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# Electrochemical study of multilayer films built on glassy carbon electrode with polyoxometalate anions and two multi-charged molecular cationic species

**David Martel · Maurice Gross**

**Abstract** Electrochemical results are reported on complex films built onto glassy carbon electrodes. Each film involves one polyoxometalate ($PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$, $SiMo_{12}O_{40}^{4-}$ or $SiW_{12}O_{40}^{4-}$) and one or two cations : methyl viologen and meso-tetra(4N-methylpyridyl porphyrin). In a given film, layers of polyoxometalate anions alternate with layers made of one of the two cations. Electrochemical studies indicate the effective building of films with polyoxometalate and both cations present. They also demonstrate that, in the film building process, the electrochemical response of every new layer is influenced by coulombic interactions and conducting properties with the immediately underlying layer.

**Keywords** Polyoxometalate · Self-assembly · Coulombic interactions · Electrochemistry · Modified electrode

## Introduction

Molecular engineering of artificial, surface-based self-assembly with specific functions has recently attracted much interest. An example of such a desired function is provided by photoinduced electron transfers [1]. Such electron transfers take place in photosynthetic systems, and the development of artificial devices aiming at mimicking natural systems has been significant in the last decade. Another application of photoinduced electron transfer is the development of photovoltaic cells.

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Research on such nanoscale-based organized molecular systems arises from the expectation that control of their structure will allow understanding and tuning their electron transfer characteristics, thus paving the way towards nanometric information and communication devices.

Previous papers [2, 3] reported that photoinduced electron transfer occurs from the excited porphyrin cation to the methyl viologen upon light excitation. This was observed in solution [2], as well as in solid films of $TiNbO_5$ oxide [3]. In this context, we were interested in studying the redox properties of films built with an electron donor (ED: cationic porphyrin) and an electron acceptor (EA: methyl viologen) plus another redox active species—namely, polyoxometalate anions (POM)-enabling effective electron transfer between ED and EA under appropriate stimulation. This paper accounts for the redox behaviour of such three components films, in the absence of light excitation.

The self-assembling process implemented in the present paper is based on electrostatic interactions between polyoxometalates (POM) as anions and the two cations. POM are very interesting molecules owing to their stability, their well-characterized topography and the versatility of their properties [4, 5] (chemical constitution, redox characteristics). POM are also known to adsorb spontaneously on surfaces, such as carbon, gold or ITO [4, 6–8]. The building of films involving methyl viologen and POM [9], or metalled cationic porphyrins and POM [10] has already been reported in the literature. Complex films with POM have also been described [11], but there is no report to date of films simultaneously involving POM and two types of cations. The aim of this study was, therefore, to investigate the feasibility of building films with one type of POM anion ($PMo_{12}O_{40}^{3-}$ or $PW_{12}O_{40}^{3-}$ or $SiMo_{12}O_{40}^{4-}$ or $SiW_{12}O_{40}^{4-}$) and two different cations. The reported results indicate that there was no cation interchange between adjacent layers during the

film-building process. In addition, the results demonstrated that each new layer was deposited upon previously deposited materials.

## Experimental section

### Materials

The polyoxometalates $H_3PMo_{12}O_{40}$ ($PMo_{12}$), $H_3PW_{12}O_{40}$ ($PW_{12}$), $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$) and $H_4SiW_{12}O_{40}$ ($SiW_{12}$), Methyl viologen chloride ($MVCl_2$) and the cationic porphyrin (meso-tetra (4$N$ methylpyridyl porphyrin) tetra p-tosylate) salt were purchased from Aldrich Chemical. The sulfuric acid solution 0.5 M was purchased from Fischer (Chem-Lab): the pH of the latter solution, measured routinely in our laboratory, was on the range 0.2–0.3, identified in the present paper as about zero. All of these chemicals were used as received. Sulfuric acid solutions for electrochemical measurements at pH=3.25 were prepared by the addition of aliquots of 0.5 M sulfuric acid to a solution 0.1 M NaCl in ultra-pure water 18.2 $M\Omega$ $cm^{-1}$ (ELIX-Synergy millipore station). Both solutions (pH=0 and 3.25) were unbuffered. Commercial glassy carbon electrodes (Bioanalytical System, BAS) with 3 mm diameter were used.

### Instrumentation

Cyclic voltammetry (CV) experiments were carried out at ambient temperature (20+2 °C) in a two-compartment cell connected to an autolab model PGSTAT 20 potentiostat. The aqueous electrolyte was bubbled with argon during at least 10 min before use. All potentials were measured vs a commercial (Tacussel) calomel reference electrode (SCE) (KCl sat.). The platinum wire used as auxiliary electrode was placed in a separate compartment to avoid contamination of the electrolytic solution by electro-generated species. Two distinct glassy carbon working electrodes were used (one for studying the tungsten-based polyoxometalates films and the other for the molybdenum-based polyoxometalates films). These working electrodes were polished before each experiment with 0.05 μm alumina powder (micropolish, Buehler) on microcloth polishing cloth (Buehler) and further sonicated in ultra-pure water. The pH of the solutions was monitored with a pH meter Tacussel minisis 6,000 and a regular glass electrode (Radiometer).

### Building self-assembled multilayer films

The general experimental procedure used in this study for preparing mono- and multilayer polyoxometalates films has been described in detail elsewhere [7]. Typically, this procedure is based on dipping the electrode, for a given duration, in a solution containing the species to be adsorbed. The specific experimental parameters pertaining to the present study were as follows. For studies in $H_2SO_4$ 0.5 M, the concentrations of the polyoxometalate, the methyl viologen and the porphyrin solutions were $10^{-3}$, $5.10^{-3}$ and $10^{-3}$ M, respectively. The duration of dipping to build-up layers with methyl viologen and polyoxometalate, respectively, was 15 min for each species, whereas the dipping lasted 20 min for layers made of porphyrin on polyoxometalate. Between two consecutive dippings, the modified electrode was immersed 5 min in a still solution of $H_2SO_4$ 0.5 M.

