Supporting Online Information

Covalent amphiphilic polyoxometalates for the design of biphasic microemulsion systems

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1. General Methods

All chemicals were purchased from commercial sources and used as received, unless noted otherwise. $K_8[\gamma\text{–}SiW_{10}O_{36}]$[1] and $Na_{10}[\alpha\text{–}SiW_9O_{34}]$[2] were prepared following published procedures and their purities were checked by IR spectroscopy. Infrared spectra were recorded on a Bio-Rad Win-IR FTS 165 FTIR spectrophotometer with compounds sampled in KBr pellets. ^{1}H (300.1 MHz) NMR and ^{31}P $\{^1H\}$ (121.5 MHz) NMR spectra were obtained at room temperature in 5 mm o.d. tubes on a Bruker AvanceII 300 spectrometer equipped with a QNP probehead. ^{29}Si (119.3 MHz) NMR and ^{183}W (25 MHz) NMR spectra were recorded on a Bruker AvanceIII 600 spectrometer equipped with a BBFO or a low-frequency BBO probeheads at room temperature in o.d. 5 mm tubes and 10 mm tubes respectively. ^{31}P–^{183}W $\{^1H\}$ HMQC 1D and 2D experiments were acquired using home modified pulse program on a Bruker Avance II fitted with a triple resonance low-frequency special probehead (BB low γ, ^{31}P and ^{1}H). For ^{1}H, chemical shifts are referenced with respect to tetramethylsilane by using the solvent signals as secondary standard. For ^{31}P $\{^1H\}$, chemical shifts were measured by the substitution method and are given with respect to 85% H_3PO_4. Concerning ^{183}W NMR, the chemical shifts are given with respect to 2M 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 (δ= –103.8). Elemental analyses were performed by the « Service de microanalyses » from the ICSN–CNRS, Gif-sur-Yvette, France. Atomic Absorption Spectroscopy were recorded on a Perkin Elmer Analyst 100 with λ_{Na} = 589 nm and λ_K = 766.5 nm. The mass spectra were recorded on a LTQ-Orbitrap (HRMS) in ESI negative mode. The small angle x-ray scattering experiments, using Mo-radiation (λ=0.71 Å), were performed on a bench built by XENOCS. The scattered beam was recorded using a large online scanner detector (diameter: 345 mm, from MAR Research). A large Q range (3.10^{-2}-2.5Å^{-1}) was covered with an off centre detection. Pre-analysis of data was performed using FIT2D software. The scattered intensities are expressed versus the magnitude of scattering vector *q*. 2mm quartz capillaries were used as sample containers. Usual corrections for background (empty cell and detector noise) subtractions and intensity normalization using Lupolen™ as standard were applied.

2. Preparation and characterization data of the ammonium derivatives

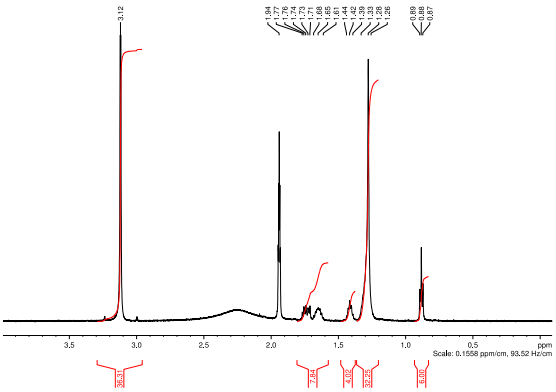
2.1. Amphiphilic hybrids POMs [1(C_n)$_2$] based on $[\gamma\text{–}SiW_{10}O_{36}]^{8-}$

General procedure for the synthesis of $TMA_3K[1\text{–}(C_n)_2]$: NMe_4Br (3.0 mmol) and $C_nH_{2n+1}PO(OH)_2$ (2.0 mmol) were suspended in 40 mL of acetonitrile. $\gamma\text{–}K_8[SiW_{10}O_{36}]$⓬$12H_2O$ (1.0 mmol) and HCl (4.0 mmol diluted in 10 mL of acetonitrile) were successively added under vigourous stirring. The mixture was further stirred at reflux overnight. The white solid was filtered off and volatiles were removed in *vacuo*. The white residue was then dissolved in 5 mL of acetonitrile and precipitated by addition of *ca*. 50 mL of water. The white solid was collected on a sintered glass filter, washed with ethanol (100 mL) and diethyl-ether (100 mL) and finally air-dried, yielding **$TMA_3K[1\text{–}(C_n)_2]$**.

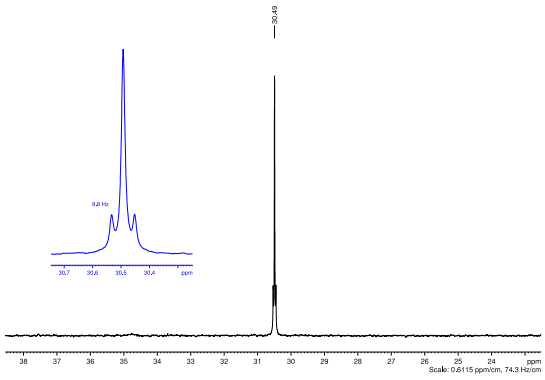
$\gamma\text{–}TMA_3K[SiW_{10}O_{36}(OPC_{12}H_{25})_2]$ ($TMA_3K[1\text{–}(C_{12})_2]$). Yield: 2.2 g (70 %). Elemental analysis calcd (%) for $C_{36}H_{86}KN_3O_{38}P_2SiW_{10}$ (3136.6): C 13.79, H 2.76, N 1.34; found: C 13.70, H 2.76, N 1.47. ^{1}H NMR (600 MHz, CD_3CN, 25°C): δ= 3.12 (s, 36H; NCH_3), 1.77–1.61 (m, 8H; CH_2 from $PC_{12}H_{25}$), 1.44–1.39 (m, 4H ; CH_2 from $PC_{12}H_{25}$), 1.39–1.26 (m, 32H; CH_2 from $PC_{12}H_{25}$), 0.89 (m, 6H; CH_3 from $PC_{12}H_{25}$). ^{31}P $\{^1H\}$ NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.6 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –104.2 (s, 2W), –113.9 (s, 4W), –152.7 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1196 (vw, $\nu_{\square\square}$C), 1060 (w, $\nu_{\square\square}$O), 1033 (w, $\nu_{\square\square}$SiO), 976 (m, $\nu_{\square\square}WO_{ter}$), 945 (s, $\nu_{\square\square}$WOW), 912 (m, $\nu_{\square\square}$WOW), 885 (vs, $\nu_{\square\square}$WOW), 837 (m, $\nu_{\square\square}$WOW), 747 (vs, $\nu_{\square\square}$WOW), 526 (m, $\delta_{\square\square}$SiO), 415 (w, $\delta_{\square\square}$WOW), 363 (m, $\delta_{\square\square}$WOW), 335 (w, $\delta_{\square\square}$WOW) cm^{-1}. HRMS (ESI): *m*/*z* (%): $\{H[1\text{–}(C_{12})_2]\}^{3-}$ 958.54 (100); $\{TMAH[1\text{–}(C_{12})_2]\}^{2-}$ 1474.35 (10).

