

Guest-Directed Supramolecular Architectures of {W₃₆} Polyoxometalate Crowns

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Abstract: The {W₃₆} isopolyoxotungstate cluster provides a stable inorganic molecular platform for the binding of inorganic and organic guest molecules. This is achieved by a binding pocket formed by six terminal oxo ligands located in the central cavity of the all-inorganic cation binding host. Previously it was shown that the cluster can specifically bind primary amines and importantly, functionalized diamines through a combination of electrostatic and hydrogen bonding interactions. Here we transform this assembly strategy to utilize the binding of long-chain alkyl-diammonium guest cations to physical-

ly define the supramolecular structure of the clusters with respect to each other and demonstrate the structure direction as a function of alkyl chain length. The systematic variation of the chain length gives access to five supramolecular assemblies which were all fully characterized using single crystal XRD, TGA, ¹H NMR, and elemental analysis. In compound **1**, diprotonated

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1,8-diaminooctane molecules link the {W₃₆} clusters into infinite 1D zigzag chains, whereas compounds **2** and **3** feature trimeric {W₃₆} assemblies directly connected through protonated 1,9-diaminononane (**2**) or 1,10-diaminododecane (**3**) linkers. Compound **4** contains dumb-bell shaped dimeric units as a result of direct center-to-center linkages between the {W₃₆} clusters formed by protonated 1,12-diaminododecane. In compound **5**, triply protonated bis(hexamethylene)triamine was employed to obtain linear 1D chains of directly connected {W₃₆} cluster units.

Introduction

Polyoxometalates (POMs) are molecular anionic transition metal oxide clusters, typically formed by the early transition metals V, Nb, Ta, Mo, and W in high oxidation states. The flexible but strong transition metal–oxygen bonds give access to a vast range of structures with up to 368 metal centers.^[1] Traditionally, POMs are formed under one-pot synthetic conditions where {MO_x} precursors are linked into polynuclear clusters by self-assembly processes which are highly dependent on precursor equilibria and competing thermodynamic and kinetic processes. Arising from this enormous complexity, predetermined strategies for cluster formation by one-pot self-assembly methods are extremely non-trivial.

However, the vast range of applications, such as catalysis,^[2] magnetism,^[3] biological systems,^[4] and molecular devices,^[5] has led to more sophisticated assembly strategies for the synthesis of POM-based systems. Highly complex molecular materials can now be built from the bottom up using pre-formed thermodynamically stable POM clusters as secondary building units (SBUs) with well-defined connectivity modes.^[6] Using this methodology of supramolecular design, it is possible to develop new structures which incorporate the shape and geometry, as well as the properties, of the pre-designed cluster units.^[7]

In this respect we have recently developed a synthetic technique where secondary building units can be assembled in a controlled manner yielding a family of novel nanosystems. The key principle is the use of bulky organic cations to kinetically stabilize metastable intermediates and prevent further re-arrangement into more thermodynamically favored, well known structure archetypes. Protonated hexamethylenetetramine (HMTAH) was successfully employed to “trap” a mixed valence polyoxomolybdate, [H₂Mo₁₆O₅₂]¹⁰⁻, with unprecedented topology, low symmetry, and high negative charge.^[8] Owing to the high nucleophilic character of this anion, we were able to utilize it as a platform for an-

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choring 3d transition metals to the cluster shell.^[9] A similar approach, which employed protonated triethanolamine (TEAH), provided access to a new molybdenum sulfite cluster system, $[\text{Mo}_{18}\text{O}_{54}(\text{SO}_3)_2]^{6-}$, based on the Dawson-type $\{\text{Mo}_{18}\}$ structure.^[10] The redox-active cluster can be used as a thermochromic device^[10] and it was demonstrated that the unit can be employed as a molecular probe as it shows distinctive electronic responses when it is deposited on various surfaces.^[11] In general, we could demonstrate that the use of bulky organic cations can prevent precursor aggregation into highly symmetrical cluster types, thereby giving access to a fundamentally more diverse set of structures which can subsequently be employed as SBUs with unprecedented topologies.

Furthermore, we have found that the utilisation of bulky organic counterions can be used as a key strategy for the isolation of new cluster types based on polyoxotungstates^[12] and, in particular, to tungsten-based isopolyanions^[13] which are purely based on $\{\text{WO}_x\}$ units and contain no additional heteroatoms. The basic isopolyoxotungstate SBUs present in aqueous solution as a function of pH are well understood^[14] and we were therefore able to establish a combined “2-in-1” strategy where the clusters are formed and subsequently linked in a one-pot reaction. The synthetic conditions are deliberately adjusted so as to form the desired cluster and subsequently, these pre-formed clusters are then linked into larger molecular structures by additional linking units present in the reaction mixture. This approach allowed us to isolate the largest isopolyoxotungstate known to date.^[15] The cluster, $[\text{H}_{12}\text{W}_{36}\text{O}_{120}]^{12-}$ ($=\{\text{W}_{36}\}$) represents a high nuclearity “inorganic crown ether” as it contains a central binding pocket almost identical to the well-known organic analogue 18-Crown-6.^[16] The principal SBUs of the cluster are three $[\text{H}_2\text{W}_{11}\text{O}_{38}]^{8-}$ ψ -metatungstate units ($=\{\text{W}_{11}\}$)^[14,17] which are linked by a set of three connecting $[\text{WO}_6]$ octahedra ($=\{\text{W}_1\}$), allowing the rationalisation of the cluster as $\{\text{W}_{36}\} = \{\text{W}_1\}_3\{\text{W}_{11}\}_3$, see Figure 1.