For studies at pH=3.25, the multilayer film was built via three consecutive steps : the first step was implemented in an aqueous solution of $H_2SO_4$ 0.5 M until a film made of five polyoxometalate layers and four methyl viologen layers was prepared, the ultimate layer being made of polyoxometalate. In this first step the aqueous solutions of POM and of methyl viologen were $10^{-3}$ M and $5.10^{-3}$ M, respectively, and the dipping duration was 15 min in POM solution and in methyl viologen solution as well. In a second step, the electrode was transferred for 1 h in a still standing aqueous solution of $H_2SO_4$ (pH=3.25). Then, a CV was recorded in the latter solution for monitoring the redox characteristics of the multilayer adsorbed film. This method led to a stable electrochemical response of the multilayer system [12]. The electrode was further dipped in a solution of polyoxometalate (pH=3.25) to restore—whenever necessary—the sole presence of polyoxometalate at the interface with the solution. The third step followed the same protocol as in sulfuric acid 0.5 M with concentrations of polyoxometalate, methyl viologen and cationic porphyrin equal to $10^{-4}$ M (in ultra-pure water solution of $H_2SO_4$, pH=3.25), $5.10^{-3}$ and $10^{-3}$ M, respectively. The duration of dipping was 40, 15 and 20 min in polyoxometalate, methyl viologen and porphyrin solutions, respectively. The successive layers built in this third step were, therefore, added to those already deposited in the first step.

### Electrochemical measurements

This work reports the electrochemical behaviour of multilayer systems containing two different cations and polyoxometalate (POM) anions in the same film. Except otherwise indicated, three types of CVs curves were obtained depending on the film studied (Scheme 1). The first, thick line (no. 1) corresponded to the redox response obtained in the presence of a monolayer built with POM only. On this POM first monolayer, four additional layers of polyoxometalate—POM—(two layers) and of methyl viologen—$MV^{2+}$—(two layers) were further added alternately, POM being the ultimate layer, namely, the layer interfacing the film with the solution. The second kind of CV (thin line no. 2) corresponded to the redox response obtained from this multilayer system. When one layer of cationic porphyrin—

P(0)$^{n+}$—plus one layer of polyoxometalate—POM—were further added, a third kind of CV (dotted line no. 3) was obtained.

The latter two processes (on one hand elaboration of four layers alternating polyoxometalate and methyl viologen, on the other hand, addition of two layers, one of which was made of cationic porphyrin and the second was made of polyoxometalate) were repeated on the above-described structure.
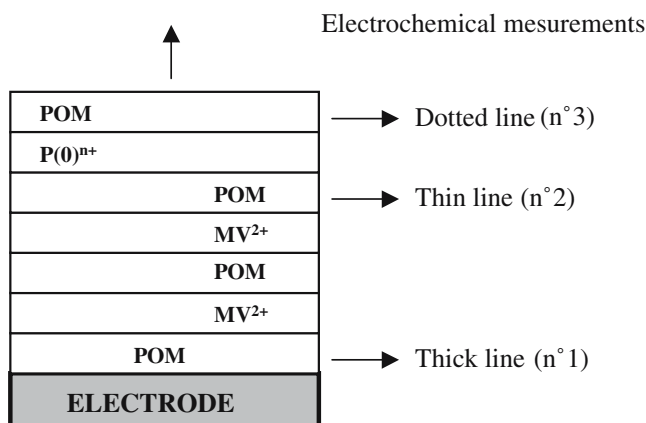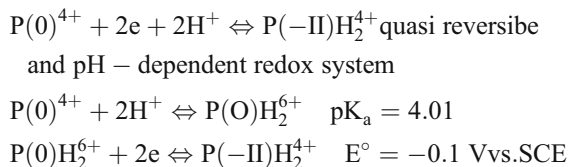
Hence, the CV curves reported in the present paper will be an alternation of CV curves corresponding to nos. (2) and (3) identified in Scheme 1.

On all figures (except where otherwise indicated), the CV curves were not the first recorded: in all CV experiments on a given film, a preliminary set of cyclic polarisations was carried out (typically ten cycles for Mo and five cycles for W-based polyoxometalates) before recording, so that the recorded CV for a given film was identical and reproducible.

In this paper, we identified as "ultimate layer" or "outermost layer" the last layer in the film, interfacing it with the solution

## Results and discussion

– The acid-base and the electrochemical characteristics of the porphyrin cation have been reported in detail [13]; they may be summarised as follows for the redox reductive processes:

$$P(0)^{4+} + 2e + 2H^+ \Leftrightarrow P(-II)H_2^{4+} \text{quasi reversibe}$$
$$\text{and pH} - \text{dependent redox system}$$
$$P(0)^{4+} + 2H^+ \Leftrightarrow P(O)H_2^{6+} \quad pK_a = 4.01$$
$$P(0)H_2^{6+} + 2e \Leftrightarrow P(-II)H_2^{4+} \quad E° = -0.1 \text{ Vvs.SCE}$$

Scheme 1 Schematic representation of films in H$_2$SO$_4$ 0.5 M with the signification of every cyclic voltammetric curves. The numbers in brackets correspond to the curve numbers in Fig. 1a

At potentials more negative than −0.6 V/SCE, an irreversible reduction of the porphyrin cation occurs, which generates porphyrinogen moieties.

