Electronic Supplementary Information

Impact of metal exchange on the electronic structure and optical properties of isostructural octa-coordinated Mo^{IV}/Cd^{II} and W^{IV}/Cd^{II} polynuclear cyanide polymers

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1 Bader charge analysis

Table S 1: Bader charge analysis. The showed values correspond with the HSE06 density functional computations. For the M and Cd metals the average value of the total of Bader charges is shown. For the cyano ligands cases (CN) the total average (CN_{avg}) is showed together with the charge values of four different types of CN ligands differentiated by their positions in the dodecahedron, as it is depicted in Figure 1 of ESI.

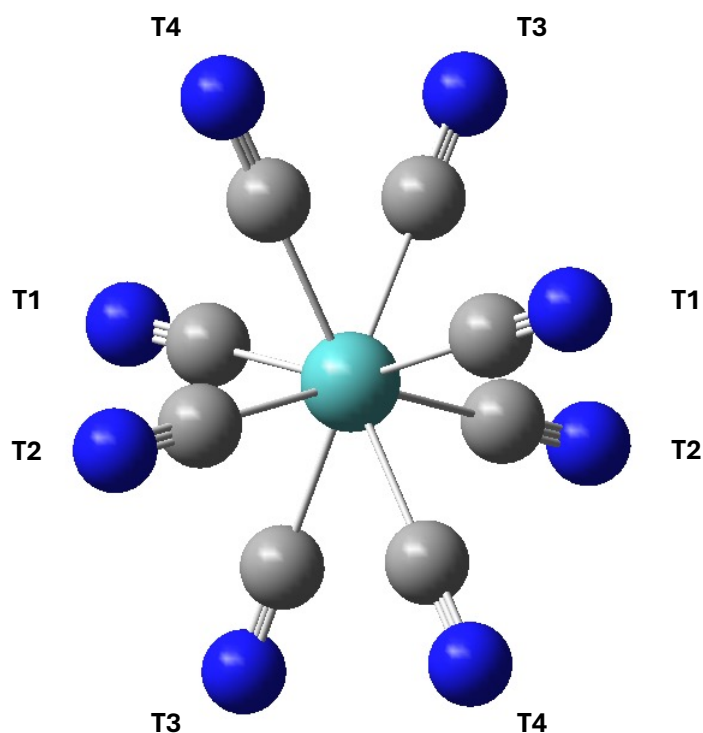| Bader charge analysis, [$bohr^{-3}$]							
System	M	Cd	CN_{avg}	CN_{T1}	CN_{T2}	CN_{T3}	CN_{T4}
Cd-Mo ($Cd_2(H_2O)_4[Mo(CN)_8]\cdot2H_2O$)	1.804	1.424	-0.582	-0.595	-0.577	-0.573	-0.582
Cd-W ($Cd_2(H_2O)_4[W(CN)_8]\cdot2H_2O$)	1.822	1.420	-0.583	-0.597	-0.577	-0.574	-0.585

