

Research Article

A comparative study on the immobilization of organic-inorganic polyoxometalates hybrids onto gold electrodes: Direct versus indirect, covalent versus electrostatic grafting

Maxime Laurans,^{1,†} Kevin Dalla Francesca,¹ Laure Fillaud,² Emmanuel Maisonhaute,^{2,‡} Richard Villanneau,¹ Vincent Humblot,^{3,⊥} Guillaume Izzet,¹ Florence Volatron,¹ and Anna Proust^{1*}

¹ Institut Parisien de Chimie Moléculaire (IPCM), CNRS, Sorbonne Université, 4 Place Jussieu, F-75005 Paris, France

² Laboratoire Interfaces et Systèmes Electrochimiques (LISE), CNRS, Sorbonne Université, 4 Place Jussieu, F-75005 Paris, France

³ Laboratoire de Réactivité de Surface (LRS), CNRS, Sorbonne Université, 4 Place Jussieu, F-75005 Paris, France

[†] Present address: Université Paris-Saclay, UVSQ, CNRS, Institut Lavoisier de Versailles, Versailles 78000, France

[‡] Present address: Institut Parisien de Chimie Moléculaire (IPCM), CNRS, Sorbonne Université, 4 Place Jussieu, F-75005 Paris, France

[⊥] Present address: FEMTO-ST Institute, UMR CNRS 6174, Université Bourgogne Franche-Comté, 15B avenue des Montboucons, 25030 Besançon Cedex, France

Received: 21 July 2026; **Revised:** 12 October 2026; **Accepted:** 13 October 2026

*Address correspondence to anna.proust@sorbonne-universite.fr

Cite This: *Polyoxometalates*, 2027, 6, 9140167 <https://doi.org/10.26599/POM.2026.9140167>

Abstract

We explored the conditions of the covalent grafting of organic-inorganic polyoxometalate hybrids onto gold using two basic reactions: the peptide-type coupling between a functionalized POM and a preformed organic self-assembled monolayer and the direct attachment of a thiol-terminated POM. We aimed at demonstrating that the variability of the POM loading is an inherent parameter of chemical reactions carried out under heterogeneous conditions that should be systematically assessed. Mitigation measures include a careful preparation and characterization of the substrates at every step before the final POM anchoring. Moreover, a very fast electron transfer across a gold microelectrode and a POM layer was achieved in the case of a very short tether.

Keywords: molecular oxides, organic-inorganic hybrids, self-assembled monolayers, interfacial electron transfer, surface immobilization, heterogeneous coupling

1 Introduction

Polyoxometalates (POMs) are photo-sensitive and redox-active molecular oxides of the early transition metals. They are well-poised to meet the ever-growing demand for multifunctional molecular materials, provided a preliminary shaping process. Various supports have been used, from porous frameworks to flat electrodes,¹ to incorporate POM active layers in applied systems for environmental and energy related fields up to nano-electronics.² Among all possible supports, Au materials stand out. Pristine as well as organic-inorganic POM-based hybrids have been shown to stabilize Au nanoparticles for use in catalytic reactions.^{3–7} In the field of nano-electronics, metallic gold electrodes have been widely used,

for systems as diverse as single POM transistor or rectifier,^{8,9} isolated POMs for resistive-switching characterization,^{10–12} or larger POM modified electrodes^{13,14} and nanojunctions.^{15–21} POMs have also been integrated in (bio)sensors detection interfaces, either on Au nanoparticles or Au substrates.^{22,23} Various strategies have been developed to incorporate POMs into devices.²⁴ Drop casting or spin coating on a substrate and embedding in a polymer matrix are the most common. The electrostatic deposition of POMs onto positively-charged surfaces by counter cations exchange is also a straightforward approach. Besides, the covalent anchoring of functionalized organic-inorganic POM-based hybrids onto a substrate ensures a better control on the POM loading density and distribution and a fine engineering of the POM-substrate interface, as we have previously reported.^{25–27} Regarding covalent grafting onto Au substrates, thiol and diazonium functions are particularly relevant. The diazonium route usually yields high surface coating, yet it generally requires an electrochemical activation and is prone to form multilayers,²⁸ while the formation of alkyl-thiol self-assembled monolayers (SAMs) has been thoroughly described and is well mastered.^{29,30} Therefore, a two-step grafting approach is appealing: first a thiolated SAM with functional headgroups is prepared, which can later be coupled to hybrid POMs bearing a complementary function. This would guarantee the protection of the electrode and a good quality of the ultimate molecular layer grown on the seeding SAM. One common reaction is the peptide coupling between amine and carboxylic acid, in the presence of a metal-free coupling reagent. It is largely used in biology as well as in molecular electronics, albeit the yield of the heterogeneous process is rarely given. On our side, we have observed that it can be very low.³¹ This prompted us to reinvestigate this reaction, working on Au because it allows the use of various characterization techniques to monitor the different steps. We have thus followed the two-step covalent grafting of $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{NH}_2\}]$ ($\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$, TBA stands for the tetrabutylammonium cation) by peptide-type coupling to a preformed 8-mercapto-1-octanoic acid SAM (**SAM-COOH**) onto gold substrates (see Scheme 1). We used a statistical approach to assess the coupling efficiency and we have drawn the conclusion that the peptide coupling can indeed be pushed to the formation of a densely-packed POM monolayer but is also subjected to surface chemistry variability. We will also underline that the relative position of the reactive carboxylic acid and amine functions is crucial since the reaction between $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{COOH}\}]$ ($\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$) and a SAM of 8-amino-1-octanethiol (**SAM-NH₂**) rather yields electrostatic deposition, probably because of partial protonation of the amine headgroups to ammonium.

Since POMs are redox-active molecules, electrochemistry is a technique of choice to characterize their molecular materials. We have shown that cyclic-voltammetry at variable scan rate applied to POM-modified electrodes not only gives the POM surface coverage but also some insights about the kinetics of the interfacial electron transfer, from the electrode to the POM layer.^{31–34} Previously, we reported the spontaneous adsorption of two thioester-terminated Keggin-type hybrids to gold macro-disks, albeit with a low surface coverage and rather modest interfacial electron transfer rates, between 100 to 170 s⁻¹.^{1,13} The low surface coverage could be due to the low reactivity of thioester, while the modest transfer

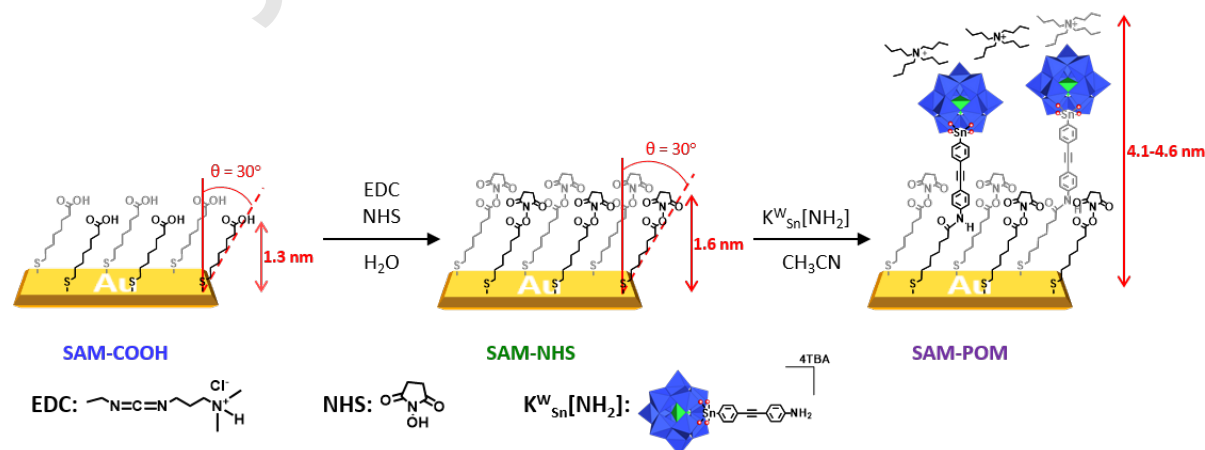
rates could be due to the length of the organic tether. This prompted us to complete these initial studies by the direct grafting of the POM hybrid $\text{TBA}_3[\text{PW}_{11}\text{O}_{39}\{\text{O}(\text{Si}(\text{CH}_2)_3\text{SH})_2\}] \text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ with thiol-terminated groups, expected to be more reactive, and short alkyl chains, to speed up the electron transfer. Indeed, a two order of magnitude higher electron transfer rate constant of $150\,000\text{ s}^{-1}$ was inferred at gold micro-electrodes but the POM coverage density at the electrode remained low.

Building on these two studies illustrating the POM processing onto gold electrodes and previous reports, we will discuss immobilization strategies, comparing direct (one-step) versus indirect (two-step) covalent grafting to identify plausible trends from the broader context.

2 Results and discussion

2.1 Indirect or two-step grafting: peptide-type coupling reaction onto pre-functionalized electrodes

The direct formation of thioalkyl SAMs onto gold from thiolates has been thoroughly studied and it is commonly admitted that it proceeds through a large reorganization of the initially formed disordered layer to maximalize van der Waals interactions between the aliphatic chains.^{29,30} In the case of POM hybrids bearing terminal thiol groups, this reorganization, crucial to get a well-organized and dense layer, is expected to be hindered by the POM steric size. The indirect or two-step POM deposition could thus appear as a valuable alternative. Therefore, we have investigated the peptide-type coupling of the amino-terminated POM $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{NH}_2\}] (\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2])$, TBA stands for the tetrabutylammonium cation) on a preformed 8-mercapto-1-octanoic acid SAM (**SAM-COOH**). To test the coupling from the carboxylic-acid functionalized POM $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{COOH}\}] (\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}])$, a 8-amino-1-octanethiol SAM (**SAM-NH₂**) has also been prepared. The POM hybrids $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ and $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ were prepared as previously reported (see SI).^{35, 26} The multi-step grafting procedure has been monitored by ellipsometry, PM-RAIRS and AFM. Note that two types of substrates have been used depending on the technique's requirements: Au on silicon substrates for ellipsometry, while Au onto glass or mica substrates, allowing flame treatment to reconstruct atomically plane substrate before functionalization, was used for AFM. They were typically immersed simultaneously in the same solution bath to enable parallel analysis.



Scheme 1. Schematic illustration of a Au-substrate modification by an activated SAM and subsequent POM peptide-coupling.

