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Exploring the solvent mediated assembly and redox activity of a POM–organic hybrid $[\text{Na}(\text{SO}_3)_2(\text{PhPO}_3)_4\text{Mo}_4^{\text{V}}\text{Mo}_{14}^{\text{VI}}\text{O}_{49}]^{5-}$

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We report the electrochemical activity and the mechanism of formation of a mixed valence polyoxometalate-based organic hybrid cluster with the formula $[\text{Na}(\text{SO}_3)_2(\text{PhPO}_3)_4\text{Mo}_4^{\text{V}}\text{Mo}_{14}^{\text{VI}}\text{O}_{49}]^{5-}$ (**1**). Electrochemical investigations of the mixed valence compound **1** showed three redox couples, in which the electrons were mainly delocalized over eight Mo sites. Furthermore, the synthesis was investigated using ³¹P-NMR, which showed that the self-assembly of cluster **1** was triggered by the addition of organic solvents, and was largely independent of the nature of the solvents, suggesting that a decrease in the concentration of water promoted cluster assembly. Finally the stability of **1** was explored and we concluded that the use of phenylphosphonate allowed the covalent stabilization of the $[\text{Mo}_4^{\text{V}}\text{Mo}_{14}^{\text{VI}}]$ core.

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Introduction

Polyoxometalates (POMs) are a class of discrete metal oxide molecules that consist of early high oxidation state transition metals such as V, Mo, W and Nb.^{1–11} Nowadays they have a strong presence as well-defined platforms for developing nano-scale molecules with interesting properties including multiple electron transfers. This is because their structures (cluster topology, size, charge and composition) are capable of being tuned and defined at the molecular level. Inorganic–organic hybrid-based clusters have recently been the focus since it is possible to integrate well-defined organic units.³

Several protocols have been established that allow the covalent grafting of organic moieties onto POM surfaces to give hybrids (class-II according to traditional classification).³ In most cases, the POM clusters were reacted with organic guest molecules, for example, by reaction of organometallic compounds with lacunary POM or Tris ligands (tris(hydroxymethyl)amino-methane) with Anderson or V-capped Dawson clusters.^{12–16} Commonly, the formation of these hybrids requires multi-step reactions of the Mo, W, and V precursors to class-II hybrids through the formation of lacunary POM clusters or Anderson types. Some hybrids are made under hydrothermal conditions,

but these tend to lead to compounds with limited redox activities and require thermally stable guests. Furthermore, the redox performances of the lacunary species and Anderson clusters tend to be limited if they are compared to that of traditional hetero-POMs of Keggin and Dawson types. From this point of view, a hybrid fabricated through intermolecular forces (class-I type hybrid) with traditional POMs is easily prepared in a one-step ion-exchange reaction with an inorganic POM such as a Keggin type and a cationic organic guest.

Recently, we revealed that the reaction of MoO_4^{2-} (for Mo precursor of Mo–POM) and phenylphosphonate (PhPO_3^{2-}) yields a class-II type hybrid in a one-step reaction. This was achieved by considering the reactivity of the template anions which controls the formation of hetero-POMs.¹⁷ An oxo-anion of hetero atoms (such as PO_4^{3-} , SO_4^{2-} and SO_3^{2-}) usually undergoes template self-assembly from MoO_4^{2-} to give hetero-POM clusters. We showed that (i) reduced conditions and (ii) mixed aqueous non-aqueous solvent systems could be used to enhance the reactivity of the template anions. In addition, (iii) the Lewis basic strength of the template anion plays a critical role in controlling its reactivity. Using these approaches, we successfully obtained a new type of mixed-valence POM–organic hybrid: $(\text{TBA})_5[\text{Na}(\text{SO}_3)_2(\text{PhPO}_3)_4\text{Mo}_4^{\text{V}}\text{Mo}_{14}^{\text{VI}}\text{O}_{49}] \cdot n\text{MeCN}$ (=TBA₅·1·nMeCN). This POM–organic hybrid is a class-II hybrid anion, and is formed through a one-step template reaction of the SO_3^{2-} anion and an external surface of the mixed-valence Mo–O cluster shell, which is decorated by four PhPO_3^{2-} units. This is because of the cooperative effect of two anions (SO_3^{2-} and PhPO_3^{2-}), which possesses comparable Lewis basicity and thus stabilises the shell.

