Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting materials

Table S1. Parameters of 0.4 g (C = 0.029 M), 1 day

	$K_7[HNb_6O_{19}]\cdot 13H_2O$	H_2WO_4	Final pH
1:1	0.4 g	0.073	11.05
1:2	0.4 g	0.146	9.40
1:3	0.4 g	0.222	9.01
1:4	0.4 g	0.292	8.70
1:5	0.4 g	0.365	8.52
1:6	0.4 g	0.438	8.33

Table S2. Parameters of 0.4 g (C = 0.029 M), 2 days

	$K_7[HNb_6O_{19}]\cdot 13H_2O$	H_2WO_4	Final pH
1:1	0.4 g	0.073	11.05
1:2	0.4 g	0.146	9.53
1:3	0.4 g	0.222	9.06
1:4	0.4 g	0.292	8.66
1:5	0.4 g	0.365	8.43
1:6	0.4 g	0.438	8.29

Table S3. Parameters of 0.1 g (C = 0.009 M), 1 day

	$K_7[HNb_6O_{19}]\cdot 13H_2O$	H_2WO_4	Final pH
1:1	0.1 g	0.018	10.23
1:2	0.1 g	0.037	9.03
1:3	0.1 g	0.056	8.48
1:4	0.1 g	0.073	8.20
1:5	0.1 g	0.091	7.88
1:6	0.1 g	0.110	7.44

Table S4. Parameters of 0.1 g (C = 0.0087 M), 1 day

	$K_6[HTeNb_5O_{19}]\cdot 13H_2O$	H_2WO_4	Final pH
1:1	0.1 g	0.017	8.71
1:2	0.1 g	0.035	8.36
1:3	0.1 g	0.052	7.95
1:4	0.1 g	0.069	7.64
1:5	0.1 g	0.087	7.20
1:6	0.1 g	0.104	6.71

Table S5. Parameters of 0.1 g (C = 0.0087 M), 2 days

	$K_6[HTeNb_5O_{19}]\cdot 13H_2O$	H_2WO_4	Final pH
1:1	0.1 g	0.017	8.53
1:2	0.1 g	0.035	8.37
1:3	0.1 g	0.052	7.97
1:4	0.1 g	0.069	7.56
1:5	0.1 g	0.087	7.06
1:6	0.1 g	0.104	6.54

Table S6. Parameters of 0.1 g (C = 7 mM), 12 hours, 60°C

	$H_3PMo_{12}O_{40}$	$(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$	Final pH
1:1	0.1 g	0.022 g	11.05
1:2	0.1 g	0.043 g	9.53
1:3	0.1 g	0.065 g	9.06

Table S7. Parameters of 12 hours, 60°C, pH = 3, 5 mL of water

	$Na_2MoO_4\cdot 2H_2O$	$(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$	H_3PO_4
12:1:1	0.145 g	0.019 g	0.012 mL
12:2:1	0.145 g	0.039 g	0.012 mL
12:3:1	0.145 g	0.059 g	0.012 mL

