Supporting Information

Single-atom control of electrical conductance and thermopower through single-cluster junctions

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1. Synthesis and characterization of target compounds

1.1 General methods and materials

The synthesis of tris functionalized Anderson polyoxometalate $[TBA]_3\{Fe[NH_2C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 1**):

A mixture of $[TBA]_3[Fe(OH)_6Mo_6O_{18}]$ (1.748 g 1 mmol) with hydrochloride salt of $(HOCH_2)_3CNH_2$ (0.314 g, 2 mmol) was dissolved in 25 mL acetonitrile and ethanol mixed solvent with volume ratio 1:1 and refluxing at 80 ºC for 6 h. The reaction solution was cooled down to room temperature to remove the precipitates by filtration and a red solution was obtained. Then the filtrate was poured into ether, resulting in precipitation. After the solution became clear, the supernatant liquid was poured off. The red powder product was obatained (88% yield based on Mo). $C_{56}H_{124}FeMo_6N_5O_{24}$ M_r = 1883.11, H 6.60 C 35.76 N 3.69 Fe 2.99 Mo 30.56 while calcd H 6.64 C 35.72 N 3.72 Fe 2.97 Mo 30.57.

The synthesis of tris functionalized Anderson polyoxometalate $[TBA]_3\{Co[NH_2C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 2**):

The synthesis process is similar to that of compound **1** but using $[TBA]_3[Co(OH)_6Mo_6O_{18}]$ instead of $[TBA]_3[Fe(OH)_6Mo_6O_{18}]$. The darkgreen powder product was obatained (86% yield based on Mo). $C_{56}H_{124}CoMo_6N_5O_{24}$ M_r = 1886.19, H 6.59 C 35.62 N 3.73 Co 3.10 Mo 30.53 while calcd H 6.63 C 35.66 N 3.71 Co 3.12 Mo 30.52.

The synthesis of tris functionalized Anderson polyoxometalate $[TBA]_2\{Ni[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 3**):

The synthesis process is similar to that of compound **1** but using $[TBA]_4[Ni(OH)_6Mo_6O_{18}]$ instead of $[TBA]_3[Fe(OH)_6Mo_6O_{18}]$. The turquoise powder product was obatained (80% yield based on Mo). $C_{40}H_{90}Mo_6N_4NiO_{24}$ M_r = 1645.50, H 5.55 C 29.15 N 3.43 Ni 3.59 Mo 34.96 while calcd H 5.51 C 29.20 N 3.40 Ni 3.57 Mo 34.98.

The synthesis of tris functionalized Anderson polyoxometalate $[TBA]_2\{Zn[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 4**):

The synthesis process is similar to that of compound **1** but using $[TBA]_4[Zn(OH)_6Mo_6O_{18}]$ instead of $[TBA]_3[Fe(OH)_6Mo_6O_{18}]$. The white powder product was obatained (82% yield based on Mo). $C_{40}H_{90}Mo_6N_4O_{24}Zn$ M_r = 1652.19, H 5.54 C 29.12 N 3.36 Zn 3.98 Mo 34.82 while calcd H 5.49 C 29.08 N 3.39 Zn 3.96 Mo 34.84.

1.2 Crystal structure determination and refinement by powder X-ray diffraction

Crystal Data for $[TBA]_3\{Fe[NH_2C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 1**), space group P21/c (no. 14), a = 25.3155(5) Å, b = 13.4971(3) Å, c = 24.9444(4) Å, α =γ =90°, β = 88.60°, V = 8520.6(3) Å3, Rp = 3.14;Rwp= 6.91; $\chi 2$= 1.03.

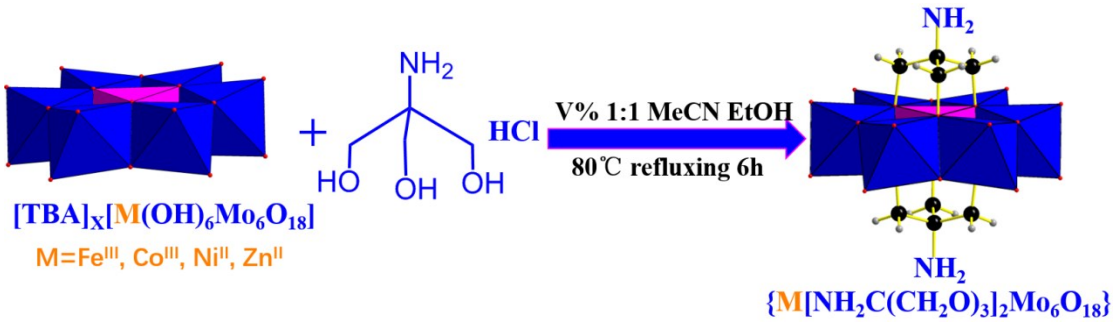
Crystal Data for $[TBA]_3\{Co[NH_2C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 2**), space group P21/c (no. 14), a = 25.1135(5) Å, b = 13.56218(20) Å, c = 25.0882(5) Å, α =γ =90°, β = 92.40°, V = 8537.4(3) Å3, Rp = 3.83;Rwp= 6.34; $\chi 2$= 1.02.

Crystal Data for $[TBA]_2\{Ni[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 3**), space group P21/c (no. 14), a = 25.510(3) Å, b = 13.3195(16) Å, c = 25.066(3) Å, α =γ =90°, β = 93.21°, V = 8503.5(18) Å3, Rp = 5.41;Rwp= 8.34; $\chi 2$= 2.73.