The $\{\text{W}_{36}\}$ cluster has an idealized C_{3v} -symmetric tungsten oxide shell with a triangular topology and, most interestingly, a central binding pocket created by six terminal oxygens located on the $\{\text{W}_1\}$ and $\{\text{W}_{11}\}$ units. The cluster assembly is driven by the presence of a central templating cation which allows the arrangement of the building blocks into the ring shaped $\{\text{W}_{36}\}$ anion. No guest-free $\{\text{W}_{36}\}$ unit can be obtained in the absence of templating cations, and successful complexation has been achieved for K^+ , Rb^+ , Cs^+ , NH_4^+ , Sr^{2+} , and Ba^{2+} .^[18] This family of $\{\text{W}_{36}\}$ based host–guest systems with purely inorganic cations, has been successfully extended into the organic domain as the rigid arrangement of the six terminal oxygen binding sites creates an ideal environment for both coordinating and hydrogen bonding guests. Previously, four hybrid organic–inorganic host–guest systems have been successfully isolated and characterized and it was shown that by using bifunctional guest molecules, supramolecular frameworks can be obtained.^[19] The use of 1,6-diaminohexane (DAH), for example, gave an infinite hydrogen-bonded system where one of the DAH amine groups

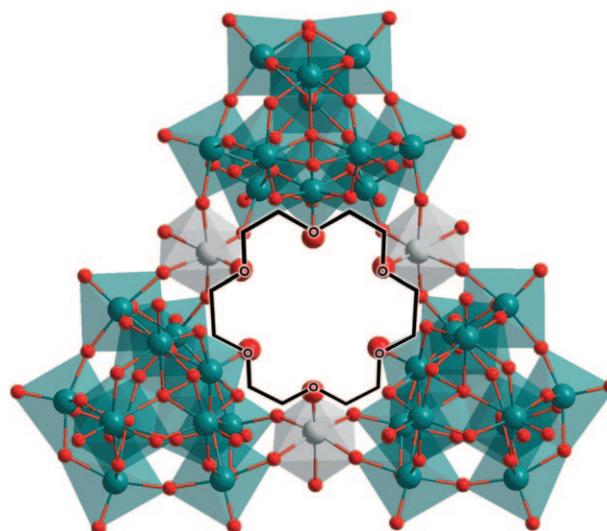


Figure 1. Representation of the $\{\text{W}_{36}\}$ cluster unit highlighting the $\{\text{W}_{11}\}$ (teal polyhedra) and $\{\text{W}_1\}$ (grey polyhedra) building blocks. The six oxygen atoms which make up the central binding cavity have been enlarged for clarity and have been superimposed with the structure of 18-Crown-6 (to scale), highlighting the almost identical coordination environment. Color scheme: O: red spheres, W: teal, and grey spheres.

is bound to the central binding site of a $\{\text{W}_{36}\}$ unit while the second amine protrudes from the cluster shell and docks on to the periphery of an adjacent $\{\text{W}_{36}\}$ cluster through electrostatic and hydrogen bonding interactions. Based on these initial studies we hypothesized that by varying the length and bulk of the organic spacer units between the terminal amine groups, it should in principle be possible to direct the arrangement of the inorganic host $\{\text{W}_{36}\}$ units and thus control the structures and properties of these complex systems.

Herein we report the synthesis of five $\{\text{W}_{36}\}$ -based systems incorporating protonated long-chain organic amines where the supramolecular structural arrangement of the inorganic cluster units is controlled by variation of the alkyl chain length of the guest molecules which are bound in the cavity of the clusters as protonated primary amines. In this way, we were able to isolate dimeric dumb-bell shaped units, triangular superstructures, and infinite 1D chains using 1,8-diaminooctane (**1**), 1,9-diaminononane (**2**), 1,10-diaminododecane (**3**), 1,12-diaminododecane (**4**), and bis(hexamethylene)tri-amine (**5**), thereby revealing a new approach to direct the supramolecular assembly of ‘hard’ nanoscale metal oxides using ‘soft’ long-chain amines.

Results and Discussion

Compounds **1–5** were obtained as crystalline materials and structural analysis using single crystal X-ray diffraction methods showed that all compounds contain the $\{\text{W}_{36}\}$ cluster as principal inorganic SBU, and one key feature is that the clusters presented here are exclusively charge balanced using only organic cations. As previously mentioned, the

$\{W_{36}\}$ cluster is constructed from three $\{W_{11}\}$ subunits linked together by three $\{W_1\}$ bridges with all tungsten centers being fully oxidized in oxidation state +VI. The $\{W_{11}\}$ ψ -metatungstate units^[14,17] consist of a ring of six apical W positions, a W position in the center of this ring, and four basal W positions in a butterfly configuration. Invariably, two protons are present in the central cavity of the $\{W_{11}\}$ unit. The three $\{W_1\}$ subunits between the $\{W_{11}\}$ fragments share four bridging oxo ligands in the equatorial plane and each $\{W_1\}$ fragment also has a single water ligand which points away from the center of the cluster. Each of the six subunits features one terminal oxo ligand which points into the central cavity so that a hexagonal array of six oxygens is created, suitable of binding positively charged guests. Furthermore, although the long-chain amines are disordered to some extent in each of the structures **1–5**, the main cluster units are absolutely well defined and the use of the different cations definitely confirms the supramolecular direction approach using pure organo-cations.

