Chemical Science

Winner of the ALPSP Award for Best New Journal 2011

RSCPublishing

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Exploring the mobility of nanoscale polyoxometalates using gel electrophoresis†

Ryo Tsunashima,[a] Craig Richmond[b] and Leroy Cronin[*b]

Polyoxometalate clusters encompass a vast library of molecular metal-oxo anions with a large range of mass, size, and charge and are generally formed under one-pot conditions, where many species may exist in solution at any given time. Herein we demonstrate that conventional gel electrophoresis can be used to separate metal oxide based nanomaterials from mixtures, and as a result identify cluster types as a function of their surface charge density. In particular we demonstrate that the nanoscale clusters, contrary to current understanding, have mobility that is a function of the surface charge density at high concentrations. This means that when considering the structural diversity of metal oxide nanomaterials, the variation of charge, size, shape or other structural properties causes a difference in mobility that can be used to both characterise and separate the nanoscale oxides in solution.

Introduction

The study of molecular metal oxides or polyoxometalates (POMs), which are polymeric clusters of oxo anions (MO_x where $M = Mo$, W, V, Nb and $x = 4$–7), defines a huge area of scientific research and is of major contemporary interest due to the plethora of shapes, sizes, physical properties, and applications they have. Examples of such applications include photo-induced water splitting, electronics, catalysis, nanotechnology and medicine.[1–11] The structures and range of sizes for some of the most studied and fundamentally important POM species are given in Fig. 1.[12]

The structural diversity among POMs can however present a major problem when attempting to discover and characterise unknown clusters, either in the solid state or even more so in solution. This difficulty can be elegantly illustrated when one considers the discovery of "molybdenum blue", first mentioned in Carl Scheele's report from 1783 but only structurally defined over two centuries later in 1995 when Achim Müller and co-workers were able to use single crystal XRD to solve the structure. The structure was revealed to be a molecular wheel *ca.* 3.6 nm in diameter containing 154 molybdenum atoms and over 500 oxygen-based ligands.[12] This discovery opened the fields of

nanomolecular and supramolecular chemistry based on these gigantic metal oxide clusters.

The reasons for the delay between the initial observations and solving the structure of 'molybdenum blue' were not only due to the inherent technical limitations of that time but also the difficulties involved in the crystallisation of such large clusters, especially when they are present as mixtures; even simple 1 : 1 mixtures are virtually impossible to crystallise. Simple and quick analytical techniques that allow us to identify and separate clusters from mixtures, such as TLC and HPLC, are clearly indispensable in organic synthesis and the development of similar techniques would be greatly beneficial for the study of POMs.
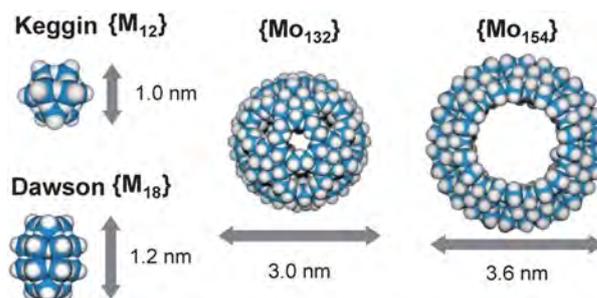
Fig. 1 Structures and relative sizes of four nanoscale polyoxometalate clusters represented by space filling models, where the blue and white spheres correspond to the metal ($M = Mo$ or W) and oxygen ligands respectively. The chemical formulae of the $\{Mo_{132}\}$ and $\{Mo_{154}\}$ complexes are $(NH_4)_{42}[Mo_{132}O_{372}(CH_3CO_2)_{30}(H_2O)_{72}]\cdot ca.300H_2O\cdot ca.10CH_3COONH_4$ and $Na_{15}[Mo_{154}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo_{152}O_{457}H_{14}(H_2O)_{68}]_{0.5}\cdot ca.400H_2O$, respectively, and the formulae of the $\{M_{12}\}$ and $\{M_{18}\}$ complexes can be $Na_3\{M_{12}O_{40}P\}$ and $Na_6\{M_{18}O_{62}P_2\}$, giving a large range of charge surface densities when one considers the charges of the anionic clusters.

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These advances could potentially open up new synthetic approaches and provide greater synthetic detail, leading to increased understanding of reaction mechanisms, improvement of yields and the discovery of new clusters and materials.

