Experimental

Materials

Solvents including triethylamine were dried over suitable reagents and freshly distilled under argon before use. Reactions, unless otherwise mentionned, were carried out under dry argon by using Schlenk-tube techniques.

Tetrabutylammonium tetrafluoroborate was synthesized from commercial (Aldrich) sodium tetrafluoroborate and tetrabutylammonium hydrogen sulfate. The reagents $K_7[PW_{11}O_{39}],14H_2O$,[1] $[Pd(PPh_3)_2Cl_2]$,[2] 1-iodo-4-(triethoxysilyl)benzene[3] and 4′-(4-Ethynylphenyl)-2,2′:6′,2″-terpyridine[4] were synthesized according to the published procedures. Chemical analyses were performed by the Service de Microanalyses (Université Pierre et Marie Curie, Paris, France) and the Laboratoire Central d'Analyses du CNRS (Vernaison, France).

Instrumentation

Microwave assisted syntheses were performed at ambient pressured reactor (Milestone Start S) equipped with a temperature control unit. IR spectra were recorded from KBr pellets on a Bruker Tensor 27 FTIR spectrophotometer. ^{31}P NMR spectra (121.5 MHz) were obtained at room temperature in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead. ^{31}P chemical shifts are given with respect to 85 % H_3PO_4 (measured by the substitution method). ^{183}W NMR (12.5 MHz) spectra were recorded at 300 K in 10 mm o.d. tubes on the same spectrometer equipped with a low-frequency special VSP probe head. ^{183}W chemical shifts are given with respect to a 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 a secondary standard (d = -103.8 ppm). Cyclic voltammetry at a carbon electrode was carried out using the EG&G model 273A system. A standard three electrode cell was used,

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[1] Souchay, P. *Polyanions et polycations*; Gauthier-Villars: Paris, 1963.

[2] O. Dangles, F. Guibe, G. Balavoine, S. Lavielle, and A. Marquet G., *J. Org. Chem.*, 1987, **52**, 4984-4993.

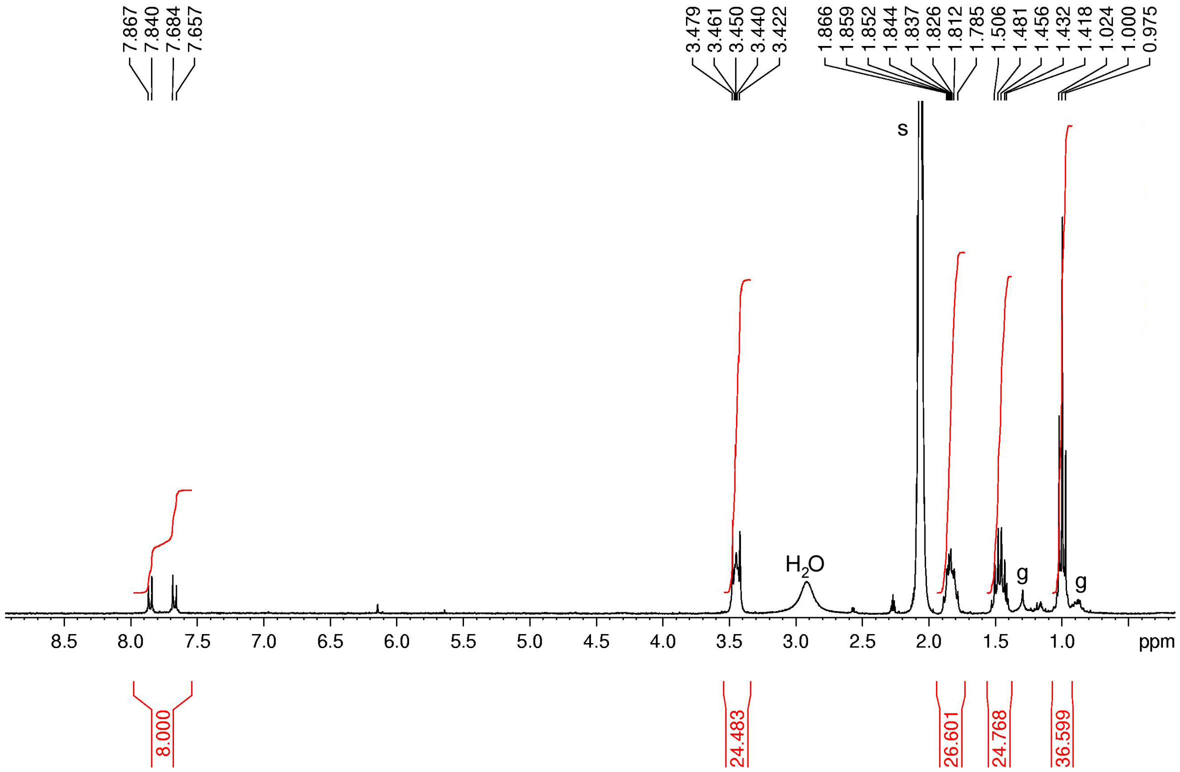
[3] Y. Maegawa, T. Nagano, T. Yabuno, H. Nakagawa and T. Shimada,, *Tetrahedron*, 2007, **63**, 11467–11474

[4] (a) J. Wang, G. S. Hanan, *Synlett*, 2005, **8**, 1251-1254. (b) Vincent Grosshenny, Francisco M. Romero, and Raymond Ziessel, J. Org. Chem. 1997, 62, 1491-1500.

