

Supporting Information

Surfactant-assisted Fabrication and Supercapacitor Performances of 12-phosphomolybdate-pillared Metal-Organic Framework Containing Helix and its SWNT Nanocomposites

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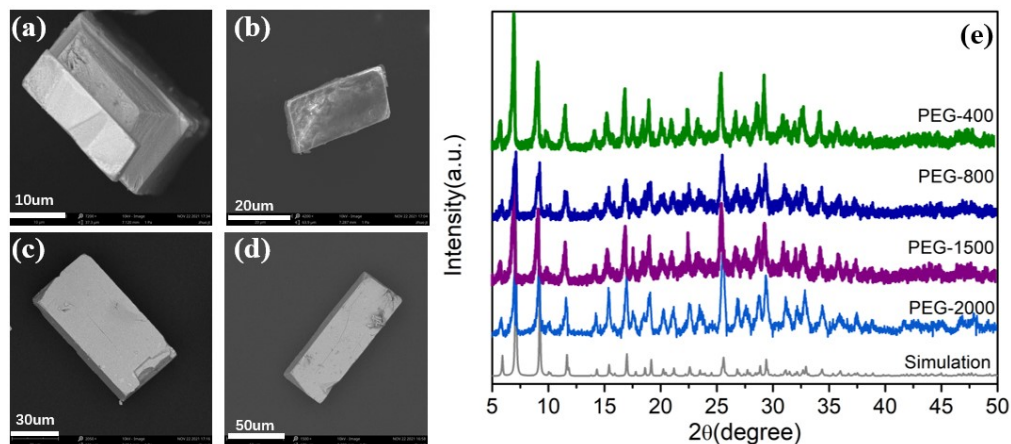


Fig. S1 SEM(a)-(d) and XRD (e) of crystalline compound NiPMo₁₂ obtained at different PEG molecular weight (400, 800, 1500, 2000).

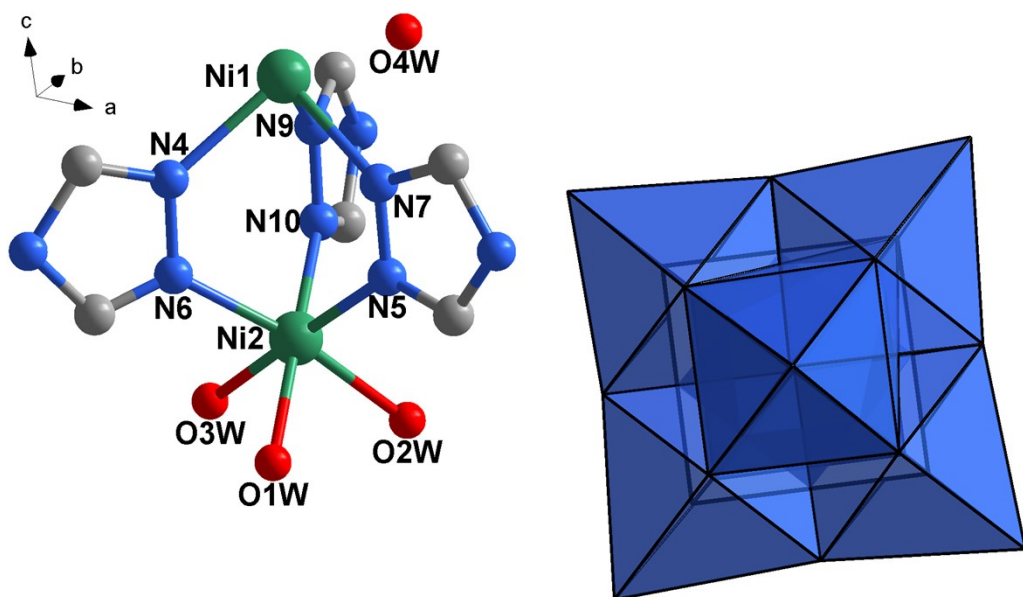


Fig. S2 Combined ball and stick representation of the asymmetric unit of compound $[\text{Ni}_3(1,2,4\text{-Tri})_6(\text{H}_2\text{O})_8][\text{H}_2\text{W}_6\text{O}_{19}]_2$. Water molecules and all hydrogen atoms are omitted for clarity.

