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Polymer-containing Organo-Polyoxometalate: Towards New Catalytic Objects

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Dedicated to Philippe Renaud, in appreciation for his mentoring

Abstract: Polyoxometalates (POMs) are early transition metal oxide clusters, which form a diverse family of compounds with highly tunable shapes, sizes, charges, *etc.* Generating hybrid structures is an attractive path to increase the structural diversity of POMs. The present article is a personal account that retraces how we inserted polyoxometallic platforms onto polymeric chains. We focused on two main families of functionalized organo-POMs: the organotin-substituted Dawson polyoxotunstates α1 and α2-$[P_2W_{17}O_{61}(SnR)]^{7-}$ and the Dawson vanadotungstates $[P_2V_3W_{15}O_{59}\{(OCH_2)_2\text{-}C(Et)NHC(=O)R\}]^{5-}$. Herein we discuss how the connection of POMs to polymers affects the self-assembly of the polymers and the catalytic properties of the polyoxometalates.

Keywords: Catalysis · Hybrid materials · Organic–inorganic hybrids · Polymers · Polyoxometalates

Foreword

I came to Switzerland as a '*scientifique-chercheur*'. Born in 1972, I had to complete military service. Rather than spend this forced break from my doctoral work in some army barrack, I chose to apply to the *scientifique-chercheur* program. In exchange for a longer term (16 months rather than 10), one could spend time to get trained in academic labs abroad, while reporting to the local French embassy. We were asked to write reports on scientific advances in the academic institutions of the host countries. I chose Switzerland at the invitation of Philippe Renaud, then at the University of Fribourg, to work on free radical reactions. Switzerland has always been close to my heart as I have family in the Zurich area, where I have spent several weeks every year since early childhood. The perspective of getting a higher education in a country which meant joyful summer vacations to me was particularly appealing. I was also lucky to be in the country when the joint graduate programs were introduced, which we learned about ahead of time thanks to the embassy. Given that my Swiss research was not too far from the topic of my Paris PhD, I was lucky enough to qualify for one of the very first '*thèses en cotutelle*' ever defended. As will be obvious from what is described below, radical chemistry is my background. That is due in no small part to my connection to Switzerland. That is why I am particularly happy to contribute to this special 'bridge' issue of *CHIMIA*. I thank Frédéric Leroux for the invitation. I hope readers will enjoy reading it as much as I did writing it.

1. Introduction

Polyoxometalates (POMs) are early transition metal oxide clusters. They form a wonderfully diverse family of compounds with highly tunable shapes, sizes, charges, *etc.* This rich structural diversity — *controllable through synthesis* — and the presence of transition metals can be harnessed for catalytic and photocatalytic applications. Some POMs are even bioactive. This was what stimulated our interest in POM chemistry. Generating hybrid structures is an attractive path to increase the structural diversity of POMs. Our general objective is thus to add organic appendages to polyoxometalates and examine how the POM-specific properties (redox properties, heavy-metal based spectroscopy, *etc.*) might be combined with the possibilities offered by multifunctional organic molecules and polymers to design new and/or better catalysts. We have developed two main families of functionalized organo-POMs: the organotin-substituted Dawson polyoxotunstates α_1 and α_2-$[P_2W_{17}O_{61}(SnR)]^{7-}$ and the Dawson vanadotunsgtates $[P_2V_3W_{15}O_{59}\{(OCH_2)_2\text{-}C(Et)NHC(=O)R\}]^{5-}$ (Fig. 1). The present article is a personal account that retraces how we inserted these two polyoxometallic platforms onto polymeric chains and what the consequences are on their catalytic properties.

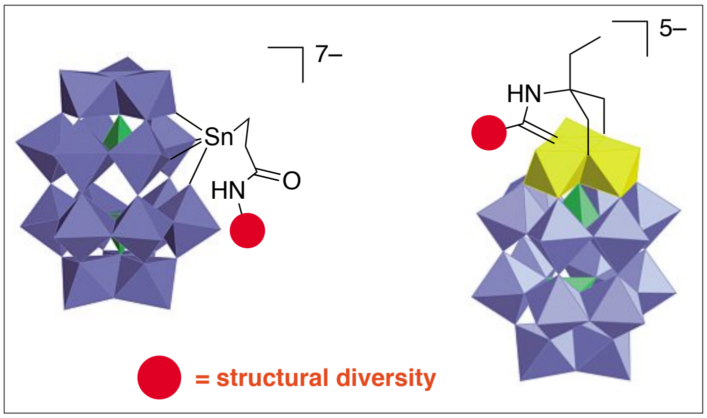

Fig. 1. The two organo-POM platforms of study.

