

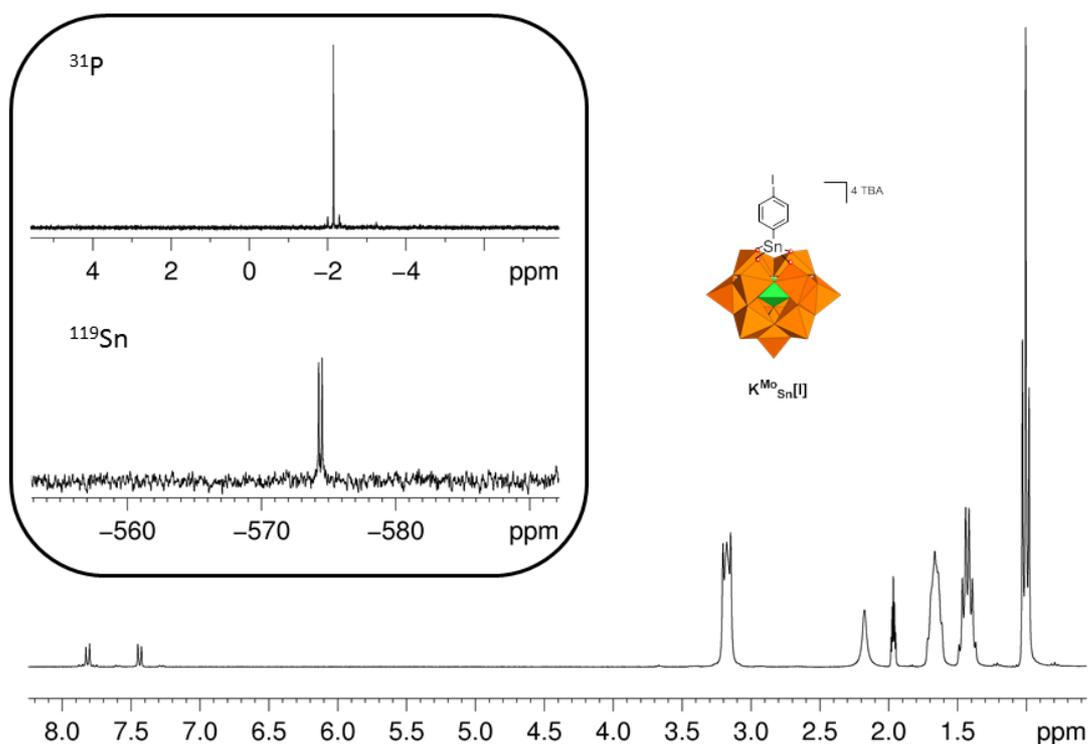
## Supporting information

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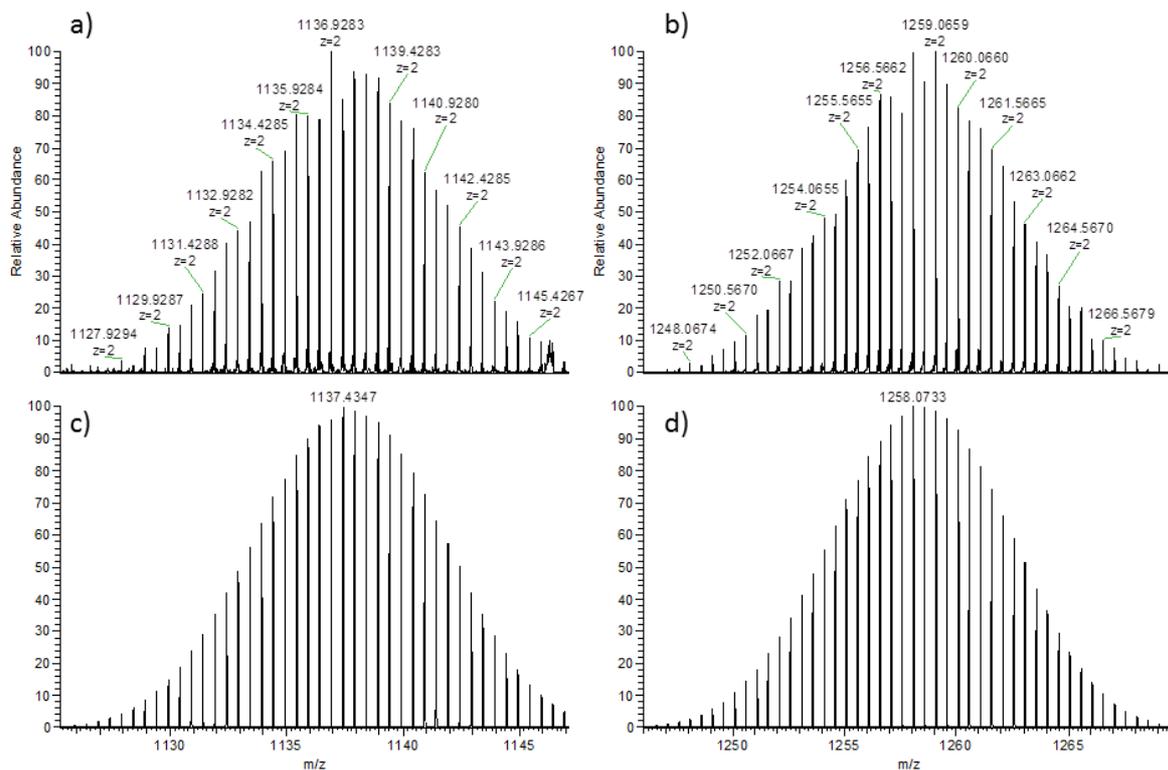
**Materials and methods:** Manipulation of all air-sensitive compounds was carried out using standard Schlenk techniques. Triethylamine was distilled from  $\text{CaH}_2$ . Dimethylformamide was purchased stored under argon over molecular sieve.  $\text{TBA}_4\text{H}_3[\text{PMo}_{11}\text{O}_{39}]$ ,<sup>[1]</sup>  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ <sup>[2]</sup> and 1-iodo-4-(trichlorotin)benzene<sup>[3]</sup> were prepared according to published procedures. All other reagents were used as supplied. NMR spectra were recorded either on a Bruker AvanceII 300 spectrometer equipped with a QNP probe head or a Bruker Avance III nanobay 400 spectrometer equipped with a BBFO probe head.  $^1\text{H}$  chemical shifts are quoted as parts per million [ppm] relative to tetramethylsilane by using the solvent signals as secondary standard (s=singlet, d=doublet, t=triplet, sex=sextet, m=multiplet) and coupling constants (J) are quoted in Hertz [Hz].  $^{31}\text{P}$  chemical shifts are quoted relative to 85%  $\text{H}_3\text{PO}_4$ .  $^{119}\text{Sn}$  chemical shifts are quoted relative to  $\text{SnMe}_4$ . IR spectra were recorded from KBr pellets on a Jasco FT/IR 4100 spectrometer. ESI mass spectra were recorded by using an LTQ Orbitrap hybrid mass spectrometer (Thermofisher Scientific, Bremen, Germany) equipped with an external ESI source operated in the negative ion mode. Spray conditions included a spray voltage of 3 kV, a capillary temperature maintained at 280 °C, a capillary voltage of -30 V and a tube lens offset of -90 V. Sample solutions ( $10 \text{ pmol} \cdot \mu\text{L}^{-1}$ ) were infused into the ESI source by using a syringe pump at a flow rate of  $180 \mu\text{L} \cdot \text{h}^{-1}$ . Elemental analyses were performed at the Institut de Chimie des Substances Naturelles, Gif sur Yvette, France. Electrochemical studies were performed on an Autolab PGSTAT 100 work station (Metrohm) or a CH660 potentiostat (CH Instruments) by using a standard three-electrode setup. Working glassy carbon electrodes (2 and 3 mm diameter) were polished with 6  $\mu\text{m}$  diamond paste, sonicated in ethanol for 5 min and dried with an argon flow. Platinum wire and saturated calomel electrode equipped with a double junction were used as auxiliary and reference electrodes, respectively.

