Supplementary Information

Insights into of the Lithium-Diffusion Process in Defect Porous Crystalline POM@MOF Anode Material

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1. Supplementary Figures of crystalline POM@MOFs material

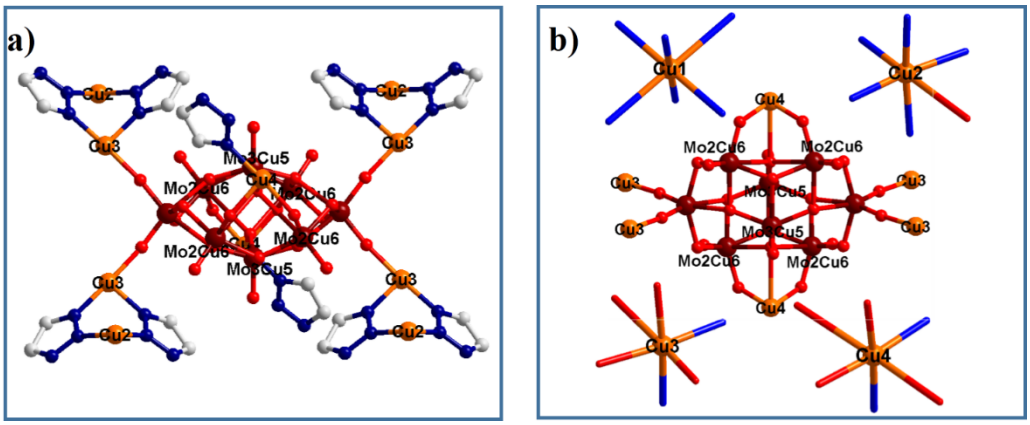

Figure S1. Representation of the asymmetric unit (a) and the coordination information (b) of POM nano- clusters and Cu in the crystalline POM@MOFs material.

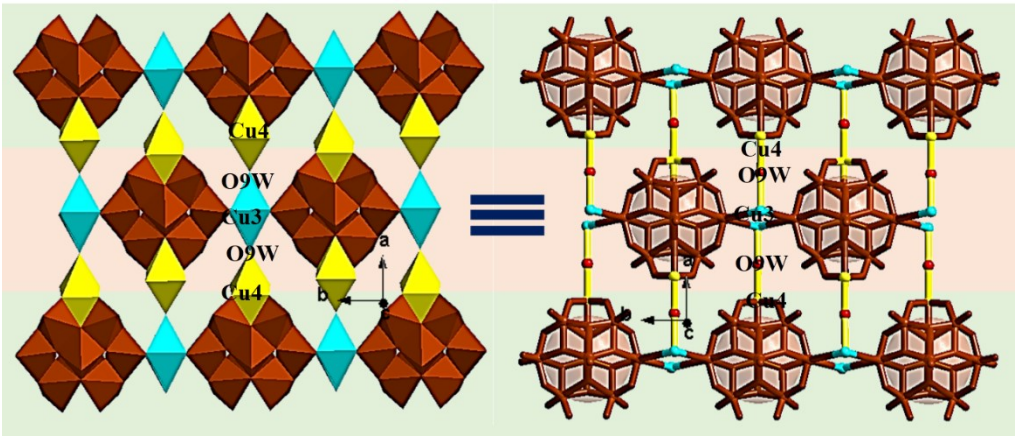

Figure S2. Representation of the 2D pure inorganic sheet or layers generated by 1D {-Mo8-Cu3-} chain structure *via* the -Cu4-O9W- fragment in crystalline POM@MOFs material.

