SUPPLEMENTARY INFORMATION

Synthesis, Structure, Electrochemistry and Magnetism of Cobalt-, Nickel- and Zinc-Containing $[M_4(OH)_3(H_2O)_2(\alpha\text{-}SiW_{10}O_{36.5})_2]^{13-}$ ($M = Co^{2+}, Ni^{2+}, Zn^{2+}$)

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Table S1. Selected bond valence sum (BVS) values for polyanions **1-3**.

$[Co_4(OH)_3(H_2O)_2(SiW_{10}O_{36.5})_2]^{13-}$ (1)

μ_3-O (3Co-O)	**BVS Value**	**Co**	**BVS value**
O4C2	1.06	Co1	1.98
Co-O_t		Co2	2.00
O5C2	0.30		
µ-O (W-O-Co)			
O1C1	1.62		
O3C2	1.64		

$[Ni_4(OH)_3(H_2O)_2(SiW_{10}O_{36.5})_2]^{13-}$ (2)

μ_3-O (3Ni-O)	**BVS Value**	**Ni**	**BVS value**
O2N1	1.04	Ni1	1.99
Ni-O_t		Ni2	2.00
O1TN	0.32		
µ-O (W-O-Ni)			
O1N2	1.74		
O2N2	1.73		
O3N1	1.71		

$[Zn_4(OH)_3(H_2O)_2(SiW_{10}O_{36.5})_2]^{13-}$ (3)

μ_3-O (3Zn-O)	**BVS Value**	**Zn**	**BVS value**
O5Z2	1.03	Zn1	1.98
Zn-O_t		Zn2	2.00
O1Z2	0.33		
µ-O (W-O-Ni)			
O1Z1	1.74		
O2Z1	1.67		
O3Z1	1.74		

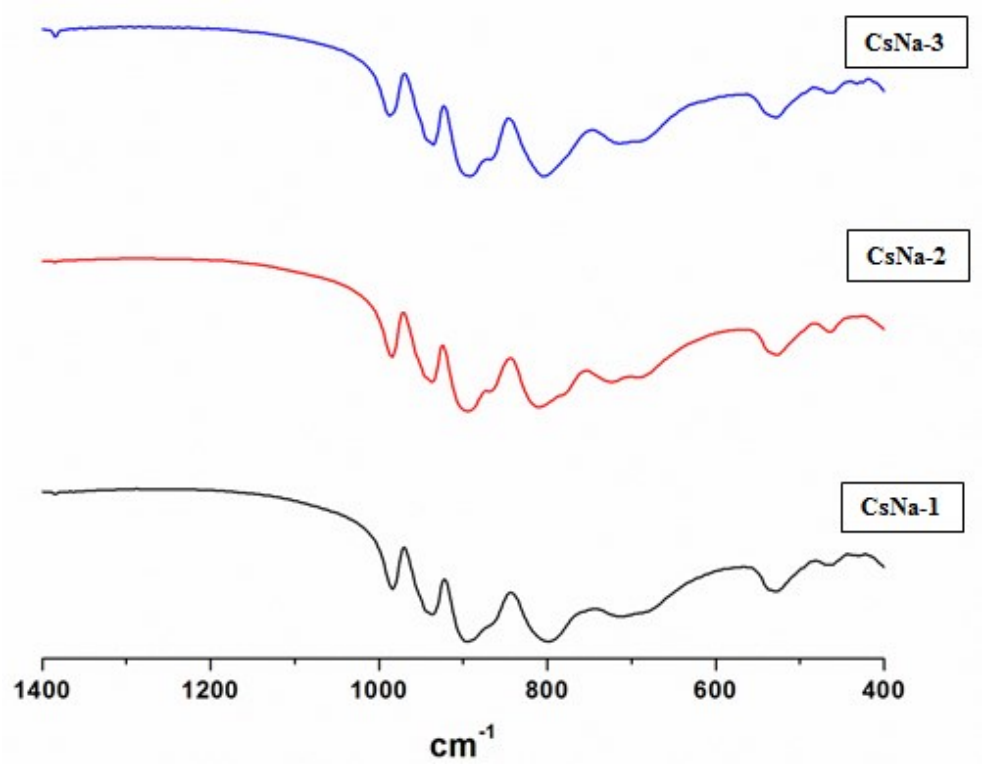

Figure S1. FT-IR spectra of **CsNa-1** (black), **CsNa-2** (red), and **CsNa-3** (blue).

