

Electronic Supplementary Information

Exploring the Mobility of Nanoscale Polyoxometalates using Gel Electrophoresis

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1. Details of electrophoresis study

a) Electrophoresis

Unless otherwise stated, all electrophoresis experiments were carried out as follows: The electrophoresis studies were performed using a commercially available submarine-type electrophoresis system (Pt-wire electrodes set at a distance of 13 cm). Acetic acid/sodium acetate buffer (pH 5.0; 0.05 M HOAc and 0.05 M NaOAc mixed 20:50 by volume) was applied and agarose (Purchased from Sigma Aldrich and used without further purification) gels were prepared using the same buffer by cooling an agarose solution from boiling temperature. A POM solution (20 mM in buffer) was prepared and injected into slots in the gels in 5 μ L portions and a voltage (100V) was applied to the system for 1-10 minutes.

In the case of non-buffered systems, the experiments were run as above but replacing the buffer solutions with distilled water. Under these non-buffered conditions some of the POMs (particularly $\{Mo_{132}\}$ and $\{Mo_{154}\}$) decomposed quickly and lost their colours due to the increased pH to 9 after 10 min of run (figure S1-1). Further runs of electrophoresis over 20 minutes also resulted in similar decomposition of these clusters even in the buffered system. Therefore we found that the best conditions to avoid decomposition of POMs were in buffer solutions with a maximum time limit for the experiment of 10 minutes.

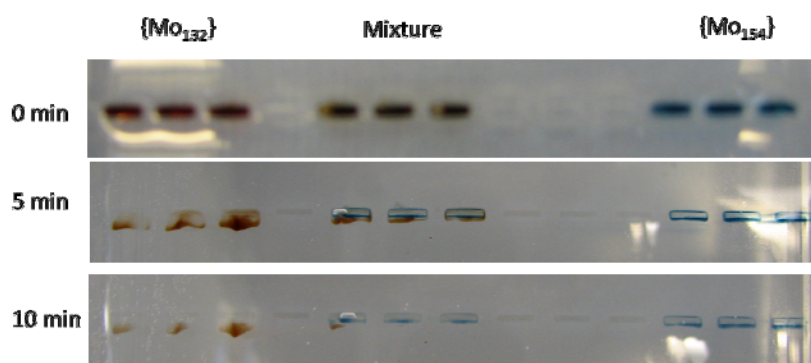


Figure S1-1. Photograph of non-buffered gels under electrophoresis taken at 0, 5 and 10 min of run. Each column is $\{Mo_{132}\}$, 1:1 mixture of $\{Mo_{132}\}$ and $\{Mo_{154}\}$, and $\{Mo_{154}\}$ at 20 mM concentrations. Here, the conditions are the same as those seen in figure 2 except that gels are prepared from water without any buffering. The colour of clusters fades progressively with time elapsed, indicating decomposition of clusters.

b) Dyeing process and estimation of mobility

The dyeing process is performed by casting a $Na_2S_2O_4$ solution (1 wt%) with a few drops of HCl (6M) onto the gel. Although some POMs can be dyed by reduction without the addition of HCl, mixtures with reducing agent and acid gave the most effective dyeing. After casting these solutions onto the gels, blue, green or brown bands appeared after 1-3 minutes, which provided the visible position of the cluster bands and enabled estimation of the distance between the initial loading position and forward edge of the bands by analysis of the photograph of the gel.

c) Extraction of the POMs from gel

For characterisation by UV-vis spectroscopy and DLS, POMs embedded in gels (after migration) were extracted using two methods, A and B: immersing the cut segment of gels into water. Method A (extraction) involved submersing cut segments of the gel into water (5 mL), allowing the clusters to diffuse out from gel matrix. After several hours (1 h of extraction was enough to obtain UV-vis spectra) POMs in gels had diffused into water. Method B (collection slot) used a second slot prepared at the anode-side of the gel, where the POM can migrate toward and then be directly removed by pipette. The solution obtained by method B was more concentrated than that of method A.