Crystal Data for $[TBA]_2\{Zn[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}$(**compound 4**), space group P21/c (no. 14), a = 25.4577(5) Å, b = 13.5783(3) Å, c = 24.7852(5) Å, α =γ =90°, β = 87.59°, V = 8560.0(3) Å3, Rp = 3.32;Rwp= 6.36; $\chi 2$= 1.03.

CCDC-2010192-2010195 contain the supplementary crystallographic data for these tris functionalized Anderson polyoxometalate nanocluster in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

1.3 Synthesis protocol of tris functionalized Anderson polyoxometalate nanocluster



1.4 Crystallographical structures

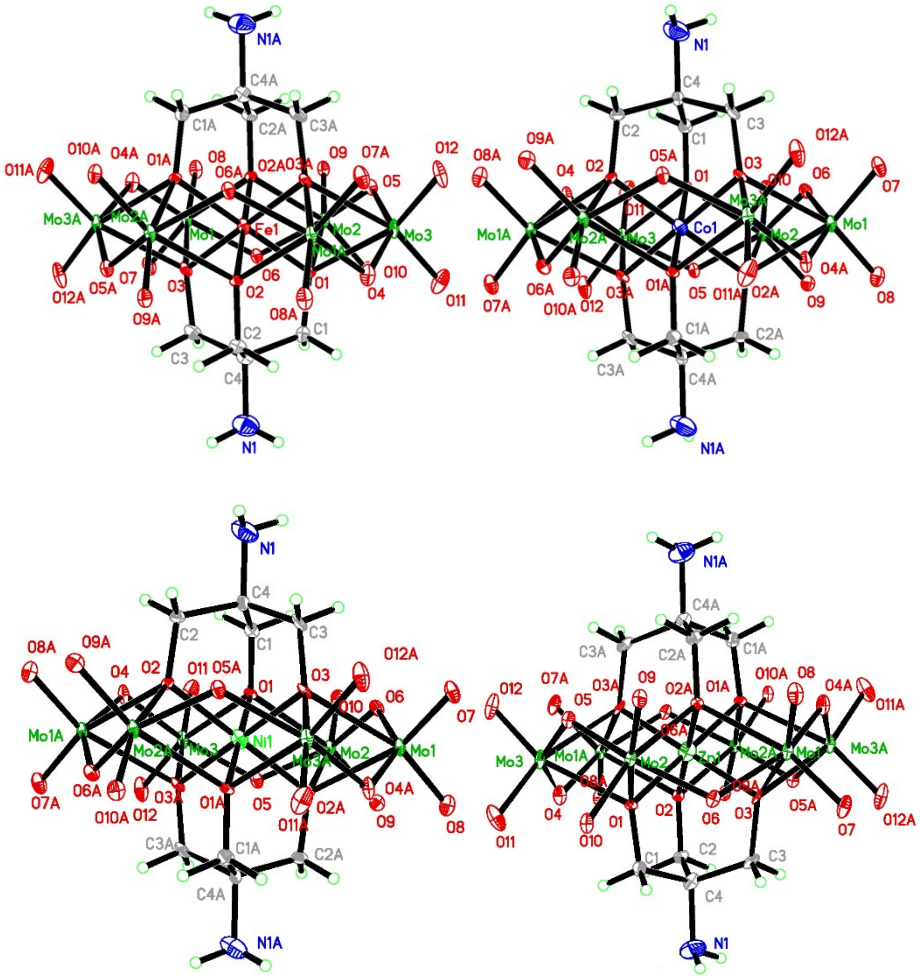


Figure S1-1. ORTEP drawings of cluster anions of the **tris functionalized Anderson polyoxometalate nanocluster**: compounds **1** (Upper left), **2** (Upper right) **1** (Bottom left) and **4** (Bottom right). Thermal ellipsoids at the 30% probability level.

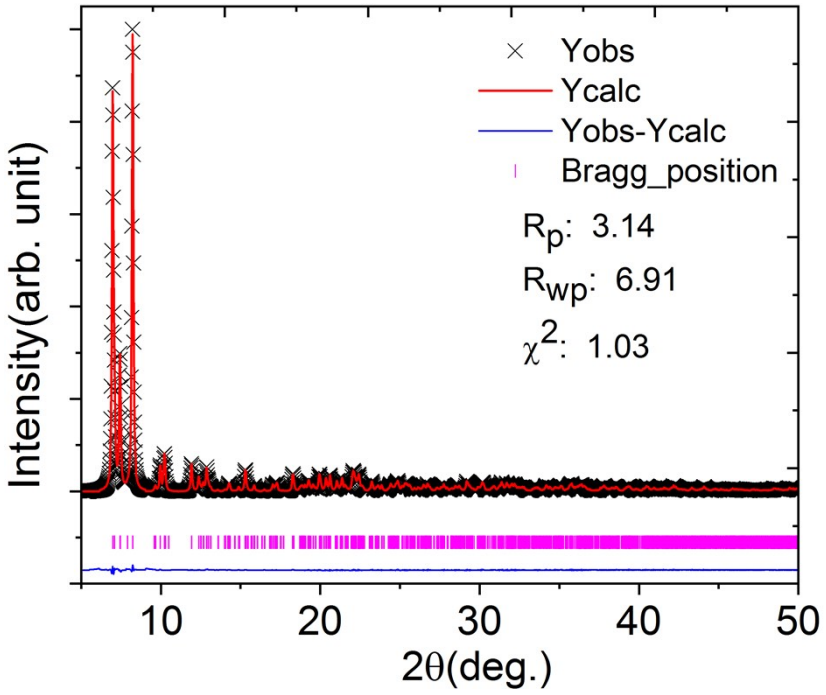


Figure S1-2 powder X-ray diffraction crystal structure Retrieved refinement of $[TBA]_3\{Fe[NH_2C(CH_2O)_3]_2Mo_6O_{18}\}$.