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2. Synthesis of POM–Polymer Conjugates

2.1 *Organotin-substituted Dawson Family*

We first targeted POM–poly(*N*,*N*-diethylacrylamide) conjugates (POM–PDEAAm). Our first synthesis relied on the attachment of a separately prepared PDEAAm polymer that had been end-functionalized with a primary amino group (Fig. 2a).[1] This *grafting to* approach used our standard POM post-synthetic modification.[2] The polymer was prepared by controlled radical RAFT (Reversible Addition-Fragmentation chain Transfer) polymerization of *N*,*N*-diethylacrylamide in the presence of a trithiocarbonate (TTC) RAFT agent. The coupling $TBA_6[\alpha_2\text{-}P_2W_{17}O_{61}\{SnCH_2CH_2C(=O)]$ was carried out using a small excess of PDEAAm in MeCN for 3 days at rt. The polymer organo-POM was isolated by precipitation in diethyl ether and centrifugation in 90% yield. The SEC signal for the POM–polymer was shifted to lower elution volume, which indicates a higher molar mass than the starting materials. It was symmetric and narrow, which supports the absence of any free PDEAAm or starting POM. This was also further confirmed by MALDI-TOF MS analysis.

However, the *grafting to* method generally suffers from the intrinsic dilution imposed by the molar mass of the polymer. Only low mass polymers react quantitatively at their chain end. As properties usually depend on molar masses, this is a limitation of the post-synthetic method, made worse by the fact that separation of the unreacted polymer and/or POM from the hybrid is generally difficult, if not impossible. In our initial report, we could couple a polymer of below 40 monomer units (Mn = 5500 g.mol^{-1}), roughly the same molecular mass of the POM platform (approx. 4500 g.mol^{-1}). That led us to look for an alternative strategy to access longer-chain POM-polymer conjugates.

In the *grafting from* strategy, the polymer is grown from a suitable structure capable of initiating the polymerization of a monomer. Translated to POM chemistry, this meant that we had to functionalize a POM platform to install that structure, and devise a polymerization reaction compatible with it. The former was not a problem given the versatility of our coupling method, but the latter meant that we had to extend the scope of the reactions compatible with a polyoxometalate. We chose radical chemistry and examined the RAFT polymerization of N,N-diethylacrylamide in the presence of a POM-containing RAFT agent (Fig. 2b).[3] RAFT is generally a more versatile controlled polymerization technique than ATRP (Atom Transfer Radical Polymerization), which requires metal catalysts. In that case, the interaction of the metal ions with the anionic POM surface might later on be a problem for catalytic applications. We thus first attached a TTC to the POM using a combination of our grafting methods (amide formation[2]/click[4]), to serve as reversible transfer agent in the polymerization.

