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Utilizing Single-Crystalline Transformations for Precise Atom Placement in Multicomponent Cluster-Based Coordination Networks

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Abstract. The assembly of cluster or superatom building blocks into extended solids has revolutionized materials design, enabling the synthesis of modular semiconductors with well-defined structures and tunable electronic, magnetic, and optical properties. This strategy has recently advanced the synthesis of complex metal oxides with multifunctional or emergent behaviors but precise atom placement of multiple elements with similar chemistries or preferred coordination environments remains a significant challenge in the design of novel complex metal oxides. Here, we present a strategy for synthesizing polyoxometalate (POM)-based coordination networks with up to three different cations in precisely defined positions. Our approach leverages a single-crystal-to-single-crystal (SCSC) transformation in which the spatial placement of cations is governed by their availability at distinct stages of crystallization and transformation. Specifically, $[\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{(15-n)-}$ ($\text{Z} = \text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Ag}^+, \text{Bi}^{3+}, \text{Y}^{3+}$, any Ln^{3+} , Th^{4+}) is coordinatively assembled with various bridging metal cations (Y^{3+} , any Ln^{3+} , Th^{4+}). By using the encapsulated cation (Z) to “label” the POM, we track the phase-transformation and confirm the retention of single crystallinity. The integrated use of POM labeling and SCSC transformation enables rational control over cation distribution and establishes a versatile strategy for constructing multicomponent materials with high compositional and spatial precision.

Introduction

The bottom-up assembly of cluster or superatom building-blocks has emerged as a powerful strategy for synthesizing extended solids with well-defined structures and tailored electronic, magnetic, or optical properties.¹⁻¹⁷ The ability to leverage diverse components with independently tunable features imparts the atomic precision of molecular chemistry on the design of materials with multifunctional or emergent phenomena.³⁻¹⁷ This level of structural control is particularly attractive for multicomponent frameworks or coordination networks, where rational design of local

environments could enable unique combinations of functionality.¹⁸⁻²⁴ Precise integration of components with similar size and chemistry, however, remains difficult, as statistical incorporation leads to averaged compositions and complicates efforts to resolve structure–property relationships.^{13, 20, 25-28} For example, despite intense interest in mixed-metal metal–organic frameworks (MOFs), the relative spatial distribution of metal ions within these materials is often difficult to determine.²⁰⁻²⁴ Existing strategies for preparing mixed-metal frameworks or coordination networks, such as one-pot mixed-metal synthesis,^{20, 25} post-synthetic exchange,²⁹⁻³¹ and kinetically controlled crystallization²⁶⁻²⁷ frequently lack the fidelity required to distinguish and position individual ions at specific crystallographic sites. These limitations are even more pronounced in solution-phase syntheses, where multiple ions compete for similar coordination environments during nucleation and growth.^{29, 32-42} Developing strategies that enable different metal ions to be positioned in distinct and identifiable crystallographic sites thus represents a critical challenge for advancing complexity in atomically precise materials.

Our laboratory has previously developed methods for synthesizing one-, two- and three-dimensionally connected coordination networks or frameworks based on Preyssler-type ($\{ZP_5W_{30}\}$ or $\{ZP_5MoW_{29}\}$; $\{ZP_5W_{30}\} = [ZP_5W_{30}O_{110}]^{(15-n)-}$; $Z = Na^+, Bi^{3+}, Sm^{3+}$) polyoxometalate (POM) clusters bridged with first-row transition metal ions (Mn^{2+} , $Fe^{2+/3+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and mixtures thereof).^{25, 43-46} In our diffusion-controlled syntheses,^{25, 43-45} these assemblies form when aqueous mixtures of the POM and transition-metal salts are exposed to MeOH vapor, leading to solvent exchange that induces crystallization. In these cases, mixed-metal bridging ions are assumed to be statistically distributed.²⁵ Direct extension of this method to lanthanide or actinide bridging ions has been challenging because strong ion-pairing with $\{ZP_5W_{30}\}$ promotes precipitation of the cation-decorated POM. Here, we take advantage of this reduced solubility to access POM-based coordination networks in which up to three different cations occupy distinct crystallographic positions. Specifically, we drive a single-crystal-to-single-crystal (SCSC) transformation during the assembly of $\{ZP_5W_{30}\}$ ($Z = Ca^{2+}, Ln^{3+}$) with various decorating and bridging metal cations (Y^{3+} , La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , Lu^{3+} , Th^{4+}). This SCSC transformation converts cation-decorated (0D) clusters into cation-bridged (1D) networks, placing two different cations in crystallographically distinct positions. Importantly, the central cation, Z , is used to “label” the POM throughout the process, providing an unprecedented method to track and confirm the SCSC transition. This central

cation defines a third distinct and tunable site within the networks, offering an additional independent handle for ion placement in the assembled materials.