Initial experiments into extending our long-chain diamine approach involved the use of diprotonated 1,8-diaminooctane $C_8H_{16}(NH_3)_2^{2+}$ (=DAO) as a guest in the $\{W_{36}\}$ system. A new crystalline product was obtained with the formula $(TEAH)_9Na_1\{(C_8H_{16}(NH_3)_2)C[H_{12}W_{36}O_{120}]\}\cdot ca. 17H_2O$ (= $(TEAH)_{10}\mathbf{1a}\cdot ca. 17H_2O$). Structural analysis showed that the supramolecular arrangement of the clusters in **1** is topologically identical to the arrangement in a previously reported 1,6-diaminohexane (DAH)-based compound^[19] and gave us indication that the DAO chains are not long enough to force a new structure type, as they can still be accommodated within this supramolecular assembly. In detail, compound **1** features $\{W_{36}\}$ -based 1D zigzag chains in which the DAO guest molecules connect two neighboring clusters through interactions with the central cavity on one cluster and with the peripheral tungsten-oxo shell on a neighboring cluster. One protonated amine of the DAO guest molecule is located in the $\{W_{36}\}$ central binding pocket, with short, hydrogen-bonded $N\cdots O$ distances of ca. 2.7–2.8 Å between the DAO nitrogen and the three terminal oxygen sites on the $\{W_{11}\}$ fragments, and longer $N\cdots O$ distances to the oxygen ligands located on the $\{W_1\}$ linking units of ca. 3.2–3.3 Å. These distances replicate those observed in previous systems^[19] and were observed in all five compounds **1** to **5**. In addition, we also examined the effect of the long-chain organic substituents on the binding mode of the protonated primary amine within the central cavity. This evaluation was achieved by comparison of the displacement of the nitrogen atom of the protonated guest amine to the mean plane formed by the six oxygen atoms of the binding site. This distance was contrasted with the situation in the sterically non-hindered parent compound, $NH_4^+C\{W_{36}\}$, which features a separation of $d_{N-center} = 0.97$ Å.^[18] For the five systems described in this study (**1–5**), the distances ranged from 1.22 to 1.34 Å—values which are consistent with our previous study^[19] and indicate that primary amines introduce only a minor steric hindrance as compared to the non-substituted NH_4^+ -based parent compound.^[18]

As this initial study on long-chain amines showed that longer alkyl-chains are required to introduce a new structure ordering, our second experimental approach used diprotonated 1,9-diaminononane $C_9H_{18}(NH_3)_2^{2+}$ (=DAN) under standard $\{W_{36}\}$ reaction conditions and allowed us to isolate compound **2** as a single crystalline product. Structural analysis of **2** yielded the formula $(TEAH)_{10}\{(C_9H_{18}(NH_3)_2)C[H_{12}W_{36}O_{120}]\}\cdot ca. 30H_2O$ (= $(TEAH)_{10}\mathbf{2a}\cdot ca. 30H_2O$). Intriguingly, the variation of the chain lengths between **1** and **2** by one carbon atom (i.e., changing the effective chain length by less than 2 Å) results in a completely different supramolecular arrangement and yielded a supra-molecular trimeric unit, $[\{W_{36}\}_3(DAN)_3]$. Structural analysis showed that the DAN guest molecules are bound to the $\{W_{36}\}$ central binding pocket with one terminal protonated amine group. The second terminal amino function of the organic guest is available for further supramolecular interactions and ‘docks’ on to the cluster shell of an adjacent $\{W_{36}\}$ unit, giving rise to a characteristic bending of the aliphatic chain (intra-chain angle ca. 103°), see Figure 2. This pendant

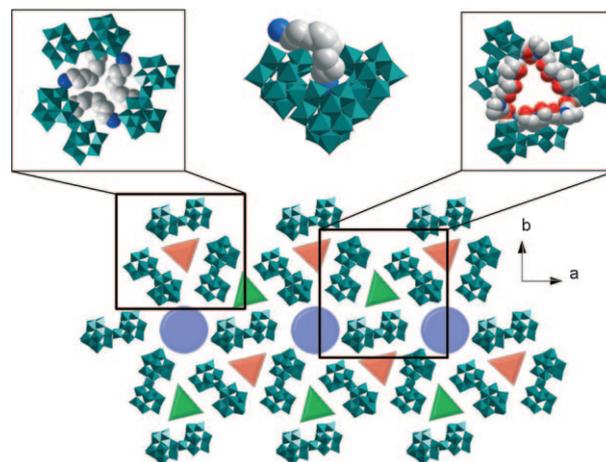


Figure 2. Top: Building units of the supramolecular network. Left: Illustration of the trimeric unit formed by the characteristic bending and hydrogen bonding of the protruding DAN linking unit. Middle: Side view of the cluster anion **2a**, $DAN\{W_{36}\}$. Right: Illustration of the trimeric unit containing the TEAH cations. Bottom: View along the crystallographic c -axis. The triangular features have been highlighted using geometric shapes to represent their arrangement whilst containing either DAN linkers or TEAH cations. C: grey, N: blue, O: red, $\{W_{36}\}$ cluster units: teal polyhedra. Trimers containing DAN linkers contain a pale red triangle, trimers containing TEAH cations contain a green triangle and the pale blue circles represent the large circular voids.

