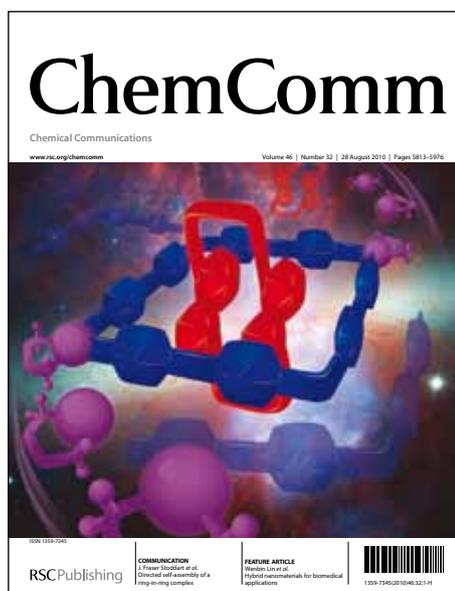


# ChemComm

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shared basal edge. The peripheral pyramids provide ligand-accessible coordination sites for four phosphonate or -arsonate functionalities that adopt O,O'-*syn,syn*-bidentate bridging modes. The convex nature of the subunit allows the formation of capsular entities when rigid bifunctional organophosphonate ligands are employed in the reaction system.<sup>5a,d</sup> The stability of the {V<sub>5</sub>O<sub>9</sub>} unit in aqueous systems not only allows the incorporation of conventional benzene-, biphenyl- or naphthyl-bisphosphonates, but it also permits the incorporation of significantly elongated ligands such as bis(4-phosphonophenyl)ethyne (H<sub>4</sub>L<sup>1</sup>) and 1,1'-bis(4-phosphonophenyl)butadiyne (H<sub>4</sub>L<sup>2</sup>), to form [V<sub>10</sub>O<sub>18</sub>L<sub>4</sub>]<sup>10-</sup> (**1**) and [V<sub>10</sub>O<sub>18</sub>L<sub>2</sub>]<sup>10-</sup> (**2**), which crystallise phase-pure and in good yields from corresponding reaction systems. The two acetylene-based organophosphonate ligands were synthesised through a one-pot double Sonogashira coupling reaction (H<sub>4</sub>L<sup>1</sup>) and a combination of Sonogashira and Eglinton coupling reactions (H<sub>4</sub>L<sup>2</sup>) involving diethyl-4-bromophenylphosphonate and ethynyltrimethylsilane.<sup>10</sup> **1** and **2** form in aqueous solution upon partial reduction of NaVO<sub>3</sub> in the presence of the organophosphonates and N<sub>2</sub>H<sub>4</sub>. Despite small crystal sizes and weak diffraction patterns the single crystal X-ray diffraction analysis provided a good structural understanding of the compounds to give the constitutional assignments of H<sub>6</sub>Na<sub>6</sub>[(N<sub>3</sub>)<sub>2</sub>⊃**1**]·42H<sub>2</sub>O and H<sub>6</sub>Na<sub>6</sub>[(N<sub>3</sub>)<sub>2</sub>⊃**2**]·40H<sub>2</sub>O.

