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## COMMUNICATION

## Coordination-driven self-assembly of polyoxometalates into discrete supramolecular triangles†

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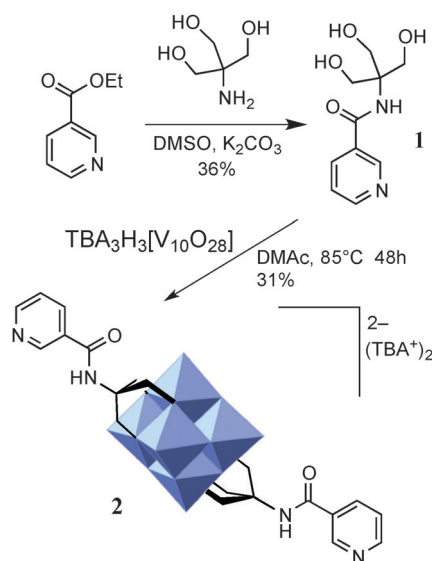
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**Pd(II)-directed self-assembly of a 3-pyridyl grafted Lindqvist hexavanadate led to the formation of a unique trimeric species, as confirmed by a variety of techniques, including pulsed-field gradient NMR spectroscopy and high-resolution ESI mass spectrometry.**

Discrete supramolecular architectures are often constructed with building-blocks presenting specific coordination sites in a pre-designed geometric orientation.<sup>1</sup> Triangles, squares and hexagons are among the “simplest” assemblies obtained through metal ion coordination with building blocks that present a 60°, 90° or 120° angle between coordination sites, respectively.<sup>2</sup> Such building blocks are usually organic molecules with suitable metal-binding domains.<sup>3</sup> The resulting geometrical arrays are of continued interest in the rational design of *functional* nano-architectures, with applications in analytical chemistry and material science.<sup>4,5</sup> The concepts and principles of the self-assembly of these coordination arrays could include inorganic components, such as polyoxometalates (POMs), if they were functionalized with organic ligands. This would allow the integration of additional properties into self-assembled supramolecular structures, and bridge the gap between solid-state oxides, metal–organic frameworks and coordination compounds. For example, POMs are a large class of inorganic compounds exhibiting rich redox, conducting, magnetic, and catalytic properties.<sup>6</sup>

POMs with remote binding sites for metal ion coordination have been reported.<sup>7–9</sup> However, the self-assembly of POM arrays presents an additional advantage that they bring the properties of the coordination complexes (optical, redox) into combination with the properties from the POM, offering potentially *synergistic* effects in such hybrid systems.<sup>10</sup>

We report herein the synthesis of ligand **1** (Scheme 1) used to produce functionalized Lindqvist-type polyoxometalate



**Scheme 1** Synthesis for pyridyl-triol **1** and Lindqvist POM **2**.

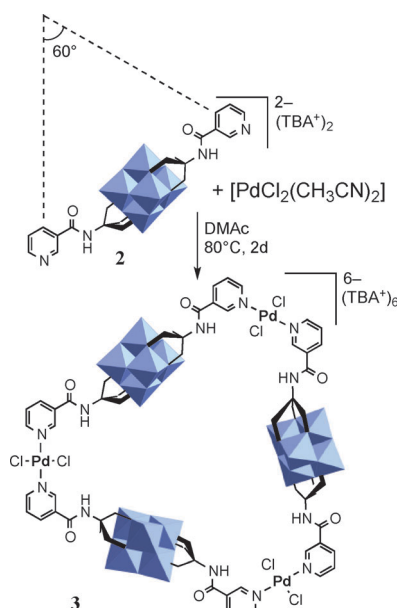
$\text{TBA}_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHC}(\text{O})\text{-}3\text{-C}_5\text{H}_4\text{N}\}_2]$  **2** (Scheme 1,  $\text{TBA}^+ = \text{tetrabutylammonium } \text{C}_{16}\text{H}_{36}\text{N}^+$ ). This new organic–inorganic hybrid constitutes a POM-based molecular building block with a 60° angle between the coordination vectors of the grafted pyridyl groups. It is expected to give, in combination with a 180° unit (*e.g.*, *trans*- $\text{PdCl}_2$ ), a supramolecular triangle **3** (Scheme 2). We report here the assembly of POM **2** directed by  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  into such an architecture.