– The redox systems associated with the other species involved in the present study are reported hereafter. The redox-specific response of POM anions that will be used throughout this paper for monitoring the characteristics of the multilayer films is well-known [4] and may be summarised as follows:
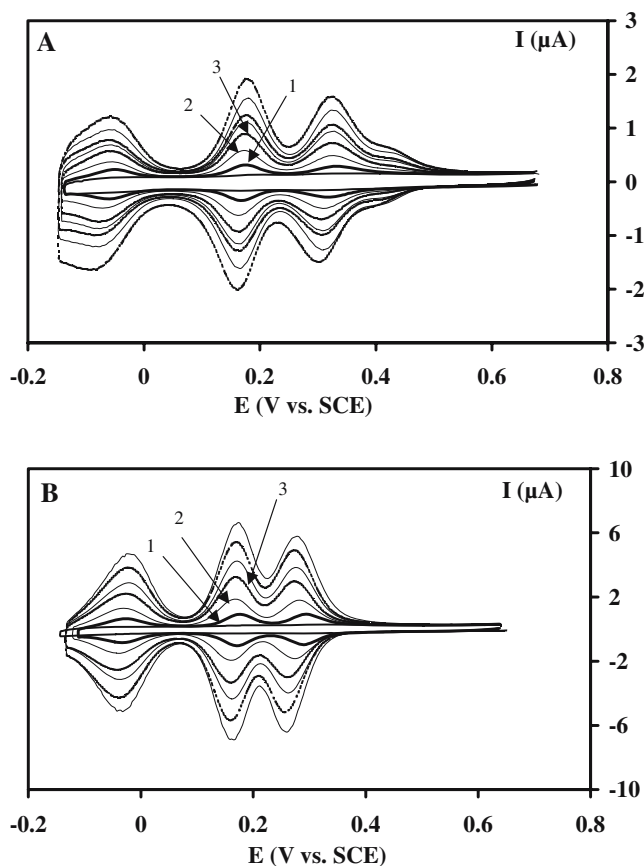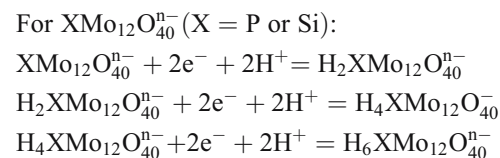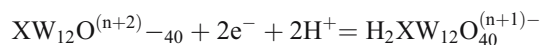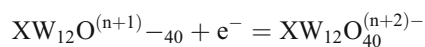
For XMo$_{12}$O$_{40}^{n-}$(X = P or Si):
$$XMo_{12}O_{40}^{n-} + 2e^- + 2H^+ = H_2XMo_{12}O_{40}^{n-}$$
$$H_2XMo_{12}O_{40}^{n-} + 2e^- + 2H^+ = H_4XMo_{12}O_{40}^-$$
$$H_4XMo_{12}O_{40}^{n-} + 2e^- + 2H^+ = H_6XMo_{12}O_{40}^{n-}$$

Fig. 1 Cyclic voltammetry of the films built up with MV$^{2+}$ and P(0)H$_2^{6+}$ as cation and **a** PMo$_{12}$ and **b** SiMo$_{12}$ as anions. Each CV was recorded with POM as outermost layer. $\nu$=100 mVs$^{-1}$, H$_2$SO$_4$ 0.5 M. As explained in the experimental part, curve no. 1 represents the electrochemical response of the first adsorbed monolayer of POM on the electrode surface, curve no. 2 is the response of the POM ultimate layer with underlying alternate layers of POM and MV$^{2+}$, while curve no. 3 corresponds to the POM ultimate layer with an immediately subjacent layer of porphyrin cation (Scheme 1)

For $XW_{12}O_{40}^{n-}$ (X = P or Si):

$$XW_{12}O_{40}^{n-} + e^- = XW_{12}O_{40}^{(n+1)-}$$

$$XW_{12}O^{(n+1)}-_{40} + e^- = XW_{12}O_{40}^{(n+2)-}$$

$$XW_{12}O^{(n+2)}-_{40} + 2e^- + 2H^+ = H_2XW_{12}O_{40}^{(n+1)-}$$
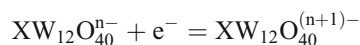
## Redox studies in aqueous sulfuric acid 0.5 M

Films with $PMo_{12}O_{40}^{3-}$ and $SiMo_{12}O_{40}^{3-}$

Figure 1 shows the cyclic voltammograms obtained for multilayer structures built according to Scheme 1 with $PMo_{12}O_{40}^{3-}$ (Fig. 1a) and $SiMo_{12}O_{40}^{4-}$ (Fig. 1b). As frequently observed in previous studies of multilayer films, these results document the increasing amount of adsorbed polyoxometalate on the electrode surface after each dipping step: this is materialised by the increase in the surface of the peaks. It is worthwhile to remind that, if no cations were adsorbed after building a given anionic (POM) layer on the electrode surface, no additional POM layer could be further adsorbed beyond the first layer. Then, in such a case no change would occur in the electrochemical pattern [4] of POM (three-stepwise two electron reductions) except for the third reduction in $PMo_{12}$-based films (this subject will be addressed below).