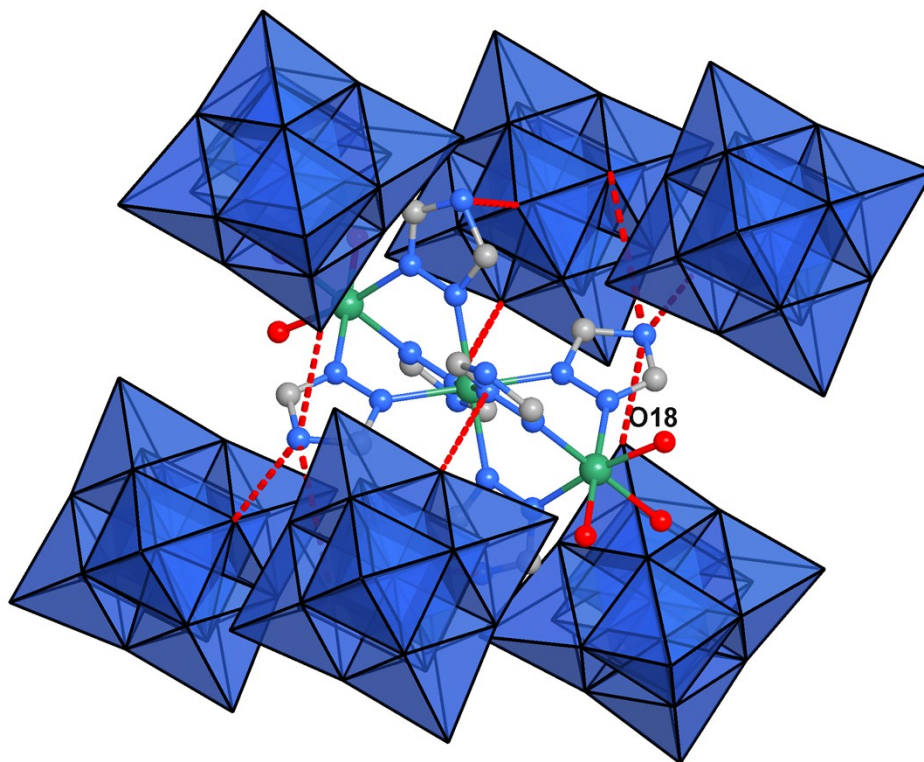


Fig. S3 Combined ball and stick representation of the linking mode between $[\text{W}_6\text{O}_{19}]^{4-}$ and $[\text{Ni}_3(1,2,4\text{Tri})_6]^{3+}$ subunits

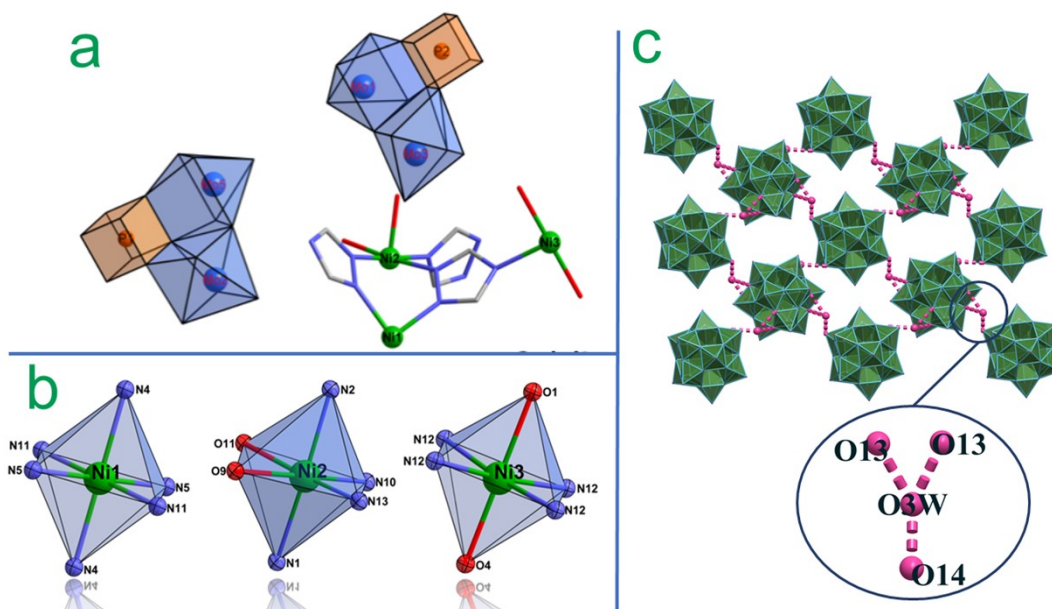


Fig.S4 (a) Combined polyhedral representation of the molecular structure unit of compound Ni PMo₁₂. (b) Coordination fashions of three crystallographic unique Ni^{II} ions. (c) adjacent PMo₁₂ are linked each other by 2O13...O3W...O14 supramolecular bonds.