γ–$TMA_3K[SiW_{10}O_{36}(OPC_{10}H_{21})_2]$ ($TMA_3K[1–(C_{10})_2]$). Yield: 2.04 g (66 %). Elemental analysis calcd (%) for $C_{32}H_{78}KN_3O_{38}P_2SiW_{10}$ (3080.5): C 12.48, H 2.55, N 1.36; found: C 12.35, H 2.53, N 1.16. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 3.12 (s, 36H; NCH_3), 1.77–1.59 (m, 8H; CH_2 from $PC_{10}H_{21}$), 1.44–1.39 (m, 4H ; CH_2 from $PC_{10}H_{21}$), 1.39–1.26 (m, 24H; CH_2 from $PC_{10}H_{21}$), 0.88 (m, 6H; CH_3 from $PC_{10}H_{21}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.7 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –104.4 (s, 2W), –113.9 (s, 4W), –152.9 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1195 (vw, $\nu_{□□}$□C), 1062 (w, $\nu_{□□}$□O), 1010 (w, $\nu_{□□}$SiO), 974 (m, $\nu_{□□}WO_{ter}$), 945 (m, $\nu_{□□}$WOW), 912 (m, $\nu_{□□}$WOW), 883 (s, $\nu_{□□}$WOW), 835 (m, $\nu_{□□}$WOW), 745 (vs, $\nu_{□□}$WOW), 523 (m, $\delta_{□□}$SiO), 412 (w, $\delta_{□□}$WOW), 363 (m, $\delta_{□□}$WOW), 334 (w, $\delta_{□□}$WOW) cm^{-1}. HRMS (ESI): *m/z* (%): $\{H[1–(C_{10})_2]\}^{3–}$ 939.51 (100); $\{TMAH[1–(C_{10})_2]\}^{2–}$ 1446.82 (10).

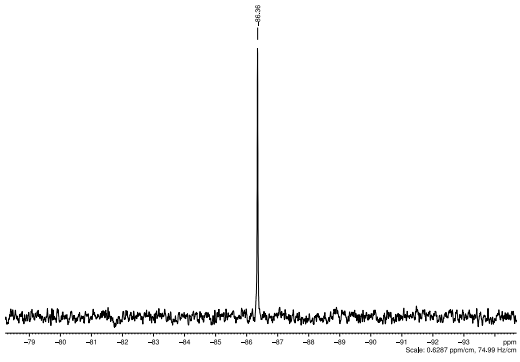
γ–$TMA_3K[SiW_{10}O_{36}(OPC_8H_{17})_2]$ ($TMA_3K[1–(C_8)_2]$). Yield: 1.9 g (63 %). Elemental analysis calcd (%) for $C_{28}H_{70}KN_3O_{38}P_2SiW_{10}$ (3024.4): C 11.12, H 2.33, N 1.39; found: C 11.40, H 2.38, N 1.68. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 3.12 (s, 36H; NCH_3), 1.77–1.59 (m, 8H; CH_2 from PC_8H_{17}), 1.44–1.39 (m, 4H ; CH_2 from PC_8H_{17}), 1.39–1.26 (m, 16H; CH_2 from PC_8H_{17}), 0.88 (m, 6H; CH_3 from PC_8H_{17}). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.7 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –104.4 (s, 2W), –113.9 (s, 4W), –152.9 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1191 (vw, $\nu_{□□}$□C), 1060 (w, $\nu_{□□}$□O), 1009 (w, $\nu_{□□}$SiO), 975 (m, $\nu_{□□}WO_{ter}$), 945 (m, $\nu_{□□}$WOW), 912 (m, $\nu_{□□}$WOW), 884 (s, $\nu_{□□}$WOW), 835 (m, $\nu_{□□}$WOW), 750 (vs, $\nu_{□□}$WOW), 524 (m, $\delta_{□□}$SiO), 413 (w, $\delta_{□□}$WOW), 364 (m, $\delta_{□□}$WOW), 334 (w, $\delta_{□□}$WOW) cm^{-1}. HRMS (ESI): *m/z* (%): $\{H[1–(C_8)_2]\}^{3–}$ 921.49 (100); $\{TMAH[1–(C_8)_2]\}^{2–}$ 1419.3 (10).



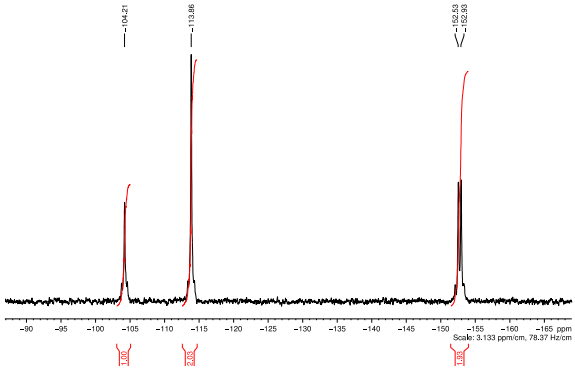
^{1}H NMR (CD_3CN)



^{31}P {^{1}H} NMR (CD_3CN)



^{29}Si NMR (CD_3CN)



^{183}W NMR (CH_3CN/CD_3CN)

Fig S1. ^{1}H, ^{31}P {^{1}H}, ^{183}W and ^{29}Si NMR patterns of the $TMA_3K[\gamma–SiW_{10}O_{36}(OPC_{12}H_{21})_2]$ hybrid POM.

2.2. Amphiphilic hybrids POMs [1(C_n)$_2$] based on [αA−SiW_9O_{34}]$^{10-}$

General procedure for the synthesis of $TMA_{2.5}Na_{3.5}$[2–(C_n)$_2$]: NMe_4Br (3.0 mmol), $C_nH_{2n+1}PO(OH)_2$ (2.0 mmol) and $Na_{10}[SiW_9O_{34}]$ (1.0 mmol) were suspended in 25 mL of N,N-dimethylformamide. HCl (4.0 mmol, 4 M) was added dropwise under vigourous stirring. The mixture was further stirred at 100°C overnight. The white solid was filtered off, the solution was concentrated under reduced pressure and the product was precipitated by adding 250 mL of diethyl-ether. The white residue was then dissolved in 50 mL of acetonitrile, filtrated and the solvent was evaporated. The white solid was collected on a sintered glass filter, washed with diethyl-ether (100 mL) and finally air-dried, yielding **$TMA_{2.5}Na_{3.5}$ [2–(C_n)$_2$]**.
The number of the alkali counterions for each sample was assessed by atomic absorption spectroscopy.

