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Shrink wrapping redox-active crystals of polyoxometalate open frameworks with organic polymers *via* crystal induced polymerisation†

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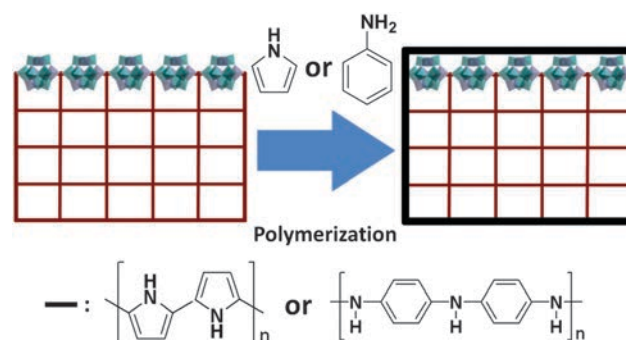
We report examples of crystal surface modification of polyoxometalate open frameworks whereby the use of pyrrole or aniline as monomers leads to the formation of the corresponding polymers *via* an oxidative polymerization process initiated by the redox active POM scaffolds. Guest-exchange experiments demonstrate that the polymers can finely tune the guest exchange rate and their structural integrity is retained after the surface modifications. In addition, the formation of polyoxometalate-based self-fabricating tubes by the dissolution of Keggin-based network crystals were also modulated by the polymers, allowing a new type of hybrid inorganic polymer with an organic coating to be fabricated.

Functionalized polyoxometalate (POM) clusters and their POM-based network derivatives are an important class of materials with many potential applications such as storage, separation, and heterogeneous catalysis due to the vast potential for programming different structures.^{1,2} Specifically, polyoxometalate-based (POM) frameworks have potential as functional materials, due to their intrinsic redox and catalytic activity and modularity arising from the ability to use different cluster building units.^{3,4} Also, in spite of the many positive developments for a general synthetic approach to the design of POM based networks, the fine tuning of their properties by post-functionalization either within the inner walls of the network or at the crystal surface is still lacking. As such, we reasoned that the assembly of porous redox active POMs into extended networks could provide a unique approach for the post-crystallization modification of the framework by using the redox-active properties of the polyoxometalate to drive a polymerization reaction to coat the surface of the polyoxometalate crystal in an organic polymer. This is because this route promises not only to enable the modification of the inside of the open network, but also add entirely new functionalities to the POM-network crystals without changing the

characteristic features of the crystal itself. However for this process to work both a redox active polyoxometalate-based material, and suitable reactivity to monomers be found.⁵

Herein, we demonstrate the crystal surface modifications of a polyoxometalate framework by the redox-driven polymerization of organic monomers, see Scheme 1. One of the major difficulties limiting the potential for the direct outer crystal surface modifications of porous materials is to prevent the unwanted modifications occurring inside the pores, especially if the pores are large so that the monomers can easily diffuse into the pores and react internally with the framework.⁶

Additionally, in the case of polymerisation, it is also necessary to prevent the reaction in the surrounding medium because otherwise the final product would contain a mixture of both 'free' polymer and polymer-decorated crystals. A possible strategy to circumvent this drawback is to promote the local polymerization on the crystal surface.⁷ To overcome these problems, we chose examples from a group of 3D POM networks recently reported by us, that show appropriate redox activity and hence should enable the necessary surface-selective polymerisation chemistry.^{3a-e} The framework is constructed from three- and four-connected Mn or Co-substituted Keggin clusters with Mn(Co)-O-W bonds, giving cubic structures with elliptical pockets



Scheme 1 Scheme showing the surface modification of the POM network crystals (red) with an organic polymer (black), whereby the POM network itself acts as an oxidant for the polymerization reaction.