In this paper, we report our investigation of the formation and electrochemical properties of **1**. Studies using cyclic

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voltammetry revealed that the anions showed three reversible processes. Bond valence sum calculations based on the crystal structure of the cluster anion **1** showed that electrons are not equally delocalized over the 18 Mo sites, but that four electrons are partially delocalized over eight Mo sites. This corresponds well to that reported in the similar basket-like POM anion $[\text{K}(\text{PO}_4)_6\text{Mo}_3^{\text{V}}\text{Mo}_{15}^{\text{VI}}\text{O}_{49}]^{10-}$. In addition to the investigation of electrochemical performance, the mechanism of formation was explored as a function of solvent composition. This was done using ^{31}P -NMR studies of reaction solutions that form **1**, which revealed that the compound is not stable in aqueous solvents. However, there are studies in which mixtures of organic solvents including methanol, ethanol, 2-propanol, acetone, acetonitrile and DMF can be shown to trigger the formation of **1**. Since these organic solvents have different dielectric constants (ϵ) and protic natures, it is interesting that any mixed solvent triggers the formation of **1**. This can be explained by considering that the reaction equilibrium between molybdate and POM releases water as part of the reaction mechanism *via* a condensation process. Since the addition of organic solvent effectively reduces the water concentration, the equilibrium is shifted to the product side. By considering the *W* value (defined as the molar ratio between the molybdate and the water product), the reaction leading to **1** has a larger *W* value than that of cooperative formation of gigantic Mo-wheels. Here, the addition of acetonitrile shifts the equilibrium to generate yet more water giving a larger *W*. The functionalization of the POM with phenyl moieties allows us to design more effective covalent-grafting protocols for the formation of mixed-valence POM-based class-II hybrids, where the solvent composition tunes cluster formation.

Results and discussion

Single crystals of $\text{TBA}_5 \cdot 1 \cdot n\text{MeCN}$ prepared as given in our previous reports were utilized for the following characterization and measurements.¹⁷

Electrochemical redox activity

The cyclic voltammetry (CV) for the redox cycle (3 cycles) of TBA salt of **1** in CH_3CN (0.5 M of Bu_4NClO_4) is shown in Fig. 1. Three reversible redox processes were observed for the oxidation process starting from **1**. The midpoint potential (E_{mid}) was observed at -0.63 (I), 0.24 (II) and 0.67 (III) V (*vs.* Ag/Ag^+), where $E_{\text{mid}} = (E_{\text{ox}} + E_{\text{red}})/2$, E_{ox} and E_{red} are the oxidation and reduction peak-potentials, respectively. The separation of the E_{ox} and E_{red} values are 103, 62 and 77 mV for processes (I), (II) and (III), respectively, which indicates at least three electron transfer reactions, for example:

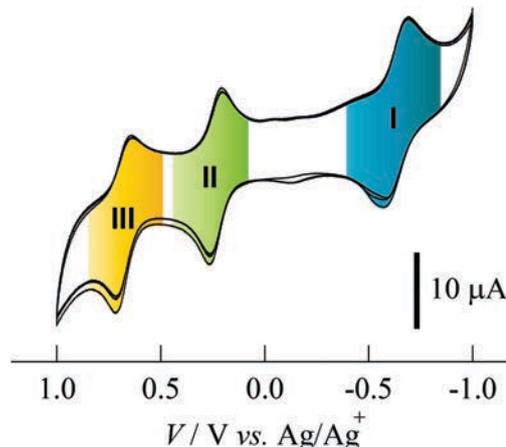
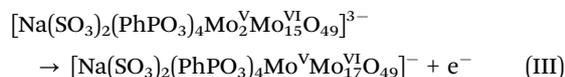
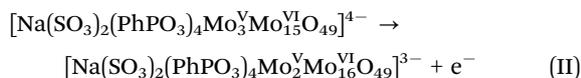
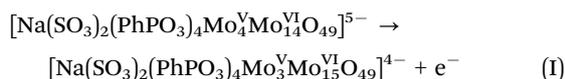


Fig. 1 CV of **1** in acetonitrile.