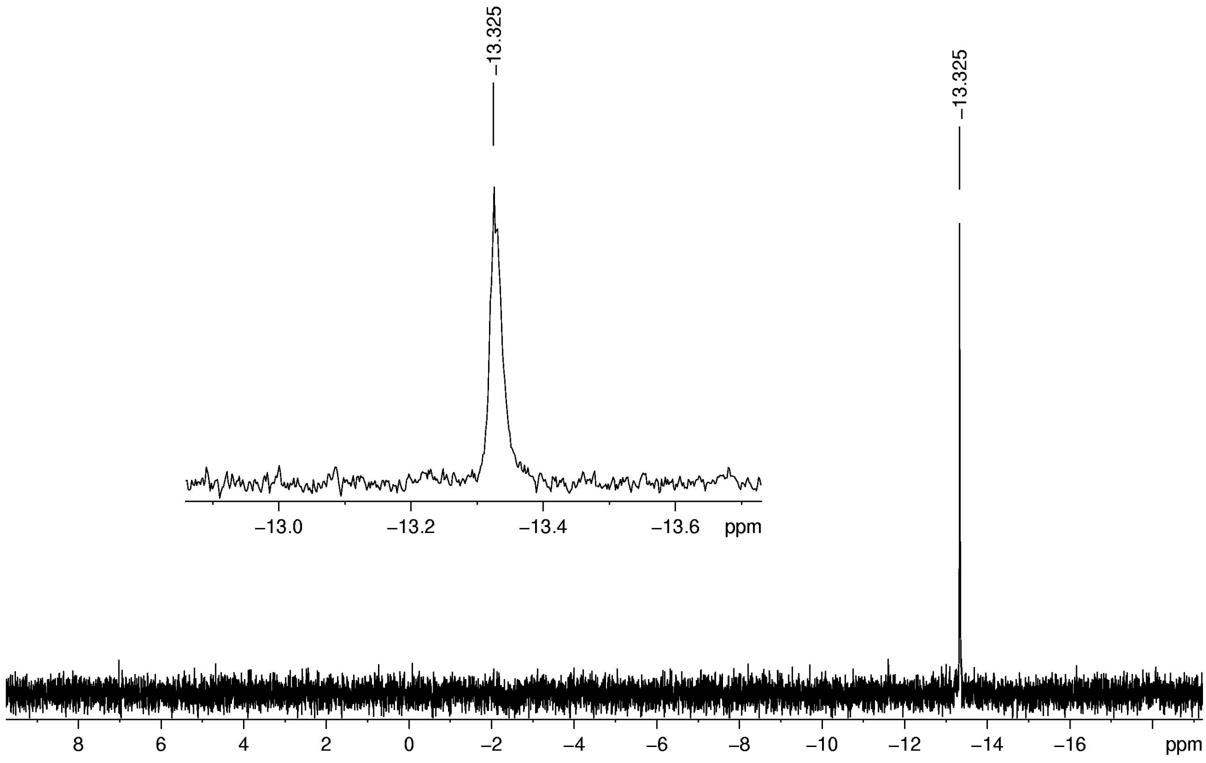
which consisted of the working vitrous carbon electrode, an auxiliary platinum electrode, and an aqueous saturated calomel electrode (SCE) equipped with a double junction. The scan rate was 100 mV/s. Each studied product was dissolved in distilled acetonitrile or dimethylformamide at a concentration of 10^{-3} M using tetrabutylammonium tetrafluoroborate as electrolyte (10^{-1} M). The ESI mass spectra were recorded by using an ion-trap mass spectrometer (Bruker Esquire 3000, Bremen, Germany) equipped with an orthogonal ESI source operated in the negative ion mode. The capillary high voltage was set to +3500 V. The capillary exit, skimmer 1 and skimmer 2, were typically set to -40, -10 and -6 V, respectively, in order to minimize insource decomposition. Sample solutions (10 pmol.μL^{-1} in acetonitrile) were infused into the ESI source by using a syringe pump at a flow rate of 120 $\mu L.h^{-1}$.

Synthesis of TBA-1 ($TBA_3[PW_{11}O_{40}\{SiPhI\}_2]$).