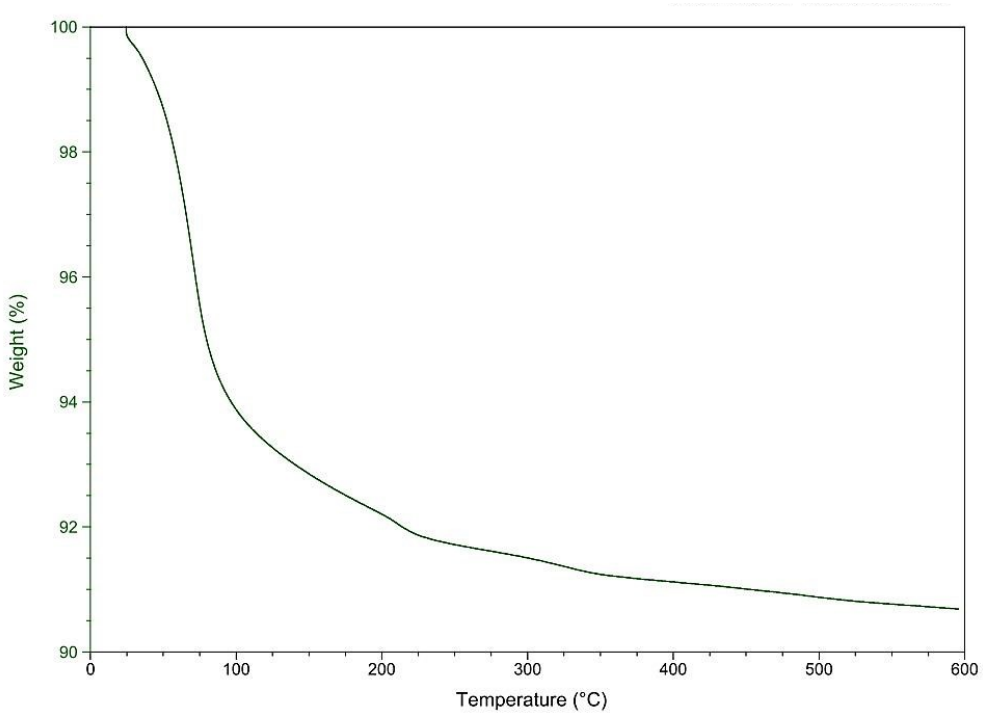

Figure S2. Thermogram for **CsNa-1** from room temperature to 600 °C.

