Supporting information

Table S1. BVS results of the independent W atoms in compounds **1**-**2** and **4**-**5**

Compound **1**			
W(1)	6.27	W(7)	6.14
W(2)	6.23	W(8)	5.74
W(3)	6.78	W(9)	6.64
W(4)	5.98	W(10)	6.59
W(5)	6.48	W(11)	5.67
W(6)	6.67	W(12)	6.43
Compound **2**			
W(1)	6.33	W(5)	6.66
W(2)	6.58	W(6)	6.72
W(3)	6.28	W(7)	6.93
W(4)	6.08	W(8)	5.95
Compound **4**			
W(1)	5.96	W(7)	6.08
W(2)	6.36	W(8)	6.11
W(3)	5.84	W(9)	5.62
W(4)	6.03	W(10)	6.07
W(5)	5.98	W(11)	6.00
W(6)	5.93	W(12)	5.49
Compound **5**			
W(1)	6.07	W(7)	6.23
W(2)	6.11	W(8)	6.16
W(3)	6.26	W(9)	6.05
W(4)	6.17	W(10)	6.16
W(5)	6.10	W(11)	6.17
W(6)	6.14	W(12)	6.05
For compound **1**, **2** and **5**, the equations used for the BVS of W are s=exp[(1.917-r)/0.37], while for compound **4**, the equations used for the BVS of V are $s=10^{(-0.5*(R-R_0)/R)}$, and R_0=1.917.			

Table S2. Crystal Data of Compounds

	Compound **1**	Compound **2**	Compound **4**
Empirical formula	$C_{50}H_{49}O_{52}N_{10}Cu_5Cl_2P_3W_{12}$	$C_{81}H_{104.5}O_{112.75}N_{15}Cu_{4.5}P_2W_{24}$	$C_{72}H_{58}O_{45}N_{12}Zn_2PW_{12}$
Formula weight	4309.15	7852.56	4179.21
Crystal system	triclinic	trigonal	triclinic
Space group	P-1	R-3	P1
a (Å)	10.9802(5)	35.2928(4)	12.0386(11)
b (Å)	12.7843(5)	35.2928(4)	13.6743(12)
c (Å)	15.3506(7)	22.6516(7)	14.7316(13)
α (°)	88.0280(10)	90	105.088(3)
β (°)	84.1660(10)	90	90.564(3)
γ (°)	80.5840(10)	120	97.682(3)
Volume (Å^3)	2114.44(16)	24434.4(9)	2318.0(4)
Z	1	6	1
Dc (Mg·m^{-3})	3.385	3.202	2.994
μ (mm^{-1})	17.696	17.569	15.440
F(000)	1947.0	21204.0	1897.0
2θ for data collection	4.832 to 50.758	4.616 to 50.734	4.776 to 50.834
Reflections collection	19273	24355	21389
Reflections unique	12131	9895	13403
R(int)	0.0599	0.0859	0.0539
Completeness to θ	0.986	0.993	0.990
parameters	1089	777	1210
GOF on F^2	1.045	1.034	1.048
R^a[I>2σ(I)]	R_1= 0.0556	R_1=0.0891	R_1=0.0664
R^b(all data)	ωR_2= 0.1564	ωR_2=0.2724	ωR_2=0.1940

	Compound **5**	Compound **6**
Empirical formula	$C_{48}H_{40}O_{44}N_8Zn_2SiW_{12}$	$C_{40}H_{32}O_{40}N_8Zn_2SiW_{12}$
Formula weight	3797.91	3629.76
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a (Å)	12.2370(9)	13.6089(7)
b (Å)	14.0325(10)	12.1703(5)
c (Å)	22.9061(15)	18.8970(8)
α (°)	83.241(2)	90
β (°)	84.184(2)	93.463(2)
γ (°)	65.508(2)	90
Volume (Å^3)	3548.5(4)	3124.1(2)
Z	2	2
Dc (Mg·m^{-3})	3.554	3.859
μ (mm^{-1})	20.143	22.865
F(000)	3396.0	3220.0
2θ for data collection	4.604 to 50.858	4.906 to 50.812
Reflections collection	33027	20771
Reflections unique	12921	5632
R(int)	0.0563	0.0630
Completeness to θ	0.989	1.134
parameters	1036	439
GOF on F^2	1.058	1.134
R^a[I>2σ(I)]	R_1= 0.0502	R_1=0.1434
R^b(all data)	ωR_2= 0.1432	ωR_2=0.3402

