In-depth understanding of the electrochemical energy storage efficiency between a series of new 3d-4d mixed metal polyoxometalates: Experimental and Theoretical Investigations

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Supporting Information

Table S1. Bond Valence Sum (BVS) calculations for vanadium and molybdenum atoms in polyanion **1**, $[(Mo^{VI}_2O_5)_2(V^{III}O_2)\{O_3P\text{-}C(O)(CH_2\text{-}4\text{-}C_5H_4N)\text{-}PO_3\}_2]^{7-}$.

Bond	Bond Length	Bond Valence	Bond Valence Sum
V1-O2P2	2.019 (5)	0.474	∑(V1) = 3.029
V1-O2P1	2.012 (5)	0.472	
V1-O1V1	1.952 (5)	0.568	
V1-O2P2	2.019 (5)	0.474	
V1-O2P1	2.012 (5)	0.472	
V1-O1V1	1.952 (5)	0.568	

Bond	Bond Length	Bond Valence	Bond Valence Sum
Mo1-O1P1	2.399 (5)	0.265	∑(Mo1) = 6.078
Mo1-O12	1.942 (5)	0.909	
Mo1-O1P2	2.340 (5)	0.310	
Mo1-O1V1	1.865 (5)	1.121	
Mo1-O1B	1.701 (6)	1.747	
Mo1-O1A	1.704 (6)	1.730	

Bond	Bond Length	Bond Valence	Bond Valence Sum
Mo2-O1P1	2.305 (5)	0.341	∑(Mo2) = 6.125
Mo2-O1P2	2.333 (5)	0.316	
Mo2-O12	1.789 (6)	1.375	
Mo2-O1C	2.037 (5)	0.703	
Mo2-O2B	1.711 (6)	1.695	
Mo2-O2A	1.712 (6)	1.693	

Table S2. Bond Valence Sum (BVS) calculations for chromium and molybdenum atoms in polyanion **2**, $[(Mo^{VI}_2O_5)_2(Cr^{III}O_2)\{O_3P\text{-}C(O)(CH_2\text{-}4\text{-}C_5H_4N)\text{-}PO_3\}_2]^{7-}$.

Bond	Bond Length	Bond Valence	Bond Valence Sum
Cr1-O1CR	1.938 (2)	0.558	∑(Cr1) = 3.088
Cr1-O1CR	1.938 (2)	0.558	
Cr1-O2P1	1.989 (2)	0.489	
Cr1-O2P1	1.989 (2)	0.489	
Cr1-O1P2	1.985 (2)	0.497	
Cr1-O1P2	1.985 (2)	0.497	

Bond	Bond Length	Bond Valence	Bond Valence Sum
Mo1-O1B	1.720 (3)	1.657	∑(Mo1) = 5.958
Mo1-O1A	1.733 (3)	1.602	
Mo1-O12	2.036 (3)	0.705	
Mo1-O1CR	1.787 (2)	0.382	
Mo1-O2P2	2.347 (2)	0.304	
Mo1-O3P1	2.343 (2)	0.308	

Bond	Bond Length	Bond Valence	Bond Valence Sum
Mo2-O2B	1.720 (3)	1.656	∑(Mo2) = 5.949
Mo2-O2A	1.714 (3)	1.684	
Mo2-O12	1.853 (3)	1.156	
Mo2-O1C	1.944 (2)	0.904	
Mo2-O2P2	2.370 (2)	0.286	
Mo2-O3P1	2.402 (2)	0.266	

Table S3. Bond Valence Sum (BVS) calculations for vanadium and molybdenum atoms in polyanion **3**, $[(Mo^{VI}_2O_5)_2(Mn^{III}O_2)\{O_3P\text{-}C(O)(CH_2\text{-}4\text{-}C_5H_4N)\text{-}PO_3\}_2]^{7-}$.

Bond	**Bond Length**	**Bond Valence**	**Bond Valence Sum**
Mn1-O1MN	1.919 (3)	0.654	∑(Mn1) = 2.974
Mn1-O1P2	2.028 (3)	0.487	
Mn1-O1P1	2.152 (3)	0.346	
Mn1-O1MN	1.919 (3)	0.654	
Mn1-O1P2	2.028 (3)	0.487	
Mn1-O1P1	2.152 (3)	0.346	

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Bond	**Bond Length**	**Bond Valence**	**Bond Valence Sum**
Mo1-O1B	1.724 (4)	1.639	∑(Mo1) = 5.960
Mo1-O1A	1.725 (4)	1.634	
Mo1-O1MN	1.801 (3)	1.331	
Mo1-O12	2.026 (4)	0.726	
Mo1-O2P2	2.331 (3)	0.318	
Mo1-O1P1	2.338 (3)	0.312	

Bond	**Bond Length**	**Bond Valence**	**Bond Valence Sum**
Mo2-O2A	1.707 (4)	1.718	∑(Mo2) = 6.019
Mo2-O2B	1.720 (4)	1.657	
Mo2-O12	1.851 (4)	1.162	
Mo2-O2P1	2.360 (3)	0.294	
Mo2-O2P2	2.394 (3)	0.268	
Mo2-O1C	1.937 (3)	0.920	

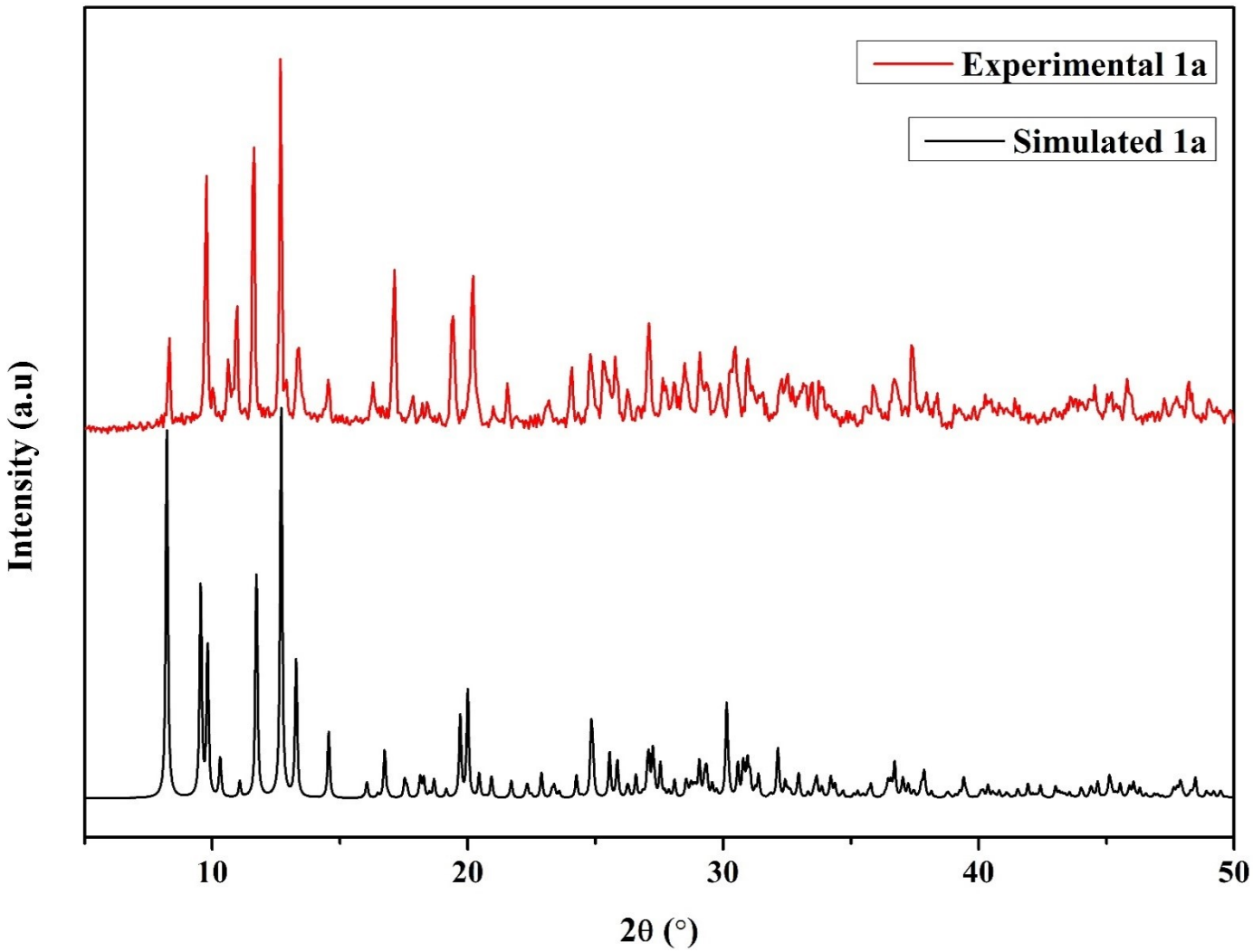


Figure S1. Comparative PXRD of compound **1a** (simulated *vs* experimental).

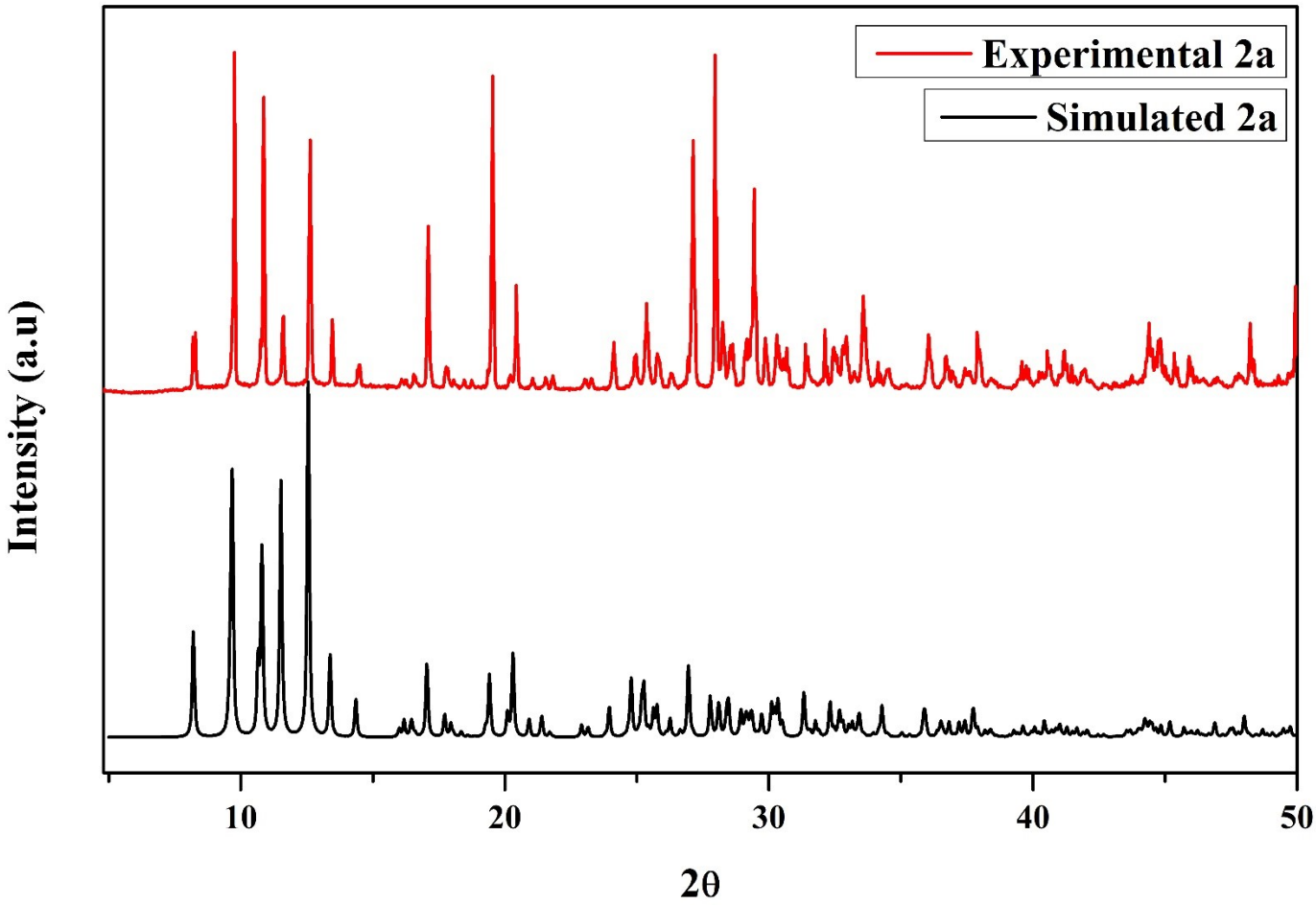


Figure S2. Comparative PXRD of compound **2a** (simulated *vs* experimental).

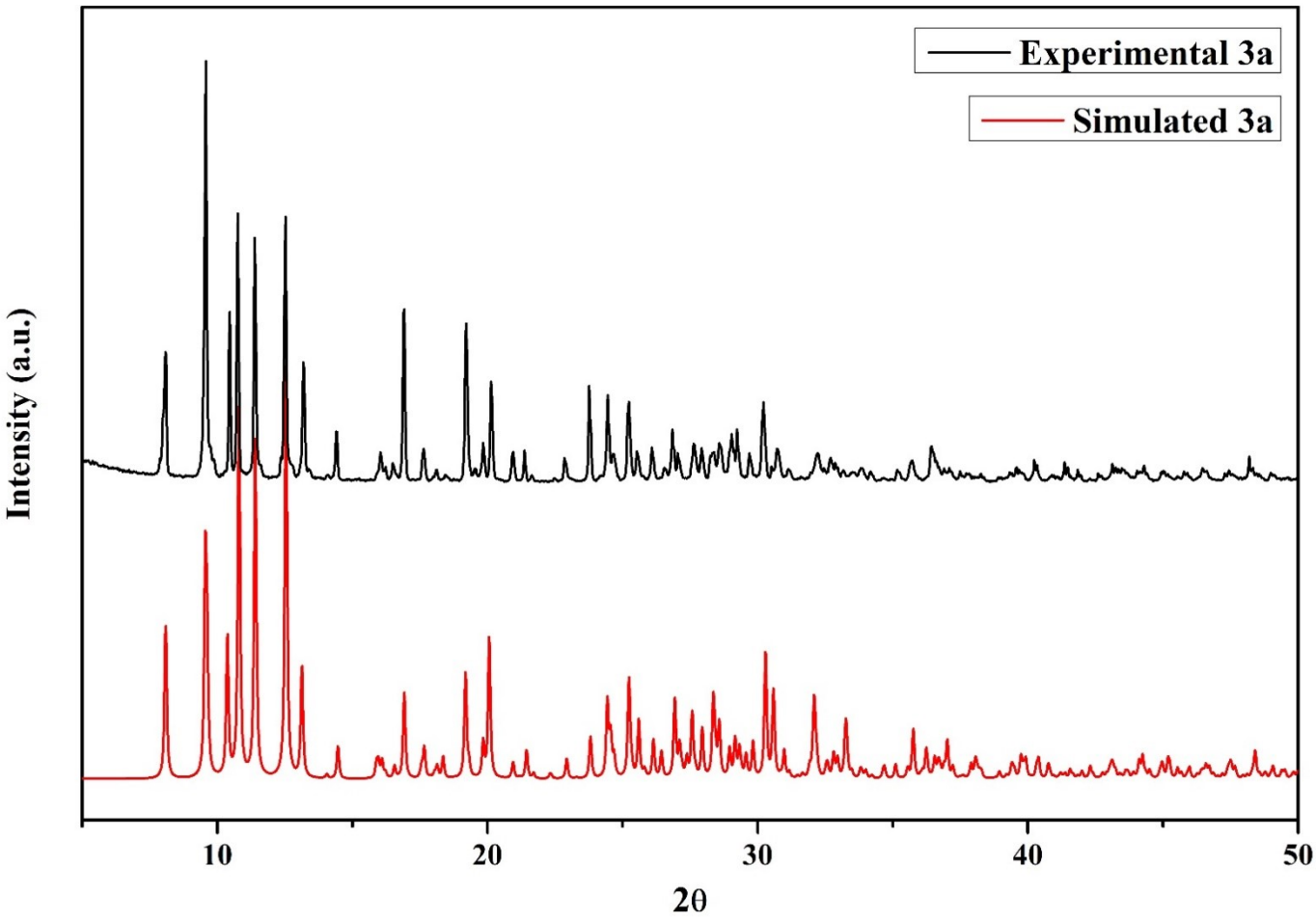


Figure S3. Comparative PXRD of compound **3a** (simulated *vs* experimental).

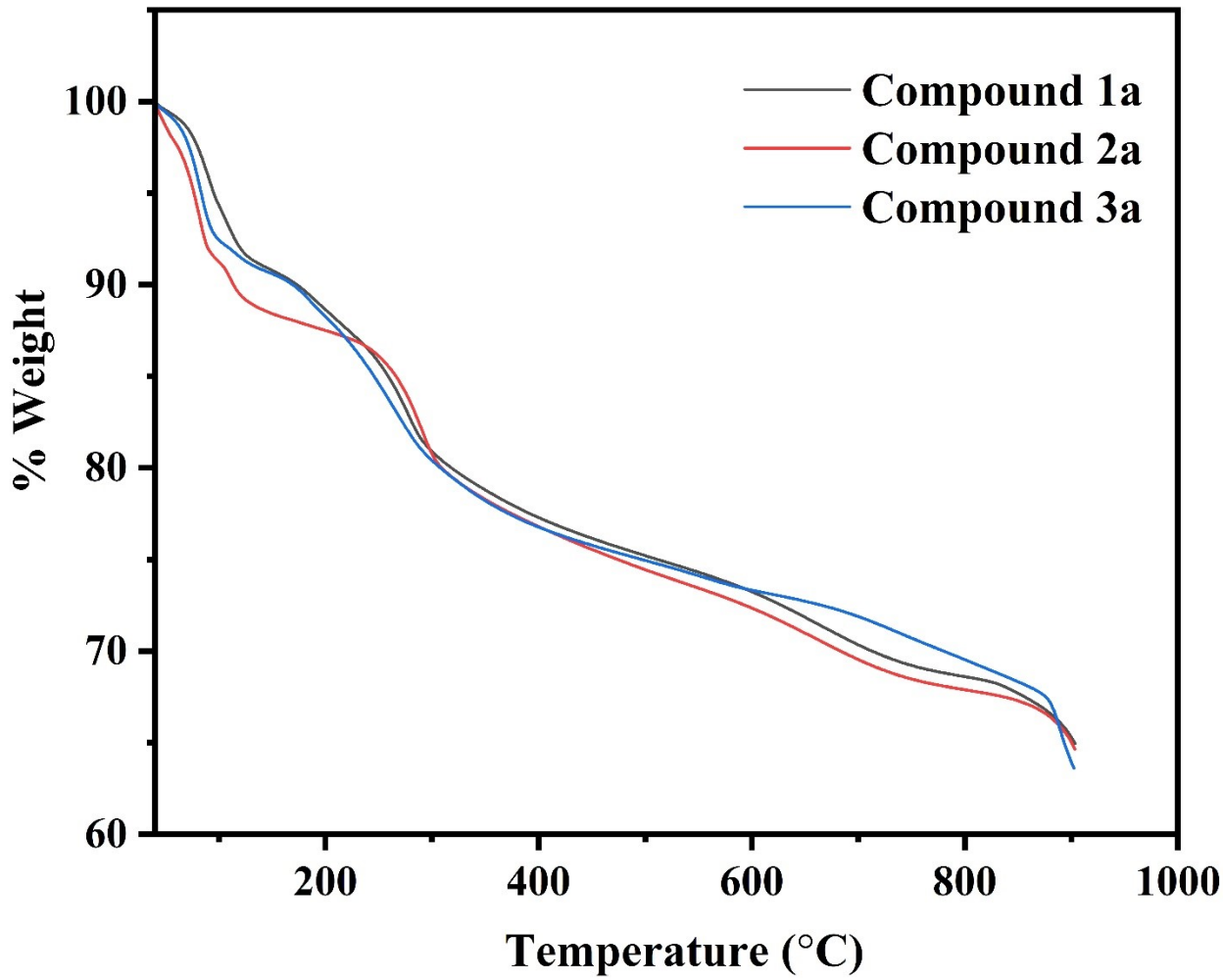


Figure S4. Comparative thermal analysis plots of compounds **1a**, **2a** and **3a**.

Theoretical calculations

The geometry optimization of compounds, namely **1′**$^{+}$ performed in its doublet, **1′** in triplet, **2′** and **1′**$^{-}$ are quartet, **3′** and **2′**$^{-}$ in the quintet, **3′**$^{-}$ in sextet state at the B3LYP-D3(BJ)/Def2-SVP[S1] level of theory using the Gaussian 16 program[S2] package in the gaseous phase as well as in water medium with the use of Density Functional Theory[S3] (DFT). B3LYP is a hybrid functional that combines the Becke three-parameter exchange functional (B3) with the Lee-Yang-Parr correlation functional (LYP). B3LYP includes a fraction of exact exchange (20-30%), which is based on Hartree-Fock's theory. The inclusion of exact exchange performs well for a broad range of molecular properties, including reaction energies, vibrational frequencies, and electronic transitions.

Table S4: The different molecules in their total charge and spin multiplicity used for optimisation of polyanionic species $[(Mo^{VI}_2O_5)_2(M^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{7-}$ (**1′ - 3′**) and $[(Mo^{VI}_2O_5)_2(M^{II}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{8-}$ (**1′**$^{-}$ **- 3′**$^{-}$) at the B3LYP-D3(BJ)/Def2-SVP level of theory using (DFT).