Results and Discussion

Lanthanide–POM Assemblies with Tunable Compositions. In a typical synthesis, EuCl₃ (0.580 mmol) and K₁₂[EuP₅W₃₀O₁₁₀]•15H₂O (0.0156 mmol) were dissolved in aqueous LiCl (1 M, 7 ml) and refluxed for 20 h. The resulting solution was concentrated to ~2 ml and placed in a methanol (MeOH) environment to induce crystallization. After ~1 h, colorless, rod-shaped crystals were observed. These crystals have a monoclinic *P*2₁/*m* unit cell (Table S1) containing {EuP₅W₃₀} decorated with four Eu³⁺ (Figures 1A, S1A), thus denoted {EuP₅W₃₀}-Eu₄ (or 0D, due to the lack of inter-POM connectivity). The Eu³⁺ occupancies and average bond distances to the terminal O atoms of {EuP₅W₃₀} (O_{POM}) are detailed in Table S2. Unlike previously synthesized lanthanide-decorated {NaP₅W₃₀} species,⁴⁷⁻⁴⁸ these assemblies require no additional Na⁺ or K⁺ for charge-balance.

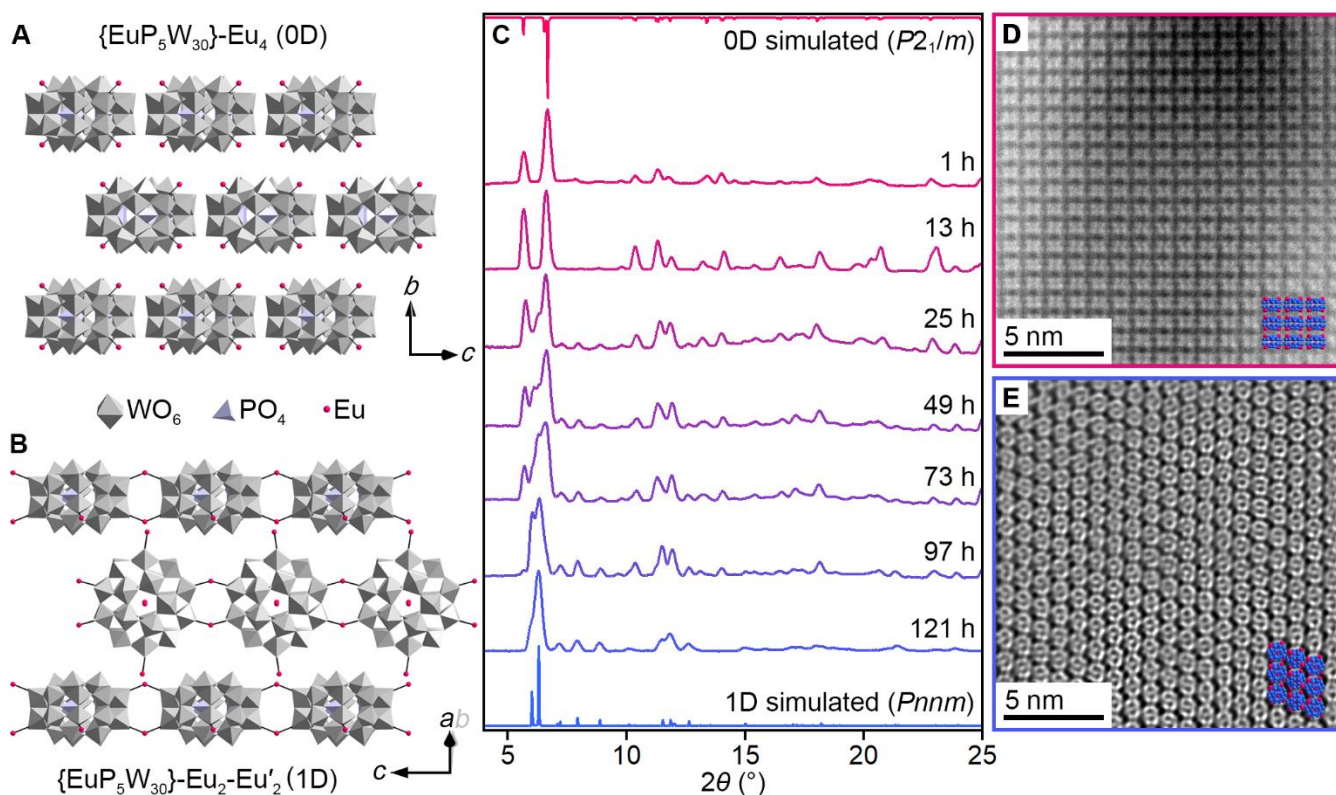


Figure 1. Crystals structures of (A) {EuP₅W₃₀}-Eu₄ (0D) and (B) {EuP₅W₃₀}-Eu₂-Eu'₂ (1D). Water molecules are omitted for clarity. (C) Powder X-ray diffraction patterns for crystals collected as soon as product is observed (1 h) and at (top to bottom) 13, 25, 49, 73, 97 and 121 h after synthesis. The patterns simulated from single-crystal data of {EuP₅W₃₀}-Eu₄ (0D, top) and {EuP₅W₃₀}-Eu₂-Eu'₂ (1D, bottom) are plotted for comparison. (D, E) Fourier-enhanced MAADF-STEM micrograph of {EuP₅W₃₀}-Eu₄ and {EuP₅W₃₀}-Eu₂-Eu'₂, respectively. Original STEM images and FFTs are provided in Figure S2.