$^aR_1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$. $^b\omega R_2=\{[w(F0_2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

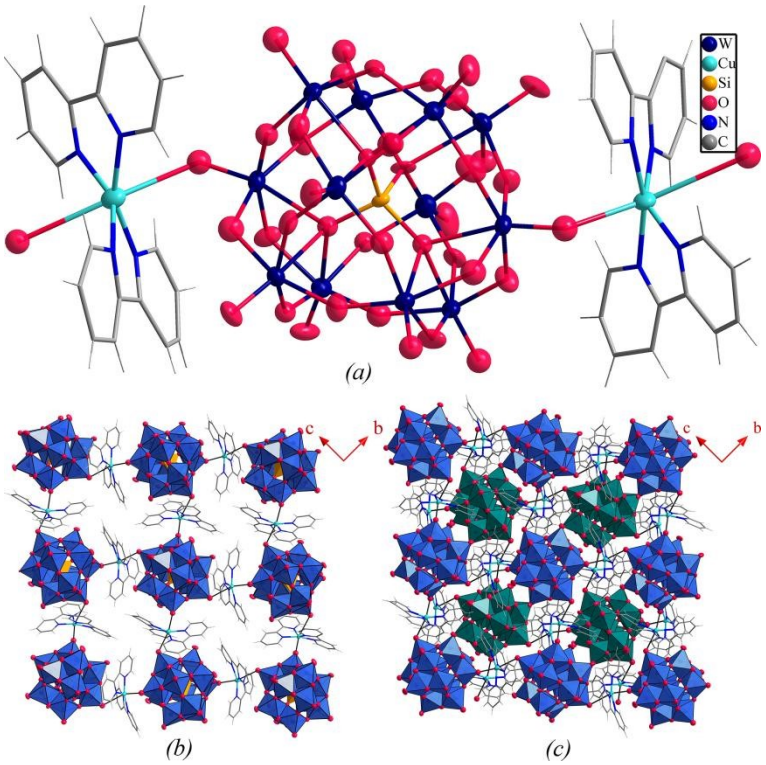

Figure S1. (a) The Ball-stick representation of coordination environment in **3** (b) View of the 2D structure of compound **3**. (c) View of the 3D stacking structure of compound **3**.