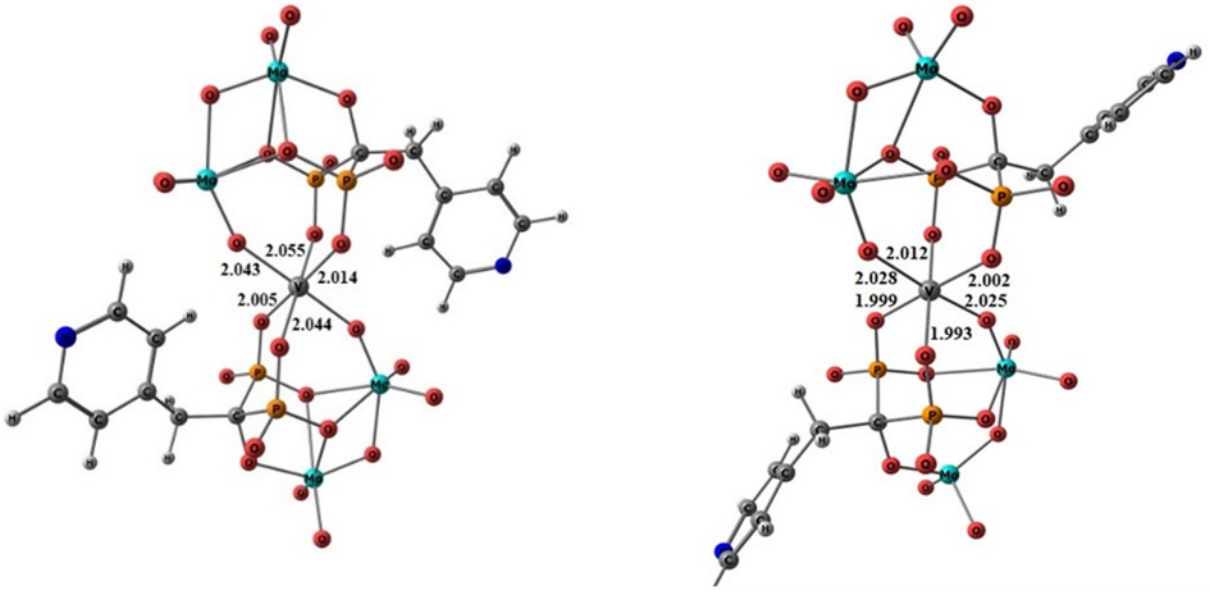
Complexes	Total Charge (q)	Spin Multiplicity (2S+1)
V^{3+} (**1′**)	-7	3 (S = 1)
Cr^{3+} (**2′**)	-7	4 (S = 3/2)
Mn^{3+} (**3′**)	-7	5 (S = 2)
V^{2+} (**1′**$^{-}$)	-8	4 (S = 3/2)
Cr^{2+} (**2′**$^{-}$)	-8	5 (S = 2)
Mn^{2+} (**3′**$^{-}$)	-8	6 (S = 5/2)
V^{4+} (**1′**$^{+}$)	-6	2 (S = 1/2)

Table S5. HOMO-LUMO energy gap of polyanionic species $[(Mo^{VI}_2O_5)_2(M^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{7-}$ (**1′ - 3′**) and $[(Mo^{VI}_2O_5)_2(M^{II}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{8-}$ (**1′⁻ - 3′⁻**) in the gas phase and water as a solvent medium at B3LYP-D3(BJ)/Def2-SVP level of theory

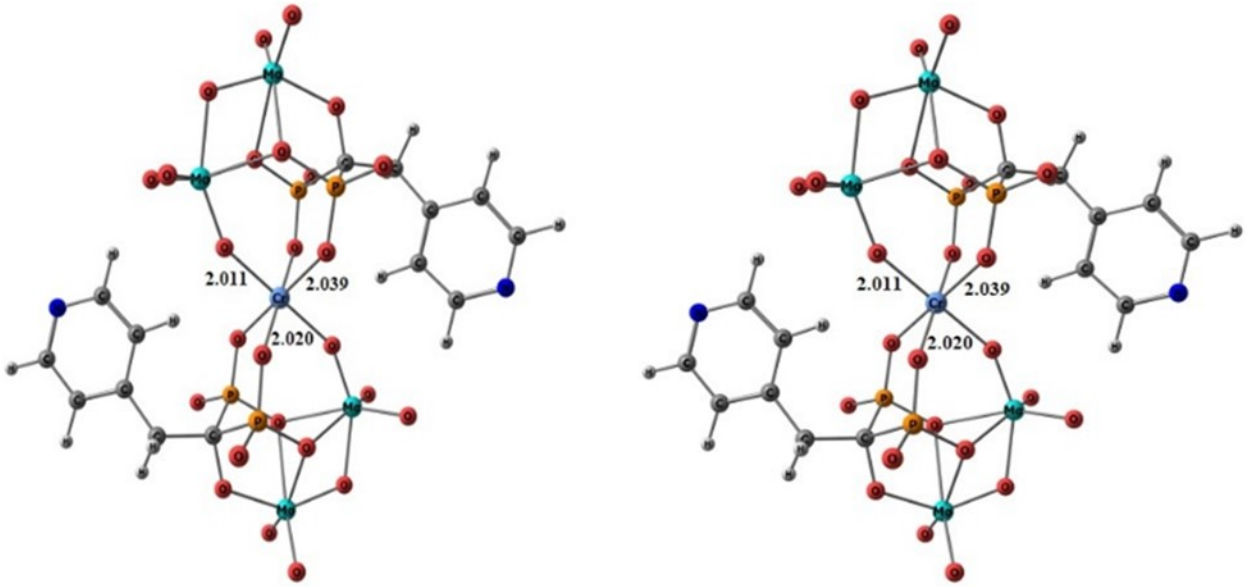
Complexes	HOMO – LUMO Energy Difference in the gas phase (eV)	HOMO – LUMO Energy Difference in water medium (eV)
V^{3+} (**1′**)	2.43	3.42
Cr^{3+} (**2′**)	3.23	4.60
Mn^{3+} (**3′**)	3.03	3.43
V^{2+} (**1′⁻**)	0.20	1.90
Cr^{2+} (**2′⁻**)	0.20	3.62
Mn^{2+} (**3′⁻**)	2.22	3.06
V^{4+} (**1′⁺**)	3.10	3.30

Table S6. Calculation of difference of energy upon reduction in the gas phase and water medium at B3LYP-D3(BJ)/Def2-SVP level of theory. All the values are in kcal/mol.

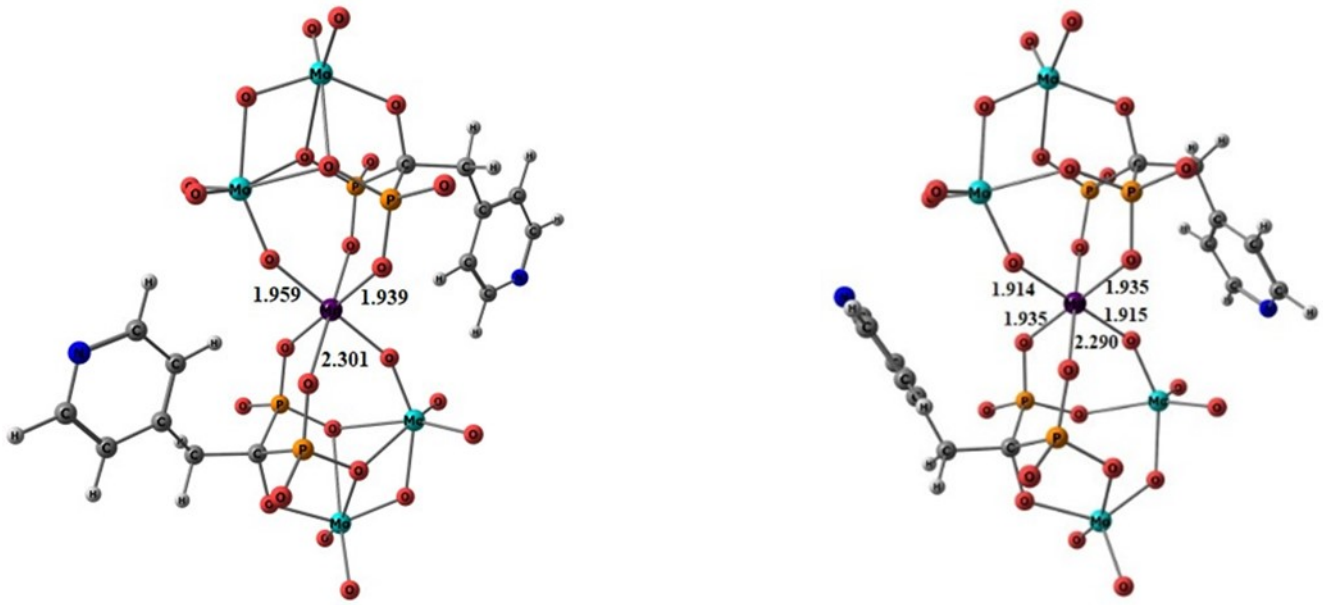
Reduction process	Δ*E* (gas phase)	Δ*E* (water medium)
V^{3+} (**1′**) to V^{2+} (**1′⁻**)	308.77	-47.85
Cr^{3+} (**2′**) to Cr^{2+} (**2′⁻**)	310.70	-58.31
Mn^{3+} (**3′**) to Mn^{2+} (**3′⁻**)	327.89	-81.32
V^{4+} (**1′⁺**) to V^{3+} (**1′**)	264.42	-67.21


2.055
2.043
2.014
2.005
2.044
2.012
2.028
2.002
1.999
2.025
1.993

(a)


2.011
2.039
2.020
2.011
2.039
2.020

(b)



(c)

Figure S5. Optimized geometries in gas phase (left) and water medium (right) of polyanion **(a)** $[(Mo^{VI}_2O_5)_2(V^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{7-}$ (**1′**), for M = V^{III}, S = 1, q = -7; **(b)** $[(Mo^{VI}_2O_5)_2(Cr^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{7-}$ (**2′**) , for M = Cr^{III}, S = 3/2, q = -7; **(c)** $[(Mo^{VI}_2O_5)_2(Mn^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{7-}$ (**3′**), for M = Mn^{III}, S = 2, q = -7; at B3LYP-D3(BJ)/Def2-SVP level of theory. Bond lengths are in Å.

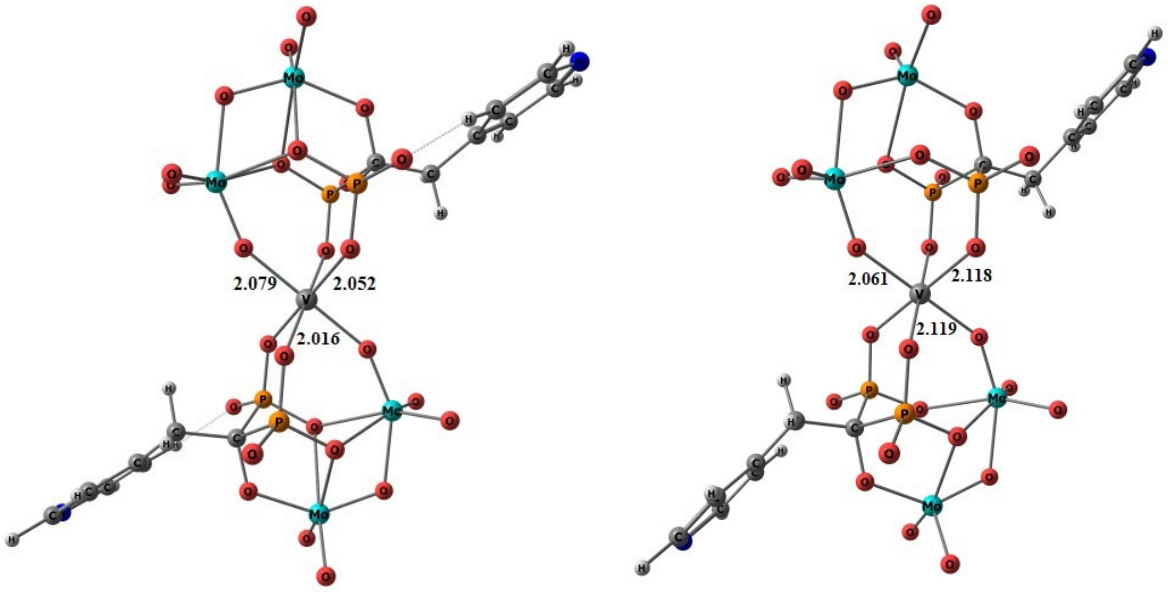


Figure S6. Optimized geometries in gas phase (left) and water medium (right) of polyanion $[(Mo^{VI}_2O_5)_2(V^{II}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{8-}$ (**1′⁻**) at B3LYP-D3(BJ)/Def2-SVP level of theory. M = V^{II} (**1′⁻**); S = 3/2, q = -8. Bond lengths are in Å.

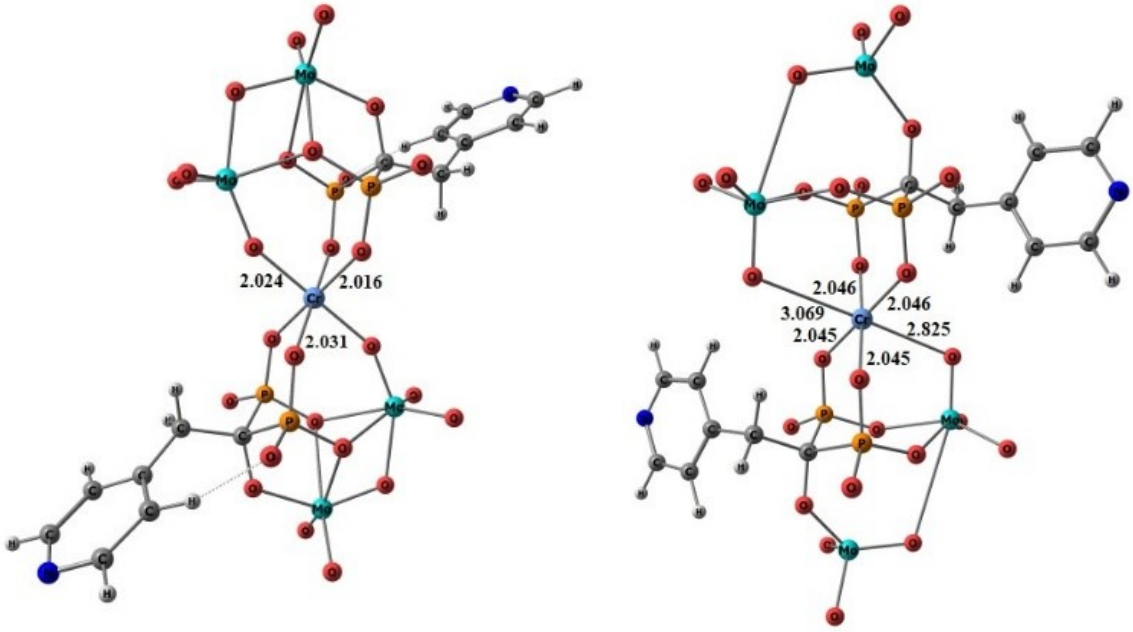


Figure S7. Optimized geometries in gas phase (left) and water medium (right) of polyanion $[(Mo^{VI}_2O_5)_2(Cr^{II}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{8-}$ (**2′⁻**) at B3LYP-D3(BJ)/def2-SVP level of theory. M = Cr^{II} (**2′⁻**); S = 2, q = -8. Bond lengths are in Å.

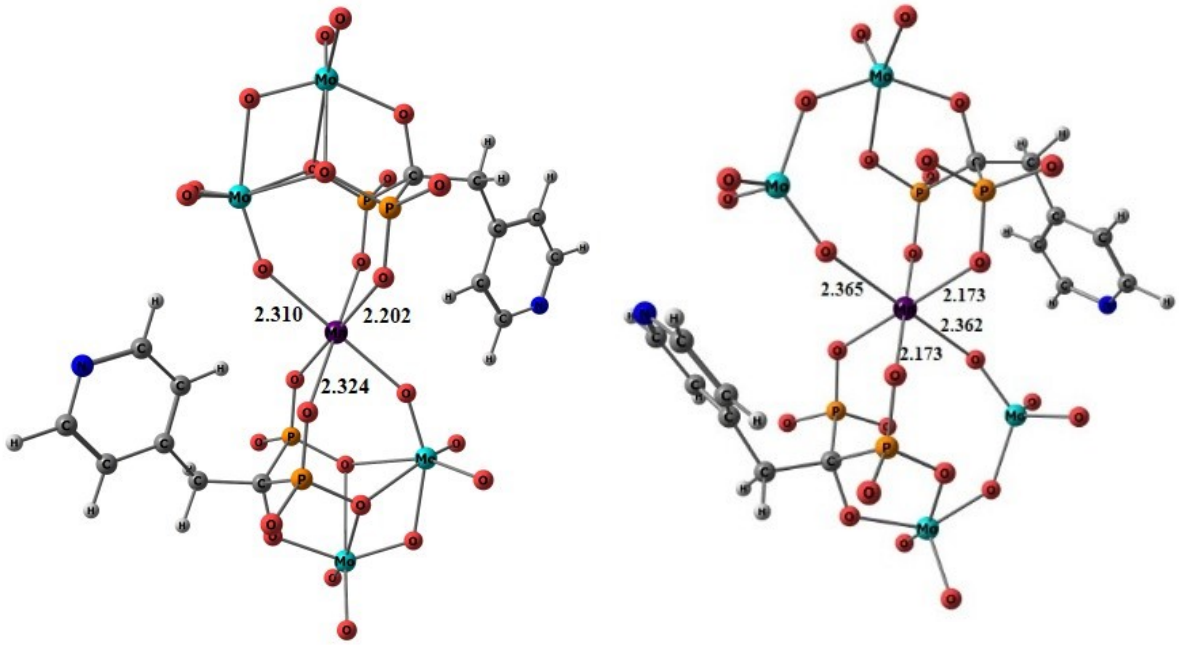


Figure S8. Optimized geometries in gas phase (left) and water medium (right) of polyanion $[(Mo^{VI}_2O_5)_2(Mn^{II}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{8-}$ (**3′**$^{-}$) at B3LYP-D3(BJ)/Def2-SVP level of theory. M = Mn^{II} (**3′**$^{-}$); S = 5/2, q = -8. Bond lengths are in Å.

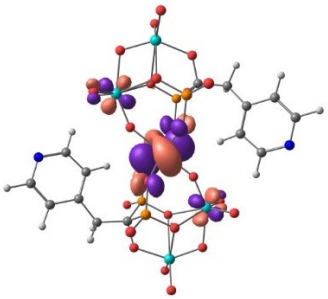
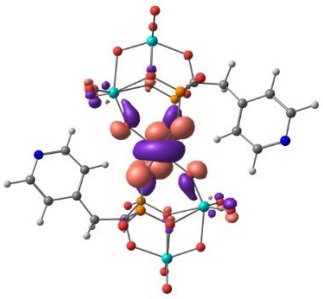
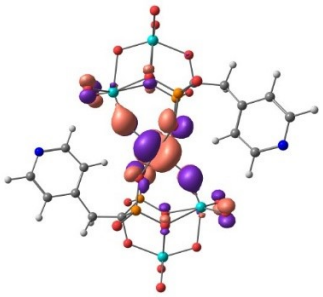
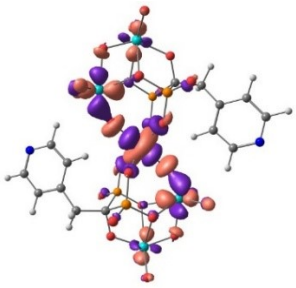
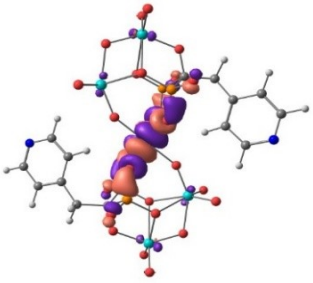
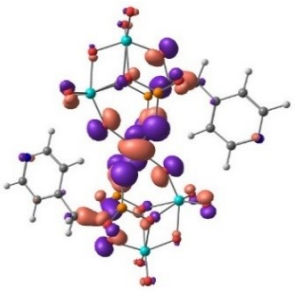
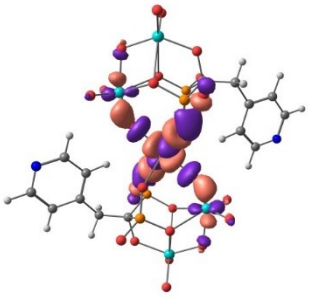
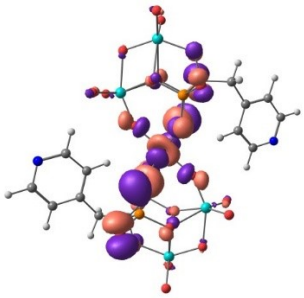
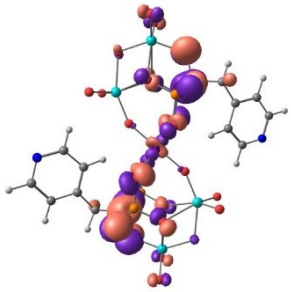
1′  LUMO (ε = -1.812 eV)	 α-SOMO (ε = -5.312 eV)	 α-SOMO-1 (ε = -5.332 eV)
2′  LUMO (ε = -1.448 eV)	 LUMO+1 (ε = -1.185 eV)	 α-SOMO-4 (ε = -6.532 eV)
3′  LUMO (ε = -2.716 eV)	 α-SOMO-2 (ε = -5.959 eV)	 α-SOMO (ε = -5.713 eV)

Figure S9. NBO figures of complexes $[(Mo^{VI}_2O_5)_2(M^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_3\}_2]^{7-}$ $M^{III} = V^{III}$ (**1′**), Cr^{III} (**2′**) and Mn^{III} (**3′**) at B3LYP-D3(BJ)/Def2-SVP level of theory in the water medium.