$TMA_{2,5}Na_{3,5}[SiW_9O_{34}(OPC_{12}H_{25})_2]$●0.5DMF ($TMA_{2,5}Na_{3,5}$[2–($C_{12}$)$_2$]). Yield: 2.06 g (70 %). Elemental analysis calcd (%) for $C_{35.5}H_{83.5}N_3Na_{3.5}O_{36.5}P_2SiW_9$ (2961.6): C 14.40, H 2.84, N 1.42; found: C 14.37, H 2.90, N 1.42. ^{1}H NMR (600 MHz, CD_3CN, 25°C): δ= 7.96 (s, 0.5H; C(O)H from DMF), 3.22 (s, 30H; NCH_3 from TMA), 2.92 (s, 1.5H; NCH_3 from DMF), 2.80 (s, 1.5H ; NCH_3 from DMF), 1.80–1.55 (m, 8H; CH_2 from $PC_{12}H_{25}$), 1.50–1.20 (m, 36H; CH_2 from $PC_{12}H_{25}$), 0.88 (m, 6H; CH_3 from $PC_{12}H_{25}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.84 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –84,55 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –14.2 (1W), –88.5 (2W), –154.7 (2W), –163.6 (2W), –180.0 (2W). (KBr) : ν= 1151 (m), 949 (s), 917 (s), 878 (s), 738 (s), 563 (m), 521 (m), 472 (w), 417 (w), 367 (m), 334 (m) cm^{-1}.

$TMA_{2,5}Na_{3,5}[SiW_9O_{34}(OPC_{10}H_{21})_2]$●0.5DMF ($TMA_{2,5}Na_{3,5}$[2–($C_{10}$)$_2$]). Yield: 2.25 g (78 %). Elemental analysis calcd (%) for $C_{31.5}H_{75.5}N_3Na_{3.5}O_{36.5}P_2SiW_9$ (2905.5): C 13.02, H 2.62, N 1.45; found: C 12.99, H 2.68, N 1.44. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 7.96 (s, 0.5H; C(O)H from DMF), 3.22 (s, 30H; NCH_3 from TMA), 2.92 (s, 1.5H; NCH_3 from DMF), 2.80 (s, 1.5H ; NCH_3 from DMF), 1.80–1.55 (m, 8H; CH_2 from $PC_{10}H_{21}$), 1.50–1.20 (m, 28H; CH_2 from $PC_{10}H_{21}$), 0.88 (m, 6H; CH_3 from $PC_{10}H_{21}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.2. ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –84.3 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –14.2 (1W), –89.4 (2W), –158.9 (2W), –163.8 (2W), –179.4 (2W). IR (KBr) : ν= 1151 (m), 950 (s), 919 (s), 878 (s), 738 (s), 563 (m), 521 (m), 472 (w), 416 (w), 367 (m), 334 (m) cm^{-1}.

$TMA_{2,5}Na_{3,5}[SiW_9O_{34}(OPC_8H_{17})_2]$●0.5DMF ($TMA_{2,5}Na_{3,5}$[2–($C_8$)$_2$]). Yield: 1.73 g (61 %). Elemental analysis calcd (%) for $C_{27.5}H_{67.5}N_3Na_{3.5}O_{36.5}P_2SiW_9$ (2849.4): C 11.59, H 2.39, N 1.47; found: C 11.52, H 2.44, N 1.47. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 7.96 (s, 0.5H; C(O)H from DMF), 3.22 (s, 30H; NCH_3 from TMA), 2.92 (s, 1.5H; NCH_3 from DMF), 2.80 (s, 1.5H ; NCH_3 from DMF), 1.80–1.55 (m, 8H; CH_2 from PC_8H_{17}), 1.50–1.20 (m, 20H; CH_2 from PC_8H_{17}), 0.88 (m, 6H; CH_3 from PC_8H_{17}). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.3. ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –84.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –18.7 (1W), –95.8 (2W), –160.0 (2W), –161.0 (2W), –183.6 (2W). IR (KBr) : ν= 1148 (m), 949 (s), 881 (s), 845 (s), 737 (s), 562 (m), 521 (m), 472 (w), 367 (m), 334 (m) cm^{-1}.

3. Preparation and characterization data of the alkaline derivatives

3.1. Using cationic exchange methods for the [1(C_n)$_2$] derivatives

General procedure for the cation exchanges:
H^+ can be a substitute for TMA^+ thanks to the use of a cation-exchange resin Dowex 50WX8-100 (purchased from Alfa Aesar). In a typical experiment, **$TMA_3K[1–(C_{12})_2]$** (0.89 g, 0.284 mmol) was dissolved in 15 mL of acetonitrile and *ca.* 10 mL (ie 17 millieq.) of the wet acidic resin were added to this solution. Monitoring of the methyl signal from TMA^+ by ^{1}H NMR allows us to observe a complete exchange for TMA^+ after two hours. The resin was filtered on a sintered glass filter and washed with acetonitrile. The formulation **$H_4[1–(C_{12})_2]$** was assigned on the basis of ^{31}P {^{1}H} NMR and ESI-MS analysis of the obtained solution (see below) since testing of product recovery by solvent evaporation has always led to a partial degradation.

The proton counterions can be further replaced with sodium or potassium using a saturated NaCl or KCl aqueous solution. In a typical experiment, an acetonitrile solution of **$H_4[1–(C_{12})_2]$** (37 mL, 0.28 mmol) was poured in *ca.* 150 mL of a saturated NaCl aqueous solution. After one night under stirring, the two phases were separated. The aqueous has become acidic (1<pH<2). Volatiles of the organic phase were removed *in vacuo* to give a white residue that was dissolved again in a few mL of acetonitrile. Some residual NaCl salts were filtered off and the solution was evaporated to dryness to give **$Na_{3-x}H_{1+x}[1–(C_{12})_2]$** (0.76 g, 90 %). The number of alkali counterions for each sample was assessed by atomic absorption spectroscopy.

$H_4[\gamma$–$SiW_{10}O_{36}(OPC_{12}H_{25})_2]$ ($H_4[1–(C_{12})_2]$). ^{31}P {^{1}H} NMR (121.5 MHz, CH_3CN/CD_3CN, 25°C): δ= 30.6 (^2J(W,P)= 10 Hz). HRMS (ESI): *m*/*z* (%): $\{H[1–(C_{12})_2]\}^{3–}$ 958.54 (100); $\{H_2[1–(C_{12})_2]\}^{2–}$ 1438.81 (35).

