Organic – Inorganic Hybrids Based on Polyoxometalates: Part 7[‡]

Bis- and Tetrakis(organosilyl) Decatungstosilicate, $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSi})_2\text{O}]^{4-}$ and $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSiO})_4]^{4-}$: Synthesis and Structural Determination by Multinuclear NMR Spectroscopy and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

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Abstract: The high propensity of organosilanes towards polycondensation and reaction with nucleophilic moieties has facilitated the formation of new organic – inorganic hybrids based on the lacunary divacant heteropolyanion $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$. Depending on the experimental conditions two different types of derivatives were obtained with the general formula $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSi})_2\text{O}]^{4-}$ (**1**) (> 90 % yield) and $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSiO})_4]^{4-}$ (**2**) (> 85 % yield) (R = H (**1a**, **2a**), vinyl (**1b**), $\text{-C}_3\text{H}_6\text{OC(O)C(Me)=CH}_2$ (**1c**, **2c**), phenyl (**1d**, **2d**)). The structures of the hybrid anions have been inferred from spectroscopic data, in particular from multinuclear (^{29}Si and ^{183}W) NMR solution studies and from MALDI-TOF mass spectrometry. Both species correspond to the grafting of an oxo-bridged siloxane unit onto the surface of the lacunary polyoxoanion.

Keywords: mass spectrometry • NMR spectroscopy • organic – inorganic hybrid composites • polyoxometalates • silicon

Introduction

The synthesis of organic – inorganic hybrid materials is a fast growing field of research. The interest in these materials lies in their specific properties which result from a synergy between both organic and inorganic parts. The properties of hybrid materials are strongly dependent on the nature of the interaction between the two components: either weak nondirectional links such as van der Waals and electrostatic interactions[2] or strongly oriented covalently links.[3] In order to obtain covalently linked hybrid materials in a rationalized fashion, it is necessary to synthesize organic – inorganic molecular precursors. These molecular building blocks may be connected together providing they contain reactive groups. Organic and organometallic derivatives of polyoxometalates (POM) appear especially suitable for obtaining hybrid materials: as a consequence of the intrinsic properties and the widespread field of applications (i.e. catalysis, chemotherapy, molecular sciences)[4] of the polyoxometalates, functionalized POMs may lead to composite materials of great potential.

Grafting of electrophilic groups such as RSn^{3+}, RSi^{3+}, and RPO^{2+} onto lacunary di- and trivacant polyoxotungstates has led to functionalized POMs such as $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2(\text{PhSnOH})_2]^{8-}$,[5] $[\gamma\text{-PW}_{10}\text{O}_{36}(t\text{BuSiOH})_2]^{3-}$,[1] $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RPO})_2]^{4-}$,[6] $[\text{PW}_9\text{O}_{34}(t\text{BuSiOH})_3]^{3-}$,[7] and $[\text{PW}_9\text{O}_{34}(\text{RPO})_2]^{5-}$.[8] In all cases the organostannyl, organosilyl, or organophosphoryl group is linked to the POM surface through E-O-W μ-oxo bridges (E = Sn^{IV}, Si^{IV}, P^{V}). The possibility of obtaining hybrid materials by sol – gel processes[3] in silicon chemistry may be of further interest with regard to the Si/POM system.

Herein we describe the synthesis of organosilyl derivatives of the divacant tungstosilicate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ which presents four nucleophilic surface oxygen atoms. Depending on the synthetic conditions, we can control the nature of the oligomeric organosiloxane framework grafted onto the POM surface, that is either a dimeric group $(\text{RSi})_2\text{O}^{4+}$ in $[\text{SiW}_{10}\text{O}_{36}(\text{RSi})_2\text{O}]^{4-}$ (**1**) or a cyclic tetrameric group $[(\text{RSiO})_4]^{4+}$ in $[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{RSiO})_4]^{4-}$ (**2**) (R = H (**1a**, **2a**),

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vinyl (**1b**), -$C_3H_6OC(O)C(Me){=}CH_2$ (**1c**, **2c**), phenyl (**1d**, **2d**)). The two families are easily distinguished by multinuclear NMR spectroscopy (^{29}Si, ^{183}W) and by MALDI-TOF mass spectrometry.

Results and Discussion

In an acetonitrile/water mixture, the divacant anion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ reacts with trimethoxy- or triethoxysilanes in the presence of hydrochloric acid to give $[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]^{4-}$ (**1**) and $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$ (**2**) (Equations 1, 2, and 3 in Scheme 1). The stoichiometry of reactants directs the preferential formation of either **1** with $SiW_{10}/RSi = \frac{1}{2}$ or **2** with $SiW_{10}/RSi = \frac{1}{4}$. However the isolation of **1** in pure form requires addition of Bu_4NBr before acidification.

$$RSi(OR')_3 + 3\,H_2O \longrightarrow RSi(OH)_3 + 3\,R'OH \qquad (1)$$

$$[\gamma\text{-}SiW_{10}O_{36}]^{8-} + 2\,RSi(OH)_3 + 4\,H^+ \longrightarrow \underset{\mathbf{1}}{[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]^{4-}} + 5\,H_2O \qquad (2)$$

$$[\gamma\text{-}SiW_{10}O_{36}]^{8-} + 4\,RSi(OH)_3 + 4\,H^+ \longrightarrow \underset{\mathbf{2}}{[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}} + 8\,H_2O \qquad (3)$$

Scheme 1. Synthesis of **1** and **2**.