Table S7: Hydrogen-bonding parameters for compound 1a

Donor - H ⋯ Acceptor	D – H (Å)	H ⋯ A (Å)	D ⋯ A (Å)
C4 - H4···O2B$^{\#1}$	0.93	2.52	3.097
C4 - H4···O2A$^{\#1}$	0.93	2.40	3.179

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$: ½ - x, -½ + y, ½ - z

Table S8: Hydrogen-bonding parameters for compound 2a

Donor - H ⋯ Acceptor	D – H (Å)	H ⋯ A (Å)	D ⋯ A (Å)
C2 - H2B···O2A$^{\#1}$	0.97	2.44	3.362
C5 – H5···N1H$^{\#2}$	0.93	2.47	3.140
C6 - H6··· O2A$^{\#3}$	0.93	2.40	3.050

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$: 3/2 - x, -½ + y, ½ - z
$^{\#2}$: 1 - x, - y, - z
$^{\#3}$: -½ + x, ½ - y, -½ + z

Table S9: Hydrogen-bonding parameters for compound 3a

Donor - H ⋯ Acceptor	D – H (Å)	H ⋯ A (Å)	D ⋯ A (Å)
C2 – H2A···O2A$^{\#1}$	0.99	2.46	3.432
C5 – H5···O2A$^{\#2}$	0.95	2.44	3.145

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$: 3/2 - x, ½ + y, ½ - z
$^{\#2}$: ½ + x, ½ - y, ½ + z

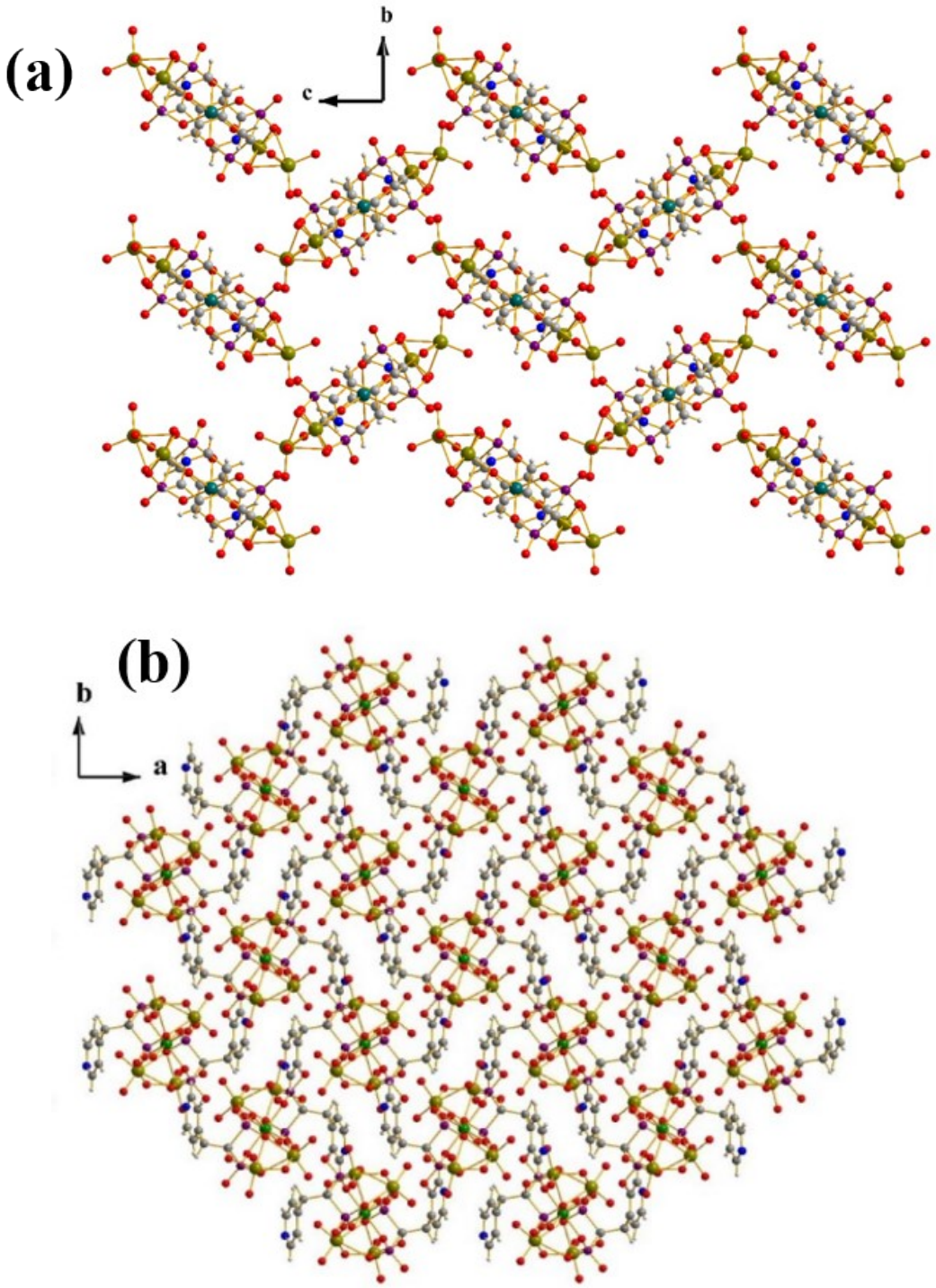
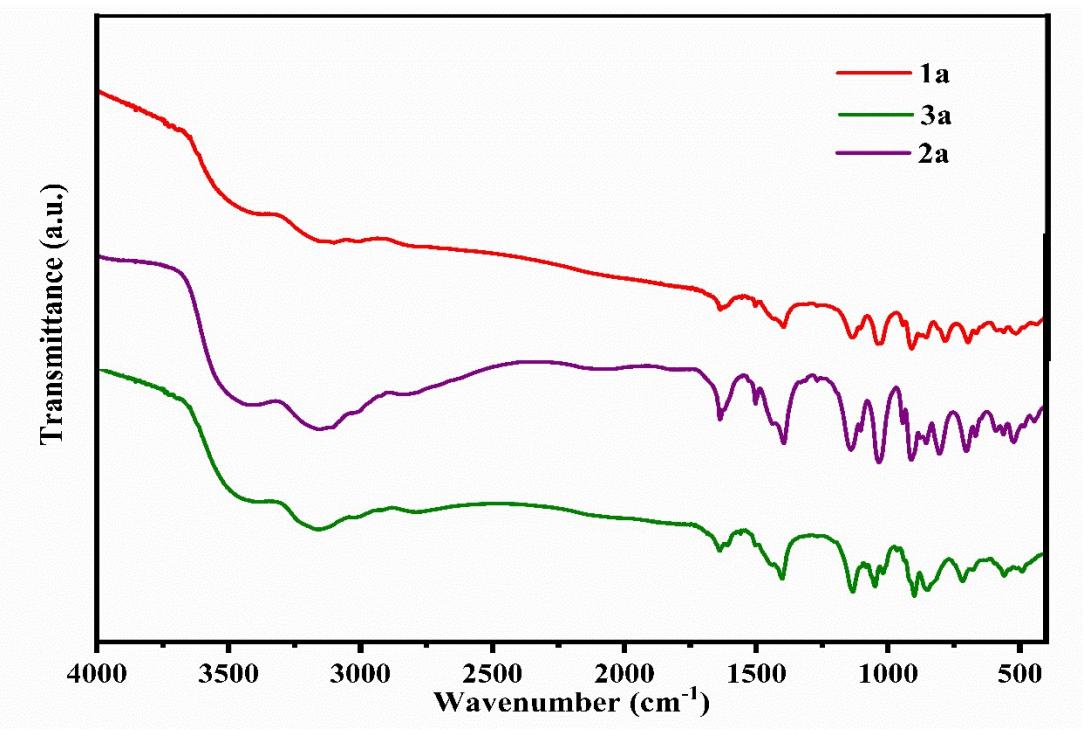
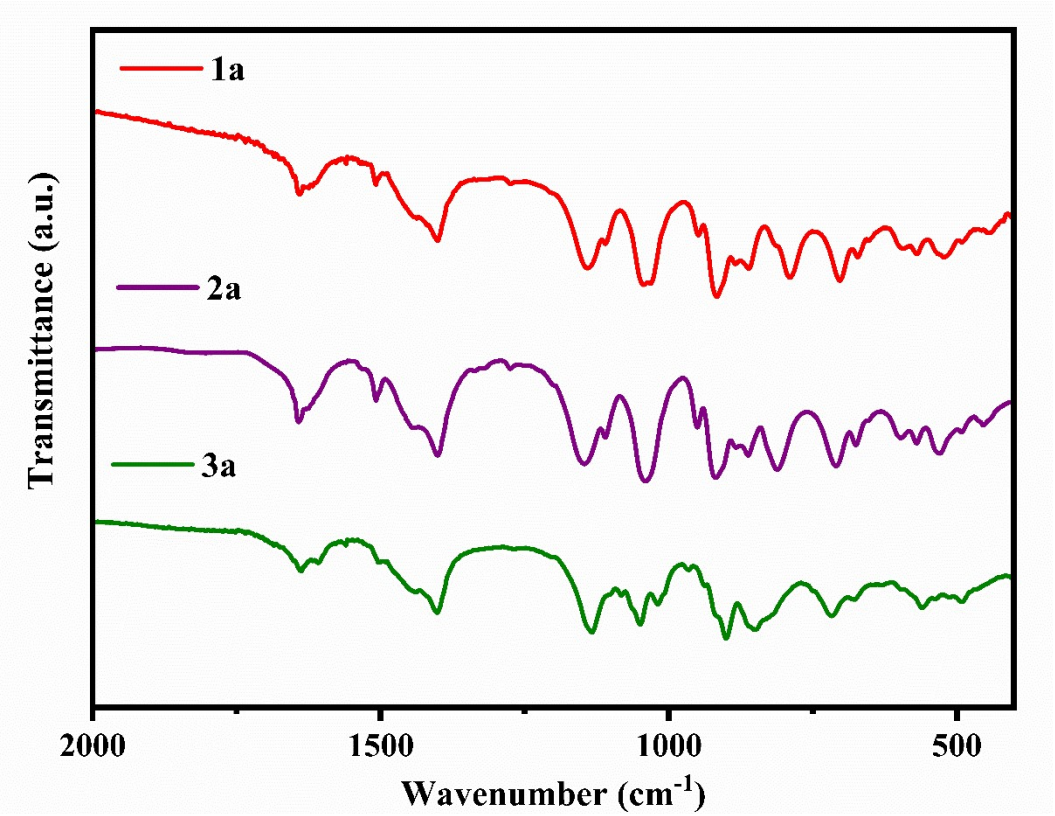


Figure S10. Crystal packing arrangement for polyanions **1**, **2** and **3 (a)** of along the a-axis, **(b)** along the c-axis.



(a)



(b)

Figure S11. Comparative infrared spectra of compound **1a – 3a**, **(a)** complete spectra, **(b)** fingerprint region.

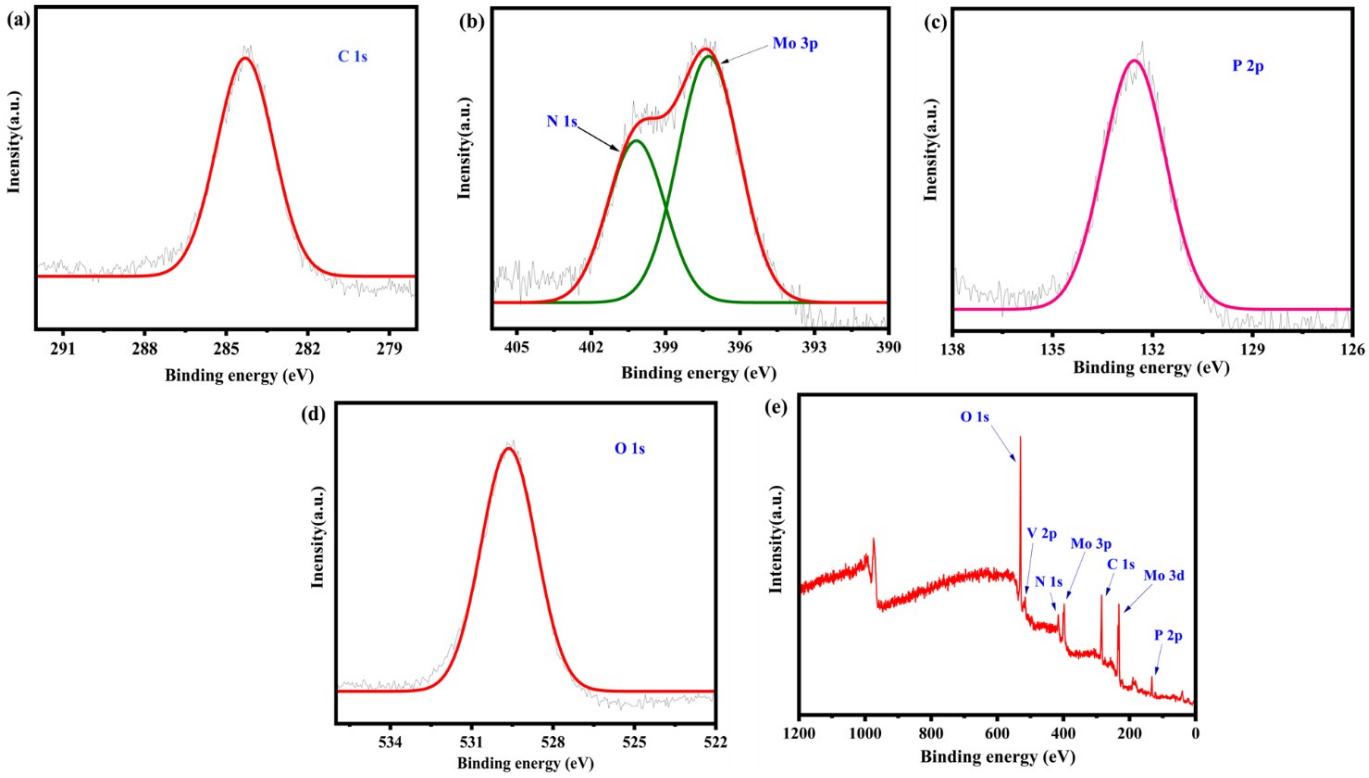


Figure S12. XPS Spectra of compound **1a**, **(a)** C 1s, **(b)** Mo 3p and N 1s, **(c)** P 2p, **(d)** O 1s and, **(e)** Survey spectrum.

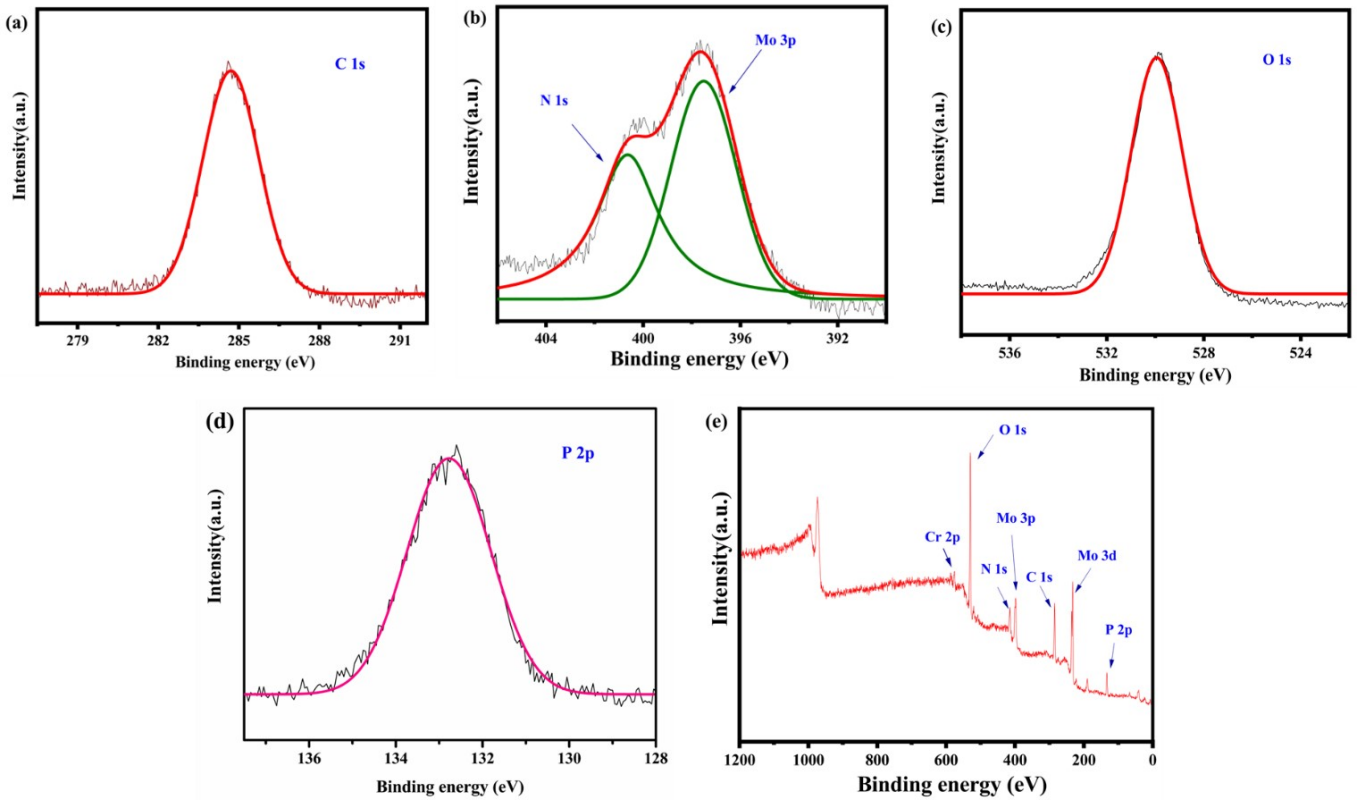


Figure S13. XPS Spectra of compound **2a**, **(a)** C 1s, **(b)** Mo 3p and N 1s, **(c)** O 1s, **(d)** P 2p and, **(e)** Survey spectrum.

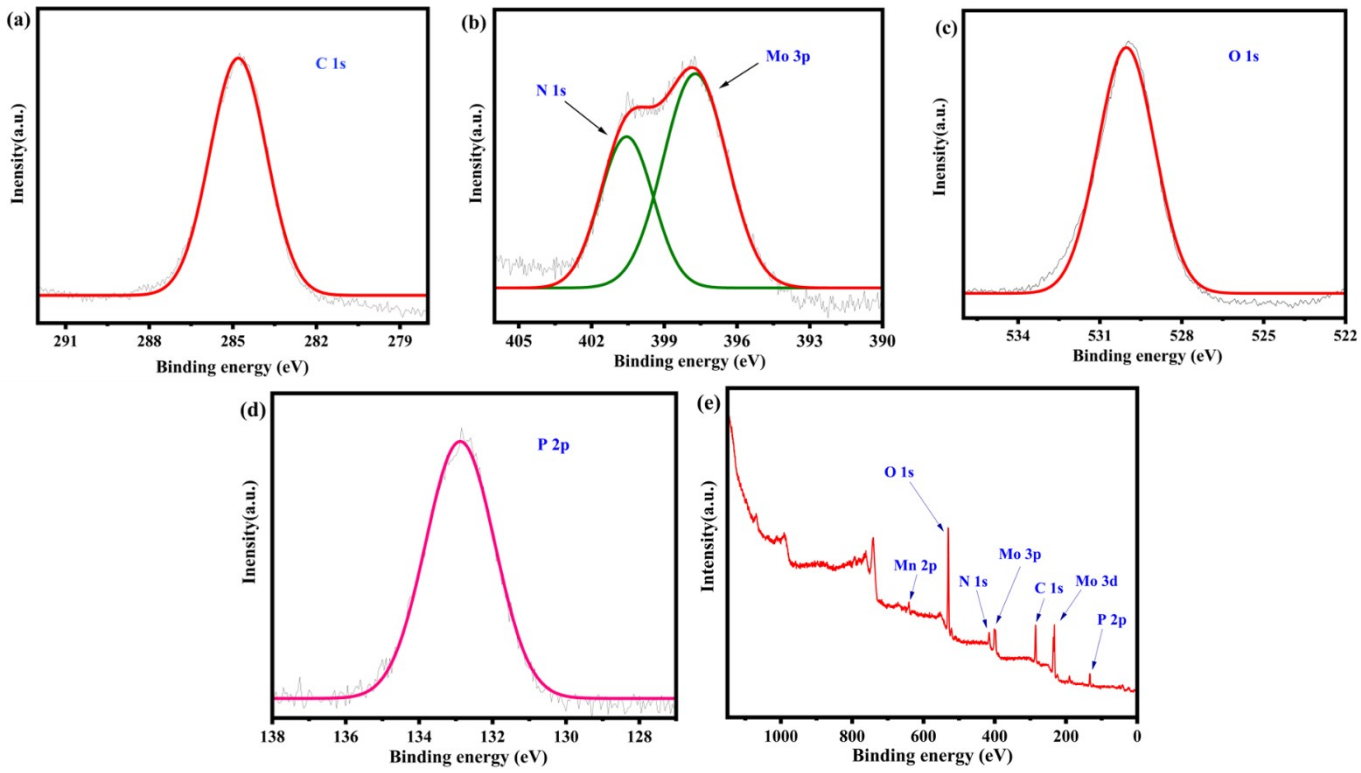
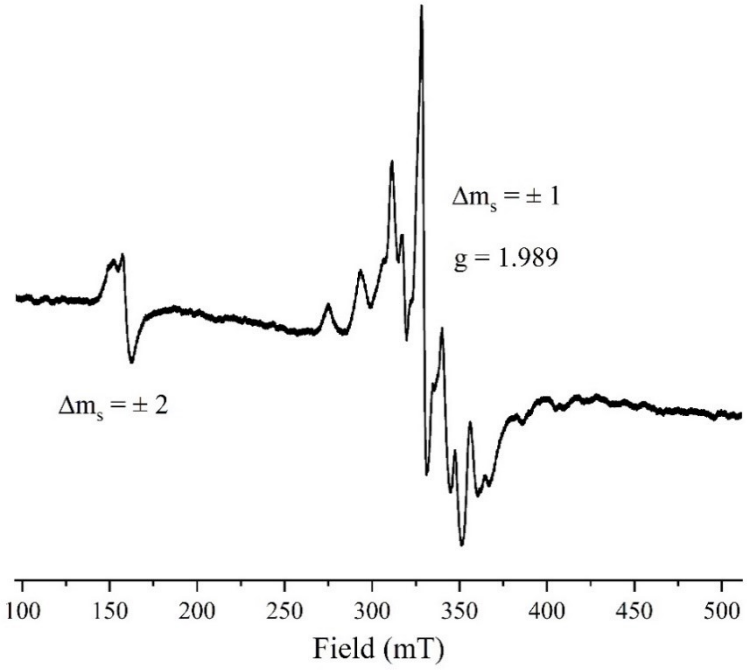
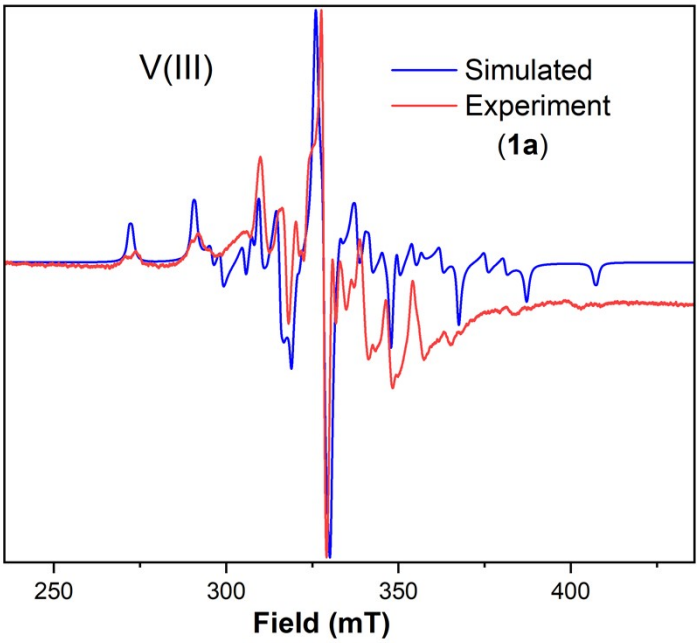


Figure S14. XPS Spectra of compound **3a**, **(a)** C 1s, **(b)** Mo 3p and N 1s, **(c)** O 1s, **(d)** P 2p and, **(e)** Survey spectrum.