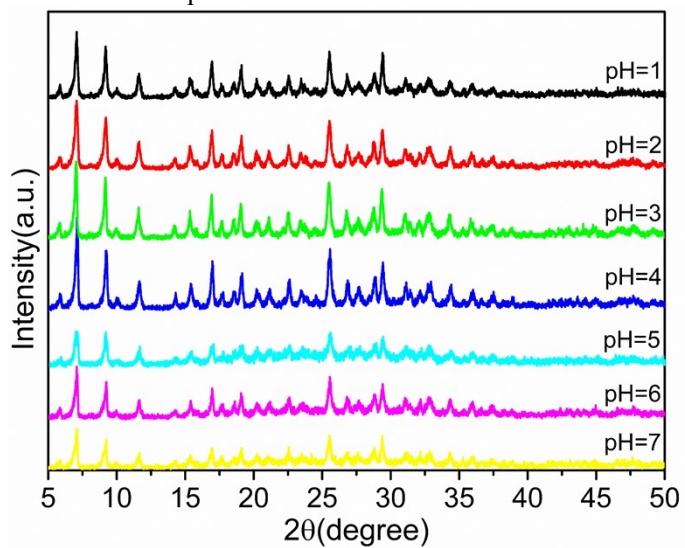


Fig. S5 PXRD of Ni PMo₁₂ in different pH.

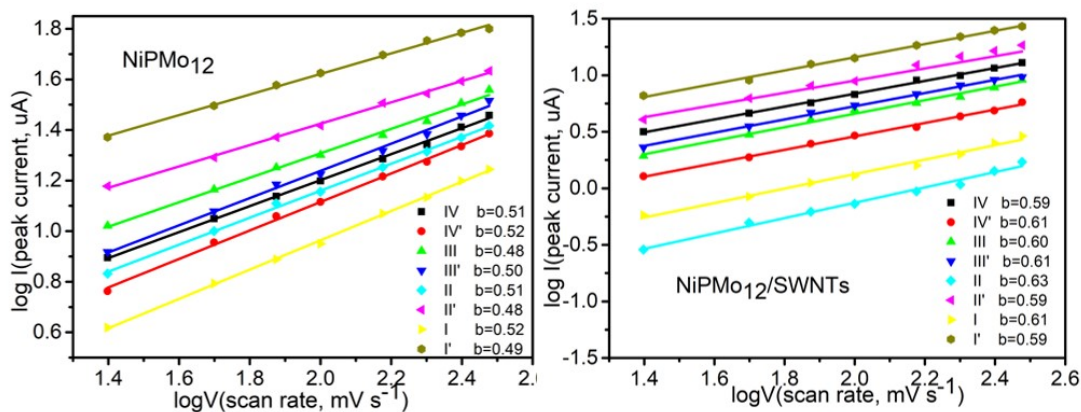


Fig. S6 The calculated b-values for the NiPMo₁₂ and NiPMo₁₂/SWNTs nanocomposite

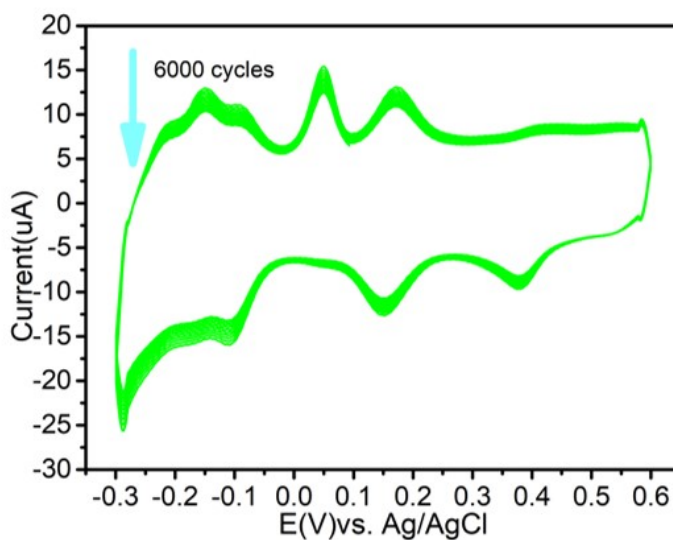


Fig. S7 CV curves of the 1st to 6000th cycle toward the NiPMo₁₂/SWNTs sample at the scan rate of 125mV s⁻¹

Table S1. Selected bond lengths (Å) and bond angles (°) for NiPMo₁₂.

