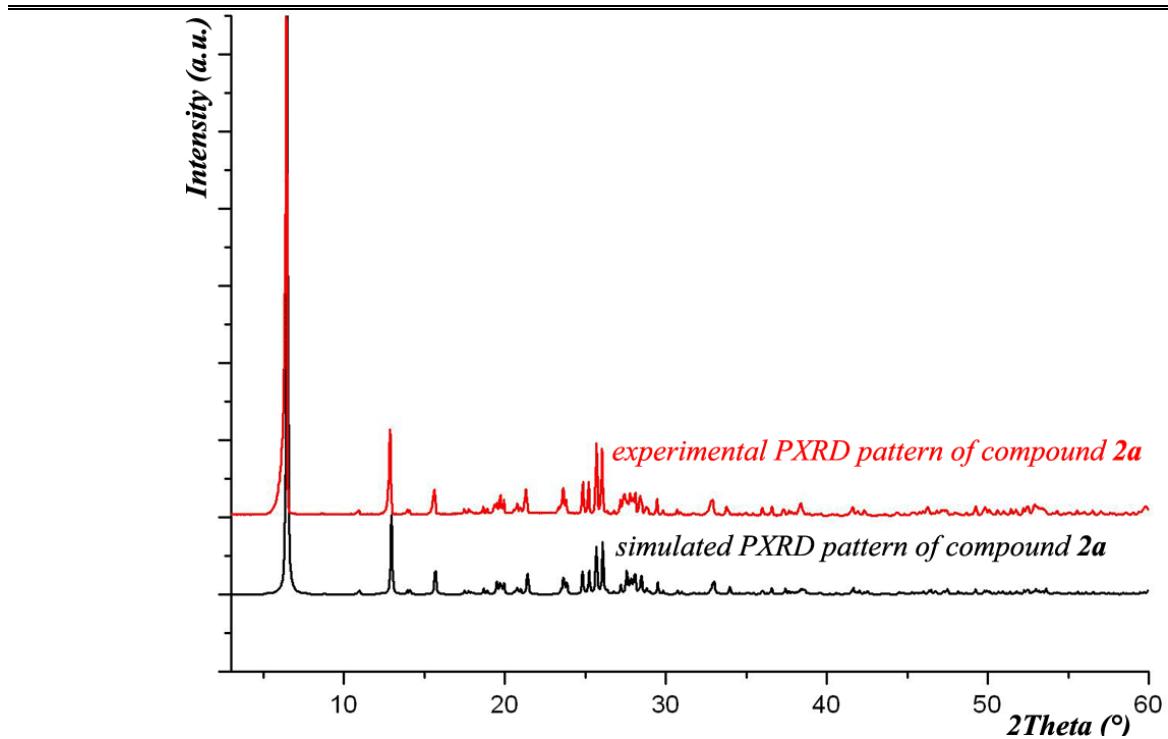
**Figure S13.** DTA/TG-MS data for compound  $[Mo_2O_6(trethbz)_2]\cdot H_2O$  (1).



**Figure S14.** a). ECD spectra recorded for (S)-trethbz in MeCN solution or KBr pellet and for compound  $[Mo_2O_6(trethbz)_2]\cdot H_2O$  (1) dispersed in paraffin oil. b) Absorption spectra of trethbz and  $[Mo_2O_6(trethbz)_2]\cdot H_2O$  (1) in paraffin oil.