When {EuP₅W₃₀}-Eu₄ crystals were left in the mother liquor under MeOH vapor for several days, a different structure was observed. Figure 1B and S1B show the structure of crystals collected after 121 h of MeOH diffusion. This structure has an orthorhombic *Pnnm* unit cell (Table S1) containing {EuP₅W₃₀} connected by Eu³⁺. Specifically, {EuP₅W₃₀} clusters form linear chains along the *c*-direction, in which each pair of {EuP₅W₃₀} is bridged by 2 Eu³⁺. Additionally, 2 Eu³⁺ per {EuP₅W₃₀} remain at decorating positions. This structure is thus denoted {EuP₅W₃₀}-Eu₂-Eu'₂ (or 1D, due to the inter-POM connectivity along one dimension). The chains stack along the *b*-directions to form alternating layers that are rotated ~90° with respect to each other along the *a*-direction (Figure S1B). The Eu occupancies and average bond distances to O_{POM} are detailed in Table S3. The change in structure as a function of time was monitored with powder X-ray diffraction (Figure 1C), showing a gradual shift from 0D to 1D crystals over ~120 h.

Figure 1D shows a Fourier-enhanced medium-angle annular dark-field scanning transmission electron microscope (MAADF-STEM) image of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$. The observed rectangular lattice corresponds to a projection of the (0 0 1) plane of the monoclinic $P2_1/m$ lattice. The bright rectangular spots can be assigned to the W and Eu atoms (Figure 1D, inset; Figure S2A). d -spacings for the (1 0 0) and (0 2 0) lattice planes (Figure S2A) determined from this image are provided in Table S4. The original MAADF-STEM image and selected-area fast Fourier transformation (FFT) are provided in Figures S2B and S2C, respectively. Figure 1E shows a Fourier-enhanced MAADF-STEM image of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_2\text{-Eu}'_2$. The ordered oval arrangement corresponds to the projection of the (1 $\bar{1}$ 1) plane of the $Pnmm$ lattice, where bright spots again correspond to the W and Eu atoms (Figure S2D). The intense spots at the center and edges of the oval are attributed to the overlapping of Eu atoms in this view (Figure S2D). d -spacings for the (0 1 1) and (1 1 0) lattice planes (Figure S2D) determined from this image are provided in Table S4. The original MAADF-STEM image and selected-area fast FFT are shown in Figures S2E and S2F, respectively. For both assemblies, the d -spacings determined by STEM are smaller than those observed by X-ray diffraction (Table S4). Similar lattice contraction has been previously reported in POM networks upon removal from the mother liquor^{25, 43} and after heating under vacuum,²⁵ and is corroborated here by powder X-ray diffraction (Figure S3). The larger contraction observed in the STEM measurements is expected due to the ultra-high vacuum. These images are among the clearest atomic-scale visualizations of assembled POM materials reported thus far.⁴⁹⁻⁵² As has been observed with other coordination networks⁵³⁻⁵⁶ and POM-containing materials,⁵⁷⁻⁵⁸ the network is perturbed by the electron beam, losing crystallinity after several scans. The ability to obtain clear images, however, is likely due to the relative stability and rigidity of $\{\text{ZP}_5\text{W}_{30}\}$,⁵⁹ as well as the use of reduced electron beam dosage.

The same 1D network structures can be synthesized with a variety of bridging and central ions. Specifically, replacing EuCl_3 with LnCl_3 ($\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}$), YCl_3 or $\text{Th}(\text{NO}_3)_4$ and/or replacing $\{\text{EuP}_5\text{W}_{30}\}$ with $\{\text{CaP}_5\text{W}_{30}\}$ or $\{\text{ErP}_5\text{W}_{30}\}$ results in isostructural networks (Figures S4–7). Powder X-ray diffraction patterns at select times with varying central or bridging cation combinations (Figures S5–7) indicate that the phase-transformation process is also comparable for all combinations evaluated. These results suggest that the various decorating/bridging ions and $\{\text{ZP}_5\text{W}_{30}\}$ each constitute a set of

interchangeable building blocks such that any combination, or mixtures thereof, can be used to access isostructural networks with diverse compositions.

“Labeled” Clusters Reveal a Single-Crystalline Phase-Transformation. SCSC transformations have attracted attention as a post-synthetic modification strategy to access atomically precise materials that are difficult to achieve via conventional solution-based methods.^{29, 32-42} Most reported SCSC transformations involve isolated crystals exposed to external stimuli (e.g., irradiation,⁶⁰ temperature variation,⁶¹ gas introduction,⁶² or soaking in solvents⁶³) and followed by single-crystal X-ray diffraction to elucidate the structural changes.³⁷ Typically, these studies avoid complex media to prevent crystal decomposition, dissolution, or recrystallization, enabling accurate tracking of structural transformations. In practical scenarios, however, many crystals form and undergo transformations in solution. Under such circumstances, tracking structural changes requires characterizing one crystal throughout the entire transformation, a process which can be hindered by decreasing crystallinity, increasing disorder and incomplete or heterogeneous transformations. Understanding SCSC transformations under these complex conditions is both essential and experimentally demanding.