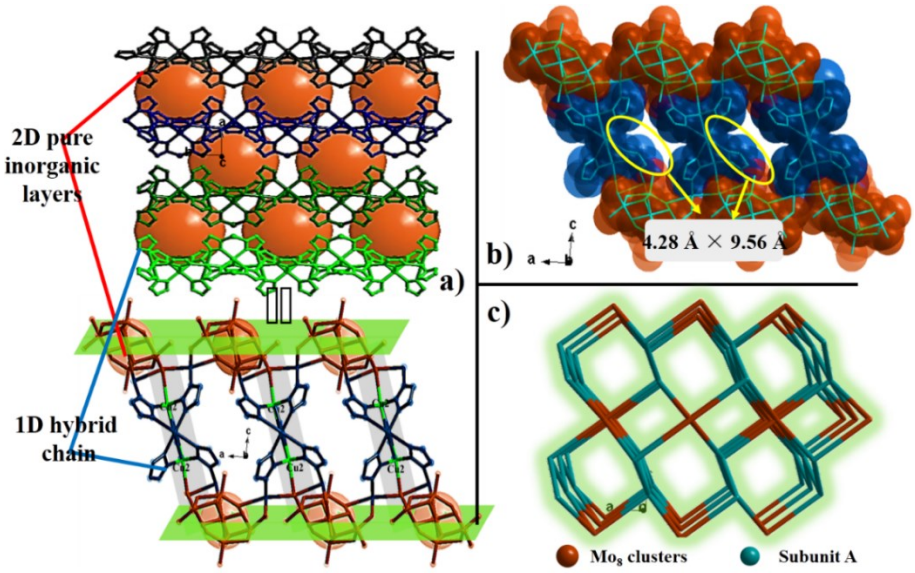

Figure S3. Combined ball/stick, stacked and topologic representation of the 3D pillared hybrid frameworks with opening feature formed by 1D hybrid chain and 2D pure inorganic layers in crystalline POM@MOFs.

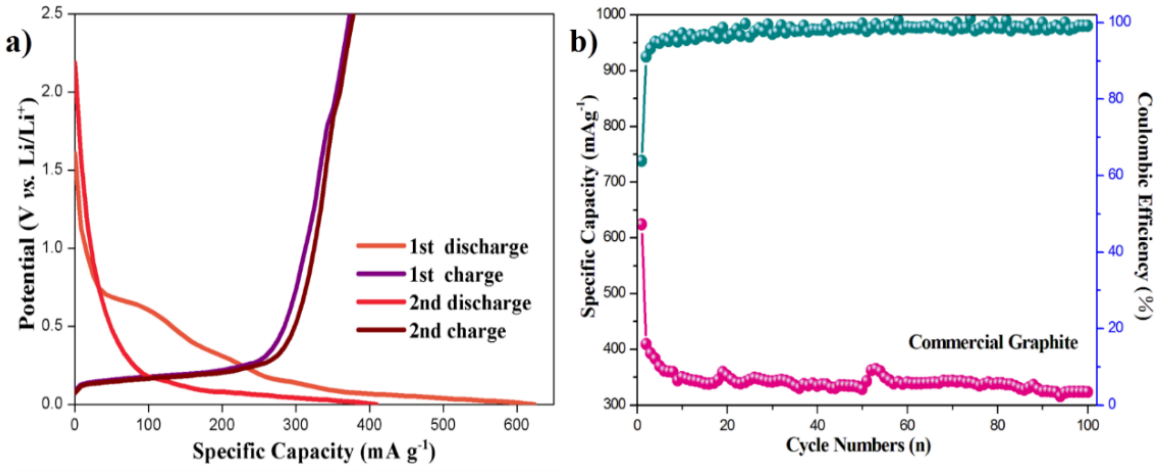

Figure S4. The charge-charge curve, cycle stabilities and columbic efficiency of commercial graphite.

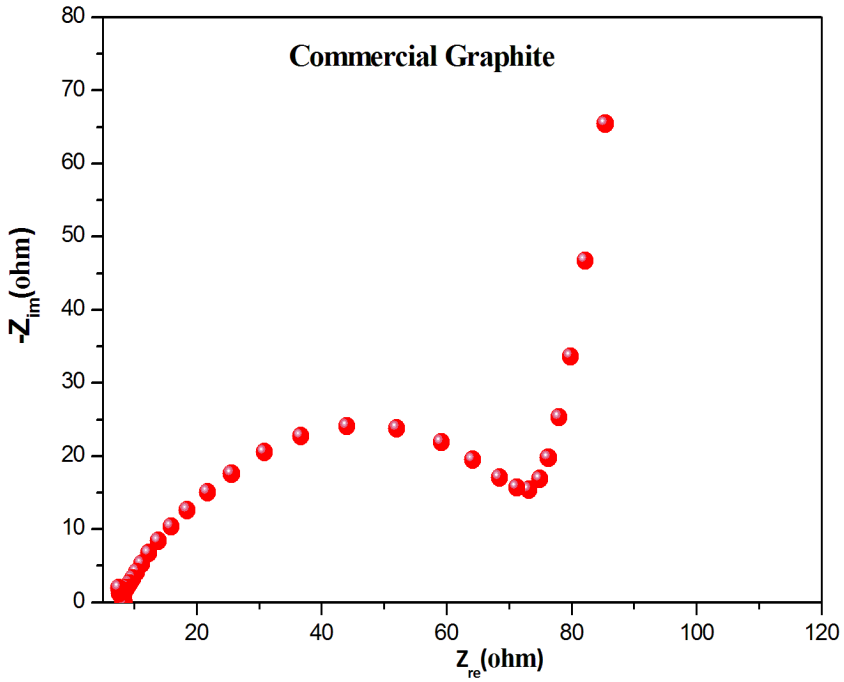

Figure S5. Nyquist plots and fitting plots after the first discharge-charge process of commercial graphite anode.

