

Supporting Information for:

Characterization of the first Peacock-Weakley polyoxometalate containing a transplutonium element: curium *bis*-pentatungstate [Cm(W₅O₁₈)₂]⁹⁻

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Experimental Section

Precaution: all isotopes for curium are highly radioactive and toxic! Extreme caution and appropriate procedures should be taken. All experiments involving radionuclides were conducted at Lawrence Livermore National Laboratory, in facilities designed for the safe handling of long-lived and short-lived radioactive materials and associated waste.

Materials: Curium samples (97% ^{248}Cm + 3% ^{246}Cm + 0.01% ^{247}Cm) were prepared from a primary source purchased from Oak Ridge National Laboratory (USA). NaCH_3COO ($\geq 99.9\%$), cesium chloride ($>99.99\%$), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ($\geq 99\%$), phosphoric acid, and lanthanide trichloride salts ($>99.9\%$) were purchased from chemical providers (VWR and Millipore Sigma) and used as received. All solutions were prepared using deionized water purified by reverse osmosis cartridge system ($\geq 18.2 \text{ M}\Omega\cdot\text{cm}$). All experiments were performed in a temperature-controlled room (22°C).

Synthesis of Cs-CmW₅: The synthesis procedure was adapted from our first report of POM-based microscale synthesis.¹ First, $^{247/246/248}\text{Cm}^{3+}$ from a parent stock solution in HCl is added to a $100 \mu\text{M}$ W_{10} (i.e. a 1 mM Na_2WO_4) solution in 0.1 M acetate buffer at pH 5.5. A 1:10 stoichiometric addition of actinide to WO_4^{2-} is made by adding the Cm solution dropwise. For crystallization, $50 \mu\text{L}$ 6 M CsCl is added to $50 \mu\text{L}$ of the parent solution. The total amount of $^{247/246/248}\text{Cm}$ in the test was $1.24 \mu\text{g}$. After two weeks at ambient conditions, several single crystals of the CmW₅ are visible to the naked eyes and fluoresce under UV light. Upon inspection with an optical microscope, XRD-quality crystals are mounted and characterized via small molecule single crystal XRD, while the rest are kept for Raman microscopy and fluorescence analysis.

Synthesis of Cs-NdW₅: The synthesis procedure was a modified version of Peacock and Weakley synthesis.² 5 g of Na_2WO_4 were added 10 mL of boiling H_2O . Then, 0.07 g of $\text{NdCl}_3 \cdot 7\text{H}_2\text{O}$ was added to 1 mL H_2O , this solution was then added dropwise to the boiling tungstate solution. After complete addition, the solution was cooled to room temperature and filtered to remove any unwanted paratungstates. After filtering, 5 g of CsCl were added and a precipitate was isolated. The precipitate was redissolved in boiling water and left to slowly cool. After about 5 minutes crystals suitable for scXRD appeared.

Raman Microscopy. Raman spectra were collected using a Senterra II confocal Raman microscope (Bruker), equipped with high resolution gratings ($1,200 \text{ lines/mm}$) and a 532 nm laser source (operated at 15 mW), and a TE-cooled CCD detector. Reported spectra are the average of at least 2-5 different spots per sample, each spot analysis consisting of 16 scans. The integration time was set to 400 ms per scan. No damage to the sample was observed due to the laser irradiation.

Fluorescence spectroscopy. Steady-state fluorescence spectra and fluorescence lifetimes were measured with a FLS1000 spectrometer (Edinburgh Instruments) equipped with a double

monochromator on the excitation arm and emission arm. A 450 W Xenon lamp was used as light source for the steady-state measurements and a 60 W microsecond flashlamp was used for lifetime measurements (MCS mode). Each lifetime decay curve contains 2,000 data points, with the maximum count per channel set to at least 1,000. The timespan of the acquisition was set so that the signal was measured until its return to background level. Lifetimes were calculated based on the dataset fit using the Fluoracle computer program (Edinburgh Instruments). Fluorescence data for liquid samples were measured in sealed quartz cuvettes or quartz tube inside a quartz Dewar (for liquid nitrogen temperature), and the emission was collected at 90° relative to the excitation. Fluorescence spectra for solid samples were measured at 45° relative to the sample.

