Steam-assisted assemblies of {Ni₆PW₉}-based inorganic-organic hybrid

chains: synthesis, crystal structures and properties

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complex	1	2	3			
Formula	$C_{18}H_{31}N_{11}Ni_7O_{45}PW_9$	$C_{12}H_{22}N_6Ni_6O_{45}PSW_9$	$C_{18}H_{0.50}N_4NaNi_7O_{90}P_2W_{21}$			
М	3351.42	3147.51	6238.58			
т/к	296 (2)	296(2)	294(2)			
Crystal system	orthorhombic	orthorhombic	Triclinic			
Space group	P212121	P212121	P-1			
a/Å	13.407(5)	13.280(4)	12.947(3)			
b/Å	14.365(5)	19.351(6)	20.737(5)			
c/Å	35.826(13)	23.254(7)	22.751(4)			
α / °	90	90	97.442			
β / °	90	90	90.630			
γ/°	90	90	93.308			
V/Å ³	6900(4)	5976(3)	6045(2)			
Z	4	4	2			
ρ _{calcd} g/cm ³	3.226	3.498	3.427			
µ/mm⁻¹	16.923	19.255	21.072			
F(000)	6152	5712	5532			
θRange/°	2.154 - 29.757	1.766 - 24.788	2.486 to 25.149			
Reflections collected	29574	32048	172794			
Independent reflections	18097	10227	21441			
R _{int}	0.0474	0.1023	0.0952			
Goodness-of-fit on F ²	1.009	1.023	1.030			
R ₁ [I>=2σ (I)] ^a	0.0436	0.0546	0.0893			
wR ₂ (all data) ^b	0.0989	0.1442	0.2539			
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} . {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}.$						

Table S1. Crystal Data and Structure Refinements for 1-3.

General Considerations. Na₉[A- α -PW₉O₃₄]·7H₂O was synthesized according to the literature method (*Inorg. Chem.* 1977, *16*, 2115). All commercially obtained reagent, including H₂N-bdc, tda, 1,4-bdc, en, sodium acetate, NiCl₂·6H₂O, NaOH, and HCl were purchased from Aldrich and used without further purification. Deionized water was used throughout the study. A pHS-25B pH meter was used for pH measurements.

Single-crystal X-ray diffraction: Single-crystal X-ray diffraction data for **1-3** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 296(2) K. Absorption corrections were applied using multiscan technique and performed by using the SADABS program¹. The structures of **1-3** were solved by direct methods and refined on F_2 by full-matrix leastsquares methods by using the SHELXTL package.² All the non-hydrogen atoms were refined anisotropically. The numbers of lattice water molecules and counter cations for **1-3** was estimated by the results of elemental analyses, TG curves, and calculations of electron count in the voids with SQUEEZE³. CCDC 1856071 (**1**), 1856072 (**2**), and 1856073 (**3**) contain the supplementary crystallographic data for this paper.

References:

[1] Sheldrick, G. SADABS; ver. 2.10; University of Gottingen: Göttingen, Germany,2003.

[2] Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structure; University of Gottingen: Göttingen, Germany, **1993**.

[3] Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, **2003**.

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Ni(1)-O(2)	1.991(12)	Ni(1)-O(1)	2.020(11)	Ni(1)-O(5)	2.028(11)	Ni(1)-O(6)#1	2.077(11)
Ni(1)-O(4)	2.087(12)	Ni(1)-O(14)	2.220(11)	Ni(2)-O(3)	1.994(11)	Ni(2)-O(2)	2.018(11)
Ni(2)-O(26)	2.040(13)	Ni(2)-O(20)	2.060(12)	Ni(2)-O(10)	2.072(11)	Ni(2)-O(14)	2.217(12)
Ni(3)-O(29)	2.022(12)	Ni(3)-O(2)#2	2.043(10)	Ni(3)-N(2)	2.048(16)	Ni(3)-O(5)#2	2.077(12)
Ni(3)-N(3)	2.112(15)	Ni(3)-O(10)#2	2.171(11)	Ni(4)-O(3)	1.964(12)	Ni(4)-O(1)	2.026(11)
Ni(4)-O(38)	2.041(12)	Ni(4)-O(8)	2.044(13)	Ni(4)-O(18)	2.076(12)	Ni(4)-O(14)	2.159(11)
Ni(5)-O(1)	2.017(12)	Ni(5)-N(1)	2.057(17)	Ni(5)-N(4)	2.088(17)	Ni(5)-O(4)	2.122(12)
Ni(5)-O(30)	2.136(15)	Ni(5)-O(8)	2.182(12)	Ni(6)-O(3)	1.997(11)	Ni(6)-N(5)	2.050(17)
Ni(6)-O(18)	2.055(12)	Ni(6)-N(6)	2.091(16)	Ni(6)-O(33)	2.117(12)	Ni(6)-O(20)	2.274(12)