d) Migration of original counter cation of POM under electrophoresis

To investigate migration of the original counter-cation of POMs, we prepared a water soluble Ni salt of the $\{\text{SiW}_{12}\}$ POM, $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{SiW}_{12}\text{O}_{40}]$, which enabled us to follow where the counter-cations were throughout the electrophoresis (Ni ions change colour from green to brown upon dyeing of the gel). After electrophoresis of $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{SiW}_{12}\text{O}_{40}]$ followed by reduction for dyeing, a brown band had migrated towards the cathode. A similar band was observed for a Nickel nitrate solution, therefore it can be considered that the Ni ions that were the original counter cations of the POM had separated and migrated toward the cathode. A blue band could also be observed for the reduced $\{\text{SiW}_{12}\}$, which had migrated towards the anode, identical to $\text{Na}_4[\text{SiW}_{12}\text{O}_{40}]$. The “buffer cations” displaced the original Ni cations without altering the behaviour of the POM anion.

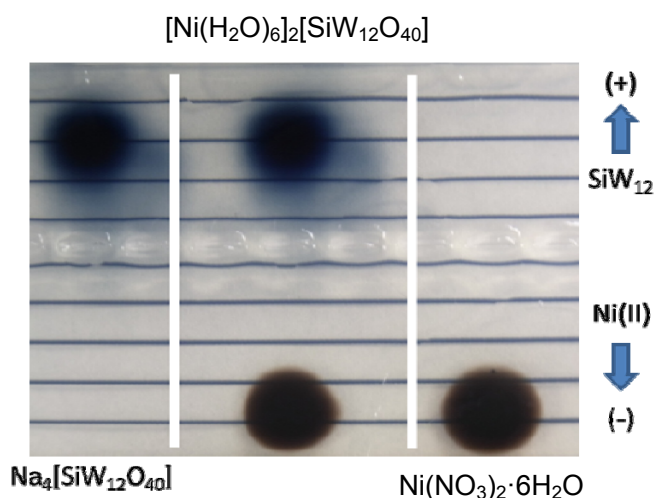


Figure S1-2. Photograph of gels after electrophoresis and dyeing process. Samples are; (left) $\text{Na}_4[\text{SiW}_{12}\text{O}_{40}]$; (middle) $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{SiW}_{12}]$; and (right) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The anionic POM migrated towards the anode while Ni cations migrated towards the cathode.

2. UV-vis spectra and DLS plots

Figure S2-1 shows UV-vis spectra of $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{154}\}$ solutions before and after gel electrophoresis (10 min run, in NaOAc/HOAc buffer). POMs after electrophoresis are extracted by immersing the cut fragment of gel containing the coloured band into water (5 mL). Both clusters show similar spectra in UV-vis regions after electrophoresis, suggesting that the redox states of cluster are not affected by electrophoresis. Figure S2-2 shows size distributions of the same solutions characterised by dynamic light scattering (DLS). The extracted POM solutions show slightly larger particle sizes and wider size distributions than the POM solutions measured before electrophoresis. This is believed to be caused by the formation of complexes of the POMs with components of the gel matrix; the POM clusters are still intact but their hydrodynamic radius has increased due to the associated gel components. Figure S2-3 shows the IR spectra of the $\{\text{Mo}_{132}\}$ precipitate obtained by addition of acetone to the aqueous extract of the $\{\text{Mo}_{132}\}$ gel band. Agarose peaks can be seen in the IR spectrum of the $\{\text{Mo}_{132}\}$ precipitate obtained after gel electrophoresis confirming its presence in the precipitate. The characteristic IR bands of $\{\text{Mo}_{132}\}$ can also be seen in the IR spectrum of the precipitate which also confirms the presence of the intact $\{\text{Mo}_{132}\}$ cluster.