At this point, two questions arise from the simultaneous presence of two types of cations (methyl viologen ($MV^{2+}$) and porphyrin $P(0)H_2^{6+}$) in the film, instead of only one. The first question to be addressed was the following: Given a multilayer film built according to Scheme 1 with POM and only one type of cation, the ultimate layer being made with POM, does a dipping of this film in a solution containing a second type of cation generate an ultimate layer made of this second cation over the POM layer, or does this dipping replace (in part or totally) the subjacent first cation by the second cation, thus expelling the first cation to the solution. In such a case, replacing cations of
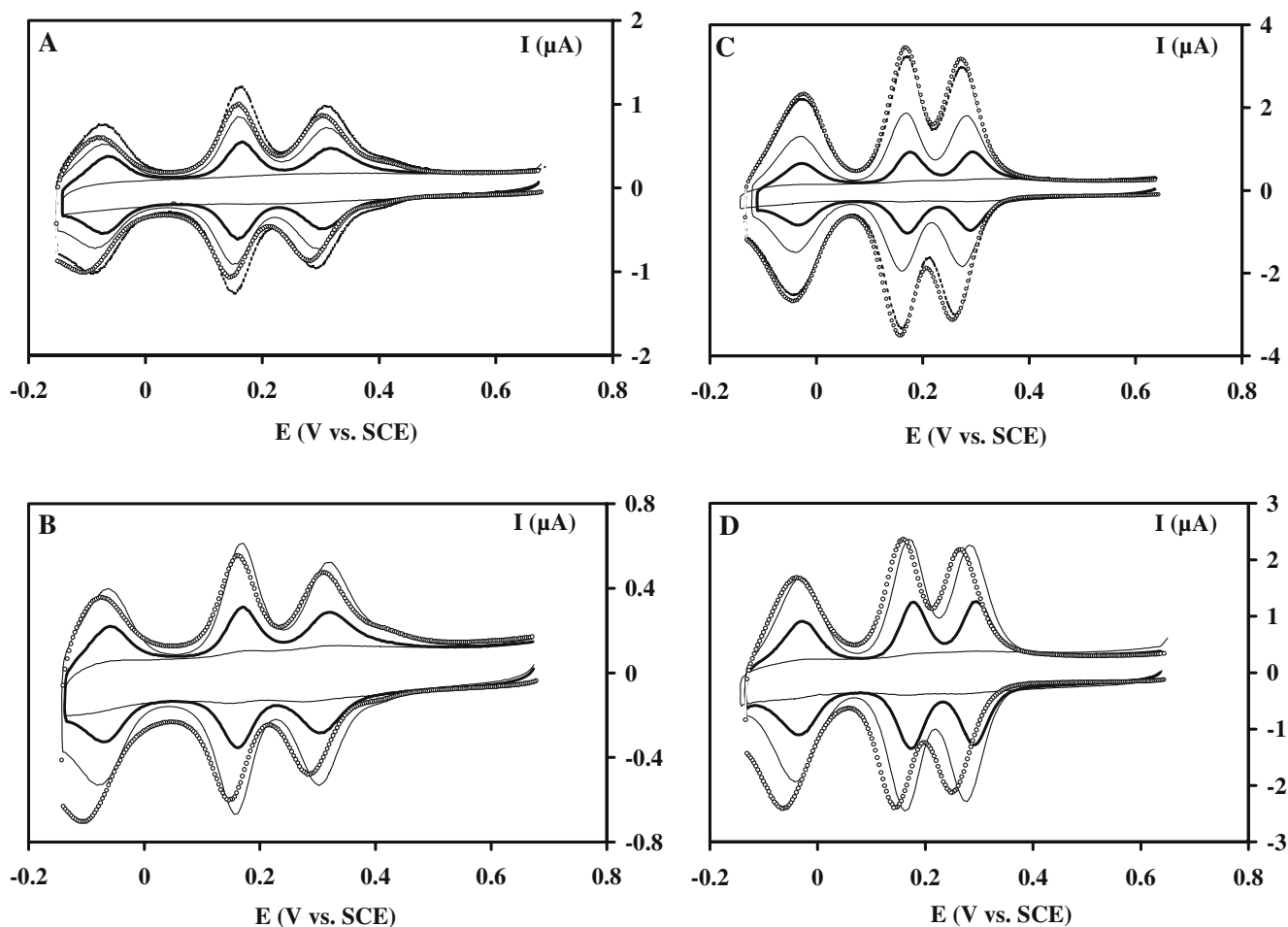


**Fig. 2** Cyclic voltammetry of films built up with $MV^{2+}$ and $P(0)H_2^{6+}$ as cations and **a b** $PMo_{12}$-based and **c d** $SiMo_{12}$−based POM as anions. The curves "*oooo*" (first cycle) in **a** and **c** correspond to $MV^{2+}$ as ultimate layer. The curves "*oooo*" in **b** and **d** correspond to $P(0)H_2^{6+}$ as ultimate layer. For other curves, POM was the ultimate layer, and their identification stands as indicated for Fig. 1 above. $v$=100 mVs$^{-1}$, $H_2SO_4$ 0.5 M
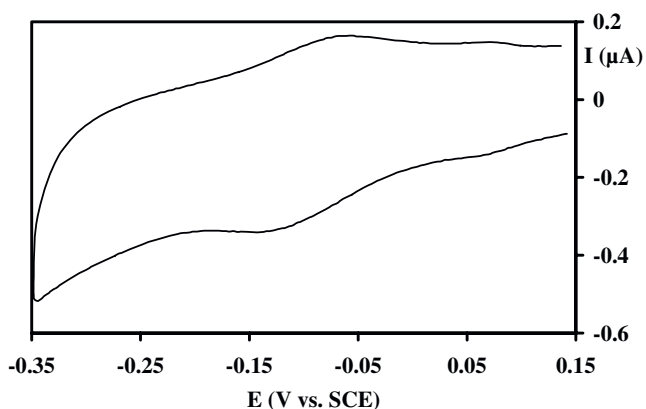
**Fig. 3** Cyclic voltammetry of the porphyrin cation $P(0)H_2^{6+}$ adsorbed onto bare glassy carbon electrode. $\nu$=100 mVs$^{-1}$, $H_2SO_4$ 0.5 M

the first type by cations of the second type would modify coulombic interactions with POM due to the difference in the nominal electric charge of each cation and, therefore, the amount of POM in the ultimate layer will be modified.

The second question aims at clarifying whether the building process of a given layer occurred (at least in part) on the previously adsorbed, becoming subjacent layer or parts of it. The latter question arises from the known characteristics of porphyrin cations to adsorb on glassy carbon [14], and because we do not focus in this paper on obtaining close-packed monolayers.

To answer the first question above, we studied the electrochemical behaviour of the multilayer film when the outermost layer was either porphyrin or methyl viologen, instead of POM anions. We, therefore, studied the two systems $POM/MV^{2+}-POM-MV^{2+}-POM/P(0)H_2^{6+}$ and $POM/MV^{2+}-POM-MV^{2+}-POM/P(0)H_2^{6+}-POM/MV^{2+}$. It was expected that intercomparisons of the results obtained would provide indications on possible interchange between the two cations $MV^{2+}$ and $P(0)H_2^{6+}$, because such exchanges would involve the destruction of a part of the film built up with the cation to be "expelled" and further adsorption of the other "incoming" cation instead. Such intercomparisons may rely on monitoring changes in the quantity of POM adsorbed in the layer subjacent to the ultimate layer of cations, as such changes, would be induced by the expulsion of subjacent cations. Figure 2 illustrates the results obtained on films built with either of the two polyoxometalates. In both cases, the ultimate layer made either with $MV^{2+}$ or with $P(0)H_2^{6+}$, the reduction peak potentials of POM were shifted toward more negative values [15] if compared with the data characterising a film ending with POM as ultimate layer. This shift may be explained by the fact that the cations (either $MV^{2+}$ or $P(0)H_2^{6+}$w) were the last components adsorbed, being, therefore, in contact with the bulk solution and also by the fact that the reduction of the subjacent POMs needed protons [4] from the bulk solution.