Pre-functionalized electrodes SAM-COOH and SAM-NH₂ onto Au

The Au substrates were incubated in a 10^{-3} M solution of 8-mercapto-1-octanoic acid in ethanol for one night, in the dark. The substrates were then gently rinsed and sonicated in ethanol to eliminate extra molecules deposited by physisorption. After air drying, the thickness of the **SAM-COOH** layer was first macroscopically probed by ellipsometry. If the measures obtained at five different points at the surface did not differ more than 0.2 nm, the SAM was considered to be homogeneous and a mean value was calculated. On this basis, 30 modified substrates over 35 were found suitable. Their mean thickness distribution is displayed on Figure S4a. The expected value for a regularly ordered SAM with a tilt angle of 30° from the normal to the surface is 1.3 nm. Accordingly, more than 67 % of the substrates had a mean value in the range 1.3 ± 0.2 nm. However, subsequent imaging by AFM has revealed the presence of large aggregates (100-150 nm large and 15-35 nm thick) dispersed on the surface. The roughness is comparable to that of the naked gold substrates (see Fig. S5b). Fortunately, subsequent treatment of the **SAM-COOH** with the coupling agents (see below) has resulted in the apparent elimination of the aggregates (see Fig. S5c).

The **SAM-NH₂** have been similarly prepared by soaking of gold substrates in a 10^{-4} M solution of 8-amino-1-octanethiol hydrochloride in ethanol for 24h, in the dark, followed by thorough rinsing and sonication in ethanol. The distribution of the mean thicknesses deduced from ellipsometry was in the range of the expected value (1.3 nm with a tilt angle of 30° , 13 substrates see Fig. S4c). As previously for the SAM-COOH the AFM images disclosed the presence of dispersed aggregates (see Fig. S5d). Furthermore, the protonation of the amine functions in the hydrochloride precursor could be detrimental to the peptide coupling. Therefore, the as prepared SAM-NH₂ were further treated by immersion in a solution of TBAOH 1 M in methanol for 45-60s, then thoroughly rinsed with methanol. Characterization by AFM showed the positive effect on the quality of the SAM with the elimination of the aggregates and a determined roughness of 0.5 nm on the Au terraces, consistent with the formation of a monolayer (See Fig. S5d). Comparison of the thickness distribution before and after treatment with TBAOH further confirmed the preservation of the **SAM-NH₂** (see Fig. S4c). Whereas it was difficult to draw any conclusion from the evolution of the PM-RAIRS spectra, XPS provided definitive insights about the deprotonation of the ammonium groups. The high resolution N1s signals before and after treatment with TBAOH 0.1 M are displayed on Figure 1. They consist in two peaks at 401.6 eV and 399.4 eV, attributed to ammonium and amine functions respectively. Peak deconvolution gave an ammonium/amine ratio of 45.9/54.1 before the treatment and 17.4/82.6 after. A longer exposition of the SAM to TBAOH was precluded as it can lead to SAM degradation.

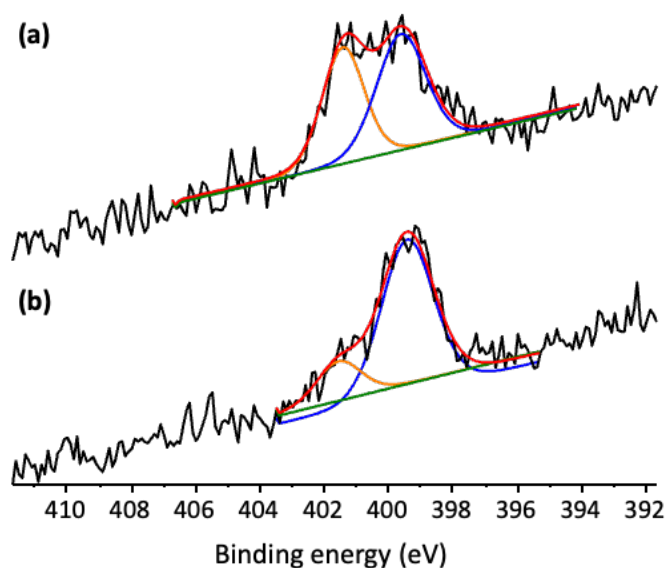


Figure 1. High resolution N1s XP spectra of a SAM-NH₂ before (a) and after (b) treatment with TBAOH 0.1 M for 1 minute.

Peptide-type coupling reaction between SAM-COOH and K^W_{Sn}[NH₂]

The peptide coupling refers to the reaction between an amine and a carboxylic acid in the presence of a coupling reagent, aimed at activating the acid function. Various coupling reagents are available, with one commonly used being the *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC). It is supplied as the hydrochloride form, which explains that it is often used in the presence of a base (dimethylaminopyridine DMAP or diisopropylethylamine DIPEA) or *N*-hydroxysuccinimide (NHS), generally in aqueous medium. In organic solvent, like acetonitrile, several possible activation systems have been tested on Dawson-type POMs functionalized with a tin-aliphatic acid tether. Isobutyl chloroformate, in the presence of a base (potassium *tert*-butoxide, triethylamine) stood out because it didn't require any separation of urea by-products (N,N'-di-isopropylcarbodiimide DIC/NHS, N,N'-dicyclohexylcarbodiimide DCC/NHS) nor heating (2-ethoxy-1-ethoxycarbonyl-1,2-Dihydroquinoline EEDQ).³⁶ Following previous reports involving hybrid POMs derivatized with amino groups,^{37–39} we have chosen the EDC/NHS system. Substrates coated with a **SAM-COOH** were immersed in an aqueous solution of EDC/NHS (30/60 mM) for 1.25 hours, then sonicated and thoroughly washed with distilled water. AFM images recorded on the activated SAMs (**SAM-NHS**) confirm the disappearance of most of the aggregates observed on the starting **SAM-COOH** (see Fig. S5c) and that the **SAM-NHS** are suitable for further reaction with the POM hybrids. A systematic characterization by ellipsometry was carried out on 19 **SAM-NHS** and the results are disclosed on Figure S4b. Using the criteria described above, more than 80% of the **SAM-NHS** displayed a mean thickness compliant with the expected value (1.6 ± 0.2 nm).

Ellipsometry has provided a useful tool to optimize the conditions for the subsequent K^W_{Sn}[NH₂] covalent grafting, given that a mean thickness above 4 nm is expected for a densely packed POM monolayer. The organization of the tetrabutylammonium counter cations is still speculative, their

location on top of the POM layer would give a total thickness between 4.1 and 4.6 nm (see Scheme 1). This was achieved after a 72 hours immersion of a **SAM-NHS** in a 10^{-3} M solution of $\text{K}^{\text{W}}_{\text{sn}}[\text{NH}_2]$ in acetonitrile, followed by sonication and thorough rinsing with the same solvent. Decreasing the POM concentration ($5 \cdot 10^{-4}$ M) or the incubation time (24 hours) resulted in thinner layers (3.1-3.4 nm and 4.1 nm, respectively). We also found out that a careful preparation of the $\text{K}^{\text{W}}_{\text{sn}}[\text{NH}_2]$ is essential: when the final washing with ethyl-acetate had not been carried out at the end of the workup, subsequent grafting generally resulted in multilayers. On the experiments carried out on 31 **SAM-NHS** modified substrates to optimize the experimental conditions, 9 substrates have met all the three optimal conditions for the peptide coupling (72h-immersion of the substrates, in a 1 mM solution of $\text{K}^{\text{W}}_{\text{sn}}[\text{NH}_2]$, preliminary washed with ethyl-acetate). These 9 substrates were related to 6 different experiments (1, 1, 1, 1, 1 and 4 substrates respectively immersed in a given bath). For these 6 experiments, mono-layers were obtained in 33% of cases (4.2-5.0 nm), and sub-monolayers (2.5-3.0 nm) in the remaining 66%. From the whole set of experiments, it is worth pointing out that whatever the number of substrates dipped into a given POM solution (up to six), the outcome of the grafting, monolayers *versus* submonolayers, was identical (see Table S1). It means that the grafting is experiment-dependent but not substrate-dependent. The 1:2 monolayer:submonolayer ratio given above has thus been calculated on the basis of the number of experiments carried out. Moreover, on each substrate, the thicknesses measured on 5 different points did not vary more than 0.2 nm, consistent with a uniform distribution. No significant variation in the thickness was observed upon sonication of the final **SAM-POM** in the presence of 0.1 M TBAPF₆, confirming both the robustness of the covalent link and the formation of a single POM layer. The occurrence of densely-packed monolayers consists in a real improvement compared to previous studies.³¹ Moreover, we were also able to monitor the various steps of the **SAM-POM** elaboration by PM-RAIRS to confirm the presence of the POMs.

Polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) characterization of the SAMs

The PM-RAIRS spectra of the **SAM-COOH**, **SAM-NHS** and **SAM-POM** are presented on Figure 2. The **SAM-COOH** spectrum displayed the characteristic asymmetric and symmetric stretching vibrations of carboxylate groups $\square(\text{COO}^-)$ at $1634\text{-}1569\text{ cm}^{-1}$ and 1446 cm^{-1} , respectively. After activation of the acid functions, a decrease of the $\square(\text{COO}^-)$ bands was observed and the characteristic features of the $\text{O}=\text{C}-\text{O}-\text{NR}$ groups appeared, with a strong $\square(\text{C}=\text{O})$ feature at 1744 cm^{-1} and very weak carbonyl stretching vibrations for the succinimide ring at 1822 and 1788 cm^{-1} . These bands weakened upon reaction with $\text{K}^{\text{W}}_{\text{sn}}[\text{NH}_2]$, while a broad pattern grew in the $1700\text{-}1500\text{ cm}^{-1}$ range, assigned to amide bands at 1641 cm^{-1} (amide I, $\square(\text{C}=\text{O})$) and 1543 cm^{-1} (amide II, $\square(\text{NH})$), together with the characteristic signature of the POM at 1090 cm^{-1} ($\square(\text{P}=\text{O})$) and 959 cm^{-1} ($\square(\text{WO})$). Given that the optical window is limited at low wavenumber (KBr and ZnSe optics, MCT detector) and the small quantity of POMs on the substrate, a low signal/noise ratio prevented the identification of the other POM vibrational modes. However, these were clearly observed in the case of a POM multi-layer with a higher POM

coating (see SI, Figure S6). Finally, the $\nu(\text{CH})$ stretching bands attributed to the methylene of the alkyl chain and the tetrabutylammonium cations are clearly present at 2923 and 2846 cm^{-1} .