Crystallographic studies. The CmW₅ and NdW₅ structures were collected at LLNL's radiochemistry laboratories using a Rigaku Synergy Custom single crystal diffractometer, equipped with a kappa goniometer and using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) with a FWHM of $\sim 200 \text{ \mu m}$ at the sample from a MicroMax-007 HF microfocus rotating anode source. Images were recorded on a Dectris Pilatus 3R (300K – CdTe) detector and processed using CrysAlis^{Pro}. After integration both analytical absorption and empirical absorption (spherical harmonic, image scaling, detector scaling) corrections were applied.³ All structures were solved by Intrinsic Phasing method from SHELXT program⁴, developed by successive difference Fourier syntheses, and refined by full-matrix least square on all F² data using SHELX⁵ via OLEX2 interface.⁶

Crystallographic information for the six reported structures can be obtained free of charge from the Cambridge Crystallographic Data Center (<https://www.ccdc.cam.ac.uk/>) upon referencing CCDC numbers in the crystallographic tables below.

Notes on crystal structures, refinement, modeling of disorder, and solvent void space. Due to safety protocol any curium containing crystals were collected under the MicroRT Capillaries 37mm. Although x-ray transparent at certain angles the background intensity increased resulting in poor signal-to-noise ratio, resulting in the use of some restraints.

Absorption correction was performed using Empirical absorption correction applied before frame scaling. Several other methods were employed, such as numerical absorption with a Gaussian grid (based on the crystal system), or analytical absorption correction after the Clark and Reid method before ultimately using a combination of Gaussian grid absorption correction and “Mutli-scan” using the Scale3 Abspack.³ All of these methods relied on measuring the face of the crystal using CCD images capture before collection. The resulting R_{int} after absorption correction dropped for each structure by approximately 3%. Nevertheless, large residual electron density less than 1 \AA away from the tungsten atoms remained.

Furthermore, individual hydrogen atoms could not be refined, as such they have been omitted in the reported molecular weight.

Table S1. Single crystal XRD structures previously reported for trivalent lanthanides with the Peacock-Weakley POM, as well as the first trivalent actinide structure reported in the present study.

	Central cation	Formula	Reference
Actinides	Cm ³⁺	NaCs ₈ [Cm(W ₅ O ₁₈) ₂]·14H ₂ O	This study
Lanthanides with Cs⁺ counter ion	Nd ³⁺	Na ₃ Cs ₆ [Nd(W ₅ O ₁₈) ₂]·18H ₂ O	This study
	Ce ³⁺	Na ₉ [Ce(W ₅ O ₁₈)]·NaCl·30H ₂ O	10
	Nd ³⁺	Na ₉ [Nd(W ₅ O ₁₈) ₂]·32H ₂ O	1,11
	Sm ³⁺	Na ₆ H ₃ [Sm(W ₅ O ₁₈) ₂]·28H ₂ O	12
	Eu ³⁺	Na ₉ [Eu(W ₅ O ₁₈) ₂]·32H ₂ O	13
		Na ₉ [Eu(W ₅ O ₁₈) ₂]·34H ₂ O	1
	Gd ³⁺	Na ₉ [Gd(W ₅ O ₁₈) ₂]·35H ₂ O	14
		Na ₈ H[Gd(W ₅ O ₁₈) ₂]·35H ₂ O	15
	Dy ³⁺	Na ₉ [Dy(W ₅ O ₁₈) ₂]·35H ₂ O	16
	Ho ³⁺	Na ₉ [Ho _x Y _(1-x) (W ₅ O ₁₈) ₂]·nH ₂ O	17
	Er ³⁺	Na ₉ [Er(W ₅ O ₁₈) ₂]·34H ₂ O	18
		Na ₉ [Er(W ₅ O ₁₈) ₂]·35H ₂ O	14 19
	Tm ³⁺	Na ₉ [Tm(W ₅ O ₁₈) ₂]·35H ₂ O	20
	Yb ³⁺	Na ₉ [Yb(W ₅ O ₁₈) ₂]·35H ₂ O	20
	Lanthanides with Na⁺, K⁺ and NH₄⁺ counter ion	La ³⁺	Na ₂ (NH ₄) ₇ [La(W ₅ O ₁₈) ₂]·16H ₂ O
Sm ³⁺		Na ₄ K ₃ H ₂ [Sm(W ₅ O ₁₈) ₂]·22H ₂ O	22
Pr ³⁺ , Nd ³⁺ , Sm ³⁺ , Gd ³⁺ , Tb ³⁺ , Dy ³⁺		Na ₄ K ₃ H ₂ [Ln(W ₅ O ₁₈) ₂]·nH ₂ O	23
Tb ³⁺		Na ₄ K ₃ H ₂ [Tb(W ₅ O ₁₈) ₂]·20H ₂ O	24