According to fine differences in mobility, DNA and proteins can be separated and identified from complex mixtures. The mobility of these materials is usually described by their molecular weight, however this is because in these cases molecular weight is proportional to the surface charge density which actually governs mobility. The differences in the molecular weights of the DNA therefore results in fine differences in electrophoretic mobility which is further amplified by molecular sieving effects. Reported here for first time are the electrophoretic mobilities in agarose gels for POMs of a range of sizes, charges and structural morphologies. It was found that the mobilities of the clusters correspond closely to the clusters in terms of surface charge density, $\sigma = Z/A$ (where Z and A represent cluster charge and surface area respectively) and as a result can be used to separate and characterise aqueous mixtures of POM clusters.

Although electrophoretic techniques have been used to investigate POMs before,[13] the correlation of size and charge, in the form of surface charge densities, with mobility for a variety of POM clusters (see Fig. 1) are revealed here for the first time. This finding opens up the possibility of using gel electrophoresis as a genuine analytical technique for the investigation of the cluster species in solution. The differences in mobilities allowed the evaluation of POM mixtures by obtaining both the number of species in the mixture and the respective surface charges of the separated components. The measurements can be performed directly on solutions of pure crystalline samples for reference and directly on crude products and reaction solutions. As mentioned previously, such analytical techniques have great potential for characterising complex self-assembly reactions such as those of the gigantic "molybdenum blue" clusters. The application of gel electrophoresis for the investigation of syntheses of the gigantic {Mo154} wheel cluster is therefore also demonstrated. The yield was improved by tuning the reaction conditions based on observations from gel electrophoresis analysis.

Results and discussion

Gel electrophoresis of gigantic POMs: Mo-brown ball and Mo-blue wheel

Since the "Mo-brown ball" {Mo132} and "Mo-blue wheel" {Mo154} have very large sizes and charges, these clusters are ideal candidates for investigation by electrophoresis. Therefore the clusters were applied (individually and as a mixture) to an agarose gel buffered at pH 5 and a voltage of 100 V was applied for between 1 and 10 min. Fig. 2a shows pictures of the gel during electrophoresis taken at 0, 6 and 10 min. This shows that both POMs moved toward the anode with different mobilities, each following a linear relationship between displacement of the band as a function of time (Fig. 2b) but that the {Mo132} sphere moves faster than the {Mo154} wheel. The higher mobility of the {Mo132} ball can be rationalised when one considers its smaller size and higher charge than those of the {Mo154} wheel. The charge and crystallographic diameter of {Mo132} are −42 and 3.0 nm and those of {Mo154} are −14 and 3.6 nm. A mixed
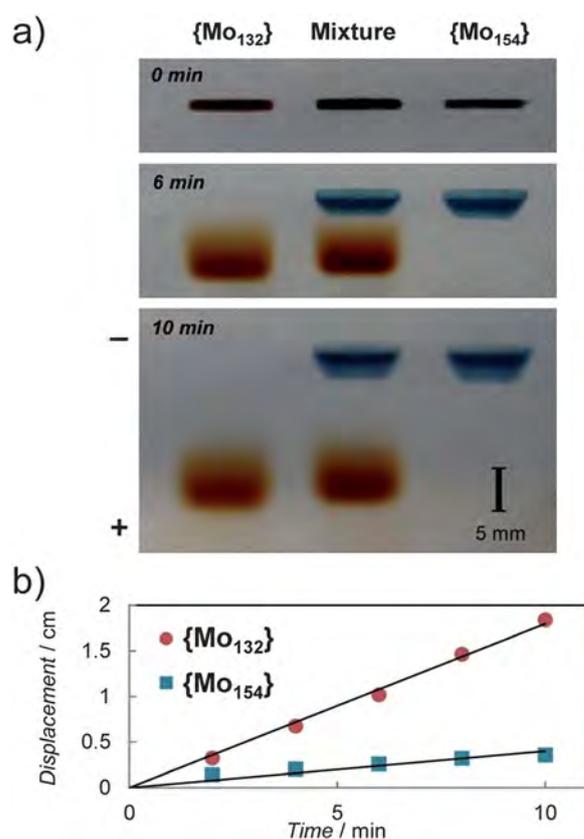
Fig. 2 (a) Photographs of a gel for electrophoretic separation of molybdenum blue and molybdenum brown taken at 0, 6 and 10 min intervals during the run. Each column is: (left) {Mo132}; (middle) 1 : 1 mixture of {Mo132} and {Mo154}; and (right) {Mo154}, all at 2.0 mM concentrations. (b) Linear plots of cluster band displacement against time for the electrophoresis experiment.

solution of the two clusters can therefore be separated into the distinct brown and blue bands, and their different mobility behaviour can be attributed to their relative size and charge.