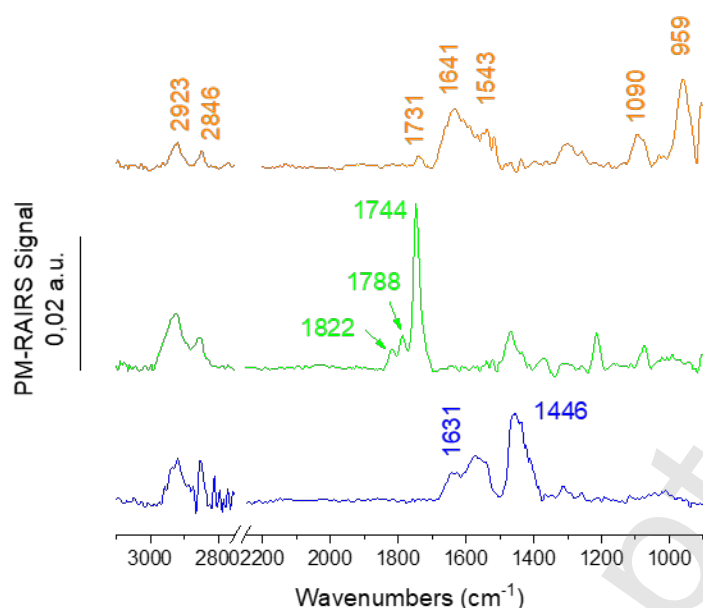
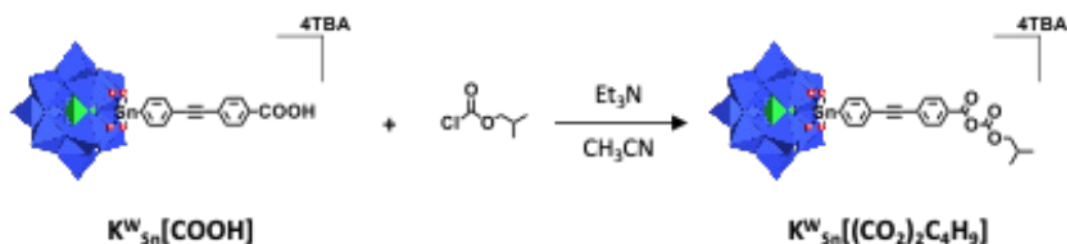


Figure 2. PM-RAIRS monitoring of the POM coupling : **SAM-COOH** (blue-bottom), **SAM-NHS** (green-middle) and **SAM-POM** (orange-top).

Immobilization of $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ or $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ onto SAM- NH_2 : indication of electrostatic deposition

In the case of $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ the aromatic amine is less reactive than an aliphatic one towards the aminolysis of N-hydroxysuccinimide esters.⁴⁰ This led us to investigate the reverse grafting, starting with the POM hybrid $\text{TBA}_{4.4}[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{COOH}_{0.6}\}]$ ($\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$) bearing a remote carboxylic acid moiety. Its ability to form a peptide bond after activation by isobutyl chloroformate, in the presence of triethylamine, in acetonitrile, was demonstrated by its reaction with hexylamine (conversion 94%). It was therefore qualified for grafting to a preformed SAM of 8-amino-1-octanethiol (**SAM-NH₂**). To make the heterogeneous reaction as straightforward as possible and avoid the liberation of by-products that could contaminate the surface, like triethylammonium chloride, we have also isolated the mixed anhydride POM hybrid $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{C}(\text{O})\text{OC}(\text{O})\text{OC}_4\text{H}_9\}]$ $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$, resulting from the carboxyl activation of $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ with isobutylchloroformate (see Scheme 2). As expected, the homogeneous reaction between $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ and hexylamine also yielded the coupling product, with a 83% yield. This non-quantitative yield was explained by the sensitivity of $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ towards hydrolysis (see SI for further details).



Scheme 2. Activation of $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ by isobutyl chloroformate in view of its immobilization onto a SAM- NH_2 .

However, our subsequent efforts to couple either a SAM- NH_2 and $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ or a SAM- NH_2 and $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ were not conclusive. The SAM was typically immersed in a $2.5 \cdot 10^{-4}$ M solution of $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ in acetonitrile for 24h. The 0.7 to 1 nm thicknesses measured by ellipsometry were much lower than expected, with no apparent effect of the POM concentration, nor of the addition of Et_3N (TEA) in excess (5 to 20 equivalents, added to push further the deprotonation of the SAM). Degradation of $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ was also observed in some cases. Furthermore, a control experiment carried out with $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{I}\}] \text{K}^{\text{W}}_{\text{Sn}}[\text{I}]$ yielded a similar thickness of 1 nm. This strongly supports a competitive electrostatic deposition/physiosorption in the reaction between a SAM- NH_2 and $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ or $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$, rather than the formation of covalent peptide bonds. This at variance with a recent report on the covalent grafting of the related $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Ge}(\text{CH}_2)_2\text{COOH}\}]$ onto Si(111) electrodes chemically modified with $\text{Ar}(\text{CH}_2)_2\text{NH}_2$.⁴¹ Yet, in that case, the POM surface coverage was $10^{-12} \text{ mol.cm}^{-2}$, which is more than one order of magnitude lower than the value around $10^{-10} \text{ mol.cm}^{-2}$ that we previously determined for a POM covalently grafted onto Si(100) and which was close to the theoretical value for a densely-packed POM monolayer.^{32,42,43} This suggests that the coupling reaction was not complete.

Several conclusions on the efficiency of the peptide coupling reaction can be drawn from these studies run in parallel either with the SAM-COOH/ $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ or SAM- NH_2 / $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ (or $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$) combinations:

- the ellipsometry technique is easy to implement and gives first insights about the progress and the performance of the grafting. The homogeneity of the POM distribution can be assessed by measures taken at various locations on the substrate, yet at a macroscopic scale.
- AFM characterization provides information down to a few nano-meter scale but, in turn, is not representative of the whole substrate, which will be ultimately engaged in the targeted application. Characterization by complementary techniques, at various length-scales is thus highly advisable.
- in the literature, the POM packing density is rarely assessed, surface coverage deduced from electrochemical characterization rather pointing to sub-monolayers. This is the case either for the coupling between the analogous $\text{K}^{\text{W}}_{\text{Ge}}[\text{NH}_2]$ and a SAM-aryl carboxylic acid prepared on glassy carbon from the 4-carboxybenzediazonium (one tenth of a closely packed monolayer)³¹

or, in the reverse grafting, between $[\text{PW}_{11}\text{O}_{39}\{\text{Ge}(\text{CH}_2)_2\text{COOH}\}]^{4-}$ and a SAM-amine (see above).⁴¹ In this work, we have demonstrated that we were able to improve the grafting density. We also underlined that reproducibility in surface functionalization is to be evaluated in terms of statistics data with a variance higher than in the case of reactions carried out under homogeneous conditions. This should be more systematically reported in studies dealing with POM-based device fabrication.

- the transposition of reactions from homogeneous to heterogeneous conditions is never straightforward: $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ and $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ show the expected reactivity towards amines in solution, which appears to be inhibited at the solid state. This is probably related to an inappropriate state of the **SAM-NH₂** such as partial protonation.
- special efforts should be paid to the preparation and characterization of the preformed SAMs. The high proportion of densely packed POM monolayers obtained through the coupling between $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ and **SAM-COOH** is probably to be attributed to quality of the intermediate **SAM-NHS** layers after carboxy activation. This underlines the importance to be paid to every step of the elaboration of the seeding SAMs and generally to the cleaning of the substrates before subsequent modifications.
- as POMs are polyanions, electrostatic deposition is a serious competitive path, probably at work in the case of **SAM-NH₂**, prone to be protonated. Abundant rinsing/sonication, including in the presence of an electrolyte such as a tetrabutylammonium salt in organic solvent, is therefore recommended. After such a work-up, observation of low thicknesses is indicative of electrostatic deposition/physiosorption, rather than covalent coupling.

2-2 Direct grafting of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ onto gold electrodes

In the previous section, we came to the conclusion that the combination **SAM-COOH**/ $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ prevails over the alternative **SAM-NH₂**/ $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ to achieve an efficient peptide coupling. Another way to bypass the POM electrostatic deposition is to harness the high affinity of Au for sulfur molecules through the direct grafting of a thiolated-POM hybrid. This prompted us to investigate the formation of covalent layers from $\text{TBA}_3[\text{PW}_{11}\text{O}_{39}\{\text{Si}(\text{CH}_2)_3\text{SH}\}_2\text{O}\}]$ $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$, which we initially prepared for adsorption on HgSe quantum dots⁴⁴ and Pt nanoparticles.⁴⁵ Stabilization of Au-nanoparticles with such thiol-terminated POM hybrids as capping agents is precedented, in the Keggin^{3 46} or the Dawson series,⁷ with an enhanced stability compared to electrostatic assemblies reported in the latter case. Covalent functionalization of flat Au substrates has been achieved through di-sulfide^{14 20} or thioester¹³ terminated POMs with a tight packing in the first case,²⁰ whereas a low coverage was deduced from electrochemical studies in the latter.¹³ In both cases, the organic tether of these POM hybrids were rather long because they were obtained by post-functionalization of primo POM hybrid platforms. Here we preferred short alkyl chains terminated by the reactive thiol function to steer the SAM formation and to enhance the electronic communication between the POMs and the electrode. The grafting has been first implemented

onto flat Au substrates to determine the best conditions and then extended to micro-electrodes to investigate the interfacial electron transfer.

Characterization of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ grafting onto Au planar substrates

Optimization of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ grafting - ellipsometry and AFM monitoring

The thiol-terminated POM hybrid was prepared using a procedure we previously reported.⁴⁴ It was then immobilized onto Au planar substrates by incubating the substrates in a solution of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ in acetonitrile, followed by thorough rinsing. The concentration was varied from 5×10^{-4} to 10^{-4} and 10^{-3} M and the incubation time from 24 to 48 and 72 hours, in the dark. The efficiency of the immobilization was first probed by ellipsometry to determine the optimum conditions, which were found to be a 24h incubation in a 5×10^{-4} M solution of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$, giving a mean thickness of 1.6 nm for the POM layer (Au/Si substrates). We also noted that operating under an argon atmosphere did not yield any improvement. Once the immobilization conditions were fixed, the homogeneity of the layer was checked by AFM. A representative image is displayed on Figure 3, showing well-identified terraces and an apparent absence of POM aggregates, with a root mean square roughness of 0.52 nm. The PM-RAIRS spectrum disclosed vibrational features at 1109, 1040, 998 and 991 cm^{-1} , which are in close agreement with the IR spectrum of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ diluted in a KBr pellet, and respectively assigned to the $\nu(\text{Si-O-Si})$, $\nu(\text{PO})$ and $\nu(\text{W=O})$ stretching vibrations (see Figure S7).