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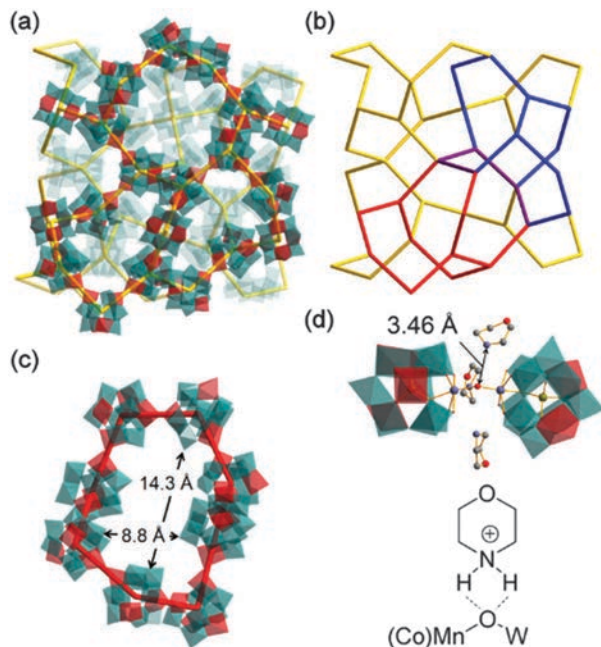


Fig. 1 (a) Framework of $(C_4H_{10}NO)_mH_n[W_{72}M_{12}X_7O_{268}]$ ($M = Co$ or Mn ; $X = Si$ or Ge) constructed from transition metal substituted Keggin clusters. Morpholinium cations and water are omitted. (b) Simplified framework. The units with pockets are coloured red and blue respectively. Shared bonds are purple. (c) Close up of pore aperture structure. (d) Local structure of POM network with morpholinium cations. Colour code: distinct WO_6 , green polyhedral; $Mn(Co)O_6$ or WO_6 units connected next to each other, purple polyhedral; Si, dark yellow; O, red.

of $27.17 \times 15.60 \times 8.46$ Å with an 14.3×8.8 Å aperture in which solvent molecules and morpholinium cations are accommodated (see Fig. 1a–c). Twelve of the morpholinium cations occupy a well-defined position, being hydrogen bonded to the M–O–M bridges, which link the Keggin ions together (Fig. 1d). Structure **1**: $[(C_4H_{10}NO)_{40}(W_{72}Mn_{12}O_{268}Ge_7)]_n$ shows single-crystal to single-crystal (SC–SC) redox transformation where **1** is easily reduced to $[(C_4H_{10}NO)_{40}H_{12}(W_{72}Mn_{12}O_{268}Ge_7)]_n$ (**1'**) by ascorbic acid, whilst the network retains its structural integrity. This result clearly indicates that **1** itself can be utilized as an oxidant promoting the polymerization without any pre-treatment.⁸ In addition, the isostructural compound, $[(C_4H_{10}NO)_{46}H_6(W_{72}Co_{12}O_{268}Ge_7)]_n$ (**2**), in which the manganese ions are replaced by cobalt ions, was also synthesized for comparison with **1**; here the $Co(II)$ species on the framework cannot be reduced by ascorbic acid, confirming its lower oxidation potential. In this work, pyrrole and aniline were used as monomers for polymerization. Those monomers are known to show the polymerizations with oxidants such as $FeCl_3$ and $(NH_4)_2S_2O_8$.⁹

Polymer-coated POM network (**1-Py**, **1** covered with polypyrrole; **1-ANI**, **1** covered with polyaniline) were successfully synthesized by heating fresh crystals of **1** in the presence of pyrrole or aniline monomers. No polymer coating was detected in the case of **2**. This shows that the $Mn(III)$ species on the crystal surface of **1** performed as an oxidant for the polymerization reaction, as expected, whereas the oxidation potential of **2** is insufficient to initiate polymerization of either monomer. Additionally, no precipitate