It is interesting to note that a similar POM cluster $[\text{K}(\text{PO}_4)_6\text{Mo}_3^{\text{V}}\text{Mo}_{15}^{\text{VI}}\text{O}_{49}]^{10-}$, where all $\{\text{PhPO}_3\}$ moieties and SO_3^{2-} anions were replaced by PO_4^{3-} , also showed the corresponding three redox cycles with peak-to-peak separations of 120, 94 and 81 mV.¹⁸

Bond valence sum analyses

To help us understand the delocalization of the electrons and the mixed valence state of **1**, bond valence sum (BVS) values were estimated for all Mo atoms using the crystallographically determined bond lengths. An order of the values was Mo_5 (5.4) < Mo_1 (5.5) < Mo_3, Mo_6 (5.7) < Mo_2, Mo_4 (5.8) < Mo_9 (5.9) < Mo_8 (6.0) < Mo_7 (6.2). The fact that each Mo has a different valence from the average valence of Mo at 5.78 ($=5 \times 4/18 + 6 \times 14/18$) suggests that the electrons are not equally delocalized over the 18 Mo atoms.

Fig. 2 shows the structure of **1** with different colours to show the BVS values. Lower oxidation states than 5.78 were observed for Mo atoms in $\text{Mo}_1, \text{Mo}_3, \text{Mo}_5$ and Mo_6 , which are positioned at the middle 'belt' of the molecule, indicating that electrons are mainly delocalized around them. Our results for **1** can be

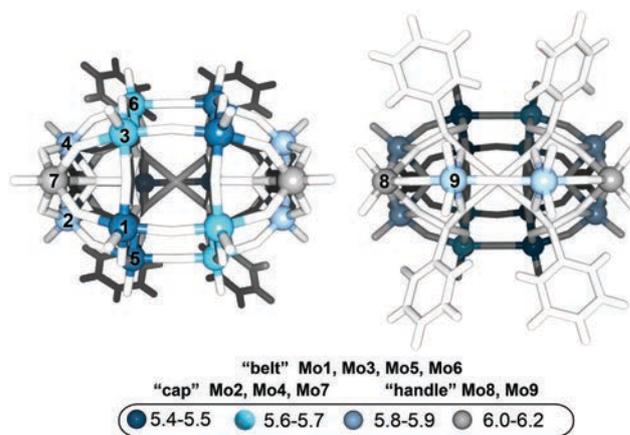


Fig. 2 Structure of **1** with different coloured graduations for BVS values on Mo atoms. Only Mo atoms (numbers for Mo are given) are shown using the ball model (other atoms are shown using the stick model for clarity).

compared to that for $[\text{K}(\text{PO}_4)_6\text{Mo}_3\text{Mo}_{15}\text{O}_{49}]^{10-}$ characterized by molecular orbital calculations. The LUMO orbitals are delocalized over the Mo sites in the belt part rather than other capping and outer moieties, showing a similar electron distribution to that of **1**.¹⁹

³¹P-NMR study

Since cluster **1** exhibits the ability to undergo multiple redox reactions as seen for the more traditional hetero-POMs, it is interesting that the formation of a POM-based class-II hybrid with the inclusion of the phenyl phosphonate moieties is possible. We achieved this by designing the reaction tuning the Lewis basic strength of template anion and guest organic phosphonate to decorate the Mo–O molecular cage. According to the reaction recipe reported, we found an enhancement of reactivity by the addition of acetonitrile to the reaction solution.¹⁷ Since it is well known that P-containing hetero-POMs exhibit reasonable chemical shift differences as a function of structure¹¹ (e.g. the structural isomers between $[\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and $[\beta\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ can be distinguished in solution), we opted to explore the NMR spectrum of compound **1** under different conditions (mixed solvents).

Reaction in water–acetonitrile mixed solvents

Cluster **1** was synthesized from a reaction of Na_2MoO_4 hydrate through a one-step reaction in a water–acetonitrile mixed solvent system. The pH of an aqueous solution of MoO_4^{2-} (12.6 mmol, 25 ml) was adjusted to 1 by the addition of HCl_{aq} (32%), followed by the addition of reductant, $\text{Na}_2\text{S}_2\text{O}_4$ (2.30 mmol), phenylphosphonic acid (3.0 mmol) and acetonitrile (10 ml) were mixed (named as solution-I) under stirring. After three days of stirring in a sealed flask, addition of tetrabutylammonium bromide

yielded a blue precipitate (the filtrate was named as solution-II). The blue precipitate obtained was then dissolved in acetonitrile (solution-III) and bluish single crystals were obtained after several days.

