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## COMMUNICATION

## Covalent amphiphilic polyoxometalates for the design of biphasic microemulsion systems

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**Covalent amphiphilic polyoxometalates generated from alkylphosphonic acids have been synthesized, characterized and monitored by multinuclear NMR spectroscopy. Among them,  $K_3H[\gamma-SiW_{10}O_{36}(C_{12}H_{25}PO)_2]$ , has been successfully used as surfactant for the stabilization of a Winsor I type microemulsion system.**

Self-assembly of polyoxometalates (POMs), nanoscaled negatively charged molecular metal oxide clusters of the early transition metals, is highly valued since it provides new supramolecular architectures to further exploit their remarkable properties and to enlarge the scope of their applications toward nanofunctional devices and materials, thus bypassing their low processability.<sup>1</sup> For example, giant POMs are able to assemble into nanoblackberries in cation driven processes.<sup>2</sup> The association of POMs and surfactant cations has also retained much attention: LB films are formed at the air/water interface,<sup>3</sup> while in solution, assemblies of surfactant-encapsulated polyoxometalates<sup>4</sup> displaying various shapes have been built on solvophobic interactions.<sup>5</sup> These result from different arrangements of the surfactant cations around the POMs, that can be triggered by changing the medium polarity,<sup>5b</sup> the redox state of the POM,<sup>6</sup> or the external pressure.<sup>7</sup> Light driven assembly / disassembly has also been reported.<sup>8</sup> In the case of covalent amphiphiles, where hydrophilic POMs and hydrophobic alkyl tails are covalently linked,<sup>9</sup> micelles<sup>10</sup> and hollow vesicles have also been described,<sup>11</sup> while increasing the concentration of the amphiphiles could lead to the formation of lyotropic liquid crystal phases.<sup>12a</sup> Beyond the structural diversity encountered in these self-assembled architectures, the possible emergences of new properties or synergistic effects have been pointed out.<sup>13</sup>

Our long-standing interest in POM hybrids<sup>14</sup> led us to consider the synthesis of covalent POM amphiphiles and to study their

aggregation in solution. While this field has been covered by recent reviews,<sup>2b</sup> applications of such assemblies are still underdeveloped,<sup>15</sup> especially have their catalytic activities been seldom mentioned.<sup>12</sup> Recently some of us designed balanced catalytic surfactant for oxidation reactions of organic substrates by  $H_2O_2$  in thermodynamically stable microemulsions ( $\mu$ ems).<sup>16</sup> Long chain mono- or bis-alkyl ammonium salts of  $[MoO_4]^{2-}$  and  $[WO_4]^{2-}$  were found to be effective in the peroxidation and epoxidation of various compounds. Formation of a  $\mu$ em allows i) an increase of the oil-water interface in the intermediate phase ( $10^5$  times compared with a classical biphasic system), ii) the presence of excess organic and/or water phases, which facilitates the recovery of the organic products and prevents the demixing potentially arising from an excess of  $H_2O_2$ . If oxidation of organic substrates by  $H_2O_2$  in the presence of POMs has been extensively studied, in homogeneous, under phase transfer conditions<sup>17</sup> and also in emulsions,<sup>18</sup> no example addresses their reactivity in  $\mu$ ems,<sup>19</sup> at least to our knowledge, and, a fortiori, the potential ability of amphiphilic POMs to stabilize such reaction media. In this contribution, we report our approach to the preparation of covalent POM amphiphiles based on lacunary Keggin type scaffolds and how they allow the formation of a Winsor I type  $\mu$ em which structure has been disclosed by SAXS measurements, notably.