Bond	Lengths	Bond	Lengths
C(1)-N(1)	1.336(11)	Mo(1)-O(10)	1.904(8)
C(1)-N(2)	1.340(11)	Mo(1)-O(12)3	2.463(12)
C(2)-N(1)	1.347(11)	Mo(1)-O(12)	2.463(12)
C(2)-N(3)	1.312(11)	Mo(3)-O(7)	1.615(7)
C(3)-N(7)	1.347(11)	Mo(3)-O(8)	1.890(8)
C(3)-N(8)	1.319(12)	Mo(3)-O(10)4	1.882(8)
C(4)-N(7)	1.348(12)	Mo(3)-O(11)5	1.899(8)
C(4)-N(9)1	1.334(11)	Mo(3)-O(11)	1.913(8)
C(5)-N(4)	1.296(12)	Mo(3)-O(12)	2.428(12)
C(5)-N(6)	1.371(15)	Mo(3)-O(12)5	2.462(12)
C(6)-N(5)	1.312(14)	O(12)-O(12)3	1.77(2)
C(6)-N(6)	1.337(14)	O(12)-O(12)2	1.781(16)
N(1)-Ni(2)	2.080(7)	O(12)-O(12)5	1.781(16)
N(2)-N(3)	1.369(10)	O(12)-P(1)	1.539(11)

N(2)-Ni(1)	2.064(7)	Mo(2)-O(2)	1.954(9)
N(3)-Ni(3)	2.065(7)	Mo(2)-O(3)	1.644(8)
N(4)-N(5)	1.381(11)	Mo(2)-O(4)	1.854(9)
N(4)-Ni(1)	2.121(8)	Mo(2)-O(4)5	1.940(9)
N(5)-Ni(3)	2.090(8)	Mo(2)-O(5)	1.852(8)
N(7)-Ni(3)	2.098(7)	Mo(2)-O(6)2	2.442(12)
N(8)-N(9)1	1.373(10)	Mo(2)-O(6)	2.474(12)
N(8)-Ni(1)2	2.116(7)	Mo(4)-O(1)	1.625(11)
N(9)-Ni(3)	2.054(8)	Mo(4)-O(2)6	1.880(8)
Ni(2)-O(13)	2.074(14)	Mo(4)-O(2)	1.880(8)
Ni(2)-O(14)	2.099(12)	Mo(4)-O(5)5	1.922(9)
Ni(3)-O(15)	2.094(7)	Mo(4)-O(5)7	1.922(9)
Ni(3)-O(16)	2.144(7)	Mo(4)-O(6)	2.430(13)
O(18)-O(18)3	0.79(7)	Mo(4)-O(6)6	2.430(13)
Mo(1)-O(8)	1.867(8)	O(6)-O(6)2	1.775(18)
Mo(1)-O(8)3	1.867(8)	O(6)-O(6)5	1.775(18)
Mo(1)-O(9)	1.655(11)	O(6)-O(6)6	1.75(2)
Mo(1)-O(10)3	1.904(8)	O(6)-P(2)	1.530(12)