In aqueous solution, the methacrylate derivative **2c** behaves as a surfactant with a surface tension of 43.5 $mN\,m^{-1}$ and critical agregate concentration of $4.3 \times 10^{-4}\ mol\,L^{-1}$. Therefore, for the spectroscopic analysis the acidic forms of **2** were converted to their $[Bu_4N]^+$ salts by precipitation with Bu_4NBr followed by recrystallization from DMF or acetonitrile. Elemental analyses of the onium salts are consistent with the formula $(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]$ and $(Bu_4N)_{4-x}H_x$-$[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]$ (R = H, $x = 0.4$ **2a**; R = -$C_3H_6OC(O)$-$C(Me){=}CH_2$, $x = 1$ **2c**; R = phenyl, $x = 0.5$ **2d**). The molecular structures of the hybrid anions have been deduced from the spectroscopic results (Figure 1).

Abstract in French: *La forte aptitude des organoalkoxosilanes à former des oligomères et à réagir avec des entités nucléophiles a été mise à profit pour synthètiser de nouveaux hybrides organiques inorganiques basés sur le polyoxotungstate divacant $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$. En fonction des conditions expérimentales, deux types de composés ont été obtenus, dont les formules générales sont : $[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]^{4-}$ **1** (rendement > 90 %) et $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$ **2** (rendement > 85 %) (R = H (**1a**, **2a**), vinyle (**1b**), -$C_3H_6OC(O)C(Me){=}CH_2$ (**1c**, **2c**), phényle (**1d**, **2d**)) Les structures moléculaires des anions hybrides ont été déduites des données spectroscopiques, en particulier de l'analyse par résonance magnétique multinucléaire en solution (^{29}Si et ^{183}W) et par spectrométrie de masse MALDI-TOF. Dans les deux cas, l'espèce hybride est constituée d'un motif siloxane greffé à la surface du polyoxotungstate lacunaire.*

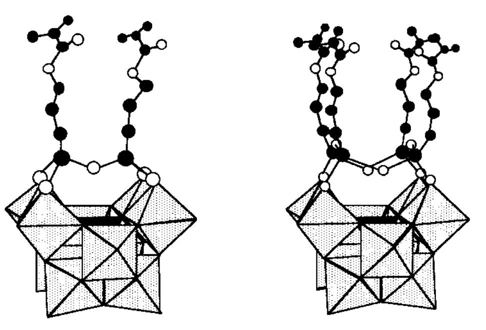

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Figure 1. Proposed structures for $[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]^{4-}$ (**1**) and $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$ (**2**).

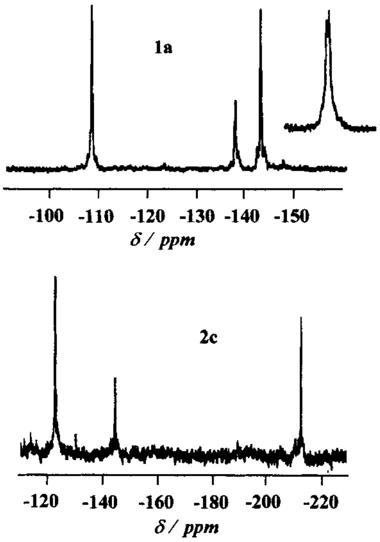


Figure 2. ^{183}W NMR (12.5 MHz) spectra of **1a** and **2c**. For **1a** {^1H}-decoupled full spectrum and abscissa expansion of the shielded line of the undecoupled spectrum showing the $^3J(W,H)$ coupling.

The ^{183}W NMR spectra of all compounds present three lines with relative intensities of 2:1:2 (Figure 2). This agrees with a retention of the C_{2v} symmetry of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ framework when grafting the siloxane units. Each series presents a characteristic ^{183}W NMR spectrum: for **1** all resonances appear in a relatively narrow range ($\Delta\delta < 35$ ppm), but for **2** the spectrum spans about 90 ppm.

The ^{183}W resonances were assigned with the help of homonuclear tungsten–tungsten couplings.[9] For both families the different resonances present the same pattern of coupling constants (Table 1). Therefore the resonances have been assigned for **2c** only and this assignment is transposable to **1** compounds. In the further discussion, we will use the following symbolism for equivalent W(*i*) tungsten atoms:[10]

Table 1. ^{183}W Chemical shifts/coupling constants connectivity matrix for **1b** and **2c**. Diagonal terms: chemical shifts, δ in ppm. Off-diagonal terms: $^2J(W,W)$ in Hz.