Ligand **1**, containing a triol moiety for POM grafting and pyridine for transition metal complexation (Scheme 1), was synthesized in two steps.<sup>9</sup> The bifunctional ligand **1** was then reacted with the decavanadate POM by adapting reported condensation procedures,<sup>8,11–13</sup> affording the Lindqvist-type POM  $\text{TBA}_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHC}(\text{O})\text{-}3\text{-C}_5\text{H}_4\text{N}\}_2]$  **2**. The successful incorporation of the triol into the POM framework can be deduced in  $^1\text{H}$  NMR from the deshielding of the methylene protons by 1.7 ppm from the free ligand **1** to the grafted ligand in **2**. IR spectroscopy confirms the inorganic POM structure by the observation of the characteristic metal-oxo vibrational bands between 600 and 1000  $\text{cm}^{-1}$ . The most characteristic signatures for the ligand are the two amide

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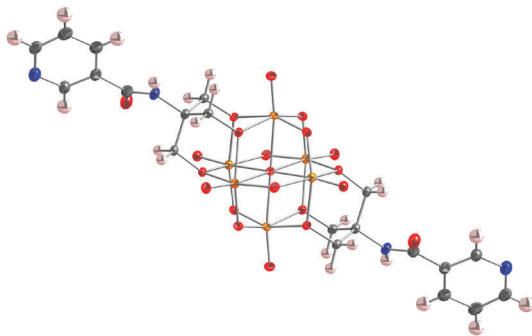


**Scheme 2** Synthesis of triangle **3** from functionalized POM derivative **2** and  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ .

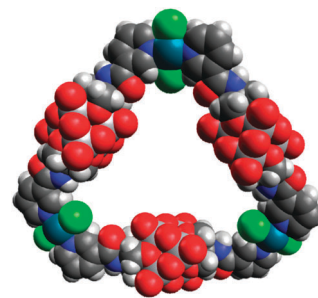
vibrations around  $1670$  and  $1540\text{ cm}^{-1}$  (full data in ESI<sup>†</sup>). High-resolution ESI mass spectrometry further confirms the identity of the compound. The Lindqvist **2** is seen at  $m/z$  959.7438 (simulated 959.7420) and 479.8722 (simulated 479.8713) for the  $\{\text{M}-\text{TBA}\}^-$  and  $\{\text{M}-2\text{TBA}\}^{2-}$  species, respectively. Single crystals of **2** for X-ray diffraction were obtained by diffusion of  $\text{Et}_2\text{O}$  into a DMF solution. For trialkoxo functionalized Lindqvist structures, *cis* and *trans* isomers exist.<sup>12,14</sup> Here, the expected *trans* isomer was confirmed (Fig. 1).

In the crystal of **2**, the anion rests on an inversion centre. The asymmetric unit is constituted of half an anion, one  $\text{TBA}^+$  counter-ion and two co-crystallized DMF molecules. Interatomic distances in the cluster are typical of such Lindqvist structures. The distance between the two pyridyl nitrogens, in *transoid* conformation, is  $20\text{ \AA}$ . Both coordination sites are accessible without steric hindrance from the POM, thus confirming that simple single bond rotation can lead to the desired *Z*-conformation of the pyridine N lone pairs.

The reaction of **2** with  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  in *N,N'*-dimethylacetamide (DMAc, Scheme 2) initially afforded a complicated mixture of species, however, after 48 hours at  $80\text{ }^\circ\text{C}$ , the



**Fig. 1** Crystal structure of **2** (thermal ellipsoids drawn at 50% probability), confirming the *trans* POM substitution. TBA cations and solvent have been omitted for clarity.

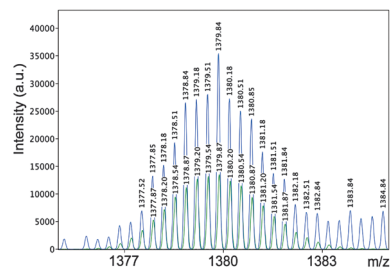


**Fig. 2** CPK model of optimized geometry for **3** (using Avogadro software and UFF parameters). No over-tension of the cycle is visible.

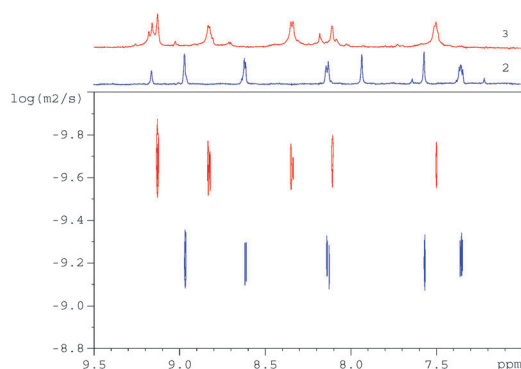
formation of *one* assembly was evident by  $^1\text{H}$  NMR. The product was isolated as a solid by precipitation in ether and trituration with acetone to wash away unreacted starting materials and soluble impurities.  $^1\text{H}$  NMR showed one set of signals for both organic ligands on the POM, *i.e.*, both sides of each POM are in the same environment. Chemical shifts are in agreement with coordination of the pyridyl-nitrogen to the  $\{\text{Pd}^{\text{II}}\text{Cl}_2\}$  motif, as confirmed by comparison with the complex  $[\text{PdCl}_2(\text{N-tert-butylnicotinamide})_2]$  (**5**) obtained from  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  and *N-tert-butylnicotinamide* (**4**) (see ESI<sup>†</sup>).<sup>15</sup>