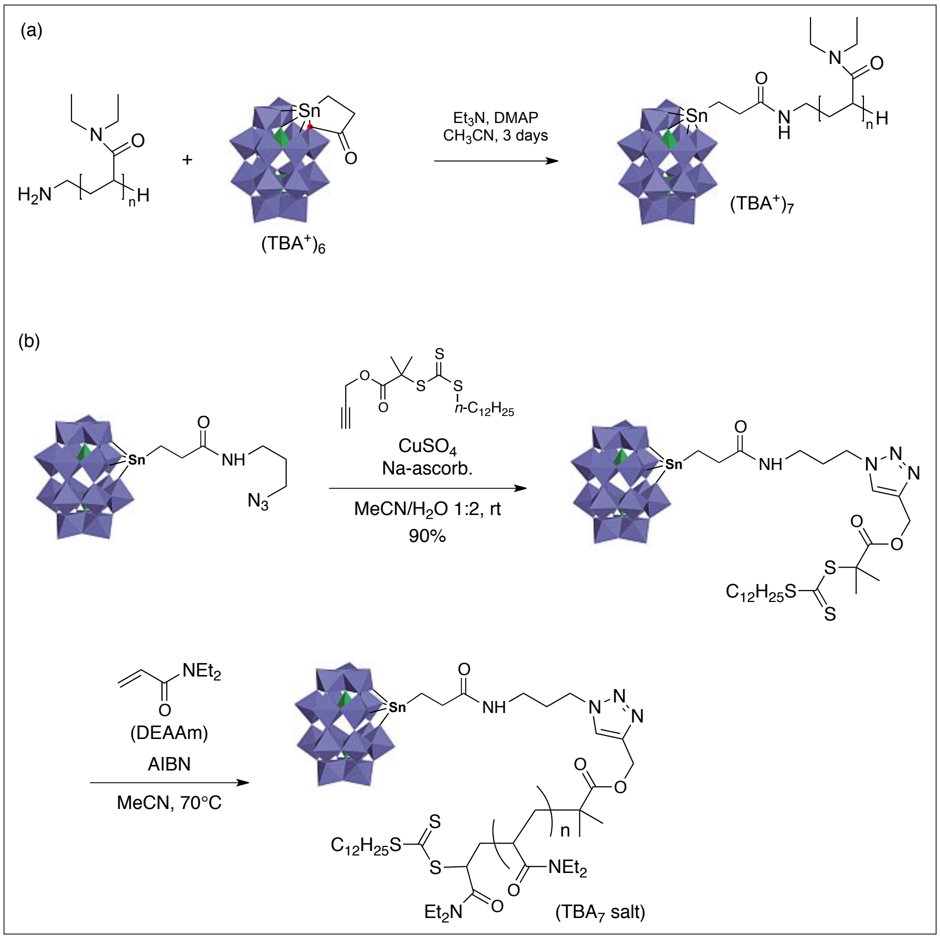

Fig. 2. *Grafting to* (a) and *grafting from* (b) approaches for the synthesis of POM–PDEAAm conjugates.

The polymerization of DEAAm in the presence of the POM-TTC RAFT agent was performed at 70 °C initiated by AIBN. Different initial molar ratios of $[DEAAm]_0/[POM\text{-}TTC]_0$ were used (150, 200, 500, 800), keeping the concentrations of RAFT agent and AIBN constant and varying the monomer concentration. The molar masses of the polymers were in the range of 10 to 100 kg mol^{-1} and molar mass dispersions of the composites were low ($M_w/M_n < 1.5$). The RAFT-polymerization of DEAAm with POM-TTC is a controlled radical polymerization. Gratifyingly, this meant that POMs do not profoundly disturb the RAFT mechanism.

The strategies depicted in Fig. 2 were carried out in an organic solvent. In parallel to that we examined the formation of hybrids *via* radical emulsion polymerization. This process is initiated in the water phase by a radical initiator and requires monomer diffusion through the water phase. The presence of a surfactant leads to polymer nanoparticles stabilized by the surfactant. Since POMs are polyanionic, we believed specifically tailored organo-POMs (with hydrophobic tails) could be used as surfactant in radical polymerizations in emulsion delivering latexes of POMs anchored or attached at the surface of polystyrene particles. During the course of our work a report by Polarz appeared, which suggested that an amphiphilic silyl-substituted Keggin organo-heteropolyacid allowed the cationic miniemulsion polymerization of styrene, confirming our assumption.[5] The latter is suggested to be initiated by the H^+ counterions of the Keggin POM surfactant present at the monomer droplet/water interface. It is carried out directly inside the micelles, which is different from the emulsion approach.