Sample		A	C	B
	A (W_7, W_8, W_9, W_{10})	**−107.6**	5.6	20.7
1b	C (W_5, W_6)	5.6	**−137.1**	19.4
	B (W_1, W_2, W_3, W_4)	20.7	19.4	**−142.3**
	A (W_7, W_8, W_9, W_{10})	**−123.9**	6.9	22.3
2c	C (W_5, W_6)	6.9	**−145.4**	20.1
	B (W_1, W_2, W_3, W_4)	22.4	19.8	**−212.7**

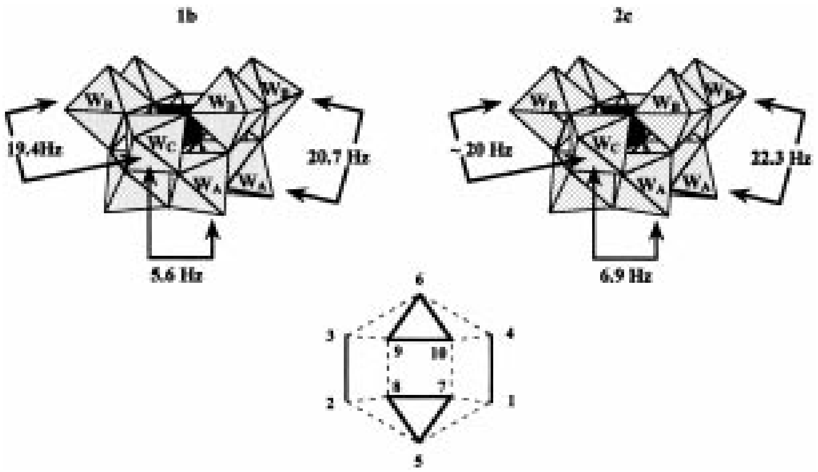


Figure 3. Polyhedral and planar representations of the polytungstate framework,[10] with corner and edge ^2J(W,W) coupling constants for **1b** and **2c**. On the schematic planar structures, heavy and dotted lines represent edge and corner junctions, respectively. The atoms are numbered according to the IUPAC convention.[11]

W_A for $i = 7, 8, 9, 10$, W_B for $i = 1, 2, 3, 4$, and W_C for $i = 5, 6$ (Figure 3).

The line of relative intensity 1, at $\delta = -145.4$, is assigned unambiguously to W_C atoms. This signal presents two different coupling constants ^2J(W,W). The small value of 6.9 Hz corresponds to edge coupling between W_C and W_A; the large value of 20.1 Hz is assigned to corner coupling between W_C and W_B (Figure 3). The line at $\delta = -123.9$ exhibits the same small coupling of 6.9 Hz, therefore it must be assigned to W_A. Consistently the third line, at $\delta = -212.7$, corresponds to W_B. It presents two pairs of satellites with ^2J(W,W) coupling constants of 22.4 and 19.8 Hz. Both correspond to corner couplings with W_A and W_C, respectively. This is in agreement with the observation of a pair of satellites around the W_A line with ^2J(W,W) = 22.3 Hz (Table 1).

The large corner coupling between W_A and W_B observed for both series **1** and **2** (> 20 Hz) has to be compared to the low value (4.6 Hz) in the divacant parent anion [γ-$SiW_{10}O_{36}$]$^{8-}$.[10] For this last compound, the small coupling was interpreted by a large W_B–O distance (220 pm) induced by the *trans* influence of the terminal oxygen atoms of the lacuna.[10] In the organosilyl derivatives these oxygen atoms are engaged in μ-oxo bridges Si-O-W, and the *trans* W_B–O distances become considerably shortened.[1, 7] Therefore the large $^2J(W_A,W_B)$ coupling in **1** and **2** confirms that the lacunary anion [γ-$SiW_{10}O_{36}$]$^{8-}$ is saturated by grafting of siloxane moieties.

This is consistent with the fact that in the spectra of **1a** and **2a** the line assigned to W_B appears as a doublet: this reflects heteronuclear coupling through the W-O-Si-H chain (^3J(W,H) = 5.1 Hz for **1a** and 5.8 Hz for **2a**).

As shown in Table 1, the analogous coupling constants are slightly different for both families. Actually for **1** all ^2J(W,W) values are significantly smaller than their corresponding values in **2**: according to the well-established correlation between ^2J(W,W) and the angle at the μ-oxo group[12] all W-O-W bridges might be larger in **2** than in **1**, which reflects a slightly different geometrical arrangement of the POM framework when grafting either four or two RSi groups.