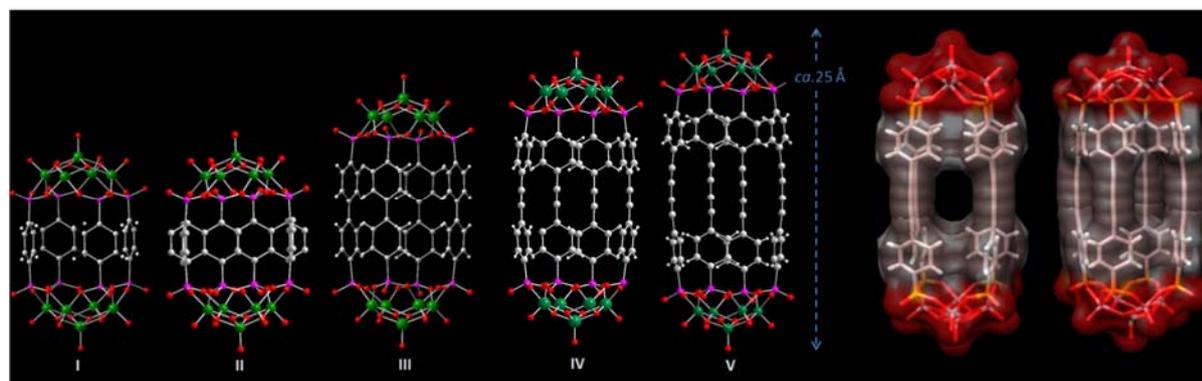
The compounds crystallise in the tetragonal space group *P4/mnc* and their asymmetric units contain 1/4 of the capsular entities with the remainder generated through symmetry operations. The lengths of the capsular entities **1** and **2** as defined by the O...O distance of the terminal oxo ligands residing in the apical positions are 22.371(2) Å and 24.836(9) Å for **1** and **2**, respectively. Their inner cavities are characterised by square cuboid arrangements of the 8 P atoms with edge dimensions of 13.202(2) x 5.568(1) Å<sup>2</sup> and 15.776(6) x 5.544(1) Å<sup>2</sup>. For both cages, the acetylene moieties bend significantly outwards whereby the average inter-plane distances between parallel aligned, opposite located phenyl rings are *ca.* 8.5. At their widest part both capsular entities have a radial diameter of *ca.* 8.8 Å. In contrast to the smaller homologues, the incorporation of acetylene moieties now gives rise to openings at the organic side-walls of the capsules (Fig. 2). The openings in **2** have dimensions of 6.7 x 6.1 Å<sup>2</sup> thus demonstrating that it is feasible to design entities that selectively incorporate or release small guests. In their pristine form, **1** and **2** encapsulate two stabilising azide ions that may act as templates during the formation of the convex

capping units (closest V-N distances 3.02 and 3.06 Å for **1** and **2**, respectively).<sup>5b,8</sup> The capsules assemble in the crystal structures to give dense lamellar packing motifs in which hydrophilic inorganic and hydrophobic organic areas are segregated. Partially hydrated sodium counterions bind to the terminal and bridging oxo ligands of the {V<sub>5</sub>O<sub>9</sub>} units and to O-donors of the stabilising phosphonate ligands. These counterions connect the hydrophilic, inorganic ends of the molecular entities within the (001) plane; organophosphonate ligands pillar between these planes.

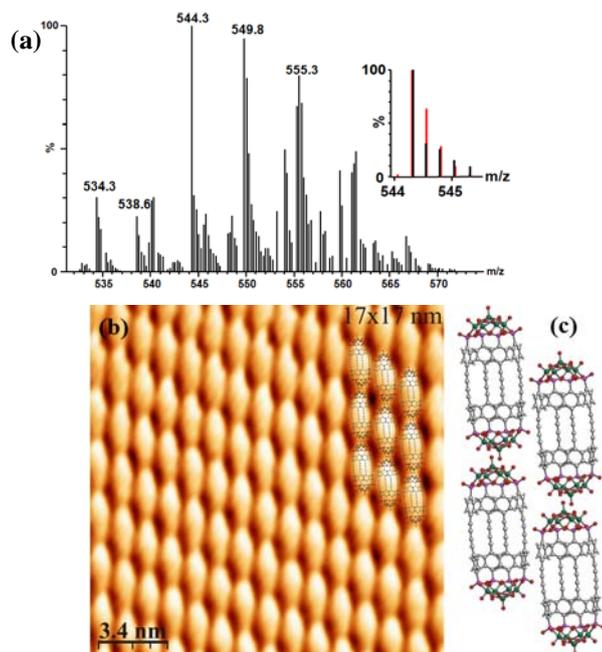
The results demonstrate that the capsular entities can systematically be extended (Fig. 2) and it appears plausible that even longer homologues of the rigid organophosphonate ligands can be incorporated. Limitations may arise from the poor solubility of extended ligands in the polar reaction mixtures that are required to prepare the {V<sub>5</sub>O<sub>9</sub>} building unit.