To determine whether phase-conversion occurs via SCSC transformation or dissolution and recrystallization process, we took advantage of the central cation, Z, of $\{ZP_5W_{30}\}$, which can be readily exchanged for a variety of cations.⁶⁴⁻⁶⁷ For these studies, the central cation was exchanged to “label” the cluster with either Er^{3+} or Ca^{2+} . Both $\{ErP_5W_{30}\}$ and $\{CaP_5W_{30}\}$ form 0D and 1D assemblies analogous to those observed for $\{EuP_5W_{30}\}$ (Figure S6) and thus all three forms of the POM are considered to be interchangeable building-blocks that can be used to follow the structural evolution during the phase-transformation (Figure 2A). To do so, $\{CaP_5W_{30}\}$ -Eu₄ (Figure 2Ai) and $\{ErP_5W_{30}\}$ -Eu₄ (Figure 2Aii) were first synthesized in parallel. After 1 h of MeOH diffusion, both sets of crystals were collected and confirmed to be in the 0D phase without detectable transformation to the 1D phase (Figure S8). Then, the $\{CaP_5W_{30}\}$ -Eu₄ crystals were added to the mother liquor from the $\{ErP_5W_{30}\}$ -Eu₄ synthesis (Figure 2Aiii) and placed in a MeOH environment for an additional 120 h. Powder X-ray diffraction (Figure S8) confirmed that the crystals transformed to the 1D phase. In the final crystals, the presence of Er (from $\{ErP_5W_{30}\}$) was used to evaluate the phase-conversion pathway. If the $\{CaP_5W_{30}\}$ -Eu₄ crystals underwent a SCSC transformation, the final product is expected to be $\{CaP_5W_{30}\}$ -Eu₂-Eu'₂, with no detectable Er (Figure 2Aiv). In contrast, if the $\{CaP_5W_{30}\}$ -Eu₄ dissolved and recrystallized in the presence of

$\{\text{ErP}_5\text{W}_{30}\}$, Er would be incorporated into the final crystals ($\{\text{ErP}_5\text{W}_{30}\}_x\{\text{CaP}_5\text{W}_{30}\}_{1-x}\text{-Eu}_2\text{-Eu}'_2$, Figure 2Av).

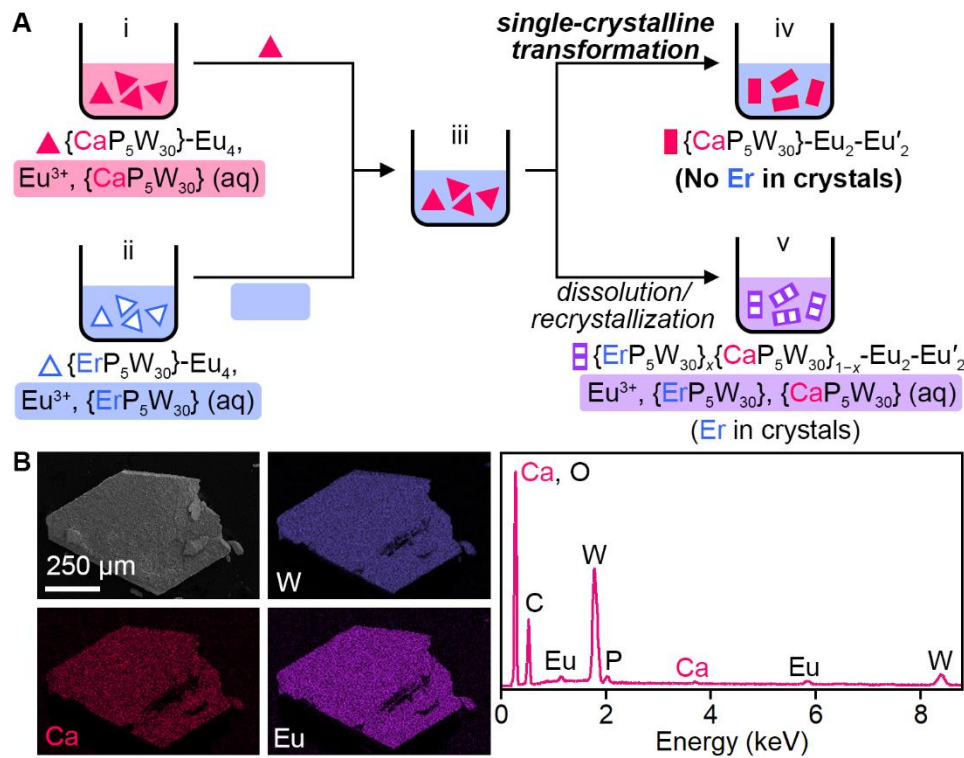


Figure 2. (A) Schematic depiction of “labeling” experiments used to determine whether phase-transformation is single-crystalline or via dissolution and recrystallization. First, (i) $\{\text{CaP}_5\text{W}_{30}\}\text{-Eu}_4$ and (ii) $\{\text{ErP}_5\text{W}_{30}\}\text{-Eu}_4$ were synthesized in parallel. (iii) $\{\text{CaP}_5\text{W}_{30}\}\text{-Eu}_4$ crystals were placed in the mother liquor from the $\{\text{ErP}_5\text{W}_{30}\}\text{-Eu}_4$ synthesis for conversion to 1D networks. The lack of Er in the final crystals suggests the crystals are undergoing a (iv) single-crystalline phase-transformation rather than (v) dissolving and recrystallizing. (B) SEM mapping images and energy dispersive spectrum of crystal from experiment depicted in A.