Moreover, the geometry of the organosiloxane moiety has been deduced from the different ^{29}Si NMR spectra. Indeed, the ^{29}Si NMR spectra of all species exhibit two signals with relative intensities of 2:1 for **1** or 4:1 for **2**, in agreement with the chemical analysis. Figure 4 displays the inverse-gate decoupled ^{29}Si spectrum of **2d**. Under broad band proton decoupling the high frequency signal presents a pair of satellites due to heteronuclear coupling between the Si nucleus of the organosilyl moiety and the W_B atom. This heteronuclear coupling differs strongly in the two families: it is 5.6 Hz in **1** and 15–17 Hz in **2** (see Figure 4). For comparison, in [γ-$PW_{10}O_{36}$(tBuSiOH)$_2$]$^{3-}$ where two independent monomeric tBuSiOH groups are linked to the divacant anion [γ-$PW_{10}O_{36}$]$^{7-}$, the ^2J(W,Si) coupling has an intermediate value of 9.7 Hz.[1]

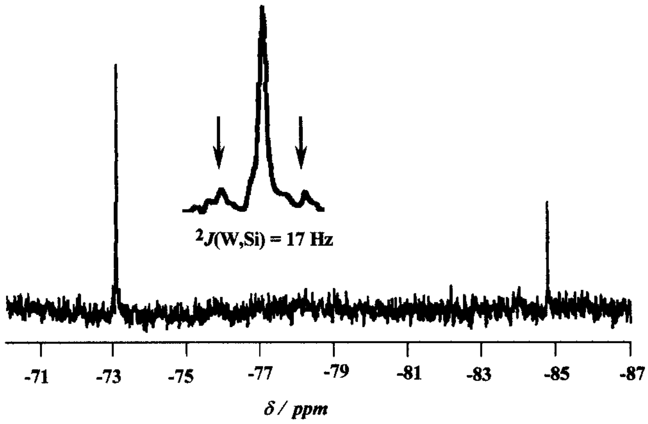


Figure 4. Inverse-gated decoupled ^{29}Si NMR spectrum (99.4 MHz) of **2d**, with abscissa expansion of the high frequency RSi signal showing the tungsten satellites (arrows).

The structure of the siloxane moieties can be deduced from the proton-coupled spectra of **1a** and **2a** (Figure 5). Actually each component of the antiphase doublet of the INEPT spectrum of **1a** ($\delta = -80.5$, ^1J(Si,H) = 286.7 Hz) is a doublet (^3J(Si,H) = 2.6 Hz): this corresponds to a small coupling through the Si-O-Si bridge of the $(HSi)_2O$ group. For the SiH resonance of **2a** ($\delta = -77.8$, ^1J(Si,H) = 293.2 Hz) it appears as a doublet of doublets (^3J(Si,H) = 5.3 Hz and 1.3 Hz): this implies that each Si atom is connected through two different μ-oxo bridges to two adjacent SiH groups. Therefore the four equivalent Si atoms are disposed according to a cyclic tetramer unit. Moreover in the lacunary [γ-$SiW_{10}O_{36}$]$^{8-}$ ion (C_{2v} symmetry), there are two different O–O distances between the oxygen atoms of the lacuna (315 pm and 530 pm):[10] therefore the tetrasiloxane unit must rearrange in order to fit the POM surface. This results in

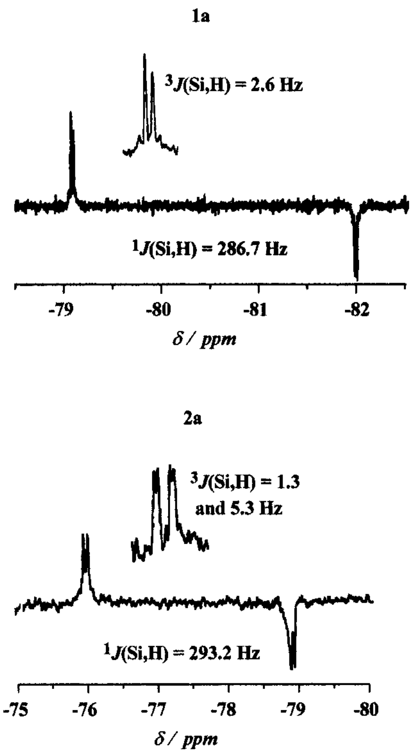
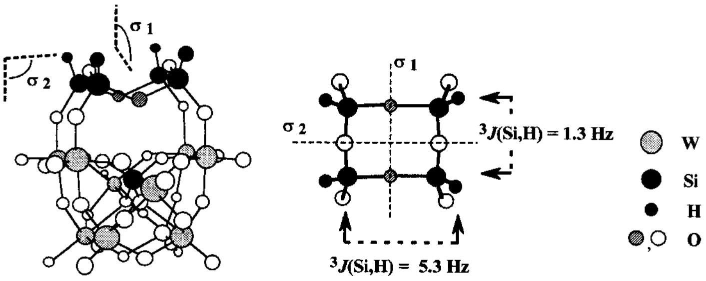


Figure 5. Proton-coupled INEPT ^{29}Si NMR spectra (99.4 MHz) of **1a** and **2a**, with abscissa expansion of the left part of the antiphase doublet.

different Si-O-Si angles and consequently in different ^3J(Si,H) coupling constants. Most likely the smaller one, corresponding to a small Si-O-Si angle, is related to two Si atoms connected to the same ditungstic group (O–O ≈315 pm) (Scheme 2).