Table S2. Selected bond lengths of Ni-O distance (Å) for 1

Table S3. Selected bond lengths of Ni-O distance (Å) for 2

Ni(1)-O(4)	1.948(16)	Ni(1)-O(3)	2.037(15)	Ni(1)-O(27)	2.071(15)	Ni(1)-O(24)	2.091(17)
Ni(1)-O(41)	2.095(16)	Ni(1)-O(1)	2.173(15)	Ni(2)-O(8)	1.992(15)	Ni(2)-O(7)	2.035(17)
Ni(2)-O(31)	2.043(15)	Ni(2)-O(4)	2.056(16)	Ni(2)-O(18)	2.070(16)	Ni(2)-O(1)	2.206(16)
Ni(3)-O(4)	2.005(15)	Ni(3)-O(10)	2.052(17)	Ni(3)-N(2)	2.08(2)	Ni(3)-N(1)	2.09(2)
Ni(3)-O(31)	2.110(16)	Ni(3)-O(27)	2.228(16)	Ni(4)-O(8)	2.018(16)	Ni(4)-N(4)	2.04(2)
Ni(4)-O(29)	2.085(17)	Ni(4)-N(5)	2.09(2)	Ni(4)-O(16)	2.116(16)	Ni(4)-O(18)	2.177(15)
Ni(5)-O(36)	1.996(16)	Ni(5)-O(3)	2.025(16)	Ni(5)-O(8)	2.042(16)	Ni(5)-O(19)	2.068(16)
Ni(5)-O(16)	2.085(16)	Ni(5)-O(1)	2.200(15)	Ni(6)-O(3)	2.013(16)	Ni(6)-N(3)	2.07(2)
Ni(6)-N(6)	2.08(2)	Ni(6)-O(26)	2.090(16)	Ni(6)-O(19)	2.100(16)	Ni(6)-O(24)	2.260(15)

Ni(0M)-O(00Y)	2.02(2)	Ni(0M)-O(01L)	2.03(2)	Ni(0M)-O(01B)	2.03(2)	Ni(0M)-O(016)	2.05(2)
Ni(0M)-O(010)	2.06(2)	Ni(0M)-O(00V)	2.19(2)	Ni(0N)-O(00Z)	2.00(2)	Ni(0N)-O(01O)	2.04(2)
Ni(0N)-O(01K)	2.05(2)	Ni(0N)-O(010)	2.05(2)	Ni(0N)-O(00X)	2.07(2)	Ni(0N)-O(00V)	2.18(2)
Ni(00)-O(00Y)	1.98(2)	Ni(00)-O(00Z)	2.00(2)	Ni(00)-O(017)	2.07(2)	Ni(00)-O(012)	2.07(2)
Ni(00)-O(01A)	2.08(2)	Ni(0O)-O(00V)	2.24(2)	Ni(0P)-O(00Z)	2.04(2)	Ni(0P)-O(01Q)	2.06(2)
Ni(0P)-O(01K)	2.07(2)	Ni(0P)-N(02H)	2.10(3)	Ni(OP)-N(O2L)	2.10(3)	Ni(0P)-O(017)	2.26(2)
Ni(0Q)-O(00Y)	2.05(2)	Ni(0Q)-O(019)	2.05(2)	Ni(0Q)-N(025)	2.05(3)	Ni(0Q)-N(02D)	2.10(3)
Ni(0Q)-O(01L)	2.11(2)	Ni(0Q)-O(01A)	2.25(2)	Ni(0R)-O(010)	2.03(2)	Ni(0R)-N(03D)	2.07(3)
Ni(0R)-N(02N)	2.07(3)	Ni(0R)-O(02M)	2.08(2)	Ni(0R)-O(016)	2.14(2)	Ni(0R)-O(00X)	2.15(2)
Ni(0S)-N(03G)	2.05(4)	Ni(0S)-N(18)	2.05(3)	Ni(0S)-N(10)	2.09(4)	Ni(0S)-O(036	2.12(3)
Ni(0S)-N(12)	2.12(3)	Ni(0S)-O(0AA)	2.21(3)				