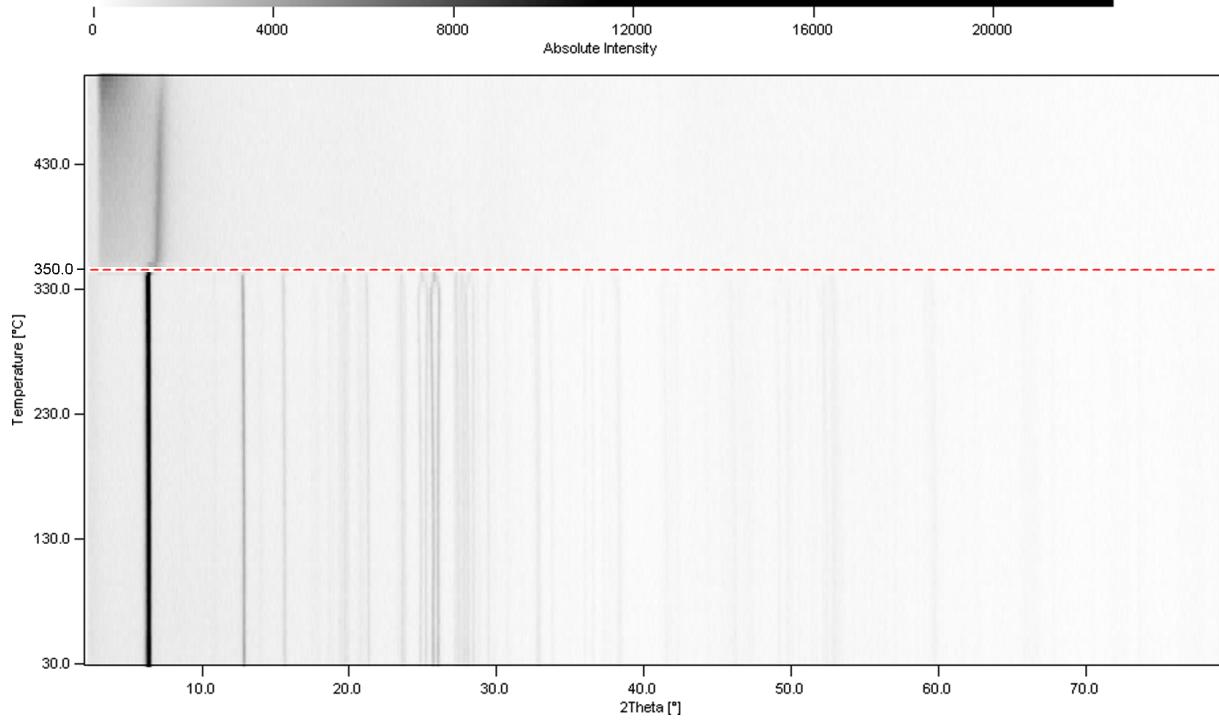
**Figure S15.** FTIR and VCD spectra of  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**) in KBr.



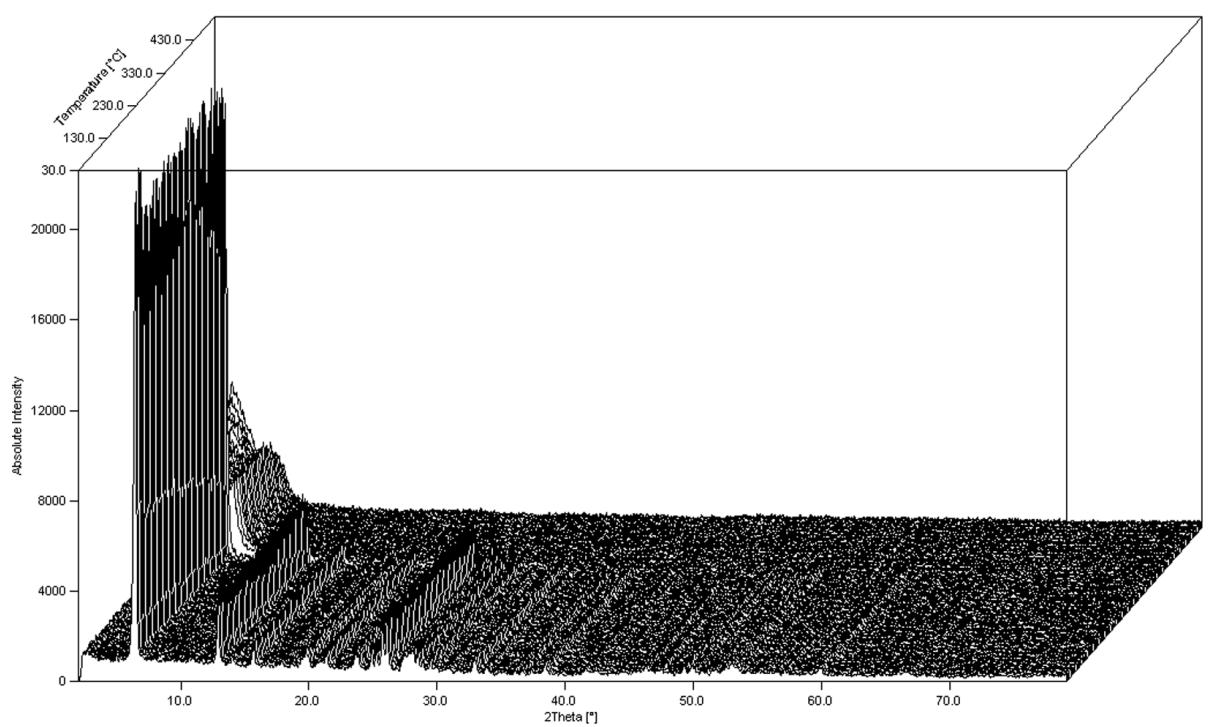
**Figure S16.** The observed and simulated PXRD patterns of compound  $[\text{Mo}_4\text{O}_{12}(\text{trC}_6\text{H}_4\text{CO}_2\text{H})_2]\cdot 0.5\text{H}_2\text{O}$  (**2a**) ( $2\theta = 3\text{--}60^\circ$ ).