Figure 2B shows scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS) mapping images and a spectrum collected on a single-crystal at the end of the phase-transformation. Importantly, W, Eu, and Ca were detected while Er was not (Table S5), indicating that the final crystals were formed via a SCSC transformation. Complementary analysis by inductively coupled plasma-mass spectrometry (ICP–MS) revealed the presence of trace Er (~ 3 Er per 100 $\{\text{CaP}_5\text{W}_{30}\}$, Table S5). We hypothesize that this signal is due to imperfect removal of Er from the mother liquor by washing with MeOH. Such signal could, however, be attributed to limited interfacial processes, such as surface exchange or shallow partial dissolution at step or edge

sites, without altering the SCSC interpretation. These possibilities align with prior discussions distinguishing SCSC transformations from dissolution–recrystallization pathways.⁶⁸

To confirm that $\{\text{ErP}_5\text{W}_{30}\}$ and $\{\text{CaP}_5\text{W}_{30}\}$ would co-crystallize together, a control experiment was performed in which an equimolar amount of both clusters was included in the initial solution (Figure S9A). Crystals were then synthesized following the procedure described for $\{\text{EuP}_5\text{W}_{30}\}$ -Eu₂-Eu'₂. The crystals were confirmed by powder X-ray diffraction to be the 1D product (Figure S10). SEM–EDS on a single crystal (Figure S9B) reveals a homogeneous distribution of W, Eu, Er, and Ca with Er/Ca = 1.1. This ratio was corroborated by ICP–MS (Er/Ca = 1.03). These results confirm that $\{\text{ZrP}_5\text{W}_{30}\}$ does not preferentially crystallize with clusters containing the same central cation. Thus, the negligible Er incorporation into crystals transformed in the presence of $\{\text{ErP}_5\text{W}_{30}\}$ can be attributed to a SCSC transformation (Figure 2A).

An Intercalated Intermediate. Given that no fully 1D connected crystals were isolated during the initial hours of MeOH diffusion, we hypothesized a continuous structural evolution, supported by observations of gradual changes in the diffraction patterns. Indeed, a perturbed structure collected after 24 h MeOH diffusion was successfully solved (Figures 3A, S11). The crystals adopt a monoclinic $P2_1/m$ unit cell (Table S1) with 2 different layers alternating along the b -direction. In one layer, $\{\text{EuP}_5\text{W}_{30}\}$ are decorated with 4 Eu³⁺, with no connections between the POMs, similar to $\{\text{EuP}_5\text{W}_{30}\}$ -Eu₄. The $\{\text{EuP}_5\text{W}_{30}\}$ within these layers have at least four possible disorder positions, whereas the disorder in $\{\text{EuP}_5\text{W}_{30}\}$ -Eu₄ can be modeled with 2 symmetry-related positions. This increased disorder in the intercalated structure likely reflects ongoing structural transformations as the material progresses toward its final phase. In the other layer, multiple Eu³⁺ begin to occupy positions intercalated between 2 $\{\text{EuP}_5\text{W}_{30}\}$, forming O_{POM}–Eu–O_{POM} connections. Compared to the layer without intercalated Eu³⁺, the intercalated layers exhibit less disorder, which may be due to the increased charge-compensation. Overall, the intermediate structure has decreasing decorating Eu³⁺ and emerging bridging (intercalating) Eu³⁺ and is thus denoted $\{\text{EuP}_5\text{W}_{30}\}$ -Eu_{4-x}-Eu_xⁱ. The Eu occupancies and average bond distances to O_{POM} are detailed in Table S6.