Table S2. Crystallographic and refinement information for NaCs₈Cm(W₅O₁₈)₂·14H₂O (**CmW₅**).

Identification code	CmW₅
Empirical formula	CmCs ₈ NaO ₅₀ W ₁₀ H ₂₈
CCDC ID	2333195
Formula weight	3997.01
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	11.46121(14)
b/Å	14.46007(19)
c/Å	17.5536(2)
α/°	101.1099(11)
β/°	99.4298(11)
γ/°	103.2930(11)
Volume/Å³	2711.36(6)
Z	2
ρ_{calc}/cm³	4.861
μ/mm⁻¹	28.007
F(000)	3374.0
Crystal size/mm³	0.131 × 0.106 × 0.036
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	6.724 to 64.154
Index ranges	-15 ≤ h ≤ 16, -17 ≤ k ≤ 21, -24 ≤ l ≤ 25
Reflections collected	53460
Independent reflections	15597 [R _{int} = 0.0714, R _{sigma} = 0.0550]
Data/restraints/parameters	15597/0/631
Goodness-of-fit on F²	1.042
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0568, wR ₂ = 0.1514
Final R indexes [all data]	R ₁ = 0.0638, wR ₂ = 0.1557
Largest diff. peak/hole / e Å⁻³	8.41/-10.50

Table S3. Crystallographic and refinement information for Na₃Cs₆[Nd(W₅O₁₈)₂]·18H₂O (Cs-NdW₅).

Identification code	NdW5-Cs
Empirical formula	Cs ₆ Na ₃ NdO ₅₄ W ₁₀ H ₃₆
CCDC ID	2326544
Formula weight	3749.47
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	11.35520(10)
b/Å	15.4905(2)
c/Å	16.9027(2)
α/°	101.3710(10)
β/°	104.4240(10)
γ/°	91.7010(10)
Volume/Å³	2813.17(6)
Z	2
ρ_{calc}/cm³	4.384
μ/mm⁻¹	25.216
F(000)	3190.0
Crystal size/mm³	0.011 × 0.012 × 0.009
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	7.03 to 60.968
Index ranges	-15 ≤ h ≤ 15, -20 ≤ k ≤ 20, -24 ≤ l ≤ 24
Reflections collected	42850
Independent reflections	14633 [R _{int} = 0.0689, R _{sigma} = 0.0598]
Data/restraints/parameters	14633/0/667
Goodness-of-fit on F²	1.014
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0515, wR ₂ = 0.1388
Final R indexes [all data]	R ₁ = 0.0585, wR ₂ = 0.1433
Largest diff. peak/hole / e Å⁻³	4.81/-4.23