The PS-POM hybrid latexes were prepared in the presence of either an amphiphilic organo-POM derivative substituted by a hydrophobic C_{12}-alkyl chain, or an amphiphilic RAFT analogue POM-TTC (Fig. 3).[6] Fluid latexes of stable polystyrene nanoparticles without coagulum were obtained with more than 0.1 mol% of POM-C_{12}. The size of the nanoparticles decreased with increasing amount of POM-

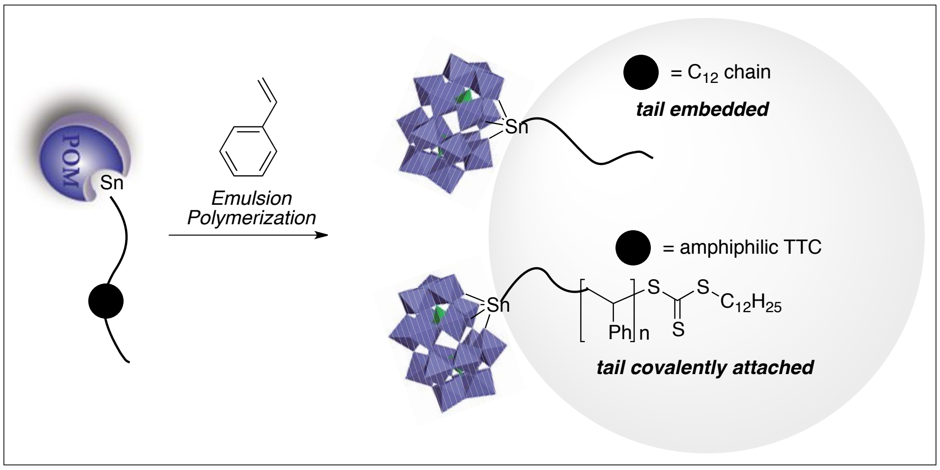

Fig. 3. Two strategies for radical emulsion polymerization using amphiphilic POMs.

C_{12}, which showed that it acted as a stabilizing surfactant. RAFT polymerization in emulsion of the analogue POM-TTC also delivered stable latexes.

The latexes were purified by successive centrifugations with a cut-off of 300 kDa. This purification step was meant to remove any organo-POMs that were not strongly adsorbed or covalently linked to the particles. It did not change the particle diameter. In the event, the majority of unreacted POM-TTC-C_{12} had already been removed in the first centrifugation step. No POM could be detected in the fourth filtrate, demonstrating the (expected) robust anchoring of the POM in the particles. In contrast, a small quantity (< 5%) of POM-C_{12} was still present in the last filtrate of the latex obtained from the POM-C_{12} amphiphile. We concluded that the latex formed *via* the RAFT polymerization was characterized by a strong covalent linkage between the POM and the PS chains. In contrast, the surfactant approach led to a weaker, non-covalent insertion of the alkyl chains in the PS particles, resulting in some leaching.

2.2 *Vanadotunstate Dawson Family*

POMs have a rich photoredox chemistry. Typically, light irradiation promotes electrons from an O-centered 2p orbital to an empty d-orbital on the metals. This creates a reactive state with strong charge-separation. The photoexcited POM is a strong oxidant that can oxidize organic substrates, in particular *via* C–H bond cleavage. The POM is then converted into its one-electron reduced form, which can be exploited for further reactions (see below), regenerating what is now a photo-redox catalyst. POMs are robust, multi-metallic species. They can thus often store reversibly multiple electrons and enter multielectron photoredox processes without decomposition. Yet, for most POMs the ligand-to-metal charge transfer band lies in the UV region. It would be important to be able to use the more practical and cheaper visible light to achieve the same goals. One way of doing this is to link POMs to visible light sensitive molecules.

We have studied the formation of a mixed covalently bonded POM–porphyrin copolymer film *via* an electropolymerization/deposition process.[7] This strategy relies on the electro-copolymerization of zinc octaethylporphyrin (ZnOEP) with several bis-pyridine-capped $[P_2W_{15}V_3O_{62}]^{9-}$ (Fig. 4). The organo-POM monomers have a versatile design that allows to control the conjugation, conformation, distance, *etc.* between the POM and the pyridine. In this way, we hoped to be able to control the properties of the film in a precise way. Compared to our previous results, the organo-POMs are co-monomers that can lead to crosslinking.

Exhaustive electro-oxidation of ZnOEP at a potential of the first porphyrin oxidation in the presence of nucleophiles leads to mono-addition adducts with the latter (ZnOEP(Nu)+). When the nucleophile is difunctional (as it is in our case) and the anodic potential is high enough to generate the porphyrin dications, one can generate polymers. The electropolymerizations were carried out by iterative scans, which generated the desired films.