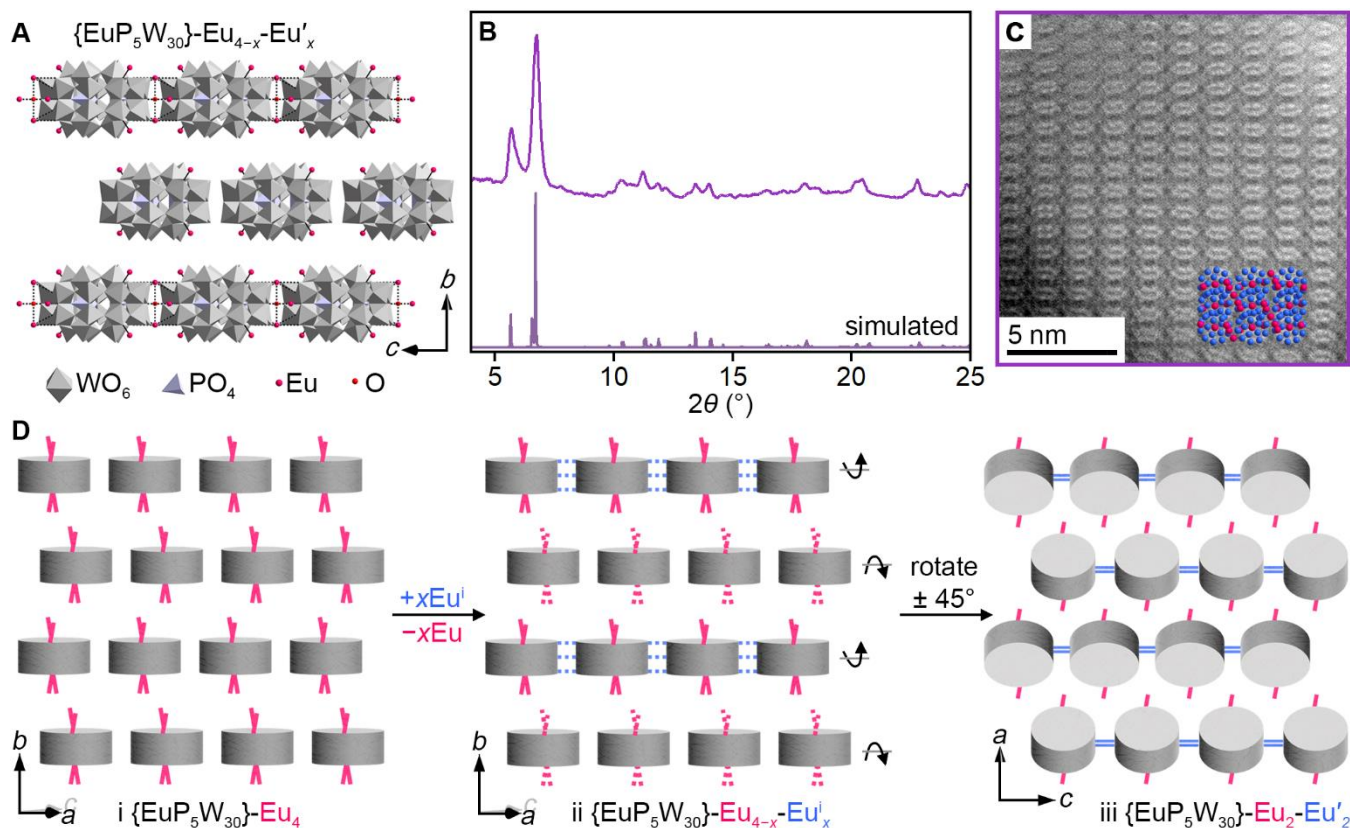


Figure 3. (A) Crystal structure, (B) powder-X-ray diffraction pattern and (C) Fourier-enhanced MAADF-STEM micrograph of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_{4-x}\text{-Eu}'_x$. Original images and FFTs are shown in Figure S12. (D) Schematic representation of the phase-transformation process. (i) Cartoon representation of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ with layers stacking along the b -direction. Additional ions (Eu^{i}) are intercalated into alternating layers, while some decorating Eu are lost in the opposite layers, to form $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_{4-x}\text{-Eu}'_x$ (ii). The partial occupancies of decorating Eu and intercalated Eu^{i} are indicated by dashed lines. After reaching a critical concentration of Eu^{i} , layers rotate in alternating directions $\pm 45^\circ$ to form the 1D-connected $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_2\text{-Eu}'_2$.

Figure 3B shows a Fourier-enhanced MAADF-STEM image of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_3\text{-Eu}^{\text{i}}$. The observed rectangular lattice corresponds to a projection of the $(0\ -1\ 0)$ plane of the monoclinic $\text{P2}/m$ lattice. The bright fusiform spots can be assigned to the W and Eu atoms for the overlap of $2\ \{\text{EuP}_5\text{W}_{30}\}$ (Figure 3C, inset; Figure S12A). d -spacings for the $(1\ 0\ 0)$ and $(1\ 0\ -1)$ lattice planes (Figure S12A) determined from this image are provided in Table S4. The original MAADF-STEM image and selected-area fast FFT are provided in Figures S12B and S12C, respectively. The observation of the $(1\ 0\ -1)$ plane in the structure of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_{4-x}\text{-Eu}'_x$ indicates a reduction in symmetry compared to $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$. Specifically, the screw axis present in $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ is lost due to intercalation of Eu in alternating layers.

Atomically Precise Placement of Distinct Ions. Throughout the phase-transformation, the number of decorating Eu^{3+} decreases from 4 to 2, while the number of bridging Eu^{3+} increases from 0 to 2. As the phase-transformation occurs in a mother-liquor containing Eu^{3+} , we designed additional experiments to determine whether the Eu^{3+} was simply migrating or if intercalating/bridging Eu^{3+} was introduced from the mother liquor. Specifically, we performed the phase-transformation in a mother-liquor containing Y^{3+} (Figure 4A), which was chosen because it shares similar chemical coordination properties with Ln^{3+} , yet differs significantly in electron density, allowing for clear differentiation in crystallographic analysis. As discussed above, powder X-ray diffraction confirmed that networks synthesized with YCl_3 transitioned from 0D to the 1D phase on timescale analogous to those synthesized with EuCl_3 (Figure S5), suggesting that Y^{3+} and Eu^{3+} follow comparable transformation pathways.