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- [2] O. Dangles, F. Guibe, G. Balavoine, S. Lavielle, A. Marquet, *J. Org. Chem.* **1987**, *52*, 4984.
- [3] B. Matt, J. Moussa, L. M. Chamoreau, C. Afonso, A. Proust, H. Amouri, G. Izzet, *Organometallics* **2012**, *31*, 35.

**Synthesis of TBA<sub>4</sub>[PMo<sub>11</sub>O<sub>39</sub>{Sn(C<sub>6</sub>H<sub>4</sub>)I}] (K<sup>Mo</sup><sub>Sn</sub>[I]):** TBA<sub>4</sub>H<sub>3</sub>[PMo<sub>11</sub>O<sub>39</sub>] (500 mg, 18.6 mmol, 1 eq.) was dissolved in 12.5 mL of CH<sub>3</sub>CN. Triethylamine (52 μL, 37.3 mmol, 2 eq.) was added to the solution. A solution of 1-iodo-4-(trichlorotin)benzene (120 mg, 27.9 mmol, 1.5 eq.) in CH<sub>3</sub>CN (2.5 mL) was added, and the cloudy mixture was stirred 15 min at room temperature. TBABr (180 mg, 55.8 mmol, 3 eq.) was added and the solution was filtrated to eliminate the insoluble residues. A 50 mL mixture of THF/Ether (1:1) was added to precipitate a yellow-green powder. The crude product was washed with water (50 mL) and THF (50 mL) to afford 370 mg of a yellow solid (66 %). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ = 7.81 (d + dd, <sup>3</sup>J(H,H)=7.5 Hz, <sup>4</sup>J(Sn,H)=30.5 Hz, 2H; Ar-H), 7.43 (d + dd, <sup>3</sup>J(H,H)=7.5 Hz, <sup>3</sup>J(Sn,H)=94.5 Hz, 2H; Ar-H), 3.17 (m, 32H; N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.66 (m, 32H; N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.43 (sex, <sup>3</sup>J(H,H)=7.0 Hz, 32H; N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 1.00 (t, <sup>3</sup>J(H,H)=7.0 Hz, 48H; N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>); <sup>31</sup>P NMR (121 MHz, CD<sub>3</sub>CN) δ = -2.15 (s + d, <sup>2</sup>J(Sn,P)=36.0 Hz); IR (KBr pellet, cm<sup>-1</sup>): 2959 (m), 2931 (m), 2872 (m), 1482 (m), 1380 (w), 1061 (m), 1035 (m), 943 (s), 866 (m), 806 (vs), 785 (vs), 385 (m); MS (ESI<sup>-</sup>) *m/z* (%): 1135.4 (X) [M+TBA+H]<sup>2-</sup> requires 1137.3, 1259.1 (X) [M+2TBA]<sup>2-</sup> requires 1258.6; elemental analysis calcd (%) for C<sub>70</sub>H<sub>148</sub>SnIN<sub>4</sub>O<sub>39</sub>PMo<sub>11</sub>: C 28.01, H 4.97, N 1.87; found: C 28.01, H 5.21, N 1.82.