2. Calculation of Theoretical Capacity

The theoretical capacities were calculated according to equation (**1**): [1]

$$Q = \frac{nF}{3.6M_W} = \frac{96500n}{3.6M_W} = 26805.56\frac{n}{M_W} \qquad (1)$$

Q: Reversible charging-discharging capacity; n: Number of electrons; F: Faraday constant; M_w: Molecular weight.

Owing to the intercalation mechanism for Li storage, the redox reactions of metal ions (Mo and Cu) could be considered according to the equations (**2**) and (**3**).

$$Mo^{6+} \leftrightarrow Mo^{5+} \leftrightarrow Mo^{4+} \qquad (2)$$

$$Cu^{2+} \leftrightarrow Cu^{+} \leftrightarrow Cu \qquad (3)$$

If two Mo (VI) atoms and six Cu (II) ions in the material are reduced to Mo^{4+} and metallic copper, respectively. So, maximum of n = 16, Q = 354 mAh g^{-1}.

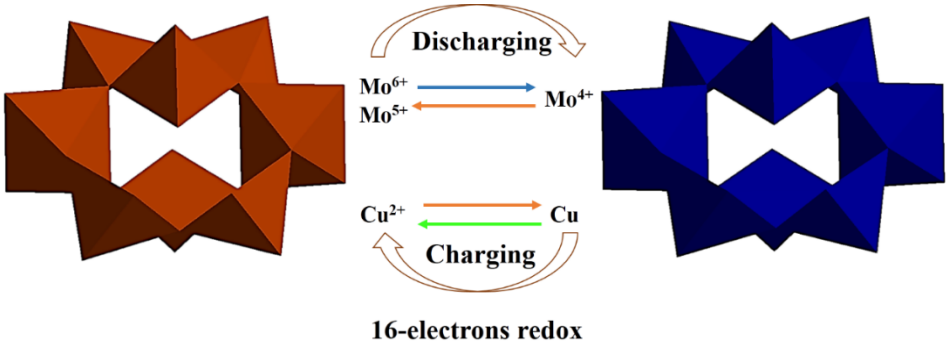

Figure S6. The schematic of the Calculation of the theoretical capacities of the crystalline POM@MOFs.

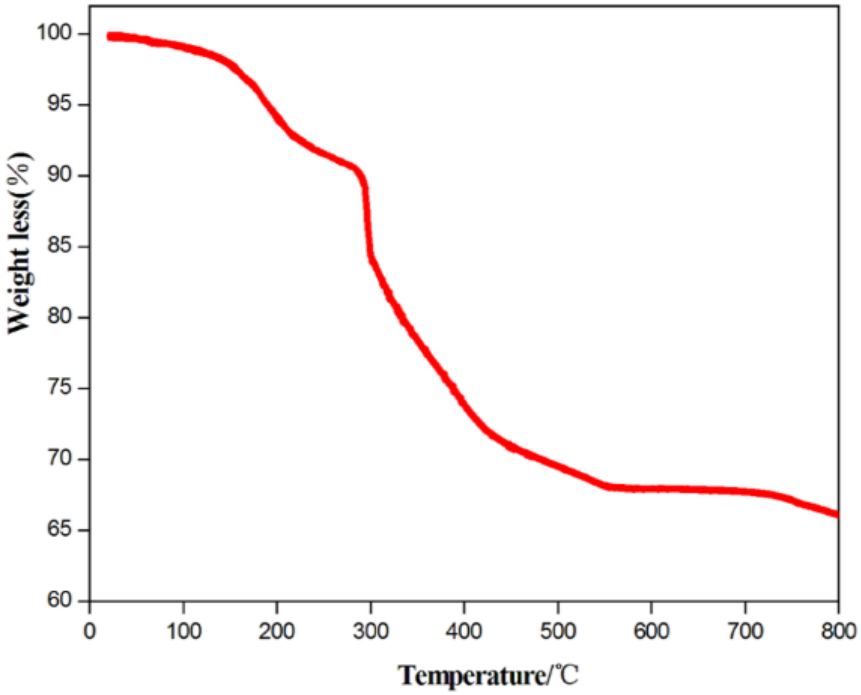

Figure S7. The TGA curve (thermal stability) of the porous crystalline POM@MOFs material.