$H_4[\gamma$–$SiW_{10}O_{36}(OPC_{10}H_{21})_2]$ ($H_4[1–(C_{10})_2]$). ^{31}P {^{1}H} NMR (121.5 MHz, CH_3CN/CD_3CN, 25°C): δ= 30.7 (^2J(W,P)= 10 Hz). HRMS (ESI): *m*/*z* (%): $\{H[1–(C_{10})_2]\}^{3–}$ 939.52 (100); $\{H_2[1–(C_{10})_2]\}^{2–}$ 1410.28 (50).

$H_4[\gamma$–$SiW_{10}O_{36}(OPC_8H_{17})_2]$ ($H_4[1–(C_8)_2]$). ^{31}P {^{1}H} NMR (121.5 MHz, CH_3CN/CD_3CN, 25°C): δ= 30.7 (^2J(W,P)= 10 Hz). HRMS (ESI): *m*/*z* (%): $\{H[1–(C_8)_2]\}^{3–}$ 921.50 (100); $\{H_2[1–(C_8)_2]\}^{2–}$ 1382.76 (50).

$Na_{2.6}H_{1.4}[\gamma$–$SiW_{10}O_{36}(OPC_{12}H_{25})_2]$❿$3H_2O$ ($Na_{2,6}H_{1,4}[1–(C_{12})_2]$). Elemental analysis calcd (%) for $C_{24}H_{57.4}Na_{2.6}O_{41}P_2SiW_{10}$ (2990.3): C 9.64, H 1.93; found: C 9.70, H 2.01. ^{1}H NMR (600 MHz, CD_3CN, 25°C): δ= 1.77–1.61 (m, 8H; CH_2 from $PC_{12}H_{25}$), 1.44–1.39 (m, 4H ; CH_2 from $PC_{12}H_{25}$), 1.39–1.26 (m, 32H; CH_2 from $PC_{12}H_{25}$), 0.89 (m, 6H; CH_3 from $PC_{12}H_{25}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.6 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –108.1 (s, 2W), –119.7 (s, 4W), –156.3 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : *ν*= 1176 (vw, $\nu_{□□}$□C), 1068 (w, $\nu_{□□}$□O), 1035 (w, $\nu_{□□}$SiO), 977 (m, $\nu_{□□}WO_{ter}$), 945 (m, $\nu_{□□}$WOW), 918 (m, $\nu_{□□}$WOW), 884 (s, $\nu_{□□}$WOW), 836 (m, $\nu_{□□}$WOW), 752 (vs, $\nu_{□□}$WOW), 526 (m, $\delta_{□□}$SiO), 410 (w, $\delta_{□□}$WOW), 352 (m, $\delta_{□□}$WOW), 334 (w, $\delta_{□□}$WOW) cm^{-1}.

$Na_{2.6}H_{1.4}[\gamma$–$SiW_{10}O_{36}(OPC_{10}H_{21})_2]$❿$6H_2O$ ($Na_{2,6}H_{1,4}[1–(C_{10})_2]$). Elemental analysis calcd (%) for $C_{20}H_{55.4}Na_{2.6}O_{44}P_2SiW_{10}$ (2988.2): C 8.04, H 1.87; found: C 8.03, H 2.04. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 1.77–1.59 (m, 8H; CH_2 from $PC_{10}H_{21}$), 1.44–1.39 (m, 4H ; CH_2 from $PC_{10}H_{21}$), 1.39–1.26 (m, 24H; CH_2 from $PC_{10}H_{21}$), 0.88 (m, 6H; CH_3 from $PC_{10}H_{21}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.6 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –107.3 (s, 2W), –118.7 (s, 4W), –155.5 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : *ν*= 1176 (vw, $\nu_{□□}$□C), 1067 (w, $\nu_{□□}$□O), 1035 (w, $\nu_{□□}$SiO), 977 (m, $\nu_{□□}WO_{ter}$), 944 (m, $\nu_{□□}$WOW), 918 (m, $\nu_{□□}$WOW), 884 (s, $\nu_{□□}$WOW), 835 (m, $\nu_{□□}$WOW),

750 (vs, νWOW), 526 (m, δSiO), 410 (w, δWOW), 358 (m, δWOW), 334 (w, δWOW) cm^{-1}.

$Na_{2.6}H_{1.4}[\gamma$-$SiW_{10}O_{36}(OPC_8H_{17})_2]$❿$3H_2O$ ($Na_{2,6}H_{1,4}[1$-$(C_8)_2]$). Elemental analysis calcd (%) for $C_{16}H_{41.4}Na_{2.6}O_{41}P_2SiW_{10}$ (2878.1): C 6.68, H 1.45; found: C 6.62, H 1.69. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 1.77–1.59 (m, 8H; CH_2 from PC_8H_{17}), 1.44–1.39 (m, 4H ; CH_2 from PC_8H_{17}), 1.39–1.26 (m, 16H; CH_2 from PC_8H_{17}), 0.88 (m, 6H; CH_3 from PC_8H_{17}). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.6 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.4 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –107.7 (s, 2W), –119.1 (s, 4W), –155.7 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1178 (vw, ν□□□C), 1066 (w, ν□□□O), 1036 (w, ν□□SiO), 977 (m, ν□□WO_{ter}), 945 (m, ν□□WOW), 919 (m, ν□□WOW), 884 (s, ν□□WOW), 836 (m, ν□□WOW), 751 (vs, ν□□WOW), 522 (m, δ□□SiO), 410 (w, δ□□WOW), 358 (m, δ□□WOW), 334 (w, δ□□WOW) cm^{-1}.

$K_3H[\gamma$-$SiW_{10}O_{36}(OPC_{12}H_{25})_2]$ ($K_3H[1$-$(C_{12})_2]$). Elemental analysis calcd (%) for $C_{24}H_{51}K_3O_{38}P_2SiW_{10}$ (2993.4): C 9.63, H 1.72; found: C 9.65, H 1.71. ^{1}H NMR (600 MHz, CD_3CN, 25°C): δ= 1.77–1.61 (m, 8H; CH_2 from $PC_{12}H_{25}$), 1.44–1.39 (m, 4H ; CH_2 from $PC_{12}H_{25}$), 1.39–1.26 (m, 32H; CH_2 from $PC_{12}H_{25}$), 0.89 (m, 6H; CH_3 from $PC_{12}H_{25}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 31,1 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.2 (SiO_4). ^{183}W NMR (12.5 MHz, CH_3CN/CD_3CN, 25°C): δ= –108.1 (s, 2W), –119.7 (s, 4W), –155.3 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1180 (vw, ν□□□C), 1070 (w, ν□□□O), 1033 (w, ν□□SiO), 975 (m, ν□□WO_{ter}), 946 (s, ν□□WOW), 918 (m, ν□□WOW), 886 (vs, ν□□WOW), 834 (m, ν□□WOW), 744 (vs, ν□□WOW), 521 (m, δ□□SiO), 410 (w, δ□□WOW), 359 (m, δ□□WOW), 334 (w, δ□□WOW) cm^{-1}.