Let us return to the differences in the coupling constants for the two series. The small μ-oxo bridged $(RSi)_2O$ unit of **1** induces larger steric constraints than the tetracyclosiloxane $(RSiO)_4$ unit in **2**. In fact, in **1** the grafting of $(RSi)_2O$ probably implies the displacement of both W_B and its terminal oxygen atoms towards the C_2 axis; this results in closing of the Si-O-W_B, W_B-O-W_C and W_B-O-W_A bridges and consequently in relatively small ^2J(W,Si) and ^2J(W,W) values. In contrast, the large tetracyclosiloxane unit forces W_B and its terminal oxygen atoms to move apart and this induces the extension of the whole POM framework, with consequently large ^2J coupling constants.

Note that different geometries of the $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ framework in both organosilyl-saturated species are also likely responsible for the large differences in ^{183}W chemical shifts (see above).



Scheme 2. Ball-and-stick representation of **2a** with a top view of the cyclic tetrasiloxane showing the two different coupling constants ^3J(Si,H).

An alternative analytical tool is MALDI-TOF mass spectrometry.[13] Figure 6 presents the positive-mode spectra of **1c** and **2c** which are characteristic of cationic monocharged species. All the observed signals are relatively broad: this is attributed to a partially resolved isotopic mass pattern due to the presence of the different isotopes of W and Si in natural abundance (Figures 6b and 6d). The signals are regularly spaced with $\Delta m/z \approx 242$, which corresponds to the mass of the NBu_4 fragment. They are assigned to the cationic entities $[M{+}x\,NBu_4{+}(5-x)\,H]^+$ ($M = [\gamma\text{-SiW}_{10}O_{36}$(3-methacryloxypropylSi$)_2$O] for **1c** and [$\gamma$-SiW$_{10}O_{36}$(3-methacryloxypropylSiO$)_4$] for **2c**; $x = 3-5$). The observed m/z values are in agreement with the calculated molecular mass for the different cations (see Experimental Section).

In conclusion, these results demonstrate the formation of novel molecular precursors for the synthesis of hybrid organic–inorganic materials, and illustrate the power of spectroscopic methods such as multinuclear NMR associated with mass spectrometry to infer the structure of these molecular derivatives.

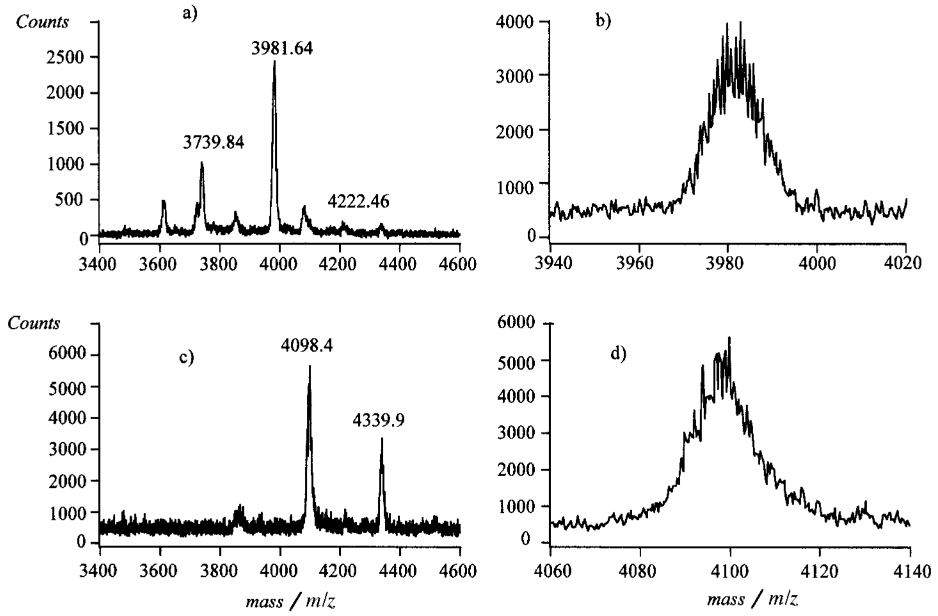


Figure 6. MALDI-TOF mass spectra of **1c** and **2c** : a) full spectrum of **1c** in delayed extraction and linear mode experimental conditions are : $V_{acc} = 20$ kV, delay time = 400 ns, laser energy: 8.5 μJ/pulse; b) expansion of signal at m/z 3981.64, in reflectron mode, experimental conditions are: $V_{acc} = 20$ kV, delay time = 275 ns, laser energy: 10 μJ/pulse; c) full spectrum of **2c** in delayed extraction and reflectron mode, experimental conditions are: $V_{acc} =$ 20 kV, delay time 200 ns; d) expansion of the signal at m/z 4098.4 of **2c**, under the same conditions.

