

Cation-controlled capture of polyoxovanadate-based organic–inorganic 1D architectures†

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Metal cations are used to control the selective crystallization of organic–inorganic supramolecular polymers. Two complementary monomers, a dodecanuclear vanadate $[V_{12}O_{32}(NO_3)]^{5-}$ and the organic macrocycle cyclen assemble into hybrid host–guest aggregates. In the presence of Ba^{2+} or La^{3+} , supramolecular polymerization and crystallization is driven by a complex interplay of cyclene protonation, hydrogen-bonding and electrostatics.

Molecular metal oxides, or polyoxometalates (POMs) are the molecular analogues of solid-state metal oxides. Their applications range from molecular electronics and spintronics¹ to catalysis,² energy storage³ and bio-medicine.⁴ POMs are atomically precise metal oxo clusters based on early, high-valent transition metals in their highest oxidation states (*e.g.*, $Mo(v/vi)$, $W(v/vi)$, $V(v/v)$). This compound class offers vast structural and chemical variability, so that task-specific structure and function tuning becomes possible.⁵ In the realm of supramolecular chemistry, structure and function control in POMs has been achieved using internal (often anionic) templates,^{6–8} as well as external structure-directing molecules.^{9–13}

Over the last decade, polyoxovanadate (POV) chemistry has undergone a tremendous developments;^{3,14,15} while pioneering work in the late 20th century was dominated by structural and magnetic studies,^{14,16,17} the field has now expanded to energy conversion and energy storage,^{3,18,19} catalysis,^{20,21} sensing,^{22,23} spintronics^{24,25} and solid-state reactivity models.^{26,27} This is in part due to novel synthetic approaches which enable polyoxovanadate functionalization with metals,^{28–30} semimetals^{15,31}

or organic moieties,^{32,33} often working under non-aqueous conditions in organic solvents.³⁴

Despite much progress, controlling the molecular self-assembly and supramolecular aggregation of POVs is still a major challenge. Often, inorganic anions such as oxoanions (Fig. 1), halides or pseudohalides (*e.g.* cyanate or azide) are used as internal templates to direct POV self-assembly.¹⁷ In one pioneering example, Klemperer and co-workers reported that charge-neutral coordinating organic nitriles (*e.g.* acetonitrile or benzonitrile) can be employed to template POV assembly, leading to hybrid structures $R-CN@[V_{12}O_{32}]^{4-}$ ($= R-CN@V_{12}$, $R = Me, Ph$; Fig. 1).^{35,36} Building on this work, Hayashi, Kikukawa and co-workers demonstrated that the $\{V_{12}\}$ framework can also be accessed using nitromethane as charge-neutral template,²³ and that exchange of the nitromethane with templates ranging from halides to acetic acid is possible by careful tuning of the reaction conditions.^{23,37} In a subsequent study, the group showed that $\{V_{12}\}$ can even be isolated with an empty inner cavity and act as a binding site for guest molecules, *e.g.*, Br_2 , leading to a unique polarization and chemical activation of the Br_2 molecule.^{20,38} To-date, these pioneering studies have mainly focused on using anionic or charge-neutral internal templates to control POV self-assembly, while the use of organic cations as external templates to control supramolecular POV aggregation is still in its infancy. However, the use of organic external templates is a key for accessing functional POV

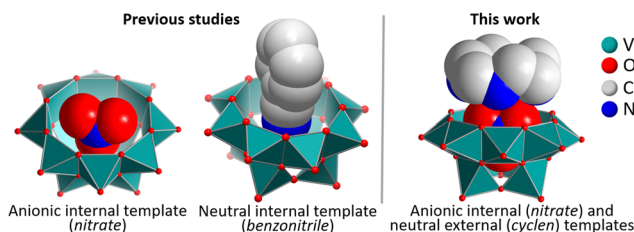


Fig. 1 Overview of previous studies focusing on internal templates within the $\{V_{12}\}$ structure,^{23,35} and the current study highlighting the use of external templates for structure aggregation.