Structural stability for electrophoresis

Unlike some traditional POMs such as the stable Keggin clusters, some of the larger gigantic POMs are rather sensitive to oxidation and high pH in aqueous solution. This was indicated by a slight fading of the intense blue and brown colours of {Mo154} and {Mo132} during extended (15–20 min) electrophoresis runs, indicating partial oxidation of the samples. This oxidative degradation is even more evident when the experiment is run in aqueous gels without buffer (see Fig. S1-1 in ESI†). However, spectroscopic investigations, including UV-vis, IR, and dynamic light scattering (DLS), show that by using a buffer (pH 5) and limiting the time of the electrophoresis experiment to no more than 10 min then there is no noticeable colour fading and oxidative decomposition.

To assess the stability of POMs during electrophoresis, clusters were first isolated from the gel matrix by two methods (Fig. 3): Method A (extraction) involved submersing cut segments of the gel into water, allowing the clusters to diffuse out from the gel matrix. Method B (collection slot) used a second slot prepared at the anode-side of the gel, where the POM can migrate toward
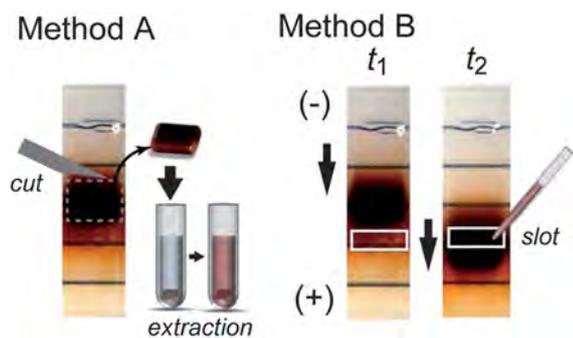
Fig. 3 Photographs of gels and schematic demonstration of extraction methods A and B, where $t_2 > t_1$.

and then be directly removed by pipette. The solution obtained by method B was more concentrated than that of method A.

The extracted solutions were suitable for characterisation by spectroscopy, namely UV-vis and DLS (see ESI for UV-vis spectra and DLS plots†). Decreasing the solubility of the POMs in the extracted solutions by addition of a potassium salt, alkylammonium salt and/or polar organic solvent led to formation of a precipitate, which could be filtered, dried and further characterised by IR spectroscopy (see ESI for IR spectra†).

The solutions of $\{Mo_{154}\}$ and $\{Mo_{132}\}$ prepared by method A showed similar UV-vis spectra to those of dilute solutions of the preloaded pure samples. The DLS plots showed a slightly larger particle size and wider size distributions for the samples after electrophoresis. This is presumably because the POMs have associated with some of the sugar-based components of the gel matrix *via* hydrogen bonding and/or direct displacement of the metal oxo-ligands by the abundant alkoxy groups.[14] The IR spectrum of the $\{Mo_{132}\}$ precipitate prepared by extraction method A followed by addition of acetone gave a similar spectrum to that of the preloaded $\{Mo_{132}\}$ but with additional peaks corresponding to agarose, confirming the association of the agarose and POM. Samples of $\{Mo_{154}\}$ and $\{Mo_{132}\}$ precipitated after electrophoresis were obtained by extraction method B followed by addition of dimethylstearylammonium bromide and acetone and KCl and acetone respectively. Precipitates of Keggin and Dawson clusters were similarly prepared as tetrabutylammonium and tetraethanolammonium salts (see ESI†). The IR spectra for samples prepared after electrophoresis showed good correspondence with the spectra of those of the control samples prepared directly by cation exchange of the original loading solutions. The spectral data therefore support the hypothesis that the POM clusters are stable during electrophoresis experiments when the pH is buffered to pH 5 and the experiment duration is limited to 10 min.