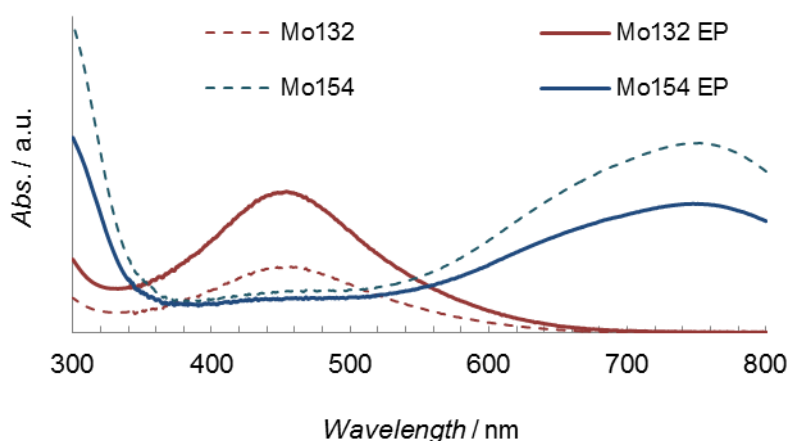


Figure S2-1. UV-vis spectra of $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{154}\}$ solution before and after gel electrophoresis. “EP” signifies spectra for samples characterised after electrophoresis.

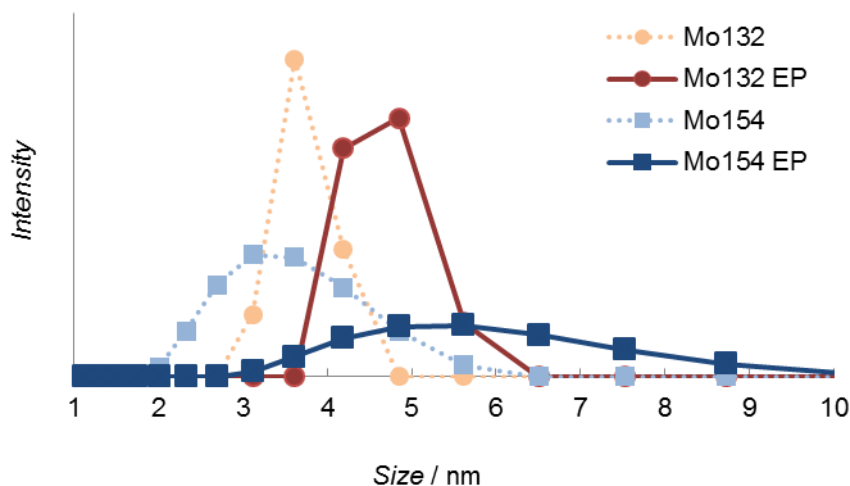


Figure S2-2. Size distribution of $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{154}\}$ solution before and after electrophoresis characterised by dynamic light scattering. “EP” signifies data for samples characterised after electrophoresis.