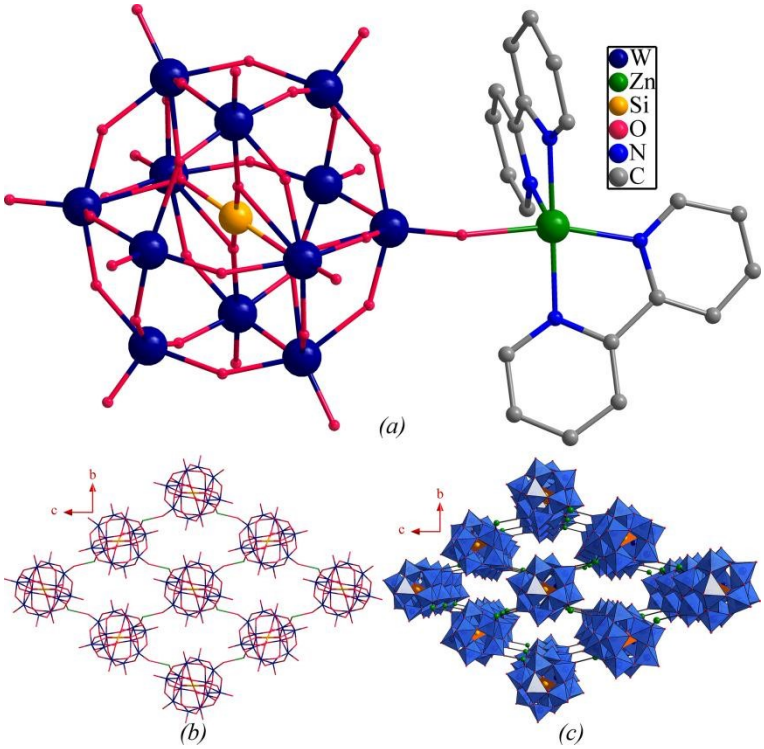

Figure S2. (a) The Ball-stick representation of coordination environment in **6**. (b) View of the 2D structure of compound **6**. (c) View of the 3D stacking structure of compound **6**.

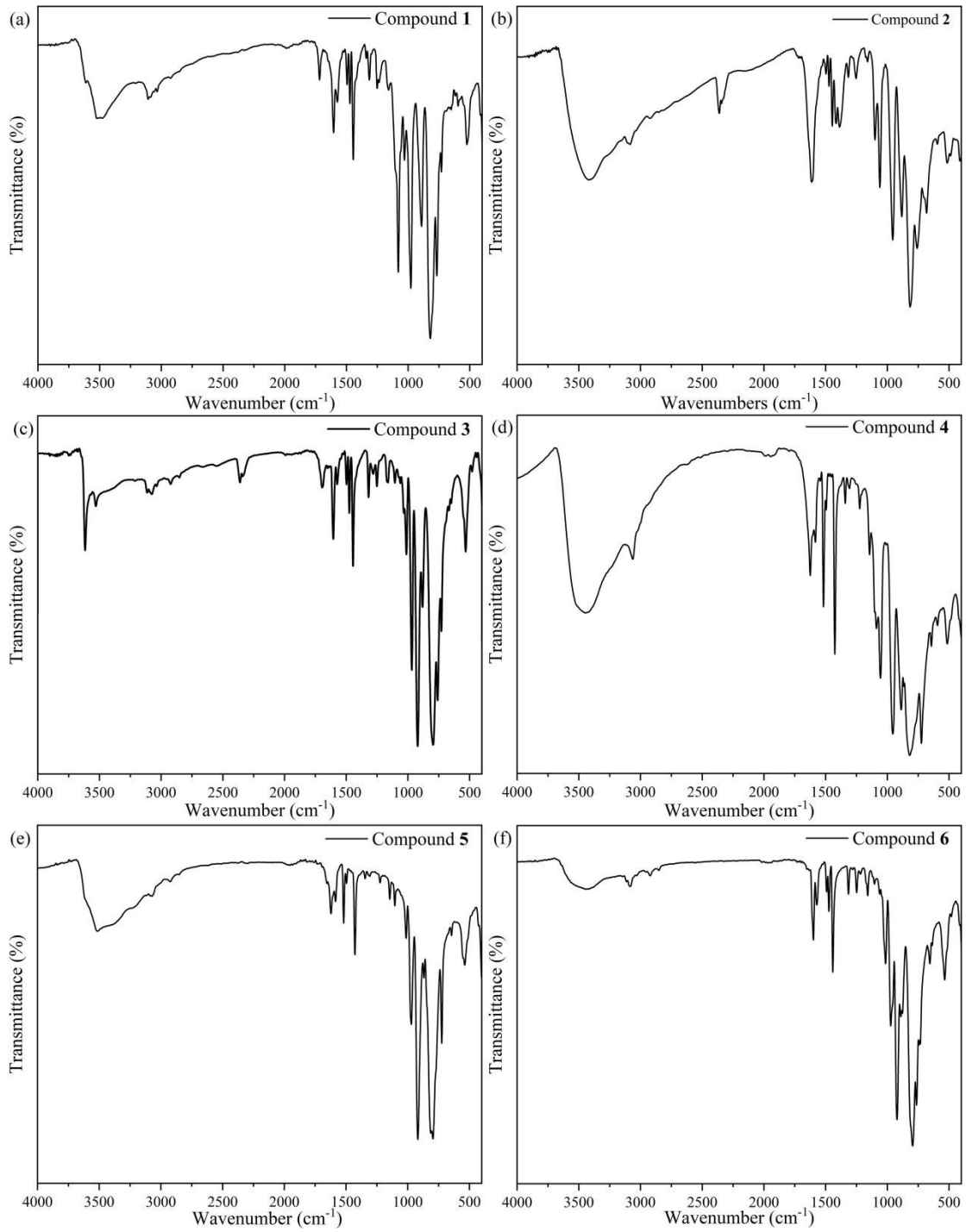

Figure S3. (a-f) FT-IR spectra of compounds **1-6**.