Table S4. Selected bond lengths of Ni-O distance (Å) for 3



Fig. S1 Two analogous hybrid {Ni₆PW₉} SBUs in **2** (a) and {[Ni₆(μ_3 -OH)₃(H₂O)(en)₄(B- α -PW₉O₃₄)](tda)} reported by Yang *et al.* (b).



Fig. S2 The W=O-Ni linkage of {(Ni₆PW₉)PW₁₂} monomer.



Fig. S3 Schematic diagram of the reaction vessels for POM hybrids synthesis. Left: hydrothermal synthesis, and right: SAC method. Ligands: tda, H₂N-bdc, or 1,4-bdc.

Here, three POM hybrids are made through the SAC method. During this synthesis, the starting material is a solid phase hybrid containing desired POMs elements that is physically separated from a small quantity of water in an autoclave reactor. We called this SAC device a holed-Teflon plate (home-built) inside a Teflonlined autoclave in our main text. Schematic diagram (Fig. S3) provides well-defined reaction vessels for both hydro(solvo)thermal and SAC methods. Unlike the hydrothermal method in which the materials contact directly with water, the solid and liquid phase in the SAC method is apparent separation, and therefore the solid phase presents a concentration gradient with the transportion of water vapor. Environmentally friendly aqueous medium is normally used in SAC method according to many other reported works (for example, Microporous Mesoporous Mater., 2002, 56, 1–10; Bull. Chem. Soc. Jpn., 2010, 83, 69–74; Microporous Mesoporous Mater., 2013, **182**, 40–49). From the properties of such water solution, during our synthesis, it is estimated that the autogenous pressure (7.9147 atm) inside the Teflonlined autoclaves at 170°C would be sufficient to make H₂O steam fill it. Simultaneously, transformation (solid phase) may proceed through the intermediate formation of a eutectic mixture. Once H_2O steam is formed, it can penetrate into the surface of eutectic mixtures. In this case, because the amount of water added was insufficient to dissolve the solid reactants, the water steam formed under the autogenous pressure actually still interacted with eutectic mixtures, hence the reaction, by nature, is vapor-solid mechanism identical to that of SAC (J. Mater. Chem., 2010, 20, 6764–6771; J. Mater. Chem. A, 2014, 2, 1247–1251). So this process can be viewed as a SAC mechanism. Besides, our group succeeded in obtaining POM-encapsulating metal azolate materials in this SAC manner for the first time (Chem. Eur. J., 2015, 21, 13058–13064). It is meaningful to adopt this alternative method to prepare {Ni₆XW₉}-based inorganic-organic hybrids.



Fig. S4 Thermogravimetric (TG) curves of ${\bf 1,2}$ and ${\bf 3.}$



Fig. S5 CVs of **2** and **3** in aqueous 0.5 M H_2SO_4/Na_2SO_4 solutions (pH = 4.80) at different scan rates from inside to out: 30, 50, 100, and 200 mV s⁻¹.



Fig. S6 $(\alpha hv)^{1/2}$ versus hv curve of **1** (a) , **2** (b) and **3** (c). The red dashed lines are the tangents of the curves. The intersection value is the band gap.



Fig. S7 IR curves of 1, 2 and 3.