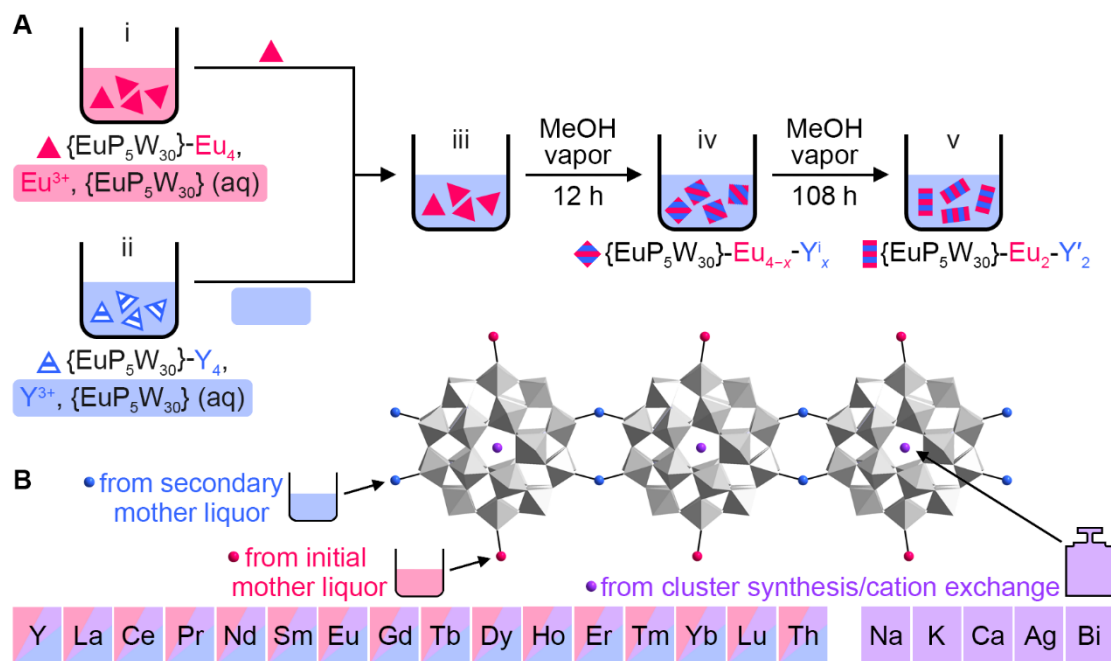


Figure 4. (A) Schematic depiction of “mother liquor exchange” experiments designed to determine the origin and evolution of ions at different positions within the final structure. First, $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ (i) and $\{\text{EuP}_5\text{W}_{30}\}\text{-Y}_4$ (ii) were synthesized in parallel. $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ crystals were then placed in the mother liquor from the $\{\text{EuP}_5\text{W}_{30}\}\text{-Y}_4$ synthesis for conversion to 1D networks (iii–v). Y^{3+} ions exclusively occupied the bridging positions, while none were found in the decorating positions, suggesting that the bridging ions originated from the secondary mother liquor, whereas the decorating ions remained from the initial mother liquor. (B) Crystals structures of $\text{Y}_2\text{Eu}_2[\text{EuP}_5\text{W}_{30}\text{O}_{110}]\cdot 62\text{H}_2\text{O}$ ($\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_2\text{-Y}'_2$). Water omitted for clarity. Ions at different positions are color-coded for clarity. Pink represents ions in the decorating positions, originating from the initial mother liquor, while blue represents bridging ions derived from the secondary mother liquor. Purple represents the center ions, which can be set prior to assembly. The colors of the elements below correspond to their ability to be precisely synthesized at the respective positions shown by the matching colors.

Initially, $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ (Figure 4Ai) and $\{\text{EuP}_5\text{W}_{30}\}\text{-Y}_4$ (Figure 4Aii) were synthesized in parallel. Following 1 h of MeOH diffusion, $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ crystals were isolated and confirmed to be in the 0D phase (Figure S14A). Subsequently, the $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ crystals were added to the mother liquor from the $\{\text{EuP}_5\text{W}_{30}\}\text{-Y}_4$ synthesis (Figure 4Aiii) and subjected to an additional 108 h of MeOH diffusion (Figure 4Aiv–v). Powder X-ray diffraction (Figure S14A) confirmed that the resulting crystals had transformed to the 1D phase. Single-crystal X-ray diffraction of the final crystals revealed that they are isostructural with $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_2\text{-Eu}'_2$ (Tables S1, S7). Notably, however, the bridging positions are occupied only by Y^{3+} , while no Y^{3+} was found in the decorating

positions. Elemental analysis throughout the phase-transformation (Figure S14B) revealed that, upon introduction of the Y^{3+} solution, the number of $Eu^{3+}/\{EuP_5W_{30}\}$ quickly dropped from 5 to 3 (one being from the central ion, plus 2 in the decorating position), while the $Y^{3+}/\{EuP_5W_{30}\}$ concomitantly increased to 2. Combined with the single-crystal structure, these data indicate that, during intercalation, 2 decorating Eu^{3+} are readily replaced by Y^{3+} , which then form the bridging metal ions in the final 1D structure. A repeat of this experiment with additional timepoints (Figure S15) further confirmed these conclusions. These results indicate that the identities of the decorating, bridging and central ions can be independently controlled based on the ions available at different times during the synthesis, enabling atomically precise placement in complex compositions (Figure 4B).