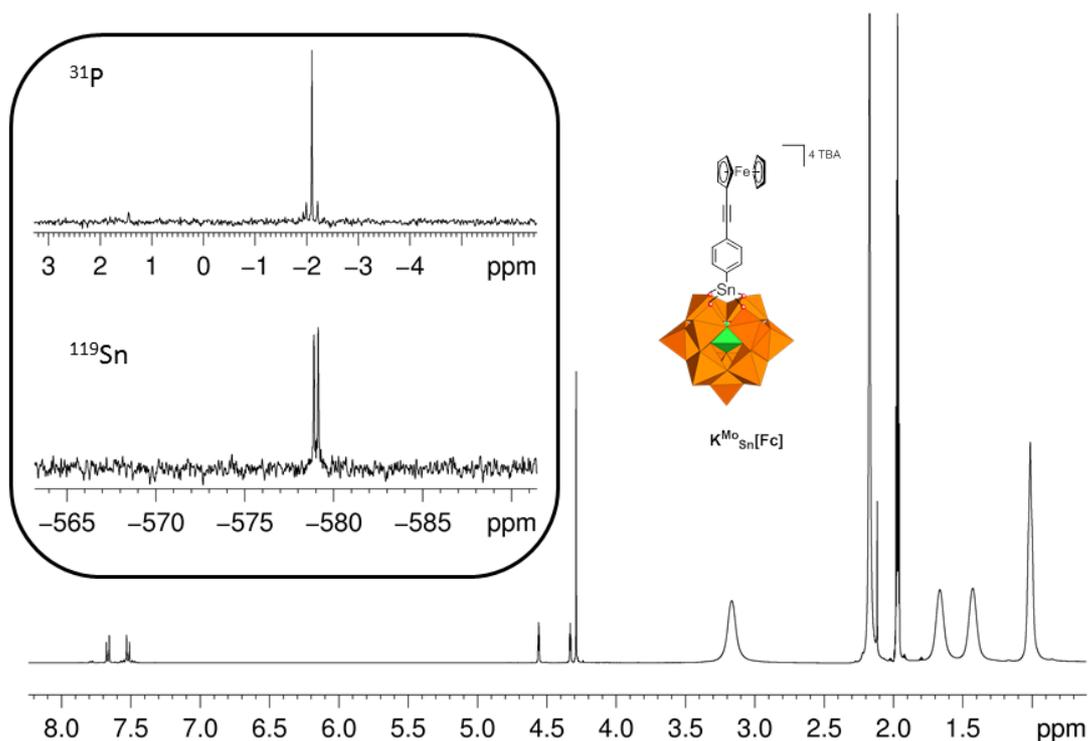


**Figure S1:** <sup>1</sup>H NMR (300 MHz) <sup>31</sup>P and <sup>119</sup>Sn NMR (121 and 149 MHz respectively, framed inset) spectra of K<sup>Mo</sup><sub>Sn</sub>[I] in CD<sub>3</sub>CN.