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systems: Streb and co-workers developed the dodecavanadate (${}^t\text{Bu}_4\text{N}_3$)[$(\text{Me}_2\text{NH}_2)_2\text{V}_{12}\text{O}_{32}\text{Cl}$], where two dimethylammonium cations act as external templates to generate and block metal cation binding sites on the POV cluster surface.^{28,39} Reaction of this cluster with various metal cations³ has led to applications ranging from molecular magnetism³⁹ to (photo)catalysis^{40,41} and energy storage.^{42,43}

Here, we build on these studies and explore supramolecular POV aggregation in the presence of organic macrocyclic cations as external “templates”. The study is inspired by groundbreaking works by Cadot, Haouas, Falaise and co-workers who reported spectacular supramolecular host-guest aggregates based on POMs (tungstates and molybdates) and γ -cyclodextrin: the authors reported that the systems are stabilized by a combination of hydrogen bonding and chaotropic effects.^{44–46}

Here, we decided to study POV-based host-guest formation using the macrocyclic aza-crownether cyclen (1,4,7,10-tetraazacyclododecane, $\text{C}_8\text{H}_{20}\text{N}_4$) as guest. We chose cyclen as it has similar diameter and similar C_4 -symmetry to $\{\text{V}_{12}\}$, features four independent protonation sites⁴⁷ and offers an ideal balance between structural rigidity (due to the ethylene bridges) and adaptability (due to the absence of bulky substituents). In addition, we targeted nitrate-templated $\{\text{V}_{12}\}$ as the inorganic “host” as we hypothesised that hydrogen-bonding between nitrate and protonated cyclen under self-assembly conditions could facilitate the simultaneous $\{\text{V}_{12}\}$ formation and host-guest assembly.

In this study, we report that cyclen can act as external organic template cation to form organic-inorganic host-guest complexes with $\{\text{V}_{12}\}$. Structural matching between N-H hydrogen-bond donors on cyclen V-O hydrogen bond acceptors

on $\{\text{V}_{12}\}$ results in the selective aggregation and growth of 1D chains. The study provides initial insights into structure formation and the role of cyclen protonation as well as counter-cations for supramolecular structure aggregation.

Initial synthetic efforts into the cyclen-POV system in organic solvents showed significant challenges including solubility incompatibilities and component precipitation. Reaction optimization led to the reaction of cyclen with the vanadate precursor $[\text{V}_4\text{O}_{12}]^{4-}$ ($=\{\text{V}_4\}$)⁴⁸ in DMSO solution in the presence of $\text{Ba}(\text{NO}_3)_2$ as additional counter-cation. The reaction was carried out at 80 °C for 4 h. After cooling to room temperature, the solution was acidified using aqueous HNO_3 (3 M). Storage under dark, ambient conditions over night resulted in the formation of orange-red block crystals of **1** (yield: 40% based on V). For synthetic details see ESI.† Single-crystal X-ray diffraction (SC-XRD) showed that **1** crystallizes in the tetragonal space group $P4/n$ with $a = b = 19.6114(12)$ Å, $c = 11.0115(9)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 4235.1(6)$ Å³ (for crystallographic details see ESI.†).‡ Structure analysis of **1** gave the formula $[\text{Ba}(\text{DMSO})_8][(\text{C}_8\text{H}_{23}\text{N}_4)\text{V}_{12}\text{O}_{32}(\text{NO}_3)]$. Infrared spectroscopy, thermogravimetric analysis and energy-dispersive X-ray spectroscopy support this assignment and confirm sample composition, for details see ESI.†

Structural analysis of **1** shows, that the cyclen acts as an external “cap” for the $\{\text{V}_{12}\}$, and is held in place by a combination of electrostatic and hydrogen bonding interactions. Based on structural and charge-balancing considerations, the cyclen is 3-fold protonated (*i.e.*, charge: 3+); however, protonation is not unambiguously observable by SC-XRD due to the low scattering of hydrogen atoms. The five-fold negative charge of $\{\text{V}_{12}\}$ is further compensated by a $[\text{Ba}(\text{DMSO})_8]^{2+}$ counter-cation in the crystal lattice. This species does show specific (*i.e.*, coordinative or hydrogen bonding) interactions with the cyclen