Bond	Angles	Bond	Angles
N(1)-C(1)-N(2)	113.3(8)	O(12)7-O(12)-Mo(3)	131.0(3)
N(3)-C(2)-N(1)	113.4(8)	O(12)7-O(12)-O(12)2	90.001(3)
N(8)-C(3)-N(7)	113.9(8)	O(12)5-O(12)-O(12)2	90.003(2)
N(9)1-C(4)-N(7)	112.9(8)	O(12)7-O(12)-O(12)5	90.001(1)
N(4)-C(5)-N(6)	109.3(9)	P(1)-O(12)-Mo(1)	123.8(6)
N(5)-C(6)-N(6)	109.3(9)	P(1)-O(12)-Mo(3)	124.4(6)
C(1)-N(1)-C(2)	109.4(10)	P(1)-O(12)-Mo(3)2	122.3(6)
C(1)-N(1)-Ni(2)	102.0(7)	P(1)-O(12)-O(12)5	54.7(2)
C(2)-N(1)-Ni(2)	133.7(6)	P(1)-O(12)-O(12)7	54.9(4)
C(1)-N(2)-N(3)	123.7(6)	O(12)-P(1)-O(12)10	180
C(1)-N(2)-Ni(1)	104.9(7)	O(12)6-P(1)-O(12)2	70.7(4)
N(3)-N(2)-Ni(1)	131.6(6)	O(12)2-P(1)-O(12)8	180.0(7)
C(2)-N(3)-N(2)	122.6(5)	O(12)10-P(1)-O(12)2	109.3(4)
C(2)-N(3)-Ni(3)	106.4(7)	O(12)9-P(1)-O(12)8	109.3(4)
N(2)-N(3)-Ni(3)	126.8(6)	O(12)7-P(1)-O(12)2	109.7(9)
C(5)-N(4)-N(5)	126.4(6)	O(12)9-P(1)-O(12)2	109.3(4)
C(5)-N(4)-Ni(1)	107.4(8)	O(12)10-P(1)-O(12)5	70.3(9)
N(5)-N(4)-Ni(1)	107.4(8)	O(12)-P(1)-O(12)8	109.3(4)
C(6)-N(5)-N(4)	124.0(7)	O(12)10-P(1)-O(12)6	109.3(4)
C(6)-N(5)-Ni(3)	128.6(6)	O(12)6-P(1)-O(12)8	109.3(4)
N(4)-N(5)-Ni(3)	107.6(8)	O(12)5-P(1)-O(12)2	70.3(9)
C(6)-N(6)-C(5)	132.5(7)	O(12)-P(1)-O(12)5	109.3(4)
C(3)-N(7)-C(4)	119.7(6)	O(12)-P(1)-O(12)9	109.7(9)
C(3)-N(7)-Ni(3)	106.2(9)	O(12)9-P(1)-O(12)5	70.7(4)
C(4)-N(7)-Ni(3)	101.8(7)	O(12)10-P(1)-O(12)8	70.7(4)
C(3)-N(8)-N(9)1	129.5(6)	O(12)-P(1)-O(12)6	180.0(7)
C(3)-N(8)-Ni(1)2	128.1(6)	O(12)5-P(1)-O(12)8	70.7(4)
N(9)1-N(8)-Ni(1)2	105.6(7)	O(12)9-P(1)-O(12)6	109.7(9)
C(4)3-N(9)-N(8)3	130.3(6)	O(12)-P(1)-O(12)7	70.3(9)
C(4)3-N(9)-Ni(3)	122.1(5)	O(12)5-P(1)-O(12)6	109.7(9)
N(8)3-N(9)-Ni(3)		O(12)7-P(1)-O(12)8	70.3(9)
N(2)-Ni(1)-N(2)4			