In this case, an additional energy and, therefore, an overpotential, is expected for enabling protons to overcome their repulsive interactions with the cations ($MV^{2+}$ or $P(0)H_2^{6+}$) in the outermost layer to be crossed before reaching POM. This explanation is consistent with the observed slightly higher potential shift (see, for instance, the first reduction peak) when the terminal layer was built with cations bearing a higher electrical charge ($P(0)H_2^{6+}$: Fig. 2b and d), than when the terminal layer was built with $MV^{2+}$ cations (Fig. 2a and c).

Another interesting result was that the peak areas corresponding to the two first redox steps of POM anions remained almost unchanged, in the case of $SiMo_{12}$−based POM, whether or not the ultimate layer was built with POM or with one of the cations $MV^{2+}$ or ($P(0)H_2^{6+}$ (Fig. 2c and d). This indicated that the amount of POM anions in the subjacent POM layer, which was responsible for the redox pattern, remained unaffected after building the terminal cationic layer.

On the contrary, when the subjacent POM layer was made with $PMo_{12}O_{40}^{3-}$ (Fig. 2a,b), the peak areas corresponding to the two first redox steps of POM were smaller than those measured when the ultimate layer was made with $SiMo_{12}O_{40}^{4-}$. This was an indication that some POM ($PMo_{12}O_{40}^{3-}$) was lost or expelled from the subjacent layer, when an ultimate layer built with cations $MV^{2+}$ or ($P(0)H_2^{6+}$ was superimposed to it.

Additionally, when the terminal layer was built with porphyrin cations ($P(O)H_2^{6+}$), an enhanced/distorted third reduction peak was obtained with both $SiMo_{12}$-based and $PMo_{12}$-based POM (Fig. 2b and d) as subjacent layer.

This enhancement/distortion may be correlated with the observation (Fig. 3) that the adsorbed porphyrin cations ($P(0)H_2^{6+}$) are reduced at about −0.1 V/SCE, therefore, close to the potential of the third reduction of POM. In addition, as documented in Fig. 3, the reduction of the adsorbed porphyrin cations occurred with a significant capacitive contribution to the measured current. It is, therefore, reasonable to ascribe the observed enhancement (Fig. 2) in the third reduction peak areas to the simulta- neous of reductions of POM and of porphyrin cations $P(0)H_2^{6+}$. Interestingly, we observed, for a comparable capacitive current, a higher distortion/enhancement with $SiMo_{12}$-based POM (Fig. 2d) as subjacent layer, compared with $PMo_{12}$ (Fig. 2b). This is a reliable indication that on identical electrode surfaces, more porphyrin cations were adsorbed when the subjacent layer was made of $SiMo_{12}$- based POM, thus indicating also a more efficient monolayer adsorption of $SiMo_{12}$ in comparison with $PMo_{12}$. In addition, it shall be noticed that, even when POM was the terminal layer interfacing the film with bulk solution, the third reduction peak was distorted when POM was $PMo_{12}O_{40}^{3-}$ (Fig. 1a), although no such distortion occurred
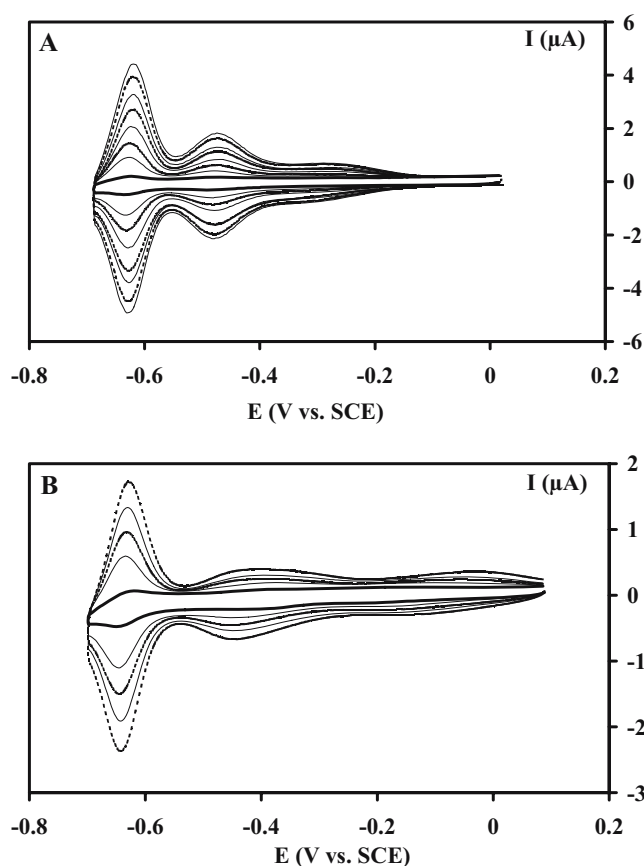
**Fig. 4** Cyclic voltammetry of the films built up with both cations $MV^{2+}$ and $P(0)H_2^{6+}$ (according to Scheme 1) and **a** $SiW_{12}$-based and **b** $PW_{12}$-based POM as anions. Each CV was recorded with POM as the outermost layer. For identifying corresponding curves, see experimental part and Scheme 1. $\nu=100$ mVs$^{-1}$, H$_2$SO$_4$ 0.5 M

with $SiMo_{12}O_{40}^{4-}$ (Fig. 1b). The latter observation is consistent with the above assumption that reduction of the porphyrin cation comes into play in this third reductive step, as the third reduction of POM in Fig. 1a occurs at potentials close to that of porphyrin cations (Fig. 3), whereas the third reduction peak potential of POM ($PMo_{12}$-based) is slightly less negative (Fig. 1b) than that of porphyrin cation (Fig. 3).

Nevertheless, in the window of potentials scanned, we could have expected a similar deformation in the presence of both types of POM anions. The obtained result indicates that specific parameters of POM, such as charge and/or chemical identity, do contribute to the global redox pattern.