protonated amino group acts as a supramolecular linker between two adjacent $\{W_{36}\}$ units through a set of three hydrogen-bonding interactions. One of the hydrogen-bonded terminal oxo ligands is found on the original $\{W_{36}\}$ unit from which the DAN group is protruding; the remaining two oxygen ligands are located on the neighboring cluster so that, in effect, an idealized equilateral triangular oxygen en-

environment is established, giving $N\cdots O$ hydrogen bonded distances in the range of 2.80 to 2.91 Å. This supramolecular linking pattern is repeated and results in the arrangement of three clusters in a unique triangular hydrogen-bonded superstructure with internal and external dimensions of 1.45 and 2.34 nm, respectively, as illustrated in Figure 2. In addition, this arrangement maximizes the attractive van der Waals interactions between the alkyl chains of the DAN guest molecules in the center of the triangle which facilitate the superstructure formation and result in a hydrophobic central pocket (red triangles in Figure 2).

The arrangement of these triangular structures in the crystal lattice reveals the presence of a second set of triangular features created on the opposite cluster hemisphere which is occupied by TEAH cations and results in the formation of hydrophilic pockets (green triangles in Figure 2). The periodic assembly of the two triangular features in the crystal lattice gives rise to a system of channels, enclosed by six $\{W_{36}\}$ cluster units in a hexagonal fashion (blue circles in Figure 2). The channel itself is almost circular with an inner diameter of ca. 1.98 nm. Interestingly, although the smaller, triangular cavities are dominated by the presence of alkyl chains from coordination of the amine or protonated TEAH cations, the larger channels contain disordered TEAH counterions together with the bulk solvent water. In the lattice these nanoscale channels are aligned along the crystallographic *c*-axis, resulting in the formation of infinite 1D pores. To investigate the accessibility of these pores, we performed an initial thermogravimetric sorption study. The solvent water was removed at elevated temperature and the material was subsequently exposed to ambient atmosphere which allowed the re-adsorption of the lost lattice water molecules. These water uptake/release experiments showed that ca. 3.5 wt. % of lattice water can reversibly be removed from the channels. Subsequent re-adsorption shows that the original material can be re-formed and the sorption cycle was repeated three times.

Following the successful preparation and characterization of compound **2**, we were interested in the possibility of tuning the cavity size by employing guest molecules with longer alkyl chains. Using diprotonated 1,10-diaminododecane $C_{10}H_{20}(NH_3)_2^{2+}$ (=DAD) we were able to isolate compound **3** and single crystal XRD gave the formula $(TEAH)_{10}\{(C_{10}H_{20}(NH_3)_2)C[H_{12}W_{36}O_{120}]\}\cdot ca. 30H_2O$ (= $(TEAH)_{10}\mathbf{3}\cdot ca. 30H_2O$). Investigation of the crystal packing of **3** showed that the clusters are arranged into a series of trimeric units similar to the situation observed for the DAN-based compound **2**, resulting in the formation of 1D channels along the crystallographic *c*-axis. Interestingly, the incorporation of the longer-chain amine DAD in compound **3** did not result in a “breathing” of the framework structure so that the crystallographic dimensions of compounds **2** and **3** are virtually identical. One intriguing detail however illustrates the sterically more strained situation in compound **3**: detailed structural analysis of the host–guest interactions demonstrate that the protonated amine in the central $\{W_{36}\}$ binding pocket is further displaced from the mean binding

plane in compound **2** ($d_{N-center}=1.31$ Å) as compared to the sterically more constrained situation in compound **3** ($d_{N-center}=1.25$ Å). This mechanism compensates for the higher steric bulk in **3** by pushing the amino group further into the central binding pocket. As a result of this compensation mechanism, the circular voids in **3** have exactly the same diameter (1.98 nm) as compared to the voids in compound **2**. These observations strongly suggest that the self-assembly of these hybrid systems is directed by the ‘soft’ organic cations but the final lattice packing and intermolecular spacings are a result of the ‘hard’ inorganic cluster building blocks.

Analysis of the steric bulk in **2** and **3** indicated that the system will not be able to accommodate any longer chain amines within the hydrophobic trimer pocket and further extension of the alkyl chain lengths will invariably lead to a different supramolecular arrangement. Using diprotonated 1,12-diaminododecane $C_{12}H_{24}(NH_3)_2^{2+}$ (=DADD) as a supramolecular guest in the $\{W_{36}\}$ reaction system gave compound **4** as a crystalline product. The formula was established by single crystal XRD and gave $(TEAH)_{11}\{(C_{12}H_{24}(NH_3)_2)_{0.5}C[H_{12}W_{36}O_{120}]\}\cdot ca. 25H_2O$ (= $(TEAH)_{11}\mathbf{4}\cdot ca. 25H_2O$). Compound **4** represents an unprecedented nanoscale dimer with a maximum dimension of 3.4 nm where two $\{W_{36}\}$ clusters are directly linked through a protonated diamine. The organic guest molecule DADD interacts with the central binding cavities of both $\{W_{36}\}$ clusters through electrostatic and hydrogen bonding interactions, showing identical binding modes on both sides, see Figure 3. The