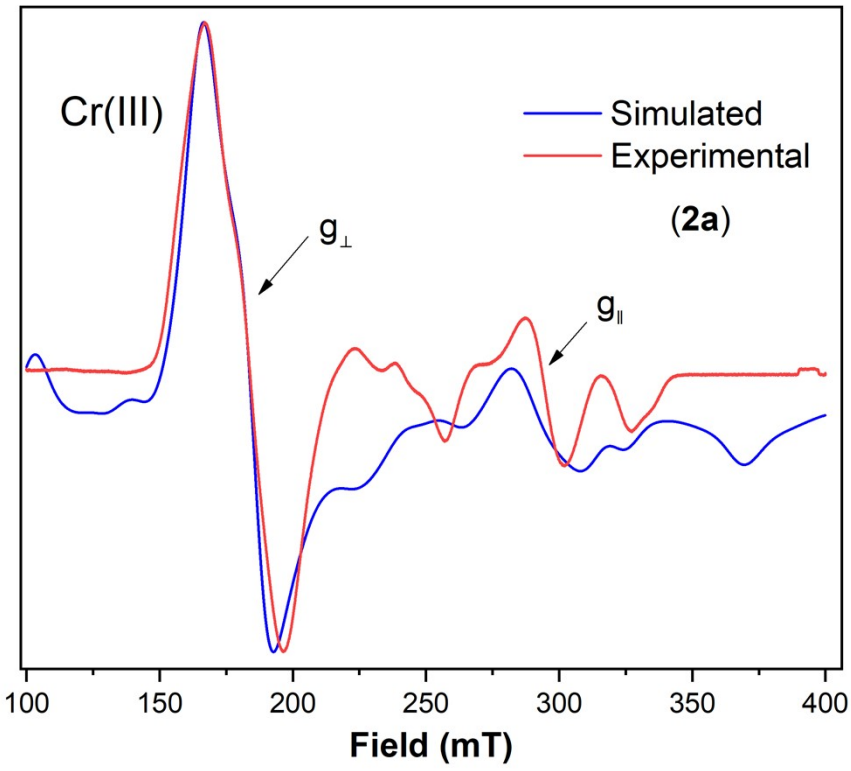


(a)

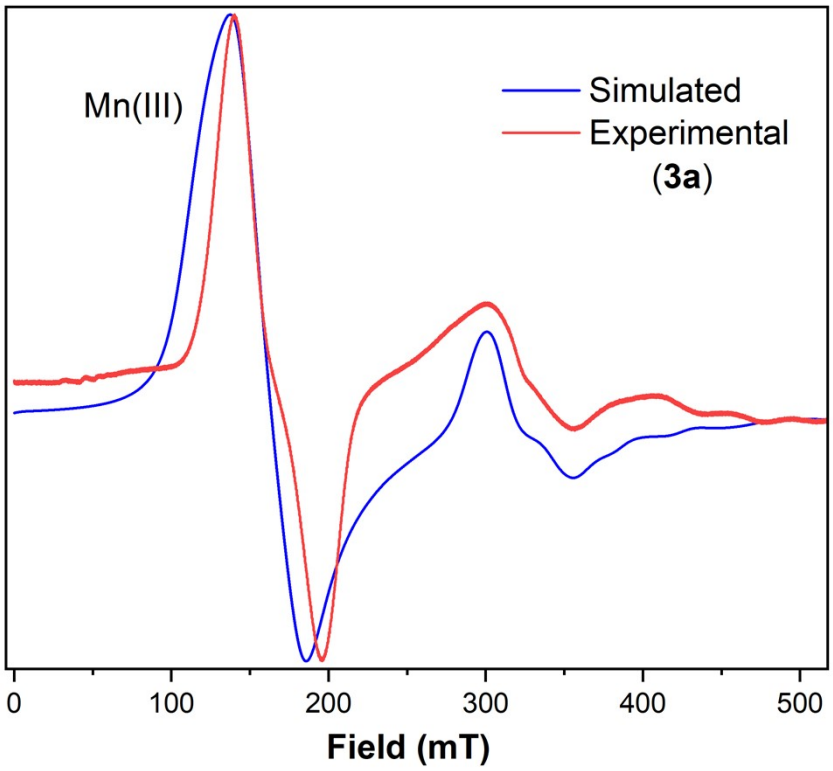


(b)

Figure S15. X-band EPR spectra of the complex $Na_2(NH_4)_5[(Mo^{VI}_2O_5)_2(V^{III}O_2)\{O_3PC(O)(CH_2\text{-}4\text{-}C_5NH_4)PO_{32}]\cdot 10H_2O$ (**1a**; V^{III}, $3d^2$) (S = 1) in the solid state at 77 K. Frequency 9.185 GHz. EPR spectrum (red, **1a**) of V(III)-complex in solid state at 77 K. Red and blue lines represent the experimental and simulated spectra of V(III)-complex using EasySpin program. [g_x = 1.9907, g_y = 1.99908, g_z = 2.03178, LWPP(1) = 0.2199 mT, LWPP(2) = 0.8177 mT, A_X = 537.269 MHz, A_Y = 322.895 MHz, A_Z = 190.087 MHz]



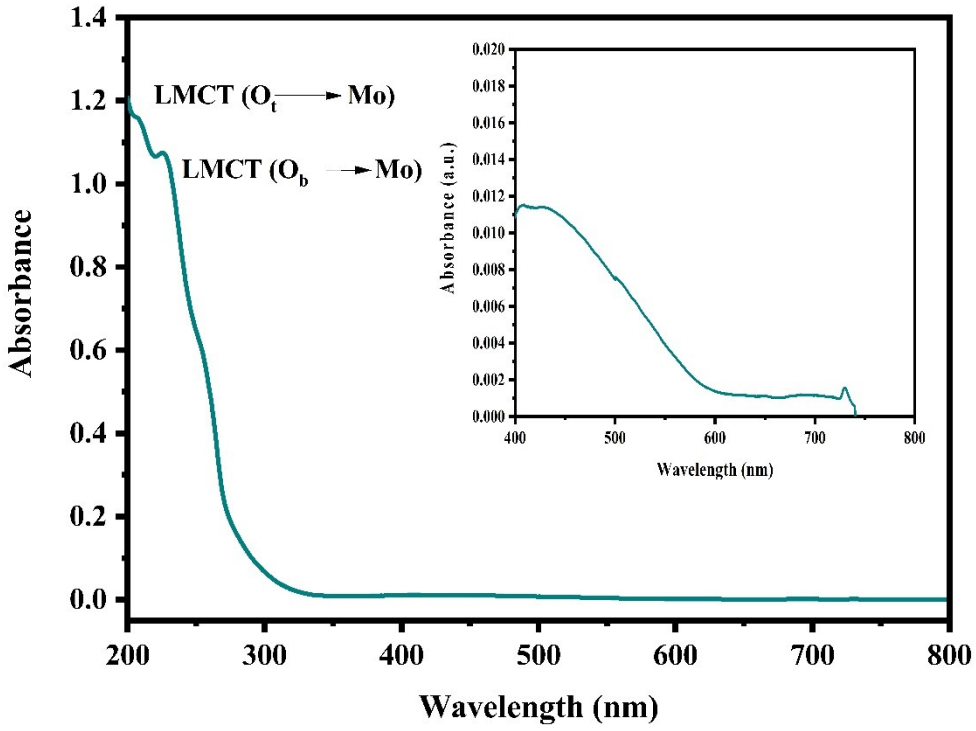
(a)



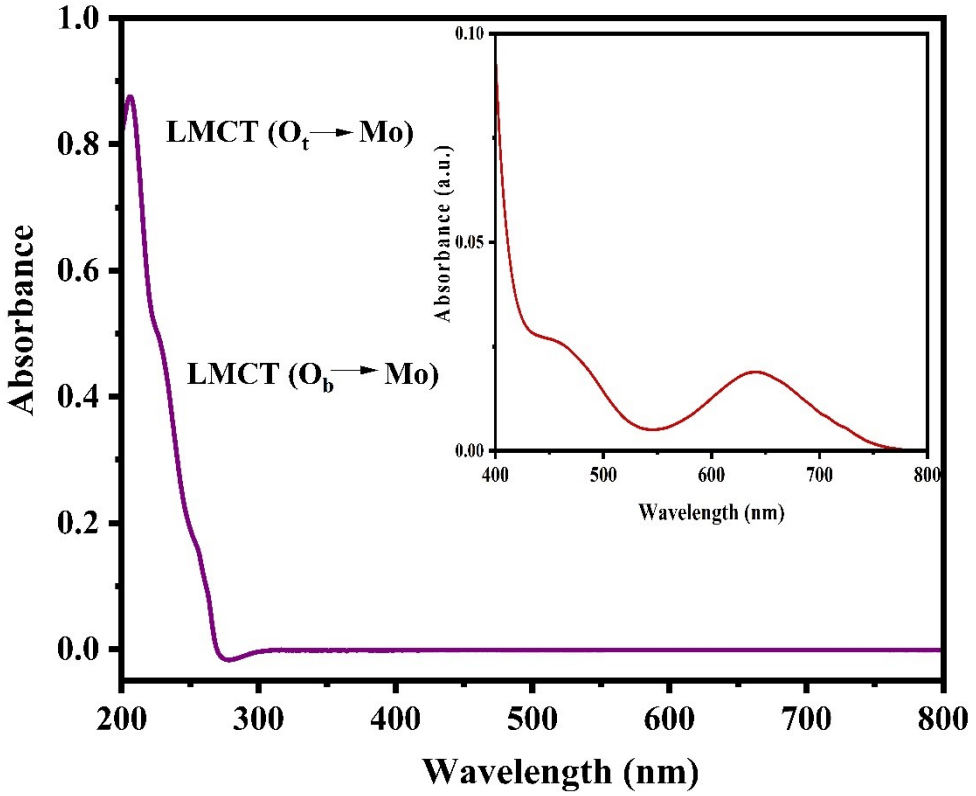
(b)

Figure S16. X-band EPR spectra, in the solid state at 77 K, of the complex (**a**) $(NH_4)_5[H_2(Mo^{VI}_2O_5)_2(Cr^{III}O_2)\{O_3P\text{-}C(O)(CH_2\text{-}4\text{-}C_5H_4N)\text{-}PO_3\}_2]\cdot 10H_2O$ (**2a**; Cr^{III}, $3d^3$) (S = 3/2) at frequency 9.182 GHz. EPR spectrum (red, **2a**) of Cr(III)-complex in solid state at 77

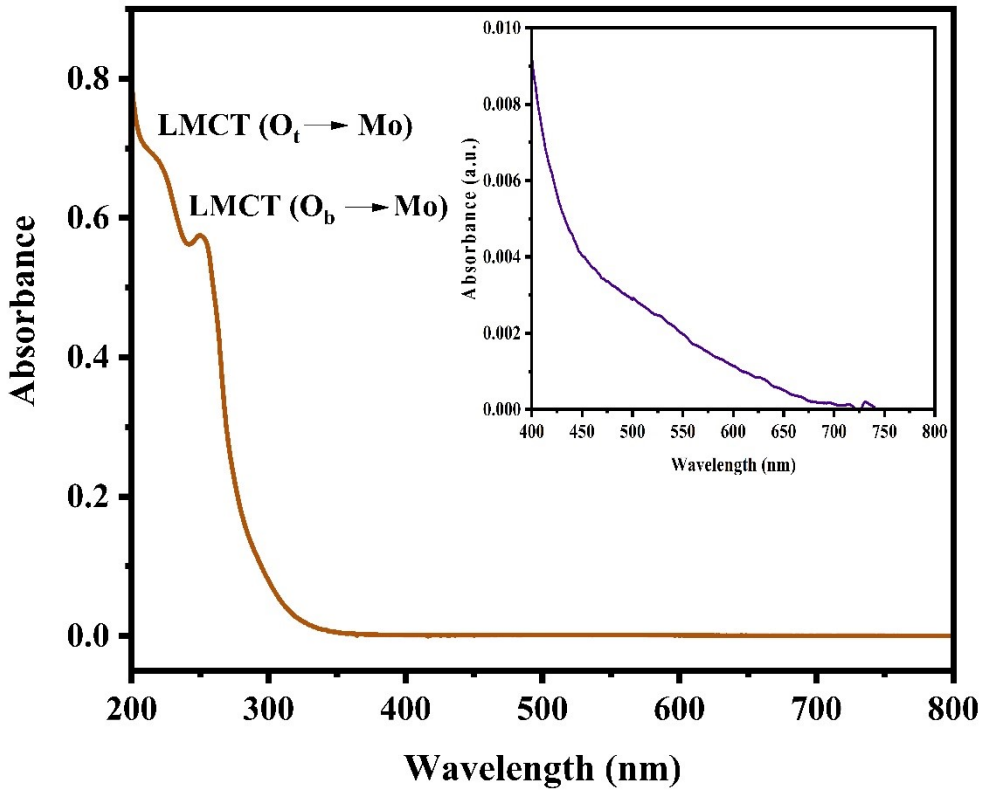
K. Red and blue lines represent the experimental and simulated spectra using EasySpin program. [g_x = 1.9186, g_y = 2.1300, g_z = 2.01047, LWPP (Gaussian broadening) = 8.0187 mT, LWPP (Lorentzian broadening) = 4.25418 mT, A_x = 428.001 MHz, A_y = 36.7313 MHz, A_z = 237.35 MHz]. (**b**) $Na(NH_4)_6[H(Mo^{VI}_2O_5)_2(Mn^{III}O_2)\{O_3P\text{-}C(O)(CH_2\text{-}4\text{-}C_5H_4N)\text{-}PO_3\}_2]\cdot 9H_2O$ (**3a**; Mn^{III}, $3d^4$) (S = 2) at frequency 9.184 GHz. EPR spectrum (red, **3a**) of Mn(III)-complex in solid state at 77 K. Red and blue lines represent the experimental and simulated spectra using EasySpin program. [g_x = 1.99472, g_y = 1.44941, g_z = 1.9210, LWPP (Gaussian broadening) = 7.02521 mT, LWPP (Lorentzian broadening) = 11.3037 mT, A_x = 190.484 MHz, A_y = 190.484 MHz, A_z = 97.143 MHZ, D = 0.59cm^{-1}, E = 0.038 cm^{-1}].


LMCT (O_t → Mo)
LMCT (O_b → Mo)
Absorbance
Wavelength (nm)
Absorbance (a.u.)
Wavelength (nm)

(a)


LMCT (O_t → Mo)
LMCT (O_b → Mo)
Absorbance
Wavelength (nm)
Absorbance (a.u.)
Wavelength (nm)

(b)



(c)

Figure S17. UV- Visible spectra in water of compounds (a) **1a,** (b) **2a** and, (c) **3a.**

TD-DFT calculations at B3LYP/def2svp level of theory:

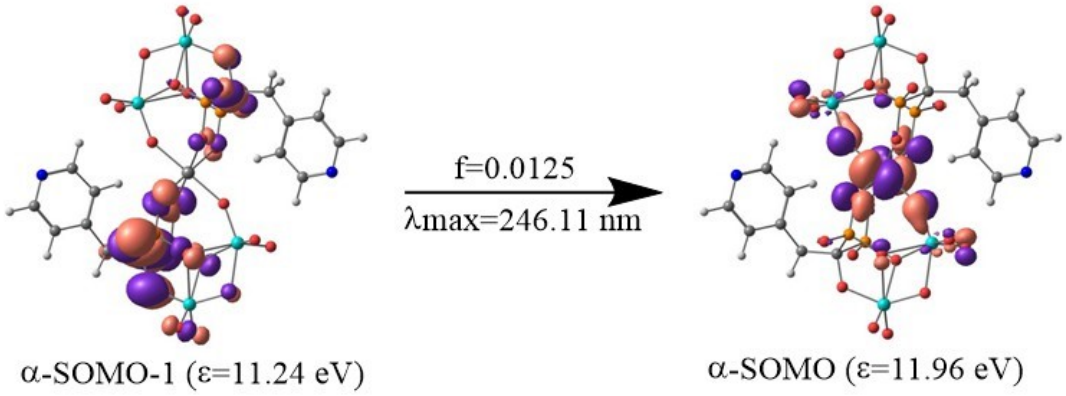


Figure S18. TD -DFT results of V(III)-complex (**1a**).

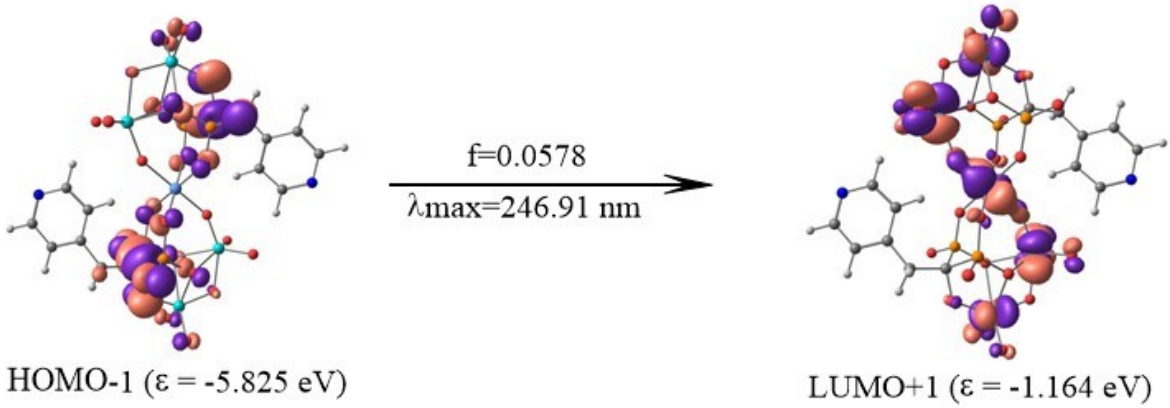


Figure S19. TD -DFT results of Cr(III)-complex (**2a**).

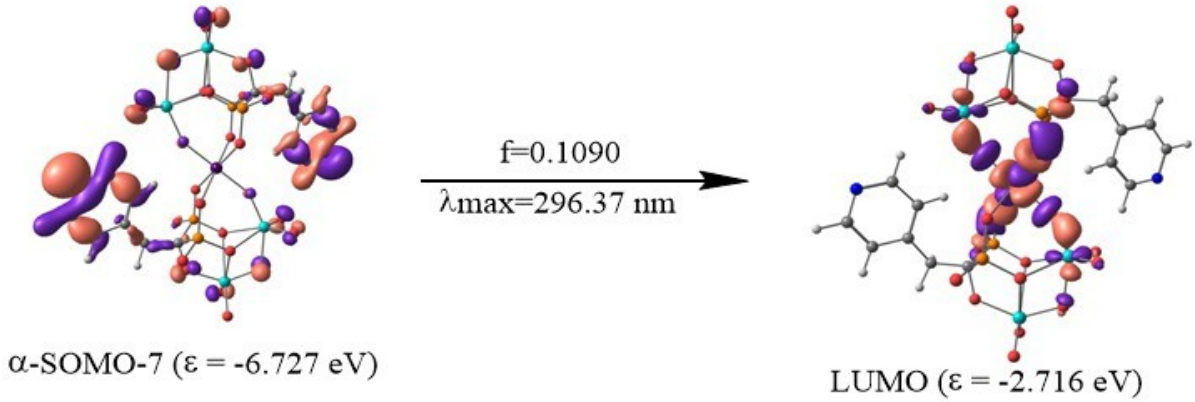


Figure S20. TD -DFT results of Mn(III) complex (**3a**).

TD DFT Results (TDDFT in B3LYP/Def2SVP) (optimised in B3LYP/def2tzvpp)