3. Properties of the Hybrid Materials

3.1 *Organotin-substituted Dawson Hybrids*

PDEAAm exhibits a lower critical solution temperature (LCST) around 43 °C in water, which depends on the molar mass, and the nature of the chain end-groups (in case of low molar mass polymers). An aqueous solution of the short-chain TBA_7[POM]-PDEAAm obtained by the *grafting to* method is slightly opalescent at rt. Upon heating, the suspension turned white. The hybrid polymer thus shows a thermoresponsive behavior, which is reversible. The ammonium salt of the same POM–polymer conjugate is fully water-soluble. Thus, its aqueous solution was transparent at 20 °C, and turbid at 70 °C. Dynamic light scattering (DLS) revealed the formation of small aggregates in the range of 100 nm. This showed that the solubility properties of the POM are controlled by the thermoresponsive polymer chains.

We studied in more depth the behavior of the POM–PDEAAm hybrids in water.[1,8] The POM–PDEAAm hybrids at 20 °C contain unimers and microgel-type swollen aggregates. Heating led to phase transition caused by the cleavage of hydrogen bonds. Mesoglobules form at around 30 °C. We evidenced an influence of the cations surrounding the POM. In water, TBA ions cannot be solvated well and are closely associated to the POM, making it more hydrophobic. The phase transition was sharper than for the 'hydrophilic' NH_4^+ salt. This difference was also

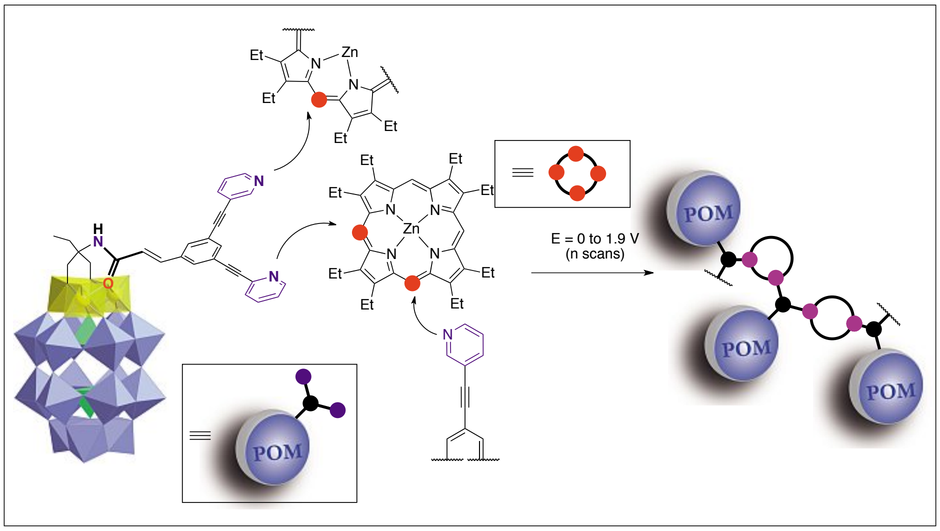

Fig. 4. Electro-copolymerization of POM–pyridines and zinc octaethylporphyrin.

evidenced on self-assembly of the hybrids. The conformation of POM–PDEAAm hybrids in water and their self-assembly into stable aggregates is thus tunable. It can be controlled by external factors, such as the temperature and the nature of counterion or the concentration.

Gratifyingly, the conjugate exhibited better catalytic efficiency for the photoreductive synthesis of silver nanoparticles (Fig. 5).[3] In the presence of sacrificial propan-2-ol the POM–polymer hybrid with the longest chain (100 kg.mol^{-1}) was a powerful photocatalyst for the reduction of Ag_2SO_4 in the presence of a sacrificial electron donor at room temperature (expt. 1). It led to smaller and monodisperse nanoparticles than UV irradiation of Ag_2SO_4 (i) in the presence of a mixture of a water-soluble 'molecular' POM $(NH_4)_7[\alpha_1\text{-}P_2W_{17}O_{61}\{SnCH_2CH_2COOH\}]$ and PDEAAm; (ii) in the presence of only $(NH_4)_7[\alpha_1\text{-}P_2W_{17}O_{61}\{SnCH_2CH_2COOH\}]$; (iii) without any photocatalyst.