Another potential route to POM destabilisation during electrophoresis could be through cation-exchange of the native POM cations with the cations present in the buffer solutions. To investigate this, a water soluble Ni salt of the $\{SiW_{12}\}$ POM, $[Ni(H_2O)_6]_2[SiW_{12}O_{40}]$, was prepared, which enabled us to follow where the counter-cations were throughout the electrophoresis (Ni ions change colour from green to brown upon dying of the gel, see Fig. S1-2 in ESI†). After electrophoresis of $[Ni(H_2O)_6]_2[SiW_{12}O_{40}]$ and reduction for dyeing (Fig. 4), a brown band had migrated towards the cathode. A similar band was

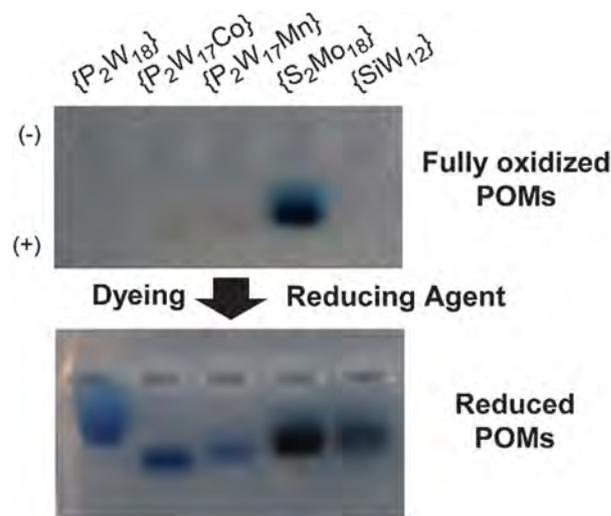**Fig. 4** Photographs of gel after electrophoresis and then after the dyeing process by casting of reducing agent. All POMs were loaded in 5 μL portions at 20 mM and show a visible band after dyeing. POMs are $\{P_2W_{18}\}$, $\{P_2W_{17}Co\}$, $\{P_2W_{17}Mn\}$, $\{S_2Mo_{18}\}$ and $\{SiW_{12}\}$, from left to right.

observed for the nickel nitrate control; the original Ni counter cations of the POM had therefore separated and migrated toward the cathode. A blue band was observed for the reduced $\{SiW_{12}\}$, which had migrated towards the anode with identical mobility to $Na_4[SiW_{12}O_{40}]$. The Na "buffer cations" displaced the original Ni cations but importantly did not alter the behaviour of the POM anion. The buffer cations therefore play a key role in stabilising the POM anion during electrophoresis and additional studies to investigate the effect these cations have on POM mobility are already underway in our lab.

### Gel electrophoresis of Keggin and Dawson clusters

To further explore the potential of gel electrophoresis in POM separation and to characterise mobility as a function of charge and size, a range of related clusters were selected. These were the Dawson and Keggin clusters of general formulae $\{P_2W_{18}\}$, $\{P_2W_{17}Co\}$, $\{P_2W_{17}Mn\}$, $\{S_2Mo_{18}\}$, $\{BW_{12}\}$, $\{SiW_{12}\}$ and $\{CoW_{12}\}$.[15] Since most of these POMs are colourless, or very light coloured in contrast to the partially reduced Mo-brown and Mo-blue clusters presented previously, a method for visualizing the fully oxidised POMs was developed by dyeing of the post-electrophoresis gels with a reducing agent. Dyeing is performed by casting a $Na_2S_2O_4$ solution (1 wt%) with a few drops of HCl (6 M) onto the gel; the reduced POMs are highly coloured and can be easily identified on the gel-plates as shown in Fig. 4. The $\{S_2Mo_{18}\}$ contains two reduced Mo centres in its native state and is therefore coloured even before the dying process.

Relating charge to electrophoretic mobility

According to the conventional theory of electrophoresis, mobility depends upon a large number of parameters; these include structural properties of the molecules (size, shape, charge and mass), applied voltage, gel concentration, pH and reagent concentrations. Here several POMs are characterised in terms of

their mobility at fixed conditions of 20 mM loading concentration, pH 5 controlled by HOAc/NaOAc buffer, and electric field strength of 7.69 V cm^{-1} applied for 10 min. Agarose gels were prepared at 1 wt% in buffer solution and mobilities were estimated by digital analysis of high resolution photographs of the gels using a CCD camera.