The hybrid anions consist on a $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ unit onto which is grafted a $(RSi)_2O$ μ-oxo bridged dimeric moiety (**1**) or a cyclotetrasiloxane $(RSiO)_4$ group (**2**). These hybrid anions were obtained as tetraalkylammonium salts soluble in organic solvents. Compound **2** could be isolated in an acidic form and as alkaline salts, allowing the preparation of aqueous solutions. All these hybrids are amphiphilic, with the polyanion constituting the hydrophilic part and the organic chain the hydrophobic part. This work opens the route to the preparation of composite materials in both aqueous and nonaqueous media, and we will report on these materials in forthcoming publications.

Experimental Section

General procedures and chemicals: $\gamma\text{-}K_8[SiW_{10}O_{36}]\cdot 12\,H_2O$ was prepared according to the literature.[10] Other reagents and solvents were from Aldrich and used as received. Elemental analyses were performed by the "Service central de microanalyses du CNRS", Vernaison, France. Infrared spectra were recorded on a Bio-Rad FTS 165 FT-IR spectrometer with compounds sampled in KBr pellets. The mass spectra were recorded using a Voyager Elite Time-of-Flight Mass Spectrometer (PerSeptive Biosystems, Boston, MA, USA). In this apparatus, the pulsed N_2 laser beam (337 nm, 3 ns pulse duration, repetition rate 2 Hz) was focused onto the target with an incidence angle of 45°. In all these experiments the mass spectrometer was tuned in the reflector mode using delayed extraction and a beam wire guide wire. The target voltage was set to +20 kV. The extraction delay and pulse voltage were adjusted to obtain the best mass resolution and the wire guide voltage was adjusted to obtain the best transmission. All mass spectra were recorded and averaged over 256 laser shots by a Tektronix TDS 520 oscilloscope (Beaverton, OR, USA). The samples were prepared as follows: The compound (2 mg) was dissolved in acetonitrile (500 µL; solution A), and dithranol (12 mg) was dissolved in CH_2Cl_2 (500 µL; matrix solution). Then 1 µL of solution A was added to 50 µL of the matrix solution. The samples were calibrated by external calibration (ACTH18-39 + insuline). The ^{1}H (300 MHz) NMR spectra were obtained at room temperature in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead. The chemical shifts are given according to the IUPAC convention with respect to $SiMe_4$. The 12.5 MHz ^{183}W NMR spectra were recorded at 300 K on nearly saturated DMF/CD_3CN (90/10, v/v) solutions in 10 mm o.d. tubes on the same spectrometer equipped with a low-frequency special VSP probehead. The chemical shifts are given with respect to 2 M Na_2WO_4 aqueous solution and were determined by the substitution method using a saturated D_2O solution of tungstosilicic acid $H_4SiW_{12}O_{40}$ as secondary standard ($\delta = -103.8$). The 99.35 MHz ^{29}Si NMR spectra were recorded at 300 K on nearly saturated DMF/CD_3CN (90:10, v/v) solutions in 10 mm o.d tubes on a Bruker AM 500 spectrometer. Surface tension measurements were obtained at 25 °C on a Krun KT10 tensiometer.

$(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(HSi)_2O]$ (1a): $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12\,H_2O$[10] (3 g, 1 mmol) was suspended with Bu_4NBr (0.97 g, 3 mmol) in a mixture of acetonitrile (30 mL) and water (8 mL). Trimethoxysilane (0.3 mL, 2 mmol) and HCl (12 M, 0.5 mL) were successively added under vigourous stirring. The mixture was stirred for a further six hours. The white compound $(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(HSi)_2O]$obtained after evaporation of the organic solution in a rotary evaporator was copiously washed with water. The crude compound was recrystallized in DMF or acetonitrile. Yield: 3.0 g (92 %). $C_{48}H_{111}N_3Si_3W_{10}O_{37}$ (%): calcd C 17.76, H 3.45, N 1.29, Si 2.60, O 18.23, W 56.66; found C 18.62, H 4.05, N 1.33, Si 2.66, O 16.41, W 56.93; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -108.3$ (s, 4W), -136.5 (s, 2W), -142.3 (d, ^3J(W,H) = 5.1 Hz, 4W); ^{29}Si NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -87.9$ (s, 1Si; SiO_4), -80.5 (dd, ^1J(Si,H) = 286.7 Hz, ^3J(Si,H) = 2.6 Hz, ^2J(W,Si) = 4.6 Hz, 2Si; $RSiO_3$,); ^{1}H NMR (300.13 MHz, CD_3CN, TMS): $\delta =$ 4.8 (s, 1 H); IR (KBr): $\tilde{\nu} =$ 2181 (SiH), 1120 (SiO), 1003 (SiO), 963 (WO_{ter}), 903, 842, 823, 732 (WO), 547, 512 (SiO), 418, 365 (WO) cm^{-1}.