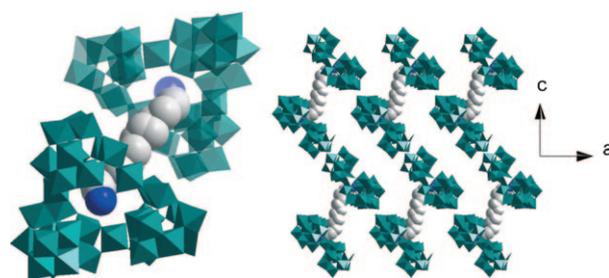


Figure 3. Left: Illustration of the dimeric dumb-bell unit in **4** formed from two $\{W_{36}\}$ cluster units and a single DADD linker. Right: View along the crystallographic *b*-axis highlighting the hydrogen-bonded coplanar arrangement of neighboring dumb-bells, resulting in a zigzag-type arrangement of the dimers. $\{W_{36}\}$: teal polyhedra, C: grey, N: blue.

dimer units, which consist of two $\{W_{36}\}$ cluster units and one linking DADD molecule, can be thought of as ‘distorted dumb-bells’ as the protruding alkyl chain extends from the central cavity at an angle of ca. 125° to the mean plane of the $\{W_{36}\}$ cluster. In this way, the opposite ends of the dumb-bells are not directly aligned; instead there is a noticeable displacement, which has a considerable effect on the crystal packing of the system.

In the crystal lattice, the dimeric dumb-bell units are stacked efficiently, in a series of zigzag chains so as to maximize inter-cluster hydrogen bonding and consequently, short

O–H...O distances of 2.96–3.12 Å are observed. As a result, the $\{W_{36}\}$ units of two adjacent dumb-bells are aligned along the mean plane of the clusters, see Figure 3.

In our next study, we set out to expand the linker chain length to see whether it is possible to construct even larger dimeric dumb-bell type structures. However, to overcome solubility issues arising from the highly non-polar nature of the alkyl chains, we opted for a secondary amine as an additional chain link and to increase solubility of the guest in aqueous solution. Triprotonated bis(hexamethylene)triamine ($C_6H_{12}NH_3)_2NH_2^{3+}$ (BIS) was added to the $\{W_{36}\}$ reaction mixture under the standard $\{W_{36}\}$ reaction conditions and resulted in the isolation of compound **5**. Single crystal XRD gave the formula $(TEAH)_8\{(C_6H_{12}NH_3)_2(NH_2)C[H_{12}W_{36}O_{120}]\cdot ca. 30H_2O (= (TEAH)_9\mathbf{5} \cdot ca. 30H_2O)$. Structurally, compound **4** is related to the dimeric assemblies in compound **3** in as far as the BIS guest links two adjacent clusters. However, the clusters are not arranged in discrete dimeric units but the BIS guest amine adopts a different binding mode which results in the formation of infinite 1D chains: one terminal protonated amine of the BIS ligand binds to the central binding site of a $\{W_{36}\}$ cluster in the standard mode observed before. However, the other terminal amine forms hydrogen bonds to the “back” of a second cluster (i.e., the side where no amine protrudes from). The second $\{W_{36}\}$ unit also contains a BIS ligand which binds in an identical fashion so that, as a result, this pattern is repeated infinitely and yields 1D chains, see Figure 4. Detailed analysis of the hydrogen-bonding motifs

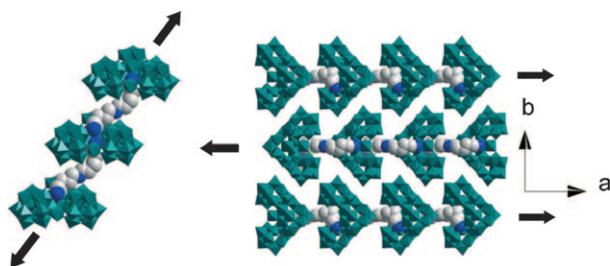


Figure 4. Left: Illustration of a section of the infinite chain with three $\{W_{36}\}$ cluster units and two BIS linkers. Right: View along the crystallographic c -axis of **5**, displaying the efficiently stacked linear chains. $\{W_{36}\}$ cluster units: teal polyhedra, C: grey, N: blue. Arrows are used to indicate the directions of the infinite chains.

show that the protruding terminal ammonium group links to the periphery on the “back” of a $\{W_{36}\}$ unit through two distinctive hydrogen bonds to oxo-ligands located on the $\{W_{11}\}$ subunit with N...O distances of 2.87 and 2.90 Å, respectively. Further stabilization of this structural arrangement is provided by the central secondary amine which also binds to the “back” side of a cluster. In essence this provides a secondary anchoring point which stabilizes the linear arrangement of the cluster with N...O spacings of 2.90 and 3.05 Å,

respectively. In the crystal lattice of **4**, the infinite chains are packed together in a co-linear, anti-parallel fashion so that the apices of the $\{W_{36}\}$ units in neighboring chains point in opposite directions (see Figure 4). In the third dimension, the chains stack above and below each other so that an infinite array of identical layers are created.