Analysis of cluster mobilities shows a general trend according to both the charge and size of the clusters. The charges of the {P$_2$W$_{18}$}, {P$_2$W$_{17}$Mn}, {P$_2$W$_{17}$Co} and {S$_2$Mo$_{18}$} Dawson clusters are −6, −7, −8 and −6, respectively and their mobilities vary proportionally with the cluster charges (Fig. 5c). A similar relationship between cluster charge and anion mobility is also observed for the Keggin clusters {SiW$_{12}$}, {BW$_{12}$}, and {CoW$_{12}$}, where the charges are −4, −5 and −6, respectively (Fig. 5b). When comparing only Keggin clusters, or only Dawson clusters, the mobility varies linearly with charge as the approximate size and surface area of the clusters remain constant for each family. However, when making comparisons across the two families, the difference in cluster size must also be accounted for: the {P$_2$W$_{18}$} and {CoW$_{12}$} clusters, compared in Fig. 5a, both have a −6 charge but have different mobilities and were able to be separated from a mixture. The reason for this is due to the smaller size of the {CoW$_{12}$} compared to the {P$_2$W$_{18}$}, resulting in the higher mobility of {CoW$_{12}$}. The diameters of the Keggin and Dawson clusters are estimated (from crystallographic data) to be 1.0 and 1.2 nm respectively.
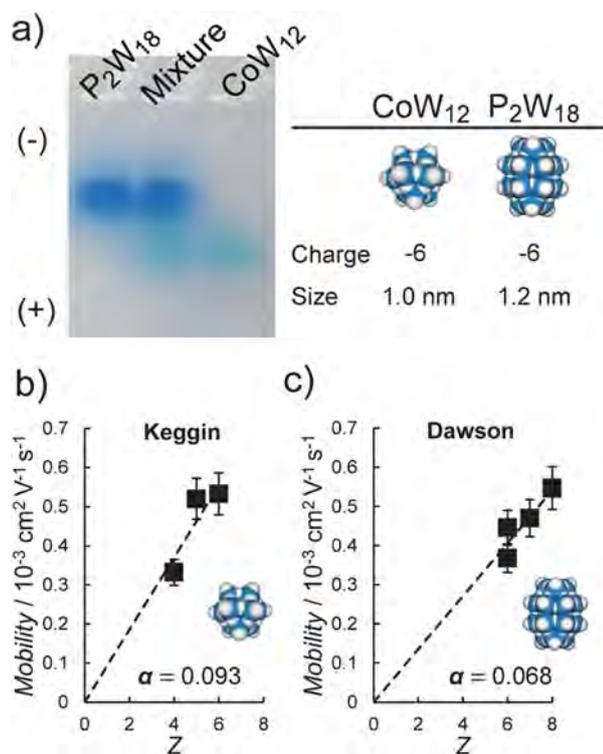
Fig. 5 (a) Photograph of a gel after the electrophoresis and dyeing process. Each column is: {P$_2$W$_{18}$}; 1 : 1 mixture of {P$_2$W$_{18}$} and {CoW$_{12}$}; and {CoW$_{12}$}. (b) Plot of mobility for Keggin clusters {SiW$_{12}$}, {BW$_{12}$} and {CoW$_{12}$} with charge (Z), where α represents its slope. (c) Plot of mobility for Dawson clusters {P$_2$W$_{18}$}, {P$_2$W$_{17}$Mn}, {P$_2$W$_{17}$Co} and {S$_2$Mo$_{18}$}. Sample loading concentrations are 20 mM. Error bars represent the standard deviations observed over multiple runs.
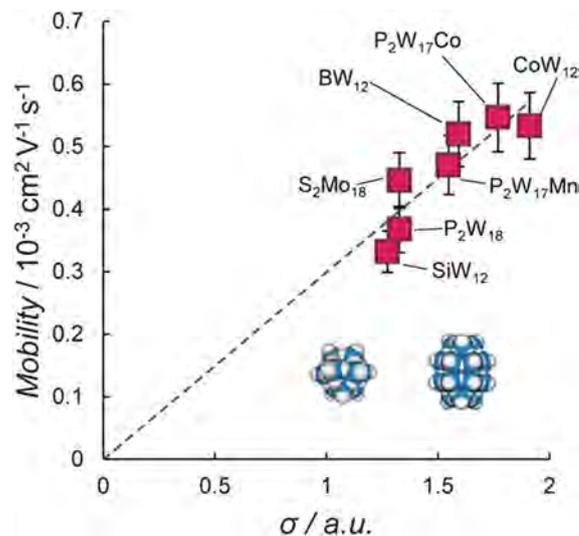
Correlation between mobility and POM structure