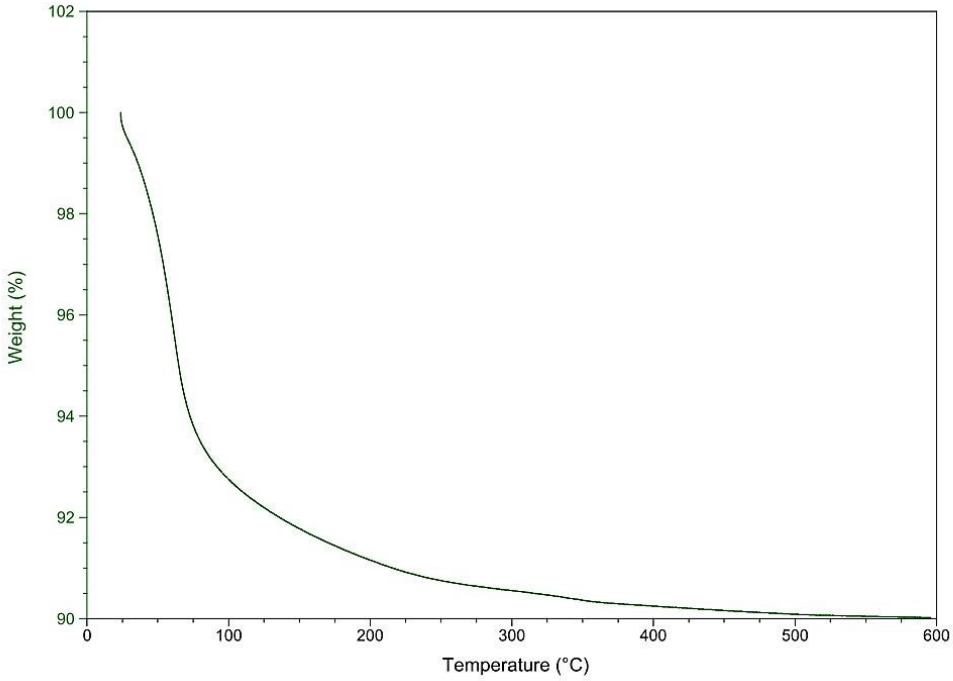

Figure S3. Thermogram of **CsNa-2** from room temperature to 600 °C.

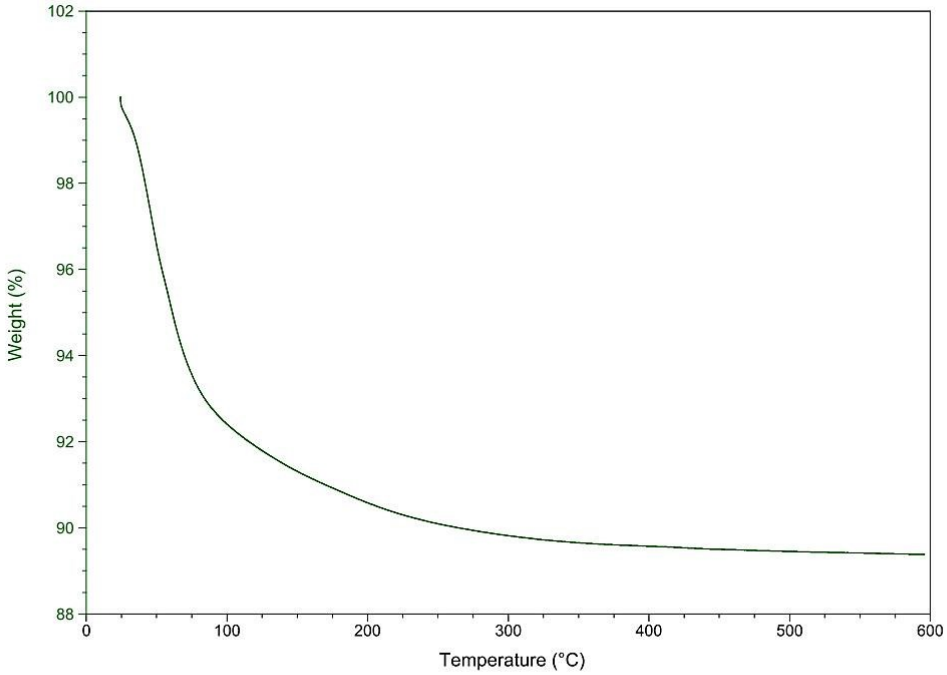

Figure S4. Thermogram of **CsNa-3** from room temperature to 600 °C.