$(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(vinylSi)_2O]$ (1b): The synthesis followed the same procedure as for compound **1a**, using vinyltriethoxysilane (0.42 mL, 2 mmol) instead of trimethoxysilane. Yield: 3.0 g (90.9 %). $C_{52}H_{115}N_3Si_3W_{10}O_{37}$ (%): calcd C 18.94, H 3.52, N 1.27, Si 2.55, O 17.94, W 55.76; found C 19.1, H 3.75, N 1.23, Si 2.62, O 18.67, W 54.63; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -107.6$ (s, 4W), -137.1 (s, 2W), -142.3 (s, 4W); ^{29}Si{^{1}H} NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -87.9$ (s, 1Si; SiO_4), -75.7 (s, 2Si: $RSiO_3$); ^{1}H NMR (300.13 MHz, CD_3CN, TMS): $\delta =$ 5.1 (s, 1 H), 5.3 (s, 1 H), 6.2 (s, 1 H); IR (KBr): $\tilde{\nu} =$ 1123 (SiC), 1100, 1005 (SiO), 963 (WO_{ter}), 903, 840, 821, 731 (WO), 547, 512 (SiO), 414, 364 (WO) cm^{-1}.

$(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(3\text{-}methacryloxypropylSi)_2O]$ (1c): The synthesis followed the same procedure as for the compound **1a**, using 3-methacryloxypropyltrimethoxysilane (0.47 mL, 2 mmol) instead of trimethoxysilane. Yield: 3.2 g (91.6 %). $C_{62}H_{131}N_3Si_3W_{10}O_{41}$ (%): calcd C 21.29, H 3.78, N 1.20, Si 2.41, O 18.74, W 52.57; found C 21.42, H 4.05, N 1.26, Si 2.48, O 17.5, W 53.29; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -107.3$ (s, 4W), -135.9 (s, 2W), -140.3 (s, 4W); ^{29}Si{^{1}H} NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -87.9$ (s, 1Si; SiO_4), -63.2 (s, 2Si; $RSiO_3$); ^{1}H NMR (300.13 MHz, CD_3CN, TMS): $\delta =$ 6.05 (d, 1 H), 5.57 (d, 1 H), 1.93 (s, 3 H), 4.09 (m, 2 H), 1.73 (m, 2 H), 0.67 (t, 3 H); IR (KBr): $\tilde{\nu} =$ 1124 (SiC), 1102, 1009 (SiO), 962 (WO_{ter}), 903, 840, 821, 732 (WO), 547, 512 (SiO), 414, 364 (WO) cm^{-1}; MS (MALDI TOF): m/z: exp.: 3498.84 $[M+3\,Bu_4N+2H]^+$, 3739.84 $[M+4\,Bu_4N+1\,H]^+$, 3981.64 $[M+5\,Bu_4N]^+$, 4222.46 $[M+6\,Bu_4N-1\,H]^+$; m/z: calcd: 3498.48 $[M+3\,Bu_4N+2\,H]^+$, 3739.95 $[M+4\,Bu_4N+1\,H]^+$, 3981.42 $[M+5\,Bu_4N]^+$, 4222.39 $[M+6\,Bu_4N-1\,H]^+$.

$(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(phenylSi)_2O]$ (1d): The synthesis followed the same procedure as for the compound **1a**, using phenyltrimethoxysilane (0.37 mL, 2 mmol) instead of trimethoxysilane. Yield: 3.1 g (91.2 %). $C_{60}H_{119}N_3Si_3W_{10}O_{37}$ (%): calcd C 21.21, H 3.54, N 1.24, Si 2.48, O 17.41, W 54.12, found: C 22.1, H 3.75, N 1.23, Si 2.62, O 16.67, W 53.63; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -107.4$ (s, 4W), -137.4 (s, 2W), -140.7 (s, 4W); ^{29}Si{^{1}H} NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -87.6$ (s, 1Si; SiO_4), -74.3 (s, 2Si; $RSiO_3$); ^{1}H NMR (300.13 MHz, CD_3CN, TMS): $\delta = 7.8$ (b, 1 H), 7.3 (d, 2 H), 7.1 (d, 2 H); IR (KBr): $\tilde{\nu} = 1124$ (SiC), 1101, 1003 (SiO), 962 (WO_{ter}), 902, 837, 818, 732 (WO), 546, 512 (SiO), 414, 365 (WO) cm^{-1}.