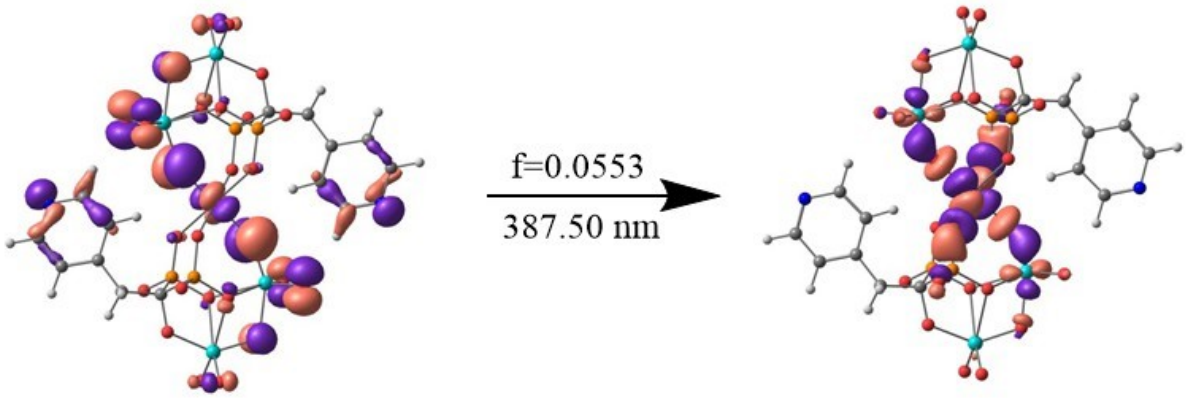
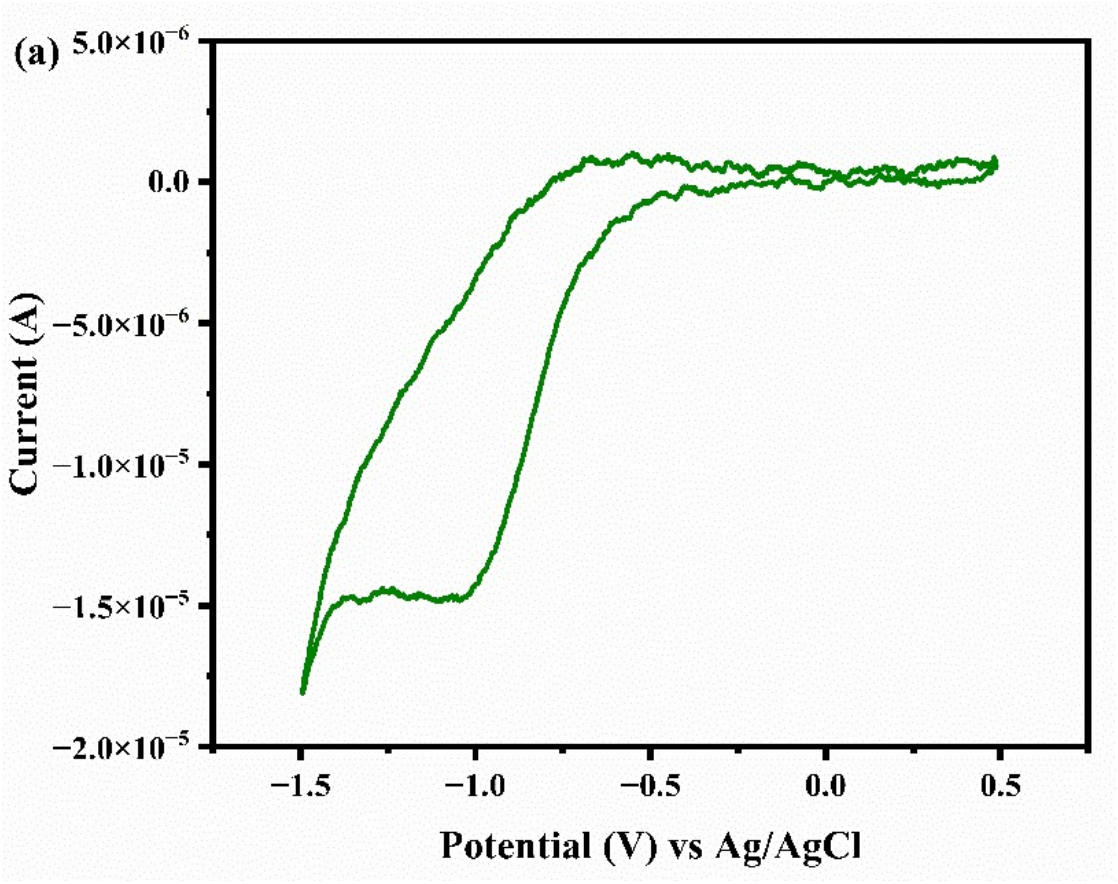
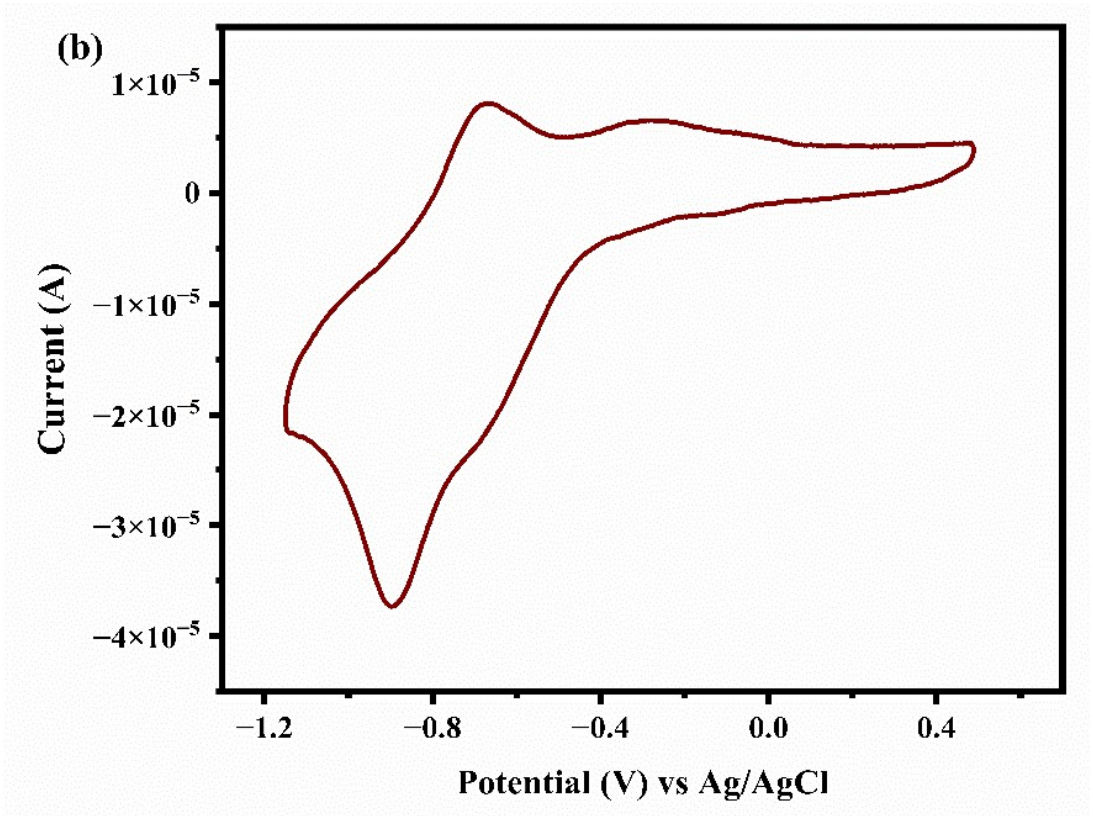


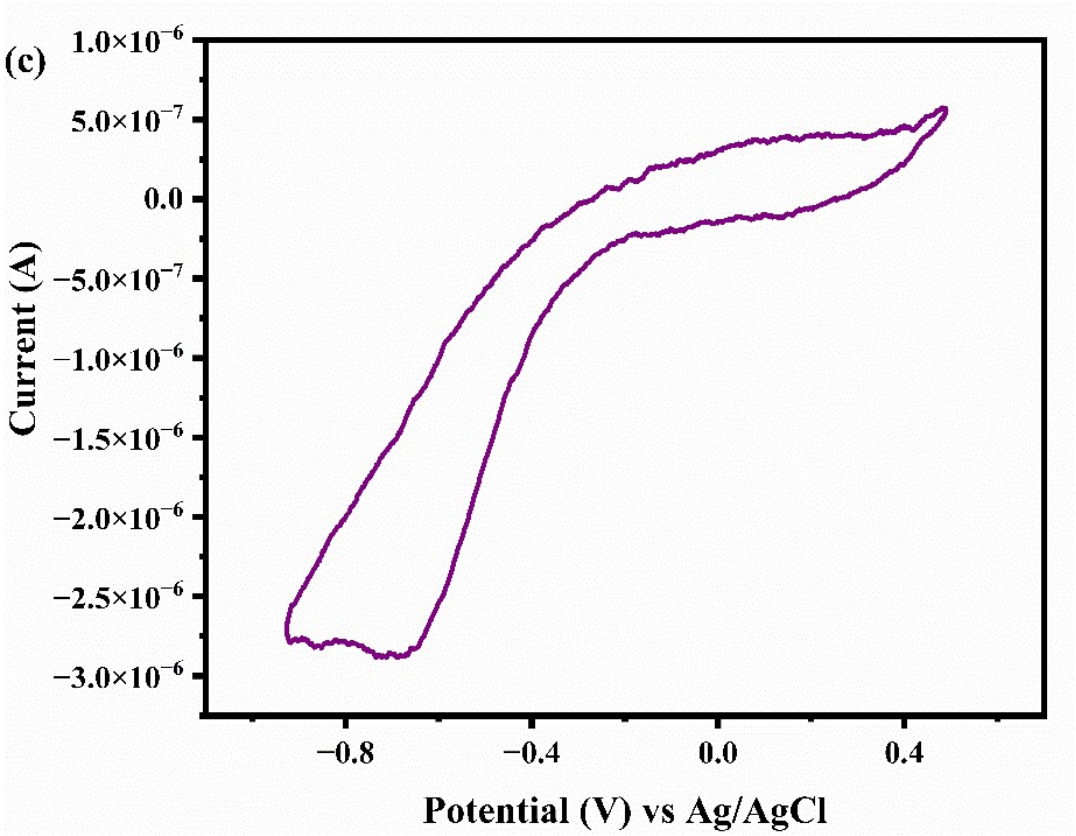
Figure S21. TD DFT results of Mn(III) complex (**3a**).


(a)
5.0×10⁻⁶
0.0
−5.0×10⁻⁶
−1.0×10⁻⁵
−1.5×10⁻⁵
−2.0×10⁻⁵
Current (A)
−1.5
−1.0
−0.5
0.0
0.5
Potential (V) vs Ag/AgCl

(a)

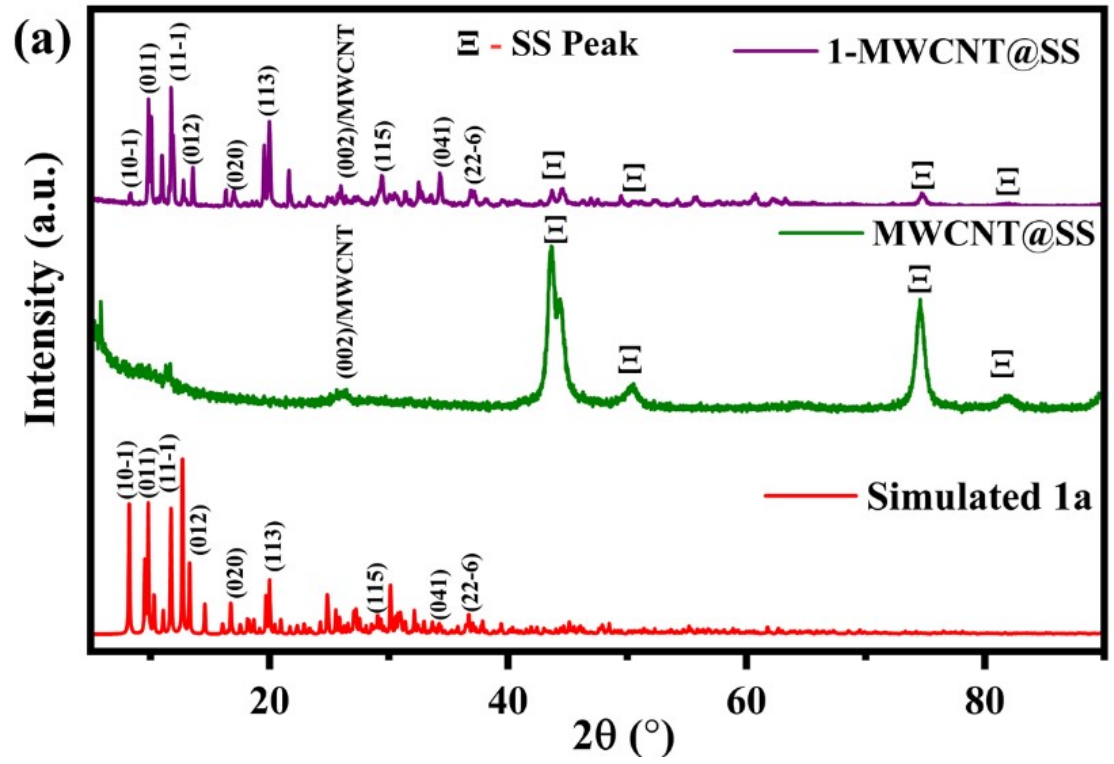

(b)
1×10⁻⁵
0
−1×10⁻⁵
−2×10⁻⁵
−3×10⁻⁵
−4×10⁻⁵
Current (A)
−1.2
−0.8
−0.4
0.0
0.4
Potential (V) vs Ag/AgCl

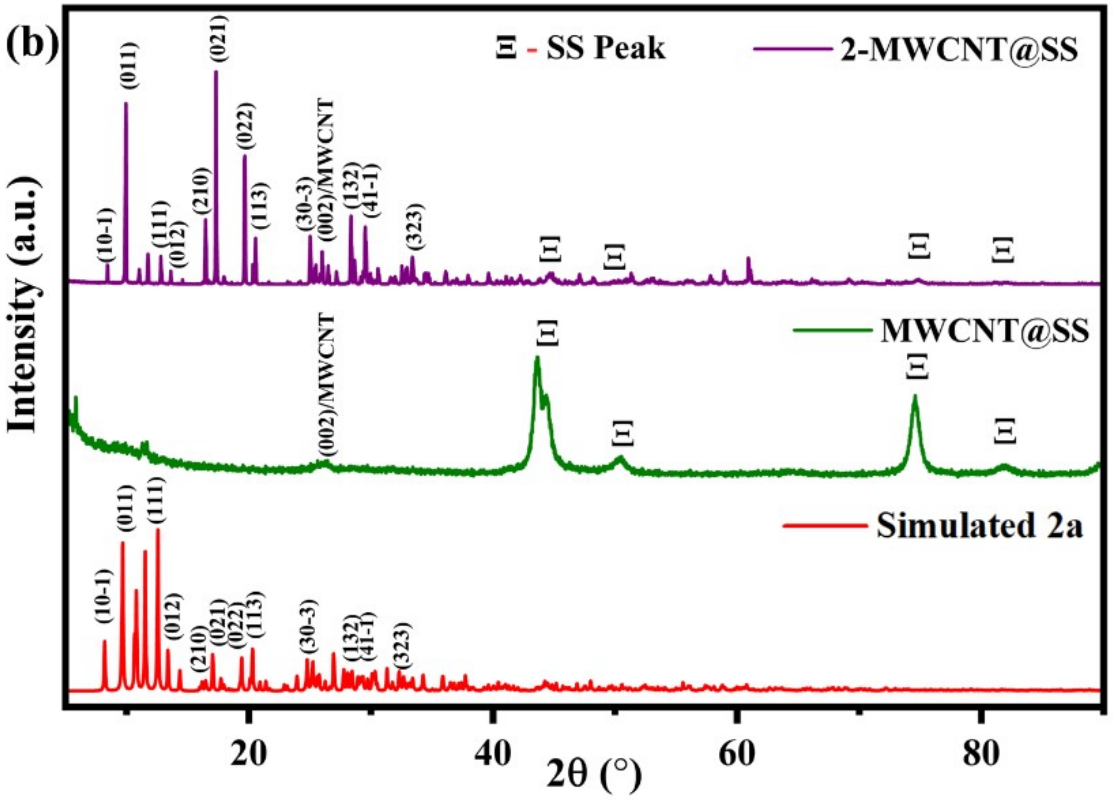
(b)



(c)

Figure S22. Electrochemical cyclic voltammogram curves for compounds **(a) 1a, (b) 2a**, and **(c) 3a** in solution of 0.5M $NaClO_4$ in the ternary solvent mixture of ethylene carbonate, propylene carbonate, and ethyl acetate in the volume ratio of 1:1:1.


(a)
Ξ - SS Peak
1-MWCNT@SS
MWCNT@SS
Simulated 1a
Intensity (a.u.)
2θ (°)
(10-1)
(011)
(11-1)
(012)
(020)
(113)
(002)/MWCNT
(115)
(041)
(22-6)
[Ξ]
20
40
60
80


(b)
Ξ - SS Peak
2-MWCNT@SS
MWCNT@SS
Simulated 2a
Intensity (a.u.)
2θ (°)
(10-1)
(011)
(111)
(012)
(210)
(021)
(022)
(113)
(30-3)
(002)/MWCNT
(132)
(41-1)
(323)
[Ξ]
20
40
60
80

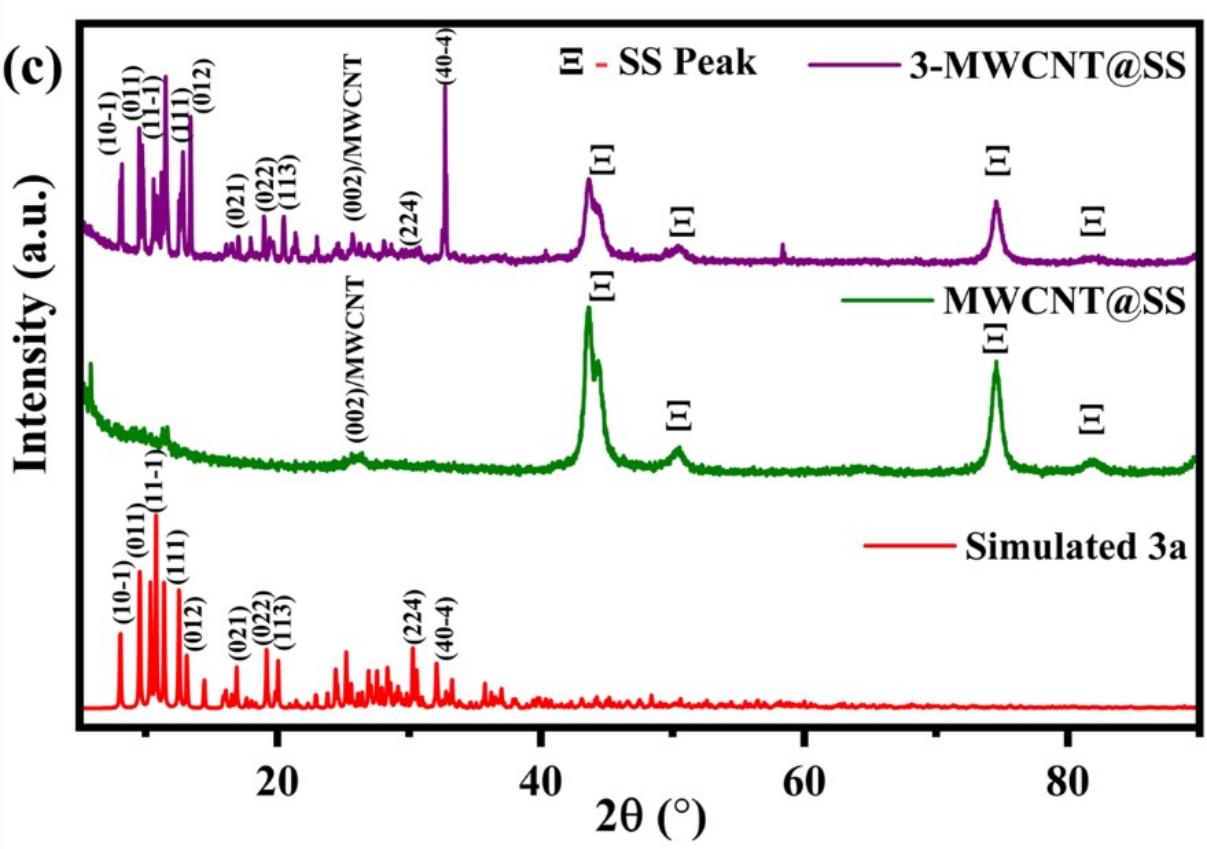
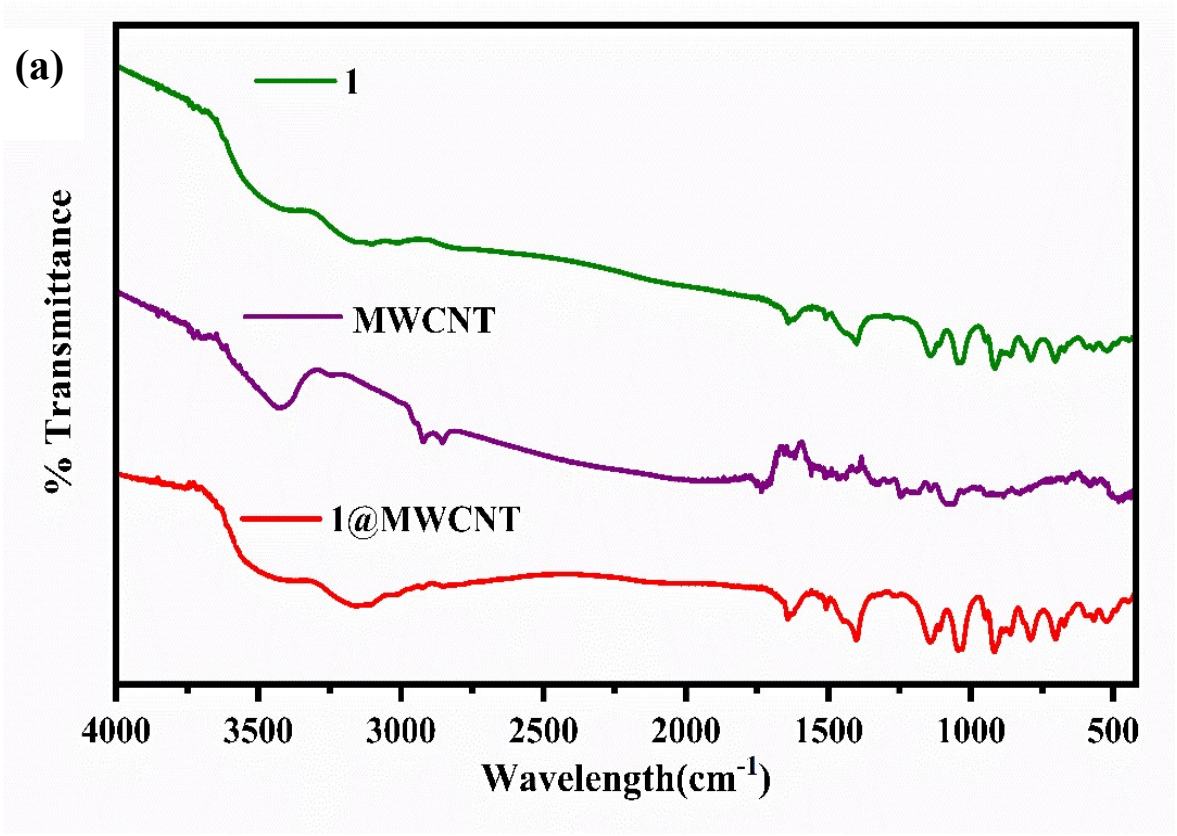
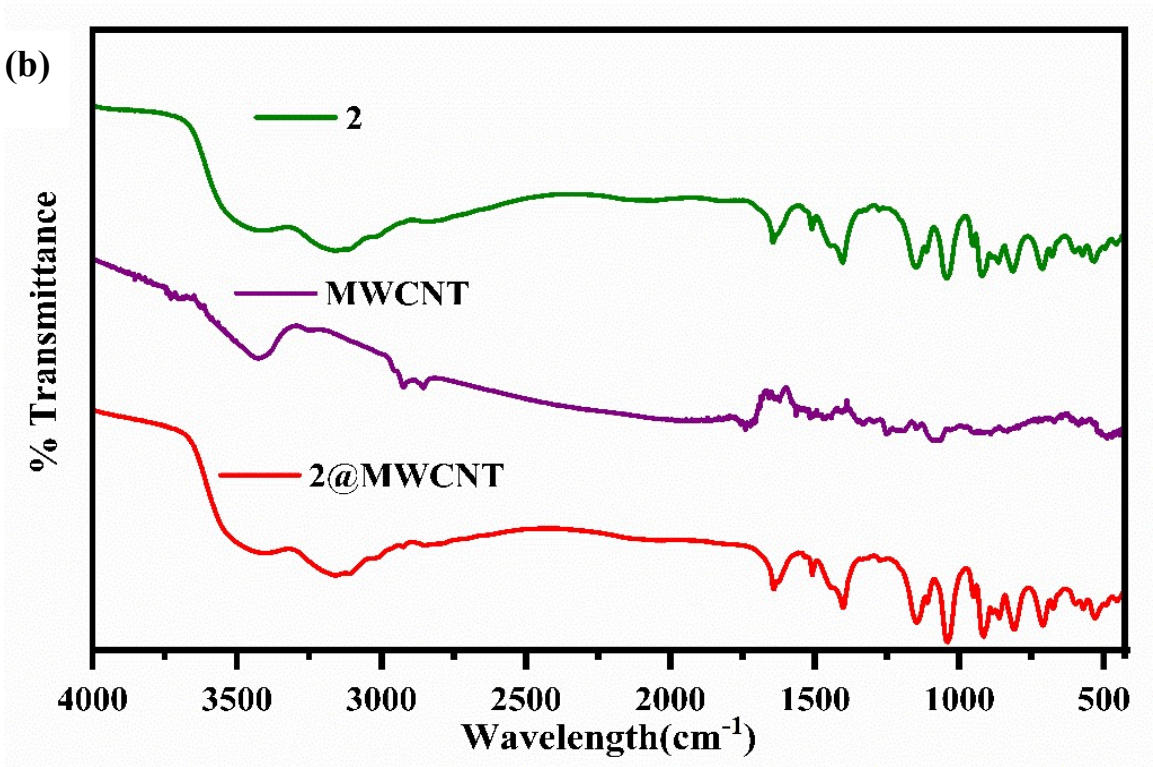


Figure S23. Comparative PXRD patterns of **(a)** simulated P-XRD pattern of **1a**, MWCNT@SS and **1-MWCNT@SS**, **(b)** simulated P-XRD pattern of **2a**, MWCNT@SS and **2-MWCNT@SS**, **(c)** simulated P-XRD pattern of **3a**, MWCNT@SS and **3-MWCNT@SS**. SS = Stainless steel.