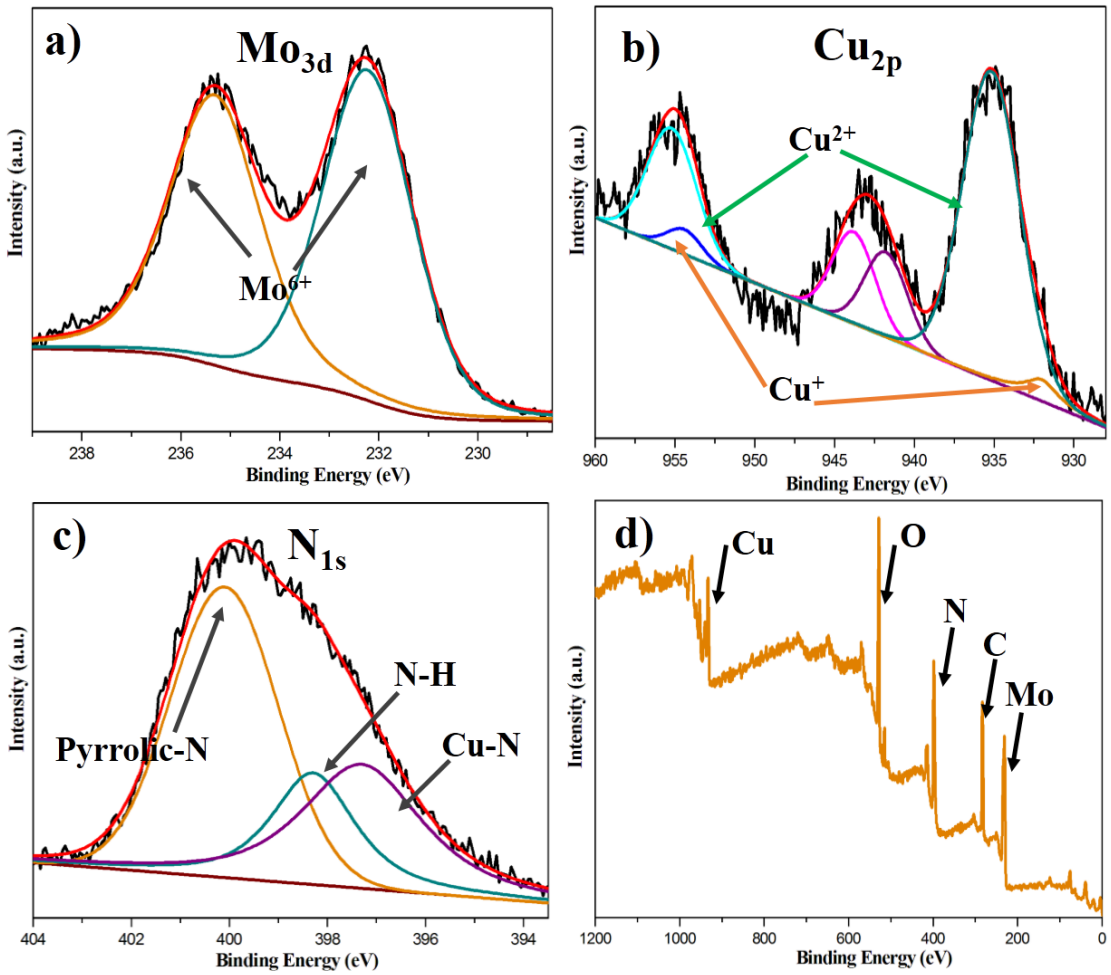

Figure S8. High-resolution XPS spectra of Mo (a), Cu (b), N (c) and XPS spectra of the fresh crystalline POM@MOFs material, respectively.