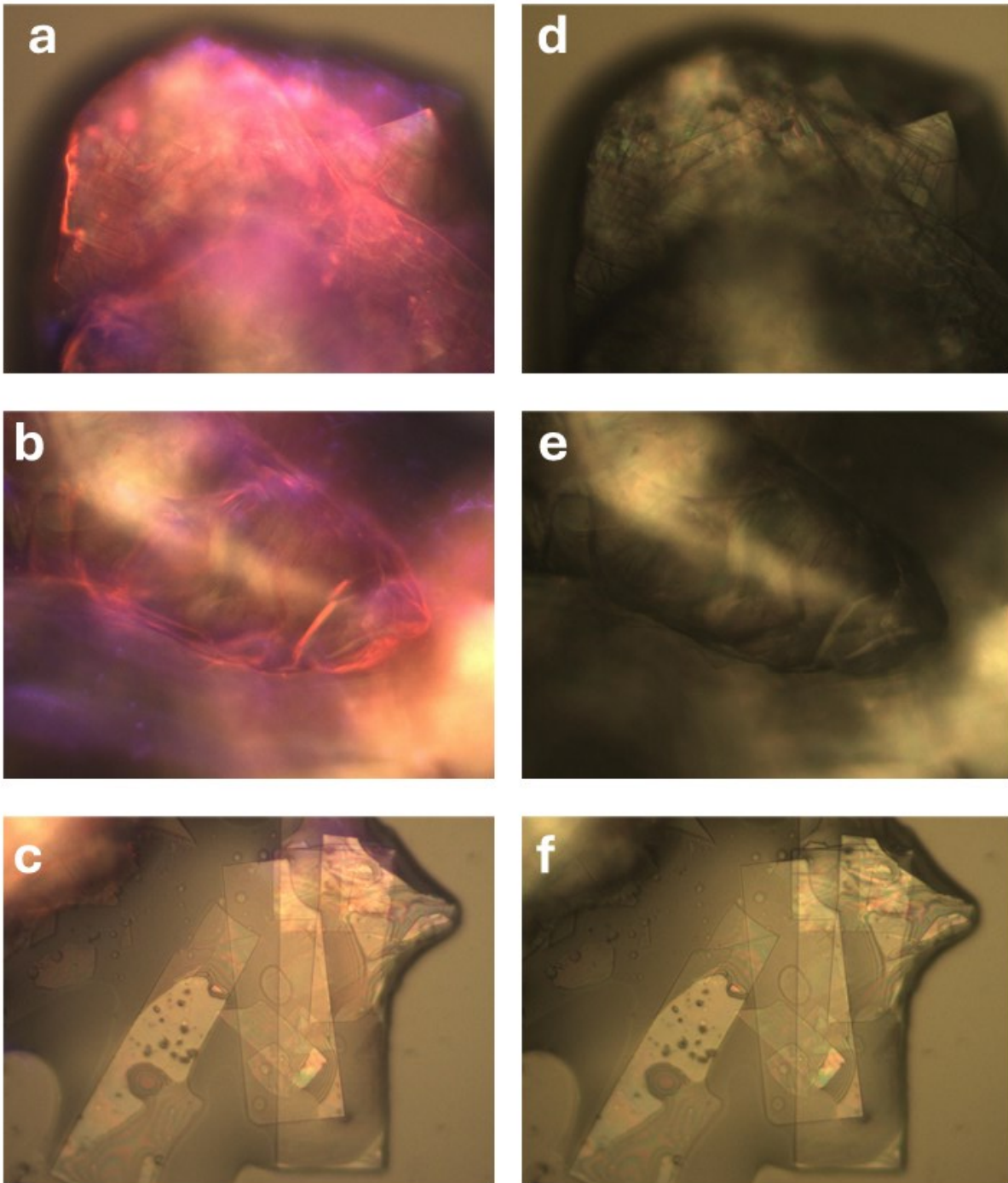


Figure S1. Microscope images of crystals of Cs-CmW₅ a-c) under UV-light d-f) under normal light. The pink-red fluorescence is characteristic of the sensitized emission from Cm³⁺ complexes.