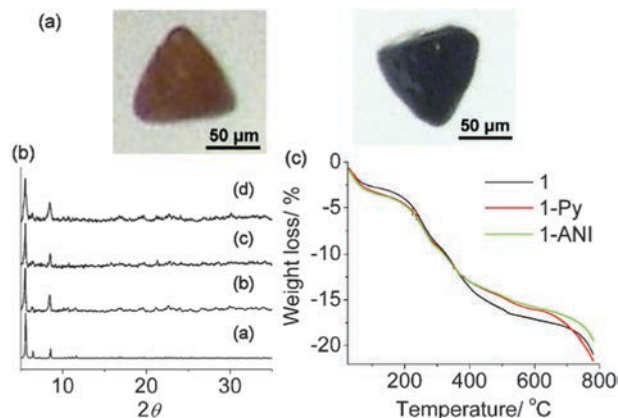


Fig. 2 (a) Optical micrographs of **1** (left) and **1-Py** (right). (b) PXRD patterns (a) simulated from crystal structure, (b) of **1**, (c) of **1-Py** and (d) of **1-ANI**. (c) TGA under N_2 atmosphere showing the weight loss in samples of **1** (black line), **1-Py** (red line) and **1-ANI** (light green line).

was observed after the polymerization in the reaction medium, which indicates that the POM network retains its molecular and crystalline integrity under the reaction conditions, as dissolved POMs would have induced undesirable polymerization in solution rather than on crystal's surface. Furthermore, successful and selective polymerization on the crystal surface was indicated by a colour change from brown to black during the reaction while the crystal shape was entirely preserved (Fig. 2a).

The as-synthesized polypyrrole–POM network (**1-Py**) and polyaniline–POM network (**1-ANI**) were thoroughly washed with methanol prior to analysis to remove any unreacted monomers. The untreated compound **1** was also washed under the same conditions before comparative measurements. Fig. 2b, shows that the powder X-ray diffraction (PXRD) patterns of **1-Py** and **1-ANI** are same as that of **1**, meaning that the native structure of **1** is retained even after surface modifications, whereas, different profiles were obtained by thermo-gravimetric analysis (TGA). As shown in Fig. 2c, the TGA profiles showed three steps in the weight loss data: (1) a minor weight loss because of guest removal (room temperature to 200 °C), (2) larger weight loss with removal of morpholinium cations (200 °C to 700 °C) and (3) decomposition of the frameworks (above 700 °C). In the first step, **1-Py** and **1-ANI** showed a slightly larger weight loss, indicative of solvent or additional guests being accommodated within the polymeric shell.

Also, the guests could be easily removed even at room temperature before the surface modification. In the second step, lower weight losses were observed for **1-Py** and **1-ANI** over *ca.* 400 °C. This is likely due to the fact that the polymer has crosslinked heavily under the inert atmosphere forming a stabilising polymer coating around the crystals.

To investigate the crystal surface, microfocussed laser Raman spectroscopy was used. As shown in Fig. 3, the Raman peaks from polymers were only observed on the crystal surface, demonstrating that the polymerisation process was confined to the crystal surface and not inside the material. In the case of **1** the main peak can be attributed to the $W=O$ symmetric vibrations of the

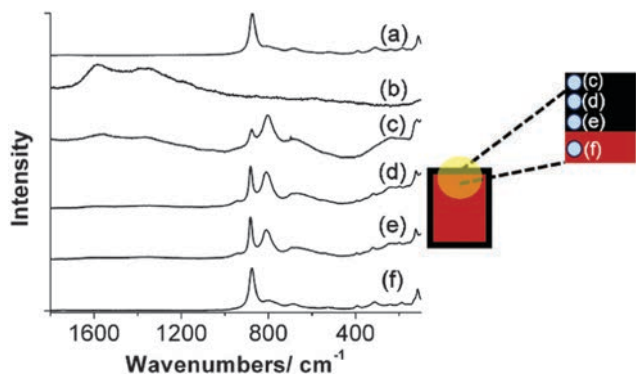


Fig. 3 Raman spectra obtained from (a) **1**, (b) polyaniline, and (c–f) **1-ANI** at various depths from the surface of the crystal.