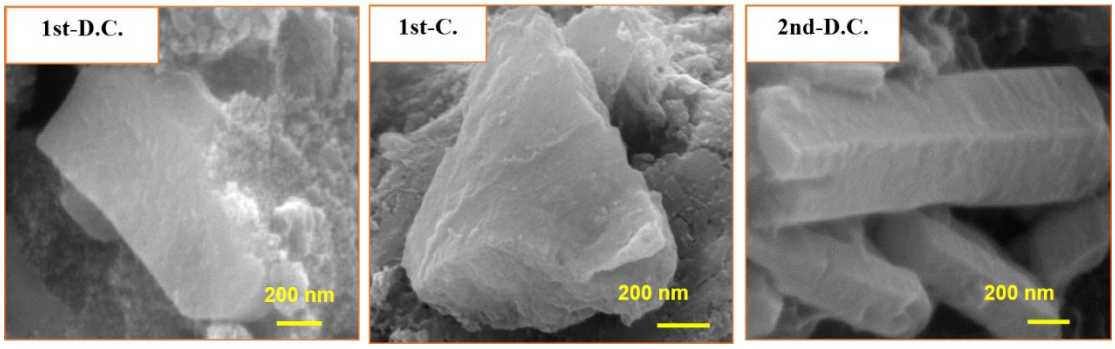

Figure S9. SEM images of the crystalline POM@MOFs material after 1st-discharge, 1st-charge and 2nd-dischage, D.C. = discharge, C. = charge.

3. Capacity Summary of Li-ion Battery Materials

Table S1. The electrochemical behavior in LIBs of different anode materials [a]

Electrode Materials	Current Density ($mA \cdot g^{-1}$)	Initial Capacity ($mAh \cdot g^{-1}$)	Cyclic Capacity ($mAh \cdot g^{-1}$)/ Cyclic Number (n)	Ref.
SnO_2/MXene	500	1463	696 (50)	*Nano Energy*, **2017**, *34*, 249-256.
Graphene/Mn_3O_4	100	1271	702 (100)	*ACS Nano*, **2016**, *10*, 6227-6234.
Ti_2C MXene	100	1015	389 (100)	*Nanoscale*, **2016**, *8*, 7580-7587
GaSe NS/SWCNT	100	1320	713 (100)	*Small*, **2017**, *13*, 1701677
Co_3O_4@Co@GC	100	1550	686 (60)	*Chem. Eng. J.*, **2017**, *321*, 495-501
CoS NS	50	954	677 (60)	*Chem. Mater.* 2**015**, 27, 5726-5735
Fe_3O_4@PEG	0.3C	550	600 (50)	*Chem. Mater*, **2016**, *28*, 6689-6697
Faceted Cu_2O	100	784	397 (50)	*CrystEngComm*, **2015**, *17*, 2110-2117
V_2O_3/Graphene	50	585	608 (100)	*ChemElectroChem*, **2019**, *6*, 493-503
$[(Bu_4N)_2[Mo_6O_{18}$-*N*-Ph-(*o*-$CH_3)_2$-*p*-SCN]	50	1678	876 (100)	*RSC Adv.*, **2014**, *4*, 7374-7379.
$TBA_{5/2}[PMo^{V}_8Mo^{VI}_4O_{37}(OH)_3Zn_4(bdc)_{1/2}(bzt)_{3/2}]3/2H_2O$	100	1389	780 (200)	*Chem. Commun.*, **2017**, 53, 10054-10057.
$(TBA)_3[PMo^{V}_8Mo^{VI}_4O_{38}(OH)_2Zn_4(PBA)_2]\cdot H_2O$	100	1008	640 (100)	*Chem. Commun.*, **2017**, *53*, 5204-5207.