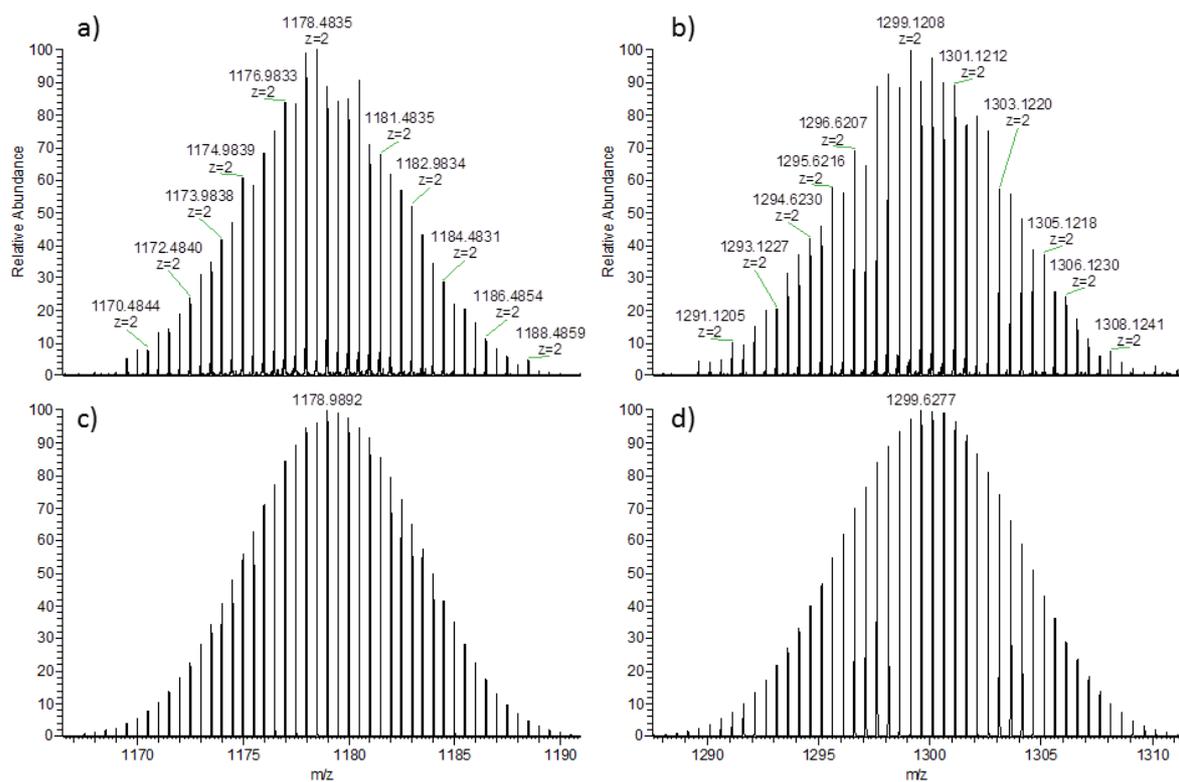


**Figure S2:** Comparison of experimental (upper traces, a and b) and calculated (lower traces, c and d) isotopic peaks for the most abundant POM-based hybrid ions of  $K^{Mo}_{Sn}[I]$ .