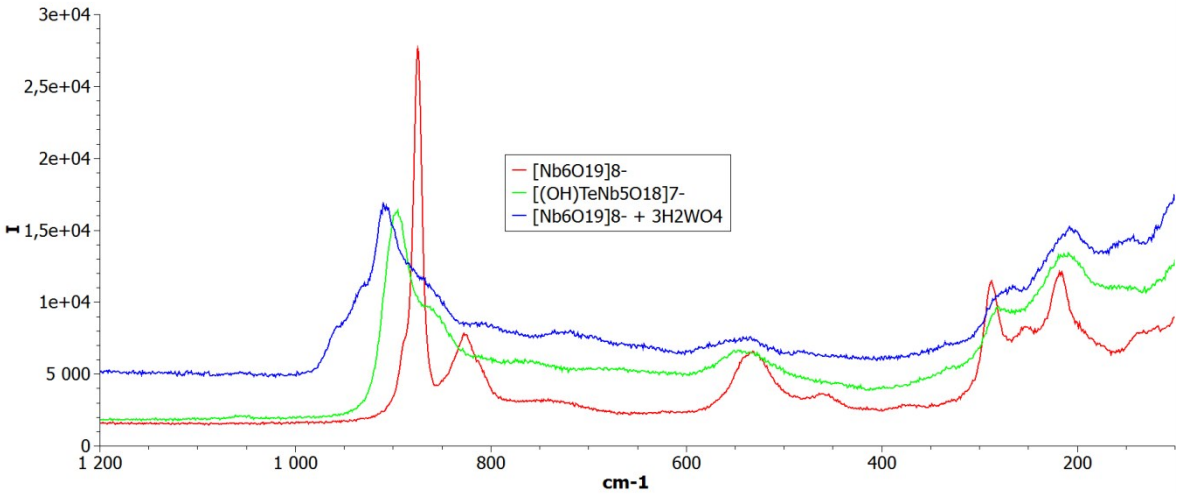

Fig. S1. Raman spectra for $[Nb_6O_{19}]^{8-}$, $[(OH)TeNb_5O_{18}]^{7-}$ and mixture isolated after the reaction of $[Nb_6O_{19}]^{8-}$ with 3 eq. of H_2WO_4.

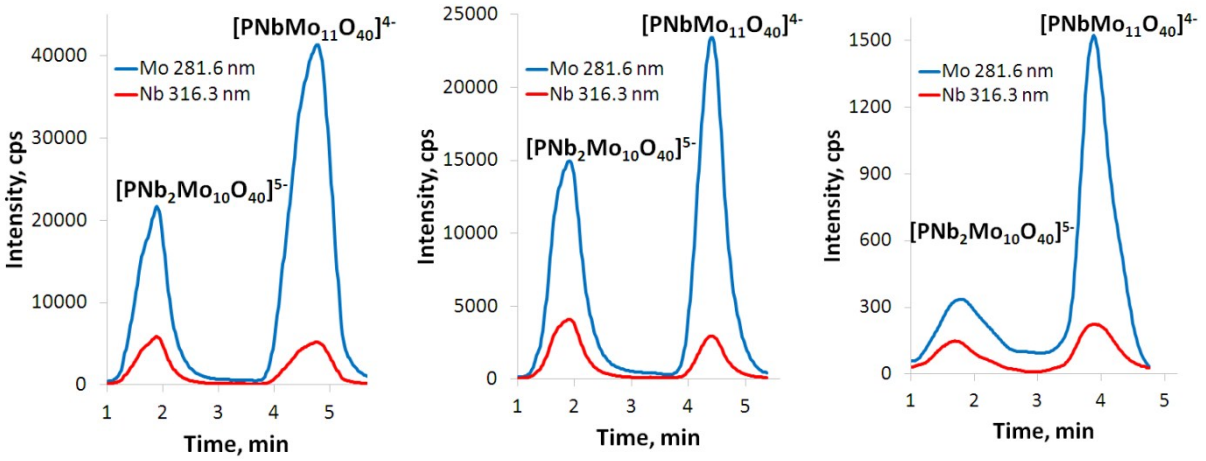

Fig. S2. The HPLC-ICP-AES chromatogram of POM mixture in coordinates “retention time–line intensity”. PMo_{12}/Nb-Ox ratio increases from 1:1 to 1:3 (from left to right).