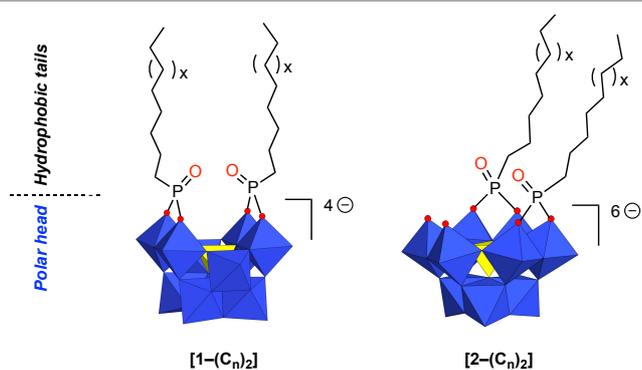


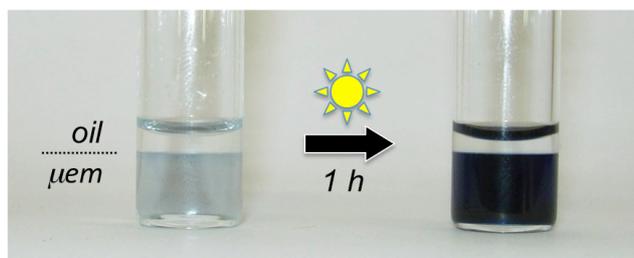
Fig 1. The double-tailed amphiphilic POMs based on the di- and tri-vacant  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  and  $[\alpha\text{-A-SiW}_9\text{O}_{34}]^{10-}$  Keggin-type scaffolds.

The compounds that we devised for these studies are displayed in Fig 1. The choice of the parent di- and tri- vacant Keggin type POMs,  $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$  and  $\text{Na}_{10}[\alpha\text{-A-SiW}_9\text{O}_{34}]$ , as hydrophilic polar heads, has been driven by, first, our expertise in their functionalization by electrophilic organic groups,<sup>20</sup> and second, by the possibility to obtain in both cases double-tailed amphiphilic POMs, and as consequence for the trivalent  $[\alpha\text{-A-SiW}_9\text{O}_{34}]^{10-}$  the opportunity to keep two  $\text{W}(=\text{O})_2$  moieties on the polyoxotungstate framework. Similar vacant sites in  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  have indeed been proposed by Mizuno *et al.*<sup>21</sup> to be the active sites in the olefin epoxidation using  $\text{H}_2\text{O}_2$ . The reactions between organophosphonic acids  $\text{RPO}(\text{OH})_2$  [ $\text{R} = \text{C}_n\text{H}_{2n+1}$  ( $n = 8, 10, 12$ )] and the lacunary POMs proceed in acetonitrile under phase transfer conditions using tetramethylammonium bromide (TMABr) leading to  $\text{TMA}_3\text{K}[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{C}_n\text{H}_{2n+1}\text{PO})_2]$ , **TMA<sub>3</sub>K[1-(C<sub>n</sub>)<sub>2</sub>]**, and  $\text{TMA}_{2.5}\text{Na}_{3.5}[\alpha\text{-A-SiW}_9\text{O}_{34}(\text{C}_n\text{H}_{2n+1}\text{PO})_2]$ , **TMA<sub>2.5</sub>Na<sub>3.5</sub>[2-(C<sub>n</sub>)<sub>2</sub>]**. Their chemical structures have been confirmed by multinuclear NMR ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{29}\text{Si}$ ,  $^{183}\text{W}$ ) and IR spectroscopies, mass spectrometry and elemental analysis (see ESI). It is worth noting that, as a result of the own phase-transfer property of the organophosphonic acids used in this study, the reactions may also be carried out in the absence of additional tetramethylammonium salts, thus directly leading to the **K<sub>3</sub>H[1-(C<sub>n</sub>)<sub>2</sub>]** and **Na<sub>6</sub>[2-(C<sub>n</sub>)<sub>2</sub>]** derivatives, both soluble in water and polar solvents. Alternatively, proton can be a substitute for TMA thanks to the use of a cation-exchange resin. The complete exchange for TMA was monitored by  $^1\text{H}$  NMR and led to **H<sub>4</sub>[1-(C<sub>n</sub>)<sub>2</sub>]** (Fig S2). The latter formulation was assigned on the basis of  $^{31}\text{P}$  NMR and ESI-MS analysis of the recovered acetonitrile solution. Transfer in water was possible, but product recovery as a solid has always led to a partial degradation. Notwithstanding, the proton can be further replaced with sodium or potassium by stirring an acetonitrile solution of **H<sub>4</sub>[1-(C<sub>n</sub>)<sub>2</sub>]** with saturated NaCl or KCl aqueous solution. Thereby, the resulting new derivatives **Na<sub>2.6</sub>H<sub>1.4</sub>[1-(C<sub>n</sub>)<sub>2</sub>]** and **K<sub>3</sub>H[1-(C<sub>n</sub>)<sub>2</sub>]** have been isolated and fully characterized. They are soluble in both acetonitrile and water (see SI).