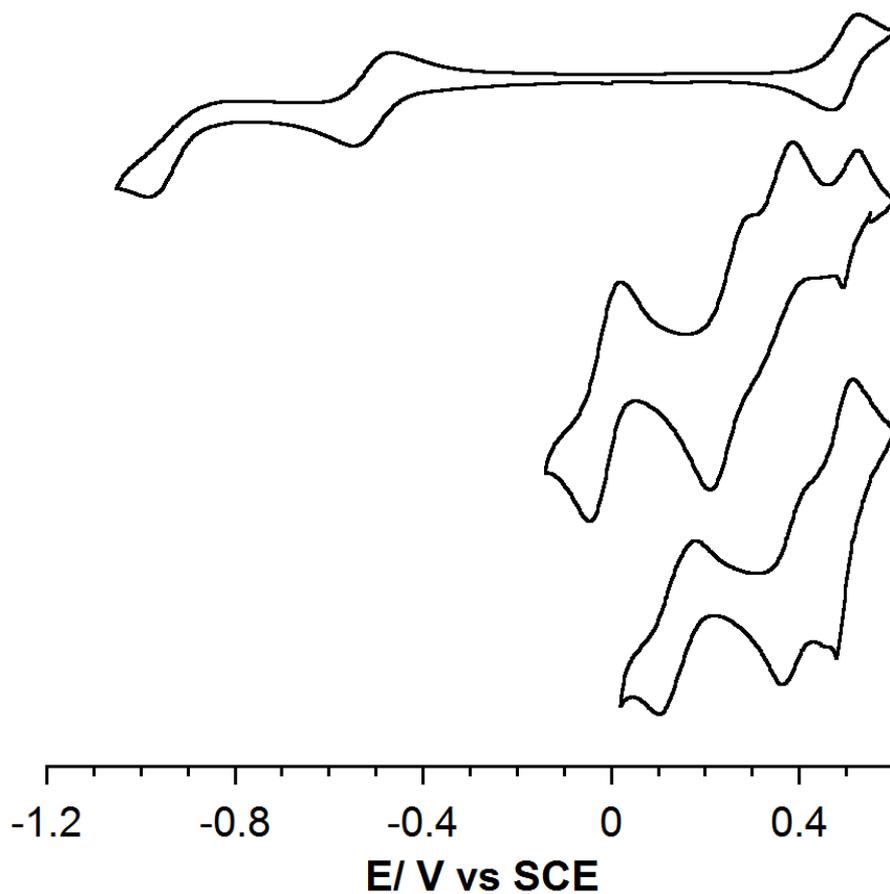
**Synthesis of  $\text{TBA}_4[\text{PMo}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}]$  ( $\text{K}^{\text{Mo}}_{\text{Sn}}[\text{Fc}]$ ):**  $\text{K}^{\text{Mo}}_{\text{Sn}}[\text{I}]$  (439 mg, 0.14 mmol), ethynylferrocene (92.0 mg, 0.44 mmol, 3 eq.), bis-(triphenylphosphine)palladium(II) dichloride (15.4 mg, 21.9  $\mu\text{mol}$ , 0.15 eq.) were introduced in a dry Schlenk flask under argon. Dry dimethylformamide (7.5 mL) was added and the solution was degassed with argon bubbling for 10 min. Freshly distilled triethylamine (0.41 mL, 2.9 mmol, 20 eq) was then added and the solution degassed for another minute. The solution was stirred at room temperature for 24 h. TBABr (0.5 g, 1.6 mmol) was added, and the mixture was centrifugated. The product was precipitated by addition of excess diethyl ether on the supernatant. After centrifugation the solid was dissolved in minimum acetonitrile and precipitated by addition of excess ethanol. The resulting suspension was centrifuged and the solid was washed with ethanol (2x50 mL) and diethyl ether (2x50 mL) to afford a brown-green solid (0.407 g, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$ =7.67 (d + dd,  $^3J(\text{H,H})=8.0$  Hz,  $^3J(\text{Sn,H})=95.5$  Hz, 2H; Ar-*H*), 7.52 (d + dd,  $^3J(\text{H,H})=8.0$  Hz,  $^4J(\text{Sn,H})=33.0$  Hz, 2H; Ar-*H*), 4.56 (t,  $^3J(\text{H,H})=3.5$  Hz, 2H, Cp-*H*), 4.33 (t,  $^3J(\text{H,H})=3.5$  Hz, 2H, Cp-*H*), 4.29 (s, 5H, Cp-*H*) 3.17 (s, 32H; N- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.66 (s, 32H; N- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.43 (s, 32H; N- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ ), 1.01 (s, 48H; N- $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ );  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ = -2.10 (s + d,  $^2J(\text{Sn,P})=35.0$  Hz); IR (KBr pellet,  $\text{cm}^{-1}$ ): 2960 (m), 2935 (m), 2872 (m), 2202 (w), 1482 (m), 1380 (w), 1061 (m), 1035 (m), 943 (s), 867 (m), 802 (vs), 787 (vs), 383 (m); MS (ESI-)  $m/z$  (%): 1178.5 (X)  $[\text{M}+\text{TBA}+\text{H}]^{2-}$  requires 1178.9, 1299.1 (X)  $[\text{M}+2\text{TBA}]^{2-}$  requires 1299.6; elemental analysis calcd (%) for  $\text{C}_{82}\text{H}_{157}\text{FeMo}_{11}\text{N}_4\text{O}_{39}\text{PSn}$ : C 31.94, H 5.13, N 1.81; found: C 31.74, H 5.24, N 1.93.



**Figure S3:**  $^1\text{H}$  NMR (400 MHz) and  $^{31}\text{P}$  and  $^{119}\text{Sn}$  NMR (162 MHz and 149 MHz respectively, framed inset) spectra of  $\text{K}^{\text{Mo}}_{\text{Sn}}[\text{Fc}]$  in  $\text{CD}_3\text{CN}$ .