When methyl viologen dications were used for building the ultimate layer, instead of porphyrin cations, we were not able to observe its redox response although it is known to be electroactive. The reason was that the electrochemical reduction of $MV^{2+}$ was expected at potentials rather negative ($-0.65$ V/SCE) that correspond to the destruction of the POM, thus producing ill-defined irreversible signals [4].

In summary, the above results indicated that POM and porphyrin cationic layers may be built on POM/$MV^{2+}$ substrate. Also, the observed potential shifts in the presence of adsorbed $P(0)H_2^{6+}$ and the unusual shape of the third POM reduction peak supports the assumption that the multilayer film self-assembled on the electrode surface involved POM and the two cations. These results did not ascertain, however, that the film was built by simple successive and alternated layers of cations ($MV^{2+}$ and/or $\left(P(0)H_2^{6+}\right)$) and POM anions. Current studies are under way for addressing this question of the film structure, of which we expect specific information on the location of POM and of the cations towards the electrode surface. The word "layer" corresponds, in this case, to the results observed after a given "dipping" step, according to the present usual experimental practice [7]. It unambiguously confirms physical addition of components to the multilayered film on the electrode surface, but it does not carry specific structural information.

The time stability of the two films built with $SiMo_{12}$-based and with $PMo_{12}$-based POM, respectively, was checked, keeping the electrode waiting at open circuit and then recording again a cyclic voltammogram. The multilayer self-assembly built with $SiMo_{12}$-based POM was stable (at least several hours), whereas the one with $PMo_{12}$-based POM was not. In the latter case, we observed already after 1 h a decrease in the amount of POM adsorbed on the electrode surface.

We speculate that the charge on $PMo_{12}O_{40}^{3-}$, less negative than $SiW_{12}O_{40}^{4-}$, might be detrimental to the coulombic forces required for stabilizing the assembly.

## Films with $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$

Figure 4 illustrates the results obtained with $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$. As in the above reported results, there was an increase of the quantity of POM on the electrode surface after each dipping of the electrode in the POM solution. The electrochemical signals of both POMs were the expected ones [4, 15] (two one-electron reductions and one two-electron reduction). Addressing the same two questions as the above with Mo-based POM, on the one hand on possible cationic exchange and on the other hand on the effect of the last layer, we repeated in this study experiments with the cations $MV^{2+}$ and $\left(P(0)H_2^{6+}\right)$ as the outermost layer. As with the above Mo-based POM, no loss of POM was detected in the layers subjacent to the cationic ultimate layer. However, at variance with the above results, we did not observe here a marked shift in the reduction potentials. This observation may be rationalised on taking into account that the electrode potential is now more negative than with Mo-based POM, thus involving significantly higher driving force on the protons for reaching
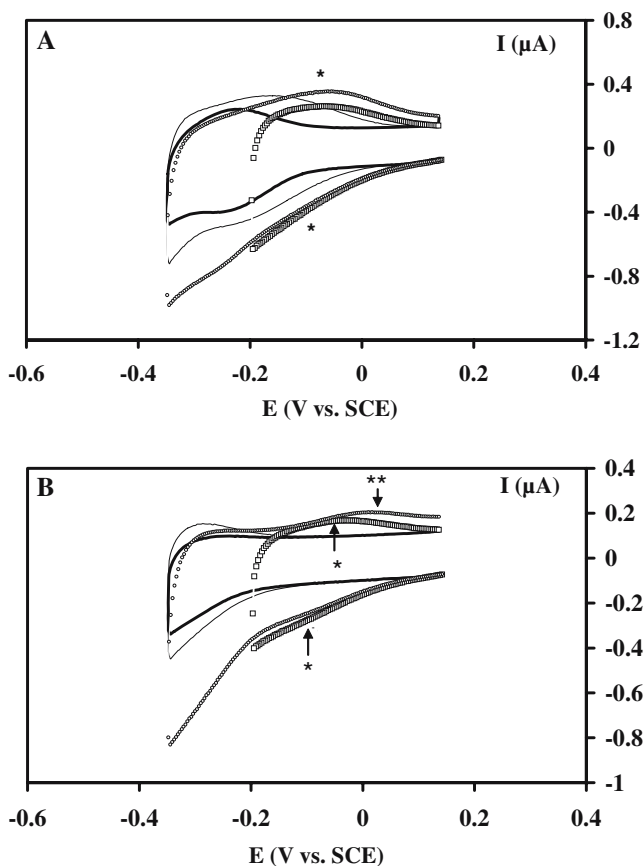
**Fig. 5** Cyclic voltammetry of films built up with $MV^{2+}$ and $P(0)H_2^{6+}$ as cations and **a** $PW_{12}$-based and **b** $SiW_{12}$-based POM as anions, the ultimate layer being made with $P(0)H_2^{6+}$. The curves "□□□□" were scanned up to −0.2 V and the curves "oooo" up to −0.35 V. For other curves, POM was the ultimate layer and their identification is given in the experimental part. $\nu=100$ mV s$^{-1}$, $H_2SO_4$ 0.5 M

subjacent POM. We also noticed, at variance with Mo-based POM, the quasi-independence of the first reduction on pH changes [4]. An information was nevertheless clearly brought: there was no cation exchange with underlying layers.

In such films involving W-based POM, an interesting feature was that the reduction of tungsten polyoxometalates occurred at more negative potentials than that of molybdenum polyoxometalates. In these conditions, it is expected that each cation may be monitored electrochemically.

For instance, the reduction of the porphyrin cation was expected around −0.1 V/SCE (Fig. 3).

Surprisingly, however, first attempts to detect any reduction signal failed when CV were carried out from +0.15 to −0.7 V/SCE, as reported in experimental part, i.e. by recording data from CV after several preliminary polarisation cycles. On the contrary, clear redox response was observed on a "blank" solution containing porphyrin cation (Fig. 3).