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a)

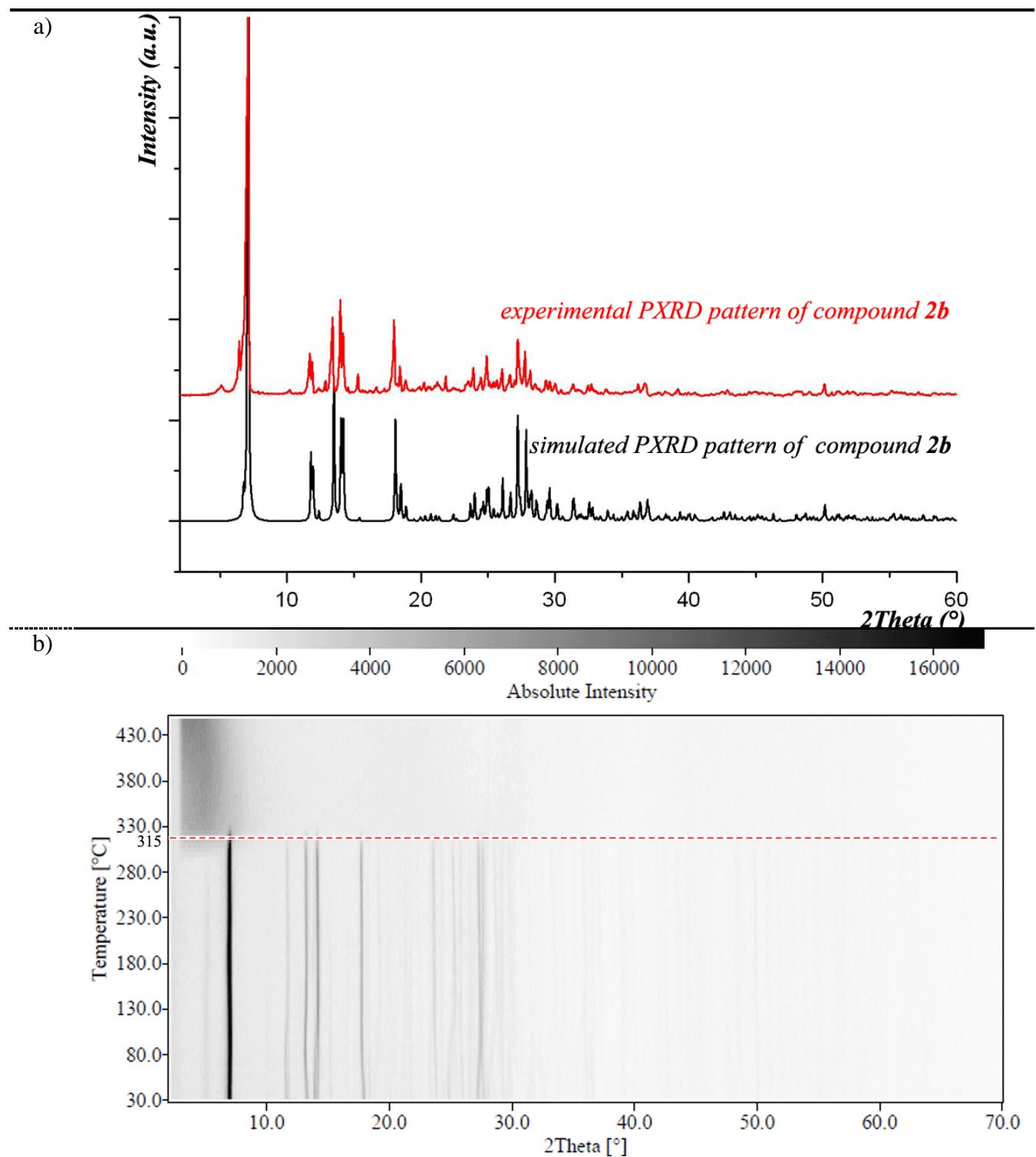


b)