Conclusions

In conclusion, we have presented five novel structures where organic bifunctional guest molecules were bound to $\{W_{36}\}$ polyoxotungstate host compounds. The systematic variation of the alkyl chain length of the guest molecules can be used as a highly effective structure directing tool to affect the supramolecular arrangement of the $\{W_{36}\}$ clusters and resulted in the assembly of five novel supramolecular assemblies, and this has not been achieved before. The study further examined the critical chain lengths, which can be incorporated in a given architecture, and examined the effects of longer chains within a certain framework structure. In detail, we demonstrated that the incorporation of 1,6-diaminohexane (DAH)^[19] and 1,8-diaminooctane (DAO) yields topologically identical infinite framework architectures where pendant amino chains connect adjacent $\{W_{36}\}$ clusters by binding to the central cavity and to the cluster periphery of neighboring $\{W_{36}\}$ units (**1**). Increasing the chain length by using 1,9-diaminononane (DAN) and 1,10-diaminododecane (DAD) results in the formation of supramolecular trimeric systems (**2** and **3**) which give rise to 1D-channel architectures with accessible pores in the mesoporous range. The use of 1,12-diaminododecane (DADD) led to the discovery of nano-sized hybrid dimers (**4**) where the amine is able to bind to the central pocket of two clusters. This binding motif was extended into co-linear chains using bis(hexamethylene)triamine (BIS) where the introduction of a central amino function introduced an additional site for hydrogen bonding (**5**). In essence, we have shown how subtle changes in the organic guest structure can be efficiently used to create a versatile range of $\{W_{36}\}$ -based supramolecular systems ranging from dimers to trimers and porous structures, see Figure 5.

Experimental Section

Compound **1** ($(TEAH)_9Na\{(C_8H_{16}(NH_3)_2)C[H_{12}W_{36}O_{120}]\cdot ca. 17H_2O\}$; $Na_2WO_4 \cdot 2H_2O$ (2.0 g, 6.1 mmol) and triethanolamine hydrochloride (TEAHCl) (2.50 g, 13.5 mmol) were dissolved in 50 mL DI water at ca. 40 °C. The pH was adjusted to 2.5 with ca. 2 mL HCl (4M) and the solution was further heated to ca. 70 °C. 1,8-diaminooctane (33 mg, 0.23 mmol) dissolved in a warmed solution of DI water (10 mL) with a few drops 4M HCl, was added to the stirred hot solution and the pH was adjusted to 2.2. This mixture was left stirring for 2 h allowing it to cool to room temperature and was then centrifuged. The clear colorless liquor was stored in a plastic vial and after ca. 2 weeks, large colorless crystalline rods were isolated using filtration, washed with cold water, and dried in vacuum. Yield: 0.806 g (78 μmol, 46.3% based on W); IR (KBr): $\tilde{\nu}$ = 3398 (br), 2925 (w), 1910 (w), 1611 (s), 1469 (s), 1385 (s), 1315 (w), 1255 (w), 1202 (vs), 1097 (vs), 1063 (w), 1031 (w), 1004 (w), 950 (s), 893 (w),

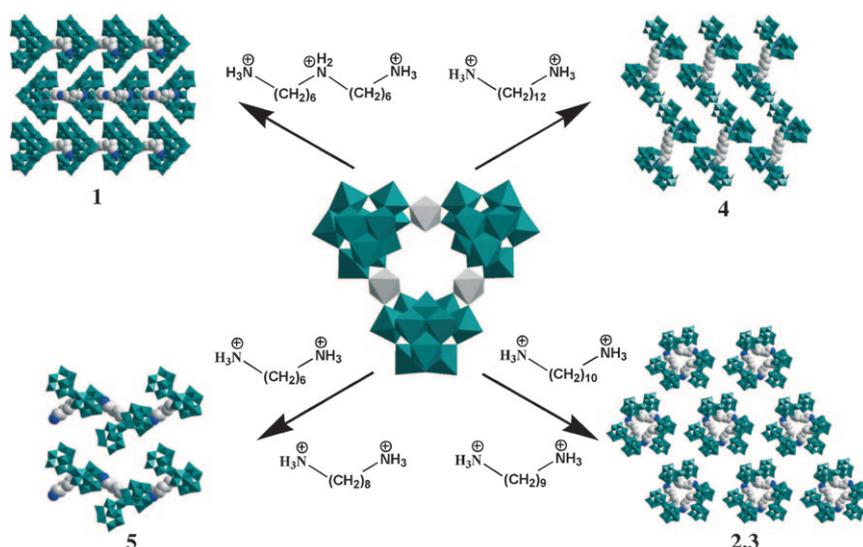


Figure 5. Summary of the four supramolecular systems engineered from the $\{W_{36}\}$ cluster and aliphatic diamines. Center: Representation of the cluster highlighting the building blocks—the $\{W_1\}$ linkers are shown in grey. Top left: Incorporation of BIS. Top right: Dimeric units formed using DADD. Bottom left: Tilted arranged formed as a result of including DAO or DAH. Bottom right: Utilisation of DAN or DAD, giving a spectacular array of large circular voids. W: teal polyhedra, C: grey spheres, N: blue spheres.

776 cm^{-1} (s); $^1\text{H NMR}$ (400 MHz, D_2O): $\delta = 3.57$ (t, 48H), 2.88 (t, 4H), 2.62 (t, 48H), 1.33 (m, 4H), 1.19 ppm (b, 8H); Elemental analysis, (dried material) in wt. % for $\text{C}_{62}\text{H}_{178}\text{N}_{11}\text{NaO}_{147}\text{W}_{36}$ (calculated values in brackets): C 7.37 (7.39), H 1.70 (1.78), N 1.51 (1.53) W 67.5 (65.71), Na 0.54 (0.23).