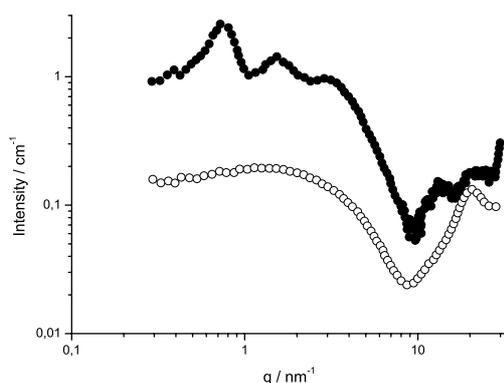
We have then investigated the ability of these covalent amphiphilic POMs to stabilize water/oil  $\mu\text{em}$ s. The ammonium salts of **1** are not soluble in water whereas the mixed TMA/Na salts of **2** are only poorly soluble in water. We recently reported that Keggin type polyoxometalates,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , associated to amphiphilic cations are not soluble in water and preferentially formed Pickering type

emulsions in water/oil mixtures<sup>22</sup> and Langmuir films when deposited at a water surface.<sup>7</sup> Although the POMs used in the present study are different (covalent vs electrostatic linkage of the amphiphilic moieties) these previous results prompted us to turn our attention to the alkaline salts of **1** and **2**, soluble in water. We observed that **K<sub>3</sub>H[1-(C<sub>12</sub>)<sub>2</sub>]**, the more hydrophobic derivative of the series based on the divacant  $[\text{SiW}_{10}\text{O}_{36}]^{8-}$  parent compound, provides a Winsor I system (WI), *i.e.* oil-in-water  $\mu\text{em}$  in equilibrium with an excess of the organic phase, when using mixtures of water/ether (diethylether or methyl *tert*-butyl ether) in equal volumes and 20wt.% of surfactant, which in fact corresponds only to 2.2wt.% of alkyl chains. Microemulsions are nanodispersed systems (nanodomains of 10-100nm) that are transparent and thermodynamically stable.