$K_7[P_{11}W_{11}O_{39}].14H_2O$ (4 g, 1.25 mmol, 1 eq.) and 1-iodo-4-(triethoxysilyl)benzene (2.74 g, 7.5 mmol, 6 eq.) were dissolved in an acetonitrile (120 mL)/water (40 mL) mixture. The pH of the suspension was fixed at 2 by dropwise addition of 1 M hydrochloric acid at 0 °C. The solution was stirred at room temperature under air atmosphere for 24 hours. NBu_4Br (1.21 g, 3.75 mmol, 3 eq.) was then added to precipitate **1** as a tetrabuylammonium salt. After partial evaporation of the acetonitrile, the solid was recovered by filtration, washed with water, ethanol, chloroform and ether to yield **TBA-1** (4,2 g, 1.10 mmol, 88 %) as an almost colorless powder. ^{1}H-RMN (acetone-d^6) δ = 7.85 (d, J = 8.1 Hz, 4H, ArH); 7.67 (d, J = 8.1 Hz, 4H, ArH); 3.45 (m, 24H, NCH_2); 1.85 (m, 24H, $\mathit{CH_2}CH_2CH_3$); 1.45 (sextuplet, 7.4 Hz, 24H, $\mathit{CH_2}CH_3$); 1.00 (t, J = 7.4 Hz, 36H, CH_3). ^{31}P-RMN (CD_3CN) δ = - 13.32 ppm. ^{183}W-RMN δ = -98.3 (d, 2W); -101.6 (d, 2W); -107.2 (d, 1W); -120.0 (d, 2W); -193.9 (d, 2W); -243.9 (d, 2W). IR (KBr, cm^{-1}) ν = 2962 (s); 2933 (s); 2873 (s); 1572 (m); 1780 (m); 1377 (m); 1111 (Si-O-Si, s); 1067 (s); 996 (s); 964 (vs); 872 (vs); 824 (s); 767 (s); 721 (s). MS (ESI): m/z calcd for $PW_{11}O_{40}Si_2C_{12}H_8I_2$ 1052.0, found 1051.8 (POM^{3-}). Anal calcd for $PW_{11}O_{40}Si_2C_{60}H_{116}I_2N_3$ C, 18.56; H, 3.01; N, 1.08. Found: C, 19.74; H, 3.24; N, 1.25.



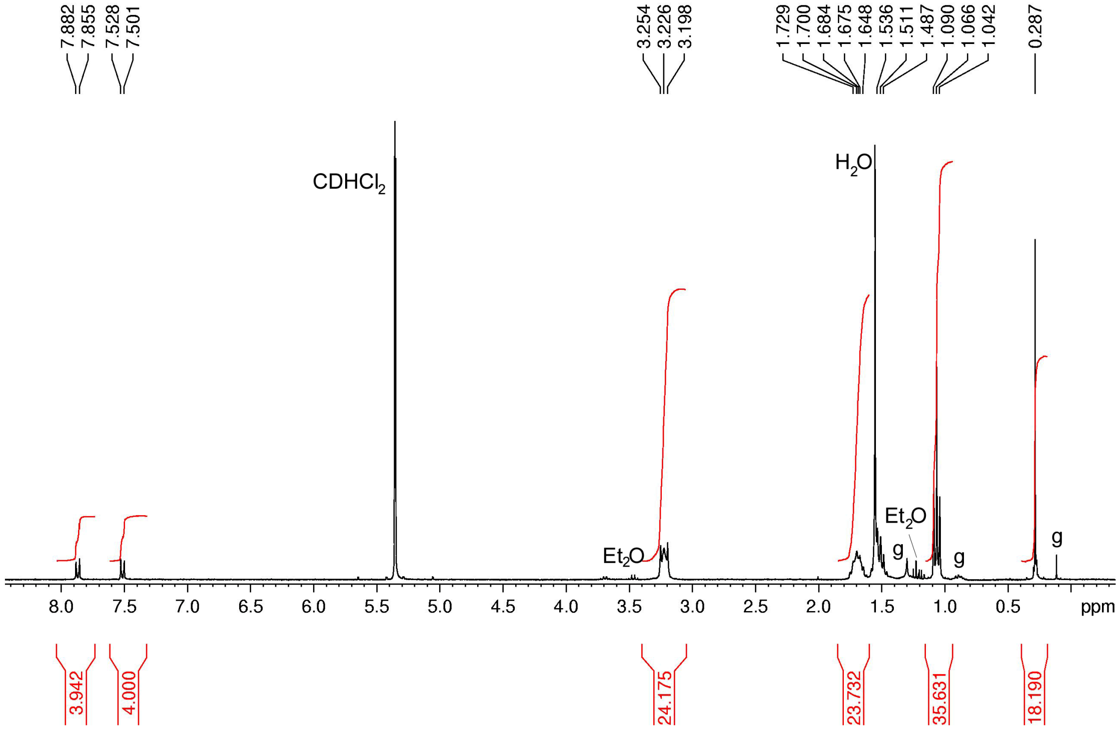
^{1}H NMR (acetone d^6, 300 MHz) spectrum of **TBA-1.** Solvent and grease peaks are labelled "s" and "g", respectively.