$[PMo_8^{V}Mo_4^{VI}O_{37}(OH)_3Zn_4][TPT]_5 \cdot 2TPT \cdot 2H_2O$	50	1322	750 (200)	*J. Mater. Chem. A*, **2017**, *5*, 8477-8483.
$[Ag_{26}(Trz)_{16}(OH)_4][P_2W_{18}O_{62}]$	100	1077	550 (100)	*J. Mater. Chem. A*, **2017**, *5*, 3371-3376.
$Na[Ag_{16}(Trz)_9(H_2O)_4][P_2W_{18}O_{62}] \cdot H_2O$	100	1094	600 (100)	
$\{(H_2bimb)[CoMo_8O_{26}]\}n$	100	1563	1083 (1000)	Chem. Commun., **2017**, *53*, 10560-10563.
$\{[Ni_6(OH)_3(H_2O)(en)_3(PW_9O_{34})][Ni_6(OH)_3(H_2O)_4(en)_3(PW_9O_{34})](BDC)_{1.5}\}[Ni(en)(H_2O)_4] \cdot H_3O$	0.25 C	1421	540 (500)	*J. Mater. Chem. A*, **2015**, *3*, 22989-22995
$[\{Cu(btp)_2\}_3\{As_2Mo_{18}\}]$/Conductive Grapheme	100	1555	878 (240)	*CrystEngComm*, **2017**, *19*, 7154-716.
$[Bu_4N]_4[SiW_{11}O_{39}\{O(SiCH_2CH_2CH_2NH_2 \cdot HCl)_2\}]$@CNTs	0.5 $mAcm^{-2}$	1189	650 (100)	*Phys. Chem. Chem. Phys.*, 2014, *16*, 19668-19673.
$[Cu_2(BTC)_{4/3}]_6[H_5PMo_{10}V_2O_{40}]$)@RGO	50	2367	1075 (400)	*Nano Energy*, 2017, *34*, 205-214.
$(Bu_4N)_4\{(SiW_{11}O_{39})[O(SiCH_2CH_2CH_2NH\text{-}COOCH_2C_{16}H_9)_2]\}$@SWNTs	0.5 $mAcm^{-2}$	1569	580 (100)	*Adv. Funct. Mater.*, **2013**, *23*, 6100-6105.
$[Ag_{10}(trz)_4(H_2O)_2][HPW_{12}O_{40}]$@ CNTs	100	2000	859 (70)	*ACS Appl. Mater. Interfaces*, **2018**, *10*, 16660-16665.

4. Crystallographic Data of Crystalline Material

Table S2. Bond lengths [Å] and angles [°] for crystalline POM@MOFs.

Bonds	Length	Bonds	Length
N(1)-Cu(1)	2.367(10)	O(6)-Cu(3)	1.953(9)
N(2)-Cu(3)	1.947(11)	O(7)-Mo(2)	1.726(9)
N(3)-Cu(2)	2.184(14)	O(7)-Cu(4)	1.935(9)
N(4)-Cu(1)	1.997(11)	O(8)-Mo(3)	1.645(15)

N(5)-Cu(2)	1.962(10)	O(9)-Cu(3)	2.245(15)
N(6)-Cu(1)	2.029(12)	Cu(1)-N(4)#4	1.997(11)
N(7)-Cu(2)	2.002(10)	Cu(1)-N(6)#4	2.029(12)
N(8)-Cu(4)	1.971(11)	Cu(1)-N(1)#4	2.367(10)
O(1)-Mo(2)	1.626(9)	Cu(2)-N(5)#1	1.962(10)
O(2)-Mo(2)#1	1.942(6)	Cu(2)-N(7)#1	2.002(10)
O(2)-Mo(2)	1.942(6)	Cu(3)-N(2)#1	1.947(11)
O(2)-Mo(3)#2	2.178(12)	Cu(3)-O(6)#1	1.953(9)
O(3)-Mo(3)#2	1.841(9)	Cu(4)-O(7)#1	1.935(9)
O(3)-Mo(2)	2.038(8)	Cu(4)-N(8)#1	1.971(11)
O(3)-Mo(1)	2.233(9)	Mo(1)-O(6)#3	1.697(9)
O(4)-Mo(3)	1.740(14)	Mo(1)-O(6)#5	1.697(9)
O(5)-Mo(1)	1.887(9)	Mo(1)-O(5)#6	1.887(9)
O(5)-Mo(2)	1.890(9)	Mo(1)-O(3)#6	2.233(9)
O(6)-Mo(1)#3	1.697(9)	Mo(3)-O(3)#6	1.841(9)
Mo(3)-O(2)#2	2.178(12)	Mo(3)-O(3)#2	1.841(9)