During the course of these synthetic procedures (Fig. 3a), ³¹P-NMR spectra of solution-I and -II were recorded where time development in solution-I was investigated at 30 minutes, 1, 2 and 3 days. The measurement of solution-I after 30 minutes showed two different ³¹P-NMR peaks at 21.2 and 20.9 ppm, and these peaks were almost unchanged during the reaction until 3 days (Fig. 3b). Furthermore, a new peak appeared at 14.8 ppm 1 day after the reaction. They were different from that of phenylphosphonic acid, which showed a peak at 15.7 ppm, confirmed by a control experiment where Na_2MoO_4 hydrate and $\text{Na}_2\text{S}_2\text{O}_4$ were excluded from the system; Fig. 3b – PhPO_3H_2 . The peak was considered to originate from **1**. A water–acetonitrile (5:2) solution of triethanolammonium (TEAH) salt of **1** showed the corresponding peak (Fig. 3b(v)). In addition, this peak was not observed in solution-II (Fig. 3b(vi)). It was suggested that **1** was formed in solution-I after 1 day of reaction and the ion exchange reaction with TBA^+ isolates **1** from the reaction mixture with enough purity for crystallization.

Reaction in a water system

To see the effect of the addition of acetonitrile, control experiments were performed in a 100% aqueous solution system (excluding acetonitrile from the reaction system) and monitored by ³¹P-NMR. Two peaks at 21.8 and 21.3 ppm were observed after 3 days of reaction (Fig. S2-3, ESI[†]). These peaks were seen after a reaction in a 5:2 water–acetonitrile mixed solvent solution; however, a peak originated from **1** was not observed after three days of reaction. This shows that cluster **1** is not stable in

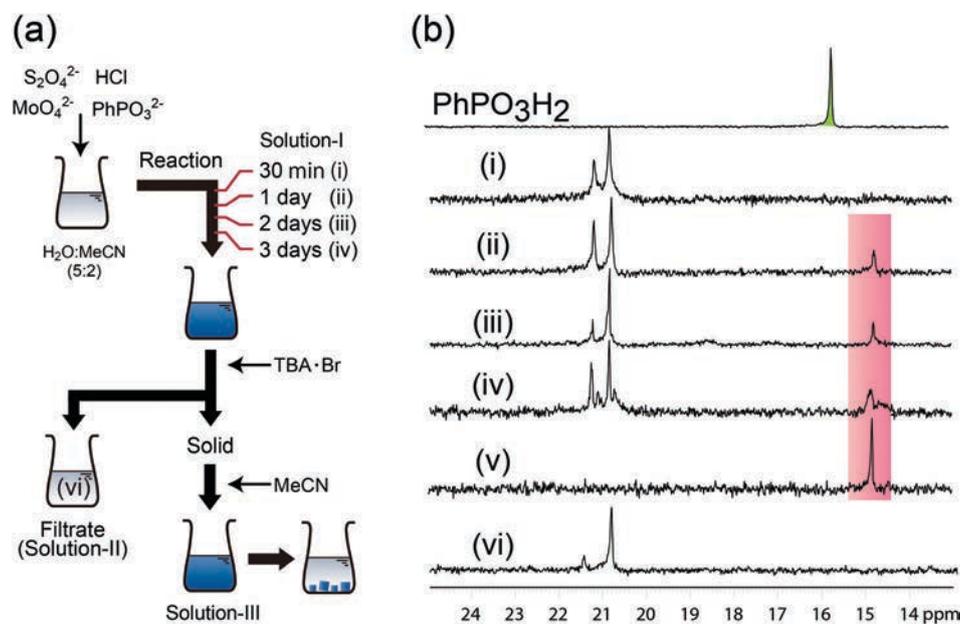


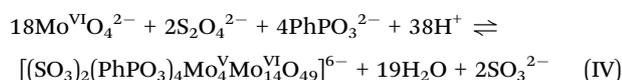
Fig. 3 (a) Scheme of the synthetic procedure where (i) to (vi) correspond to the spectra shown in (b). (b) ³¹P-NMR spectra in water–acetonitrile (5:2) mixed solvent system of PhPO_3H_2 , solution-I after reaction: (i) 30 minutes, (ii) 1 day, (iii) 2 days and (iv) 3 days with those of (v) TEAH salt of **1** and (vi) solution-II.