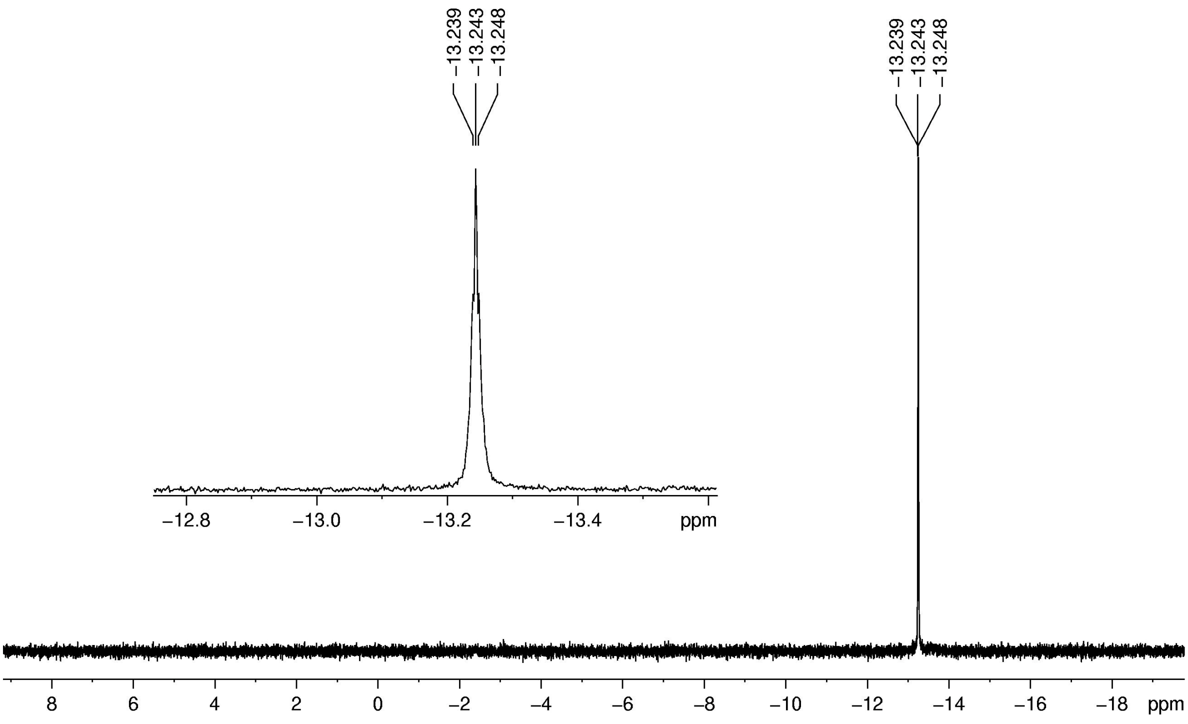
^{31}P NMR (acetone d^6, 121.5 MHz) spectrum of **TBA-1**.

Synthesis of TBA-2 ($TBA_3[PW_{11}O_{40}\{SiPhC{\equiv}CSiMe_3\}_2]$).

Under argon, **TBA-1** (400 mg, 0.103 mmol, 1 eq.), ethynyltrimethylsilane (61 mg, 0.620 mmol, 6 eq.), $[Pd(PPh_3)_2Cl_2]$ (6 mg, 8.5×10^{-3} mmol, 0.08 eq.) and copper iodide (3 mg, 1.6×10^{-2} mmol, 0.15 eq.) were dissolved in 20 mL of acetonitrile. After addition of distilled triethylamine (175 mg, 1.73 mmol, 17 eq.), the solution was heated to 50 °C under microwave activation for 4 minutes. NBu_4Br_3 (50 mg, 0.103 mmol, 1 eq.) and NBu_4Br (650 mg, 2.02 mmol, 20 eq.) were then added under argon to the resulting dark blue solution which instantly bleached. After evaporation of the solvents under reduce pressure, the resulting yellow solid was washed several times with EtOH to give a very pale brown solid (350 mg, 9.16×10^{-2} mol, 89 %). For microanalysis purpose, a crystallisation by slow diffusion of diethylether into an acetonitrile solution of **TBA-2** afforded a colourless microcrystalline precipitate that was separated from a slight amount of brownish gel. ^{1}H-RMN (CD_2Cl_2) δ = 7.87 (d, J = 8.1 Hz, 4H, ArH); 7.51 (d, J = 8.1 Hz, 4H, ArH); 3,23 (m, 24H, NCH_2); 1.68 (m, 24H, $\mathit{CH_2}CH_2CH_3$); 1.53 (sextuplet, 7.2 Hz, 24H, $\mathit{CH_2}CH_3$); 1.07 (t, J = 7.2 Hz, 36H, $CH_2\mathit{CH_3}$); 0.29 (s, 18H, $SiCH_3$). ^{31}P-RMN (CD_2Cl_2) d = -13.24 ppm. IR (KBr, cm^{-1}) n = 2963 (s); 2875 (s); 1653 (m); 1482 (m); 1382 (m); 1250 (m); 1111 (Si-O-Si, s); 1070 (s); 966 (vs); 871 (vs); 824 (vs); 767 (s); 715 (s). MS (ESI): m/z calcd for $PW_{11}O_{40}Si_4C_{22}H_{26}$ 1031.4, found 1032.0 (POM^{3-}). Anal calcd for $PW_{11}O_{40}Si_4C_{70}H_{134}N_3$ C, 21.99 H, 3.53; N, 1.10. Found: C, 22.18; H, 3.94; N, 1.16.