The partitioning of the POM surfactants between the two phases of the WI  $\mu\text{em}$  was easily disclosed by irradiation with UV or even sunlight. A blue coloration, characteristic of the resulting photochemical reduction of the POM framework,<sup>23</sup> only appeared in the  $\mu\text{em}$  phase, as shown in Fig 2. Quantification by  $^{31}\text{P}$  NMR spectroscopy clearly confirmed that the amphiphilic POMs are mainly localized in the  $\mu\text{em}$  phase (>95%). Moreover, the 2D heteronuclear chemical shift correlation between  $^{31}\text{P}$  and  $^{183}\text{W}$  nuclei observed by HMQC experiments proved that the phosphorus atom remains bonded to the POM framework (see Fig S4 in ESI). This distribution was further ascertained by using small and wide-angle X-ray scattering (SWAXS). The low transmission value of the X-ray beam in the  $\mu\text{em}$  phase (lower phase) compared to the transmission in the upper ether phase confirms that most of the amphiphilic POM is present in the  $\mu\text{em}$  phase (>95%). Moreover, the nanostructuring has been clearly evidenced by SWAXS. The spectrum of the lower phase of the WI system obtained with diethylether is shown in Fig 3. In the wide-angle part of the spectrum, for  $q$  values above  $10\text{ nm}^{-1}$ , intermolecular correlations are probed, typically in the scale range from one to some Angstroms. Two broad signals are observed in this region at  $13\text{ nm}^{-1}$  and  $20\text{ nm}^{-1}$  corresponding respectively to the scattering signals of liquid diethylether and water. The presence of two separate peaks in the high  $q$  region indicates, as it is expected in  $\mu\text{em}$ s, that diethylether and water coexist as two distinct phases in the solution. In the small-angle part of the spectrum, for  $q$  values below  $10\text{ nm}^{-1}$ , the signal observed at  $4\text{ nm}^{-1}$  corresponds to the typical scattering of a POM in solution; see the empty symbol curve in Fig 3.<sup>24</sup> The large scattered intensity at  $q$  between  $0.4$  and  $2\text{ nm}^{-1}$  corresponds in real space to distances between 3 and 16 nm that are much larger than the amphiphilic POM size and corresponds to the scattering of the  $\mu\text{em}$  namely oil droplets dispersed in water. The size of the ether droplets of the WI  $\mu\text{em}$  (Diameter = 5.0 nm) was calculated by fitting the SWAXS spectrum by a core-shell spherical model (see Fig S5 in ESI). These combined experiments provide evidences that covalent amphiphilic POMs, such as **K<sub>3</sub>H[1-(C<sub>12</sub>)<sub>2</sub>]**, are prone to self-assemble and to behave as efficient surfactants for stabilizing  $\mu\text{em}$ s.



**Fig 2.** Picture of the Winsor I type  $\mu\text{em}$  stabilized by  $\text{K}_3\text{H}[\text{1}-(\text{C}_{12})_2]$  before (left) and after (right) exposure to sunlight for one hour.



**Fig 3.** SWAXS spectra of the Winsor I microemulsion (dark symbols) and 2.5wt%  $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$  aqueous solution (open symbols).

## Conclusions

We describe two families of covalent amphiphilic POMs, with various counterions that make them accordingly soluble in water and/or organic solvents. The physico-chemical characterization of their aggregation in water will be reported elsewhere. A systematic tuning of solvent mixtures and POMs allowed us to assess the conditions of formation of a Winsor I type  $\mu\text{em}$ , namely oil droplets dispersed in water, only based on water, an appropriate solvent, and the POM surfactant. It is noteworthy that the reactivity of POMs in such media has not yet been tested. However, the fully functionalized **[1-(Cn)<sub>2</sub>]** POMs are only active under extreme conditions (high temperature, microwave irradiation)<sup>25</sup> which are not compatible with the stability of the  $\mu\text{em}$ , at variance with compounds of the **[2-(Cn)<sub>2</sub>]** family, which are active at lower temperature because of the two remaining  $\text{W}(\text{=O})_2$  sites available for catalysis.<sup>21</sup> Current efforts are now addressed to get  $\mu\text{ems}$  stabilized by these surfactants, which would circumvent the lack of miscibility of  $\text{H}_2\text{O}_2$  with the organic substrates. Therefore, the use of such  $\mu\text{ems}$  appears as promising in place of phase-transfer catalysis or emulsions that mainly prevail for the development of sustainable oxidation reactions by  $\text{H}_2\text{O}_2$ .

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## Notes and references

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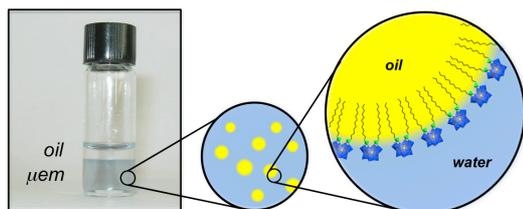
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Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data,  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{29}\text{Si}$ ,  $^{183}\text{W}$  NMR spectra of selected compounds, core-shell spherical model for the fitting of the SWAXS data, catalytic tests with  $\text{K}_3\text{H}[\text{1}-(\text{C}_{12})_2]$ . See DOI: 10.1039/b000000x/

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## Table of Content Entry



An unprecedented stabilization of a Winsor I microemulsion has been obtained using a covalent polyoxotungstate amphiphile.