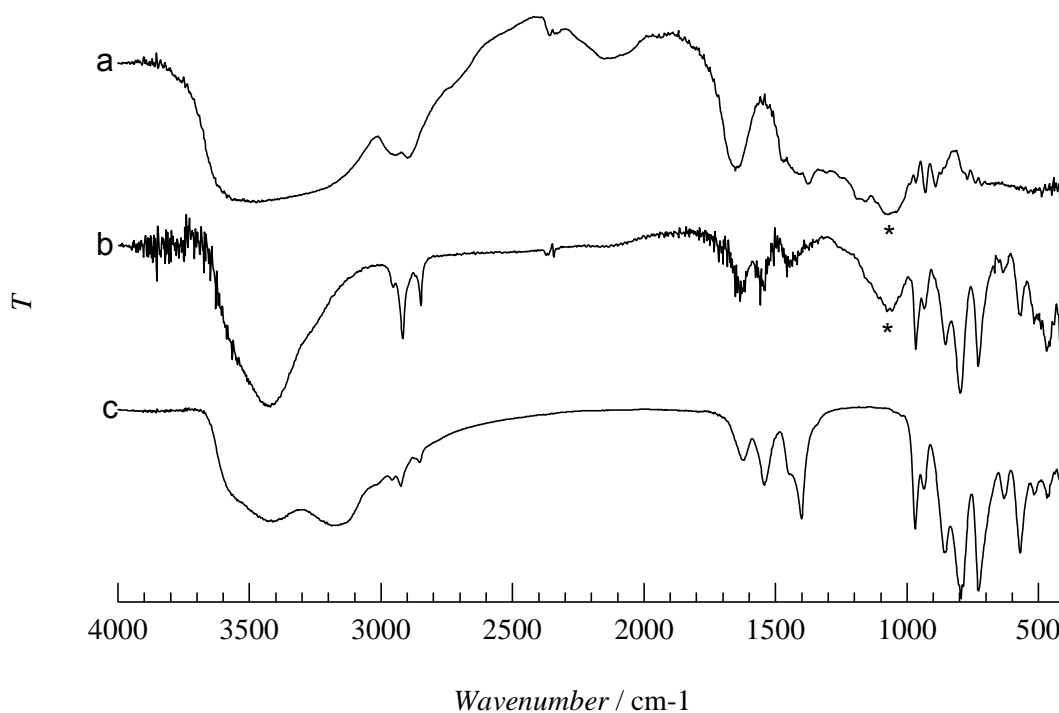


Figure S2-3. IR spectra of (a) Agarose; (b) $\{\text{Mo}_{132}\}$ -EP, which is extracted from gels into water and then precipitated by addition of acetone; and (c) $\{\text{Mo}_{132}\}$. The spectrum of $\{\text{Mo}_{132}\}$ -EP extracted from the gel has additional peaks which can be assigned to that of agarose (highlighted by asterisk), suggesting $\{\text{Mo}_{132}\}$ is still contaminated with agarose after extraction.

3. Estimation of Surface Charge Density

The surface charge density for each cluster is estimated by dividing the surface area, based on crystallographic cluster dimensions, by the charge of the cluster. Surface areas of Keggin and Dawson clusters are estimated by using a spherical model with radii of 0.5 nm and 0.6 nm, respectively (see Figure S3 below). Although the Dawson cluster is not spherical, the isotropic and effective radius has been based a spherical model with the longest cluster axis taken as the diameter. A better approximation of the surface area for the Dawson may be achieved by using different geometric models, such as a cylinder or triangular prism.

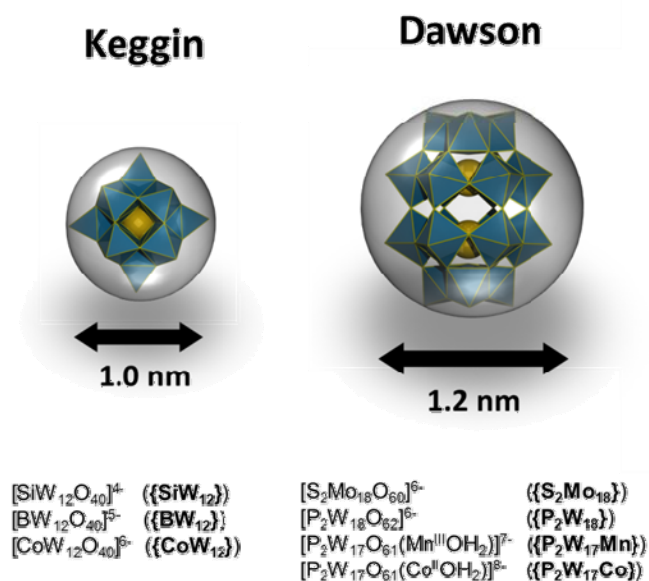


Figure S3. Cluster shape and surface area of each cluster family of Keggin and Dawson cluster with compositions of polyanions.

Table S1. Summary of charge (Z), surface charge density (σ) and mobility (μ) measured for 20 mM samples.

	Keggin Clusters			Dawson Clusters			
	$\{\{\text{SiW}_{12}\}\}$	$\{\{\text{BW}_{12}\}\}$	$\{\{\text{CoW}_{12}\}\}$	$\{\{\text{P}_2\text{W}_{18}\}\}$	$\{\{\text{P}_2\text{W}_{17}\text{Mn}\}\}$	$\{\{\text{P}_2\text{W}_{17}\text{Co}\}\}$	$\{\{\text{S}_2\text{Mo}_{18}\}\}$
Z	4	5	6	6	7	8	6
σ	1.27	1.59	1.91	1.32	1.55	1.77	1.33
$\mu / 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	0.33	0.52	0.53	0.37	0.47	0.55	0.45