Figure S 1: Octacordinated M block (M=Mo or W) with D_{2d} symmetry. Cyano ligands are labeled according to their Bader charges (see Table 1).
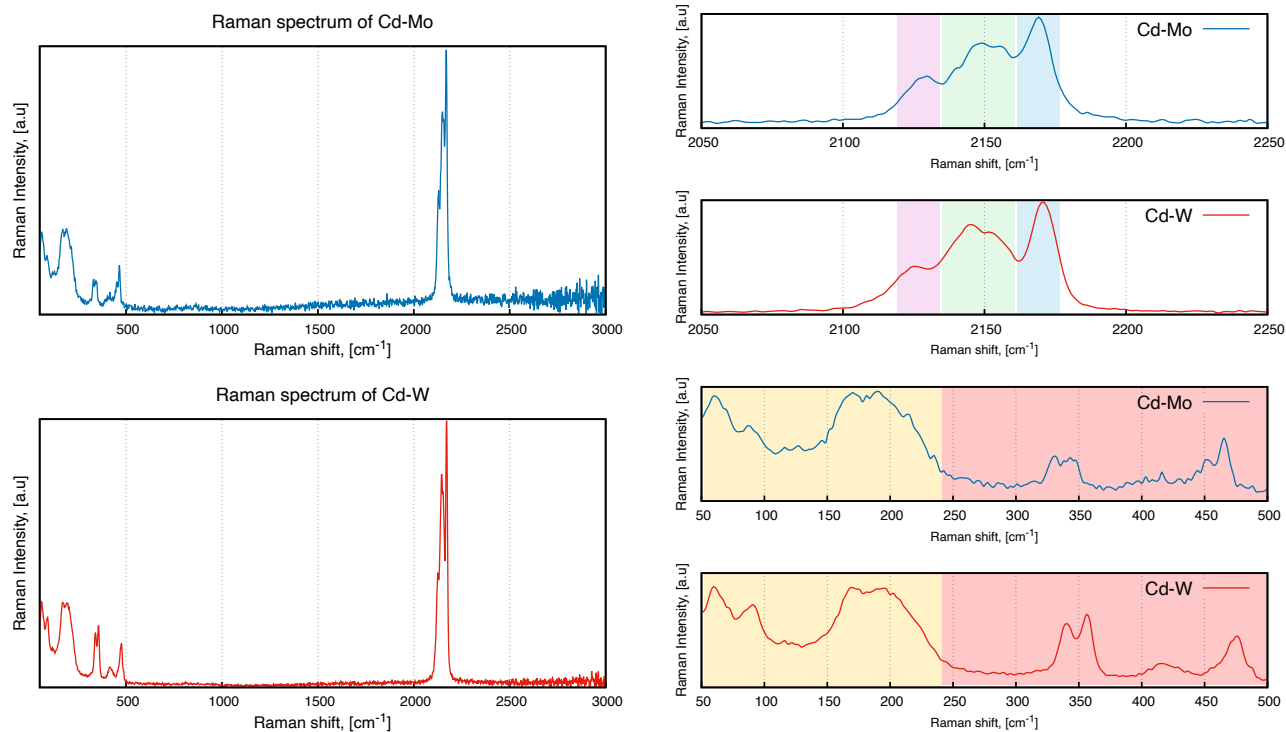
2 Raman spectroscopy

Figure S 2: Raman spectra of Cd-Mo and Cd-W (right column). The ranges 2050 - 2250 cm^{-1} [$\nu(CN)$] and 50 - 500 cm^{-1} [$\delta(C-M-C)$ and $\delta(N-Cd-N)$] are shown on the left side of the image. Raman shift values are summarized in Table S2

Table S 2: Raman signals. The showed values correspond to the spectra depicted in Figure S2 in the 2050 - 2250 cm^{-1} and 50 - 500 cm^{-1} spectral ranges.

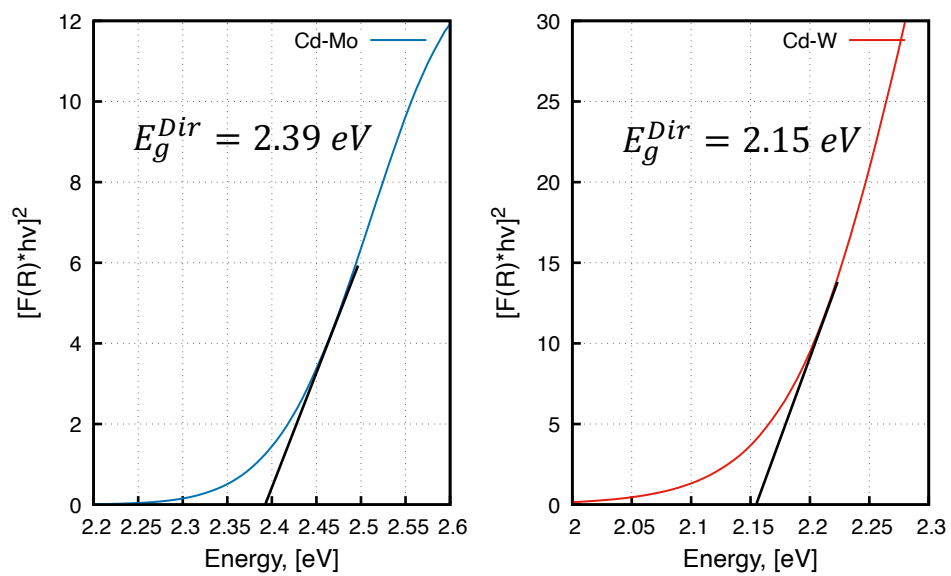| Raman shift values, [cm^{-1}]		
Active Raman Modes	**Cd-Mo**	**Cd-W**
ν(CN)	2160, 2156, 2149, 2141, 2130, 2125	2170, 2159, 2152, 2145, 2134, 2121
ν(M/Cd-), δ(-M/Cd-)	466, 417, 349, 332, 191, 169, 88, 61	476, 416, 358, 340, 197, 169, 92, 61

3 Ultraviolet-visible analysis

Figure S 3: Tauc plot of Cd-Mo (right blue) and Cd-W (left-red) for allowed direct electronic transitions.