$K_3H[\gamma$-$SiW_{10}O_{36}(OPC_{10}H_{21})_2]$ ($K_3H[1$-$(C_{10})_2]$). Elemental analysis calcd (%) for $C_{20}H_{43}K_3O_{38}P_2SiW_{10}$ (2937.3): C 8.18, H 1.48; found: C 8.17, H 1.67. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 1.77–1.59 (m, 8H; CH_2 from $PC_{10}H_{21}$), 1.44–1.39 (m, 4H ; CH_2 from $PC_{10}H_{21}$), 1.39–1.26 (m, 24H; CH_2 from $PC_{10}H_{21}$), 0.88 (m, 6H; CH_3 from $PC_{10}H_{21}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 31.3 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.3 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –107.3 (s, 2W), –118.7 (s, 4W), –155.5 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1165 (vw, ν□□□C), 1062 (w, ν□□□O), 1030 (w, ν□□SiO), 972 (m, ν□□WO_{ter}), 948 (s, ν□□WOW), 925 (m, ν□□WOW), 884 (vs, ν□□WOW), 744 (vs, ν□□WOW), 520 (m, δ□□SiO), 412 (w, δ□□WOW), 360 (m, δ□□WOW), 334 (w, δ□□WOW) cm^{-1}.

$K_3H[\gamma$-$SiW_{10}O_{36}(OPC_8H_{17})_2]$ ($K_3H[1$-$(C_8)_2]$). Elemental analysis calcd (%) for $C_{16}H_{35}K_3O_{38}P_2SiW_{10}$ (2881.1): C 6.67, H 1.22; found: C 6.83, H 1.41. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 1.77–1.59 (m, 8H; CH_2 from PC_8H_{17}), 1.44–1.39 (m, 4H ; CH_2 from PC_8H_{17}), 1.39–1.26 (m, 16H; CH_2 from PC_8H_{17}), 0.88 (m, 6H; CH_3 from PC_8H_{17}). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 31.3 (^2J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –86.3 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –107.7 (s, 2W), –119.1 (s, 4W), –155.7 (d, ^2J(W,P)= 10 Hz, 4W). IR (KBr) : ν= 1166 (vw, ν□□□C), 1062 (w, ν□□□O), 1032 (w, ν□□SiO), 975 (m, ν□□WO_{ter}), 949 (s, ν□□WOW), 923 (m, ν□□WOW), 885 (vs, ν□□WOW), 748 (vs, ν□□WOW), 523 (m, δ□□SiO), 412 (w, δ□□WOW), 362 (m, δ□□WOW), 334 (w, δ□□WOW) cm^{-1}.

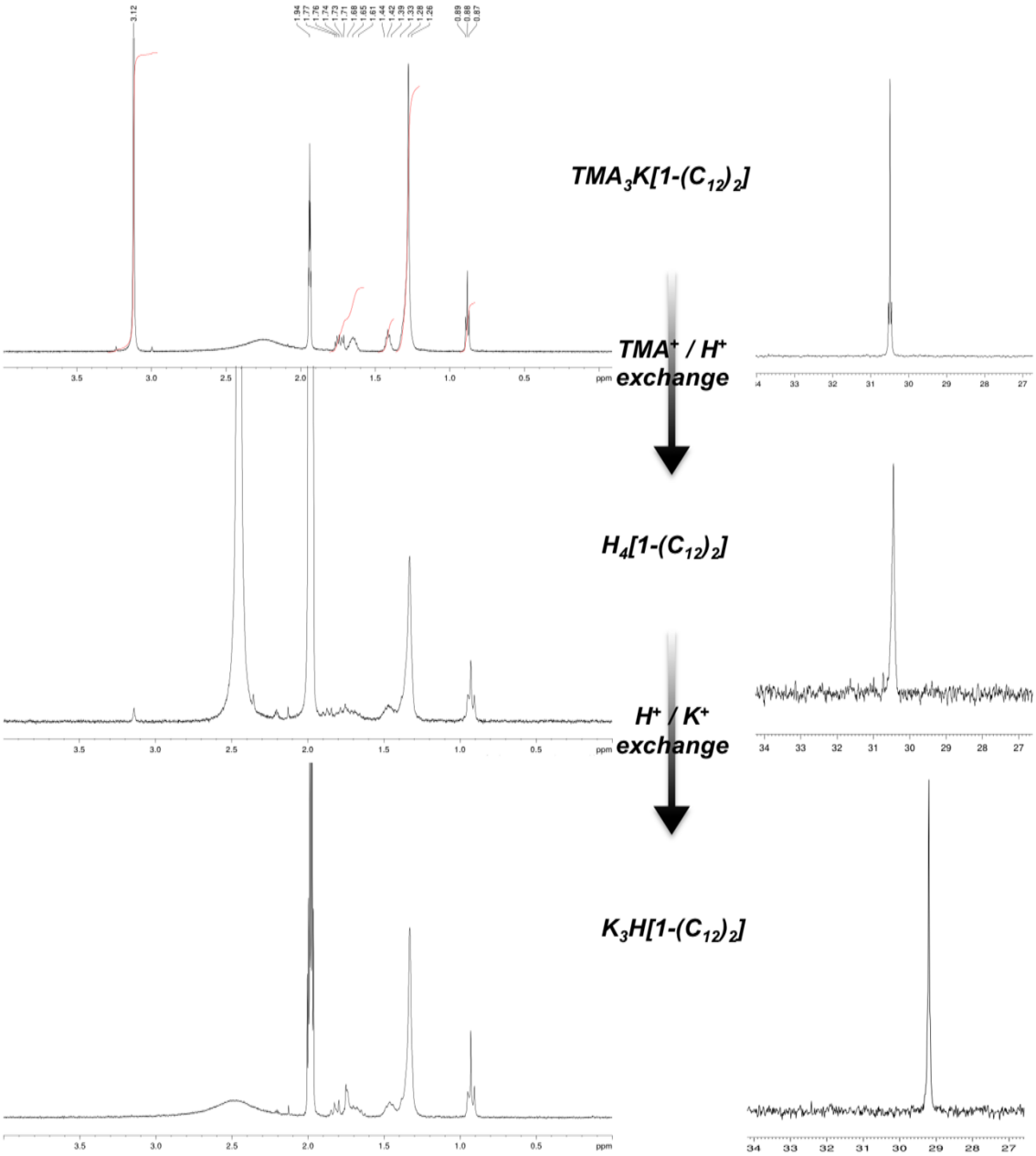


Fig S2. ^{1}H (left) and ^{31}P $\{^{1}H\}$ (right) NMR monitoring of the cation exchange for TMA in the case of $TMA_3K[\gamma\text{-}SiW_{10}O_{36}(OPC_{12}H_{21})_2]$