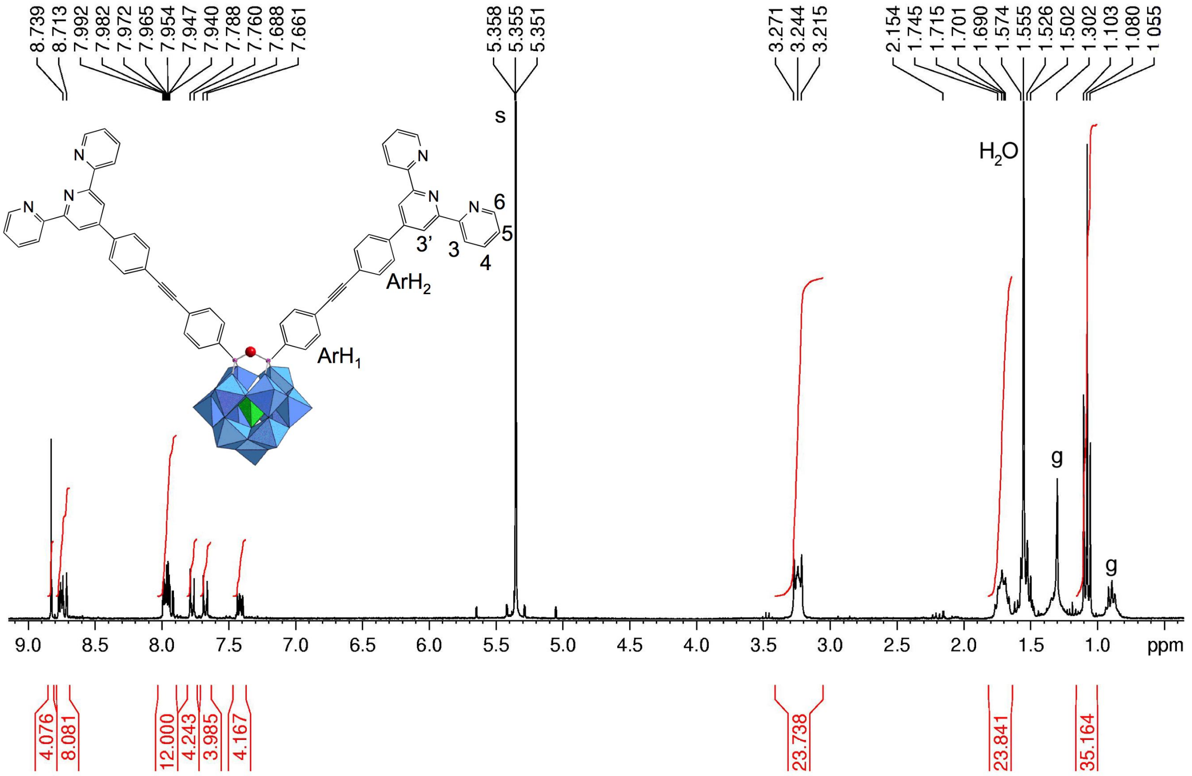
^{1}H NMR (CD_2Cl_2 d^6, 300 MHz) spectrum of **TBA-2.** Grease peaks are "g".



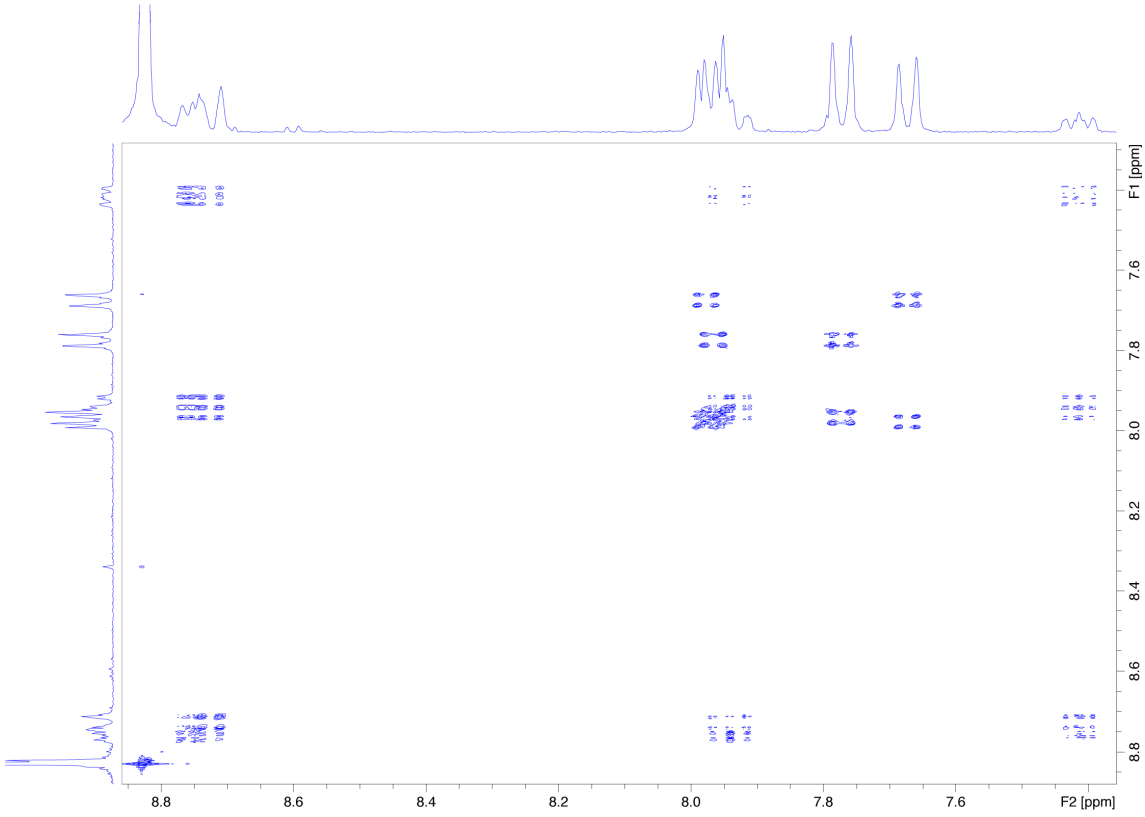
^{31}P NMR (CD_2Cl_2 d^6, 121.5 MHz) spectrum of **TBA-2**.