(a)
1
MWCNT
1@MWCNT
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavelength(cm-1)


(b)
2
MWCNT
2@MWCNT
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavelength(cm-1)

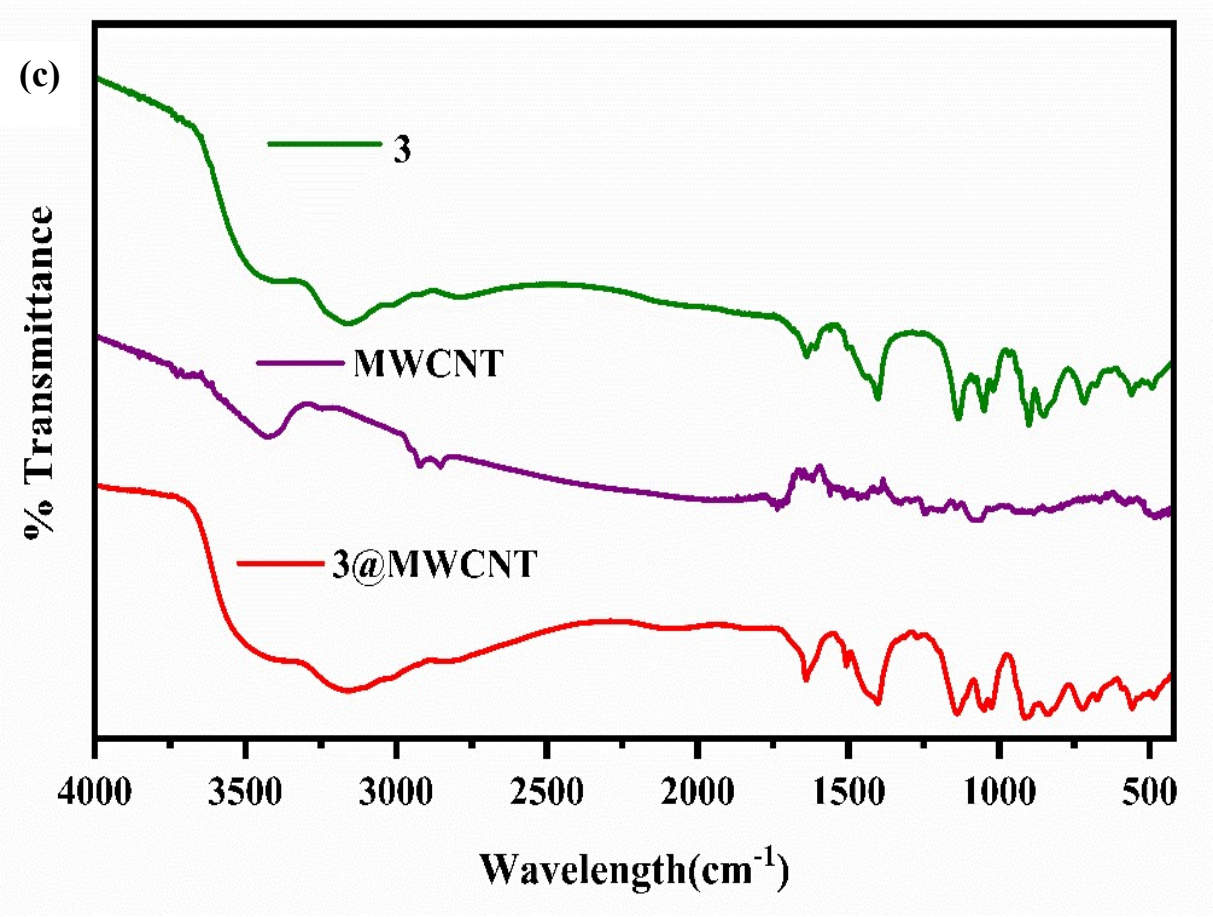


Figure S24. Comparative infrared spectra of **(a) 1a**, MWCNT@SS and **1-MWCNT@SS**, **(b) 2a**, MWCNT@SS and **2-MWCNT@SS**, **(c) 3a**, MWCNT@SS and **3-MWCNT@SS**.

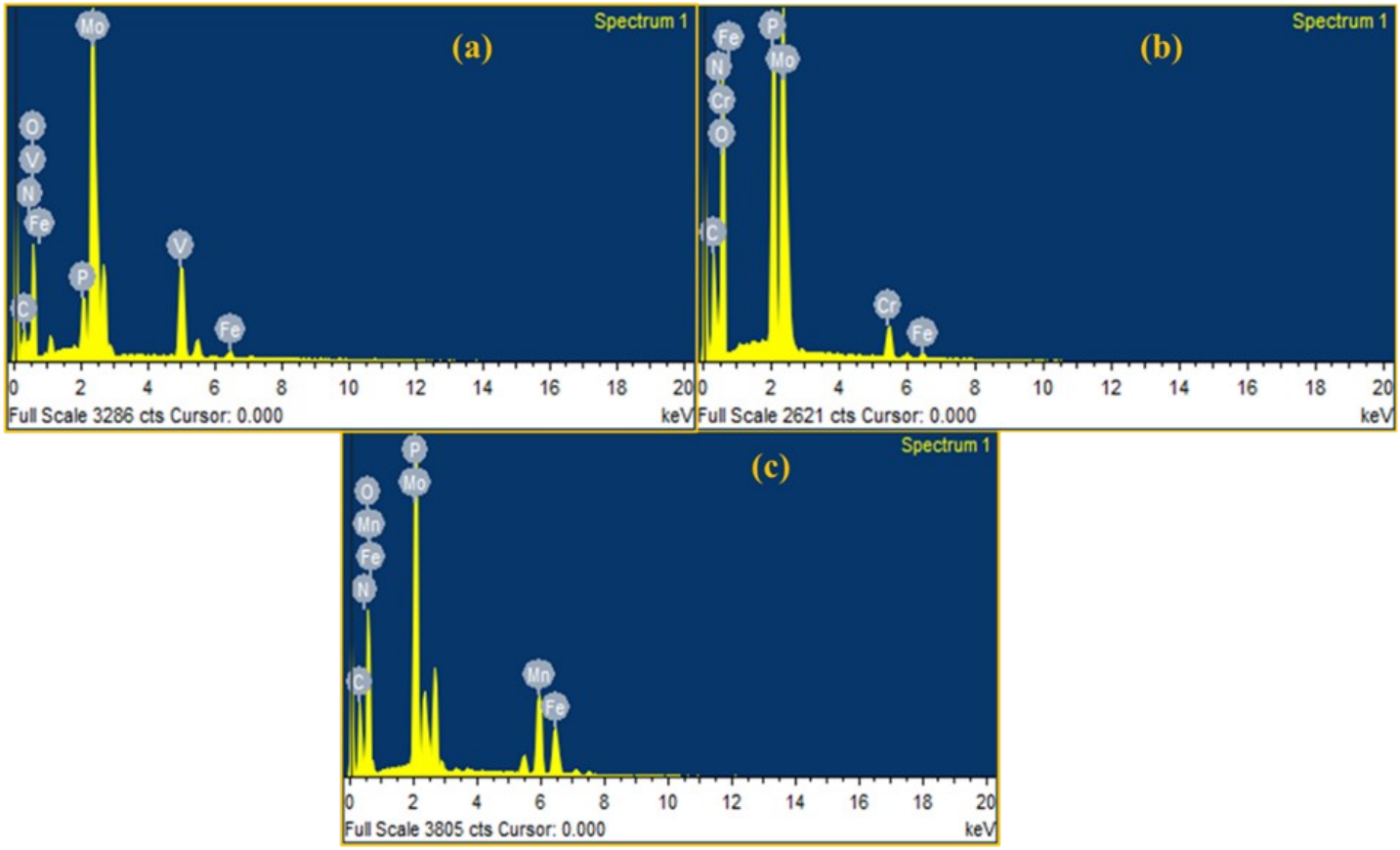


Figure S25. EDX spectra for **1-MWCNT@SS**, **(b) 2-MWCNT@SS**, and **(c) 3-MWCNT@SS**

Table S10. Elemental composition of **1-MWCNT@SS**, **2-MWCNT@SS,** and **3-MWCNT@SS.**

1-MWCNT@SS		**2-MWCNT@SS**		**3-MWCNT@SS**	
Element	**Weight %**	**Element**	**Weight %**	**Element**	**Weight %**
C	12.20	C	22.04	C	24.69
N	8.54	N	11.32	N	7.80
O	33.31	O	38.65	O	30.10
P	1.56	P	6.37	P	12.17
V	9.63	Cr	1.97	Mn	10.41
Fe	1.17	Fe	0.36	Fe	6.30
Mo	11.60	Mo	19.29	Mo	8.51

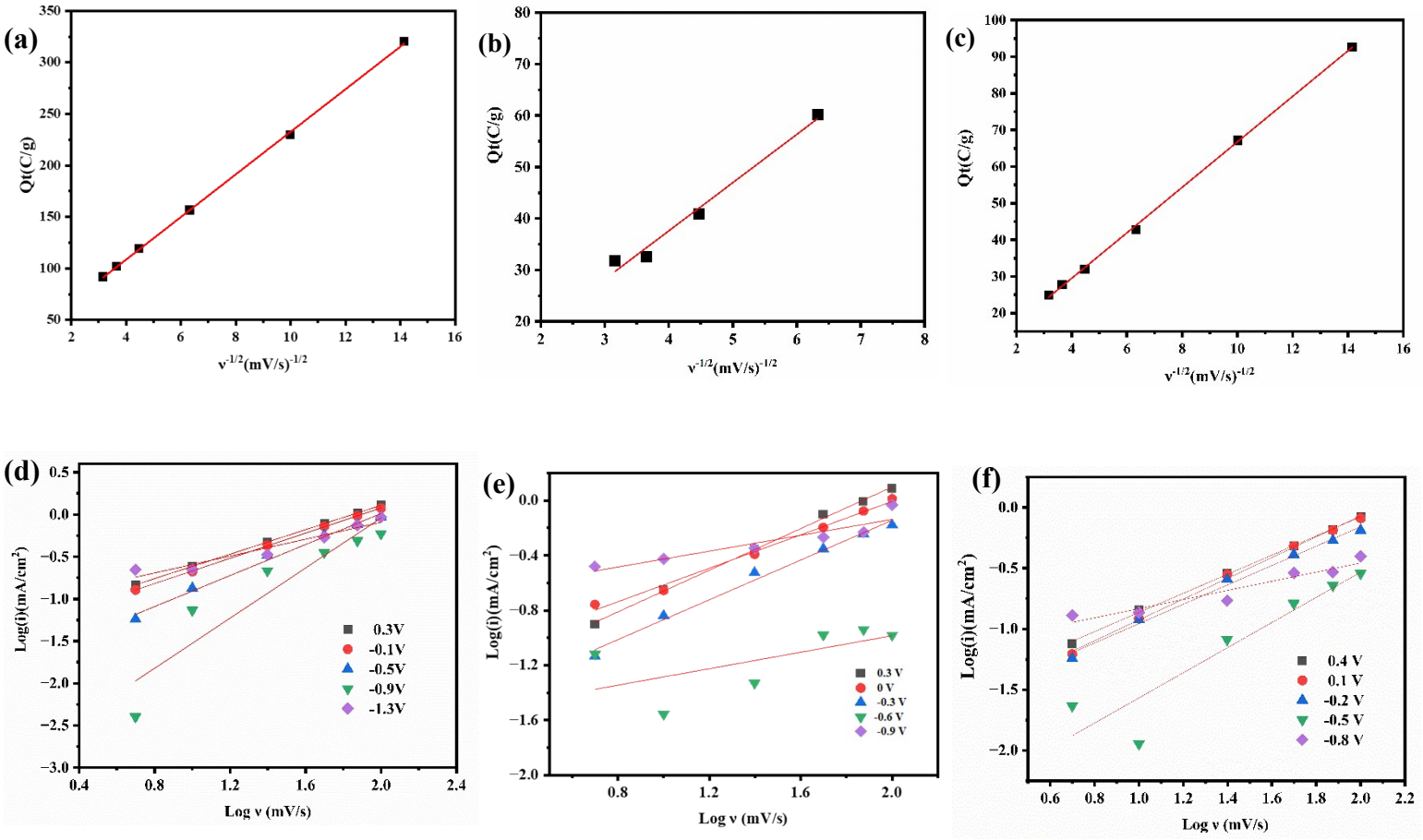


Figure S26. Electrochemical performance Q(C/g) *vs.* $v^{-1/2}(mV/s)^{-1/2}$ for **(a) 1-MWCNT@SS**, **(b) 2-MWCNT@SS**, and **(c) 3-MWCNT@SS**. Plots of log i(mA/cm^2) *vs.* log(v)(mV/s) for **(d) 1-MWCNT@SS**, **(e) 2-MWCNT@SS**, and **(f) 3-MWCNT@SS**.

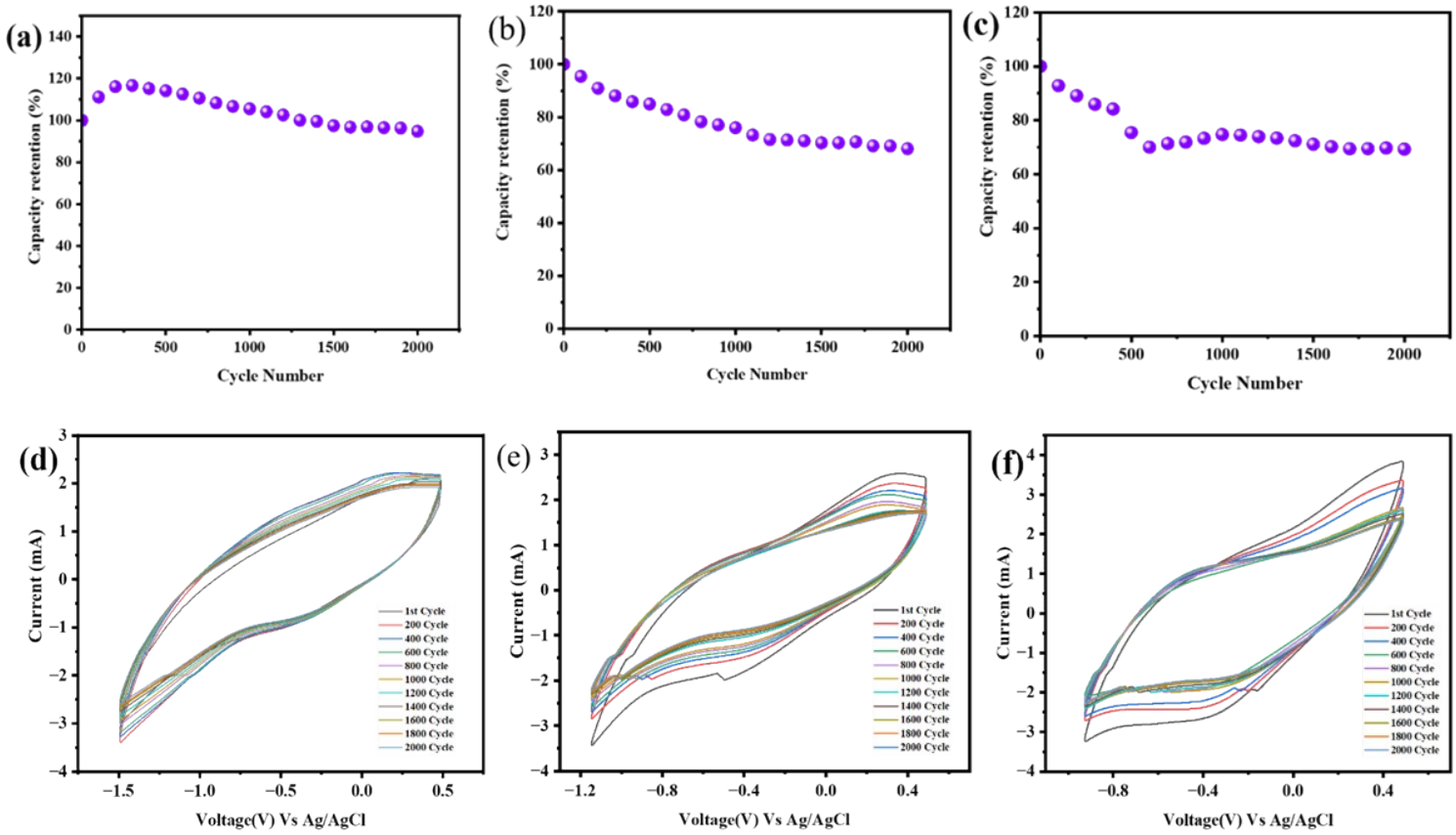


Figure S27. Capacity retention for the electrodes **(a) 1-MWCNT@SS**, **(b) 2-MWCNT@SS**, and **(c) 3-MWCNT@SS**. Cyclic stability test: Retention of stability for 2000 CV cycles for **(a) 1-MWCNT@SS**, **(b) 2-MWCNT@SS**, and **(c) 3-MWCNT@SS**.

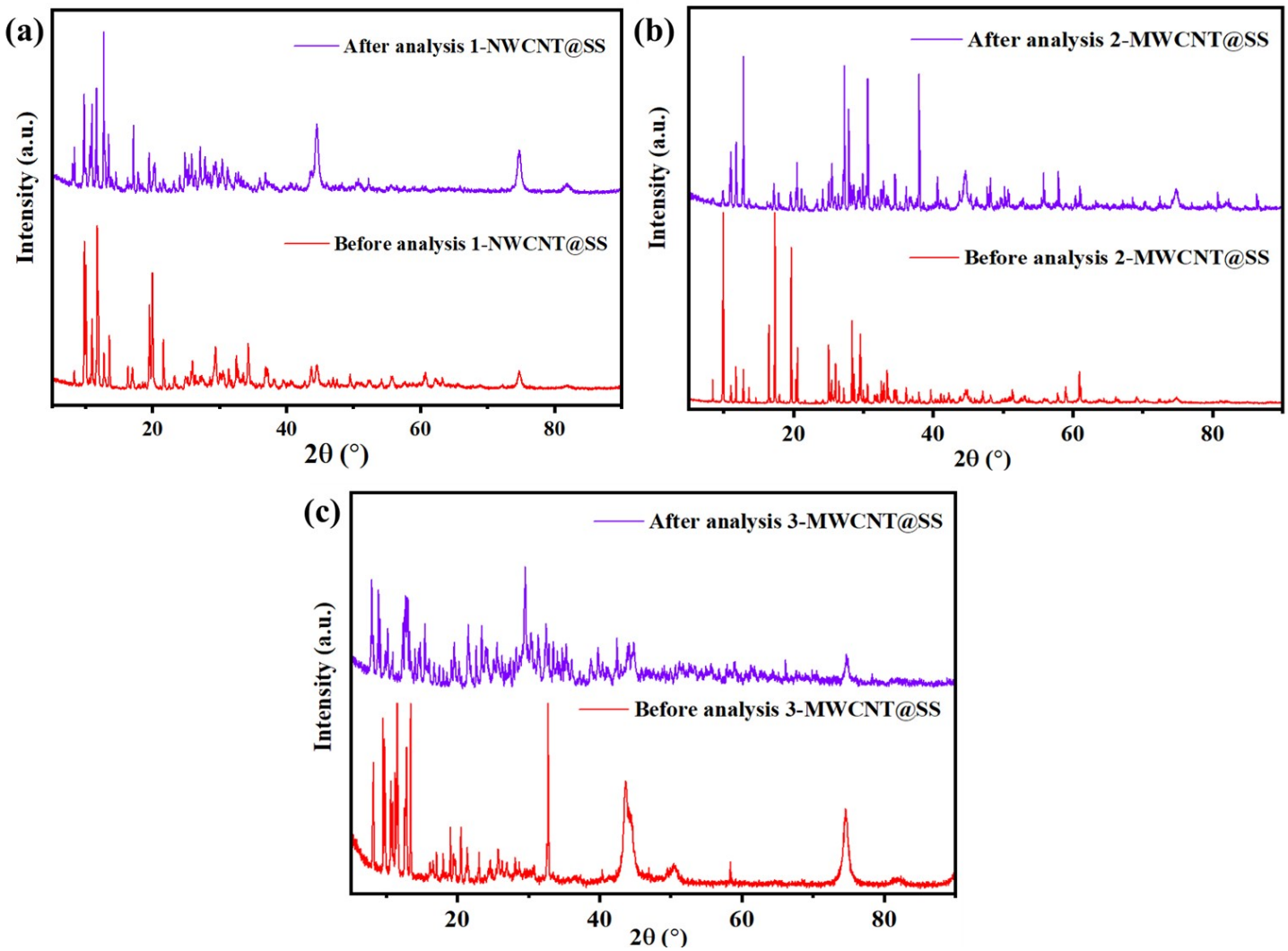


Figure S28. Comparative P-XRD patterns of **1-MWCNT@SS, 2-MWCNT@SS**, and **3-MWCNT@SS** before and after electrochemical analysis.