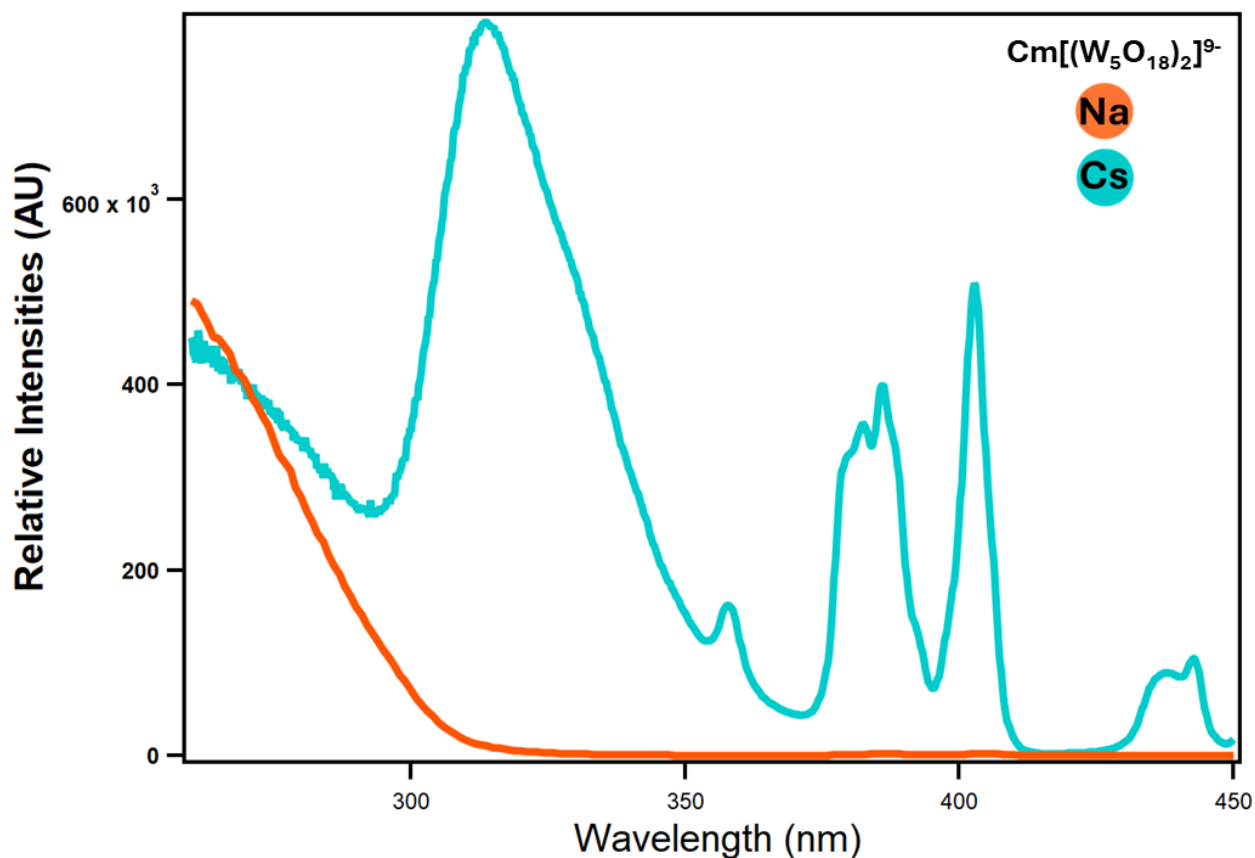


Figure S2. Excitation spectra of single crystals of Cs-CmW₅ (blue) and evaporated sample of Na-CmW₅ (orange). The large band below ~320 nm is characteristic of the W₅ POM complexed to curium. The four sharp peaks at ~360, ~380, ~405, and ~440 nm are characteristic of the 5f-5f transitions from Cm³⁺. The large band centered at ~325 nm in the case of Cs-CmW₅ is due to crystallography oil used for handling of the single crystals.