Synthesis of compound 3 (TBA$_3$[PW$_{11}$O$_{40}${SiPhC≡CPhtpy}$_2$]).

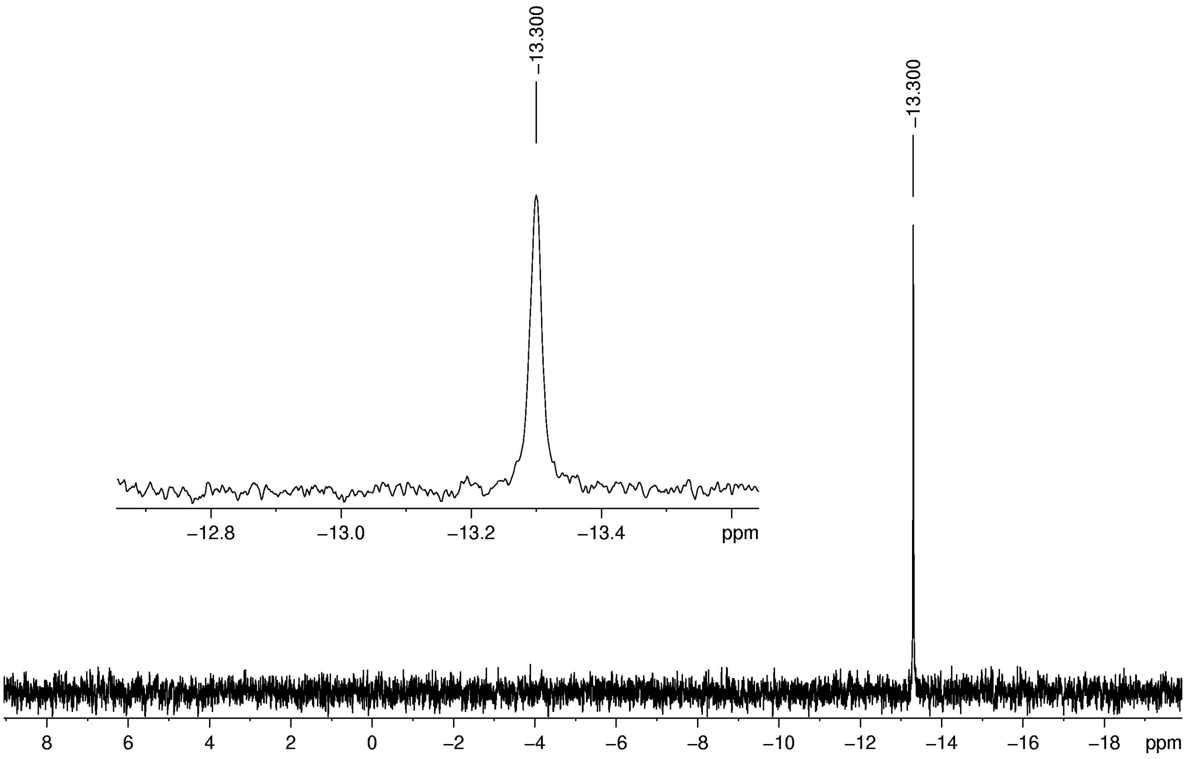
Under argon, **TBA-1** (400 mg, 0.103 mmol, 1 eq.), 4′-(4-Ethynylphenyl)-2,2′:6′,2″-terpyridine (103 mg, 0.309 mmol, 3 eq.), [Pd(PPh$_3$)$_2$Cl$_2$] (6 mg, 8.5×10^{-3} mmol, 0.08 eq.) and copper iodide (3 mg, 1.6×10^{-2} mmol, 0.15 eq.) were dissolved in 8 mL of DMF. After addition of distilled triethylamine (104 mg, 1.03 mmol, 10 eq.), the solution was heated to 70 °C under microwave activation for 40 minutes. NBu$_4$Br$_3$ (50 mg, 0.103 mmol, 1 eq.) and NBu$_4$Br (650 mg, 2.02 mmol, 20 eq.) were then added under argon to the resulting dark green solution which instantly bleached. After filtration of the solution, ethanol was added to precipitate **TBA-3** as a pale yellow solid which was washed with ethanol and ether (380 mg, 8.85×10^{-2} mmol, 86 %). ^{1}H-RMN (CD$_2$Cl$_2$) δ = 8,83 (s, 4H, H$_{3'}$); 8.75 (ddd, J = 1.2 Hz; 1.8 Hz; 4.8 Hz, 4H, H$_6$); 8.73 (dt, J = 1.2 Hz; 7.8 Hz, 4H, H$_3$); 7.98 (d, J = 8.1 Hz, 4H, ArH$_1$); 7.97 (d, J = 8.4 Hz, 4H, ArH$_2$); 7.96 (td, J = 1.8 Hz; 7.8 Hz, 4H, H$_4$); 7.77 (d, J = 8.4 Hz, 4H, ArH$_2$); 7.67 (d, J = 8.1 Hz, 4H, ArH$_1$); 7.42 (ddd, J = 1.2 Hz; 4.8 Hz; 7.5 Hz, 4H, H$_5$); 3.24 (m, 24H, NCH$_2$); 1.72 (m, 24H, *CH$_2$*CH$_2$CH$_3$); 1.54 (sextuplet, J = 7.2 Hz, 24H, *CH$_2$*CH$_3$); 1.08 (t, J = 7. 2 Hz, 36H, CH$_3$) . ^{31}P-RMN (CD$_2$Cl$_2$) δ = -13.30 ppm. IR (KBr, cm^{-1}) ν = 2963 (s); 2935 (m); 2874 (m); 1603 (m); 1584 (s); 1566 (m); 1536 (w); 1516 (w); 1469 (s); 1388 (m); 1148 (m); 1111 (Si-O-Si, s); 1066 (s); 1039 (s); 965 (vs); 872 (vs); 793 (s); 769 (s); 745 (s). MS (ESI): m/z calcd for PW$_{11}$O$_{40}$Si$_2$C$_{58}$H$_{36}$N$_6$ 1188.8, found 1188.4 (POM^{3-}). Anal calcd for PW$_{11}$O$_{40}$Si$_2$C$_{106}$H$_{144}$N$_9$ C, 29.65; H, 3.38; N, 2.94. Found: C, 31.31; H, 3.35; N, 3.56.