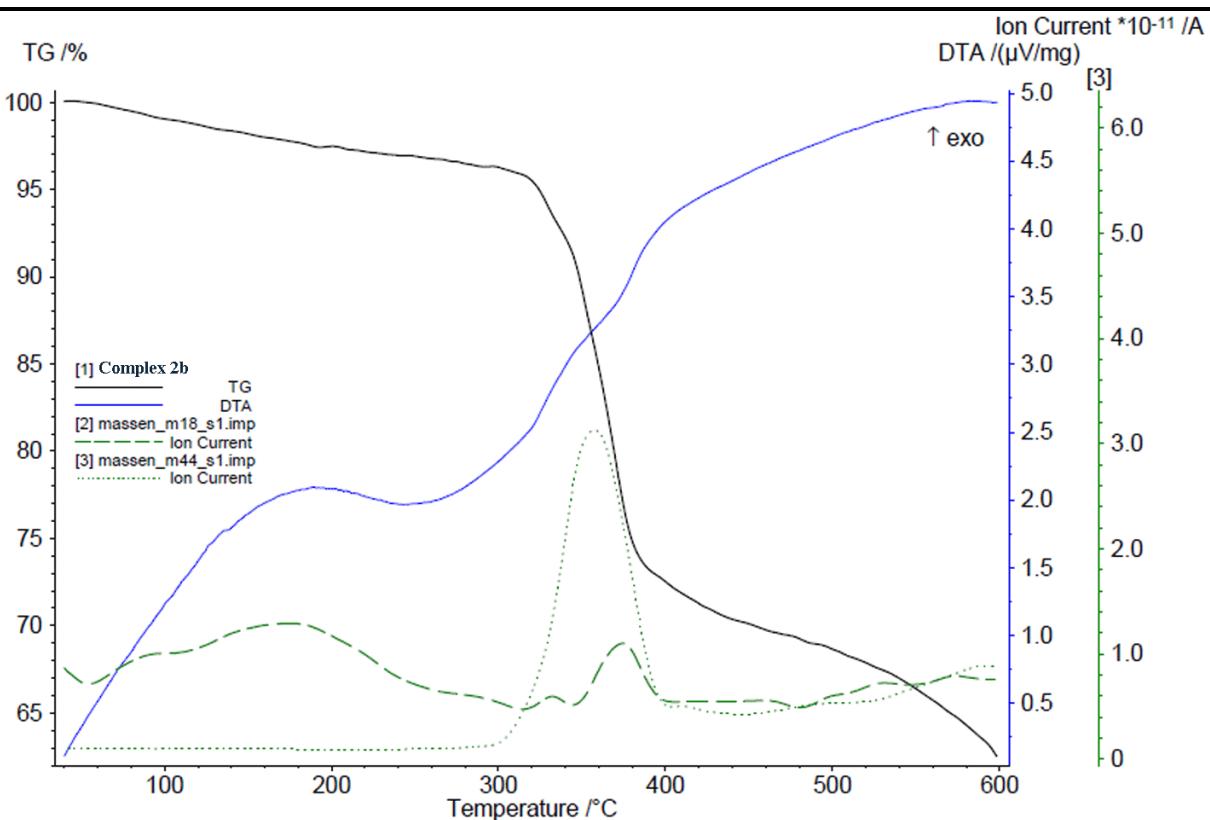


**Figure S17.** 2D/3D thermo-PXRD patterns (Cu-K $\alpha$ 1 radiation,  $2\theta = 5$ – $80^\circ$ ) for compound  $[\text{Mo}_4\text{O}_{12}(\text{trC}_6\text{H}_4\text{CO}_2\text{H})_2] \cdot 0.5\text{H}_2\text{O}$  (**2a**).