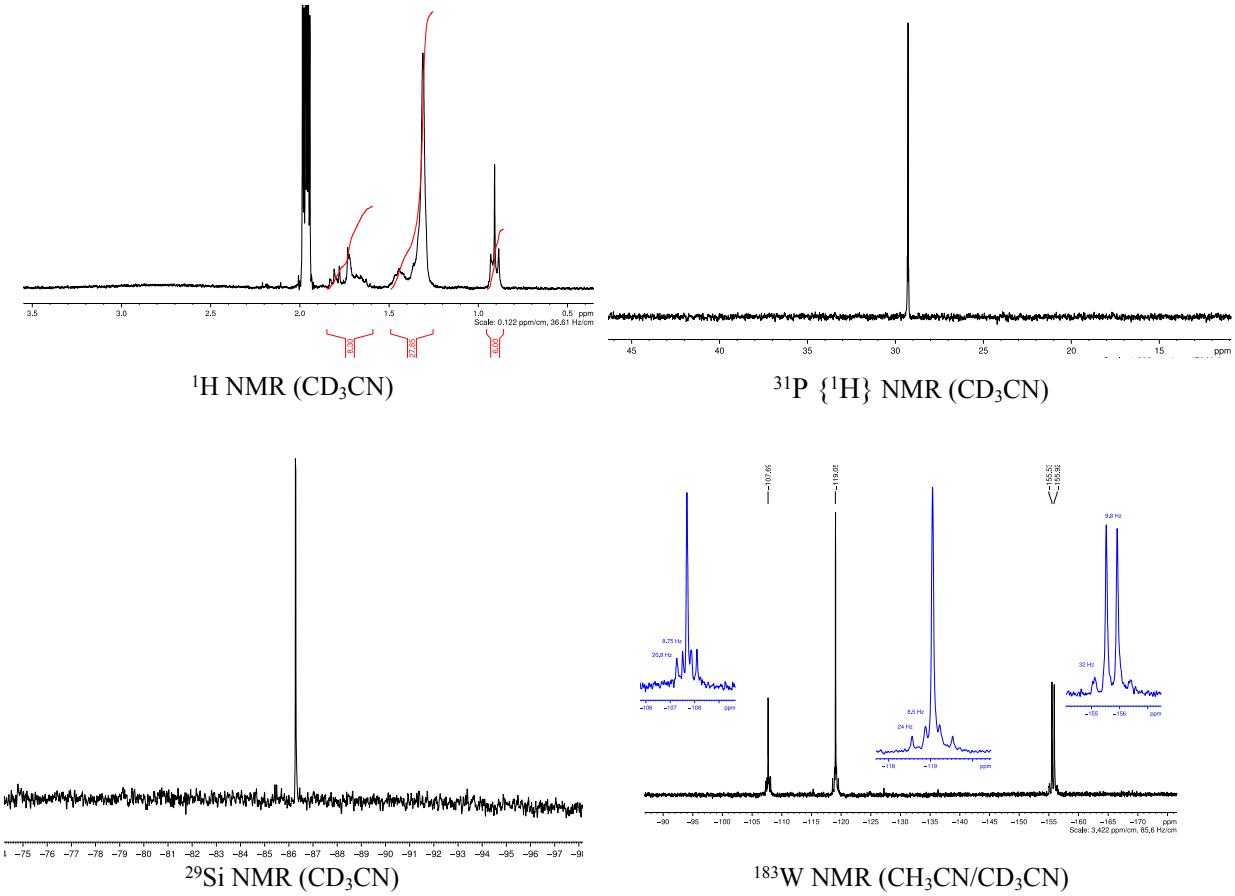


Fig S3. ^{1}H, ^{31}P {^{1}H}, ^{183}W and ^{29}Si NMR patterns of the $K_3H[\gamma\text{–}SiW_{10}O_{36}(OPC_{12}H_{21})_2]$ hybrid POM

3.2. In a direct synthetic pathway for the $[2(C_n)_2]$ compounds

General procedure for the synthesis of Na_6–$[2–(C_n)_2]$: $C_nH_{2n+1}PO(OH)_2$ (2.0 mmol) and $Na_{10}[SiW_9O_{34}]$ (1.0 mmol) were suspended in 25 mL of N,N-dimethylformamide. HCl (4.0 mmol, 4 M) was added dropwise under vigourous stirring. The mixture was further stirred at 100°C overnight. The white solid was filtered off, the solution was concentrated under reduced pressure and adding 250 mL of a saturated NaCl aqueous solution precipitated the product. The white residue was then dissolved in 50 mL of acetonitrile, filtrated and the solvent was evaporated. The white solid was collected on a sintered glass filter, washed with diethyl-ether (100 mL) and finally air-dried, yielding **$Na_6[2–(C_n)_2]$**.

$Na_6[SiW_9O_{34}(OPC_{12}H_{25})_2]$·4.5DMF ($Na_6[2–(C_{12})_2]$). Yield: 1.55 g (55 %). Elemental analysis calcd (%) for $C_{37.5}H_{81.5}N_{4.5}Na_6O_{40.5}P_2SiW_9$ (3126.1): C 14.41, H 2.63, N 2.02; found: C 14.00, H 2.54, N 1.81. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 7.96 (s, 4.5H; C(O)H from DMF), 2.92 (s, 13.5H; NCH_3 from DMF), 2.80 (s, 13.5H; NCH_3 from DMF), 1.80–1.55 (m, 8H; CH_2 from $PC_{12}H_{25}$), 1.50–1.20 (m, 36H; CH_2 from $PC_{12}H_{25}$), 0.88 (m, 6H; CH_3 from $PC_{12}H_{25}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 32.89 (^{2}J(W,P)= 10 Hz). ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –85.02 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –21.8 (1W), –99.5 (2W), –157.7 (2W), –170.9 (2W), –180.0 (2W). IR (KBr) : ν= 1231 (w), 1163 (m), 1040 (m), 953 (s), 880 (s), 737 (s), 624 (m), 561 (m), 519 (m), 474 (w), 365 (m), 321 (m) cm^{-1}. HRMS (ESI): *m/z* (%):$\{Na_2[2–(C_{12})_2]\}^{4–}$ 677.66 (100); $\{Na_2H[2–(C_{12})_2]\}^{3–}$ 904.24 (50); $\{Na_3[2–(C_{12})_2]\}^{3–}$ 911.57 (95).