N(2)-Ni(1)-N(4)4	105.8(7)	O(12)9-P(1)-O(12)7	109.3(4)
N(2)4-Ni(1)-N(4)	128.4(6)	O(12)10-P(1)-O(12)9	70.3(9)
4N(2)-Ni(1)-N(4)	125.7(5)	O(12)-P(1)-O(12)2	70.7(4)
N(2)4-Ni(1)-N(4)	180.0(4)	O(12)10-P(1)-O(12)7	70.7(4)
N(2)-Ni(1)-N(8)3	89.5(3)	O(12)6-P(1)-O(12)7	70.7(4)
N(2)4-Ni(1)-N(8)5	90.5(3)	O(12)5-P(1)-O(12)7	70.7(4)
N(2)-Ni(1)-N(8)5	90.5(3)	O(2)-Mo(2)-O(6)2	70.7(4)
N(2)4-Ni(1)-N(8)3	89.5(3)	O(2)-Mo(2)-O(6)	70.7(4)
N(4)4-Ni(1)-N(4)	89.5(3)	O(3)-Mo(2)-O(2)	109.7(9)
N(8)5-Ni(1)-N(4)	89.0(3)	O(3)-Mo(2)-O(4)5	180.0(7)
N(8)3-Ni(1)-N(4)4	89.0(3)	O(3)-Mo(2)-O(4)	109.3(4)
N(8)5-Ni(1)-N(4)4	91.0(3)	O(3)-Mo(2)-O(5)	95.3(4)
		O(3)-Mo(2)-O(6)	64.4(4)
N(8)3-Ni(1)-N(8)5	91.0(3)	O(3)-Mo(2)-O(6)2	98.7(5)
N(1)-Ni(2)-N(1)6	180	O(4)-Mo(2)-O(2)	99.6(5)
N(1)6-Ni(2)-N(1)5	89.6(3)	O(4)5-Mo(2)-O(2)	102.3(5)
N(1)-Ni(2)-N(1)2	89.6(3)	O(4)-Mo(2)-O(4)5	102.6(5)
N(1)-Ni(2)-N(1)5	90.4(3)	O(4)-Mo(2)-O(6)	156.1(4)
N(1)6-Ni(2)-N(1)2	90.4(3)	O(4)-Mo(2)-O(6)2	161.6(4)
N(1)5-Ni(2)-N(1)2	180.0(4)	O(4)5-Mo(2)-O(6)	158.5(5)
N(1)5-Ni(2)-O(14)	175.3(4)	O(5)-Mo(2)-O(2)	84.7(3)
N(1)2-Ni(2)-O(14)	89.902(19)	O(5)-Mo(2)-O(4)	87.4(6)
N(1)6-Ni(2)-O(14)	89.902(19)	O(5)-Mo(2)-O(4)5	94.2(5)
N(1)-Ni(2)-O(14)	89.902(19)	O(5)-Mo(2)-O(6)	65.3(5)
O(13)-Ni(2)-N(1)2	89.902(19)	O(5)-Mo(2)-O(6)2	93.5(5)
O(13)-Ni(2)-N(1)	89.902(19)	O(6)2-Mo(2)-O(6)	63.6(4)
O(13)-Ni(2)-N(1)5	175.3(4)	O(1)-Mo(4)-O(2)11	88.1(4)
O(13)-Ni(2)-N(1)6	87.6(2)	O(1)-Mo(4)-O(2)	91.6(4)
O(13)-Ni(2)-O(14)	87.6(2)	O(1)-Mo(4)-O(5)5	157.5(5)
N(3)-Ni(3)-N(5)	87.6(2)	O(1)-Mo(4)-O(5)12	94.1(5)
N(3)-Ni(3)-N(7)	87.6(2)	O(1)-Mo(4)-O(6)	65.9(4)
N(3)-Ni(3)-O(15)	87.6(2)	O(2)11-Mo(4)-O(2)	42.3(5)
N(3)-Ni(3)-O(16)	92.4(2)	O(2)-Mo(4)-O(5)5	99.9(5)
N(5)-Ni(3)-N(7)	92.4(2)	O(2)11-Mo(4)-O(5)5	99.9(5)
N(5)-Ni(3)-O(15)	92.4(2)	O(2)-Mo(4)-O(5)12	99.7(5)
N(5)-Ni(3)-O(16)	92.4(2)	O(2)11-Mo(4)-O(5)12	99.7(5)
N(7)-Ni(3)-O(16)	180	O(2)11-Mo(4)-O(6)	99.7(5)
N(9)-Ni(3)-N(3)	89.2(3)	O(2)-Mo(4)-O(6)	158.8(3)
N(9)-Ni(3)-N(5)	90.1(3)	O(2)11-Mo(4)-O(6)11	158.8(3)
N(9)-Ni(3)-N(7)	91.7(3)	O(2)-Mo(4)-O(6)11	91.6(5)
N(9)-Ni(3)-O(15)	174.7(3)	O(5)5-Mo(4)-O(5)12	88.5(4)
N(9)-Ni(3)-O(16)	176.5(3)	O(5)12-Mo(4)-O(6)11	160.1(5)
O(15)-Ni(3)-N(7)	87.4(3)	O(5)5-Mo(4)-O(6)	160.1(5)
O(15)-Ni(3)-O(16)	92.9(3)	O(5)12-Mo(4)-O(6)	88.5(4)
O(8)-Mo(1)-O(8)7	87.5(3)	O(6)11-Mo(4)-O(6)	96.5(5)
O(8)-Mo(1)-O(10)	95.6(3)	Mo(4)-O(2)-Mo(2)	66.3(4)
O(8)-Mo(1)-O(10)7	88.3(3)	Mo(2)-O(4)-Mo(2)2	
O(8)7-Mo(1)-O(10)	95.2(3)	Mo(2)-O(5)-Mo(4)2	
O(8)7-Mo(1)-O(10)7			
O(8)-Mo(1)-O(12)7			
O(8)7-Mo(1)-O(12)7			