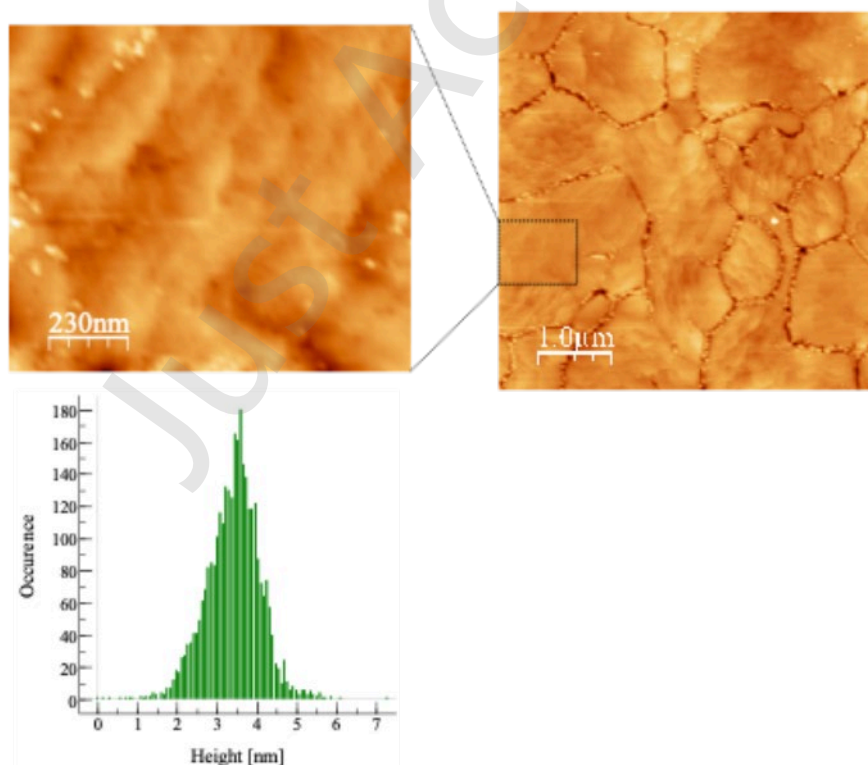


Figure 3. AFM image, zoom of the image (dashed line area) and histogram of heights of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ on Au/glass substrates.

Confirmation of covalent-attachment by XPS

The PM-RAIRS spectrum confirms the presence of the POMs on the substrate but not their covalent bonding. This was inferred from the S2p peak of XPS spectrum, as shown in Figure 4. The S2p doublet observed at 162.2 and 163.4 eV (S 2p_{3/2} and S 2p_{1/2} respectively), corresponds to S bound to Au. The presence of the POM is further revealed by the W 4f doublet at 36.2 (4f_{7/2}) and 38.4 (4f_{5/2}) consistent with previously reported values for W(VI) in polyoxotungstates.^{38,47,48,7}

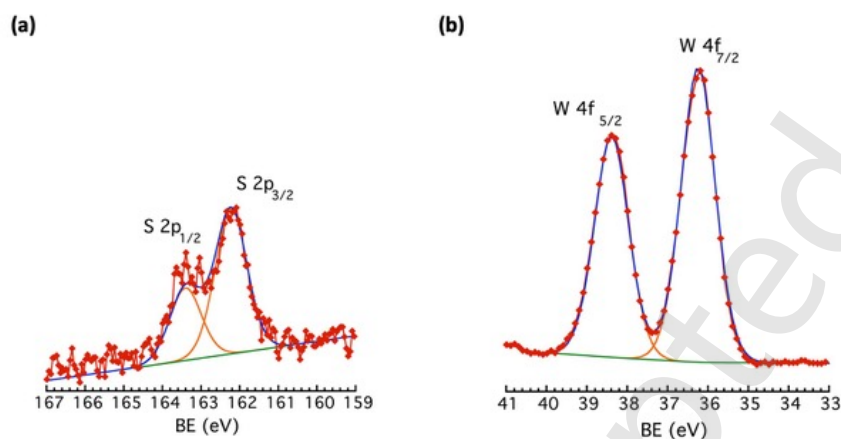


Figure 4. High resolution (a) S2p and (b) W4f XPS spectra of the $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ layer onto Au/Si substrates.

Interfacial electron transfer at a gold micro-electrode

After determining the optimal concentration of the $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ dipping solution for efficient grafting onto commercial substrates, the protocol was extended to gold-ball ultramicroelectrodes to further evaluate the POM layer electrochemically. The microelectrodes were thus soaked in a 5×10^{-4} M solution of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ in acetonitrile for 24h and gently rinsed, prior to performing electrochemical measurements in an acetonitrile solution containing 0.5 M tetraethylammonium tetrafluoroborate as supporting electrolyte. The choice of small electrodes was dictated by the necessity to reach scan rates larger than 10^4 V.s^{-1} in order to efficiently measure the electron transfer rate constant.^{49–51} The electrodes were produced by melting the protruding part (c.a. 3 mm) of a gold wire sealed in a glass pipet.⁵² This strategy produces electrodes that can be further cleaned repeatedly in a flame prior adsorption. Importantly, we could then perform experiments up to $50\,000 \text{ V.s}^{-1}$ under ohmic drop compensation conditions using our home-made potentiostat.⁵³ The reference electrode was a platinum wire.

Figure 5 presents 3 cyclic voltammograms (CVs) taken at various scan rates v . Two chemically reversible waves are observed above 200 V.s^{-1} , in agreement with the typical expected behaviour of Keggin POMs and with the CV obtained for $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ in solution (see Figure S8). The CVs at 1400 and 14000 V.s^{-1} show a one order of magnitude difference in the currents, in agreement with theory for adsorbed systems. In these conditions, integration of the voltametric wave provides the number of adsorbed molecules on the surface. We then deduced a surface coverage Γ of ca. $2 \times 10^{-11} \text{ mol.cm}^{-2}$, lower than expected. However, for larger electrodes and at lower scan rates (typically 20 V.s^{-1}), the extracted

surface coverage was higher, indicating that the number of electrochemically responsive POMs decreases as the rate increases.⁵¹ This suggests the formation of loosely packed layers, as we have also observed by direct grafting of POM hybrids initially terminated by thioacetate groups.¹³ In that case, the organic tether length has little effect. Regardless the choice of the anchoring function, the direct grafting mode might have an impact: the POM hybrid reported in this work is bi-functionalized. In a previous study dealing with the grafting of carboxylate-terminated POM hybrids onto Si/SiO₂ the SAM thickness determined by ellipsometry was lower (therefore a lower surface coverage) for a bi-functionalized POM (silyl derivative, analogous to the POM hybrid of this work with an even shorter C2-alkyl chain), compared to a mono-functionalized POM (tin derivative).²⁶ Note that a low coating was also determined from electrochemical measurements for ruthenium organometallic complexes anchored through thiol, carbodithioate or isocyanide groups,⁵⁴ whereas a higher grafting density was inferred from XPS in the case of Anderson- and Lindqvist-type POMs functionalized with terminal disulfide groups.²⁰ (see Table 1).

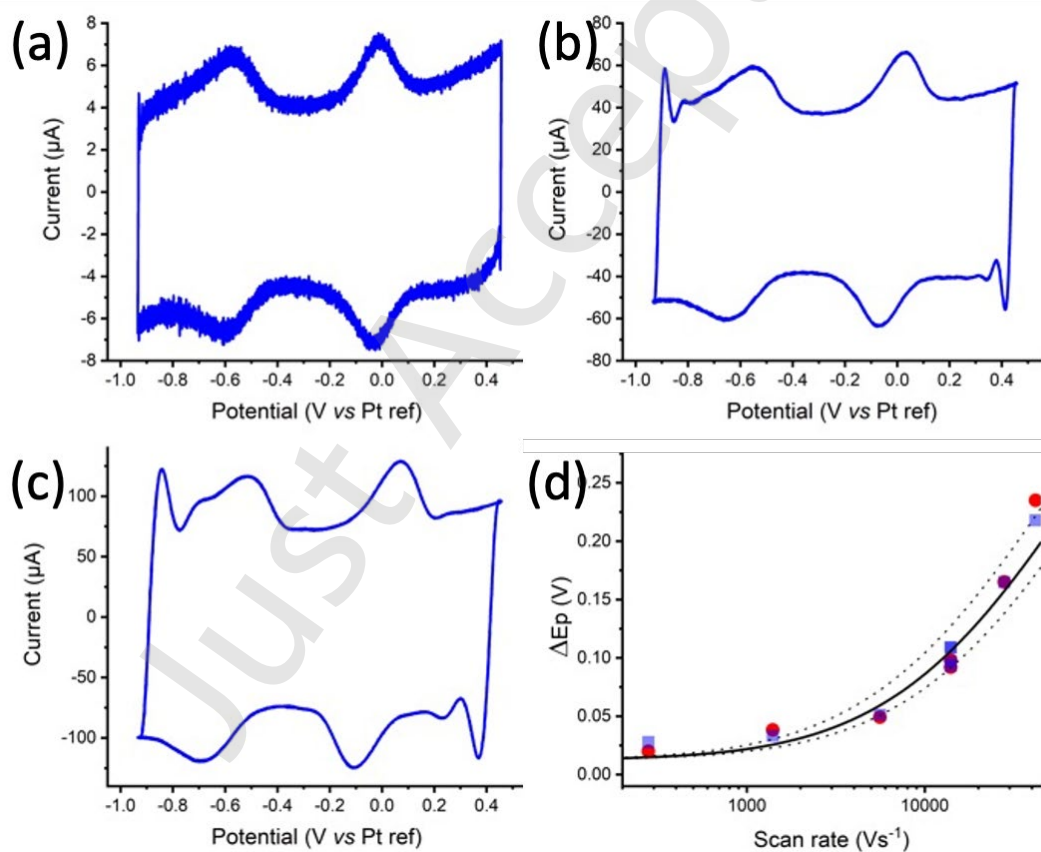


Figure 5. CVs of a gold microelectrode modified with $K^W_{Si}[SH]$ immersed in a CH_3CN solution containing $(NEt_4)BF_4$ 0.5 M as supporting electrolyte at a) 1400 $V.s^{-1}$ b) 14000 $V.s^{-1}$ c) 28000 $V.s^{-1}$. Oscillations at the inversion potential are due to online ohmic drop compensation. d) Peak to peak potential difference (ΔE_p) for the first (red circles) and second (blue squares) reduction waves. Theoretical fit for $k_{et} = 1.5 \times 10^5 s^{-1}$ (bold black line), $1.1 \times 10^5 s^{-1}$ and $1.9 \times 10^5 s^{-1}$ (dotted lines).