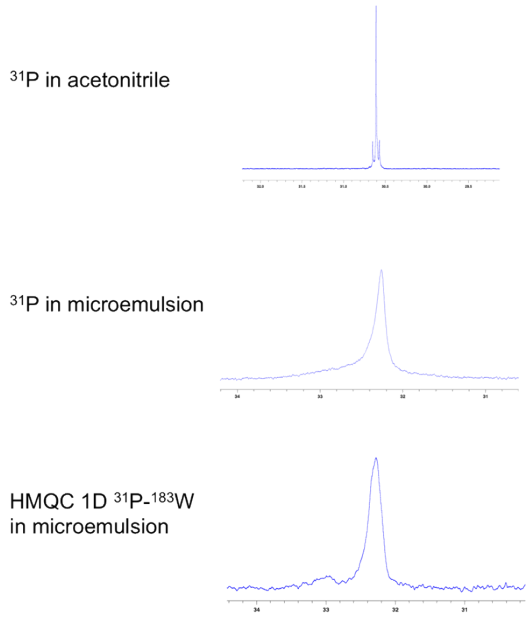
$Na_6[SiW_9O_{34}(OPC_{10}H_{21})_2]$·4DMF ($Na_6$–[2–$(C_{10})_2$]). Yield: 0.8 g (30 %). Elemental analysis calcd (%) for $C_{33.5}H_{73.5}N_{4.5}Na_6O_{40.5}P_2SiW_9$ (3033.4): C 12.67, H 2.33, N 1.85; found: C 12.22, H 2.24, N 1.64. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 7.96 (s, 4.0H; C(O)H from DMF), 2.92 (s, 12H; NCH_3 from DMF), 2.80 (s, 12H; NCH_3 from DMF), 1.80–1.55 (m, 8H; CH_2 from $PC_{10}H_{21}$), 1.50–1.20 (m, 28H; CH_2 from $PC_{10}H_{21}$), 0.88 (m, 6H; CH_3 from $PC_{10}H_{21}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 33.38. ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –84.87 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –21.1 (1W), –99.3 (2W), –157.7 (2W), –170.6 (2W), –180.1 (2W). IR (KBr) : *ν*= 1232 (w), 1162 (m), 1089 (w), 1038 (m), 952 (s), 882 (s), 735 (s), 624 (w), 561 (m), 519 (m), 471 (w), 365 (m), 322 (m) cm^{-1}. HRMS (ESI): *m*/*z* (%): $\{Na_2[2–(C_{10})_2]\}^{4–}$ 663.63 (90); $\{Na_2H[2–(C_{10})_2]\}^{3–}$ 885.53 (50); $\{Na_3[2–(C_{10})_2]\}^{3–}$ 892.20 (100).

$Na_6[SiW_9O_{34}(OPC_8H_{17})_2]$·2.5DMF ($Na_6$–[2–$(C_8)_2$]). Yield: 1.4 g (51 %). Elemental analysis calcd (%) for $C_{23.5}H_{51.5}N_{2.5}Na_6O_{38.5}P_2SiW_9$ (2868.7): C 9.84, H 1.81, N 1.22; found: C 10.34, H 1.91, N 1.45. ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 7.96 (s, 2.5H; C(O)H from DMF), 2.92 (s, 7.5H; NCH_3 from DMF), 2.80 (s, 7.5H; NCH_3 from DMF), 1.80–1.55 (m, 8H; CH_2 from PC_8H_{17}), 1.50–1.20 (m, 20H; CH_2 from PC_8H_{17}), 0.88 (m, 6H; CH_3 from PC_8H_{17}). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 30.9. ^{29}Si NMR (119.3 MHz, CD_3CN, 25°C): δ= –85.12 (SiO_4). ^{183}W NMR (25 MHz, CH_3CN/CD_3CN, 25°C): δ= –20.9 (1W), –99.4 (2W), –157.0 (2W), –170.7 (2W), –180.1 (2W). IR (KBr) : *ν*= 1162 (m), 879 (s), 799 (s), 737 (s), 624 (w), 520 (m), 366 (m), 334 (m), 322 (m) cm^{-1}. HRMS (ESI): *m*/*z* (%): $\{Na_2[2–(C_8)_2]\}^{4–}$ 649.61 (100); $\{Na_2H[2–(C_8)_2]\}^{3–}$ 866.17 (40); $\{Na_3[2–(C_8)_2]\}^{3–}$ 873.51 (95).

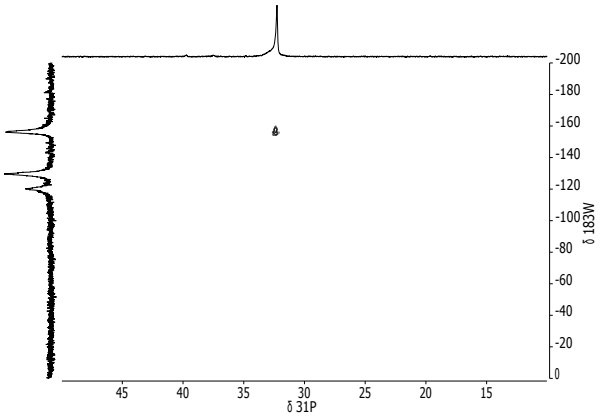
4. Preparation and characterization data of the Winsor I microemulsion system.

In a small glass vessel, 200 mg of $K_3H[\gamma\text{-}SiW_{10}O_{36}(C_{12}H_{25}PO)_2]$ are dispersed in 0.4 mL of distilled water. After adding 0.4 mL of methyl *tert*-butyl ether (or diethyl ether) and gentle agitation (by hands), the mixture becomes transparent and separate into two phases of different volumes within a few seconds. The volume of the upper etherated phase is *ca*. 0.20 mL and the lower microemulsion phase *ca*. 0.60 mL.
After one hour, aliquots of each phase (50µL) were diluted in CD_3CN and analysed by ^{1}H and ^{31}P {^{1}H} NMR spectroscopy. In the upper phase *i.e.* the organic phase, only the two singlets corresponding to methyl *tert*-butyl ether are observed, while in the lower phase, *i.e.* the µem, the presence of $K_3H[1\text{-}(C_{12})_2]$ is confirmed by similar proton and phosphorus NMR patterns than in the original compound: ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ= 3.15 (s, 50H; CH_3 from MTBE), 2.76 (s, 594H; H_2O), 1.85–1.55 (m, 8H; CH_2 from $PC_{12}H_{25}$), 1.50–1.20 (m, 36H; CH_2 from $PC_{12}H_{25}$), 1.16 (s, 150H, ^{t}Bu from MTBE), 0.88 (m, 6H; CH_3 from $PC_{12}H_{25}$). ^{31}P {^{1}H} NMR (121.5 MHz, CD_3CN, 25°C): δ= 29.2 (^2J(W,P)= 10 Hz).