Optimized Coordinates

Polyanion **1′** in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5186.3590181 hf

Mo	-2.938782000	-2.237280000	0.177840000
O	-2.903055000	-3.509786000	-1.011274000
O	-2.993387000	-3.127908000	1.660804000
O	-1.282554000	-1.584200000	0.121015000
O	-5.032866000	-2.014004000	0.054292000
O	-3.487028000	-0.569173000	-1.420669000
O	-3.587620000	-0.254965000	1.238167000
Mo	-5.536231000	-0.273421000	-0.158958000
O	-6.593066000	-0.320731000	-1.544792000
O	-6.687199000	-0.016201000	1.124019000
O	-4.816243000	1.535758000	-0.348396000
V	0.011793000	-0.011020000	-0.042538000
O	1.286091000	1.575117000	-0.223568000
O	1.256809000	-0.984824000	-1.355526000
O	-1.257551000	0.965849000	1.227052000
O	-1.164242000	0.668865000	-1.517674000
O	1.240250000	-0.704438000	1.394581000
P	-2.711166000	0.793531000	-1.731845000
O	-3.099431000	1.449631000	-3.053425000
C	-3.417666000	1.817340000	-0.316620000
P	-2.806947000	1.147211000	1.330536000
O	-3.273005000	2.041892000	2.466916000
N	-0.413222000	6.002675000	1.299058000
C	-0.033624000	4.798797000	0.811770000
C	-1.715499000	6.288920000	1.208779000
C	-3.307226000	3.338109000	-0.570379000
C	-2.278797000	4.188423000	0.124059000
H	-3.190612000	3.450348000	-1.667475000
H	-4.301779000	3.735707000	-0.310455000
C	-2.666138000	5.437228000	0.650870000
C	-0.910738000	3.880062000	0.215922000
H	-3.723811000	5.729411000	0.626058000
H	-2.037865000	7.270415000	1.615020000
H	1.029736000	4.530386000	0.895118000
H	-0.507830000	2.934547000	-0.156620000

Mo	2.933145000	2.248405000	-0.308807000
Mo	5.559585000	0.313488000	-0.074821000
O	2.935042000	3.181219000	-1.769260000
O	2.922935000	3.484949000	0.915485000
O	3.559522000	0.286393000	-1.444142000
O	3.546534000	0.547296000	1.219436000
O	5.027011000	2.048125000	-0.261502000
O	4.870069000	-1.504727000	0.094181000
O	6.655388000	0.361057000	1.278926000
O	6.675493000	0.087874000	-1.394938000
P	2.807987000	-1.127034000	-1.504459000
P	2.793280000	-0.828248000	1.566127000
C	3.474825000	-1.813984000	0.115666000
O	3.254573000	-2.023655000	-2.652159000
O	3.239074000	-1.470008000	2.871494000
C	3.477415000	-3.337686000	0.250745000
H	4.107881000	-3.549214000	1.133065000
H	4.031931000	-3.683024000	-0.644427000
C	2.248115000	-4.205344000	0.342192000
C	0.956754000	-3.872335000	-0.091630000
C	2.421748000	-5.525601000	0.813601000
H	0.725640000	-2.867904000	-0.460656000
C	-0.051737000	-4.851181000	-0.070312000
C	1.360978000	-6.425418000	0.784091000
H	3.405126000	-5.840690000	1.188063000
N	0.135543000	-6.123686000	0.341304000
H	-1.057703000	-4.576874000	-0.416157000
H	1.517527000	-7.463726000	1.143430000

Polyanion **2′** in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5286.7894563 hf

Mo	-2.890874000	2.237788000	-0.414701000
O	-2.842904000	3.592380000	0.674564000
O	-2.907240000	3.016923000	-1.961160000
O	-1.241008000	1.556711000	-0.288627000
O	-4.982105000	2.078519000	-0.305333000
O	-3.490074000	0.724375000	1.298358000
O	-3.569102000	0.195833000	-1.319173000
Mo	-5.528348000	0.371346000	0.053296000

O	-6.597440000	0.561997000	1.416558000
O	-6.672513000	0.034309000	-1.217253000
O	-4.854777000	-1.430105000	0.398113000
Cr	-0.000122000	0.000296000	0.000010000
O	1.241019000	-1.556478000	0.288885000
O	1.267158000	1.065489000	1.189815000
O	-1.266948000	-1.065418000	-1.189513000
O	-1.191054000	-0.545080000	1.537464000
O	1.190907000	0.545544000	-1.537167000
P	-2.738698000	-0.621454000	1.736268000
O	-3.160931000	-1.154108000	3.102762000
C	-3.462039000	-1.743450000	0.405795000
P	-2.819399000	-1.226786000	-1.283389000
O	-3.294118000	-2.203659000	-2.346103000
N	-0.492775000	-6.113471000	-0.725187000
C	-0.113209000	-4.859134000	-0.388288000
C	-1.795257000	-6.386215000	-0.602833000
C	-3.394348000	-3.238470000	0.786124000
C	-2.359064000	-4.166289000	0.211422000
H	-3.322993000	-3.258578000	1.892993000
H	-4.386237000	-3.639619000	0.520510000
C	-2.746148000	-5.471050000	-0.157612000
C	-0.990175000	-3.872710000	0.088534000
H	-3.804338000	-5.757497000	-0.099515000
H	-2.117589000	-7.410315000	-0.885366000
H	0.950333000	-4.604343000	-0.503898000
H	-0.588250000	-2.887884000	0.341908000
Mo	2.890691000	-2.237681000	0.414774000
Mo	5.528357000	-0.371519000	-0.053957000
O	2.907070000	-3.017115000	1.961095000
O	2.842586000	-3.592061000	-0.674791000
O	3.569061000	-0.196332000	1.319275000
O	3.489815000	-0.724311000	-1.298830000
O	4.981971000	-2.078571000	0.304790000
O	4.854861000	1.429978000	-0.398182000
O	6.597178000	-0.562254000	-1.417421000

O	6.672806000	-0.034638000	1.216401000
P	2.819657000	1.226448000	1.283594000
P	2.738560000	0.621702000	-1.736213000
C	3.462132000	1.743367000	-0.405608000
O	3.294615000	2.203134000	2.346396000
O	3.160513000	1.154732000	-3.102645000
C	3.394636000	3.238499000	-0.785451000
H	3.323447000	3.259015000	-1.892331000
H	4.386522000	3.639458000	-0.519552000
C	2.359352000	4.166256000	-0.210698000
C	2.746477000	5.470888000	0.158747000
C	0.990386000	3.872797000	-0.088242000
H	3.804706000	5.757243000	0.101009000
C	1.795549000	6.386057000	0.603904000
C	0.113417000	4.859230000	0.388496000
H	0.588456000	2.888049000	-0.341909000
N	0.493004000	6.113458000	0.725794000
H	2.117943000	7.410037000	0.886813000
H	-0.950171000	4.604541000	0.503743000

Polyanion **3′** in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5393.276736 hf

Mo	2.863793000	2.229050000	0.418537000
O	2.749660000	3.589895000	-0.653594000
O	2.877605000	2.991107000	1.970729000
O	1.219829000	1.502044000	0.306756000
O	4.949876000	2.162755000	0.239100000
O	3.419253000	0.749290000	-1.316020000
O	3.684008000	0.238244000	1.292348000
Mo	5.553802000	0.468330000	-0.102875000
O	6.555037000	0.691581000	-1.513570000
O	6.763138000	0.190906000	1.118106000
O	4.931371000	-1.347427000	-0.465627000
Mn	-0.000131000	-0.000059000	-0.000142000

O	-1.219948000	-1.502441000	-0.306863000
O	-1.454450000	1.149944000	-1.361170000
O	1.455068000	-1.150252000	1.362001000
O	1.167210000	-0.613368000	-1.421481000
O	-1.167110000	0.612557000	1.421886000
P	2.722355000	-0.634480000	-1.684823000
O	3.068535000	-1.176762000	-3.066682000
C	3.554053000	-1.717745000	-0.386112000
P	2.994478000	-1.232855000	1.343335000
O	3.654868000	-2.157930000	2.358343000
N	0.587367000	-6.091946000	0.674207000
C	0.222176000	-4.828897000	0.356051000
C	1.888564000	-6.375015000	0.561503000
C	3.534173000	-3.215609000	-0.742918000
C	2.480714000	-4.145875000	-0.205437000
H	3.515582000	-3.256553000	-1.851519000
H	4.515446000	-3.596897000	-0.415098000
C	2.852408000	-5.460302000	0.144099000
C	1.113505000	-3.841109000	-0.091634000
H	3.908893000	-5.754561000	0.093029000
H	2.198081000	-7.406941000	0.829194000
H	-0.840695000	-4.569095000	0.464523000
H	0.728669000	-2.847502000	-0.333582000
Mo	-2.864050000	-2.229086000	-0.418653000
Mo	-5.553938000	-0.468051000	0.102878000
O	-2.878025000	-2.991093000	-1.970870000
O	-2.750273000	-3.590006000	0.653397000
O	-3.683652000	-0.238136000	-1.292395000
O	-3.419326000	-0.749544000	1.315999000
O	-4.950359000	-2.162496000	-0.239209000

O	-4.930988000	1.347437000	0.465824000
O	-6.555476000	-0.691246000	1.513379000
O	-6.763017000	-0.190135000	-1.118268000
P	-2.993912000	1.232838000	-1.342954000
P	-2.722201000	0.634087000	1.685078000
C	-3.553645000	1.717582000	0.386461000
O	-3.653744000	2.158156000	-2.358072000
O	-3.068481000	1.176277000	3.066941000
C	-3.533523000	3.215448000	0.743462000
H	-3.514215000	3.256239000	1.852061000
H	-4.515021000	3.596736000	0.416347000
C	-2.480449000	4.145837000	0.205450000
C	-2.852599000	5.460019000	-0.144500000
C	-1.113162000	3.841457000	0.091600000
H	-3.909189000	5.753912000	-0.093527000
C	-1.889076000	6.374923000	-0.562219000
C	-0.222180000	4.829384000	-0.356488000
H	-0.727959000	2.848037000	0.333738000
N	-0.587798000	6.092251000	-0.674924000
H	-2.198931000	7.406669000	-0.830168000
H	0.840726000	4.569807000	-0.465024000

Polyanion **1′**$^{-}$ in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5185.8669403 hf

Mo	2.266637000	-2.959074000	-0.281263000
O	1.912686000	-4.203459000	0.879824000
O	2.119570000	-3.812462000	-1.789097000
O	0.857458000	-1.879384000	-0.232176000
O	4.369150000	-3.312890000	-0.162461000
O	3.242534000	-1.572317000	1.354187000
O	3.447865000	-1.187086000	-1.270797000

Mo	5.311653000	-1.783399000	0.137767000
O	6.296353000	-2.183006000	1.523821000
O	6.508576000	-1.804610000	-1.131989000
O	5.113513000	0.154317000	0.398720000
V	-0.000065000	-0.000080000	0.000052000
O	-0.857509000	1.879122000	0.232419000
O	-1.540558000	-0.638602000	1.196064000
O	1.540319000	0.638106000	-1.196237000
O	1.314371000	0.218541000	1.513400000
O	-1.314470000	-0.218449000	-1.513480000
P	2.837232000	-0.070076000	1.736228000
O	3.353476000	0.369788000	3.103567000
C	3.851639000	0.801329000	0.375726000
P	3.074920000	0.373611000	-1.290450000
O	3.761166000	1.122912000	-2.436910000
N	7.358730000	4.816469000	-0.720968000
C	6.933106000	4.776772000	0.576980000
C	6.665261000	3.938188000	-1.524834000
C	3.996190000	2.299534000	0.729498000
C	5.182196000	3.090206000	0.214790000
H	3.050645000	2.775911000	0.403907000
H	4.012633000	2.354763000	1.833091000
C	5.630348000	3.095463000	-1.142791000
C	5.905855000	3.966891000	1.061583000
H	5.114922000	2.415544000	-1.845298000
H	6.992346000	3.921506000	-2.581736000
H	7.469339000	5.444871000	1.285093000
H	5.645247000	4.008903000	2.127976000
Mo	-2.266517000	2.959060000	0.281646000
Mo	-5.311376000	1.783551000	-0.137683000

O	-2.119406000	3.812117000	1.789659000
O	-1.912163000	4.203580000	-0.879170000
O	-3.447911000	1.186818000	1.270861000
O	-3.242544000	1.572501000	-1.354035000
O	-4.368726000	3.313002000	0.162789000
O	-5.113582000	-0.154032000	-0.398904000
O	-6.296034000	2.183575000	-1.523654000
O	-6.508293000	1.804755000	1.132075000
P	-3.075127000	-0.373863000	1.290339000
P	-2.837294000	0.070282000	-1.736279000
C	-3.851830000	-0.801315000	-0.375906000
O	-3.761472000	-1.123243000	2.436704000
O	-3.353568000	-0.369296000	-3.103710000
C	-3.996667000	-2.299390000	-0.730036000
H	-3.051092000	-2.775909000	-0.404724000
H	-4.013281000	-2.354312000	-1.833645000
C	-5.182611000	-3.090163000	-0.215333000
C	-5.630545000	-3.095830000	1.142294000
C	-5.906439000	-3.966650000	-1.062268000
H	-5.115224000	-2.415879000	1.844850000
C	-6.665299000	-3.938739000	1.524346000
C	-6.933509000	-4.776735000	-0.577660000
H	-5.646072000	-4.008307000	-2.128732000
N	-7.358872000	-4.816924000	0.720311000
H	-6.992260000	-3.922366000	2.581282000
H	-7.469885000	-5.444582000	-1.285936000

Polyanion **2′**$^{-}$ in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5286.294311 hf

Mo	2.211079000	2.943613000	0.280093000
O	1.841539000	4.184873000	-0.877436000

O	2.044354000	3.790375000	1.788306000
O	0.811941000	1.841525000	0.223319000
O	4.301438000	3.331646000	0.174422000
O	3.212813000	1.582812000	-1.346079000
O	3.405538000	1.190945000	1.272012000
Mo	5.264436000	1.812179000	-0.130685000
O	6.250001000	2.230224000	-1.510696000
O	6.456109000	1.845124000	1.144190000
O	5.093102000	-0.126590000	-0.393926000
Cr	-0.000218000	0.000266000	0.000045000
O	-0.811718000	-1.840925000	-0.223438000
O	-1.512996000	0.645578000	-1.191089000
O	1.512349000	-0.644896000	1.191380000
O	1.296686000	-0.216807000	-1.527928000
O	-1.297146000	0.217784000	1.527771000
P	2.813971000	0.077447000	-1.737747000
O	3.343579000	-0.349304000	-3.104819000
C	3.837190000	-0.786221000	-0.379695000
P	3.045025000	-0.373390000	1.282498000
O	3.732038000	-1.122597000	2.428713000
N	7.372797000	-4.776267000	0.721617000
C	6.665047000	-3.909239000	1.525345000
C	6.956805000	-4.732318000	-0.579408000
C	3.998127000	-2.281336000	-0.739069000
C	5.187302000	-3.064310000	-0.220474000
H	3.054185000	-2.766795000	-0.422153000
H	4.022065000	-2.330687000	-1.842864000
C	5.925742000	-3.928804000	-1.066884000
C	5.625268000	-3.073800000	1.140627000
H	5.673742000	-3.966478000	-2.135548000

H	7.504698000	-5.390980000	-1.287557000
H	6.984062000	-3.896027000	2.584827000
H	5.098084000	-2.402216000	1.842683000
Mo	-2.210504000	-2.943580000	-0.279940000
Mo	-5.263787000	-1.812537000	0.130751000
O	-2.043622000	-3.790209000	-1.788207000
O	-1.840346000	-4.184652000	0.877570000
O	-3.405676000	-1.190869000	-1.271974000
O	-3.212623000	-1.582655000	1.346121000
O	-4.300404000	-3.331997000	-0.174062000
O	-5.093438000	0.126165000	0.394021000
O	-6.249437000	-2.230882000	1.510669000
O	-6.455251000	-1.846029000	-1.144359000
P	-3.045572000	0.373563000	-1.282449000
P	-2.814310000	-0.077213000	1.737754000
C	-3.837813000	0.786291000	0.379759000
O	-3.732623000	1.122437000	-2.428843000
O	-3.343869000	0.349280000	3.104924000
C	-3.999258000	2.281280000	0.739211000
H	-3.055249000	2.766904000	0.422711000
H	-4.023571000	2.330500000	1.843007000
C	-5.188349000	3.064195000	0.220302000
C	-5.926857000	3.928924000	1.066513000
C	-5.626187000	3.073557000	-1.140829000
H	-5.675012000	3.966739000	2.135211000
C	-6.957749000	4.732456000	0.578781000
C	-6.665826000	3.909034000	-1.525834000
H	-5.099083000	2.401771000	-1.842732000
N	-7.373619000	4.776322000	-0.722297000
H	-7.505656000	5.391263000	1.286808000

H	-6.984747000	3.895651000	-2.585339000

Polyanion **3′**$^{-}$ in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5392.7541922 hf

Mo	3.200713000	2.222509000	0.397521000
O	3.235717000	3.576691000	-0.708902000
O	3.348221000	3.025423000	1.940587000
O	1.527664000	1.699548000	0.333169000
O	5.390501000	1.999546000	0.228221000
O	3.735205000	0.680374000	-1.301807000
O	3.883756000	0.201756000	1.317068000
Mo	5.853122000	0.286957000	-0.086931000
O	6.913047000	0.400905000	-1.481029000
O	7.027802000	-0.068554000	1.166269000
O	5.105597000	-1.496403000	-0.392590000
Mn	0.000089000	0.000117000	-0.000190000
O	-1.527646000	-1.699582000	-0.333783000
O	-1.572719000	1.084377000	-1.323391000
O	1.572623000	-1.084022000	1.323457000
O	1.434770000	-0.609881000	-1.554880000
O	-1.434607000	0.609622000	1.554640000
P	2.974354000	-0.677289000	-1.715841000
O	3.456477000	-1.242355000	-3.061904000
C	3.705377000	-1.771855000	-0.358590000
P	3.110602000	-1.224919000	1.343462000
O	3.688785000	-2.179425000	2.392436000
N	0.373911000	-5.873997000	0.664695000
C	0.120499000	-4.600879000	0.276798000
C	1.653266000	-6.256744000	0.636217000
C	3.600175000	-3.275815000	-0.683881000
C	2.455741000	-4.112452000	-0.181260000
H	3.633171000	-3.332174000	-1.793176000
H	4.534437000	-3.721033000	-0.299074000
C	2.706871000	-5.434242000	0.242034000
C	1.108560000	-3.705922000	-0.163840000
H	3.740761000	-5.806038000	0.267923000
H	1.869186000	-7.299569000	0.959832000

H	-0.924600000	-4.264767000	0.322944000
H	0.827213000	-2.702469000	-0.491478000
Mo	-3.200714000	-2.222445000	-0.397983000
Mo	-5.853127000	-0.287030000	0.087288000
O	-3.348421000	-3.025051000	-1.941202000
O	-3.235645000	-3.576855000	0.708175000
O	-3.883729000	-0.201606000	-1.317168000
O	-3.735035000	-0.680612000	1.301612000
O	-5.390516000	-1.999529000	-0.228311000
O	-5.105603000	1.496317000	0.392974000
O	-6.912903000	-0.401261000	1.481466000
O	-7.027953000	0.068698000	-1.165723000
P	-3.110718000	1.225121000	-1.343352000
P	-2.974162000	0.677024000	1.715792000
C	-3.705376000	1.771805000	0.358829000
O	-3.689046000	2.179741000	-2.392142000
O	-3.456108000	1.241868000	3.062010000
C	-3.600154000	3.275734000	0.684273000
H	-3.633011000	3.331984000	1.793576000
H	-4.534472000	3.720970000	0.299628000
C	-2.455800000	4.112440000	0.181573000
C	-2.707014000	5.434231000	-0.241667000
C	-1.108601000	3.705975000	0.164042000
H	-3.740921000	5.805990000	-0.267447000
C	-1.653479000	6.256773000	-0.635950000
C	-0.120609000	4.600967000	-0.276679000
H	-0.827171000	2.702542000	0.491654000
N	-0.374109000	5.874071000	-0.664567000
H	-1.869465000	7.299599000	-0.959516000
H	0.924502000	4.264887000	-0.322938000

Polyanion **1′**$^{+}$ in B3LYP-D3(BJ)/Def2svp gas phase

Energy = -5186.780418 hf

Mo	2.988741000	2.014436000	-0.000796000
O	2.979764000	3.076324000	-1.348059000
O	2.980081000	3.076604000	1.346083000

O	1.255661000	1.350504000	-0.000533000
O	4.994073000	1.693737000	-0.001000000
O	3.465352000	0.142249000	-1.358254000
O	3.465615000	0.143236000	1.357734000
Mo	5.444645000	-0.102051000	-0.000450000
O	6.530570000	-0.245201000	-1.341883000
O	6.531066000	-0.244176000	1.340695000
O	4.642989000	-1.878346000	0.000439000
V	-0.000014000	-0.000080000	0.000054000
O	-1.255843000	-1.350502000	0.000570000
O	-1.083048000	0.917075000	-1.382108000
O	1.083378000	-0.917300000	1.381991000
O	1.083205000	-0.918464000	-1.381160000
O	-1.083523000	0.918360000	1.381237000
P	2.615107000	-1.199595000	-1.540770000
O	2.961094000	-2.034507000	-2.764898000
C	3.231491000	-2.063367000	0.000639000
P	2.615334000	-1.198388000	1.541437000
O	2.961445000	-2.032414000	2.766147000
N	-0.931850000	-5.352981000	0.001763000
C	-0.338415000	-4.970431000	-1.135124000
C	-0.338882000	-4.968613000	1.138302000
C	3.003770000	-3.572611000	0.001105000
C	1.580681000	-4.060099000	0.001260000
H	3.517192000	-3.952380000	-0.898044000
H	3.517208000	-3.951900000	0.900473000
C	0.897369000	-4.324020000	1.196475000
C	0.897806000	-4.325829000	-1.193793000
H	1.343447000	-3.998195000	2.140821000
H	-0.889092000	-5.181029000	2.064409000

H	-0.888166000	-5.184443000	-2.061150000
H	1.344166000	-4.001258000	-2.138432000
Mo	-2.988904000	-2.014468000	0.000663000
Mo	-5.444628000	0.102225000	-0.000772000
O	-2.979930000	-3.077048000	-1.345961000
O	-2.980354000	-3.075933000	1.348175000
O	-3.465367000	-0.143223000	-1.358407000
O	-3.465740000	-0.142205000	1.357512000
O	-4.994221000	-1.693602000	-0.000018000
O	-4.642858000	1.878402000	-0.001466000
O	-6.530951000	0.245458000	1.340339000
O	-6.530672000	0.244388000	-1.342231000
P	-2.614958000	1.198296000	-1.541850000
P	-2.615465000	1.199602000	1.540378000

Polyanion **1′** in B3LYP-D3(BJ)/Def2svp water medium

Energy = -5188.6682985 hf

Mo	-2.405218000	-2.967018000	0.130878000
O	-2.229265000	-4.185919000	-1.094654000
O	-2.318898000	-3.856890000	1.624189000
O	-0.841535000	-2.060005000	0.114886000
O	-4.521377000	-3.120619000	0.095091000
O	-3.163438000	-1.483754000	-1.397583000
O	-3.259988000	-1.221024000	1.459939000
Mo	-5.410482000	-1.539900000	-0.183542000
O	-6.334668000	-1.802548000	-1.619868000
O	-6.608713000	-1.531908000	1.064087000
O	-4.924561000	0.371266000	-0.302511000
V	0.000417000	-0.216284000	0.036423000
O	0.688917000	1.682829000	-0.100099000
O	1.369932000	-0.914294000	-1.241830000