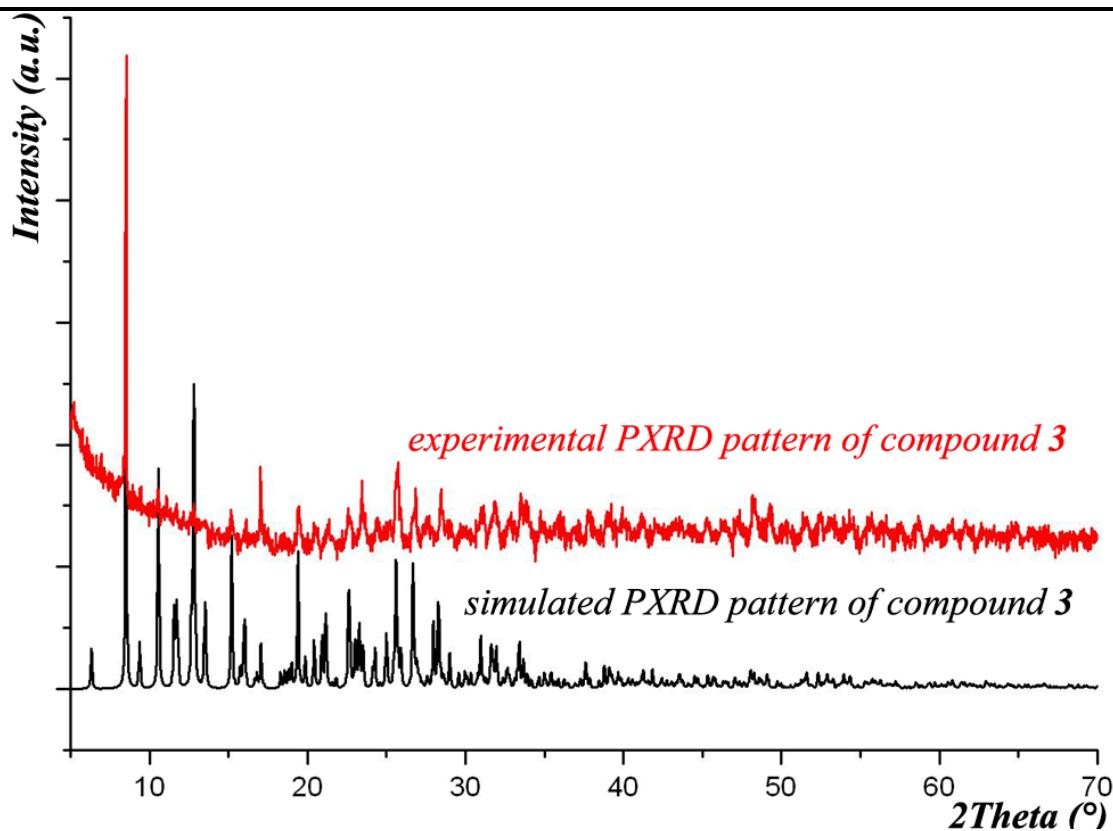
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**Figure S18.** a) The PXRD patterns (observed and simulated) and b) 2D thermo-PXRD patterns (Cu-K $\alpha$ 1 radiation,  $2\theta = 5$ – $70^\circ$ ) for compound  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot\text{H}_2\text{O}$  (**2b**).



**Figure S19.** DTA/TG-MS data for  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot\text{H}_2\text{O}$  (**2b**).



**Figure S20.** The observed and simulated PXRD patterns of compound  $[\text{Mo}_8\text{O}_{25}(\text{trhis-2H})_2(\text{trhis-H})_2]\cdot 2\text{H}_2\text{O}$  (**3**).

**Table S10.** Comparison of the catalytic results of compounds **1**, **2a** and **3\*** to literature data for molybdenum(VI) oxide hybrid polymers, tested as catalysts for the reaction of *cis*-cyclooctene (Cy) with TBHP.