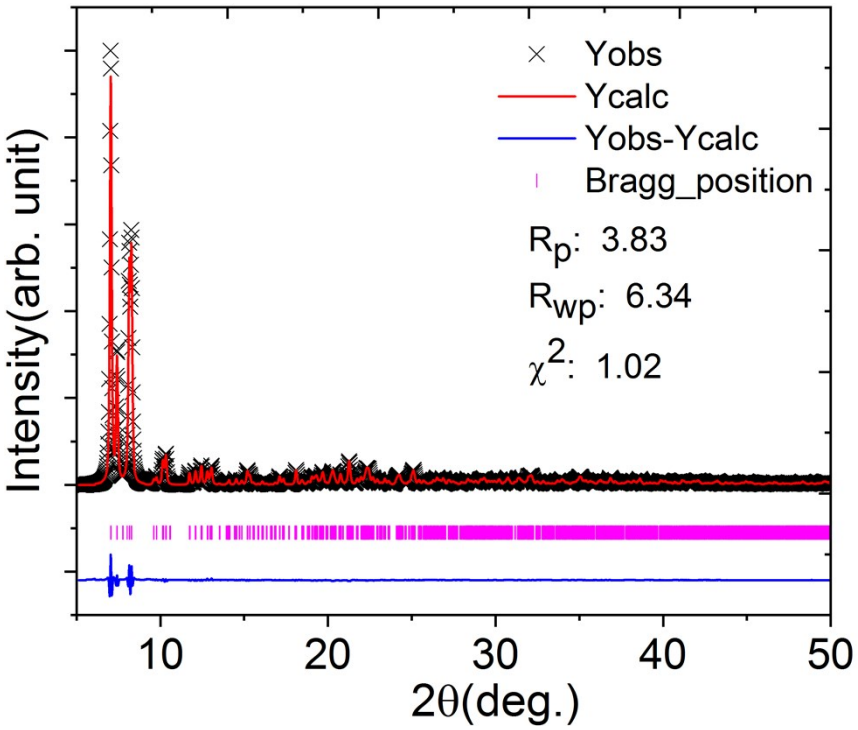


Figure S1-3 powder X-ray diffraction crystal structure Retrieved refinement of $[TBA]_3\{Co[NH_2C(CH_2O)_3]_2Mo_6O_{18}\}$.

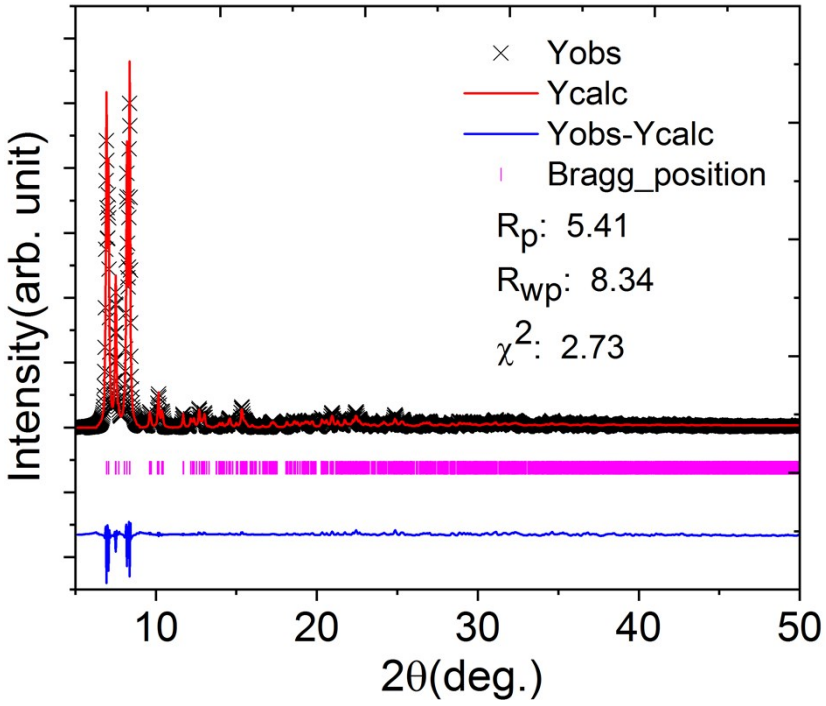


Figure S1-4 powder X-ray diffraction crystal structure Retrieved refinement of $[TBA]_2\{Ni[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}$.