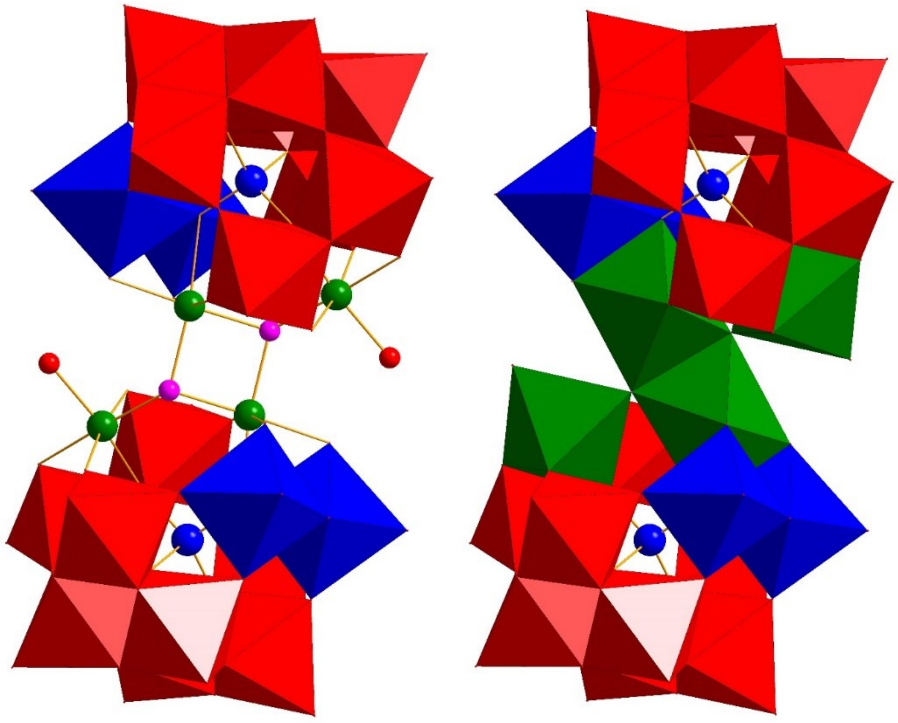

Figure S5. Mixed ball-and-stick/polyhedral (left) and full polyhedral (right) representation of $[Ni_4(OH)_4(H_2O)_2(\beta\text{-}SiW_{10}O_{36})_2]^{12-}$. The blue WO_6 octahedra are part of the rotated triad. For details see ref. 8 in the main text.

UV-vis absorption spectroscopy and stability tests

The UV-vis absorption spectra for polyanions **1-3** were recorded in a pH 7 medium (1 M CH_3COOLi / CH_3COOH) on a Shimazu U2550 spectrophotometer. In the UV region, all three polyanions exhibit intense absorption bands (at around 232 nm) attributed to oxygen-to-tungsten charge transfer transitions (Figure S6a). As expected, the absorption bands due to the Co^{2+} and Ni^{2+} centers are observed at higher wavelengths (Figure S6b). The spectrum of **1** presents a well-defined band located at 528 nm followed by a shoulder at around 500 nm while that of **2** is characterized by a broad band at around 400 nm and a very weak absorbance at around 700 nm attributed to the Ni^{2+} centers. The spectra of all three polyanions were reproducible with respect to absorbances and wavelengths for at least the period of time matching the duration of the electrochemical experiments (up to several hours).