Compound <sup>a</sup>	Reaction conditions <sup>b</sup>				Conv. <sup>c</sup> (%)	Sel. <sup>d</sup> (%)	Ref <sup>e</sup>
	Mo:Cy:TBHP	T (°C)	Solv.	t (h)			
<b>1</b>	1:100:153	55	THF	6/24	77/97	100	-
<b>1</b>	1:100:153	70	THF	6/24	98/100	100	-
<b>2a</b>	1:100:153	55	THF	6/24	44/82	100	-
<b>3*</b>	1:100:153	55	THF	6/24	12/47	100	-
[MoO <sub>3</sub> (tr) <sub>0.5</sub> ]	1:100:152	70	CH <sub>3</sub> CN	24	35	100	3g
[Mo <sub>2</sub> O <sub>6</sub> (trpzH)(H <sub>2</sub> O) <sub>2</sub> ]	1:100:153	70	THF	6/24	74/100	100	11b
[MoO <sub>3</sub> (bipy)] <sub>n</sub>	1:100:153	55	DCE	6	95	100	27
[MoO <sub>3</sub> (bipy)] <sub>n</sub>	1:100:153	75	DCE	6	100	100	27
{[MoO <sub>3</sub> (bipy)][MoO <sub>3</sub> (H <sub>2</sub> O)]} <sub>n</sub>	1:100:150	55	DCE	48	62	100	3b
{[MoO <sub>3</sub> (bipy)][MoO <sub>3</sub> (H <sub>2</sub> O)]} <sub>n</sub>	1:100:150	75	hex	24	81	100	3b
{[MoO <sub>3</sub> (bipy)][MoO <sub>3</sub> (H <sub>2</sub> O)]} <sub>n</sub>	1:100:150 <sup>f</sup>	55	-	24	24	100	3b
{[MoO <sub>3</sub> (bipy)][MoO <sub>3</sub> (H <sub>2</sub> O)]} <sub>n</sub>	1:100:153 <sup>f</sup>	70	H <sub>2</sub> O	24	38	100	32
[Mo <sub>2</sub> O <sub>6</sub> (HpypzA)] <sub>n</sub>	1:100:153	55	DCE	24	74	100	3f
[Mo <sub>2</sub> O <sub>6</sub> (HpypzA)] <sub>n</sub>	1:100:153 <sup>f</sup>	55	EtOH	24	16	100	3f
[Mo <sub>2</sub> O <sub>6</sub> (pent-pp)] <sub>n</sub>	1:113:172	55	THF	6	98	100	28
[Mo <sub>3</sub> O <sub>9</sub> (pypz)] <sub>n</sub>	1:100:153	75	THF	6/24	60/100	100	3c
[PiperazinCH <sub>2</sub> {MoO <sub>2</sub> (Salen)}] <sub>n</sub>	1:200:200	75	DCE	12	98	n.a.	S3
[PiperazinCH <sub>2</sub> {MoO <sub>2</sub> (Salen)}] <sub>n</sub>	1:200:200 <sup>g</sup>	75	DCE	12	95	98	S3
[PiperazinCH <sub>2</sub> {MoO <sub>2</sub> (Salophen)}] <sub>n</sub>	1:200:200 <sup>g</sup>	75	DCE	12	89	97	S3
[PiperazinCH <sub>2</sub> {MoO <sub>2</sub> (Salpn)}] <sub>n</sub>	1:200:200 <sup>g</sup>	75	DCE	12	93	97	S3
[MoO <sub>2</sub> (L1)] <sub>n</sub>	1:2000:4000 <sup>f</sup>	80	-	6	72	87	S4
[MoO <sub>2</sub> (L2)] <sub>n</sub>	1:2000:4000 <sup>f</sup>	80	-	6	54	87	S4
[MoO <sub>2</sub> (L3)] <sub>n</sub>	1:2000:4000 <sup>f</sup>	80	-	6	23	73	S4

<sup>a</sup> tr = 1,2,4-triazole; trpzH=4-(3,5-dimethyl-1H-pyrazol-4-yl)-1,2,4-triazole; bipy=2,2'-bipyridine; HpypzA=[3-(pyridinium-2-yl)-1H-pyrazol-1-yl]-acetate; pent-pp=2-(1-pentyl-3-pyrazolyl)pyridine; pypz=2-[3(5)-pyrazolyl]pyridine; Salen=N,N'-bis(salicylidene)ethylenediamine; Salophen=N,N'-phenylene-bis(salicylideneimine); Salpn=N,N'-propylenebis(salicylideneiminato); H2L1=pyridoxal isonicotinic acid hydrazone; H2L2=pyridoxal benzhydrazone; H2L3=pyridoxal 4-hydroxy benzhydrazone. <sup>b</sup> Initial molar ratios of Mo:Cy:TBHP; T = reaction temperature; Solv=co-solvent (TFT=a,a,a-trifluorotoluene, DCE=1,2-dichloroethane, hex=hexane, EtOH=ethanol); reaction time (t); n.a.=data not available/specify. <sup>c</sup> Conversion of *cis*-cyclooctene (Cy). <sup>d</sup> Selectivity to cyclooctene oxide (CyO). <sup>e</sup> Please also see the references in the main text. <sup>f</sup> 70% aq. TBHP was used. <sup>g</sup> 80% TBHP in di-tert-butyl peroxide/water (3:2) was used.

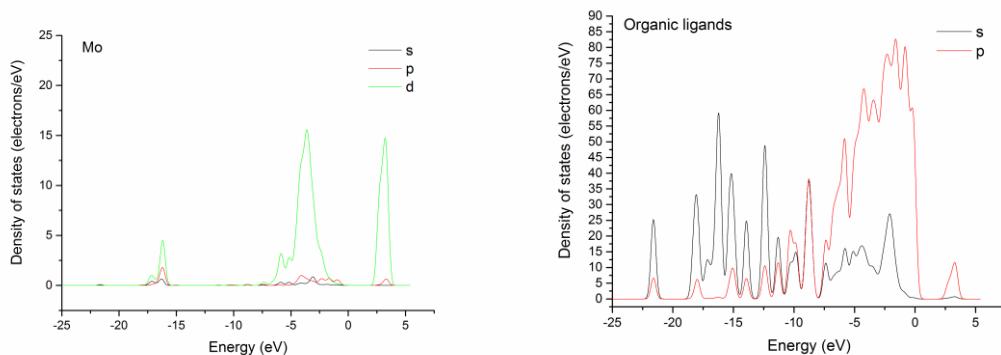
**Table S11.** Comparison of the catalytic results for  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**) to literature data for molybdenum(VI) oxide hybrid polymers, tested as catalysts for the reaction of *cis*-cyclooctene (Cy) with  $\text{H}_2\text{O}_2$ .