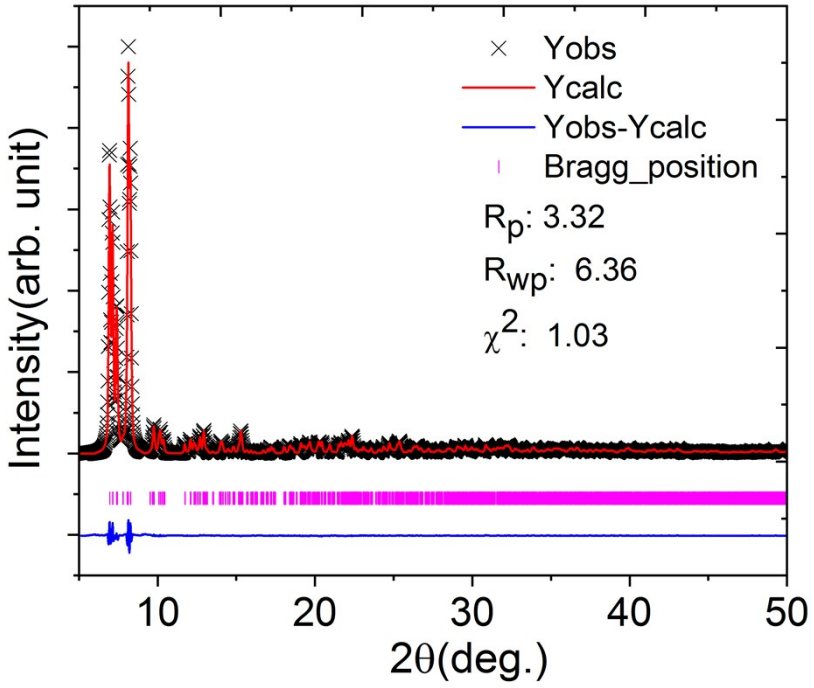


Figure S1-5 powder X-ray diffraction crystal structure Retrieved refinement of $[TBA]_2\{Zn[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}$.

2. Equipments

2.1 Scanning tunneling microscope break junction (STM-BJ) technique

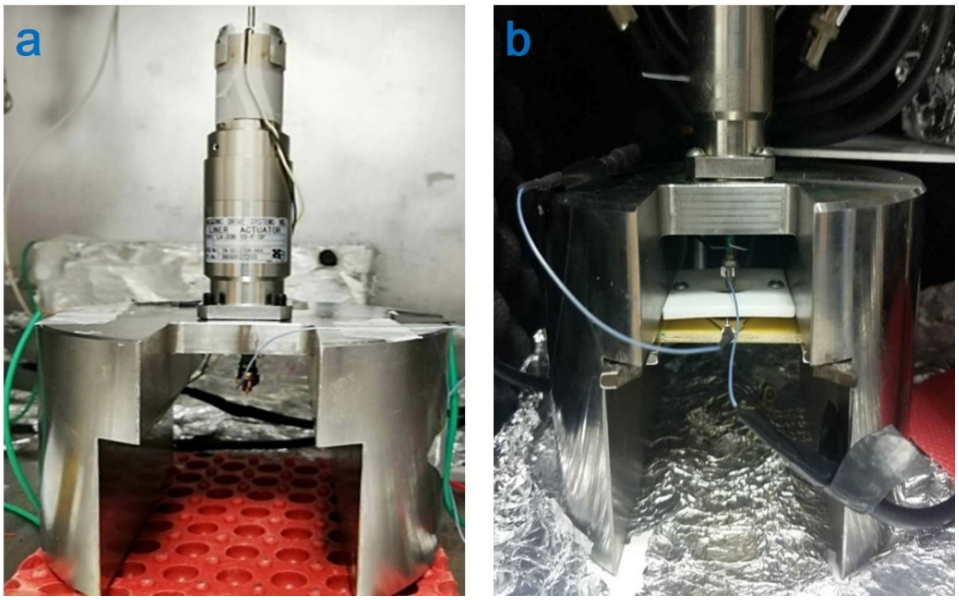


Figure S2-1. The Scanning Tunneling Microscope break junction (STM-BJ) equipment for (a) the whole graph and (b) the local close-up graph of well-prepared setup.

2.2 thermoelectricity equipment

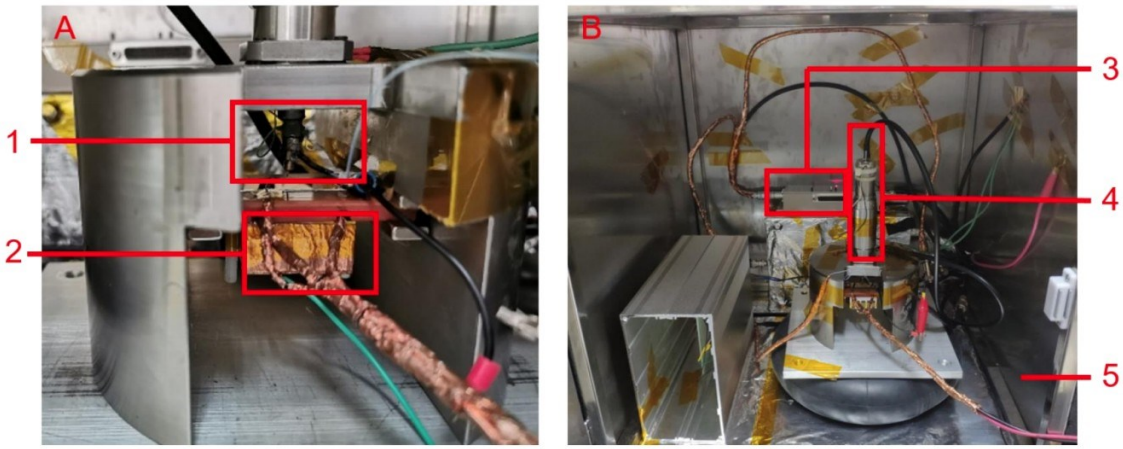


Figure S2-2. Photo of home-made the thermoelectricity equipment. (A) Close up of skeleton. (B) Overviews of the thermoelectricity equipment. 1 is the tip, 2 is the peltier device, 3 is voltage amplifier, 4 is the motor, 5 is the shield box.