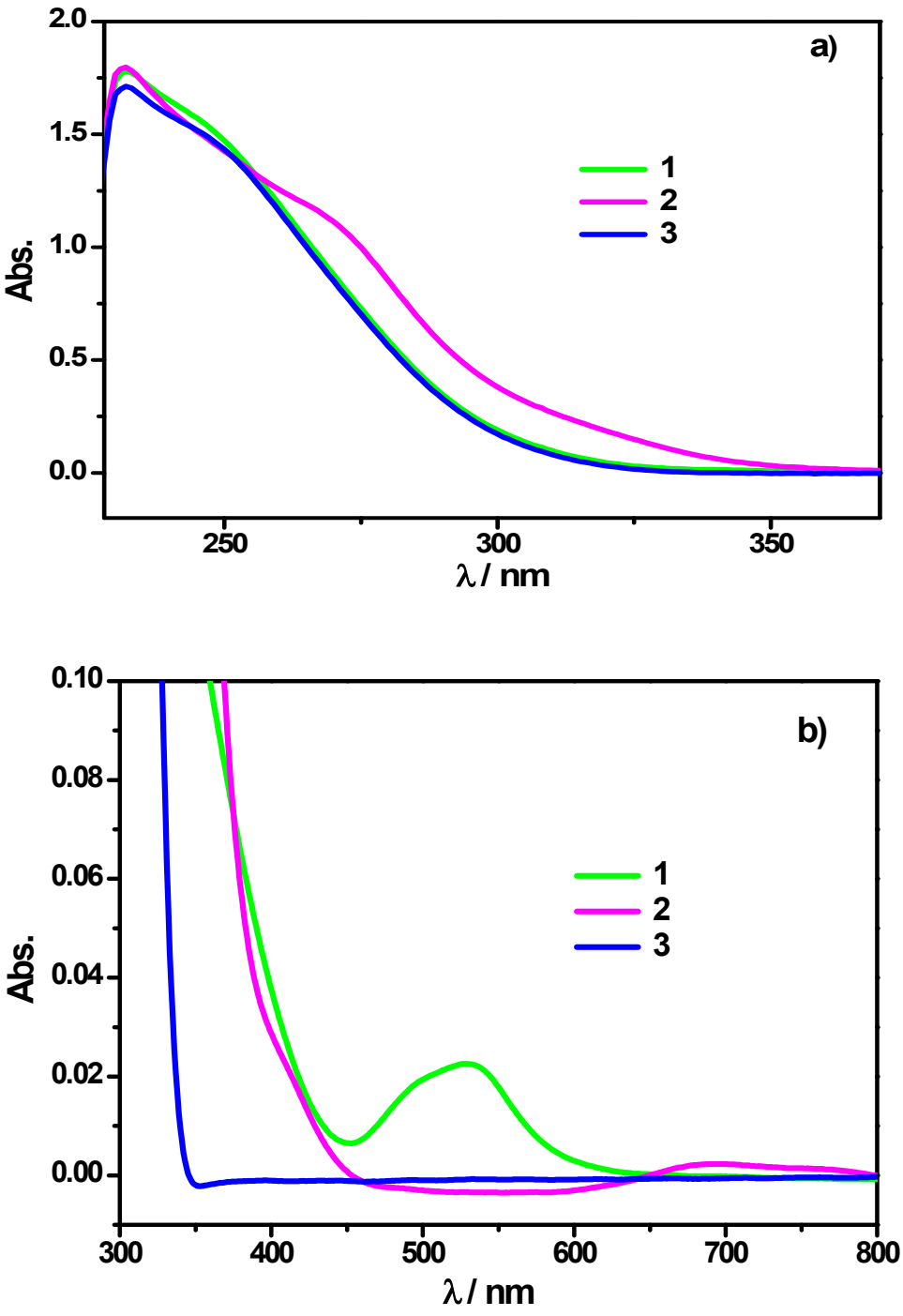

Figure S6. UV-vis spectra of polyanions **1**-**3** in a pH 7 medium (1 M CH_3COOLi / CH_3COOH) with a 1 cm optical path quartz cuvette. (a) Spectra recorded in the UV region. The concentration of the polyanions was 0.02 mM. (b) Spectra recorded in the visible-NIR region. The concentration of the polyanions was 0.2 mM.