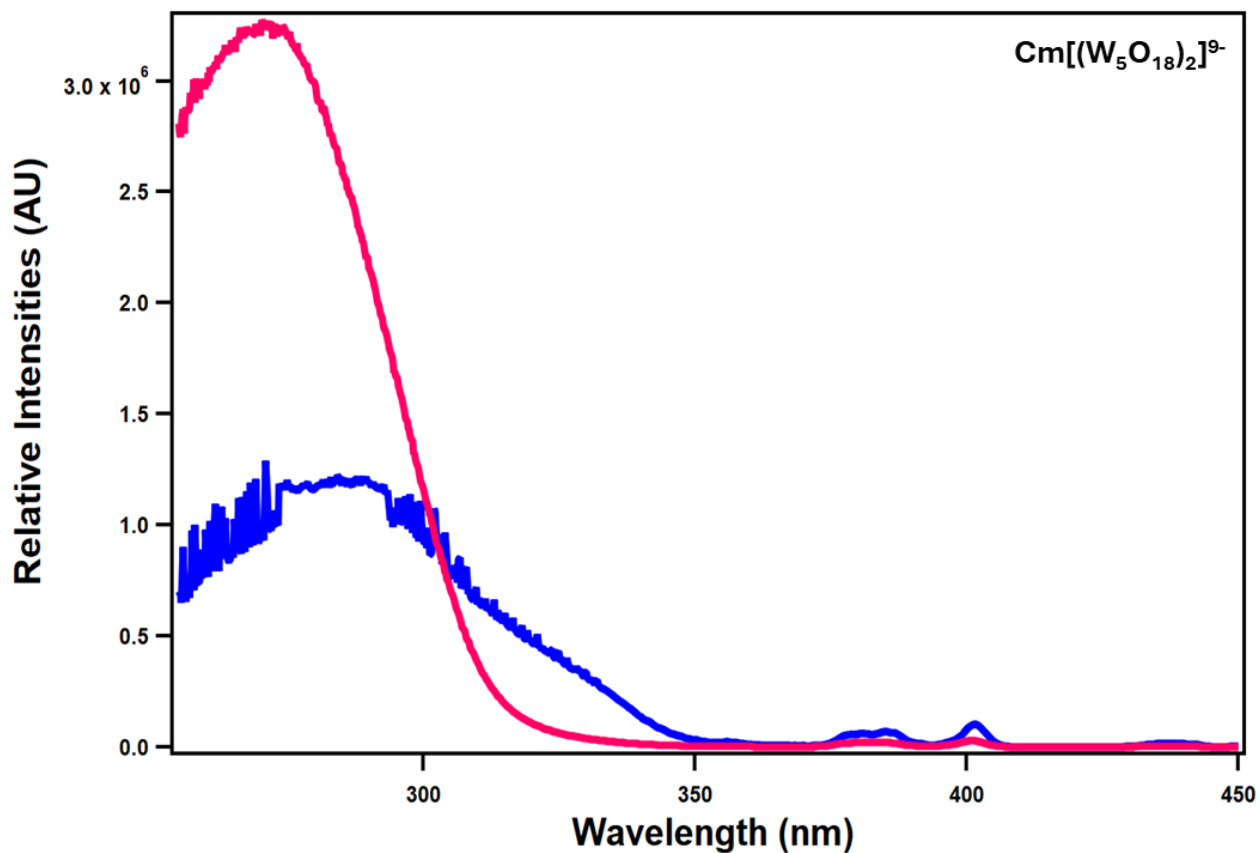


Figure S3. Excitation spectra for Na-CmW₅ in 1:4 v/v water/glycerol. Blue spectrum: liquid nitrogen temperature. Pink spectrum: Room temperature (22°C). The large band below ~320 nm is characteristic of the W₅ POM complexed to curium. This band shifts to below ~350 nm upon cooling to liquid nitrogen temperature. The four sharp peaks at ~360, ~380, ~405, and ~440 nm are characteristic of the 5f-5f transitions from Cm³⁺.