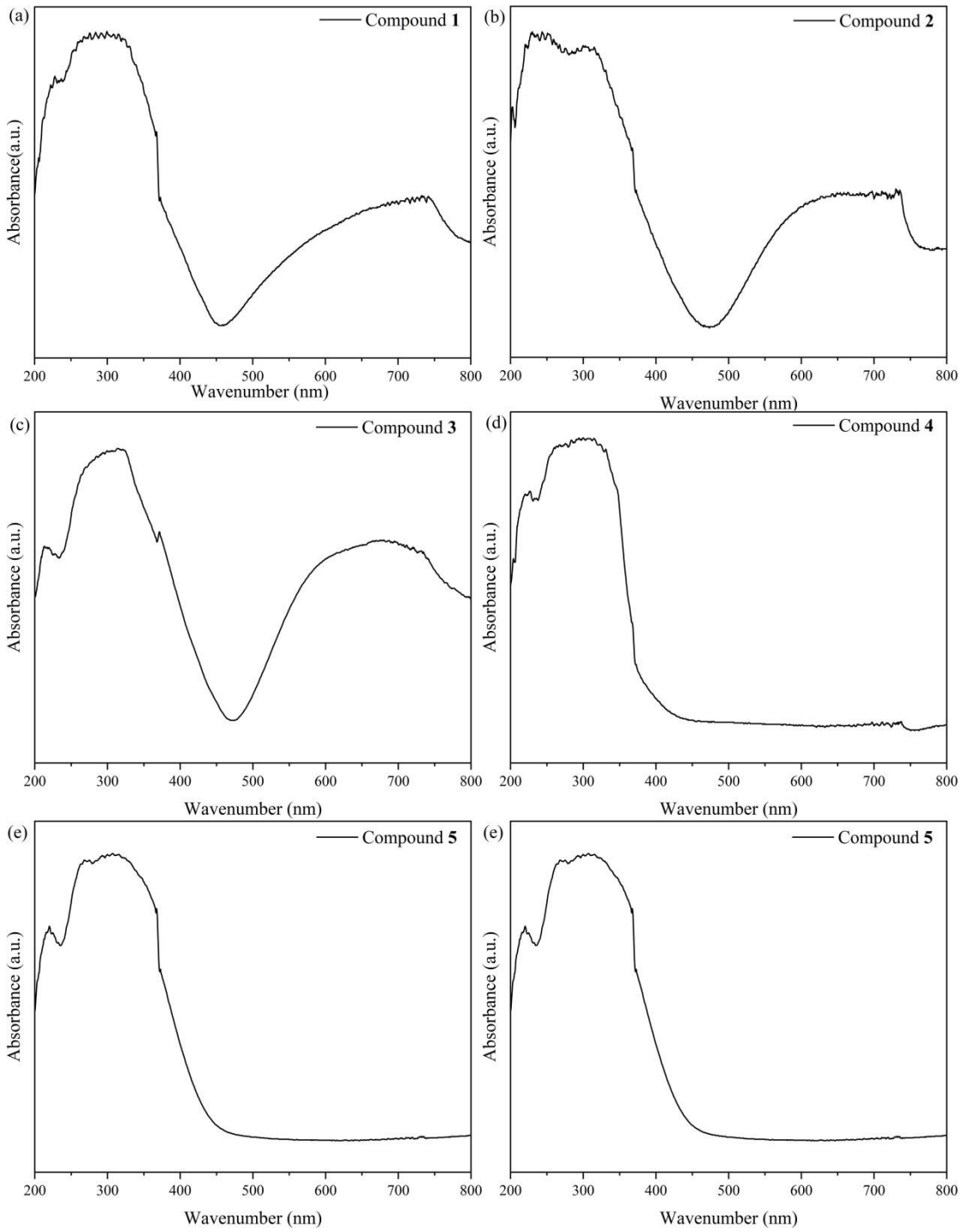

Figure S4. (a-f) FT-IR spectra of compounds **1-6**.