As a tentative explanation, it shall be remembered at this point that at potentials negative enough (i.e. beyond from −0.6 V/SCE) and in protic acidic solution, the porphyrin

cation involved in the present study is irreversibly reduced to porphyrinogen [13], thus destroying the aromaticity in the macrocycle and the electrochemical typical pattern of porphyrins. This is likely the explanation for the lack of detectable redox response associated with porphyrin cations in films involving W-based POM.

Addressing the second question (effect of the subjacent layer on to the next layer to be built) led to study the redox pattern of the film in a shorter potential window, namely, from +0.15 to −0.35 V vs SCE. On this range of potentials, only the first POM one-electron reduction (or a part of it) was observable as illustrated on Fig. 5 for $PW_{12}$-based (slightly more negative than −0.2 V vs SCE) and $SiW_{12}$-based POM (around −0.35 V vs SCE). The investigations were carried out on $POM/MV^{2+}-POM-MV^{2+}-POM/P(0)H_2^{6+}$ films. On this range of potentials, the same kind of change was detected on the CV curves as with Mo-based POM around −0.1 V/SCE (Fig. 2b,d), ascribed to the redox signal (mark *) corresponding to the porphyrin (Fig. 5a,b).

Moreover, Fig. 5b revealed the reoxidation signal of the porphyrin (on the backward scan) at potentials depending on the potential scan inversion (−0.2 or −0.35 V vs SCE).
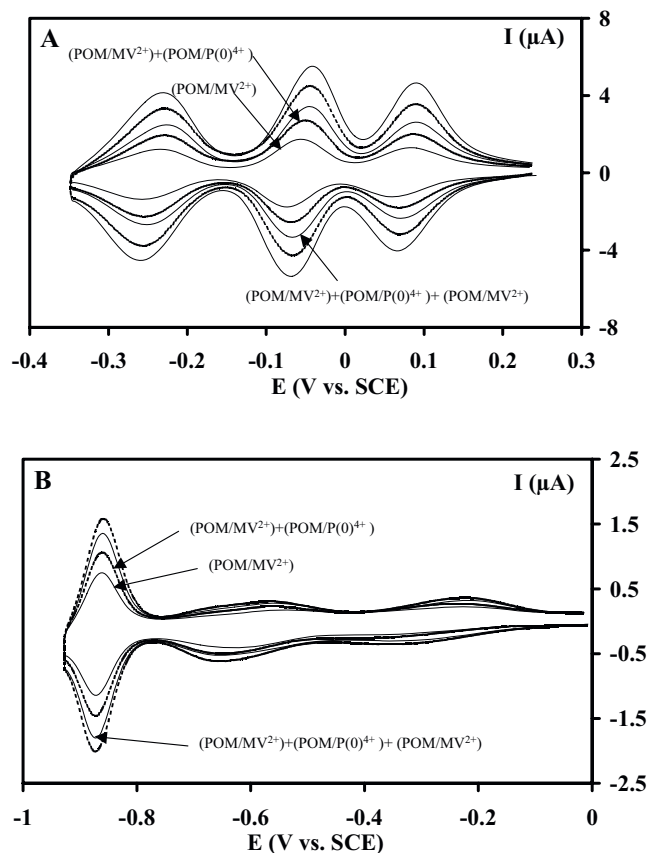


**Fig. 6** Cyclic voltammetry of the films built up with $MV^{2+}$ and $P(0)^{4+}$ as cations and **a** $SiMo_{12}$ and **b** $SiW_{12}$ as anions. Each CV is recorded with POM as the outermost layer. For corresponding curves, see experimental part and Scheme 1. $\nu=100$ mV s$^{-1}$, NaCl 0.1 M, $H_2SO_4$ pH=3.25

The signal observed when the potential scan was reverted at −0.2 V (* on Fig. 5b) was akin to the signal of the adsorbed cationic porphyrin onto bare graphite electrode (Fig. 3). A second signal (**), which corresponded to a reoxidation at more positive potential, appeared on Fig. 5b when the potential inversion was −0.35 V, i.e. when the first SiW$_{12}$-based POM reduction was allowed to occur. Comparison with Fig. 5a revealed on the latter no change in the reoxidation potential corresponding to the adsorbed porphyrin, whatever the inversion potential value was. The major difference in the redox patterns between both POM was that the potential of their first one-electron reduction is less negative for PW$_{12}$ (Fig. 5a). About the reoxidation signal (** on Fig. 5b) obtained around −0.05 V/SCE when the potential scan was reversed at −0.35 V, it is reasonable to assume that it corresponds to the reoxidation of porphyrins adsorbed on the ultimate POM layer. The absence of this signal ** in Fig. 5 may be ascribed to the semi-conducting properties of the POM in the oxidised state and to its conductive characteristics in the redox state [16, 17]. Indeed, in Fig. 5a, the reoxidation signal of porphyrin occurs on POM still conducting (i.e. still not fully reoxidised), at variance with Fig. 5b, where the reoxidation steps of porphrin occurs on semi-conducting POM (i.e. fully reoxidised).

The reoxidation signal (*) detected with SiW$_{12}$-based films at potential corresponding to the reoxidation of the adsorbed porphyrin onto bare glassy carbon electrode (Fig. 3), was more difficult to interpret. On Fig. 5, an immediate intuitive assumption was that this observed reduction/oxidation signal was due to porphyrin cations adsorbed onto bare glassy carbon electrode [on part(s) of the surface not occupied by POM]. For clarifying this point, we carried out a study after depositing an additional part of film with $P(0)H_2^{6+}$ porphyrin cations as ultimate layer $(POM/MV^{2+} − POM − MV^{2+} − POM/P(0)H_2^{6+} − POM− MV^{2+} − POM/MV^{2+} − POM/P(0)H_2^{6+})$.

The obtained results were similar to those observed on the first part of the multilayer film (i.e., identical to Fig. 5b). Then, even on the assumption that after the first dipping in the porphyrin solution some adsorption sites were left open on the bare part of the graphite electrode, the second dipping should decrease or even reduce to almost zero the number of such free sites on bare carbon. As a result, little or no free sites would be left available for adsorbing porphyrin onto bare carbon and, therefore, the redox signal at −0.1 V should disappear. Clearly, it was not the case, and the above assumption has to be revisited. Hence, the reoxidation signal at −0.05 V cannot be ascribed to porphyrin reoxidation onto bare carbon.