aqueous solution. Indeed, the aqueous solution of TEAH salt of **1** shows only a peak at 21.4 ppm (Fig. S2-1, ESI†). Since a similar peak was observed in a reaction solution of both water–acetonitrile system and aqueous solution, it can be deduced that the peak at around 21–22 ppm originates from the P-containing building blocks found in **1**, suggesting that the addition of acetonitrile stabilizes **1**.

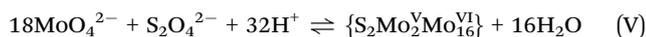
Reactions in water–organic mixed solvents

We investigated reactions in a water–organic mixed solvent system (5:2) employing a variety of organic solvents including methanol, ethanol, 2-propanol, acetone and DMF. After three days of reaction in a series of mixed solvents, similar spectra to that observed in the water–acetonitrile system were observed (Fig. S2-4–S2-8, ESI†). The organic solvents employed here have different dielectric constants from 36.7 of DMF to 18.3 of 2-propanol, as well as different polarities and protic natures, but the results do not appear to depend on these aspects. However, the addition of organic solvent triggers the formation of **1**. Similar stabilization effects of hetero-POM by organic solvents have been reported by Himeno, who reported that the $[S_2Mo_{18}O_{62}]^{4-}$ cluster was stabilized by the presence of acetonitrile, and similarly the stabilization was also observed with different organic solvents of acetone and 1,4-dioxane.²⁰ In addition, it was reported that the structural isomerization process was strongly inhibited in the water–acetonitrile mixed solvent. For instance the cluster of $[\beta\text{-PW}_{12}O_{40}]^{3-}$, which is too short-lived in 100% water, is sufficiently long-lived in water–acetonitrile mixtures to be seen by NMR.²¹ Furthermore, it has been established that quite labile POMs such as the phosphomolybdates can be stabilized in acetonitrile.^{22,23}

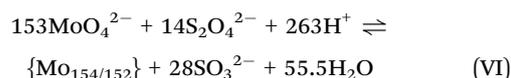
In the present reaction of MoO_4^{2-} , $S_2O_4^{2-}$ and $PhPO_3^{2-}$ in a water–organic mixed solvent, **1** was formed.



On the other hand, a similar reaction excluding $PhPO_3^{2-}$ from reaction (IV) yields $[(SO_3)_2Mo_2^VMo_{16}^V O_{54}]^{6-}$ ($\equiv \{S_2Mo_2^VMo_{16}^V\}$).²⁴



The formation of **1** is promoted by the cooperative effect between SO_3^{2-} and $PhPO_3^{2-}$ anions possessing comparable Lewis basicity, so that both anions are included in the Mo–O molecular cage. Furthermore, a reaction excluding both $PhPO_3^{2-}$ and acetonitrile results in the formation of the gigantic nanowheel of $Na_{15}[Mo_{154}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo_{152}O_{457}H_{14}(H_2O)_{68}]_{0.5} \cdot ca. 400H_2O$ ($\equiv Na_{15}\{Mo_{154/152}\} \cdot ca. 400H_2O$).²⁵

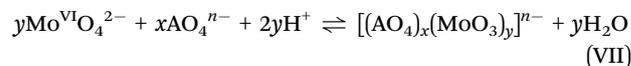


The $\{Mo_{154/152}\}$ cluster was formed in an aqueous solution through a template reaction with $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\equiv \{Mo_{36}\}$). Taking the yields of **1** in reaction (IV) at 42% based on Mo into account, the other two reactions are able to proceed, but $\{S_2Mo_2^VMo_{16}^V\}$ and $\{Mo_{154/152}\}$ are not the main products. A reason

for the addition of acetonitrile making **1** and $\{S_2Mo_2^VMo_{16}^V\}$ stable compared to $\{Mo_{154/152}\}$ is the “dilution” of water by acetonitrile as discussed below.