Keggin moieties.^{10a} Whilst the crystal of the POM network is coated, additional peaks can be observed which can be attributed to the C–C ring vibrations (1600–1200 cm⁻¹) and ring deformations (800–830 cm⁻¹) of the polymer.^{10b} To validate the potential for guests to move through the polymer layer, guest-exchange experiments were conducted with four tetraalkylammonium bromide compounds of differing alkyl chain length: tetramethylammonium bromide (TMABr), tetraethylammonium bromide (TEABr), tetrapropylammonium bromide (TPABr) and tetrabutylammonium bromide (TBABr). Three kinds of crystals, **1**, **1-Py** and **1-ANI** were separately immersed into the CD₃OD solution with the salts and the guest exchange reactions were investigated by ¹H NMR measurements. As shown in Fig. 4, the smaller TMABr and TEABr took place in guest-exchange reactions with the morpholinium cations in **1**, whereas TPABr and TBABr did not diffuse into the framework.

This size-selectivity can easily be explained by considering the pore aperture size; the size (14.3 × 8.8 Å) is bigger than TMABr (diameter, 4.0 Å) and TEABr (diameter, 7.6 Å) themselves, but smaller than TPABr (diameter, 9.2 Å) and TBABr (diameter, 11.8 Å). Similarly, **1-Py** and **1-ANI** also showed guest-exchange reactions which occurred with the same size-selectivity, meaning that the polymer coating did not hinder the diffusion process and that the pore windows kept their integrity and size. This result is critically important from the point of crystal surface modifications since crystal surfaces are often fragile, resulting in structural changes after modifications. Also, it is noteworthy that the guest-exchange reaction with **1-Py** and **1-ANI** become less efficient compared to the case of **1**, indicating that the polymers on the crystal surface could control the access of guest molecules.

To understand the kinetic process of guest-exchange, the reactions were repeated with guanidine hydrochloride and monitored after 1, 2, 4, 8 and 12 h by ¹H NMR (Fig. 5). Guanidine hydrochloride was used as a guest molecule instead of TMA because, despite its similar molecular size, it is planar (Fig. 5a), making the guest-exchange reactions easier. In addition, the three NH₂ groups on the guanidine hydrochloride should have suitable interactions with the POM framework, similar to the morpholinium cation, which makes the reaction faster. The exchange reactions were almost completed after 12 h and they showed different guest-exchange rates depending on the polymer

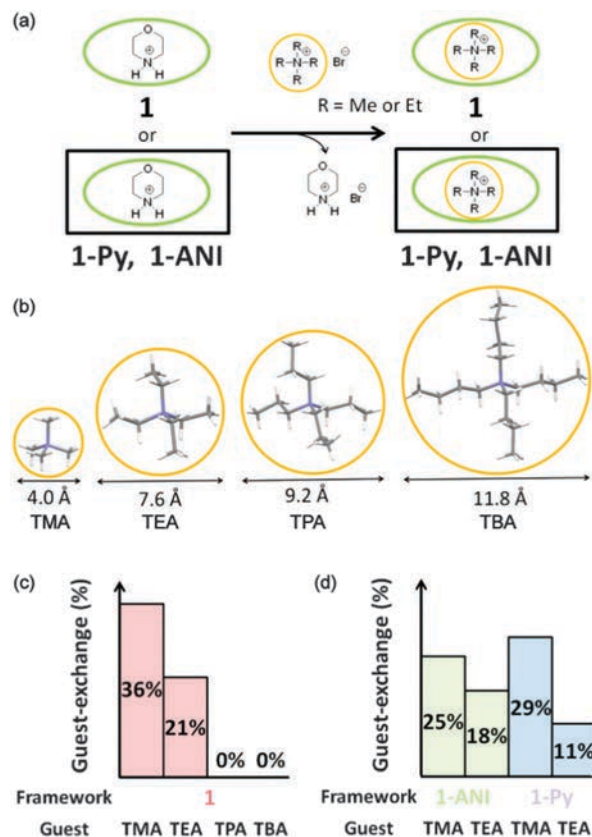


Fig. 4 (a) Guest-exchange reactions with alkylammonium bromides. (b) The size of alkylammonium cations. The yields of the guest-exchange reactions at 50 °C after 24 h with (c) **1** and (d) **1-ANI** or **1-Py**.