3 Blank experiment and additional datas

3.1 The conductance of counter ions:

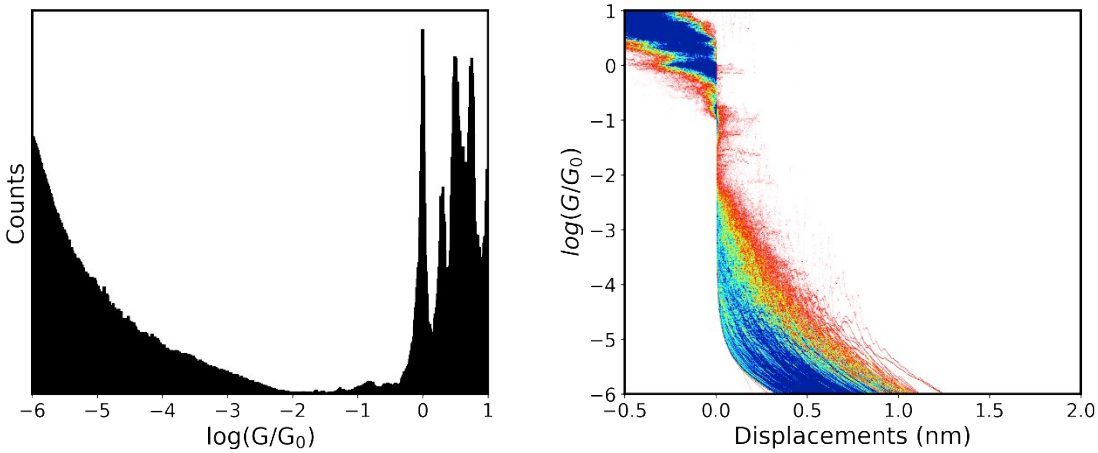


Figure S3-1. The 1D conductance histogram and 2D conductance-displacement histogram of tetrabutylammonium.

3.2 Summary of the calculated and experimentally results:

Table S1. The calculated and experimentally determined single-cluster conductance of **MoNi, MoZn, MoFe** and **MoCo**.

Cluster	Experimental conductance ($log(G/G_0)$)	Calculated conductance ($log(G/G_0)$)
MoNi	-4.21	-4.2
MoCo	-3.82	-4.1
MoFe	-3.41	-3.8
MoZn	-3.45	-3.8

3.3 2D conductance-displacement histograms of various bias voltages:

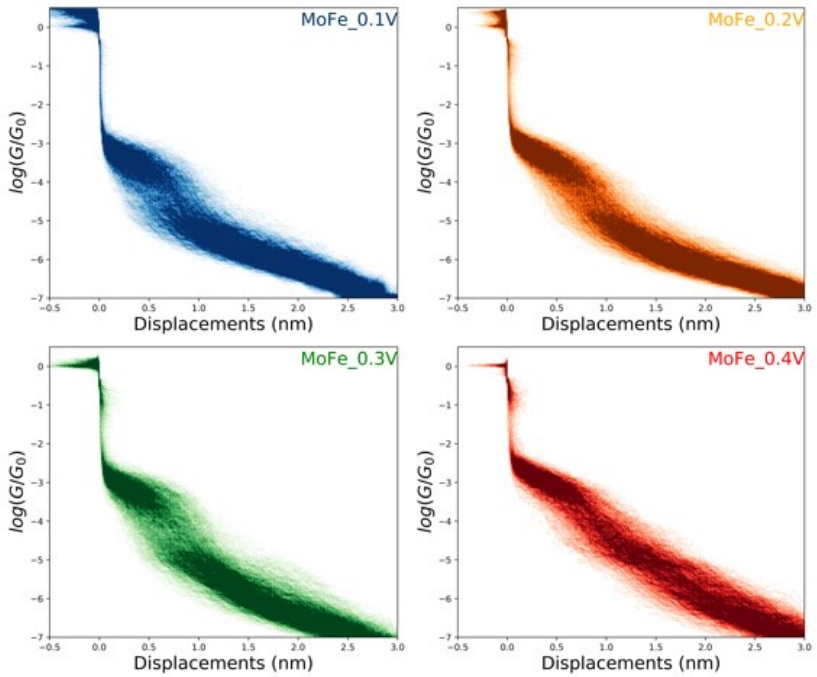


Figure S3-2. Two-dimensional conductance histograms of various bias voltages for **MoFe**.

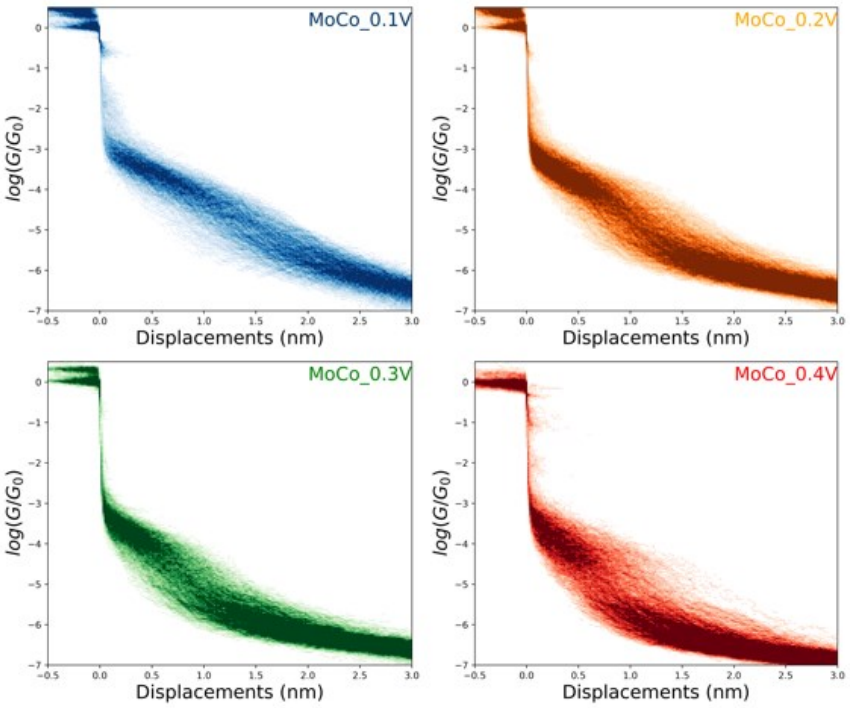


Figure S3-3. Two-dimensional conductance histograms of various bias voltages for **MoCo**.