O(8)-Mo(1)-O(12)	171.5(3)	Mo(2)5-O(6)-Mo(2)	66.3(4)
O(8)7-Mo(1)-O(12)	89.4(3)	Mo(4)-O(6)-Mo(2)5	96.5(5)
O(9)-Mo(1)-O(8)	89.2(3)	Mo(4)-O(6)-Mo(2)	84.8(6)
O(9)-Mo(1)-O(8)7	83.5(3)	O(6)2-O(6)-Mo(2)	65.3(4)
O(9)-Mo(1)-O(10)7	87.8(6)	O(6)5-O(6)-Mo(2)5	65.3(4)
O(9)-Mo(1)-O(10)	156.5(5)	O(6)2-O(6)-Mo(2)5	93.9(5)
O(9)-Mo(1)-O(12)7	88.3(4)	O(6)11-O(6)-Mo(2)5	93.9(5)
O(9)-Mo(1)-O(12)	88.3(4)	O(6)11-O(6)-Mo(2)	42.2(6)
O(10)-Mo(1)-O(10)7	156.5(5)	O(6)5-O(6)-Mo(2)	136.3(6)
O(10)7-Mo(1)-O(12)7	93.4(5)	O(6)2-O(6)-Mo(4)	138.3(6)
O(10)7-Mo(1)-O(12)	63.9(4)	O(6)11-O(6)-Mo(4)	135.8(6)
O(10)-Mo(1)-O(12)7	63.9(4)	O(6)5-O(6)-Mo(4)	92.3(4)
O(10)-Mo(1)-O(12)	93.4(5)	O(6)11-O(6)-O(6)2	91.7(4)
O(12)7-Mo(1)-O(12)	102.4(5)	O(6)5-O(6)-O(6)2	93.0(4)
O(7)-Mo(3)-O(8)	102.4(5)	O(6)11-O(6)-O(6)5	67.9(6)
O(7)-Mo(3)-O(10)8	101.1(4)	P(2)-O(6)-Mo(2)	69.8(6)
O(7)-Mo(3)-O(11)5	101.1(4)	P(2)-O(6)-Mo(2)5	131.5(3)
O(7)-Mo(3)-O(11)	158.9(3)	P(2)-O(6)-Mo(4)	131.6(3)
O(7)-Mo(3)-O(12)	158.9(3)	P(2)-O(6)-O(6)5	131.0(3)
O(7)-Mo(3)-O(12)5	86.1(6)	P(2)-O(6)-O(6)2	130.9(3)
O(8)-Mo(3)-O(11)5	93.2(4)	P(2)-O(6)-O(6)11	131.3(8)
O(8)-Mo(3)-O(11)	64.2(4)	O(6)11-P(2)-O(6)	68.9(3)
O(8)-Mo(3)-O(12)5	64.2(4)	O(6)13-P(2)-O(6)12	131.3(8)
O(8)-Mo(3)-O(12)	93.2(4)	O(6)11-P(2)-O(6)12	89.994(5)
O(10)8-Mo(3)-O(8)	42.2(5)	O(6)14-P(2)-O(6)	89.998(7)
O(10)8-Mo(3)-O(11)	101.5(5)	O(6)14-P(2)-O(6)12	89.996(6)
O(10)8-Mo(3)-O(11)5	101.9(5)	O(6)13-P(2)-O(6)14	122.5(7)
O(10)8-Mo(3)-O(12)	101.2(5)	O(6)13-P(2)-O(6)	124.3(7)
O(10)8-Mo(3)-O(12)5	100.9(5)	O(6)11-P(2)-O(6)2	124.0(6)
O(11)-Mo(3)-O(12)	158.6(4)	O(6)11-P(2)-O(6)13	54.6(2)
O(11)-Mo(3)-O(12)5	158.7(4)	O(6)5-P(2)-O(6)12	54.6(2)
O(12)-Mo(3)-O(12)5	157.3(5)	O(6)6-P(2)-O(6)13	55.1(4)
Mo(1)-O(8)-Mo(3)	87.9(3)	O(6)6-P(2)-O(6)	69.8(9)
Mo(3)9-O(10)-Mo(1)	94.8(5)	O(6)13-P(2)-O(6)5	110.2(9)
Mo(3)2-O(11)-Mo(3)	64.5(4)	O(6)14-P(2)-O(6)2	70.9(4)
Mo(3)2-O(12)-Mo(1)	88.4(4)	O(6)11-P(2)-O(6)14	180
Mo(3)-O(12)-Mo(1)	157.2(5)	O(6)5-P(2)-O(6)	70.9(4)
Mo(3)-O(12)-Mo(3)2	87.9(3)	O(6)6-P(2)-O(6)14	70.9(4)
O(12)2-O(12)-Mo(1)	94.0(4)	O(6)6-P(2)-O(6)12	70.9(4)
O(12)7-O(12)-Mo(1)	64.5(4)	O(6)12-P(2)-O(6)	109.1(4)
O(12)5-O(12)-Mo(1)	86.8(5)	O(6)11-P(2)-O(6)6	109.1(4)
O(12)5-O(12)-Mo(3)	93.5(4)	O(6)5-P(2)-O(6)14	70.9(4)
O(12)5-O(12)-Mo(3)2	63.6(4)	O(6)6-P(2)-O(6)2	69.8(9)
O(12)7-O(12)-Mo(3)2		O(6)2-P(2)-O(6)2	109.1(4)
O(12)2-O(12)-Mo(3)		O(6)5-P(2)-O(6)2	
O(12)2-O(12)-Mo(3)2			