In conventional gel electrophoresis, smaller particles should show a higher migration than larger particles of similar charge, however this is normally only possible for very large (>100 nm) species due to the molecular sieving effect of the porous gel matrix. Despite this potential limitation, it was still possible to correlate the mobility of a range of POMs with their charge and size. This was accomplished by applying the standard practice in electrophoresis, which employs surface charge density as the fundamental parameter that governs mobility if the particles fall within the Debye–Hückel limit, as shown below by eqn (1):

$$\mu = \sigma/4\pi\eta\kappa \qquad (1)$$

Where μ, σ, η and κ are mobility, surface charge density, solvent viscosity and inverse Debye length, respectively.[16] Since both the Keggin and Dawson clusters do not fit the same linear relationship when mobilities are plotted against charge, (each cluster group forms a separate linear relationship, $\alpha_{Keggin} \neq \alpha_{Dawson}$, see Fig. 5) surface charge density was plotted against mobility, which gave a good linear correlation (Fig. 6). Surface charge density, σ, was approximately estimated by dividing the cluster charge, Z, by its surface area (estimated from crystallographic data, see Fig. S3 in ESI†). This correlation is particularly important as it links the cluster mobilities to their charge and size across the different families of POM clusters.

In the case of DNA, mobility is typically described as a function of its molecular weight, because the variations in charge and surface charge density of DNA are directly proportional to its size and mass. Optimal separation is therefore only expected under conditions where the molecule or particle sizes are comparable with the pore size of the gel, as it is this that retards progression of the DNA through the gel matrix and produces the molecular sieving effect observed. At the gel concentrations used here (1 wt%) the range of pore sizes are 100–200 nm and are therefore not comparable to the size of the clusters,[16–18] however


Fig. 6 Plots of mobility against surface charge density, σ. Correlation between mobility and σ is fitted linearly. Sample concentration is 20 mM. Error bars represent the standard deviations observed over multiple runs.

the clusters can still be separated with relatively high resolution as shown previously in Fig. 2 and 5. The correlation between the cluster surface charge density and mobility must therefore be caused by another type of interaction between the POMs and the gel. These attractive interactions could be attributed to hydrogen bonding between the oxo-ligands of the POM and the hydroxyl groups of the agarose; such interactions between sugar-based polymer matrices and POMs have been previously reported.[14] These interactions would account for the linearity of the relationships observed in the absence of molecular sieving effects since compounds with lower surface charge densities would form weaker hydrogen bond interactions with the gel and thus have lower mobilities as seen here.

Tuning the synthetic conditions for gigantic polyoxometalate clusters

One of the most important applications of chromatographic techniques is reaction monitoring and conventional quick chromatography techniques, such as TLC, are indispensable for optimising organic reaction conditions. A major goal of this work was therefore to demonstrate the use of gel electrophoresis in the reaction monitoring of POM syntheses. A series of reaction conditions for the formation of the gigantic "molybdenum blue" cluster $\{Mo_{154}\}$ were characterised by gel electrophoresis and the information obtained was used to improve the isolated product yield. The $\{Mo_{154}\}$ cluster is typically prepared in a one-pot reaction from a mixture of Na_2MoO_4, acid and reducing agent, giving single crystals after one day.[15d] In contrast to its simple reaction procedure, the mechanism involves complex equilibria and self-assembly processes.[8] Ascertaining information on the species present in solution would therefore help to understand the formation mechanism and allow judicial alterations to be made for improving the synthetic procedures.