At small v , the peak positions are unchanged. A small shift between oxidation and reduction of 12 mV is observed. This slight deviation with theory is frequent in SAMs, previously observed with POM-

based SAMs,^{32,33} but does not preclude kinetic analysis. Above 1000 V.s⁻¹, the peak splitting ΔE_p increases because the voltametric timescale approaches the one of electron transfer, as observed on Figure 5d. By recording experimental ΔE_p with the scan rate, and comparing them with the numerical solution of the Butler-Volmer equation for adsorbed systems, we could deduce a rate of electron transfer $k_{et} = 1.5 \pm 0.4 \times 10^5 \text{ s}^{-1}$ for the two redox couples.⁵⁵⁻⁵⁷ At scan rates larger than 30000 V.s⁻¹, experimental ΔE_p s deviate from the theory for purely instrumental reasons, *i.e.* limitations of the electronic bandwidth of the potentiostat.

The present interfacial electron transfer rate constant $k_{et} = 150\,000 \text{ s}^{-1}$ is in the range of those determined for self-assembled monolayers of fast redox-active systems, like ferrocene or ruthenium complexes immobilized onto Au.^{54,58} However, it is more than two order of magnitude larger than the ones we previously determined for other self-assembled POM monolayers on Au (see Table 1). This is apparently not correlated to the surface coverage, the first three examples in Table 1 dealing with low surface coverage but very different values k_{et} .¹³ Under the assumption that the anchoring group has little effect,⁵⁴ this can tentatively be ascribed to a much better electronic coupling compared to other systems, due to the very short linker between the POM and the electrode. Indeed, for SAMs with redox active headgroups such as ferrocene, the attenuation of the kinetics was demonstrated to be directly related to the linker length increase.⁵⁸ Another striking feature of this study is the similar k_{et} measured for both waves. Considering an outer sphere electron transfer, this suggests that the reorganization energies are the same in the framework of Marcus theory. This is in line with the fact that the electrons added are delocalized over the whole POM backbone, inducing very little structural change.

(POM)-anchor	electrode	Surface coverage G (mol.cm ⁻²)	Interfacial electron transfer k_{et} (s ⁻¹)	Ref
(PW ₁₁)	micro electrode	2x10 ⁻¹¹ (a) (b)	150 000 (1 st and 2 nd wave)	this work
(PW ₁₁)	macro disk	1.2X10 ⁻¹¹ (a)	170 (1 st wave) 150 (2 nd wave)	13
(PW ₁₁)	macro disk	3.7X10 ⁻¹² (a)	140 (1 st wave) 100 (2 nd wave)	13
(V ₆)	Au ^{TS}	1.4X10 ⁻¹⁰ (c)	-	20
(MnMo ₆)	Au ^{TS}	2.7X10 ⁻¹⁰ (c)	-	20

(PW ₁₁)	Au plate	4x10 ⁻¹¹ (a)	-	31
---------------------	----------	-------------------------	---	----

Table 1. Electrochemical interfacial studies on some selected POM-based SAMs on Au. ^(a) Determined from electrochemistry; ^(b) lower-bound estimate (see text); ^(c) determined from XPS by S-peak integration.

3 General survey on the immobilization of POMs on flat surface

Assembling molecules is a critical step in the elaboration of molecular materials-based devices, as it ultimately strongly influences their performance. Beyond final metrics, long-term stability, reproducibility issues, and device-to-device variability are significant limitations that hinder large scale development. This requires to step back and rationalize the various immobilization strategies that have been used to prepare POM-active layers, enabling the proposal of subsequent improvements and the identification of layer fabrication - structuring relationships.

Besides conventional methods like drop-casting or spin-coating or use of POM-polymer composites,^{48,59–61} which typically produce thick layers, electrostatic deposition via dip-coating in a POM solution is often used to achieve thinner POM layers. While this method is straightforward, it can yield to the deposition of POM aggregates. Aggregation is a well-known phenomenon in POM chemistry that may occur, depending on the POM type and the nature of the cations, both in solution⁶² as well as on surfaces,⁶³ where it has been observed⁶⁴ and, later on, harnessed⁶⁵ on modified silicon substrates. Additionally, we have also shown that a meticulous preparation of modified Au substrates can enable uniform POM mono-layer coatings.^{15,66,67} Note that *soft landing* is a new and promising alternative.^{68,69} The covalent POM anchoring remains the superior approach to achieve precise control over thin layer formation, ideally a mono-layer, to ensure uniform POM distribution, and to engineer the POM/electrode interface.^{25,26,32–34,37,42,70,71} While it may require a demanding functionalization step, this method allows for the discrimination between chemi- and physisorbed species through rinsing and sonication.⁷² However, given the polyanionic nature of POMs, electrostatic deposition remains a strong competitive path, even when using POM hybrids. For instance, in the case of the reaction between $K^W_{Sn}[COOH]$ and $SAM-NH_2$, it likely hindered the intended covalent bonding. While a vast library of pristine POMs is available, organic-inorganic POM hybrids are restricted to specific structural types, which restricts the applicability of the covalent approach. In this work, we performed both the direct (one-step) grafting of $K^W_{Si}[SH]$ onto Au electrodes and the indirect (two-step) grafting of $K^W_{Sn}[NH_2]$ onto a pre-functionalized Au-substrate. Based on our prior experience with direct grafting of highly reactive functions (diazonium or carboxylate)^{25,26,32,33,35,42} and relevant literature,²⁰ we anticipated a high $K^W_{Si}[SH]$ loading, potentially forming a monolayer. However, the surface coverage derived from the electrochemical data remained modest, only slightly higher than that obtained with thioacetate-functionalized POMs, but probably underestimated at high scan rate (see above).¹³ Further investigation is needed to determine the likelihood of achieving tight packing through direct POM hybrid grafting. The indirect peptide coupling reaction seems to be more efficient, though a direct comparison between

the two approaches is challenging. The chemical reactions involved differ, and $\mathbf{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ is a bi-functionalized POM hybrid while $\mathbf{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ is monofunctionalized. Additionally, the pre-organization of the organic SAM on the substrate in the indirect method should favor higher structuring, which remains to be proved. When thicker POM layers are desired, the electrostatic strategy is generally more suitable, unless bespoke multi-functionalized POM hybrids are used.³⁵

The use of POM hybrids enables fine tuning of the tether or organic SAM design, allowing for the variation in the length (short/long), and nature (conjugated/aliphatic) of the organic moiety. In this work, we demonstrated that the short spacer in $\mathbf{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ promotes exceptionally fast electron transfer. The entanglement of the three parameters, surface coverage, interfacial electron transfer rate and tether length/grafting mode is difficult to unravel and would require more experimental data. For applications requiring minimal POM/electrode distance, direct coupling is the preferred approach. Conversely, expanding the organic spacer could electronically isolate the POMs from the electrode, which may be advantageous for applications like spintronics. XPS experiments on Au nanoparticles coated with diphosphonate POM hybrids⁷ have suggested such a shielding, while also revealing enhanced stability compared to electrostatic assemblies. Another advantage of the covalent strategy, particularly the two-step covalent grafting, is the ability to study POM-to-POM communication by progressively transitioning from a densely-packed POM monolayer to isolated POMs, through the dilution of the reactive headgroups in the pre-formed SAM.

4 Conclusions

In conclusion, we have shown that the peptide coupling reaction carried out under heterogenous conditions is effective to covalently attach a monolayer of the aniline-terminated POM hybrid $\mathbf{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ to a pre-functionalized **SAM-COOH**, resulting in densely-packed monolayers in half of the cases. The reverse reaction, attaching the carboxy-terminated POM hybrid $\mathbf{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ to a pre-functionalized **SAM-NH₂** proves more challenging and is likely charge surface dependent. Electrostatic interactions may dominate the deposition of POM hybrids onto positively charged pre-assembled SAMs. As an alternative to the peptide coupling, some of us have previously used 1,4-phenylene diisothiocyanate (PDITC) as a cross-linking agent to achieve the covalent immobilization of aniline-functionalized POM hybrids on amino-modified SBA-15 mesoporous silica.⁷³ In all cases, reproducibility or experiment-to-experiment- variability is an intrinsic parameter of surface functionalization, which should be more frequently addressed and discussed.

Characterizing the interfacial electron transfer in a wet electrochemical environment provides valuable insights into the electronic communication between the electrode and the covalently immobilized POM layer, which depends on the nature of the organic spacer. For $\mathbf{K}^{\text{W}}_{\text{Si}}[\text{SH}]$, with its short alkyl-thiol spacer, a high value of $150\,000\text{ s}^{-1}$ was determined. However, this does not necessarily predict electron transport across the molecular junction once contacted by a top electrode, nor of the response time of an electronic device. Experimental studies bridging electrochemistry and molecular electronics concepts are rare and

warrant further investigations.^{74–76} Nevertheless, the high interfacial electron transfer rate obtained in this work underscore the potential of POMs as candidates for electronic devices when integrated into molecular junctions.^{77,78} With organic or organometallic systems, it has been observed that the energy levels may be altered by conformational changes once the system is trapped in a junction, as shown by Ulstrup in scanning tunneling break junctions.⁷⁹ In comparison to other molecules, the rigid backbone of POMs may better stay unchanged, leading to more predictable properties and better robustness of potential devices.

6 Experimental part

Chemicals and solvents were supplied by Fischer or VWR and used as received. The POM hybrids $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$,³⁵ $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ ²⁶ and $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ ⁴⁵ were prepared as previously reported and their purity confirmed by ³¹P NMR spectroscopy. An additional step in the purification of $\text{K}^{\text{W}}_{\text{Sn}}[\text{NH}_2]$ was assured by dissolving the solid in a minimum of acetonitrile and the final product was obtained by fractional precipitation and thorough washing with an ethyl acetate excess.