The stability of the capsular entities **1** and **2** in H<sub>2</sub>O was demonstrated by electrospray ionisation mass spectrometry (ESI-MS, Fig. 3). A set of -4 charged species corresponding to the decavanadate cages **1** and **2** could be identified in the *m/z* = 500-600 region of the spectra. For **1**, the signal observed at *m/z* = 544.3 corresponds to a Na<sub>2</sub>H<sub>2</sub>[V<sub>4</sub><sup>IV</sup>V<sub>6</sub><sup>IV</sup>O<sub>18</sub>(O<sub>3</sub>PC<sub>14</sub>H<sub>8</sub>PO<sub>3</sub>)<sub>4</sub>]<sup>4-</sup> species. Additional signals at *m/z* = 534.3, 538.6, 549.8 and 555.3 can be assigned to H<sub>8</sub>[V<sub>10</sub><sup>IV</sup>O<sub>18</sub>(O<sub>3</sub>PC<sub>14</sub>H<sub>8</sub>PO<sub>3</sub>)<sub>4</sub>]<sup>4-</sup>, NaH<sub>2</sub>[V<sub>5</sub><sup>IV</sup>V<sub>5<sup>IV</sup>O<sub>18</sub>(O<sub>3</sub>PC<sub>14</sub>H<sub>8</sub>PO<sub>3</sub>)<sub>4</sub>]<sup>4-</sup>, Na<sub>3</sub>H[V<sub>4</sub><sup>IV</sup>V<sub>6<sup>IV</sup>O<sub>18</sub>(O<sub>3</sub>PC<sub>14</sub>H<sub>8</sub>PO<sub>3</sub>)<sub>4</sub>]<sup>4-</sup> and Na<sub>4</sub>[V<sub>4</sub><sup>IV</sup>V<sub>6<sup>IV</sup>O<sub>18</sub>(O<sub>3</sub>PC<sub>14</sub>H<sub>8</sub>PO<sub>3</sub>)<sub>4</sub>]<sup>4-</sup> species, respectively. Similarly, in the mass spectrum of **2** (Fig. 3), the signal at *m/z* = 573.6 originates from Na<sub>3</sub>[V<sub>5</sub><sup>IV</sup>V<sub>5<sup>IV</sup>O<sub>18</sub>(O<sub>3</sub>PC<sub>16</sub>H<sub>8</sub>PO<sub>3</sub>)<sub>4</sub>]<sup>4-</sup> species. Additional signals, comparable to those reported for **1**, were also observed and assigned. The experimental and modelled isotopic distributions of these anionic species are shown in Figs. 3 and S3-6(ESI). The UV-vis spectra of both, H<sub>6</sub>Na<sub>6</sub>[(N<sub>3</sub>)<sub>2</sub>⊃**1**]·42H<sub>2</sub>O and H<sub>6</sub>Na<sub>6</sub>[(N<sub>3</sub>)<sub>2</sub>⊃**2**]·40H<sub>2</sub>O dissolved in H<sub>2</sub>O give rise to characteristic bands at 621 nm with ε = 518.3 L·mol<sup>-1</sup>·cm<sup>-1</sup> and ε = 741.9 L·mol<sup>-1</sup>·cm<sup>-1</sup>, respectively.</sub></sub></sub></sub>

The solution stability of the capsular entities in polar reaction systems can be exploited for their deposition on surfaces. For this purpose an aqueous 7.8x10<sup>-6</sup> M solution of H<sub>6</sub>Na<sub>6</sub>[(N<sub>3</sub>)<sub>2</sub>⊃**2**]·40H<sub>2</sub>O was deposited by spin-coating at room temperature onto the Au(111) surface, which has been cleaned according to a standard literature procedure in vacuum prior to the deposition.<sup>11</sup> STM reveals that the molecules of **2** self-assemble on the Au(111) surface forming well-ordered molecular domains with a characteristic close-packed oblique structure.