Characterisation of the reaction filtrate (after separation of single crystals of $\{Mo_{154}\}$ after 48 h) revealed two bands (Fig. 7); a dark blue band with low mobility and a highly mobile colourless band (turns brown after dyeing for visualisation). The very low mobility and dark blue colour of the first band indicate the presence of a structure with a low surface charge density and reduced molybdenum centres, suggesting residual $\{Mo_{154}\}$. The very high mobility and lack of colour from the second band suggests a fully oxidised structure with a high surface charge density, probably $\{Mo_{36}\}$, however further analysis would be required for unambiguous assignment. When the amounts of reducing agent were varied from 0.15 g (condition A) to 0.30 (condition B) and 0.40 g (condition C), the intensity of the brown band decreased and the intensity of the blue band increased, indicating an increase in the overall reaction conversion to $\{Mo_{154}\}$. This increased conversion was corroborated by an increase in the isolated product yield from A to C (45%, 73% and 80% respectively) Single crystals suitable for crystallography were only obtained under condition A (unit cell matched for $\{Mo_{154}\}$) however the microcrystalline powder collected from conditions B and C gave IR and UV-vis spectral data consistent with the material from condition A and the reported synthesis.[15d] Furthermore, the isolated blue powders from syntheses B and C showed single bands of identical mobility to that of synthesis A and the $\{Mo_{154}\}$ reference sample, confirming product identity and purity.
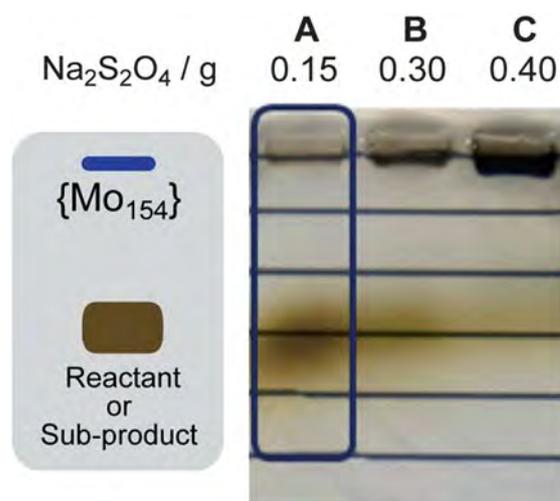
Fig. 7 Photograph of gels after electrophoretic migration of solutions A, B and C followed by dyeing process. Solutions A, B and C are the filtrates of $\{Mo_{154}\}$ reaction solutions ($Na_2MoO_4\cdot2H_2O$, 3.04 g plus 32% hydrochloric acid, 2.7 mL in water, 25 mL and $Na_2S_2O_4$, 0.15 g, 0.30 g, and 0.40 g).

Conclusions

In summary, the separation of a diverse range of nanoscale molecular metal oxide clusters using gel electrophoresis has been fully demonstrated. These studies have revealed that even though gel pore size was considerably larger than cluster size, and therefore unable to exhibit the traditional sieving effect required for separation by electrophoresis, a good correlation between the cluster migration and surface charge density was still observed. This was attributed to other physical interactions between POM clusters and the sugar-based polymer gel matrix. To demonstrate these results, nanoscale molecules of $\{Mo_{132}\}$ and $\{Mo_{154}\}$ were isolated from mixtures, where the higher charged cluster of $\{Mo_{132}\}$ showed a higher comparative mobility. The mobilities of a series of Dawson and Keggin POM anions were also studied and were shown to follow a linear relationship when plotted against their surface charge densities. This relationship provides a new means of obtaining structural information from both pure samples and solution based mixtures of POMs and could therefore play a key role in elucidating the composition of new or unknown cluster systems e.g. the new members in the recently discovered uranyl peroxide cluster systems.[19] The ability to use gel electrophoresis to measure mobility and hence characterise the surface charge density of nanoscale POM clusters therefore represents a major breakthrough and opens up new possibilities to explore a large variety of other nanoscale-clusters, -particles and -molecular aggregates e.g. MOFs or any other large nanoscale structures of high charge and large size.

Experimental

Synthesis

All of the clusters explored here have been prepared using previously reported literature examples.[15]

Electrophoresis studies

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 (sample concentration was shown in each figure caption) was prepared and injected into slots in the gels in 5 μL portions and a voltage (100 V) was applied to the system for 1–10 min.

Dyeing of POMs on gels

The dyeing process is performed by casting a $Na_2S_2O_4$ solution (1 wt%) with a few drops of HCl (6 M) 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 min, 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.

Extraction of POMs after electrophoresis

For characterisation using UV-vis spectroscopy and DLS, the POMs embedded in gels (after migration) were extracted using two methods, A and B (see Fig. 3 and ESI†).

Analytical measurements

Infrared spectra were measured using samples dispersed in a KBr disk on a Jasco FTIR-410 spectrometer. Wavenumbers are given in cm^{-1}. UV-vis spectra were collected using a Shimazu PharmaSpec UV-1700 spectrophotometer in absorbance mode using quartz cuvettes with 1.0 cm optical path length. The particle sizes were characterized using a Malvern Instruments Zetasizer Nano ZS instrument at 25 °C.

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