4. IR spectra POM precipitates

IR spectra of $\{\text{Mo}_{154}\}$ and $\{\text{Mo}_{132}\}$ precipitated samples after electrophoresis are shown in figure S4-1. $\{\text{Mo}_{132}\}$ was precipitated by addition of KCl and acetone into the solution collected after electrophoresis. The solution was collected by method B. $\{\text{Mo}_{154}\}$ was precipitated in a similar way to $\{\text{Mo}_{132}\}$ but using dimethylstearyl ammonium bromide instead of KCl. Samples after electrophoresis show good correspondence with the spectra for those of the control samples (dimethylstearyl ammonium salt of $\{\text{Mo}_{154}\}$ and K salt of $\{\text{Mo}_{132}\}$) prepared directly by cation exchange of the original loading solutions. The precipitated samples for Keggin and Dawson clusters were prepared in a similar way to the method above, except tetrabutylammonium bromide (for SiW_{12} , BW_{12} , P_2W_{18} and $\text{P}_2\text{W}_{17}\text{Co}$) and tetraethanolammonium chloride (for $\text{P}_2\text{W}_{17}\text{Mn}$ and CoW_{12}) were used for cation exchanges. Figure S4-2 shows the IR spectra for Keggin and Dawson clusters with and without electrophoresis. Again the samples after electrophoresis show good correspondence with the spectra for those of the control samples prepared directly by cation exchange of the original loading solutions.

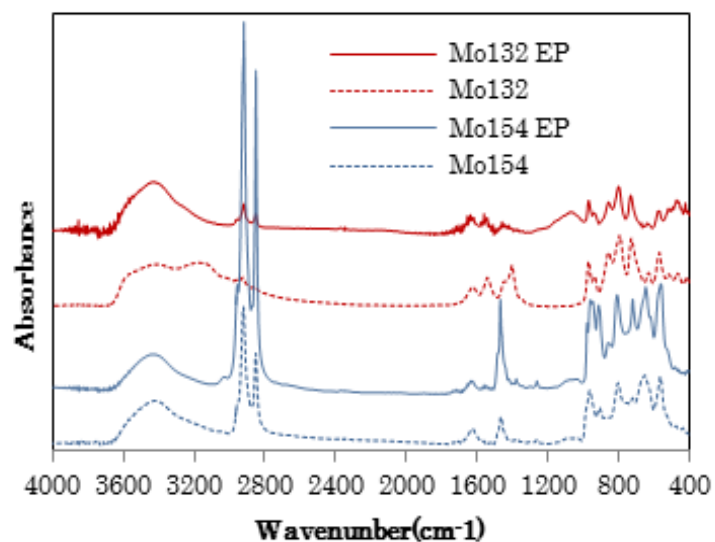


Figure S4-1. IR spectra of $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{154}\}$ prepared as K and dimethylstearyl ammonium salts respectively. “EP” refers to samples collected from gels after electrophoresis.