**Fig. 2** (a) Size comparison of [V<sub>10</sub>O<sub>18</sub>L<sub>4</sub>]<sup>10-</sup> complexes containing benzenediphosphonate (I), naphthalene diphosphonate (II), biphenyl diphosphonate (III), L<sup>1</sup> (IV) and L<sup>2</sup> (V) as stabilising ligands. (b) Space filling model for [V<sub>10</sub>O<sub>18</sub>L<sub>2</sub>]<sup>10-</sup> highlighting that the acetylene-based ligands give rise to small openings.



**Fig. 3** (a) ESI mass spectrum of  $H_6Na_6[(N_3)_2O] \cdot 42H_2O$  dissolved in  $H_2O$ . *Inset*: Comparison of experimental isotopic envelopes (black spectrum) with simulated patterns (red spectrum) for  $Na_2H_2[V_4V_6O_{18}(O_3PC_{14}H_8PO_3)_4]^{4-}$  centred at  $m/z = 544.3$ . (b) A constant current STM image of **2** deposited by spin-coating onto the Au(111) surface,  $V_{sample} = 1.4$  V,  $I = 200$  pA. (c) Schematic model of **2** on the Au(111).

Despite the inhomogeneous appearance of the total surface, it is indeed facile to image areas as shown in Fig. 3b where capsular entities typically cover large areas (i.e. 200 nm x 200 nm) and are arranged off-set to each other revealing similarity to the packing of **2** in the crystal structure when viewed in the direction of the crystallographic *a*- or *b*-axes (cf. Fig. S2). The obtained micrographs are in agreement with the presence of strong intermolecular interactions (which involve electrostatic interactions between **2** and counterions, H-bonds and  $\pi$ - $\pi$  interactions of phenyl rings) and a low diffusion barrier on this surface at room temperature, which is characteristic for low reactivity substrates such as Au.<sup>11</sup>

In summary, we demonstrate that the stability of the convex  $\{V_5O_9\}$  unit can be exploited to prepare a homologous series of capsular entities whose dimensions can be controlled by the extent of the organic ligands. Depending on the employed organophosphonate ligand, ‘windows’ in the side wall can be constructed which may facilitate the uptake and release of small guest molecules giving rise to catalytic activities or molecular recognition effects.<sup>2c</sup> These latter aspects are the subject of our current investigations. The capsular entities are stable in solution and adopt dense packing arrangements when deposited on the Au(111) surface.

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## Notes and references

<sup>a</sup> School of Chemistry & CRANN, University of Dublin, Trinity College, Dublin 2, Ireland. Tel: (+) 353-1-896-3495; E-mail: [schmittw@tcd.ie](mailto:schmittw@tcd.ie)

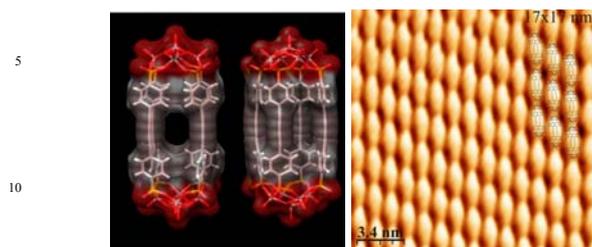
<sup>b</sup> School of Physics & CRANN, University of Dublin, Trinity College, Dublin 2, Ireland.

† Electronic Supplementary Information (ESI) available: Synthetic details; additional Figures, ESI-MS analysis, crystallographic table and data in CIF format; . See DOI: 10.1039/b000000x/

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**Graphical Abstract:**



15 The dimensions and cavities of the hybrid vanadate capsules with  
the general formula  $[V_{10}O_{18}L_4]^{10-}$  can be controlled modularly  
through variation of the employed bifunctional organophosphonate  
ligands (L). The solution-stability allows the deposition of the  
20 hollow molecular entities on the Au(111) surface giving rise to  
densely packed 2D structures that relate to packing arrangements in  
the 3D crystal structure.