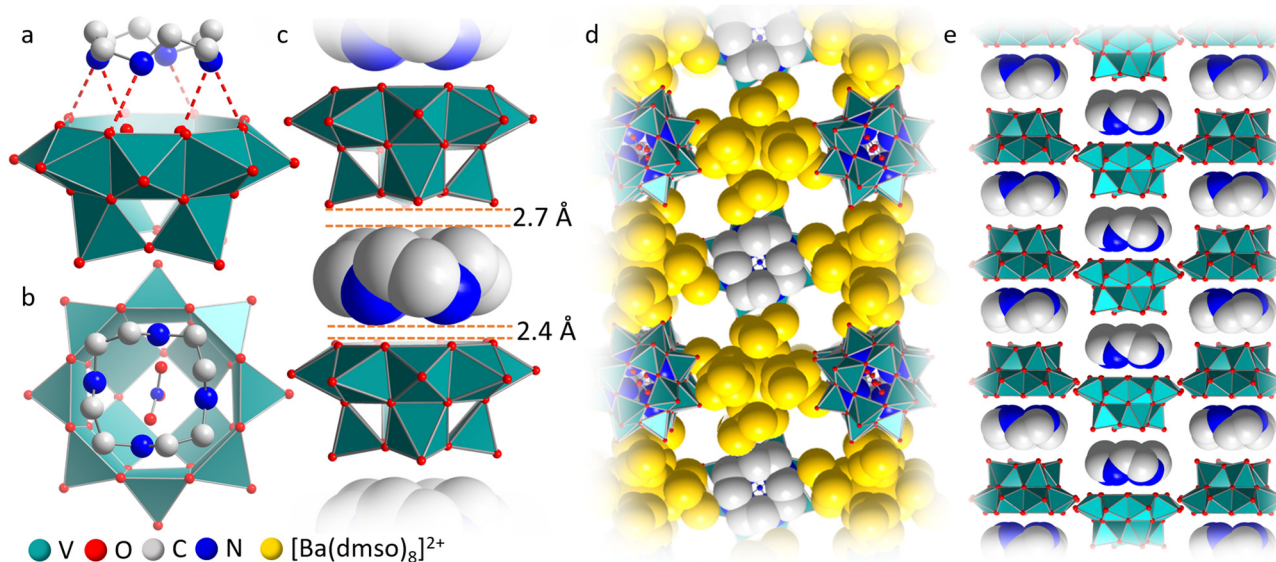


Fig. 2 Structural illustration of the organic-inorganic host-guest aggregate **1**. (a) Side view, highlighting short (< 3.0 Å) N...O contacts as possible N-H...O hydrogen bonding sites. (b) Top view showing the symmetry and size match between cyclen and $\{\text{V}_{12}\}$. (c) View of the 1D organic-inorganic chains in **1** along the crystallographic c -axis. (d) View of the antiparallel 1D supramolecular chains along the crystallographic a -axis, $[\text{Ba}(\text{DMSO})_8]^{2+}$ cations removed for clarity.

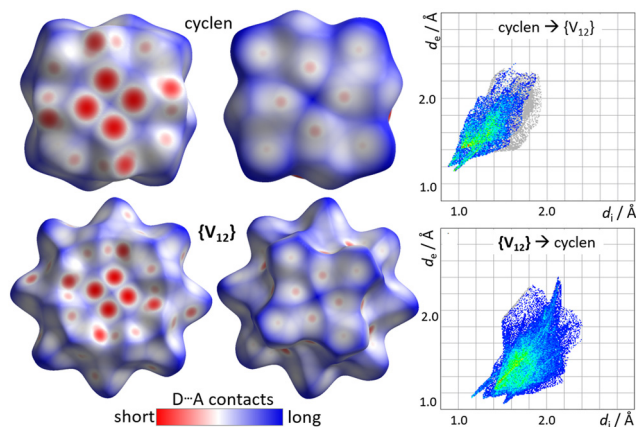


Fig. 3 Hirshfeld surface analysis (surface plot: d_{norm})^{49,50} of intermolecular interactions for cyclen (top) and $\{V_{12}\}$ (bottom), highlighting the strong interactions at the hydrogen bonded interaction sites between both components (left), and the weak interactions at the peripheral interaction sites (centre). Right: Hirshfeld interaction analyses (fingerprint plots) to identify strong and weak intermolecular interactions between cyclen and $\{V_{12}\}$ (based on analysis of d_i vs. d_e , i.e., internal and external atomic distances from the calculated Hirshfeld surface).^{49,50}