^{1}H NMR (CD$_2$Cl$_2$, 300 MHz) spectrum of **TBA-3.** Solvent and grease peaks are labelled “s” and “g”, respectively).



^{1}H NMR COSY (CD_2Cl_2, 300 MHz) spectrum of **TBA-3.**



^{31}P NMR (CD_2Cl_2 d^6, 121.5 MHz) spectrum of **TBA-3**.

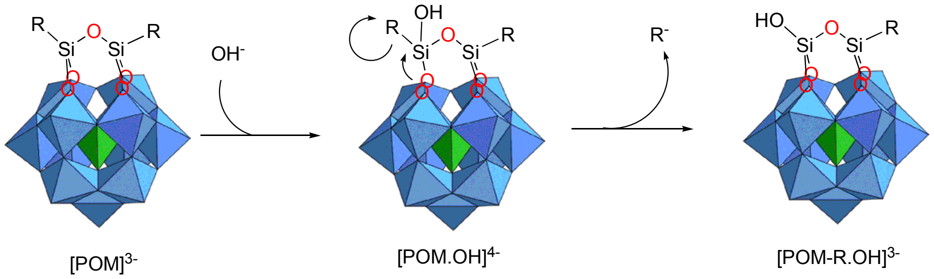
Redox potentials of 1 and 3, E / V vs SCE (ΔE / mV)

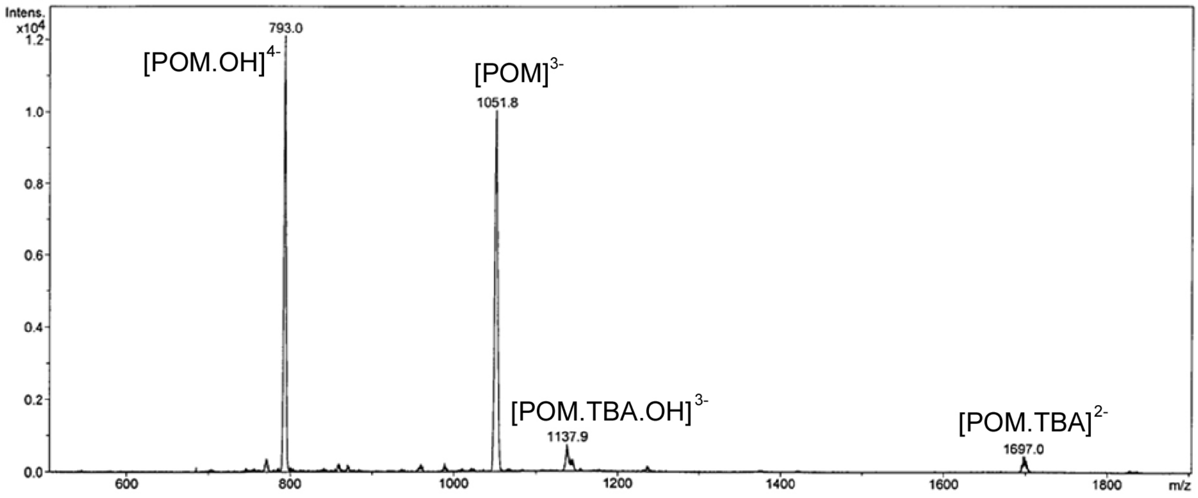
compound	E_1 (ΔE_1)	E_2 (ΔE_2)	E_3 (ΔE_3)	E_4 (ΔE_4)
1[a]	-0.292 (72)	-0.813 (74)	-1.439 (70)	
3[b]	-0.356 (76)	-0.950 (75)	-1.542	-1.746 (89)