Bonds	Angle	Bonds	Angle
N(4)-Cu(1)-N(4)#4	180	O(5)-Mo(1)-O(3)#6	85.7(3)
N(4)-Cu(1)-N(6)	91.4(4)	O(5)#6-Mo(1)-O(3)#6	72.5(3)
N(4)#4-Cu(1)-N(6)	88.6(4)	O(6)#3-Mo(1)-O(3)	89.4(4)
N(4)-Cu(1)-N(6)#4	88.6(4)	O(6)#5-Mo(1)-O(3)	164.2(4)
N(4)#4-Cu(1)-N(6)#4	91.4(4)	O(5)-Mo(1)-O(3)	72.5(3)
N(6)-Cu(1)-N(6)#4	180	O(5)#6-Mo(1)-O(3)	85.7(3)
N(4)-Cu(1)-N(1)#4	87.6(4)	O(3)#6-Mo(1)-O(3)	78.5(4)
N(4)#4-Cu(1)-N(1)#4	92.4(4)	O(1)-Mo(2)-O(7)	104.8(4)
N(6)-Cu(1)-N(1)#4	92.6(4)	O(1)-Mo(2)-O(5)	105.6(4)
N(6)#4-Cu(1)-N(1)#4	87.4(4)	O(7)-Mo(2)-O(5)	96.7(4)
N(4)-Cu(1)-N(1)	92.4(4)	O(1)-Mo(2)-O(2)	103.5(5)
N(4)#4-Cu(1)-N(1)	87.6(4)	O(7)-Mo(2)-O(2)	96.9(4)

N(6)-Cu(1)-N(1)	87.4(4)	O(5)-Mo(2)-O(2)	143.3(4)
N(6)#4-Cu(1)-N(1)	92.6(4)	O(1)-Mo(2)-O(3)	102.3(4)
N(1)#4-Cu(1)-N(1)	180	O(7)-Mo(2)-O(3)	152.8(4)
N(5)-Cu(2)-N(5)#1	88.6(6)	O(5)-Mo(2)-O(3)	77.2(4)
N(5)-Cu(2)-N(7)	172.7(4)	O(2)-Mo(2)-O(3)	75.2(4)
N(5)#1-Cu(2)-N(7)	91.4(4)	O(8)-Mo(3)-O(4)	106.8(8)
N(5)-Cu(2)-N(7)#1	91.4(4)	O(8)-Mo(3)-O(3)#6	108.4(3)
N(5)#1-Cu(2)-N(7)#1	172.7(4)	O(4)-Mo(3)-O(3)#6	95.7(3)
N(7)-Cu(2)-N(7)#1	87.7(6)	O(8)-Mo(3)-O(3)#2	108.4(3)
N(5)-Cu(2)-N(3)	96.2(4)	O(4)-Mo(3)-O(3)#2	95.7(3)
N(5)#1-Cu(2)-N(3)	96.2(4)	O(3)#6-Mo(3)-O(3)#2	136.1(6)
N(7)-Cu(2)-N(3)	91.0(4)	O(8)-Mo(3)-O(2)#2	105.7(6)
N(7)#1-Cu(2)-N(3)	91.0(4)	O(4)-Mo(3)-O(2)#2	147.4(7)
N(2)-Cu(3)-N(2)#1	92.0(6)	O(3)#6-Mo(3)-O(2)#2	73.9(3)
O(6)#1-Cu(3)-O(6)	88.1(5)	O(3)#2-Mo(3)-O(2)#2	73.9(3)
O(6)#1-Cu(3)-O(9)	88.8(4)	O(6)#3-Mo(1)-O(6)#5	104.1(6)
O(6)-Cu(3)-O(9)	88.8(4)	O(6)#3-Mo(1)-O(5)	100.6(4)
O(7)#1-Cu(4)-O(7)	83.0(5)	O(6)#5-Mo(1)-O(5)	96.6(4)
O(7)#1-Cu(4)-N(8)#1	175.4(4)	O(6)#3-Mo(1)-O(5)#6	96.6(4)
O(7)-Cu(4)-N(8)#1	93.3(4)	O(6)#5-Mo(1)-O(5)#6	100.6(4)
O(7)#1-Cu(4)-N(8)	93.3(4)	O(5)-Mo(1)-O(5)#6	151.9(6)
O(7)-Cu(4)-N(8)	175.4(4)	O(6)#3-Mo(1)-O(3)#6	164.2(4)
N(8)#1-Cu(4)-N(8)	90.3(6)	O(6)#5-Mo(1)-O(3)#6	89.4(4)

#1: x, -y+1, z; #2: -x+1, -y+1, -z; #3: -x+1/2, -y+1/2, -z; #4: -x+1/2, -y+3/2, -z+1; #5: x+1/2, -y+1/2, z; #6: -x+1, y, -z.

5. References

1 Chen, J. J.; Symes, M. D.; Fan, S. C.; Zheng, M. S.; Miras, H. N.; Dong, Q. F.; Cronin, L. *Adv. Mater.*, **2015**, *27*, 4649-4654