The electrochemical behaviour observed for methyl viologen on bare glassy carbon electrode was the one reported previously in the literature: a first one-electron

exchange occurred around −0.65 V vs SCE [18]. However, this electrochemical signal was not observed on the films based on $PW_{12}O_{40}^{3-}$P or $SiW_{12}O_{40}^{4-}$ polyoxometalates, be $MV^{2+}$ in the outermost layer or not. This observation was already made previously with Wells–Dawson type polyoxometalates (Martel and Kuhn, unpublished results). A possible explanation is that the redox signal was too small and overlapping the signal of the POM. This hypothesis is consistent with the small (smaller than on bare electrode) current associated with the electrochemical signal of the porphyrin cation in the film.

Another explanation relies on the binding coulombic interaction between $MV^{2+}$ cations and the conducting highly negatively charged reduced polyoxometalate. As a result, the expected reduction of $MV^{2+}$ around −0.65 V/SCE would only correspond to available "free" $MV^{2+}$, i.e. without binding interactions with POM. In such conditions, the major part of the signal expected at −0.65 V/SCE for the reduction of $MV^{2+}$ will be observed at more negative potentials, as well known in the redox processes involving complexation or coordination reactions. However, the occurrence of irreversible further reductions of tungsten-based POM beyond −0.7 V/SCE prevented any experimental testing of this hypothesis. Another explanation might also be that, due to interactions in the film, $MV^{2+}$ undergoes a slowed down electronic transfer, and that its electrochemical response is screened as already reported for other films [19].

The latter scheme would account for the very weak signals observed for both cations $MV^{2+}$ and $P(0)H_2^{6+}$ at the potentials corresponding to their expected reduction as uncomplexed cations.

However, in summary, films including two types of cations were reproducibly elaborated. The stability of these two films was very good with time at pH close to zero.

## Redox studies in pH=3.25: $SiMo_{12}O_{40}^{4-}$ and $SiW_{12}O_{40}^{4-}$

When the pH increases, Keggin-type polyoxometalate could be hydrolysed [4]. This is especially the case for the Phophorus-based type POM. This is the reason why we did not study films with the PMo$_{12}$ and PW$_{12}$ anions. The pH value of 3.25 has been selected because it is low enough to prevent hydrolysis of the Si-based POM, while it is high enough to avoid significant protonation of the porphyrin cation.

When pH was raised to higher values, the two-electron reduction potentials of POM were shifted towards more negative values [4], indicating that the energy of the involved orbitals was accordingly increased. For instance, at pH=3.25, the third reduction of SiW$_{12}$-POM occurred at more negative potentials than the reduction of the

methyl viologen (electron acceptor), which is not pH-dependent [20] at −0.65 V/SCE [the oxidation potential of the excited porphyrin cation (electron donor) being even more negative]. Therefore, this sequence of redox potentials was thermodynamically consistent with a scheme in which the electron transfers would be facilitated by POM from the donor (porphyrin) to the acceptor (methyl viologen).

Assuming that the behaviour of the studied films in aqueous solutions of $H_2SO_4$ at pH=3.25 resembles that in $H_2SO_4$ 0.5 M, the following results were obtained with $SiMo_{12}$ and $SiW_{12}$-based POM. We focussed on these two POMs because they carry higher electrical charge and they exhibit a better stability than P-based POM in acidic solutions. Figure 6 shows an electrochemical monitoring of the growth of two films with $SiMo_{12}$-based (6A) and $SiW_{12}$-based POM (6B), respectively. The above reported electrochemical behaviour was again observed here, however, with negative shifts in the potentials of about 200 mV for each two-electron transfer. These shifts were 60 mV per pH unit as expected [4]. Also, as in studies in $H_2SO_4$ 0.5 M, an increase in the amount of deposited POM was observed after each dipping step.

We also checked here the possibility of cationic exchanges among the layers in the film, and we reached the same conclusions as in more acidic conditions, i.e. no exchange was detected. For $SiMo_{12}$, we also observed the distortion of the third reduction peak when the cationic porphyrin was the outermost layer. We did not investigate more on the porphyrin redox process when $P(0)^{4+}$ was deposited with $SiW_{12}$-based POM. We noticed here that the reduction potentials of $SiW_{12}$-based POM are quite negative, enough to reach potentials (beyond −0.6 V/SCE) enabling the irreversible reduction of porphyrin cations to porphyrinogens. On the other hand, the redox signal of methyl viologen was not detected, as already reported in $H_2SO_4$ 0.5 M conditions. The explanation proposed above in $H_2SO_4$ 0.5 M may very well hold here also. Additionally, this signal might overlap here with the second reduction peak of POM. In summary, these results indicated that, at pH=3.25, it was clearly possible to build films with both cations inside. At open circuit, these films were chemically stable.

## Conclusion

Based on the self-assembly concept, complex films were built on carbon electrode surfaces. Each film involved two distinct molecular cations (methyl viologen and cationic porphyrin) and one given polyoxometalate as anion, held by coulombic interactions, at pH close to zero and also at pH=3.25. The corresponding scheme for the distribution of anions and cations inside the film is drawn on Scheme 1.

Electrochemical studies on the film indicated that after building a first multilayer film with one cation alternating with POM, it was further possible to extend the building process with a second, chemically distinct cation.

Electrochemical studies of films in which the ultimate layer (i.e. the layer interfacing the film with the solution) was made of a given cation indicated that no exchange occurred between both types of cations in the multilayer array and that the adsorption of each component (cation or polyoxometalate anion) occurred on the already deposited subjacent layer. Moreover, the electrochemical response of the cationic porphyrin in the films changed when the chemical composition of the polyoxometalate was modified. The obtained films were chemically stable with time for Si-based POM.

Further studies will scrutinise the effects of varying other parameters, such as the number of bilayers cation–anion in the film, the involvement of metalled cationic porphyrins [21] and analogs instead of free base porphyrin cation, as well as the physico-chemical characteristics of the electrode used as substrate.

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