Compound <sup>a</sup>	Reaction conditions <sup>b</sup>				Conv. <sup>c</sup> (%)	Sel. <sup>d</sup> (%)	Ref <sup>e</sup>
	Mo:Cy:H <sub>2</sub> O <sub>2</sub>	T (°C)	Solv.	t (h)			
<b>1</b>	1:100:152	55	CH <sub>3</sub> CN	24	77	100	
[MoO <sub>3</sub> (tr) <sub>0.5</sub> ]	1:100:152	70	CH <sub>3</sub> CN	24	98	100	-
[Mo <sub>2</sub> O <sub>6</sub> (trpzH)(H <sub>2</sub> O) <sub>2</sub> ]	1:100:153	70	CH <sub>3</sub> CN	4/24	97/100	100	<sup>11b</sup>
{[MoO <sub>3</sub> (bipy)][MoO <sub>3</sub> (H <sub>2</sub> O)]} <sub>n</sub>	1:100:153	55	-	48	11	100	<sup>3b</sup>
{[MoO <sub>3</sub> (bipy)][MoO <sub>3</sub> (H <sub>2</sub> O)]} <sub>n</sub>	1:100:153	70	CH <sub>3</sub> CN	24	79	100	<sup>29</sup>
[MoO(O <sub>2</sub> )(4,4'-bipy)] <sub>n</sub>	1:33:89	r.t.	DCM	7	~40	100	<sup>30</sup>
[MoO <sub>3</sub> (pdtc)] <sub>n</sub>	1:33:327	r.t.	DCM	7.5	63	100	<sup>S5</sup>

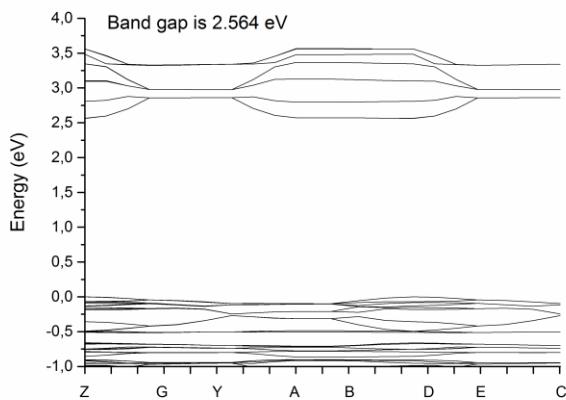
<sup>a</sup> tr = 1,2,4-triazole; trpzH=4-(3,5-dimethyl-1H-pyrazol-4-yl)-1,2,4-triazole; bipy=2,2'-bipyridine; 4,4'-bipy=4,4'-bipyridine; pdtc=pyrrolidinedithiocarbamate. <sup>b</sup> Initial molar ratios of Mo:Cy:H<sub>2</sub>O<sub>2</sub>; T = reaction temperature (r.t.=ambient temperature); Solv=co-solvent (DCM=dichloromethane); reaction time (t). <sup>c</sup> Conversion of *cis*-cyclooctene (Cy). <sup>d</sup> Selectivity to cyclooctene oxide (CyO). <sup>e</sup> please also see the references in the main text.

### Density functional theory calculations

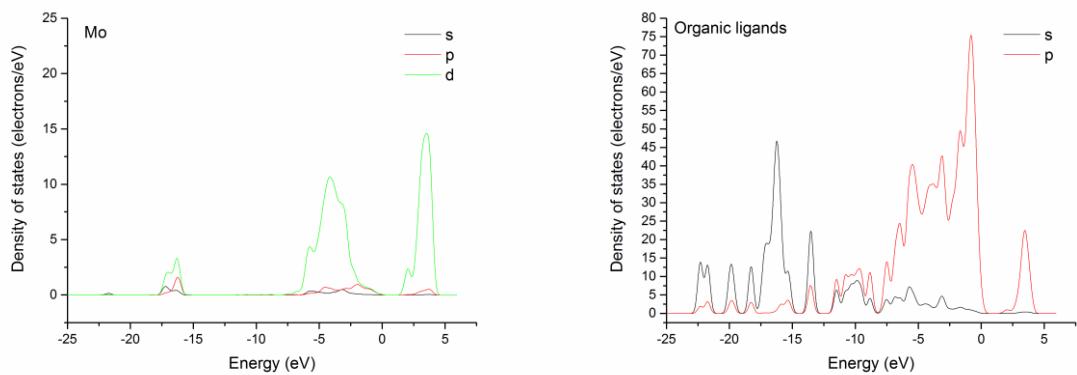
All DFT calculations were performed using a CASTEP package implemented in Materials Studio 8.0 software. Calculation were performed using the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functional.<sup>S6</sup> Band gap energy and density of states calculations were performed using geometry optimized structures with ultra-fine parameters setup.