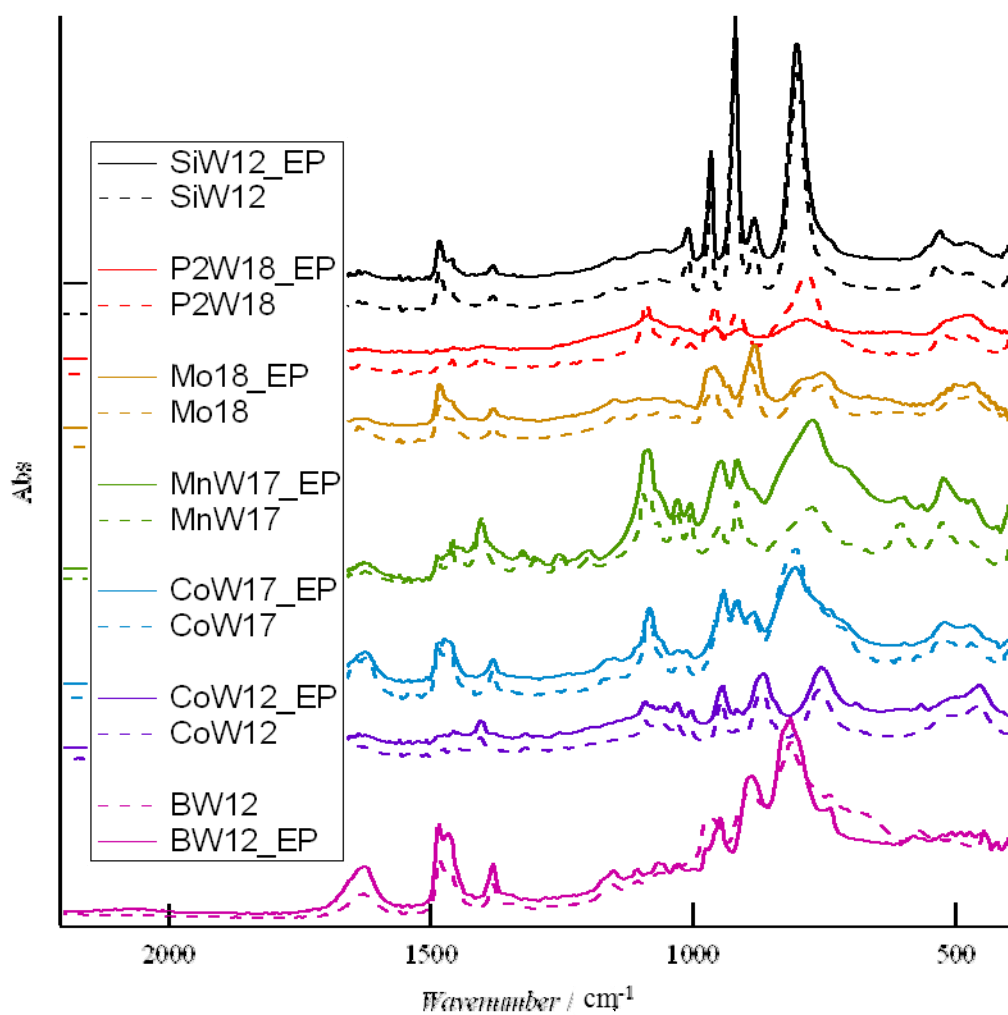


Figure S4-2. IR spectra of Keggin and Dawson clusters prepared as tetrabutylammonium and tetraethanolammonium salts. “EP” refers to samples collected from gels after electrophoresis.

5. Preparation of Ni salt of SiW₁₂

Ni salt of {SiW₁₂} was prepared by cation exchange from the Na salt of {SiW₁₂} which was commercially available. An acetonitrile solution of Na₄[SiW₁₂O₄₀] (3.3 M, 5 mL) was mixed with an acetonitrile solution of Ni(NO₃)₂•6H₂O (3.3 M, 10 mL), producing a green precipitate. Single crystals of [Ni(H₂O)₆]₂[SiW₁₂O₄₀] • ca. 6H₂O were obtained by recrystallisation of this precipitate from water. IR spectrum of the compound shows good agreement with that reported (figure S5).^[1-2]

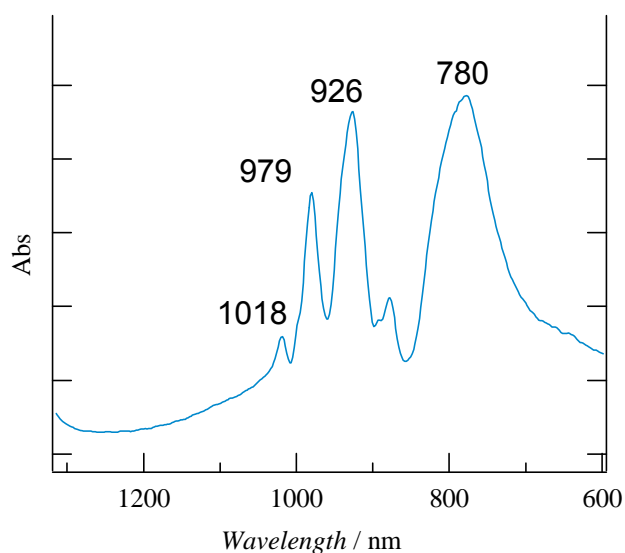


Figure S5. IR spectra of [Ni(H₂O)₆]₂[SiW₁₂O₄₀]•nH₂O.

[1] K. B. Tayeb, C. Lamonier, C. Lancelot, M. Fournier, E. Payen, A. Bonduelle, F. Bertoncini, *Catalysis Today*, **2010**, *150*, 207-212.

[2] K. B. Tayeb, C. Lamonier, C. Lancelot, M. Fournier, E. Payen, F. Bertoncini, A. Bonduelle, *C. R. Chim.*, **2009**, *12*, 692-698.