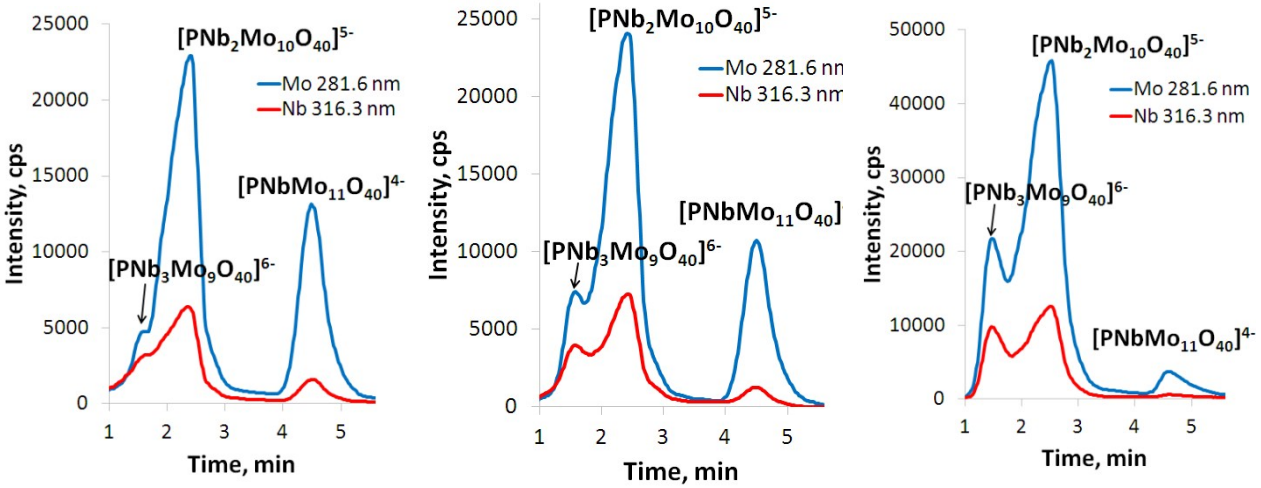

Fig. S3. The HPLC-ICP-AES chromatogram of POM mixture in coordinates “retention time–line intensity”. Na_2MoO_4/Nb-Ox ratio increases from 12:1 to 12:3 (from left to right).