The “acidity (*Z*)” of the reaction system has been employed to consider the POM reaction.¹¹ The *Z* value was defined as the ratio of proton per molybdate. Here, we define the ratio between the amounts of the water molecules generated per molybdate as *W*. The *W* values of reactions (IV)–(VI) are 1.1 (=19/18), 0.89 (=16/18) and 0.36 (=55.5/153), respectively. In addition the *Z* values are 2.1, 2.0 and 1.7, respectively, which means that reaction (VI) generates fewer water molecules than reactions (IV) and (V). Thus it can be deduced that the dilution of water (=addition of acetonitrile) biased the entire reaction system to the right side of reactions (IV) and (V), so that most numbers of water molecules are generated. And, the addition of $PhPO_3^{2-}$ proceeds *via* reaction (IV). This consideration was also supported by a fact that the solvent effect was independent of the nature of the organic solvent.¹⁷

In terms of exploring the condensation of the molybdate units, if the building blocks are reacted in the presence of templating anions, and the water concentration is reduced, these conditions favour the formation of hetero-POMs over isopoly-molybdates. In general, the formation of hetero-POMs such as Keggin and Dawson have a large *Z* value of 1.0.



Here, the Keggin and Dawson clusters are represented by ($x = 1$, $y = 12$) and ($x = 2$, $y = 18$), respectively ($A = S, P, Si$ or others). The reaction with isopolymolybdates usually has a lower *W* value than those for Keggin and Dawson clusters. This is simply because $W = 1.0$ when MoO_4^{2-} ions release one water molecule by reacting with two protons, namely giving MoO_3 . The insight reported here suggests an approach to understanding which reaction should be more favoured after dilution by an organic solvent, namely the reaction with largest *W* is desired. Not only will this allow us to understand the formation of POMs, but also lead to their rational design.

Conclusions

In summary, we have investigated here the electrochemical properties of **1** and its formation mechanism which reveal a mixed valence state and the fact that **1** exhibits three redox couples, in which the added electrons are mainly delocalized over eight Mo sites. These make **1** an important candidate for redox active class-II type polyoxometalate–organic hybrids. In addition, the formation of **1** was monitored using ^{31}P -NMR over time and as a function of the solvent system where an enhanced assembly was seen when molybdate was reacted with $S_2O_4^{2-}$ and $PhPO_3^{2-}$ in an acidified water–acetonitrile mixed solvent system. A study of the solvent effects during cluster formation revealed that addition of organic solvents (acetonitrile, DMF, acetone, methanol, ethanol and 2-propanol) triggers the formation of **1** and that **1** is not stable in pure water. The enhancement of stability may be altered

after mixing the organic solvent by “dilution” of water and can be understood by defining the W value, which is defined as the molar ratio between water molecules generated from the reaction and molybdate. The reaction to **1** has a W value of 1.1, which is larger than that of $\{\text{Mo}_{154/152}\}$, which is the main product in a reaction by removing PhPO_3^{2-} and acetonitrile, showing that larger numbers of water molecules are generated from the reaction. Thus it was deduced that the dilution of water (=addition of acetonitrile) biased the reaction system, so that it generated the largest number of water molecules. This consideration is also consistent with the fact that the solvent effect was independent of the nature of organic solvent. This means that the reaction of molybdate, acid, reductant and organic phosphonate in a water-organic mixed solvent is a promising candidate for the rational covalent-grafting of ligands onto mixed valence polyoxometalates. We can imagine that other redox active polyoxometalate-based class-II hybrids can also be made accessible, *e.g.*, by changing the phenyl moiety where the solvent system can be tuned on demand as a function of the solubility of the organic phosphonate.

Experimental

Reactions

All chemicals were used without further purification. The cluster **1** was synthesized according to our previous report.¹⁷

Electrochemical study

The redox potential in solution was measured in acetonitrile solution (1.0 mM) with 0.5 M *n*-Bu₄NClO₄ in MeCN solution as a supporting electrolyte, platinum electrodes (working- and counter-electrodes) and Ag/Ag⁺ electrode as a reference electrode with a scan rate of 50 mV s⁻¹.

NMR study

The solution ³¹P-NMR spectra were recorded at room temperature on a BRUKER SPECTROSPIN AVANCE 400S. H₃PO₄ solution (85%) was used as a chemical shift reference.

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