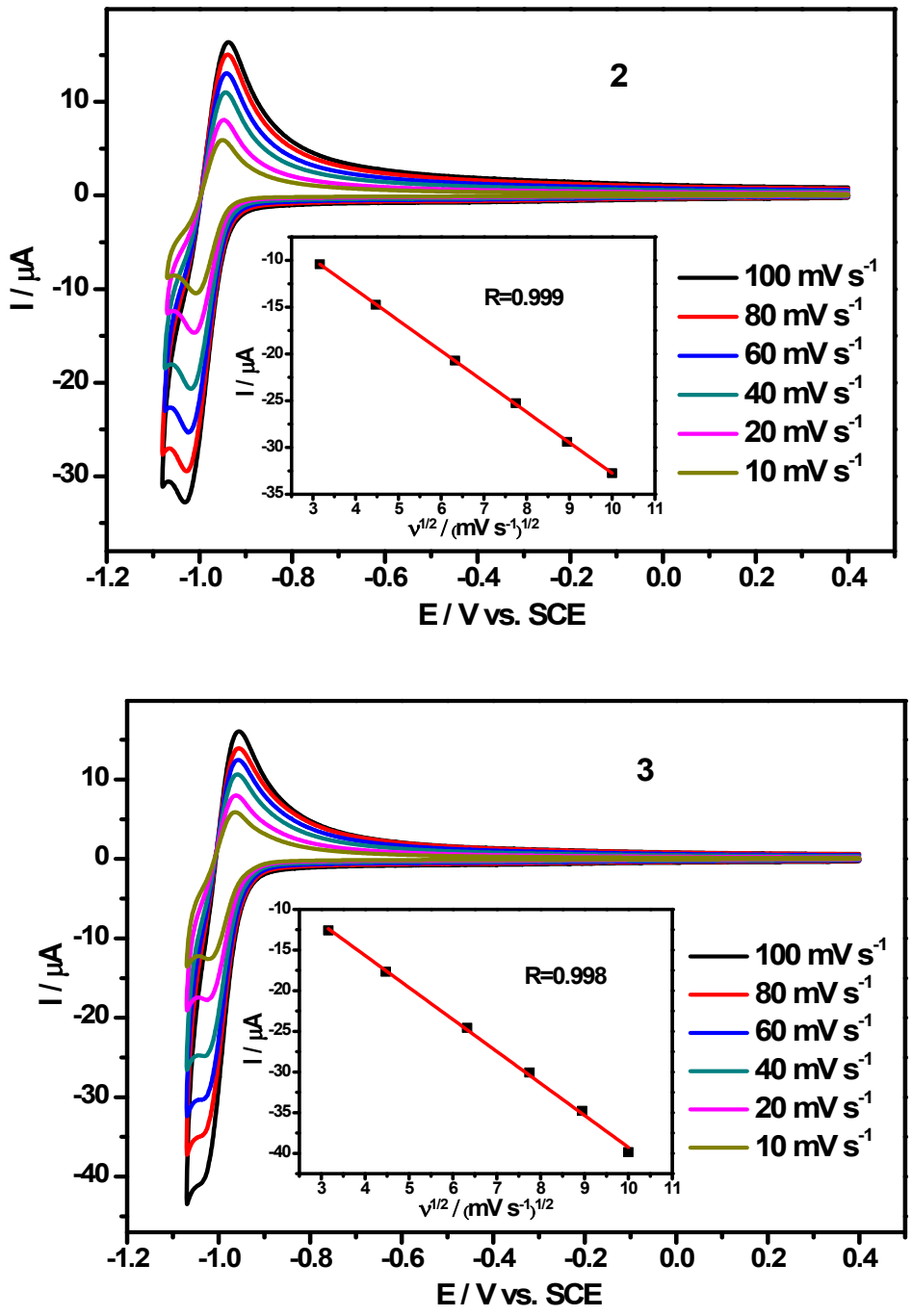

Figure S7. Cyclic voltammograms (CVs) of the first W^{VI}-wave of polyanions **2** (upper) and **3** (lower) as a function of the scan rate, run in a pH 7 (1 M CH_3COOLi / CH_3COOH) medium. The concentration of the polyanions was 0.2 mM, and the reference electrode was a saturated calomel electrode (SCE). Insets: variation of the cathodic peak current intensity as a function of the square root of the scan rate.