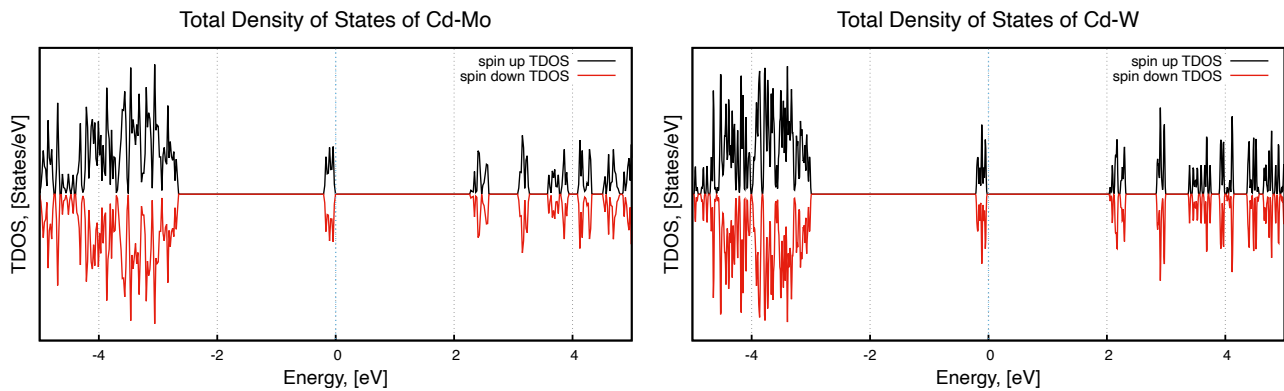# 4 Projected density of states (HSE06)

Figure S 4: Total density of states (TDOS) of Cd-Mo (left) and Cd-W (right). Spin up (black line) and spin down (red line) are symmetrical with respect 0 states/eV.
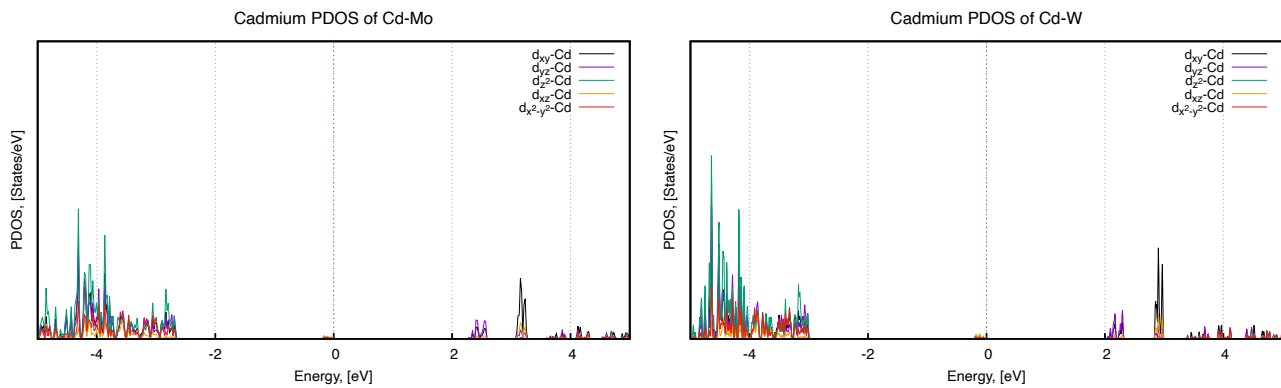