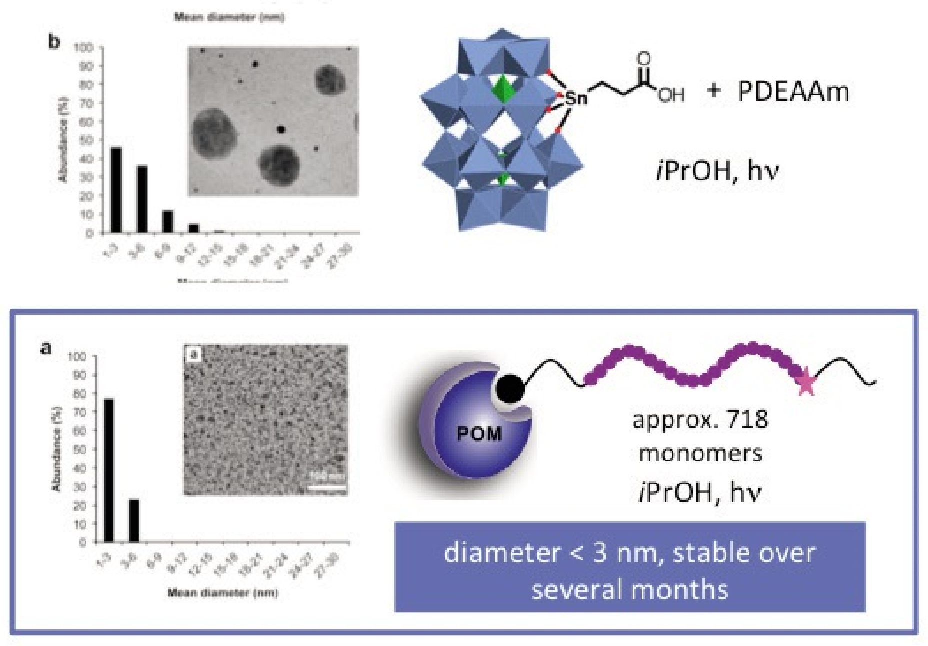

Fig. 5. TEM images and histograms (100 particles) of silver nanoparticles after UV irradiation of aqueous solutions containing 0.16 mmol L^{-1} Ag_2SO_4, 0.13 mol L^{-1} propan-2-ol and 0.05 mmol L^{-1} of photocatalyst. (a) POM–polymer covalent hybrid (Ag nanoparticles are embedded in the POM–polymer matrix); (b) mixture of $(NH_4)_7[\alpha1\text{-}P_2W_{17}O_{61}\{SnCH_2CH_2COOH\}]$ and PDEAAm (large polymer aggregates demix from Ag nanoparticles).

The POM@PS latexes were quite stable since the colloids showed no sign of coagulation after 1 year of storage at 5 °C. The strongly negative zeta potential values of both purified latexes (covalent and non-covalent, see above) support a stabilization mechanism featuring an electrostatic repulsion of the negatively charged POMs at the surface of the particles.[6] The cryo-TEM micrographs showed spherical PS nanoparticles in the size range determined by DLS. Dark spots (< 2 nm) can be observed on the nanoparticles, and not in the aqueous solution. They might indicate the presence of single or aggregated organo-POMs. Indeed, the latter strongly absorb the electrons because of the W atoms.

The previous analyses suggest that the POMs are accessible to reagents in the aqueous solution, and are not buried deeply inside the organic nanoparticles. We again sought to prove this by resorting to the photocatalyzed formation of silver nanoparticles. The latexes were irradiated (UV) in the presence of silver sulfate and propan-2-ol. Nanoparticles were formed in less than 5 min. Cryo-TEM of both latexes after photocatalysis showed the presence of silver nanoparticles associated to the PS spheres, and no silver particles were detected in the surrounding aqueous medium. Dark field scanning transmission electron microscopy combined with X-ray energy dispersive spectroscopy allowed us to localize the elements present in the medium. Silver was found only in the Ag^0 NPs, W only in the POM, and carbon in the PS nanospheres. The carbon was distributed evenly on all the PS nanospheres. In contrast, W and Ag were only observed at their periphery (Fig. 6). Since the photocatalysts are located near the surface of the polymer particles (as expected for amphiphilic species in emulsion polymerization, see above) they spatially limit the photoreduction to the PS surface, not in the aqueous phase, nor inside the hydrophobic core.