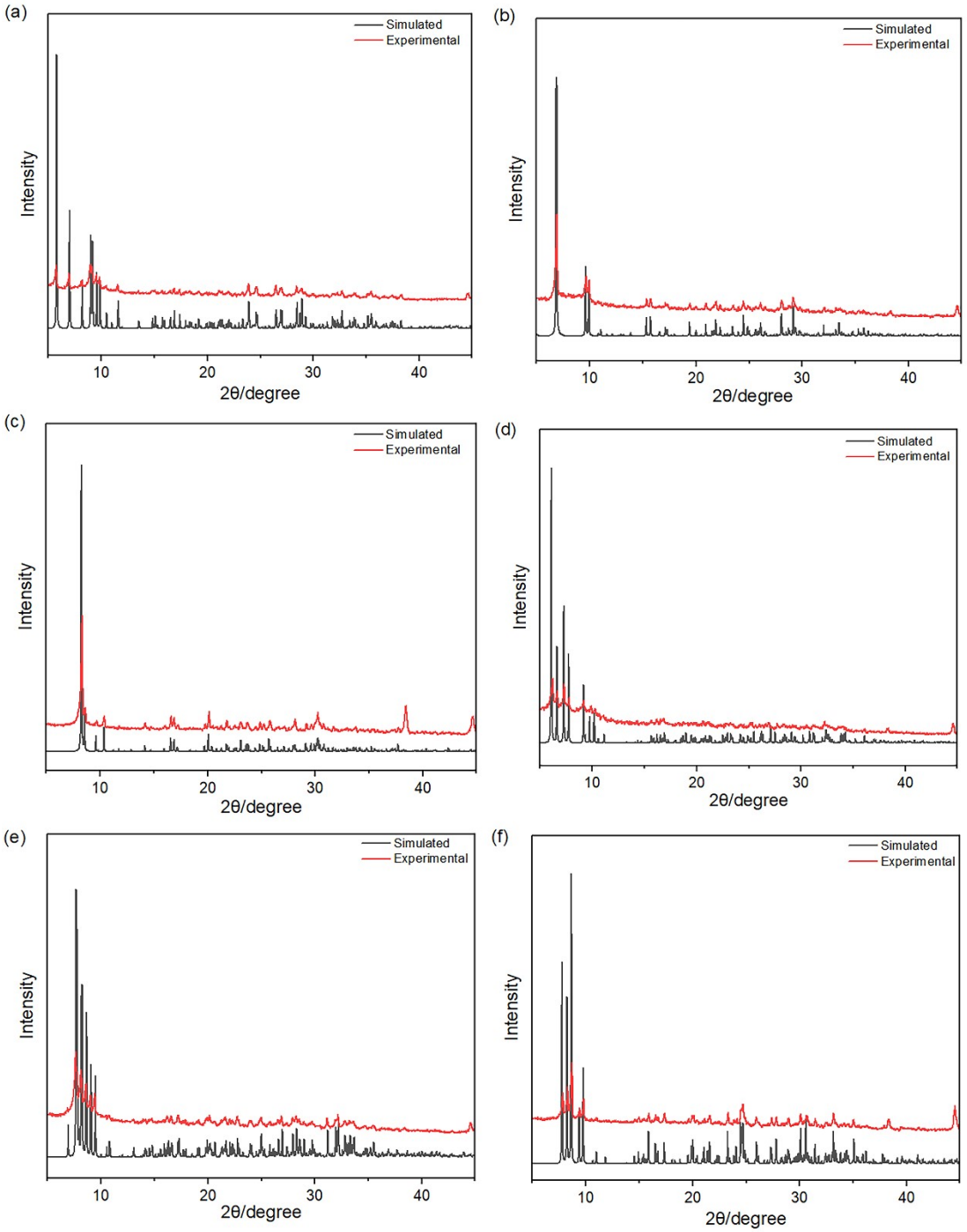

Figure S5. (a-f) the experimental and simulated XRD patterns of compounds **1-6**.