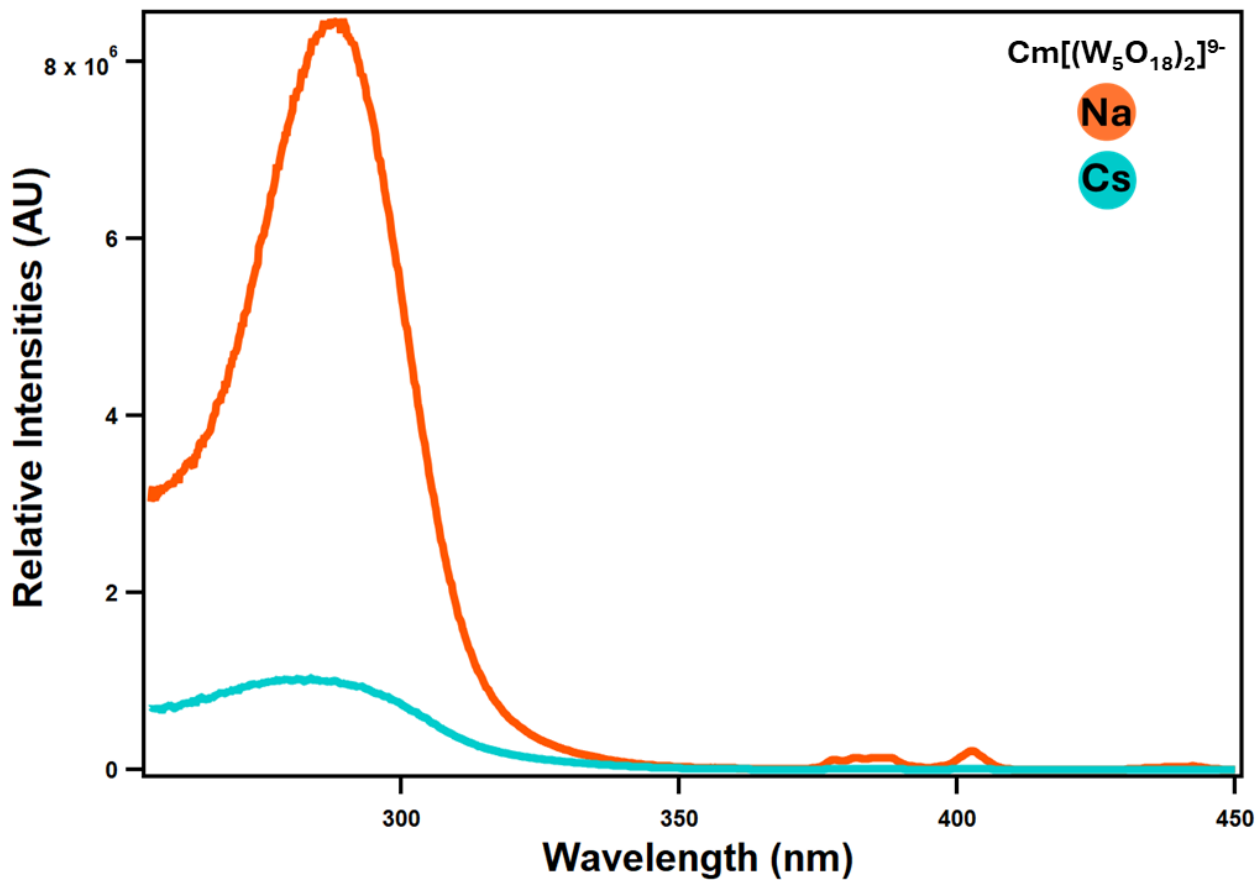


Figure S4. Excitation spectra for aqueous solutions of Cs-CmW₅ (blue) and Na-CmW₅ (Orange). pH = 5.5 (0.1 M acetate buffer). The large band below ~320 nm is characteristic of the POM. The four sharp peaks at ~360, ~380, ~405, and ~440 nm are characteristic of the 5f-5f transitions from Cm³⁺.