or $\{V_{12}\}$. Short intermolecular contacts ($d(\text{N} \cdots \text{O}) < 2.9 \text{ \AA}$) are observed between the cyclen nitrogen donors and oxygen atoms on the “open” face of $\{V_{12}\}$ (Fig. 2). In contrast, significantly longer intermolecular distances are found between the cyclen side facing the “closed” face of a neighbouring $\{V_{12}\}$, with $d(\text{C} \cdots \text{O}) > 3.3 \text{ \AA}$ (Fig. 2a). In the crystal lattice, the cyclen- $\{V_{12}\}$ host-guest systems aggregate into polymeric supramolecular 1D chains along the crystallographic c -axis (Fig. 2c and d). Neighbouring chains are aligned in an antiparallel fashion (Fig. 2c and d). Further insights into the stabilization of these chains were obtained using Hirshfeld surface analysis,^{49,50} which can be used to visualize weak and strong intermolecular interactions between cyclen and $\{V_{12}\}$ (Fig. 3). This analysis indicates that the regiospecific orientation of the cyclen (i.e., all ammonium groups face the “open” face of $\{V_{12}\}$), results in strong N-H \cdots O hydrogen bonds. Note that both cyclen and $\{V_{12}\}$ feature idealized C_4 rotational symmetry, resulting in an ideal structural match between both species. This is reflected in the Hirshfeld surface analysis where C_4 -symmetrical interaction sites are observed.

We hypothesized that selective isolation of **1** with cyclen in one specific protonation state (triprotonated) was possible due to electrostatic matching between the POV anion (charge: 5 $-$), the Ba²⁺ counter-cation (charge: 2 $+$) and the cyclen (charge: 3 $+$). Thus, we proposed that change of the counter-cation under otherwise similar reaction conditions could be used to selectively isolate other protonation states of cyclen in related structures. To this end, the original synthesis was modified to use lanthanum nitrate (La(NO₃)₃·6H₂O). Crystallization of the system gave orange-red single crystals of **2**, which crystallized in the tetragonal space group $P4/n$ with $a = b = 19.6892(16) \text{ \AA}$, $c = 10.9971(13) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 4263.2(8) \text{ \AA}^3$ (for crystallographic details see ESI[†]).§ Structural analysis of **2** gave

the formula [La(DMSO)₈][[C₈H₂₂N₄]V₁₂O₃₂(NO₃)]·DMSO. Structural comparison between **1** and **2** shows that both species are virtually isostructural. In **2**, the negative charge of the organic-inorganic 1D chains is balanced by La³⁺ counter-cations, indicating that the cyclen is present in a diprotonated state. This is substantiated by structural analyses which does not indicate any protonation on the $\{V_{12}\}$ framework. This first proof of principle study therefore suggests that cation charge can be a control parameter to selectively isolate one specific supramolecular cyclen/POM aggregate from solutions containing mixtures of different protonation states.

In summary, we demonstrate a new approach for the design of organic-inorganic 1D chains in the solid state. Specific electrostatic and hydrogen bonding interactions are used to form host-guest complexes between the protonated organic macrocycle cyclen and $\{V_{12}\}$ in solution. Selective crystallization using charge-matching between the organic-inorganic species and a suitable metal cation (here: Ba²⁺ or La³⁺) subsequently enables isolation of the aggregates as 1D polymeric chains with controllable cyclen protonation state. This principle could in future be used for targeted deposition of organic-inorganic nanostructures, e.g. on electrodes or semiconductors for sensing or catalysis.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ **1**: [Ba(DMSO)₈][[C₈H₂₃N₄]V₁₂O₃₂(NO₃)]: tetragonal, space group $P4/n$, $a = b = 19.6114(12) \text{ \AA}$, $c = 11.0115(9) \text{ \AA}$, $V = 4235.1(6) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, $\mu(\text{MoK}\alpha) = 2.101 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.911 \text{ g mm}^{-3}$, 368 824 reflections measured, 4893 unique ($R_{\text{int}} = 0.0555$) which were used in all calculations. Final $R_1 = 0.0249$ ($I > 2s(I)$); $wR_2 = 0.0711$ (all data).

§ **2**: [La(DMSO)₈][[C₈H₂₂N₄]V₁₂O₃₂(NO₃)]·DMSO: tetragonal, space group $P4/n$, $a = b = 19.6892(16) \text{ \AA}$, $c = 10.9971(13) \text{ \AA}$, $V = 4263.2(8) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, $\mu(\text{MoK}\alpha) = 2.122 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.899 \text{ g mm}^{-3}$, 189 090 reflections measured, 4937 unique ($R_{\text{int}} = 0.0942$) which were used in all calculations. Final $R_1 = 0.0374$ ($I > 2s(I)$); $wR_2 = 0.0928$ (all data).

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