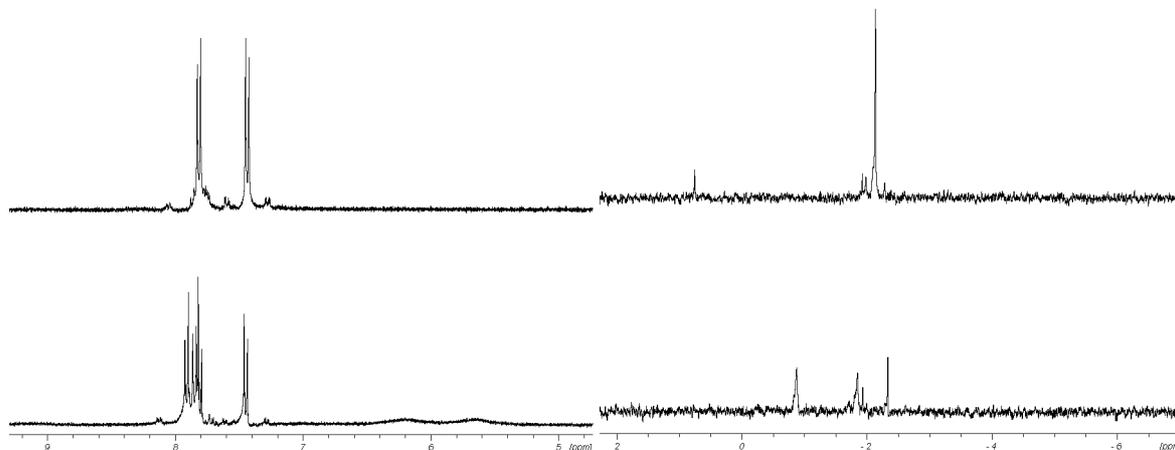
**Figure S4:** Comparison of experimental (upper traces, a and b) and calculated (lower traces, c and d) isotopic peaks for the most abundant POM-based hybrid ions of  $\text{K}^{\text{Mo}}_{\text{Sn}}[\text{Fc}]$ .



**Figure S5:** cyclic voltammograms of  $K^{M^0}_{Sn}[Fc]$  with 0 (top), 50 (middle) and 250 eq (bottom) of TFA, 1 mM solutions in MeCN containing 0.1 M TBAPF<sub>6</sub>, scan rate 20 mV.s<sup>-1</sup>. The low reversibility of the ferrocene oxidation wave is probably due to adsorption of the compound on the electrode, as its solubility decreases with the cation exchange. In dimethylformamide the wave is fully reversible in these conditions.

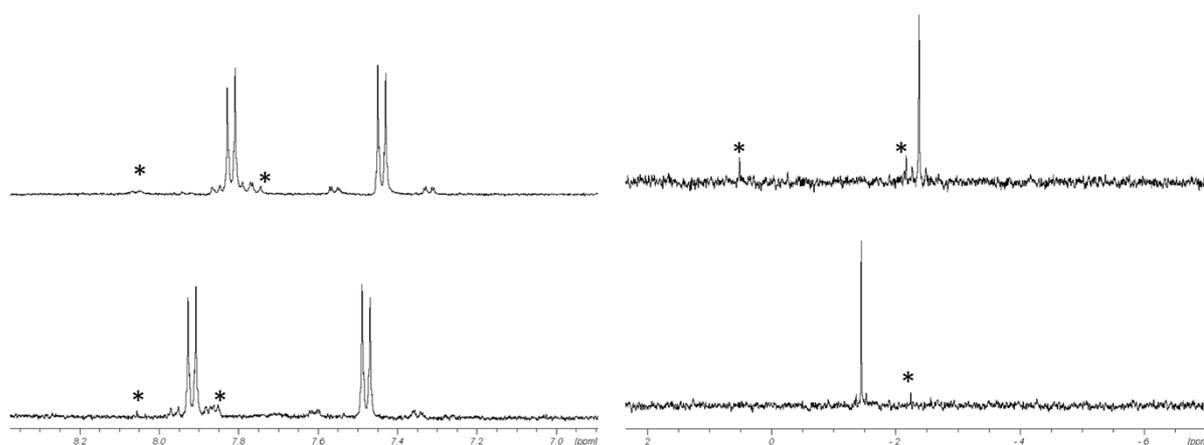
### Stability of $K^{Mo}_{Sn}[I]$ towards acids