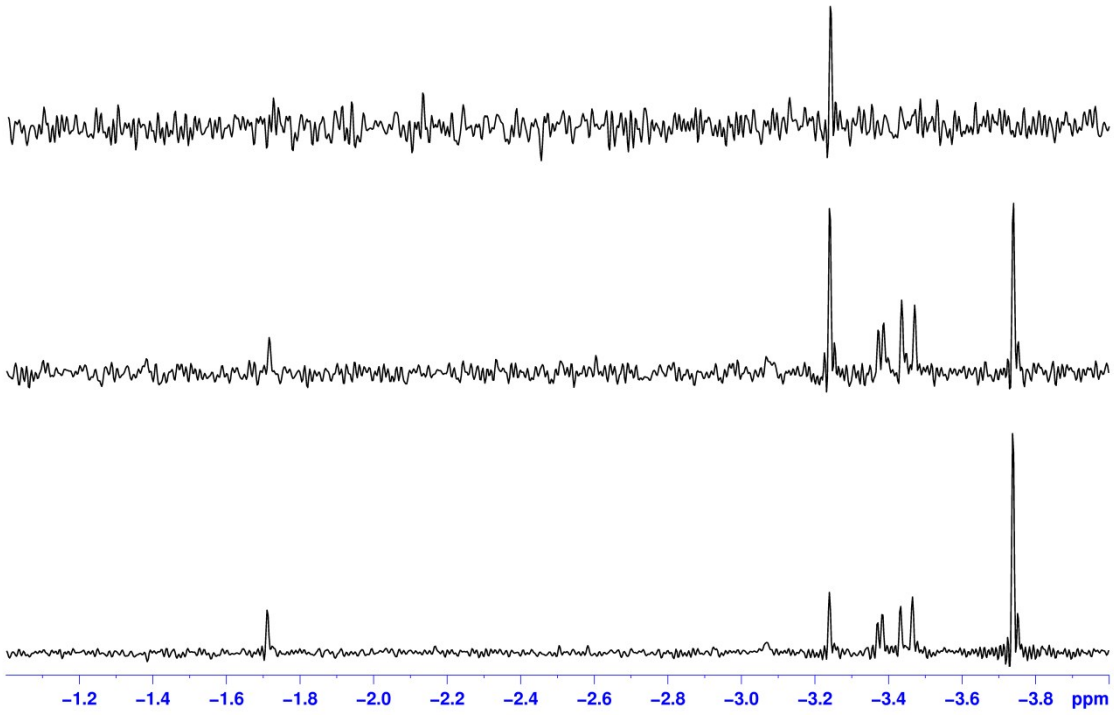

Fig. S4. ^{31}P NMR spectra of the reaction products of phosphomolybdic acid niobium oxalate. Increasing of Nb-Ox ratio from bottom to up. 4 isomers of $[PMo_{10}Nb_2O_{40}]^{5-}$ with center at -3.42 ppm. -3.25 ppm possibly peak from $[PMo_{11}NbO_{40}]^{4-}$. -3.75 ppm $[PMo_{12}O_{40}]^{3-}$.

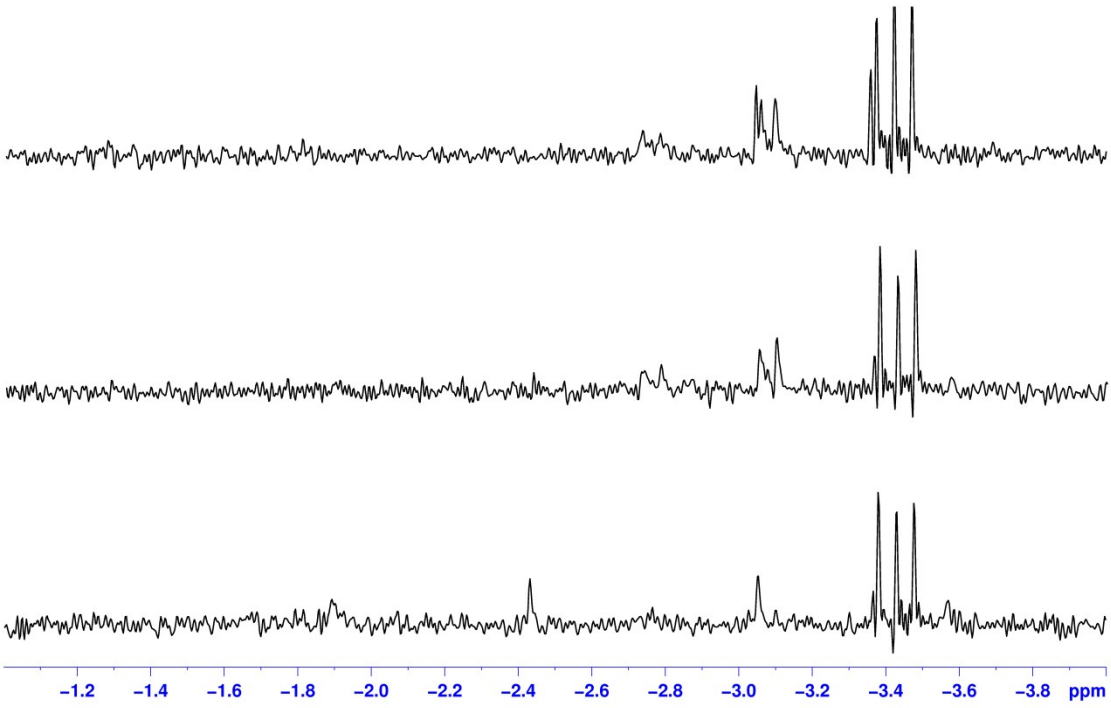

Fig. S5. ^{31}P NMR spectra of the self-assembly reaction products (area of $[PMo_{10}Nb_2O_{40}]^{5-}$ and $[PMo_9Nb_3O_{40}]^{6-}$ isomers). Increasing of Nb-Ox ratio from bottom to up.