Synthesis of $\text{TBA}_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{C}(\text{O})\text{OC}(\text{O})\text{OC}_4\text{H}_9\}] \text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$
 $\text{K}^{\text{W}}_{\text{Sn}}[\text{COOH}]$ (100 mg, 0.025 mmol) and triethylamine (5 μL , 0.034 mmol) were solubilized in 4.8 mL of dry acetonitrile and the solution placed in an ice bath. Isobutyl chloroformate (7 μL , 0.039 mmol) was added and the mixture was stirred for 30 minutes. A precipitate appeared by the addition of an excess of diethyl ether (45 mL) at room temperature and was collected by centrifugation. The solid was dissolved in a minimum of acetonitrile and a new precipitate was obtained by the addition of a DCM/Et₂O mixture (1.5/25 mL). The solid underwent further washings in suspension in diethyl ether and a final step in acetonitrile in the presence of TBA enriched Amberlyst[®] resin for 15 minutes. After the removal of the resin by a membrane filtration, the filtrate was subjected to the addition of a DCM/Et₂O mixture (1.5/25 mL) and $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ precipitated as a pale orange powder. Further washings in suspension in diethyl ether and centrifugation steps lead to pure $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$ (66%, 67.6 mg NMR ¹H (400 MHz, CD₃CN, ppm) : $\delta=8,05$ (d, ³J_{H-H}=8,69 Hz, 2H, Ar-H), $\delta=7,75$ (d+dd, ³J_{H-H}=8,19 Hz, ³J_{Sn-H}= 93,2 Hz, 2H, Ar-H), $\delta=7,72$ (d, ³J_{H-H}=8,69 Hz, 2H, Ar-H), $\delta=7,67$ (d, ³J_{H-H}=8,19 Hz, 2H, Ar-H), $\delta=4,13$ (d, ³J_{H-H}=6,64 Hz, 2H, O-CH₂-CH-(CH₃)₂), $\delta=3,12$ (m, 32H, N-CH₂-CH₂-CH₂-CH₃), $\delta=2,02$ - $2,06$ (m, 1H, O-CH₂-CH-(CH₃)₂), $\delta=1,63$ (m, 32H, N-CH₂-CH₂-CH₂-CH₃), $\delta=1,39$ (sex, ³J_{H-H}=7,40 Hz, 32H, N-CH₂-CH₂-CH₂-CH₃), $\delta=0,98$ (t, ³J_{H-H}=7,40 Hz, 54H, O-CH₂-CH-(CH₃)₂/ N-CH₂-CH₂-CH₂-CH₃). NMR ³¹P (121,5 MHz, CD₃CN, ppm) : $\delta= -10,98$ (s+d, ²J_{Sn-P}=23,64 Hz). IR (KBr, cm⁻¹): 2961 (m), 2935 (m), 2873 (m), 1802 (m), 1740 (f), 1482 (m), 1380 (f), 1199(m), 1170(m), 1069 (F), 962 (F), 886 (F), 813 (FF), 514 (f), 381 (m).

Surface functionalization

The *Au/Si substrates* were purchased from Sigma-Aldrich. They consist of a 100 nm gold layer adhered to the silicon wafer by means of a titanium adhesion layer. To remove any contamination, the substrates

were treated 2 min in pure sulfuric acid and rinsed abundantly with water and isopropanol and dried under N₂. Before immersion in the thiol solution, the substrates were exposed to UV-ozone during 20 minutes and rinsed with ethanol. Thanks to their homogeneous reflective properties, these substrates are suitable for ellipsometry and for PM-RAIRS characterization.

Au/glass substrates, coated successively with a 50 Å thick layer of chromium and a 200 nm thick layer of gold, were purchased from Arrandee (Werther, Germany). To ensure a good crystallinity of the gold top layer, the substrates were annealed in a butane flame, afterwards exposed to UV-ozone during 20 minutes and rinsed with ethanol prior to immersion in the thiol solution. Thanks to the thick Au layer suitable for reconstruction, these flat substrates were used for AFM characterization. As far as possible and to ensure cross-linked characterization, both types of Au substrates were simultaneously immersed in the same thiol or POM solution.

Preparation of the SAM-COOH The Au substrates were incubated in a 10⁻³ M solution of 8-mercaptopal-octanoic acid in absolute ethanol (8.8 mg in 50 mL) for one night, in the dark. The substrates were then thoroughly rinsed with absolute ethanol, sonicated 5 min in absolute ethanol and dried under N₂ after a last rinsing with a flow of absolute ethanol.

Preparation of the SAM-NHS To activate the SAM-COOH, a solution containing a mixture of *N,N'*-dicyclohexylcarbodiimide (30 mmol.L⁻¹) and *N*-hydroxysuccinimide (60 mmol.L⁻¹) in distilled water was prepared. One drop of this solution was deposited on the top of the SAM-COOH during 1.25 hour. The sample was then rinsed successively by a flow of distilled water, sonication (5 min) in a bath of distilled water and a last flow of distilled water before drying under N₂.

Preparation of the SAM-NH₂ The SAM-NH₂ have been prepared by incubation of gold substrates in a 1.2x10⁻⁴ M solution of 8-amino-1-octanethiol hydrochloride in absolute ethanol (1mg in 50 mL), for 24h, in the dark, followed by thorough rinsing and sonication in absolute ethanol (flow/sonication 20min/flow). They were dried under N₂.

Immobilization of K^W_{si}[SH] The Au-substrates were immersed in a 5x10⁻⁴ M solution of K^W_{si}[SH] in acetonitrile (8.9 mg in 5 mL) for 24h in the dark. They were then thoroughly rinsed with a flow of acetonitrile and dried under a N₂ flow. Most of the time, a clean substrate free of physisorbed molecules was obtained after solvent-flow rinsing and the sonication step was not necessary.

Characterization techniques

Ellipsometry Ellipsometry measurements were performed on the Au/Si substrates with a monowavelength ellipsometer SENTECH SE 400 equipped with a He-Ne laser at $\lambda = 632.8$ nm and an incident angle at 70°. The ns and ks values of the sample with bare Au were systematically measured just before immersion in the thiol solution, as various optical indices could be measured from one piece

of wafer to another. The obtained values were around 0.2 for ns and 3.5 for ks. For the 8-amino-1-octanethiol SAM, typical optical indices of an organic monolayer were used (ns = 1.5, ks = 0). To characterize the POM layer, ns = 1.48 and ks = 0 were used.³¹ At least 5 measurements were performed on a same sample in different zones, to check the homogeneity of the layer. A mean value for the thickness was calculated when the standard deviation was equal or lower than 0.2 nm.

XPS XPS analyses were performed on using an Omicron Argus X-ray photoelectron spectrometer. The monochromated AlK α radiation source ($h\nu = 1486.6$ eV) had a 300 W electron beam power. The emission of photoelectrons from the sample was analyzed at a takeoff angle of 90° under ultra-high vacuum conditions ($\leq 10^{-10}$ Torr). Spectra were recorded with a 100 eV pass energy for the survey scan and 20 eV pass energy for Au4f, P2p, W4f, C1s, O1s, N1s and S2p regions. Binding energies were calibrated against the Au4f $_{7/2}$ binding energy at 84.0 eV and element peak intensities were corrected by Scofield factors.⁸⁰ The spectra were fitted using Casa XPS v.2.3.15 software (Casa Software Ltd., U.K.) and applying a Gaussian/Lorentzian ratio G/L equal to 70/30.

AFM AFM images were recorded on Au/glass substrates using a commercial AFM (NanoScope VIII MultiMode AFM, Bruker Nano Inc., Nano Surfaces Division, Santa Barbara, CA) equipped with a $150 \times 150 \times 5$ μm scanner (J-scanner). The substrates were fixed on a steel sample puck using a small piece of double-sided adhesive tape. Images were recorded in peak force tapping mode in air at room temperature (around 22°C) using oxide-sharpened microfabricated Si $_3$ N $_4$ cantilevers (Bruker Nano Inc., Nano Surfaces Division, Santa Barbara, CA). The spring constants of the cantilevers were measured using the thermal noise method, yielding values ranging from 0.4 to 0.5 N/m. The curvature radius of silicon nitride tips was about 10 nm (manufacturer specifications). The raw data were processed using the imaging processing WSxM, mainly to correct the background slope between the tip and the gold surface. A zoomed-in image of a gold terrace was used to perform a statistical heights analysis using the software.

Polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) PM-RAIRS measurements were performed on Au/Si or Au/glass substrates using a Nicolet Nexus 5700 FT-IR spectrometer equipped with a nitrogen-cooled HgCdTe wide band detector, with an external beam configuration as follow: A ZnSe grid polarizer and a ZnSe photoelastic modulator were placed prior to the sample in order to modulate the incident beam between p and s polarizations (HINDS Instruments, PM90, modulation frequency = 36 kHz).. Infrared spectra were recorded at 8 cm $^{-1}$ resolution with co-addition of 128 scans. The sum and difference interferograms were processed and underwent Fourier-transformation to yield the PM-RAIRS signal which is the differential reflectivity $(\Delta R/R^\circ) = (R_p - R_s)/(R_p + R_s)$, where R_p is the signal parallel to the incident plane while R_s is the perpendicular contribution. The measurements were done at two different voltages applied to the modulator ZnSe

crystal to optimize the sensitivity. Finally, a base line correction was apply using the spline mode and auto y set-up from ThermoFisher OMNIC software.

Electrochemistry

Ultrafast voltammetry was performed with a home-made potentiostat⁵³ allowing online ohmic drop compensation. The gold-ball electrodes were produced following a procedure previously described.^{50–52}

Electronic Supplementary Material: Supplementary material (NMR and IR spectra of $\text{K}^{\text{W}}_{\text{Sn}}[(\text{CO}_2)_2\text{C}_4\text{H}_9]$, statistical data for the SAM formation, activation and POM coupling reaction, AFM images, additional PM-RAIRS spectra, cyclic voltammogram of $\text{K}^{\text{W}}_{\text{Si}}[\text{SH}]$ in solution) is available in the online version of this article.

Acknowledgments A. P. Acknowledges support from the CNRS and Sorbonne Université;

Data availability All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Declaration of competing interest There are no conflicts to declare.

Author contribution statement M. L. data collection, validation, writing manuscript. K. D. F. and L. F. data collection. E. M. and V. H. data collection and writing manuscript. R.V. and G. I. data validation. F. V. and A. P. supervision and writing manuscript. All the authors have approved the final manuscript.

Use of AI statement None.