Compound **2** ((TEAH) $_{10}$ ((C $_9$ H $_{18}$ (NH $_3$) $_2$)C[H $_{12}$ W $_{36}$ O $_{120}$]])·ca. 30 H $_2$ O): Na $_2$ WO $_4$ ·2H $_2$ O (2.0 g, 6.1 mmol) and triethanolamine hydrochloride (TEAHCl) (2.50 g, 13.5 mmol) were dissolved in 50 mL DI water at ca. 40 °C. The pH was adjusted to 2.5 with ca. 2 mL HCl (4M) and the solution was heated to ca. 60 °C. 1,9-diaminononane (30 mg, 0.19 mmol) was dissolved in DI water (10 mL, 40 °C) with a few drops 4M HCl and was added to the stirred hot tungstate solution; the pH was adjusted to 2.15. This mixture was left stirring for 3 h allowing it to cool to room temperature and was then centrifuged. The clear colorless liquor was stored in a plastic vial and after ca. 3 days, large colorless crystalline needles were isolated using filtration, washed with cold water, and dried in vacuum. Yield: 0.445 g (41 μmol , 24.4% based on W); IR (KBr): $\tilde{\nu} = 3417$ (br), 2924 (w), 1941 (w), 1613 (s), 1469 (w), 1385 (vs), 1316 (w), 1255 (w), 1202 (s), 1096 (vs), 1063 (w), 1031 (w), 1005 (w), 956 (vs), 893 (w), 778 cm^{-1} (s); $^1\text{H NMR}$ (400 MHz, D_2O): $\delta = 3.59$ (t, 42H), 2.84 (t, 4H), 2.63 (t, 42H), 1.52 (m, 4H), 1.23 ppm (b, 10H); Elemental analysis, (dried material) in wt. % for $\text{C}_{69}\text{H}_{226}\text{N}_{12}\text{O}_{150}\text{W}_{36}$ (calculated values in brackets): C 8.44 (8.11), H 1.98 (1.93), N 1.83 (1.65), W 62.4 (64.81).

Compound **3** ((TEAH) $_{10}$ ((C $_{10}$ H $_{20}$ (NH $_3$) $_2$)C[H $_{12}$ W $_{36}$ O $_{120}$]])·ca. 30 H $_2$ O): Na $_2$ WO $_4$ ·2H $_2$ O (2.0 g, 6.1 mmol) and triethanolamine hydrochloride (TEAHCl) (2.50 g, 13.5 mmol) were dissolved in 50 mL DI water at ca. 40 °C. The pH was adjusted to 2.5 using ca. 2 mL HCl (4M) and the solution was heated to ca. 75 °C. 1,10-diaminodecane (34 mg, 0.20 mmol), dissolved in 10 mL water (40 °C) with a few drops 4M HCl, was added to the stirred hot solution and the pH was adjusted to 2.1. This mixture was left stirring for 2 h allowing it to cool to room temperature and was then centrifuged. The clear colorless liquor was stored in a plastic vial and after ca. 6 days, very large, colorless, crystalline rods were isolated using filtration, washed with cold water, and dried in vacuum. Yield: 0.537 g (50 μmol , 29.7% based on W); IR (KBr): $\tilde{\nu} = 3442$ (br), 2925 (w), 1958 (w), 1631 (s), 1464 (w), 1385 (w), 1311 (w), 1249 (w), 1199 (w), 1098 (s), 1065 (w), 1032 (w), 1004 (w), 949 (w), 894 (w), 775 cm^{-1} (s); $^1\text{H NMR}$

(400 MHz, D_2O): $\delta = 3.58$ (t, 42H), 2.71 (t, 4H), 2.63 (t, 42H), 1.47 ppm (m, 4H), 1.21 (b, 12H); Elemental analysis, (dried material) in wt. % for $\text{C}_{70}\text{H}_{198}\text{N}_{12}\text{O}_{150}\text{W}_{36}$ (calculated values in brackets): C 8.51 (8.22), H 1.89 (1.95), N 1.69 (1.64); Tungsten analysis: W 63.5% (64.71%).

Compound **4** ((TEAH) $_{11}$ ((C $_{12}$ H $_{24}$ (NH $_3$) $_2$) $_{0.5}$ [H $_{12}$ W $_{36}$ O $_{120}$]])·ca. 25 H $_2$ O): Na $_2$ WO $_4$ ·2H $_2$ O (2.0 g, 6.1 mmol) and triethanolamine hydrochloride (TEAHCl) (2.50 g, 13.5 mmol) were dissolved in 50 mL DI water (ca. 40 °C). The pH was adjusted to 2.5 with ca. 2 mL HCl (4M) and the solution was heated to ca. 60 °C. 1,12-diaminododecane (19 mg, 0.10 mmol), dissolved in a warm DI water (10 mL) with a few drops of 4M HCl, was added to the stirred hot solution and the pH was adjusted to 2.2. This mixture was left stirring for 3 hrs, allowing it to cool to room temperature and was then centrifuged. The clear colorless liquor was stored in a plastic vial and after ca. 10 days colorless crystalline blocks were isolated using filtration, washed with cold water, and dried in vacuum. Yield: 0.475 g (44 μmol , 26.1% based on W); IR

(KBr): $\tilde{\nu} = 3426$ (br), 2923 (w), 1910 (w), 1610 (s), 1469 (s), 1385 (s), 1316 (w), 1255 (w), 1201 (s), 1097 (vs), 1063 (w), 1031 (w), 1004 (w), 949 (vs), 893 (s), 776 cm^{-1} (s); $^1\text{H NMR}$ (400 MHz, D_2O): $\delta = 3.58$ (t, 60H), 2.63 (t, 60H), 2.48 (t, 4H), 1.31 (m, 4H), 1.17 ppm (b, 16H); Elemental analysis, (dried material) in wt. % for $\text{C}_{78}\text{H}_{203}\text{N}_{12}\text{O}_{153}\text{W}_{36}$ (calculated values in brackets): C 9.08 (9.03), H 2.00 (1.91), N 1.76 (1.62), W 63.2 (63.79).