A Winsor I µem system was also successfully prepared from a mixture of methyl *tert*-butyl ether and D_2O. This allows characterizing the POM inside the µem itself by NMR spectroscopy. ^{31}P {^{1}H} NMR (300 MHz, D_2O/MTBE, 25°C): δ= 31.2 (brs). Because of the broad signal observed by ^{31}P {^{1}H} NMR, and because of the impossibility to observe the phosphorus-tungstene coupling, 1D and 2D ^{31}P-^{183}W {^{1}H} HMQC experiments were runned to ensure that the phosphorus atom is still bonded to the POM framework (see FigS4)



Monitoring of $K_3H[1\text{-}(C_{12})_2]$ by ^{31}P $\{^1H\}$ and 1D ^{31}P – ^{183}W $\{^1H\}$ HMQC in the WI type microemulsion.



2D ^{31}P – ^{183}W $\{^1H\}$ HMQC analysis of $K_3H[1\text{-}(C_{12})_2]$ in the WI type microemulsion; X-axis : ^{31}P $\{^1H\}$ NMR (D_2O/MTBE) ; Y-axis : ^{183}W NMR spectrum in microemulsion.

Fig S4. ^{31}P $\{^1H\}$ NMR and 1D and 2D ^{31}P–^{183}W $\{^1H\}$ HMQC for $K_3H[\gamma\text{–}SiW_{10}O_{36}(OPC_{12}H_{21})_2]$ in the microemulsion phase

Fitting of the microemulsion SWAXS spectrum

The Winsor I microemulsion corresponds to droplets of ether dispersed in a continuous aqueous medium. The ether droplets are stabilized by the amphiphilic POMs that are present at the ether/water interface. Some amphiphilic POMs can be present in the surrounding aqueous medium as monomers i.e. not at the ether/water interface and not present in an aggregated form. Consequently the X-ray scattered intensity of the diethylether WI microemulsion shown in Fig. 3 was modelled by using a spherical core-shell model for the micelles and a spherical model for the amphiphilic POMs dispersed in water as monomer. The scattered intensity was assumed to be the sum of the monomeric amphiphilic POM and the micelles contributions as:

$$I(q) = A \times P_{POM}(q) + B \times P_{micelle}(q) S_{micelle}(q) + I_b$$

where A and B are scaling factors, I_b is a background contribution, $P(q)$ and $S(q)$ are the form factor for a sphere and structure factor respectively. For the POM a spherical shape was considered with a radius of 0.46 nm. A core-shell structure has to be considered for micelles to take into account for the high contrast, i.e. scattering length density difference (SLD), between the core (SLD_{core}) and the shell (SLD_{shell}) of the microemulsion droplets and the surrounding medium (SLD_{water}) respectively composed of the solubilized ether, the polar head (POM) of the surfactant and water. The two contrasts considered here in the model are calculated from molecular volumes and chemical compositions: (SLD_{POM}-SLD_{water}) = 4.3 10^{-3} nm^{-2} and (SLD_{ether}-SLD_{water}) = 6.88 10^{-4} - 9.36 10^{-4} = 2.53 10^{-4} nm^{-2}.

Interparticular interactions were only considered between micelles not between POMs. The structure factor, that takes into account intermicellar interactions, could be well described by a hard sphere model for which an analytical expression for S(q) exists in the Percus-Yevick approximation which

has been shown to be reliable for many systems.[3] The fits were performed using the data analysis software Sasfit 0.92.3.
The fitting of the SWAXS spectrum was done in the small angle limit of the spectrum i.e. for $q < 8$ nm^{-1}. The radii of the core (ether droplets) and the thickness of the shell obtained from the fitting procedure are 2.5 nm and 0.9 nm. The thickness corresponds perfectly to the size of the POM confirming the validity of the core-shell model used here.

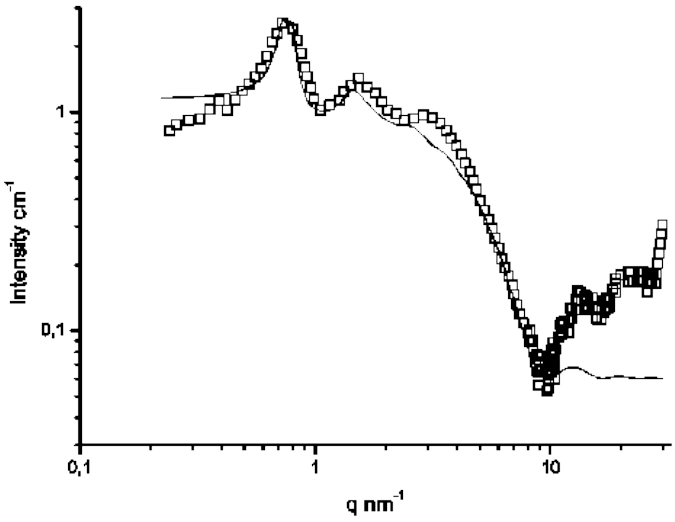
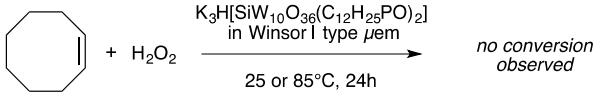


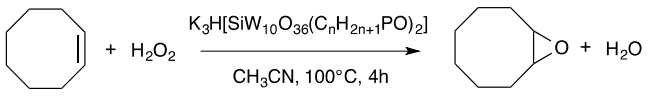
Fig S5. SWAXS spectra of the Winsor I microemulsion (empty symbols) and fit of the spectrum with a spherical core-shell form factor giving the ether droplet diameter of 5.0 nm (core) and a shell thickness of 0.9 nm corresponding to the size of a POM.

Epoxidation studies



In a preformed W I microemulsion are successively added *cis*-cyclooctene (0.1 mmol) and H_2O_2 (0.2 mmol, 50% aqueous solution), then the mixture is stirred at 750 rpm. At 25°C and at 85°C, no conversions were observed, even after 24 hours. At 85°C, the microemulsion was not stable more than a few hours.

To further evaluate the potential catalytic activity of compounds **$K_3H[1\text{-}(Cn)_2]$**, catalysis in single organic phase were also carried out, as depicted below :



Typical epoxidation procedure: A full conversion of *cis*-cyclooctene (1 mmol) in its epoxide (>99% based on GC yields) may be obtained by reacting with 2 equivalents of H_2O_2 (2 mmol, 50% aqueous solution) in acetonitrile (6 mL) in the presence of $K_3H[\mathbf{1}\text{-}(C_{12})_2]$ (0,01 mmol) as catalyst. However, this requires heating the reaction mixture at 100°C during 4 hours in a sealed vessel. Below 90°C, the conversion decreases drastically (below 15% conv. at 60°C, as example).

This lack of reactivity is in agreement with the results reported by M. Bonchio and coll.[4] with similar functionalized POMs, which appear as efficient catalysts (up to 97% conv. after 50 minutes) only under extreme conditions (in acetonitrile at 120°C and under microwaves).

5. References

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