Elemental analysis revealed the composition that corresponds to one Lindqvist POM **2** and one  $\{\text{PdCl}_2\}$  moiety. The necessary conclusion of the symmetric Pd complexation onto the pyridyl groups as shown by  $^1\text{H}$  NMR and the 1:1 stoichiometry of POM and  $\{\text{PdCl}_2\}$  is the formation of a cyclic oligomer (Fig. 2).

A common technique for the characterization of supramolecular assemblies is electrospray mass spectrometry, which has also proven its potential in POM chemistry.<sup>16</sup> The most intensive signal in HR-ESI-MS (Fig. 3 and full spectrum in Fig. 2 in ESI<sup>†</sup>) corresponds to POM **2** and a much weaker signal to POM- $\text{PdCl}_2$ . These species must form under the conditions for ESI-MS, as NMR proved their absence in solution. The spectrum shows further the molecular triangle  $[(\text{POM})_3(\text{PdCl}_2)_3(\text{TBA})_{6-z}]^z-$  at charge states  $z = 3-$  ( $m/z$  1379.84),  $4-$  ( $m/z$  974.31) and  $5-$  ( $m/z$  730.79). Each of these signals is accompanied by lower  $m/z$  signals of the same charge state (loss of  $m = 105$  is the most common), almost certainly from an exchange of TBA counterions by other cations. More importantly, no signals that would correspond to other oligomers, such as dimers, tetramers, pentamers or higher, are present. We also measured under the same conditions the coordination polymer  $\{\text{TBA}_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHC}(\text{O})-4-\text{C}_5\text{H}_4\text{N}\}_2][\text{PdCl}_2]\}_n$  that we reported earlier.<sup>9</sup> No signals for oligomers with  $n \geq 2$  were found. The trimeric species observed for **3** therefore exists in



**Fig. 3** Experimental (blue, upper trace) and calculated (green, lower trace) HR-ESI-mass spectrum for  $\{[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNHC}(\text{O})-3-\text{C}_5\text{H}_4\text{N}\}_2]_3(\text{PdCl}_2)_3(\text{TBA})_3\}^{3-}$ .



**Fig. 4**  $^1\text{H}$  NMR spectra and DOSY NMR for **2** and **3**, recorded at rt (600 MHz,  $\text{CD}_3\text{CN}:\text{DMAc}$  3:2,  $1 \times 10^{-6}$  M).

solution and is not a fragment of a longer polymer chain. This is strong evidence that the molecular triangle **3** is the only assembly formed.

Pulsed-Field Gradient (PFG) NMR experiments (diffusion ordered spectroscopy, DOSY) are based on the fact that, in a solution of given viscosity, molecules of various sizes will diffuse at different rates.<sup>13,17</sup> They were conducted for **2** and **3** at identical concentration ( $1 \times 10^{-6}$  M) and temperature (rt = 27 °C). The mixture of solvents ( $\text{CD}_3\text{CN}/\text{DMAc}$  3/2) was chosen to solubilize all species while providing the minimum viscosity possible. The diffusion coefficients  $D$  are clearly distinct between **2** and **3** (Fig. 4, standard deviation errors are estimated around 10%):  $D_2 = 6.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for **2** and  $D_3 = 2.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for **3**. This result shows that **3** is unambiguously obtained as a unique species; indeed, a mixture of several oligomeric or polymeric species would display a large distribution of diffusion coefficients. By roughly approximating the geometry to spheres, we could estimate the hydrodynamic radius as being  $r_3 = 2.7 \times r_2$  which makes sense for the postulated trimer.

In conclusion, the analytical data provide unambiguous evidence for the formation of the discrete, trimeric assembly **3**. This demonstrates that the combination of the concepts of metallosupramolecular chemistry with the synthesis of organic–inorganic POM hybrids gives access to predictable architectures. The properties of the new assemblies—such as host–guest chemistry for example—and the extension of the concept to other POMs such as polyoxomolybdates and polyoxotungstates will be reported in due course.

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