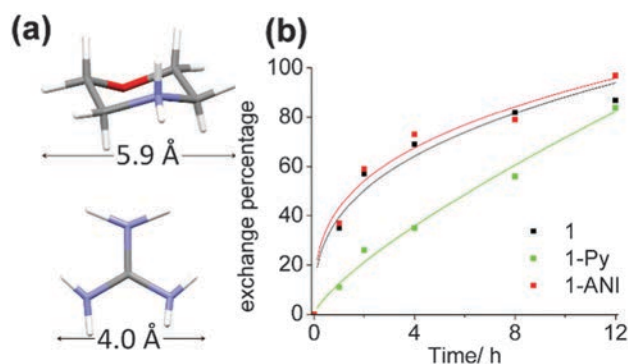


Fig. 5 (a) Molecular structures of morpholinium and guanidinium cation. (b) The guest-exchange reactions with guanidine hydrochloride at 25 °C.

used for coating. In the case of **1** and **1-ANI**, they showed very similar kinetics; initially, exchange of morpholinium cations is a rapid process with ca. 60% being replaced within two hours of exposing the crystals to the methanolic guanidine hydrochloride solution. Upon prolonged exposure, the amount of exchanged morpholine increases gradually to completion after 12 h. The reason that no significant influence of the polyaniline coating on the guest-exchange reaction rate is observed, it might be due to the polymer's assembled structure, which provides enough space for guest inclusion.¹¹ Interestingly, with **1-Py** a slower,

but constant, guest-exchange rate was observed, which shows that the guest exchange rates can be tuned independently of the pore size, by a simple post synthetic modification of the crystal's surface.

Finally, in order to explore further the effect of the polymer growth on the crystal surface, we investigated the osmotic driven growth of micro-scale tubes using polymer encapsulated POM crystals upon addition of giant organic cations. In the 'native' form of POM network, the added large cation forms a protective semi-permeable membrane around the POM crystal causing the osmotic pressure to build up inside upon guest exchange, leading to the ejection of POM anions which subsequently will ion exchange with the bulky cationic polymer, p(N-[3-(dimethylamino)propyl]methacrylamide) (p(DMAPMAM)).¹² As shown in Fig. S7 (ESI[†]), POM-based tubes were successfully obtained for all the samples after the addition of the solution of p(DMAPMAM). However, the new tubes exhibited different morphologies showing that the polymeric coating influences the growth process. The growth of long thin tubes from the surface of **1** was observed in agreement with our initial report of the phenomenon¹² indicative of a rapid and unobstructed process. In the case of **1-ANI** and **1-Py**, a higher density of tubes was observed after a longer incubation period, with larger diameters and they showed a tendency to aggregate. Thus, it would appear that coated crystals stabilize the crystal surfaces and hinder the tube formation for the initial period of time followed from a sudden growth due to increased osmotic pressure within the polymeric coating.

In conclusion, we have succeeded in making a polymer coated POM based network by exploiting its intrinsic redox activity. Microscopic Raman measurements, showed that the polymers were grown on the crystal surface, which makes it possible to tune their guest-exchange properties without compromising the structural integrity or the ion exchange properties of the network. Additionally, depending on the type of the polymer, it is possible to tune the exchange kinetics independently of the pore size. Utilization of this simple surface induced redox strategy, POM based networks can be easily modulated with various types of polymers and different functionalities, making it possible to control their sorption properties more precisely,¹³ and potentially open the field to new functionalities that polymer coatings and POM based materials can bring together, which might otherwise not be accessible by pure inorganic frameworks.

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