Table S3. Summary of POM-based composite electrodes of three-electrode supercapacitors

electrode	Electrolyte (H_2SO_4)	C_s ($F \cdot g^{-1}$)	current density ($A \cdot g^{-1}$)	references
$[Cu_5(2,2'\text{-bpy})_5(\mu_2\text{-}Cl)_2(PO_4)_2(H_2O)_2][HPW_{12}O_{40}] \cdot 2H_2O$	0.5 M	94.0	1.5	This work
$[Cu_{1.5}(2,2'\text{-bpy})_{1.5}(inic)_2(H_2O)_{1.5}]_3[H_{1.5}PW_{12}O_{40}]_2 \cdot 16.25H_2O$	0.5 M	45.8	1.5	This work
$[Cu(2,2'\text{-bpy})_2]_2[SiW_{12}O_{40}] \cdot 10H_2O$	0.5 M	18.9	1.5	This work
$[Zn(phen)_3]_2[PW^{V}W^{VI}_{11}O_{40}] \cdot 5H_2O$	0.5 M	24.4	1.5	This work
$[Zn(phen)_2(H_2O)]_2[SiW_{12}O_{40}] \cdot 2H_2O$	0.5 M	26.5	1.5	This work
$[Zn(2,2'\text{-bpy})_2]_2[SiW_{12}O_{40}]$	0.5 M	58.9	1.5	This work
$[Ag_{10}(C_2H_2N_3)_8][HVW_{12}O_{40}]$	1 M	93.5	1.5	[1]
$[Ag_{10}(C_2H_2N_3)_6][SiW_{12}O_{40}]$	1 M	47.8	1.5	[1]
$[Ag(C_2H_2N_3)][Ag_{12}(C_2H_2N_3)_9][H_2BW_{12}O_{40}]$	1 M	42.9	1.5	[1]
$(H_2bipy)[Cu^{I}_2(bipy)_2(H_3PMo_{11}CuO_{40})]$	0.5 M	407.7	1.5	[2]
$H[Cu^{I}_2(bipy)_2Cu^{I}(bipy)(\beta\text{-}Mo_8O_{26})]$	0.5 M	373.8	1.5	[2]
$[Cu^{I}H_2(C_{12}H_{12}N_6)(PMo_{12}O_{40})] \cdot [(C_6H_{15}N)(H_2O)_2]$	1 M	249.0	3	[3]
$[Cu^{II}_2(C_{12}H_{12}N_6)_4(PMo^{VI}_9Mo^{V}_3O_{39})]$	1 M	154.5	3	[3]
$(H_2bpe)(Hbpe)_2\{[Cu(pzta)(H_2O)][P_2W_{18}O_{62}]\} \cdot 5H_2O$	1 M	168	5	[4]
$[\{Ag(phen)_2\}_4\{Ag(phen)\}_2(H_2BW_{12}O_{40})_2]$	1 M	1647	2.16	[5]
$H_3[Cu_2(4\text{-dpye})_2(PMo_{12}O_{40})]$	0.1 M	260.0	0.5	[6]
$H_3[Cu_2(4\text{-dpye})_2(PMo_{12}O_{40})]$	0.1 M	196.6	0.5	[6]
$[Co(phen)_3]_2[AsW_{12}O_{40}] \cdot 2H_2O$	0.5 M	643.3	3	[7]
$(Hbipy)_2\ [Mn(bipy)_3]_2[As_2W_{18}O_{62}]$	0.5 M	789.5	3	[7]
$(H_2bib)_5[Co_4(H_2O)_2(AsW_9O_{34})_2] \cdot 2H_2O$	0.5 M	819.4	3	[7]

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