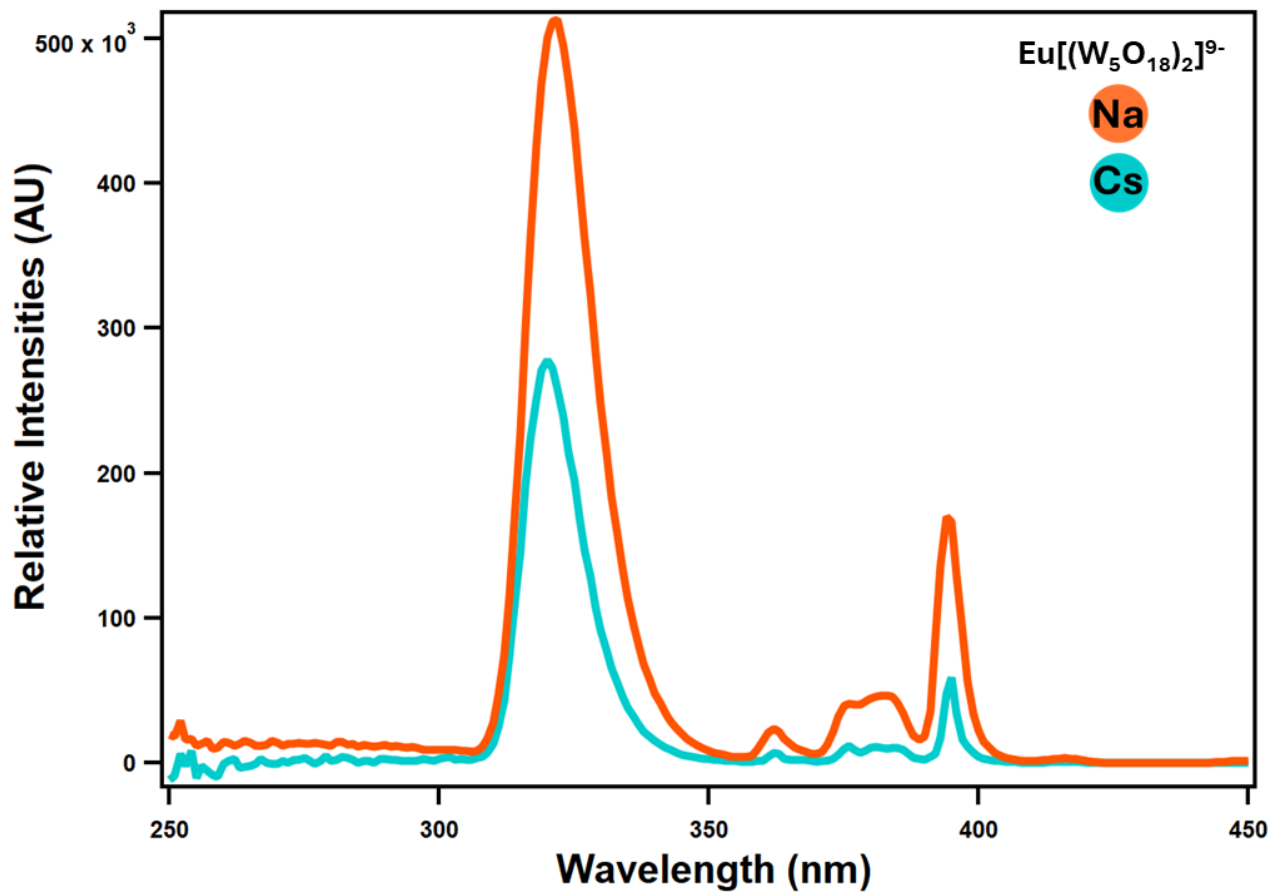


Figure S5. Excitation spectra for crystals of Cs-EuW₅ (blue) and Na-EuW₅ (Orange). The three sharp peaks at ~360, ~375, and ~395 nm are characteristic of the 4f-4f transitions from Eu³⁺.

Table S4. Summary of fluorescence emission peak positions and lifetimes as a function of the Na and Cs counterions for the $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ and $[\text{Cm}(\text{W}_5\text{O}_{18})_2]^{9-}$.

$\text{Cm}[(\text{W}_5\text{O}_{18})_2]^{9-}$	Solution Em peak (nm)	Lifetime decay (μs)	Solid Em peak (nm)	Lifetime decay (μs)
Na	605	780	605	700
Cs	606	515	608	341
(RT) Na	605	125	N/A	N/A
(LN₂) Na	605	200	N/A	N/A
$\text{Eu}[(\text{W}_5\text{O}_{18})_2]^{9-}$				
Na	701	3051	701	2240
Cs	701	3431	701	3041

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