$(Bu_4N)_{3.6}H_{0.4}[\gamma\text{-}SiW_{10}O_{36}(HSiO)_4]$ (2a): Trimethoxysilane (0.6 mL, 4 mmol) was added to a suspension of $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12\,H_2O$[10] (3 g, 1 mmol) in a mixture of CH_3CN (30 mL) and water (20 mL). Then, the mixture was acidified with hydrochloric acid (12 M, 0.4 mL) and the solution was stirred for 4 h. The crude acid compound (≈3 g), obtained after evaporation of the solution, was redissolved in water (30 mL) and then precipitated by addition of an aqueous solution containing Bu_4NBr (0.97 g, 3 mmol). The fine white precipitate recovered after filtration of the solution was dried in vacuo. Yield: 3.1 g (88.7 %). $C_{57.6}H_{134}N_{3.6}Si_5W_{10}O_{40}$ (%): calcd C 19.78, H 3.87, N 1.44, Si 4.01, W 52.58, O 18.29; found C 20.32, H 4.04, N 1.47, Si 4.19, W 53.57, O 16.41; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -124.8$ (s, 4W), -141.8 (s, 2W), -204.0 (d, ^3J(W,H) = 5.8 Hz, 4W); ^{29}Si{^{1}H} NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -84.8$ (s, 1Si; SiO_4), -77.8 (ddd, ^1J(Si,H) = 293.2 Hz, ^3J(Si,H) = 1.3 and 5.3 Hz, ^2J(W,Si) = 14.4 Hz, 4Si; $RSiO_3$); ^{1}H NMR (300.13 MHz, CD_3CN, TMS): $\delta = 4.9$ (s, 1 H); IR (KBr): $\tilde{\nu} = 2181$ (SiH), 1152, 1075, 1001 (SiO), 973 (WO_{ter}), 912, 903, 873, 821, 740 (WO), 556, 541 (SiO), 416, 359 (WO) cm^{-1}.

$(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}(3\text{-}methacryloxypropylSiO)_4]$ (2c): The compound **2c** was prepared similarly to **2a**, using 3-methacryloxypropyltrimethoxysilane (0.94 mL, 4 mmol) instead of trimethoxysilane. Yield: 3.3 g (85.6 %), white microcrystalline powder. $C_{76}H_{153}N_3Si_5W_{10}O_{48}$ (%): calcd C 23.67, H 4.00, N 1.09, Si 3.64, W 47.68, O 19.9; found C 21.37, H 3.65, N 0.89, Si 3.86, W 48.95, O 21.3; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -123.9$ (s, 4W), -145.4 (s, 2W), -212.7 (s, 4W); ^{29}Si {^{1}H} NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -85.3$ (s, 1Si; SiO_4), -61.7 (s, 4Si; $RSiO_3$, ^2J(W,Si) = 15.3 Hz); ^{1}H NMR (300.13 MHz, CD_3CN, TMS): $\delta =$ 6.05 (d, 1 H; HC=), 5.57 (d, 1 H; HC=), 4.09 (m, 2 H; -O-CH_2-), 1.9 (s, 3 H; (H_3C)-C), 1.73 (m, 2 H; -CH_2-), 0.67 (t, 3 H; -CH_2-Si); IR (KBr): $\tilde{\nu} =$ 1200 (CO), 1170 (SiC), 1108, 1081, 1058 (SiO), 1015 (CO), 989 (SiO), 963 (WO_{ter}), 925, 902, 868, 820, 748 (WO), 562, 538 (SiO), 412, 368 (WO) cm^{-1}; MS (MALDI TOF); m/z: exp.: 3856.5 $[M+3\,Bu_4N+2\,H]^+$, 4098.4 $[M+4\,Bu_4N+1\,H]^+$, 4339.9 $[M+5\,Bu_4N]^+$; m/z: calcd: 3856.59 $[M+3\,Bu_4N+2\,H]^+$, 4098.45 $[M+4\,Bu_4N+1\,H]^+$, 4339.91 $[M+5\,Bu_4N]^+$.

$(Bu_4N)_{3.5}H_{0.5}[\gamma\text{-}SiW_{10}O_{36}(PhenylSiO)_4]$ (2d): The compound **2d** was prepared similarly to **2a**, using phenyltrimethoxysilane (0.6 mL, 4 mmol) instead of trimethoxysilane. Yield : 3.2 g (84.7 %), white microcrystalline powder. $C_{80}H_{147}N_{3.5}Si_5W_{10}O_{40}$ (%): calcd C 25.44, H 3.92, N 1.29, Si 3.72, W 48.68, O 16.94; found C 26.38, H 4.08, N 1.15, Si 3.64, W 49.52, O 15.23; ^{183}W NMR (12.5 MHz, DMF/CD_3CN, 300 K, Na_2WO_4): $\delta = -123.5$ (s, 4W), -146.1 (s, 2W), -214.2 (s, 4W); ^{29}Si {^1H} NMR (99.35 MHz, DMF/CD_3CN, 300 K, TMS): $\delta = -84.7$ (s, 1Si; SiO_4), -73.0 (s, $^2J(W,Si) = 17$ Hz, 4Si; $RSiO_3$); ^1H NMR (300.13 MHz, CD_3CN, TMS): $\delta = 7.8$ (t, 1 H), 7.3 (d, 2 H), 7.1 (d, 2 H); IR (KBr): $\tilde{\nu} =$ 1135 (SiC), 1109, 1084, 1054, 998 (SiO), 966 (WO_{ter}), 911, 905, 871, 816, 739 (WO), 697 (C=CH), 551, 539 (SiO), 412, 359 (WO) cm^{-1}.

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