Compound **5** ((TEAH) $_8$ Na((C $_6$ H $_{12}$) $_2$ NH $_2$ (NH $_3$) $_2$)C[H $_{12}$ W $_{36}$ O $_{120}$]])·ca. 30 H $_2$ O): Na $_2$ WO $_4$ ·2H $_2$ O (10.0 g, 30.3 mmol) and triethanolamine hydrochloride (TEAHCl) (12.50 g, 67.3 mmol) was dissolved in 250 mL DI water (ca. 40 °C). The pH was adjusted to 2.2 with HCl (4M) and the solution was heated to ca. 60 °C. Bis(hexamethylene)triamine (0.195 g, 0.91 mmol), dissolved in hot water (50 mL) with a few drops 4M HCl, was added to the stirred tungstate solution and immediately, a white precipitate began to form. The pH was immediately re-adjusted to 2.2 and the mixture was left stirring for 2 h allowing it to cool to room temperature. After centrifugation, the clear colorless liquor was stored in plastic containers and after ca. 1 week, small colorless crystals were isolated using filtration, washed with cold water, and dried in vacuum. Yield: 1.741 g (165 μmol , 19.6% based on W); IR (KBr): $\tilde{\nu} = 3353$ (br), 2101 (w), 1906 (w), 1613 (s), 1512 (w), 1448 (s), 1385 (s), 1321 (w), 1256 (s), 1204 (s), 1094 (vs), 1005 (s), 1032 (s), 1004 (s), 949 (vs), 894 (s), 777 cm^{-1} (s); $^1\text{H NMR}$ (400 MHz, D_2O): $\delta = 3.59$ (t, 54H), 2.80 (m, 8H), 2.63 (t, 54H), 1.52 (m, 8H), 1.29 ppm (b, 8H); Elemental analysis, (dried material) in wt. % for $\text{C}_{60}\text{H}_{196}\text{N}_{11}\text{NaO}_{144}\text{W}_{36}$ (calculated values in brackets): C 7.59 (7.21), H 1.72 (1.73), N 1.61 (1.54), W 65.7 (66.23), Na 0.61 (0.23).

The crystallographic data for compounds **1–5** are presented in Table 1. For compounds **1**, **2**, and **4**, data was collected on an Oxford Diffraction Gemini CCD diffractometer and for compounds **3** and **5**, a Bruker Apex II CCD diffractometer. SHELXS-97 was used for structure solution and SHELXL-97 was used for least-squares refinement on F^2 .

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Table 1. Crystallographic data for compounds 1–5.

	1	2	3	4	5
formula	C ₆₂ H ₂₁₂ N ₁₁ NaO ₁₆₄ W ₃₆	C ₆₀ H ₂₅₆ N ₁₂ O ₁₈₀ W ₃₆	C ₇₀ H ₂₅₈ N ₁₂ O ₁₈₀ W ₃₆	C ₇₈ H ₂₅₃ N ₁₂ O ₁₇₈ W ₃₆	C ₆₀ H ₂₃₂ N ₁₁ NaO ₁₇₄ W ₃₆
<i>M_r</i> [g mol ⁻¹]	10378.02	10753.46	10767.48	10754.46	10534.16
crystal system	orthorhombic	hexagonal	hexagonal	triclinic	monoclinic
space group	<i>Pnma</i>	<i>P6₃/m</i>	<i>P6₃/m</i>	<i>P-1</i>	<i>P2₁/n</i>
<i>a</i> [Å]	27.0695(4)	33.8750(4)	34.1030(23)	20.0052(3)	15.5310(3)
<i>b</i> [Å]	35.2582(4)	33.8750(4)	34.1030(23)	20.7517(4)	34.9895(7)
<i>c</i> [Å]	21.3092(3)	35.2371(4)	35.1157(47)	31.4394(7)	40.4871(9)
<i>α</i> [°]	90	90	90	97.816(2)	90
<i>β</i> [°]	90	90	90	98.587(2)	96.966(1)
<i>γ</i> [°]	90	120	120	113.137(2)	90
<i>ρ</i> _{calcd} [g cm ⁻³]	3.389	3.060	3.033	3.076	3.204
<i>V</i> [Å ³]	20338.0(5)	35017.8(7)	35369(6)	11612.25(147)	21839.2(8)
<i>Z</i>	4	6	6	2	4
<i>μ</i> (MoK _α) [mm ⁻¹]	20.378	17.762	17.586	17.854	18.983
<i>T</i> [K]	150(2)	150(2)	100(2)	150(2)	100(2)
no. rflns (measd)	78463	86245	132784	151342	142672
no. rflns (unique)	20222	21840	20685	43052	34474
no. params	1050	1020	982	1587	1838
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0408	0.0471	0.0474	0.0739	0.0528
<i>wR</i> 2 (all data)	0.0908	0.1012	0.1304	0.2078	0.1407

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