Since molydates have a well-known propensity to rearrange, the stability of  $K^{Mo}_{Sn}[I]$  towards acids was carefully inspected. Indeed, after the addition of aqueous solutions of hydrochloric acid, the hybrid immediately loses the organotin moiety and irreversibly leads to  $[PMo_{12}O_{40}]^{3-}$  (-2.34 ppm by  $^{31}P$  NMR), together with other species (Figure S6).

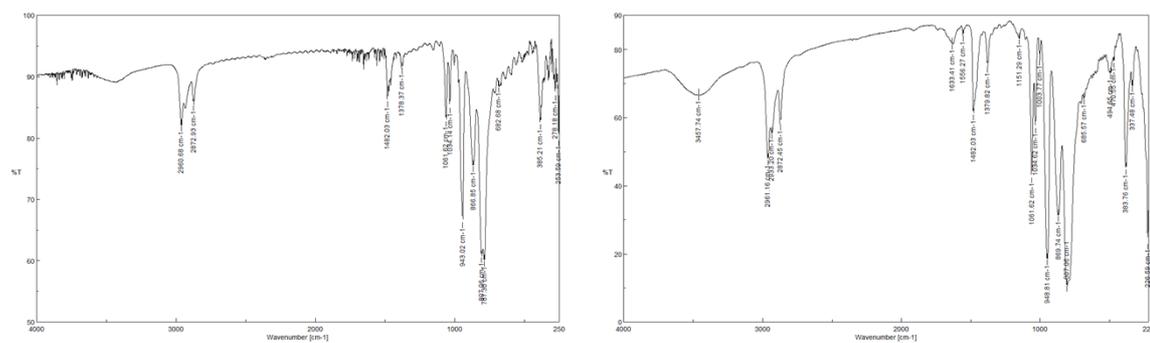


**Figure S6:**  $^1H$  (left) and  $^{31}P$  (right) NMR of  $K^{Mo}_{Sn}[I]$  ( $CD_3CN$ ) before (top) and after (bottom) the addition of 4 eq HCl.

However, the hybrid is perfectly stable in the presence of a water-free acid such as trifluoroacetic acid (TFA):  $^1H$ ,  $^{31}P$  and IR spectroscopies confirmed the preservation of the POM structure after the addition of acid. To support this statement NMR and IR spectra of the product before and after the addition of 100 eq. of TFA are presented below (Figure S7 and S8). Note that these tests have been carried out on samples containing traces of impurities (we had not found the proper conditions allowing a full purification of the hybrid at that time). The continuous change of the chemical shifts is due to the increased acidity of the solution. Importantly, the preservation of the  $J_{Sn-P}$  coupling on the  $^{31}P$  NMR spectrum indicates that the organotin moiety remains grafted onto the POM.



**Figure S7:**  $^1H$  (left) and  $^{31}P$  (right) NMR of  $K^{Mo}_{Sn}[I]$  ( $CD_3CN$ ) before (top) and after (bottom) the addition of 100 eq TFA. The peaks noted with an asterisk correspond to minor impurities initially present in the sample.



**Figure S8:** IR spectra of  $K^{Mo}_nSn[I]$  before (left) and after (right) the addition of 100 eq TFA. Note that the bands at ca. 1050  $cm^{-1}$  (attributed to P-O stretching modes) are still split after the addition of TFA, which is indicative of the low symmetry of the POM backbone ( $[P_{Mo}_{12}O_{40}]^{3-}$  displays for instance a unique band at 1063  $cm^{-1}$ ).