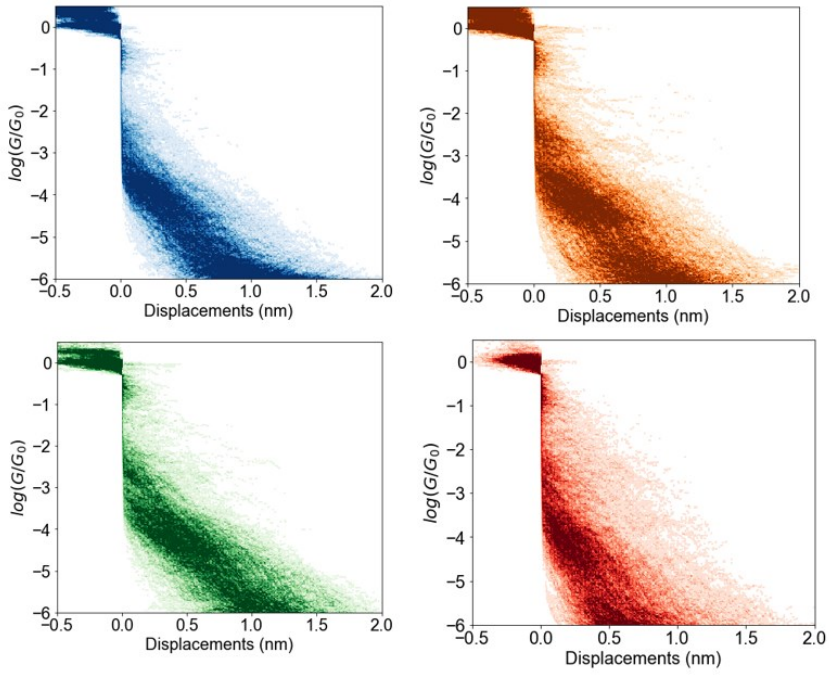


Figure S3-4. Two-dimensional conductance histograms of various bias voltages for **MoNi**.

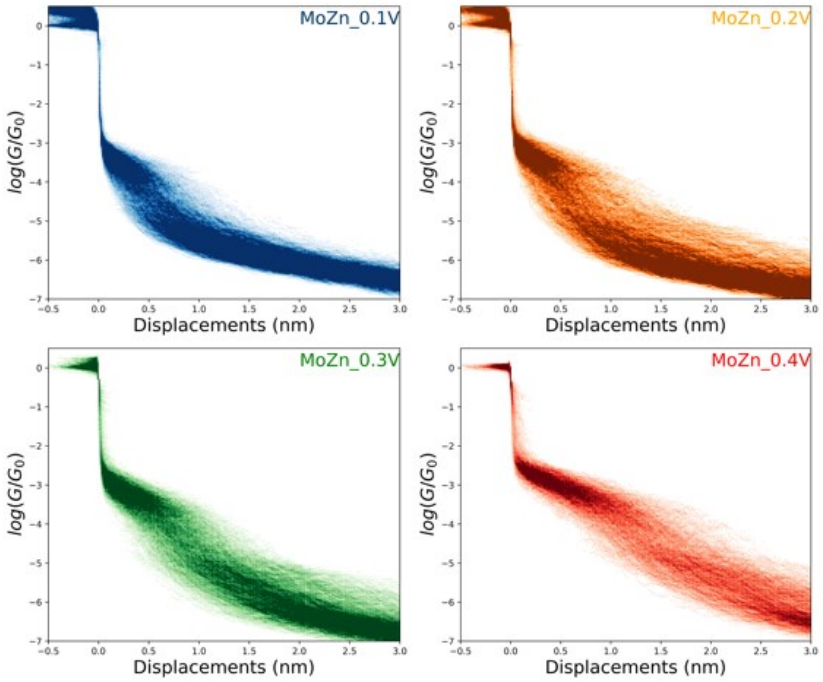


Figure S3-5. Two-dimensional conductance histograms of various bias voltages for **MoZn**

3.4 Summary of the conductances

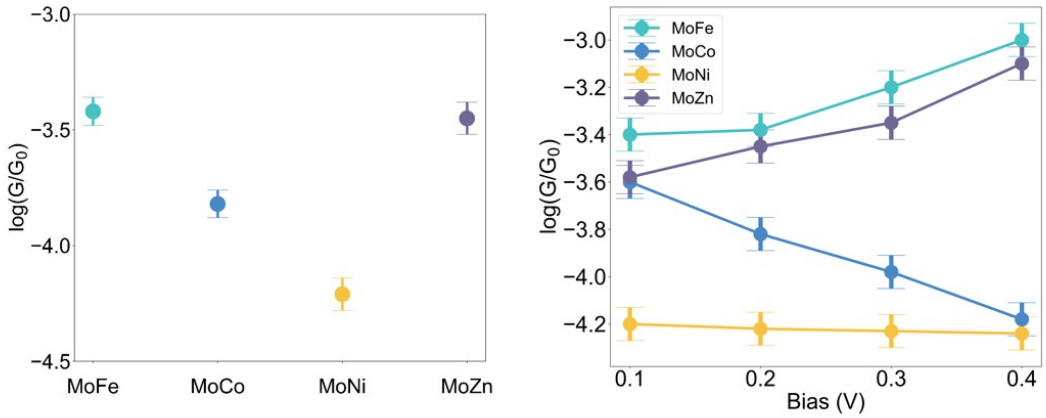


Figure S3-6. Experimental results. Left panel is the summary of conductances at 0.2 V bias voltage. Right panel is the summary of the conductances with a seirous bias voltages.