[a] recorded in MeCN
[b] recorded in DMF

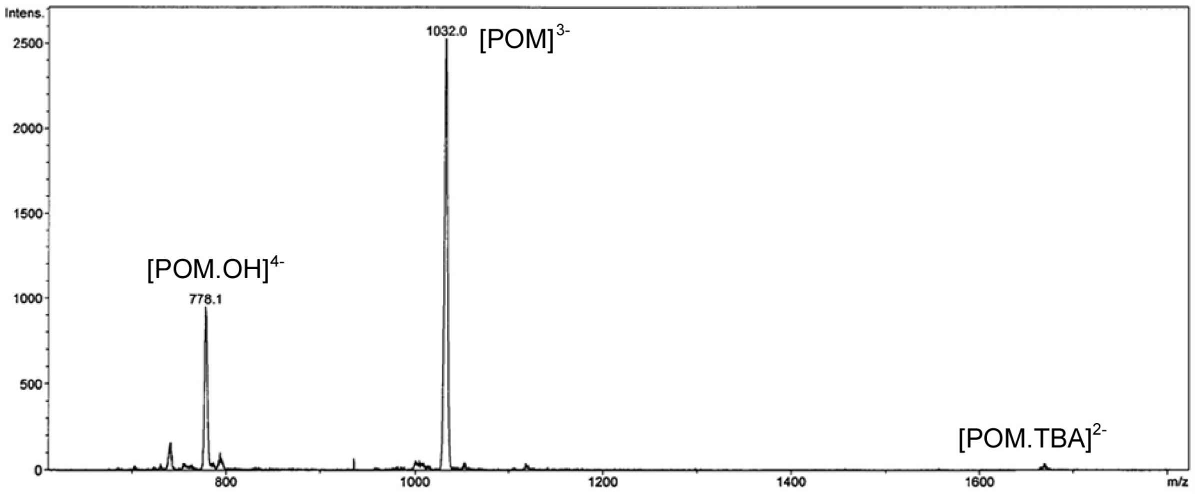
ESI MS experiments

The ESI mass spectrums of compounds **TBA-1**, **TBA-2** and **TBA-3** in MeCN (10^{-5} M) were recorded using the negative ion mode and under relatively soft desolvation conditions to avoid dissociation of the polyoxoanions. In addition to the isotopic cluster of the triply charged species, labeled POM^{3-}, another important cluster, attributed to the [POM.OH]$^{4-}$ adduct, was almost systematically observed for the 3 compounds. The charge state of the ions was confirmed by the recording of higher resolution spectra (use of slower scan speed) and examination of the isotopic cluster. The intensity of the signal corresponding to this adduct was found to be dependent on the quantity of water present in the solvent. This adduct could never be characterized by NMR spectroscopy and was attributed to in-source hydrolysis of the hybrid polyoxometalate. This may occur either in the nozzle/skimmer region during the desolvation process, or in the ion trap cell. A third minor species labeled [POM-R.OH]$^{3-}$, attributed to the loss of an organic arm, was sometime observed. An MS/MS experiment carried out on the m/z 896 ion ([POM.OH]$^{4-}$ for **TBA-3**) yielded the m/z 1059 [POM-R.OH]$^{3-}$, showing that this ion was produced through dissociation of the [POM.OH]$^{4-}$.

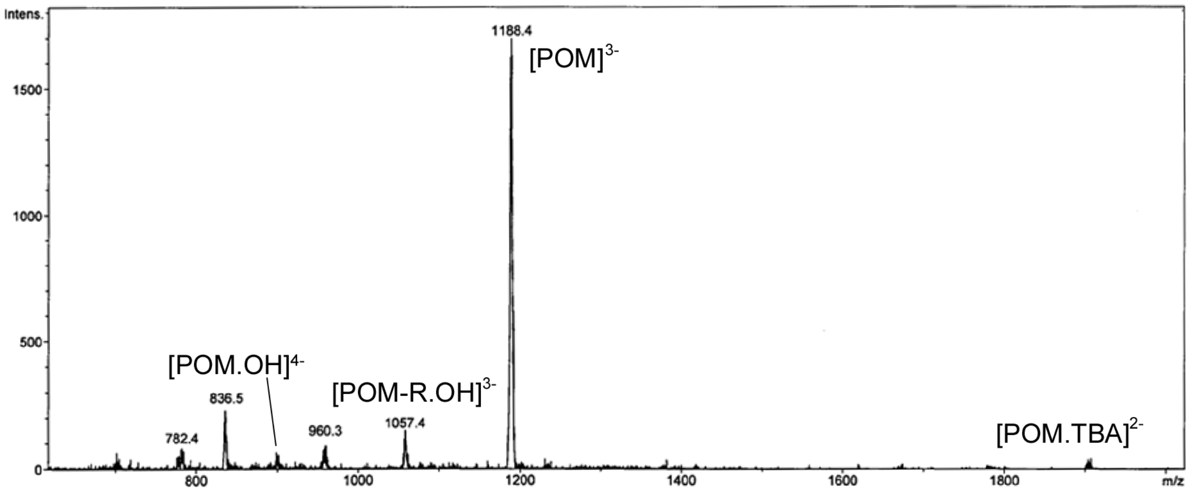




ESI spectrum of 10 µmol.L^{-1} CH_3CN solution of **TBA-1** recorded using the "extended" mass range with the negative ion mode.



ESI spectrum of 10 µmol.L^{-1} CH_3CN solution of **TBA-2** recorded using the "extended" mass range with the negative ion mode.



ESI spectrum of 10 µmol.L^{-1} CH_3CN solution of **TBA-3** recorded using the "extended" mass range with the negative ion mode.