To evaluate the generality of this approach, additional ion exchange experiments were conducted (Table S8). First, the above experiment was repeated with an additional step in which the crystals were transferred to a Ce^{3+} -containing mother liquor after 36 h of Y^{3+} intercalation (Figure S16), demonstrating that the intercalating ions can easily be replaced while the 2 decorating ions remain fixed. If, however, crystals are placed in the Ce^{3+} mother liquor only after conversion to the 1D phase, no ion exchange occurs (Figure S17), indicating that none of the ions are mobile once the 1D network is formed. If the order of the ion exchange is reversed (Figure S18), the process proceeds in the same manner, suggesting that the exchange is driven by an excess of ions rather than by ion solubility or affinity for $\{ZP_5W_{30}\}$. Additional ion combinations (Figures S19, S20) further demonstrate that the exchange is not limited by ion identity and that this method can be applied to a wide range of ions to access diverse compositions with atomically precise placement (Figure 4B). SEM-EDS line-mapping of individual crystals with select ion combinations (Figures S21, 22; Tables S9, S10) shows that the elemental distribution is homogeneous within the experimental resolution, consistent with uniform ion incorporation.

This strategy allows access to coordination networks in which “dopant” metal ions can be placed in three distinct positions: the central ion (purple) originates from the cluster synthesis,⁶⁴⁻⁶⁷ the decorating ions (pink) are retained from the initial mother liquor, and the bridging ions (blue) are introduced from the secondary mother liquor. This demonstrates a clear approach for tuning metal identity at these specific sites, enabling targeted modification of the final structure through controlled phase-transformation. Such compositional precision also offers a foundation for tailoring functional properties. For example, photoluminescence characteristics can be predictably

modulated via mixed-Ln incorporation (Figures S23, S24), providing a clear route to white light emission in these materials.

MeOH Diffusion Drives Phase-Transformation. We hypothesized that the driving force behind the ion intercalation and phase-transformation was a change in solubility due to increased MeOH content with longer diffusion times. Indeed, ^1H NMR spectroscopy collected on the mother liquor at various times revealed that the % volume MeOH initially increased rapidly in the first ~16 h, followed by a plateauing increase for the remainder of the experiment (Figures S25A, S26; Table S11). Powder X-ray diffraction on crystals collected at the same times indicated that the phase transformation was complete when the mother liquor reached ~95% MeOH by volume (Figure S25B, Table S11). To further test the role of MeOH without the influence of time, “rapid” transformation experiments were performed in which MeOH was directly added to the mother liquor prior to crystallization of $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$. A white precipitate immediately formed, which was collected by filtration, washed, and characterized. The results revealed that increasing the MeOH percentage from 80% to 95% induced a phase-transformation from $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_4$ to $\{\text{EuP}_5\text{W}_{30}\}\text{-Eu}_2\text{-Eu}'_2$ (Figure S27). These observations corroborate the difference in solubility within increasing MeOH as the driving force for the intercalation and phase-transformation, aligning with previous studies on solvent-mediated phase-transformations.⁶⁹⁻⁷¹ The rapid phase-transformation could also be applied to synthesize networks with different decorating and bridging ions. For example, $\{\text{CaP}_5\text{W}_{30}\}\text{-Eu}_4$ can be rapidly (< 1 h) transformed to $\{\text{CaP}_5\text{W}_{30}\}\text{-Eu}_2\text{-Y}'_2$ if the Y^{3+} mother liquor is adjusted to contain 95% MeOH before adding the $\{\text{CaP}_5\text{W}_{30}\}\text{-Eu}_4$ crystals (Figure S28). In contrast, when the crystals are added to a fresh Y^{3+} mother liquor and MeOH is introduced only by vapor diffusion, intercalation of Y^{3+} occurs without accompanying phase-transformation (Figure S29). These results further demonstrate that the MeOH environment, and not the ion intercalation, serves as the driving force for the phase-transformation.

Summary and Outlook

We demonstrate a synthetic strategy that leverages SCSC transformations to achieve atomically precise incorporation of multiple metal cations into POM-based coordination networks. By using the central cation to label the POM, we revealed the dynamic ion-exchange processes involved in the solubility-driven single-crystalline transformation. Understanding this transformation enabled the independent and precise placement of different cations at central,

decorating and bridging positions, overcoming conventional statistical cation distributions and allowing rational design of multicomponent networks. Extending this strategy to additional POMs and metal ions could provide a route to atomically precise coordination networks with a vast range of compositional possibilities, substantially broadening structural and compositional control in multicomponent materials.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

- Supplementary tables and figures, including crystallographic parameters and network connectivity, additional crystal structure images, powder X-ray diffraction patterns, STEM images, experimental schematics with associated elemental analysis; Experimental details including synthesis and characterization.

Accession Codes

Deposition Numbers 2434860–2434863 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe.

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