3.5 1D conductance histograms of hover measurement

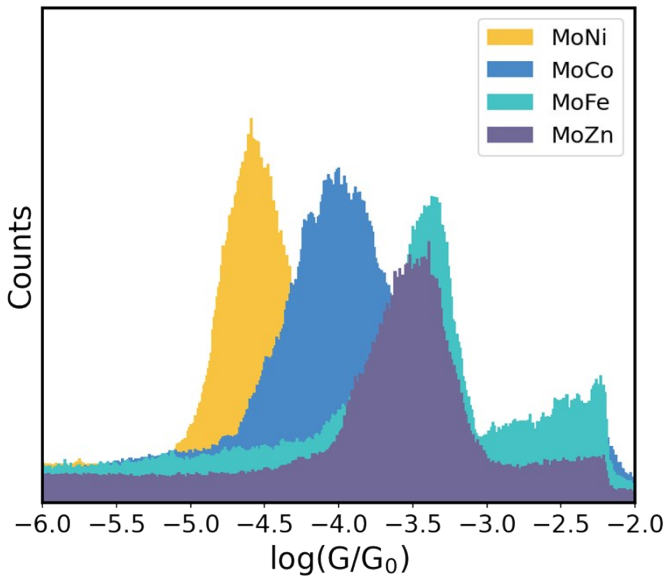


Figure S3-7. 1D conductance histograms of hover measurement for all POM clusters.

3.6 2D conductance of hover measurement

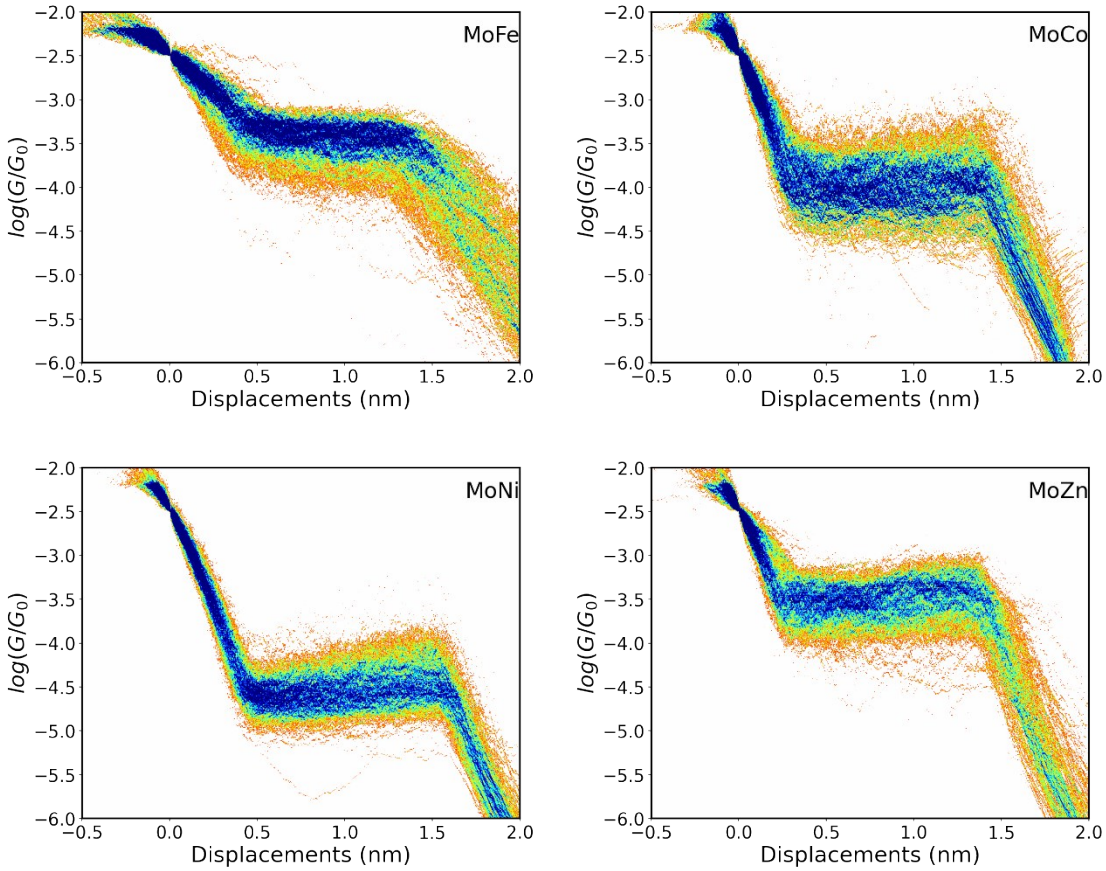


Figure S3-8. 2D conductance histograms of hover measurement for all POM clusters.