The positioning of the POMs at the surface of PS supports, that is in an area accessible to reactants, and the possibility to recover the latexes by ultrafiltration should make these systems suitable as supported catalysts in aqueous medium. By using amphiphilic POMs one can thus elaborate complex structures with predictable built-in properties.

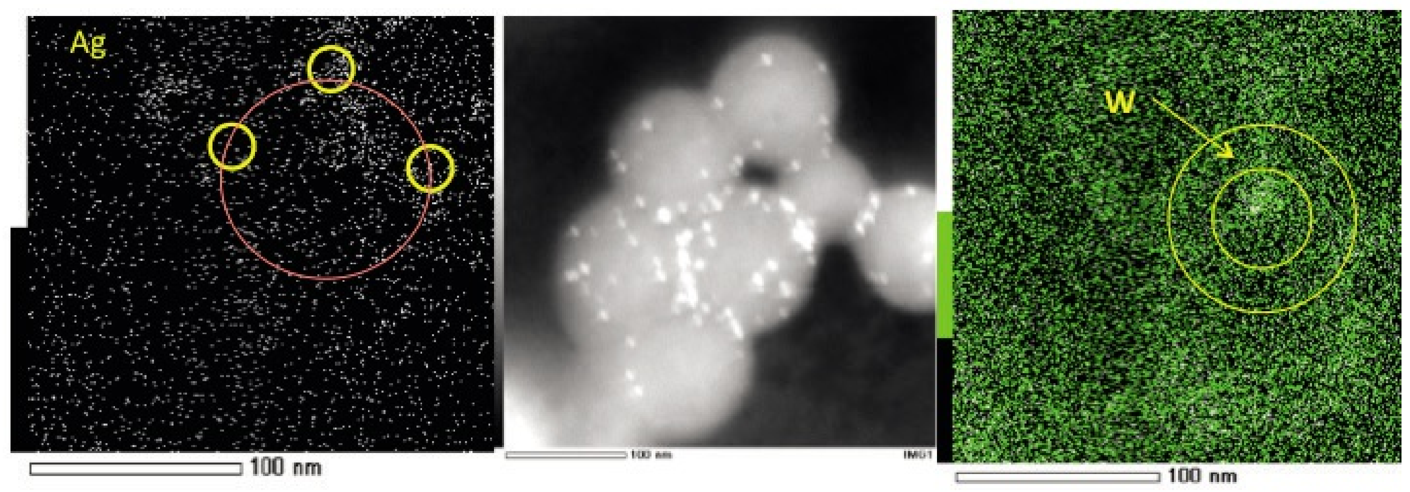

Fig. 6. Center: HAADF image of a PS–POM latex; left: X-ray mapping with detection of silver; right: X-ray mapping with detection of tungsten.

3.2 *Vanadotungstate Dawson Hybrids*

The chemical nature and geometry of the spacers in the (vanadotungstate) POM-bis-pyridine conjugates have a direct influence over the film properties, first and foremost the thickness.[7] In contrast, the conjugation of the porphyrin to the POM in the polymers may not be a crucial item. The materials were used to build new types of photovoltaic electrodes, whose performances were investigated by photocurrent transient measurements.[9] A significant photocurrent response was observed, and the charge transport through the films was rapid and homogeneous. The film thickness is strongly influencing the photocurrent generation efficiency.

4. Conclusions

To conclude this rapid tour at the border between organic, inorganic, polymer and materials chemistries, I would like to emphasize two things. The first is that no chemistry happens in a vacuum. We are *among* the pioneers of POM/polymer chemistry, but certainly not *the* pioneers. For clarity, and because it was not the point of the manuscript, (almost) no literature has been cited. The reader should go to our published articles, where proper credit is given to our precursors and competitors. Second, had we not been able to prepare the molecules we need, we could never have harvested the results presented. Organic synthesis is at the root of the program, as it should be. Core organic chemistry has matured, and some of its seeds are in the neighboring fields. I, for one, enjoy pursuing them in these less familiar surroundings.

Acknowledgements

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