References

- (1) Cherevan, A. S.; Nandan, S. P.; Roger, I.; Liu, R.; Streb, C.; Eder, D. Polyoxometalates on Functional Substrates: Concepts, Synergies, and Future Perspectives. *Adv. Sci.* **2020**, *7* (8), 1903511. <https://doi.org/10.1002/advs.201903511>.
- (2) Monakhov, K.; Petrovskii, S. K.; Long, D.; Nyman, M.; Kahnt, A.; Warneke, J.; Ritchie, C.; Parac-Vogt, T. N.; Mitchell, S. G.; Song, Y.; Moors, M.; Proust, A.; Vuillaume, D.; Sadakane, M.; Newton, G. N.; Miras, H. N. Polyoxometalates for Health, Electronics, Energy, and the Environment: Challenges, Opportunities, and Future Horizons. *ChemistryEurope* **2026**, *4* (5), e70280. <https://doi.org/10.1002/ceur.70280>.
- (3) Mayer, C. R.; Neveu, S.; Cabuil, V. A Nanoscale Hybrid System Based on Gold Nanoparticles and Heteropolyanions. *Angewandte Chemie International Edition* **2002**, *41* (3), 501–503. [https://doi.org/10.1002/1521-3773\(20020201\)41:3%3C501::AID-ANIE501%3E3.0.CO;2-Z](https://doi.org/10.1002/1521-3773(20020201)41:3%3C501::AID-ANIE501%3E3.0.CO;2-Z).
- (4) Wang, Y.; Zeiri, O.; Raula, M.; Le Ouay, B.; Stellacci, F.; Weinstock, I. A. Host–Guest Chemistry with Water-Soluble Gold Nanoparticle Supraspheres. *Nature Nanotech* **2017**, *12* (2), 170–176. <https://doi.org/10.1038/nnano.2016.233>.
- (5) Zhang, M.; Hao, J.; Neyman, A.; Wang, Y.; Weinstock, I. A. Influence of Polyoxometalate Protecting Ligands on Catalytic Aerobic Oxidation at the Surfaces of Gold Nanoparticles in Water. *Inorg. Chem.* **2017**, *56* (5), 2400–2408. <https://doi.org/10.1021/acs.inorgchem.6b02167>.
- (6) Xia, K.; Yamaguchi, K.; Suzuki, K. Recent Advances in Hybrid Materials of Metal Nanoparticles and Polyoxometalates. *Angew Chem Int Ed* **2023**, *62* (1), e202214506. <https://doi.org/10.1002/anie.202214506>.

- (7) Martin, C.; Kastner, K.; Cameron, J. M.; Hampson, E.; Alves Fernandes, J.; Gibson, E. K.; Walsh, D. A.; Sans, V.; Newton, G. N. Redox-Active Hybrid Polyoxometalate-Stabilised Gold Nanoparticles. *Angew Chem Int Ed* **2020**, *59* (34), 14331–14335. <https://doi.org/10.1002/anie.202005629>.
- (8) Wu, C.; Qiao, X.; Robertson, C. M.; Higgins, S. J.; Cai, C.; Nichols, R. J.; Vezzoli, A. A Chemically Soldered Polyoxometalate Single-Molecule Transistor. *Angew. Chem. Int. Ed.* **2020**, *59* (29), 12029–12034. <https://doi.org/10.1002/anie.202002174>.
- (9) Sherif, S.; Rubio-Bollinger, G.; Pinilla-Cienfuegos, E.; Coronado, E.; Cuevas, J. C.; Agraït, N. Current Rectification in a Single Molecule Diode: The Role of Electrode Coupling. *Nanotechnology* **2015**, *26* (29), 291001. <https://doi.org/10.1088/0957-4484/26/29/291001>.
- (10) Linnenberg, O.; Moors, M.; Notario-Estévez, A.; López, X.; De Graaf, C.; Peter, S.; Baeumer, C.; Waser, R.; Monakhov, K. Yu. Addressing Multiple Resistive States of Polyoxovanadates: Conductivity as a Function of Individual Molecular Redox States. *J. Am. Chem. Soc.* **2018**, *140* (48), 16635–16640. <https://doi.org/10.1021/jacs.8b08780>.
- (11) Yang, F.; Moors, M.; Hoang, D. A.; Schmitz, S.; Rohdenburg, M.; Knorke, H.; Charvat, A.; Wang, X.-B.; Monakhov, K. Yu.; Warneke, J. On-Surface Single-Molecule Identification of Mass-Selected Cyclodextrin-Supported Polyoxovanadates for Multistate Resistive-Switching Memory Applications. *ACS Appl. Nano Mater.* **2022**, *5* (10), 14216–14220. <https://doi.org/10.1021/acsanm.2c03025>.
- (12) Yang, F.; Kalandia, G.; Moors, M.; Lorenz, J.; Rohdenburg, M.; Wang, X.; Cao, W.; Moussawi, M. A.; Volke, D.; Hoffmann, R.; Warneke, J.; Parac-Vogt, T. N.; Monakhov, K. Yu. Ligand Substituent Effects on the Electronic Properties of Lindqvist-Type Polyoxometalate Multi-Level-Switches in the Gas Phase, Solution and on Surfaces. *Adv Materials Inter* **2024**, *11* (33), 2400411. <https://doi.org/10.1002/admi.202400411>.
- (13) Yaqub, M.; Walsh, J. J.; Keyes, T. E.; Proust, A.; Rinfray, C.; Izzet, G.; McCormac, T.; Forster, R. J. Electron Transfer to Covalently Immobilized Keggin Polyoxotungstates on Gold. *Langmuir* **2014**, *30* (15), 4509–4516. <https://doi.org/10.1021/la4048648>.
- (14) Lombana, A.; Rinfray, C.; Volatron, F.; Izzet, G.; Battaglini, N.; Alves, S.; Decorse, P.; Lang, P.; Proust, A. Surface Organization of Polyoxometalate Hybrids Steered by a 2D Supramolecular PTCDI/Melamine Network. *The Journal of Physical Chemistry C* **2016**, *120* (5), 2837–2845. <https://doi.org/10.1021/acs.jpcc.5b11945>.
- (15) Francesca, K. D.; Lenfant, S.; Laurans, M.; Volatron, F.; Izzet, G.; Humblot, V.; Methivier, C.; Guerin, D.; Proust, A.; Vuillaume, D. Charge Transport through Redox Active [H7P8W48O184]33– Polyoxometalates Self-Assembled onto Gold Surfaces and Gold Nanodots. *Nanoscale* **2019**, *11* (4), 1863–1878. <https://doi.org/10.1039/C8NR09377F>.
- (16) Velessiotis, D.; Glezos, N.; Ioannou-Sougleridis, V. Tungstate Polyoxometalates as Active Components of Molecular Devices. *Journal of Applied Physics* **2005**, *98* (8), 084503. <https://doi.org/10.1063/1.2103416>.
- (17) Yi, X.; Izarova, N. V.; Stuckart, M.; Guérin, D.; Thomas, L.; Lenfant, S.; Vuillaume, D.; Van Leusen, J.; Duchoň, T.; Nemšák, S.; Bourone, S. D. M.; Schmitz, S.; Kögerler, P. Probing Frontier Orbital Energies of {Co₉(P₂W₁₅)₃} Polyoxometalate Clusters at Molecule–Metal and Molecule–Water Interfaces. *J. Am. Chem. Soc.* **2017**, *139* (41), 14501–14510. <https://doi.org/10.1021/jacs.7b07034>.
- (18) Glöß, M.; Pütt, R.; Moors, M.; Kentzinger, E.; Karthäuser, S.; Monakhov, K. Yu. Exploring the Ligand Functionality, Electronic Band Gaps, and Switching Characteristics of Single Wells–Dawson-Type Polyoxometalates on Gold. *Adv Materials Inter* **2022**, *9* (21), 2200461. <https://doi.org/10.1002/admi.202200461>.
- (19) Soni, S.; Werner, I.; Aidi, M.; Moors, M.; Mthembu, C. L.; Zharnikov, M.; Havenith, R. W. A.; Monakhov, K. Yu.; Chiechi, R. C. Influence of Polyoxovanadate and Phthalocyanine on 4f Electron Transfer in Gold-Confined Monolayers Probed with EGaIn Top Contacts. *ACS Appl. Nano Mater.* **2023**, *6* (24), 22643–22650. <https://doi.org/10.1021/acsanm.3c05021>.
- (20) Lin, J.; Zheng, A.; Xie, Y.; Chen, N.; He, R.; Yin, B.; Lv, W.; Wei, Y.; Li, Y. Transition from Tunneling to Schottky Barriers in Molecular Junctions Based on Polyoxometalate Monolayers. *Angew Chem Int Ed* **2025**, *64* (23), e202501763. <https://doi.org/10.1002/anie.202501763>.
- (21) Glauber, J.; Moors, M.; Ryndyk, D. A.; Najafidehaghani, E.; Lorenz, J.; Maas, R.; Boysen, N.; Parala, H.; Heine, T.; Devi, A.; Monakhov, K. Tunable Electronic and Optoelectronic Properties of MoS₂ Through Molecular Coverage-Controlled Polyoxometalate Doping. *Adv Elect Materials* **2026**, *12* (4), e00706. <https://doi.org/10.1002/aelm.202500706>.
- (22) Mercier, D.; Ben Haddada, M.; Huebner, M.; Knopp, D.; Niessner, R.; Salmain, M.; Proust, A.; Boujday, S. Polyoxometalate Nanostructured Gold Surfaces for Sensitive Biosensing of Benzo[a]Pyrene. *Sens. Actuators, B* **2015**, *209*, 770–774. <https://doi.org/10.1016/j.snb.2014.12.015>.
- (23) Verissimo, M. I. S.; Evtuguin, D. V.; Gomes, M. T. S. R. Polyoxometalate Functionalized Sensors: A Review. *Front. Chem.* **2022**, *10*, 840657. <https://doi.org/10.3389/fchem.2022.840657>.
- (24) Vuillaume, D.; Proust, A. Towards Polyoxometalate Nanoelectronics. *Chem. Rev.* **2026**.