3.7 Seebeck coefficients

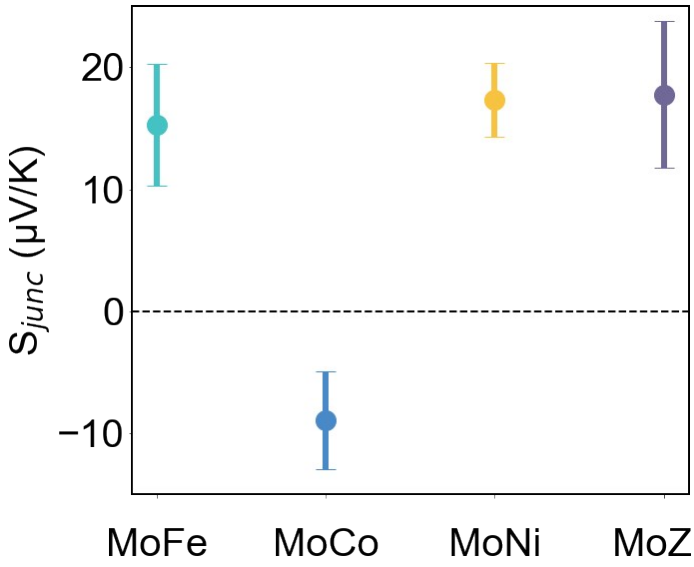


Figure S3-9. Summary of Seebeck coefficients for all POM clusters junctions.

3.8 Histograms of thermoelectric voltage measurements

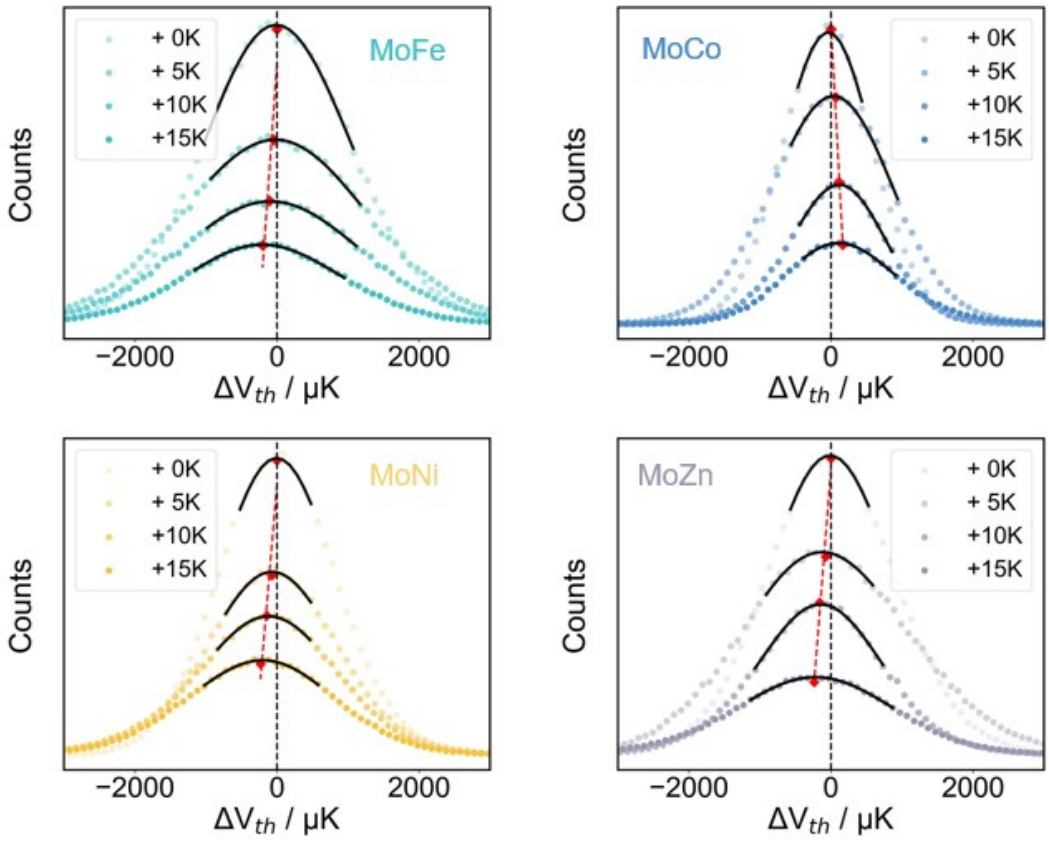


Figure S3-10. Histograms of thermoelectric voltage measurements for all POMs at a series of ΔT= 0 K, 5 K, 10 K and 15 K, respectively. Gaussian fits plotted as a black line. Red dash lines are linear fitting lines.

4 Theoretical analysis

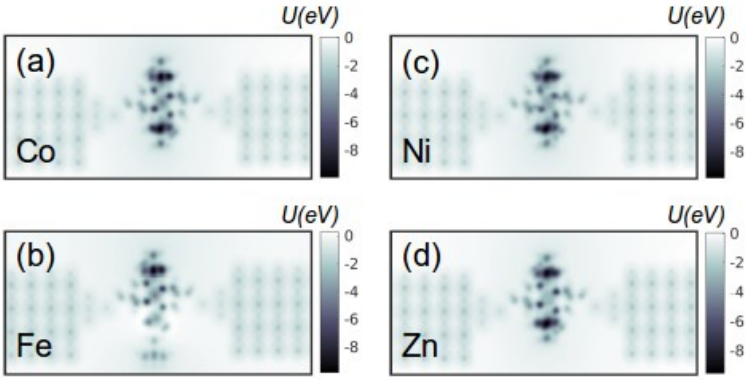


Figure S4-1. The sum of electrostatic potential profile for different POMs.