O	-1.335742000	0.520929000	1.331736000
O	-1.197025000	0.226458000	-1.518855000
O	1.248514000	-0.640341000	1.531381000
P	-2.743069000	0.027382000	-1.643163000
O	-3.310499000	0.568035000	-2.948957000
C	-3.592575000	0.868162000	-0.211436000
P	-2.889898000	0.307085000	1.428491000
O	-3.495158000	1.073581000	2.600237000
N	-7.123339000	4.630182000	0.622008000
C	-6.482670000	4.805890000	-0.540184000
C	-6.602026000	3.722507000	1.461697000
C	-3.538946000	2.400979000	-0.409643000
C	-4.788417000	3.156935000	-0.026834000
H	-2.673653000	2.786713000	0.155580000
H	-3.341333000	2.614790000	-1.469601000
C	-5.456497000	2.975734000	1.193999000
C	-5.334518000	4.101261000	-0.906335000
H	-5.070237000	2.257849000	1.918592000
H	-7.128585000	3.576762000	2.411656000
H	-6.904307000	5.547181000	-1.228149000
H	-4.868986000	4.289831000	-1.876735000
Mo	2.112662000	2.758922000	-0.226159000
Mo	5.372602000	1.711997000	0.063986000
O	1.803889000	3.658507000	-1.680048000
O	1.898361000	3.973890000	1.003405000
O	2.981907000	1.094264000	-1.560939000
O	2.861619000	1.402429000	1.572641000
O	4.198929000	3.080772000	-0.211751000
O	4.969598000	-0.184417000	0.271139000
O	6.263653000	2.099411000	1.495365000

O	6.555093000	1.810760000	-1.189485000
P	2.872185000	-0.460223000	-1.400279000
P	2.743664000	-0.151958000	1.698379000
C	3.700040000	-0.832718000	0.236004000
O	3.564607000	-1.209858000	-2.536410000
O	3.375411000	-0.696203000	2.978455000
C	3.864320000	-2.369743000	0.425281000
H	3.134794000	-2.881959000	-0.221892000
H	3.612752000	-2.632192000	1.461100000
C	5.250880000	-2.891263000	0.146414000
C	5.888483000	-2.731911000	-1.094064000
C	5.971264000	-3.562256000	1.142180000
H	5.372257000	-2.207033000	-1.899092000
C	7.174963000	-3.236219000	-1.268611000

Polyanion **2′** in B3LYP-D3(BJ)/Def2svp water medium

Energy = -5289.1265027 hf

Mo	3.030040000	-1.959278000	-0.116513000
O	3.304242000	-2.961860000	1.276976000
O	3.116246000	-3.100792000	-1.418638000
O	1.283912000	-1.524957000	0.022362000
O	5.123282000	-1.567853000	-0.176706000
O	3.419430000	-0.200030000	1.469323000
O	3.150407000	-0.278728000	-1.593637000
Mo	5.614333000	0.181068000	-0.064426000
O	6.770779000	0.318445000	1.211328000
O	6.561439000	0.450803000	-1.486473000
O	4.583584000	1.833760000	-0.076903000
Cr	-0.017353000	-0.022727000	0.081461000
O	-1.297513000	1.473908000	0.178004000
O	-1.013038000	-1.003259000	1.493577000

O	0.919458000	0.992193000	-1.347774000
O	1.067836000	0.901953000	1.477667000
O	-1.054143000	-0.954681000	-1.339835000
P	2.619072000	1.154560000	1.531241000
O	3.019212000	2.031681000	2.716756000
C	3.165240000	1.981232000	-0.049331000
P	2.466406000	1.140215000	-1.567332000
O	2.815974000	1.973602000	-2.797674000
N	-1.010643000	5.277176000	0.055478000
C	-0.353671000	4.956386000	1.178111000
C	-0.445771000	4.911064000	-1.102535000
C	2.929480000	3.500639000	-0.062669000
C	1.515820000	4.015378000	-0.021112000
H	3.477912000	3.897013000	0.804381000
H	3.419741000	3.877034000	-0.972444000
C	0.797760000	4.287330000	-1.193262000
C	0.890510000	4.327448000	1.193334000
H	1.218998000	4.034623000	-2.167342000
H	-1.001985000	5.144042000	-2.016432000
H	-0.834616000	5.227125000	2.123745000
H	1.385635000	4.105249000	2.139938000
Mo	-3.023392000	1.983816000	0.205951000
Mo	-5.555432000	-0.154311000	-0.276449000
O	-3.129459000	3.171504000	1.462513000
O	-3.148938000	2.925192000	-1.253978000
O	-3.270821000	0.267689000	1.589687000
O	-3.425268000	0.090643000	-1.435914000
O	-5.066084000	1.574188000	0.075538000
O	-4.625376000	-1.849305000	0.066656000
O	-6.344953000	-0.219951000	-1.817690000

O	-6.853742000	-0.418569000	0.839591000
P	-2.571888000	-1.143455000	1.642782000
P	-2.589796000	-1.245538000	-1.452450000
C	-3.210174000	-2.028797000	0.118543000
O	-2.971081000	-1.940558000	2.881929000
O	-2.925725000	-2.147379000	-2.638936000
C	-2.983598000	-3.547562000	0.185877000
H	-3.500514000	-3.972105000	-0.687047000
H	-3.499689000	-3.900796000	1.091018000
C	-1.559829000	-4.038206000	0.203373000
C	-0.856445000	-4.215624000	1.402474000
C	-0.895306000	-4.385505000	-0.980313000
H	-1.309729000	-3.931855000	2.353093000

Polyanion ***3′*** in B3LYP-D3(BJ)/Def2svp in water medium

Energy = -5395.6224775 hf

Mo	2.882471000	2.115724000	-0.280148000
O	2.904234000	3.351112000	-1.489813000
O	2.949515000	2.960717000	1.241183000
O	1.176319000	1.496662000	-0.218017000
O	4.868186000	1.701523000	-0.083504000
O	3.137514000	0.340813000	-1.569705000
O	3.777457000	-0.093650000	1.556540000
Mo	5.495312000	-0.024899000	0.146004000
O	6.430908000	-0.212515000	-1.307770000
O	6.704218000	-0.082303000	1.382010000
O	4.670184000	-1.807429000	-0.196784000
Mn	-0.000508000	0.001670000	-0.000106000
O	-1.175861000	-1.493391000	0.219235000
O	-1.319478000	0.927066000	-1.627682000
O	1.318438000	-0.923213000	1.627784000

O	0.942904000	-1.018767000	-1.346113000
O	-0.944777000	1.021807000	1.345521000
P	2.503970000	-1.102490000	-1.579455000
O	2.836456000	-1.856834000	-2.863704000
C	3.265772000	-2.019322000	-0.131499000
P	2.805417000	-1.354177000	1.554715000
O	3.214569000	-2.386518000	2.613392000
N	-0.857299000	-5.366775000	-0.244254000
C	-0.285896000	-4.952626000	-1.383009000
C	-0.213549000	-5.080112000	0.894710000
C	3.064027000	-3.538596000	-0.265092000
C	1.656882000	-4.075783000	-0.250704000
H	3.550959000	-3.836278000	-1.204954000
H	3.626682000	-3.989523000	0.565218000
C	1.023579000	-4.438699000	0.945282000
C	0.950368000	-4.311359000	-1.438410000
H	1.508224000	-4.248914000	1.903803000
H	-0.699768000	-5.391095000	1.824778000
H	-0.830959000	-5.157733000	-2.310505000
H	1.376309000	-4.015190000	-2.398199000
Mo	-2.880874000	-2.115738000	0.279599000
Mo	-5.495025000	0.024176000	-0.146517000
O	-2.943153000	-2.960932000	-1.242032000
O	-2.902260000	-3.351301000	1.489170000
O	-3.776999000	0.093307000	-1.554228000
O	-3.137679000	-0.340188000	1.569379000
O	-4.864882000	-1.702017000	0.080279000
O	-4.673017000	1.808929000	0.194654000
O	-6.424261000	0.205592000	1.312378000
O	-6.706840000	0.080836000	-1.379370000

P	-2.807021000	1.355652000	-1.554669000
P	-2.506069000	1.103739000	1.578880000
C	-3.268485000	2.020681000	0.130940000
O	-3.218449000	2.385987000	-2.614309000
O	-2.838737000	1.857819000	2.863266000
C	-3.066067000	3.539872000	0.264819000
H	-3.553363000	3.837723000	1.204447000
H	-3.627924000	3.991387000	-0.565726000
C	-1.658186000	4.075211000	0.251361000
C	-1.023843000	4.437337000	-0.944337000
C	-0.951877000	4.310016000	1.439341000
H	-1.508336000	4.248796000	-1.903163000
C	0.214252000	5.076880000	-0.893355000
C	0.285382000	4.949407000	1.384394000
H	-1.378650000	4.014758000	2.399019000

Polyanion **1′⁻** in B3LYP-D3(BJ)/Def2svp in water medium

Energy = -5188.7445478 hf

Mo	2.244010000	2.872603000	0.248013000
O	2.046731000	4.105392000	-0.979251000
O	2.077206000	3.762087000	1.742982000
O	0.740254000	1.917567000	0.164686000
O	4.394772000	3.198551000	0.181683000
O	3.179306000	1.480651000	-1.355808000
O	3.197543000	1.184736000	1.473711000
Mo	5.336731000	1.682137000	-0.184078000
O	6.239686000	2.014567000	-1.627914000
O	6.549718000	1.670264000	1.057078000
O	5.001254000	-0.260523000	-0.285141000
V	-0.000153000	0.000767000	0.000256000
O	-0.740746000	-1.915548000	-0.163951000

O	-1.438865000	0.739862000	-1.367232000
O	1.438508000	-0.738945000	1.367472000
O	1.310448000	-0.333693000	-1.630666000
O	-1.310893000	0.335007000	1.631043000
P	2.834430000	-0.049087000	-1.661416000
O	3.519793000	-0.512122000	-2.947676000
C	3.707679000	-0.854896000	-0.221035000
P	2.949981000	-0.379463000	1.426656000
O	3.682161000	-1.069787000	2.581727000
N	7.554984000	-4.294261000	0.526981000
C	6.975686000	-4.429157000	-0.672253000
C	6.906006000	-3.534168000	1.423056000
C	3.773587000	-2.385769000	-0.443846000
C	5.086310000	-3.038038000	-0.083010000
H	2.949566000	-2.848077000	0.124809000
H	3.585566000	-2.598375000	-1.505757000
C	5.691083000	-2.898874000	1.176063000
C	5.764791000	-3.827508000	-1.020700000
H	5.204381000	-2.285728000	1.937048000
H	7.383363000	-3.420169000	2.402996000
H	7.502388000	-5.048850000	-1.406593000
H	5.354550000	-3.973991000	-2.022780000
Mo	-2.243247000	-2.872202000	-0.248161000
Mo	-5.336310000	-1.682614000	0.184013000
O	-2.074648000	-3.761781000	-1.742852000
O	-2.045637000	-4.104757000	0.979340000
O	-3.197160000	-1.184766000	-1.473539000
O	-3.178849000	-1.480382000	1.356181000
O	-4.393759000	-3.198691000	-0.181769000
O	-5.001520000	0.260122000	0.285039000

O	-6.239133000	-2.015372000	1.627845000
O	-6.549291000	-1.671018000	-1.057134000
P	-2.950131000	0.379541000	-1.426582000
P	-2.834721000	0.049535000	1.661589000
C	-3.708095000	0.854861000	0.220998000
O	-3.682483000	1.069427000	-2.581808000
O	-3.520477000	0.512437000	2.947693000
C	-3.774502000	2.385764000	0.443609000
H	-2.950687000	2.848298000	-0.125153000
H	-3.586506000	2.598560000	1.505484000
C	-5.087502000	3.037463000	0.082757000
C	-5.691703000	2.898754000	-1.176644000
C	-5.766825000	3.825886000	1.020712000
H	-5.204336000	2.286373000	-1.937822000
C	-6.906951000	3.533419000	-1.423663000
C	-6.977990000	4.426963000	0.672220000
H	-5.357042000	3.971968000	2.023038000
N	-7.556757000	4.292484000	-0.527318000
H	-7.383858000	3.419792000	-2.403865000
H	-7.505376000	5.045820000	1.406774000

Polyanion **2'⁻** in B3LYP-D3(BJ)/Def2svp in water medium

Energy = -5289.2194269 hf

Mo	2.614878000	-2.812381000	-0.795092000
O	2.931652000	-4.271346000	0.120098000
O	3.194373000	-3.288510000	-2.376112000
O	0.883590000	-2.687647000	-0.947730000
O	5.762144000	-2.166338000	-0.229501000
O	2.989127000	-1.812827000	1.076700000
O	3.252188000	-0.826466000	-1.451358000
Mo	6.238506000	-0.571264000	0.289452000

O	7.250195000	-0.794122000	1.691483000
O	7.262385000	0.090919000	-0.965472000
O	4.908976000	0.781505000	0.753128000
Cr	-0.015442000	0.085629000	0.010431000
O	-0.898045000	2.649290000	0.802917000
O	-1.454513000	-0.826263000	1.141351000
O	1.437730000	0.988889000	-1.111071000
O	1.158599000	-0.106796000	1.675041000
O	-1.165244000	0.163122000	-1.678653000
P	2.691417000	-0.411169000	1.733509000
O	3.293569000	-0.314087000	3.134148000
C	3.502539000	0.888058000	0.669520000
P	2.972640000	0.685549000	-1.100992000
O	3.793983000	1.606063000	-2.001770000
N	3.951335000	5.653958000	-1.260001000
C	2.698358000	5.212470000	-1.081797000
C	4.919876000	5.006449000	-0.595792000
C	3.065106000	2.252179000	1.263890000
C	3.381276000	3.453656000	0.422057000
H	1.984852000	2.218041000	1.449658000
H	3.568455000	2.327424000	2.240857000
C	4.691023000	3.922426000	0.249645000
C	2.365916000	4.133115000	-0.264893000
H	5.525600000	3.434471000	0.755863000
H	5.942615000	5.371101000	-0.743187000
H	1.907795000	5.745925000	-1.621321000
H	1.327059000	3.809531000	-0.171891000
Mo	-2.634051000	2.830553000	0.713185000
Mo	-6.262121000	0.472525000	-0.262063000
O	-3.140905000	3.352982000	2.303398000

O	-2.962646000	4.277917000	-0.216624000
O	-3.364391000	0.910986000	1.377451000
O	-3.062459000	1.815943000	-1.156374000
O	-5.935132000	2.183219000	-0.103980000
O	-4.900242000	-0.833692000	-0.778349000
O	-7.511654000	0.287220000	-1.471399000
O	-6.945165000	-0.076030000	1.250931000
P	-3.000211000	-0.603370000	1.095810000
P	-2.708252000	0.408370000	-1.768046000
C	-3.491710000	-0.887345000	-0.672613000
O	-3.790495000	-1.520924000	2.024376000
O	-3.284894000	0.242764000	-3.172442000
C	-3.000184000	-2.252979000	-1.215960000
H	-1.918584000	-2.189069000	-1.385177000
H	-3.483968000	-2.375118000	-2.198046000
C	-3.292255000	-3.436188000	-0.340176000
C	-4.587354000	-3.947964000	-0.178691000
C	-2.268067000	-4.052472000	0.391810000
H	-5.428558000	-3.511342000	-0.719500000
C	-4.794158000	-5.010120000	0.699876000
C	-2.577936000	-5.114466000	1.239532000
H	-1.240355000	-3.694101000	0.306362000
N	-3.817307000	-5.596694000	1.407035000
H	-5.805553000	-5.408327000	0.838430000
H	-1.780148000	-5.598432000	1.813942000

Polyanion **3′⁻** in B3LYP-D3(BJ)/Def2svp in water medium

Energy = -5395.7520669 hf

Mo	3.157265000	2.519445000	-0.023473000
O	3.316272000	3.723411000	-1.274559000
O	3.080272000	3.360920000	1.511935000

O	1.598553000	1.725670000	-0.229147000
O	4.873872000	1.611602000	-0.074678000
O	3.198599000	-0.241778000	-1.876362000
O	3.582350000	-0.135253000	1.388866000
Mo	5.308504000	-0.246306000	0.060927000
O	6.188281000	-0.387567000	-1.430825000
O	6.539123000	-0.353511000	1.265261000
O	4.539702000	-2.042634000	-0.088246000
Mn	0.001115000	0.000624000	-0.000747000
O	-1.598870000	-1.724998000	0.230025000
O	-1.144592000	1.004963000	-1.549745000
O	1.144424000	-1.005777000	1.549679000
O	0.895104000	-1.363485000	-1.436196000
O	-0.895705000	1.362131000	1.436380000
P	2.431116000	-1.577315000	-1.658778000
O	2.726006000	-2.620899000	-2.758057000
C	3.135436000	-2.281194000	-0.052588000
P	2.637756000	-1.414643000	1.526722000
O	3.052777000	-2.290054000	2.719131000
N	-0.925858000	-5.665545000	0.171165000
C	-0.276580000	-5.487247000	-0.986140000
C	-0.364735000	-5.137399000	1.267907000
C	2.976769000	-3.806131000	0.032970000
C	1.577937000	-4.358931000	0.068885000
H	3.503243000	-4.219735000	-0.838555000
H	3.509844000	-4.127621000	0.940292000
C	0.864372000	-4.479926000	1.269765000
C	0.955929000	-4.845238000	-1.088883000
H	1.283979000	-4.090927000	2.198959000
H	-0.918250000	-5.252601000	2.205260000

H	-0.753164000	-5.891308000	-1.885714000
H	1.443177000	-4.730141000	-2.057347000
Mo	-3.157268000	-2.519075000	0.024351000
Mo	-5.308821000	0.246449000	-0.061219000
O	-3.080075000	-3.360547000	-1.511158000
O	-3.316007000	-3.722993000	1.275587000
O	-3.582563000	0.134945000	-1.388886000
O	-3.199908000	0.242012000	1.876905000
O	-4.874169000	-1.611439000	0.075572000
O	-4.539835000	2.042698000	0.087621000
O	-6.188743000	0.388333000	1.430342000
O	-6.539418000	0.353099000	-1.265591000
P	-2.637827000	1.414152000	-1.526813000
P	-2.431541000	1.576999000	1.658790000
C	-3.135484000	2.280941000	0.052399000
O	-3.052664000	2.289544000	-2.719305000
O	-2.725798000	2.621020000	2.757820000
C	-2.976473000	3.805816000	-0.033279000
H	-3.502866000	4.219553000	0.838234000
H	-3.509547000	4.127302000	-0.940601000
C	-1.577567000	4.358483000	-0.069264000
C	-0.864102000	4.479598000	-1.270218000
C	-0.955414000	4.844698000	1.088463000
H	-1.283856000	4.090662000	-2.199381000
C	0.364977000	5.137134000	-1.268477000
C	0.277075000	5.486727000	0.985618000
H	-1.442648000	4.729725000	2.056930000
N	0.926175000	5.665181000	-0.171739000
H	0.918348000	5.252515000	-2.205903000
H	0.753717000	5.890779000	1.885164000

Polyanion **1′**$^{+}$ in B3LYP-D3(BJ)/Def2svp in water medium

Energy = -5188.5611881 hf

Mo	-3.011620000	-1.987482000	-0.200623000
O	-2.871328000	-2.931301000	-1.630372000
O	-3.005251000	-3.160811000	1.063005000
O	-1.265141000	-1.291654000	0.005637000
O	-4.967916000	-1.643198000	0.018718000
O	-3.227305000	-0.224807000	-1.572757000
O	-3.362860000	-0.137589000	1.471277000
Mo	-5.494136000	0.126508000	0.319972000
O	-6.749571000	0.313124000	-0.850507000
O	-6.318587000	0.226713000	1.831382000
O	-4.588181000	1.829886000	0.016943000
V	0.001930000	0.006388000	0.015279000
O	1.266450000	1.293405000	0.007729000
O	0.975084000	-1.013075000	-1.392646000
O	-1.011301000	0.954452000	1.435119000
O	-0.977048000	1.018908000	-1.391470000
O	1.009175000	-0.951602000	1.435299000
P	-2.536802000	1.186881000	-1.571214000
O	-2.898534000	2.028259000	-2.788321000
C	-3.174578000	2.030885000	-0.025715000
P	-2.560226000	1.218801000	1.534500000
O	-2.915674000	2.083282000	2.738161000
N	0.990671000	5.297827000	-0.211920000
C	0.309505000	5.011822000	-1.328587000
C	0.442772000	4.912553000	0.948061000
C	-2.964606000	3.551643000	-0.057033000
C	-1.548532000	4.063797000	-0.115669000
H	-3.517324000	3.923916000	-0.931611000

H	-3.451828000	3.948620000	0.845762000
C	-0.804155000	4.297125000	1.048506000
C	-0.944108000	4.400999000	-1.333973000
H	-1.208979000	4.029127000	2.025623000
H	1.018183000	5.119116000	1.855771000
H	0.775798000	5.299421000	-2.276835000
H	-1.458318000	4.206825000	-2.276270000
Mo	3.021752000	1.989395000	-0.199537000
Mo	5.491879000	-0.131421000	0.320440000
O	2.881448000	2.932977000	-1.628565000
O	3.004895000	3.161792000	1.063883000
O	3.227474000	0.227185000	-1.573012000
O	3.363123000	0.136951000	1.470620000
O	4.973718000	1.645318000	0.026814000
O	4.583962000	-1.832467000	0.015981000
O	6.318410000	-0.238670000	1.829201000
O	6.745256000	-0.318225000	-0.852000000
P	2.534224000	-1.183730000	-1.572466000
P	2.557378000	-1.218293000	1.533807000
C	3.169930000	-2.030299000	-0.027271000
O	2.895256000	-2.024805000	-2.789932000
O	2.913013000	-2.083522000	2.736806000
C	2.957975000	-3.550556000	-0.059604000
H	3.445926000	-3.948563000	0.842343000
H	3.509524000	-3.922727000	-0.934967000
C	1.541865000	-4.062448000	-0.116948000
C	0.936569000	-4.399504000	-1.334791000
C	0.799498000	-4.298202000	1.048032000
H	1.449167000	-4.203204000	-2.277549000
C	-0.314913000	-5.014664000	-1.328169000

C	-0.445541000	-4.917662000	0.948757000
H	1.205036000	-4.029936000	2.024802000
N	-0.993388000	-5.304348000	-0.210803000
H	-0.781482000	-5.303128000	-2.276003000
H	-1.019084000	-5.126818000	1.857068000

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