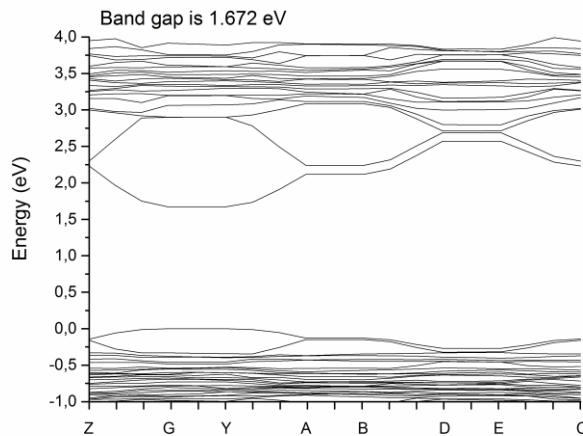
**Figure S21.** Partial densities of states calculated for molybdenum and organic ligands of  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**).



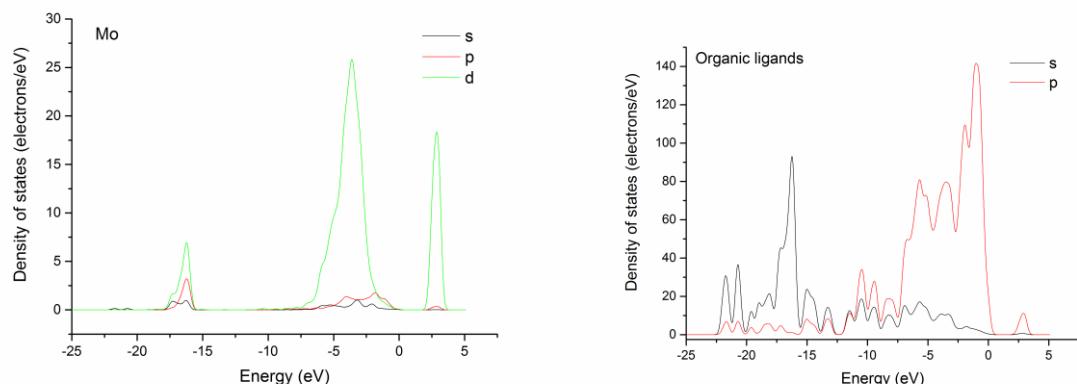
**Figure S22.** Calculated electronic band structure of complex  $[\text{Mo}_2\text{O}_6(\text{trethbz})_2]\cdot\text{H}_2\text{O}$  (**1**).



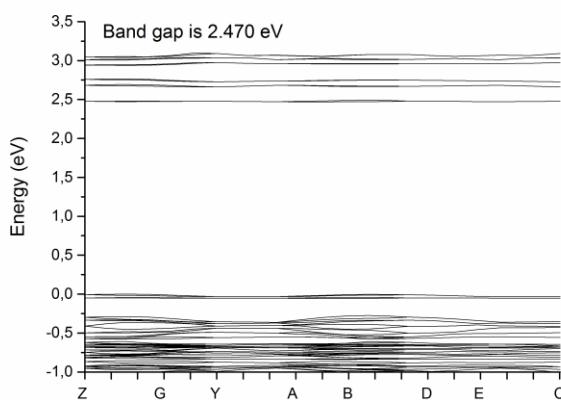
**Figure S23.** Partial densities of states calculated for molybdenum and organic ligands of complex  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot0.5\text{H}_2\text{O}$  (**2a**).



**Figure S24.** Calculated electronic band structure of  $[\text{Mo}_4\text{O}_{12}(\text{trPhCO}_2\text{H})_2]\cdot0.5\text{H}_2\text{O}$  (**2a**).



**Figure S25.** Partial densities of states calculated for molybdenum and organic ligands of  $[\text{Mo}_8\text{O}_{25}(\text{trhis})_2(\text{Htrhis})_2]\cdot 2\text{H}_2\text{O}$  (**3**).



**Figure S26.** Calculated electronic band structure of complex  $[\text{Mo}_8\text{O}_{25}(\text{trhis})_2(\text{Htrhis})_2]\cdot 2\text{H}_2\text{O}$  (**3**).

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