Symmetry transformations used to generate equivalent atoms: 2+y,1/2-x,3/2-z; 2-y,+x,+z;

3+x,+y,1-z; 4+y,-x,1-z; 5+y,-x,+z; 6+x,+y,2-z; 7+y,-x,2-z; 1-1/2+y,1/2-x,3/2-z; 2-y,+x,+z; 31/2-y,1/2+x,3/2-z; 41/2-x,1/2-y,3/2-z; 5+y,-x,+z; 6-x,-y,+z; 7+x,+y,1-z; 8+y,-x,1-z; 9-y,+x,1-z; 10-x,-y,1-z; 11+x,+y,2-z; 12+y,-x,2-z; 13-y,+x,2-z; 14-x,-Y,2-z.

Table S2 The synthesis schemes for crystalline NiPMo₁₂.

Unit (mg)	PMo ₁₂	Ni(NO ₃) ₂	1,2,4-trz	NH ₄ VO ₃	surfactant	Product
No.1	300	150	65	36	0	No crystal
No.2	300	150	65	36	PEG-2000	NiPMo ₁₂
No.3	300	150	65	36	PEG-1500	NiPMo ₁₂
No.4	300	150	65	36	PEG-800	NiPMo ₁₂
No.5	300	150	65	36	PEG-400	NiPMo ₁₂
No.6	300	150	65	36	SDBS	No crystal
No.7	300	150	65	36	PVP	No crystal
No.8	300	150	65	0	PEG*	No crystal
No.9	SiW ₁₂	150	65	36	PEG-1500*	NiW ₆ O ₁₉
No.10	SiW ₁₂	150	65	36	SDBS	No crystal
No.11	SiW ₁₂	150	65	36	PVP	No crystal

* PEG: 2000, 1500, 800, 400

Table S3 Crystallographic data and structural refinements for [Ni₃(1,2,4Tri)₆(H₂O)₈][H₂W₆O₁₉]₂.

Compounds	[Ni ₃ (1,2,4Tri) ₆ (H ₂ O) ₈][H ₂ W ₆ O ₁₉] ₂
Chemical formula	C ₁₂ H ₁₂ N ₁₈ Ni ₃ O ₄₆ W ₁₂
Formula weight	3526.55
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 21/ <i>n</i>
a(Å)	11.942(4)
b(Å)	20.015(7)
c(Å)	14.729(5)
α(°)	90
β(°)	99.586(6)
γ(°)	90
V(Å ³) / Z	3471(2) / 2
Density (g·cm ⁻³)	2.734
Abs coeff. (mm ⁻¹)	5.793
F(000)	3100.0
Data collect θ range	1.732-27.631
Reflns collected	20726
Independent reflns /R _{int}	7864/0.0612
Data/restraints/parameters	7864 / 16 / 412

Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\delta(I)$]	$R_1 = 0.0707, wR_2 = 0.2109$
R indices (all data)	$R_1 = 0.1247, wR_2 = 0.2451$
Largest diff. peak and hole (e.Å ⁻³)	7.913 and -6.013

$$R_1 = \frac{\sum(|F_0| - |F_c|)}{\sum|F_0|}, wR_2 = \frac{\sum w(|F_0|^2 - |F_c|^2)^2}{\sum w(|F_0|^2)^2}^{1/2}$$