Figure S 5: Projected density of states of cadmium atoms. No relevant orbital contributions are observed at the valence and conduction regions.
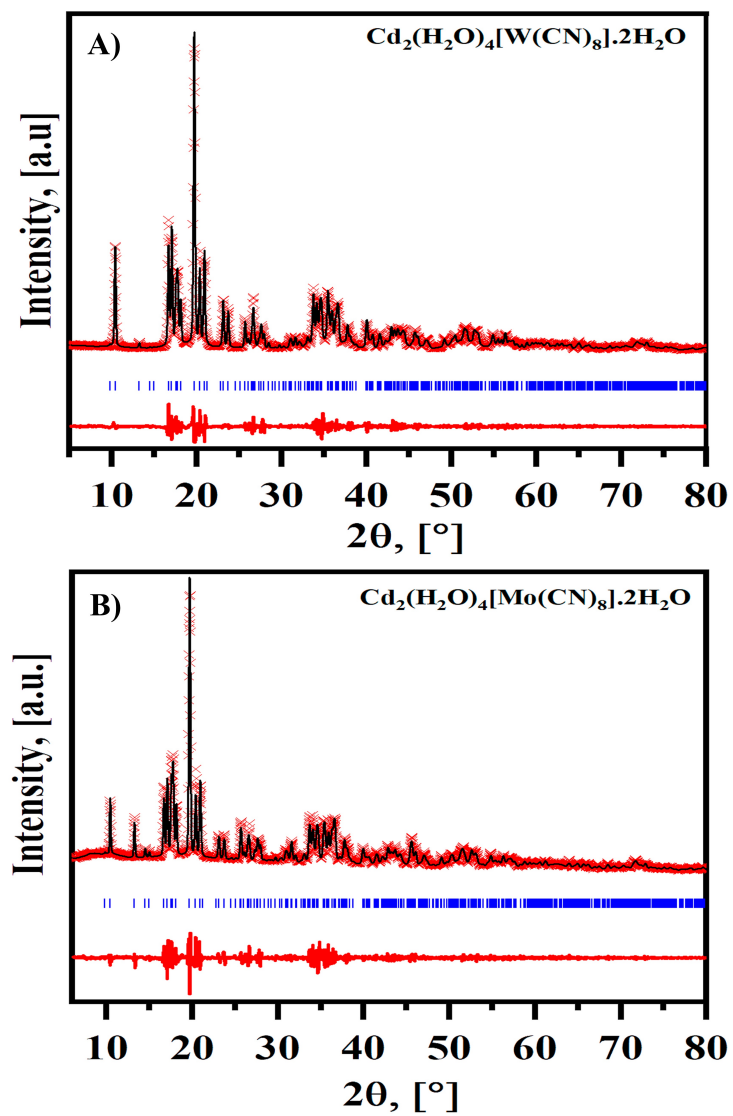
5 Powder X-Ray Diffraction Patterns (PXRD)
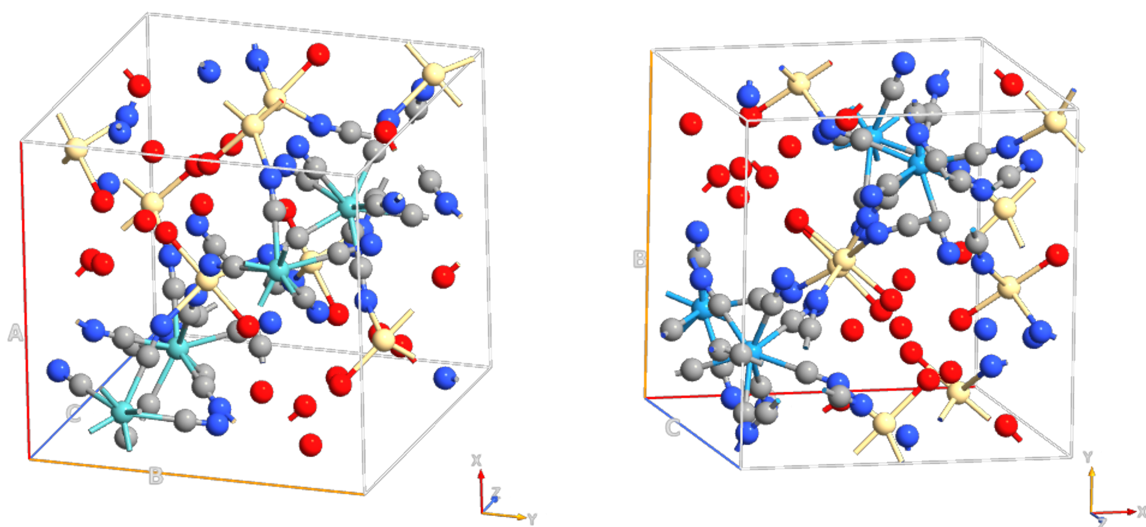

Figure S 6: Powder X-ray diffraction patterns.

Figure S 7: Unit cell structure of Cd-Mo (left) and Cd-W (right).