- (25) Laurans, M.; Dalla Francesca, K.; Volatron, F.; Izzet, G.; Guerin, D.; Vuillaume, D.; Lenfant, S.; Proust, A. Molecular Signature of Polyoxometalates in Electron Transport of Silicon-Based Molecular Junctions. *Nanoscale* **2018**, *10* (36), 17156–17165. <https://doi.org/10.1039/C8NR04946G>.
- (26) Laurans, M.; Trinh, K.; Dalla Francesca, K.; Izzet, G.; Alves, S.; Derat, E.; Humblot, V.; Pluchery, O.; Vuillaume, D.; Lenfant, S.; Volatron, F.; Proust, A. Covalent Grafting of Polyoxometalate Hybrids onto Flat Silicon/Silicon Oxide: Insights from POMs Layers on Oxides. *ACS Appl. Mater. Interfaces* **2020**, *12* (42), 48109–48123. <https://doi.org/10.1021/acsami.0c12300>.
- (27) Ben M'Barek, Y.; Rosser, T.; Sum, J.; Blanchard, S.; Volatron, F.; Izzet, G.; Salles, R.; Fize, J.; Koepf, M.; Chavarot-Kerlidou, M.; Artero, V.; Proust, A. Dye-Sensitized Photocathodes: Boosting Photoelectrochemical Performances with Polyoxometalate Electron Transfer Mediators. *ACS Appl. Energy Mater.* **2020**, *3* (1), 163–169. <https://doi.org/10.1021/acsaeem.9b02083>.
- (28) Pinson, J.; Podvorica, F. Attachment of Organic Layers to Conductive or Semiconductive Surfaces by Reduction of Diazonium Salts. *Chem. Soc. Rev.* **2005**, *34* (5), 429. <https://doi.org/10.1039/b406228k>.
- (29) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105* (4), 1103–1170. <https://doi.org/10.1021/cr0300789>.
- (30) Vericat, C.; Vela, M. E.; Benitez, G.; Carro, P.; Salvarezza, R. C. Self-Assembled Monolayers of Thiols and Dithiols on Gold: New Challenges for a Well-Known System. *Chem. Soc. Rev.* **2010**, *39* (5), 1805. <https://doi.org/10.1039/b907301a>.
- (31) Gam Derouich, S.; Rinfray, C.; Izzet, G.; Pinson, J.; Gallet, J.-J.; Kanoufi, F.; Proust, A.; Combellas, C. Control of the Grafting of Hybrid Polyoxometalates on Metal and Carbon Surfaces: Toward Submonolayers. *Langmuir* **2014**, *30* (8), 2287–2296. <https://doi.org/10.1021/la500067e>.
- (32) Rinfray, C.; Izzet, G.; Pinson, J.; Gam Derouich, S.; Ganem, J.-J.; Combellas, C.; Kanoufi, F.; Proust, A. Electrografting of Diazonium-Functionalized Polyoxometalates: Synthesis, Immobilisation and Electron-Transfer Characterisation from Glassy Carbon. *Chem. Eur. J.* **2013**, *19* (41), 13838–13846. <https://doi.org/10.1002/chem.201302304>.
- (33) Rinfray, C.; Brasiliense, V.; Izzet, G.; Volatron, F.; Alves, S.; Combellas, C.; Kanoufi, F.; Proust, A. Electron Transfer to a Phosphomolybdate Monolayer on Glassy Carbon: Ambivalent Effect of Protonation. *Inorganic Chemistry* **2016**, *55* (14), 6929–6937. <https://doi.org/10.1021/acs.inorgchem.6b00485>.
- (34) Rahman, M. A.; Guo, S.-X.; Laurans, M.; Izzet, G.; Proust, A.; Bond, A. M.; Zhang, J. Thermodynamics, Electrode Kinetics, and Mechanistic Nuances Associated with the Voltammetric Reduction of Dissolved $[n\text{-Bu}_4\text{N}]_4[\text{PW}_{11}\text{O}_{39}\{\text{Sn}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)(\text{N}_3\text{C}_4\text{H}_{10})\}]$ and a Surface-Confined Diazonium Derivative. *ACS Appl. Energy Mater.* **2020**, *3* (4), 3991–4006. <https://doi.org/10.1021/acsaeem.0c00405>.
- (35) Salles, R.; Poh, W. C.; Laurans, M.; Volatron, F.; Miche, A.; Alves, S.; Carino, C.; Torteche, L.; Izzet, G.; Lee, P. S.; Proust, A. Covalent Shaping of Polyoxometalate Molecular Films onto ITO Electrodes for Charge Trapping Induced Resistive Switching. *Inorg. Chem. Front.* **2024**, *11* (1), 255–268. <https://doi.org/10.1039/D3QI01761C>.
- (36) Bareyt, S.; Piligkos, S.; Hasenknopf, B.; Gouzerh, P.; Lacôte, E.; Thorimbert, S.; Malacria, M. Efficient Preparation of Functionalized Hybrid Organic/Inorganic Wells–Dawson-Type Polyoxotungstates. *J. Am. Chem. Soc.* **2005**, *127* (18), 6788–6794. <https://doi.org/10.1021/ja050397c>.
- (37) Song, Y.-F.; McMillan, N.; Long, D.-L.; Kane, S.; Malm, J.; Riehle, M. O.; Pradeep, C. P.; Gadegaard, N.; Cronin, L. Micropatterned Surfaces with Covalently Grafted Unsymmetrical Polyoxometalate-Hybrid Clusters Lead to Selective Cell Adhesion. *J. Am. Chem. Soc.* **2009**, *131* (4), 1340–1341. <https://doi.org/10.1021/ja807091v>.
- (38) Mercier, D.; Boujday, S.; Annabi, C.; Villanneau, R.; Pradier, C.-M.; Proust, A. Bifunctional Polyoxometalates for Planar Gold Surface Nanostructuring and Protein Immobilization. *The Journal of Physical Chemistry C* **2012**, *116* (24), 13217–13224. <https://doi.org/10.1021/jp3031623>.
- (39) Yvon, C.; Surman, A. J.; Hutin, M.; Alex, J.; Smith, B. O.; Long, D.; Cronin, L. Polyoxometalate Clusters Integrated into Peptide Chains and as Inorganic Amino Acids: Solution- and Solid-Phase Approaches. *Angew Chem Int Ed* **2014**, *53* (13), 3336–3341. <https://doi.org/10.1002/anie.201311135>.
- (40) Cline, G. W.; Hanna, S. B. The Aminolysis of N-Hydroxysuccinimide Esters. A Structure-Reactivity Study. *J. Am. Chem. Soc.* **1987**, *109* (10), 3087–3091. <https://doi.org/10.1021/ja00244a035>.
- (41) Gurrentz, J. M.; Rose, M. J. Covalent Attachment of Polyoxometalates to Passivated Si(111) Substrates: A Stable and Electronic Defect-Free Si/POM Platform. *J. Phys. Chem. C* **2021**, *125* (26), 14287–14298. <https://doi.org/10.1021/acs.jpcc.1c04015>.
- (42) Volatron, F.; Noël, J.-M.; Rinfray, C.; Decorse, P.; Combellas, C.; Kanoufi, F.; Proust, A. Electron Transfer Properties of a Monolayer of Hybrid Polyoxometalates on Silicon. *Journal of Materials Chemistry C* **2015**, *3* (24), 6266–6275. <https://doi.org/10.1039/C5TC00074B>.

- (43) Tang, Z.; Liu, S.; Wang, E.; Dong, S. Self-Assembled Monolayer of Polyoxometalate on Gold Surfaces: Quartz Crystal Microbalance, Electrochemistry, and in-Situ Scanning Tunneling Microscopy Study. *Langmuir* **2000**, *16* (11), 4946–4952. <https://doi.org/10.1021/la9907127>.
- (44) Martinez, B.; Livache, C.; Meriggio, E.; Xu, X. Z.; Cruguel, H.; Lacaze, E.; Proust, A.; Ithurria, S.; Silly, M. G.; Cabailh, G.; Volatron, F.; Lhuillier, E. Polyoxometalate as Control Agent for the Doping in HgSe Self-Doped Nanocrystals. *J. Phys. Chem. C* **2018**, *122* (46), 26680–26685. <https://doi.org/10.1021/acs.jpcc.8b07190>.
- (45) Gillet, A.; Cher, S.; Tassé, M.; Blon, T.; Alves, S.; Izzet, G.; Chaudret, B.; Proust, A.; Demont, P.; Volatron, F.; Tricard, S. Polarizability Is a Key Parameter for Molecular Electronics. *Nanoscale Horiz.* **2021**, *6* (3), 271–276. <https://doi.org/10.1039/D0NH00583E>.
- (46) Sutter, S.; Trepka, B.; Siroky, S.; Hagedorn, K.; Theiß, S.; Baum, P.; Polarz, S. Light-Triggered Boost of Activity of Catalytic Bola-Type Surfactants by a Plasmonic Metal–Support Interaction Effect. *ACS Appl. Mater. Interfaces* **2019**, *11* (17), 15936–15944. <https://doi.org/10.1021/acsami.9b03727>.
- (47) Vasilopoulou, M.; Douvas, A. M.; Palilis, L. C.; Kennou, S.; Argitis, P. Old Metal Oxide Clusters in New Applications: Spontaneous Reduction of Keggin and Dawson Polyoxometalate Layers by a Metallic Electrode for Improving Efficiency in Organic Optoelectronics. *J. Am. Chem. Soc.* **2015**, *137* (21), 6844–6856. <https://doi.org/10.1021/jacs.5b01889>.
- (48) Zhu, Q.; Paci, B.; Generosi, A.; Renaudineau, S.; Gouzerh, P.; Liang, X.; Mathieu, C.; Rountree, C.; Izzet, G.; Proust, A.; Barrett, N.; Tortech, L. Conductivity via Thermally Induced Gap States in a Polyoxometalate Thin Layer. *J. Phys. Chem. C* **2019**, *123* (3), 1922–1930. <https://doi.org/10.1021/acs.jpcc.8b08510>.
- (49) Zhou, X.-S.; Mao, B.-W.; Amatore, C.; Compton, R. G.; Marignier, J.-L.; Mostafavi, M.; Nierengarten, J.-F.; Maisonhaute, E. Transient Electrochemistry: Beyond Simply Temporal Resolution. *Chem. Commun.* **2016**, *52* (2), 251–263. <https://doi.org/10.1039/C5CC07953E>.
- (50) Boitel-Aullen, G.; Fillaud, L.; Huet, F.; Nierengarten, I.; Delavaux-Nicot, B.; Nierengarten, J.; Maisonhaute, E. Electron Transfer Inside a Decaferrocenylated Rotaxane Analyzed by Fast Scan Cyclic Voltammetry and Impedance Spectroscopy. *ChemElectroChem* **2021**, *8* (18), 3506–3511. <https://doi.org/10.1002/celec.202100738>.
- (51) Boitel-Aullen, G.; Nierengarten, I.; Nierengarten, J.-F.; Tschulik, K.; Maisonhaute, E. EIS versus CV for Adsorbed Systems with CPE and Kinetic Distributions: Physicochemical Consequences. *Electrochimica Acta* **2026**, *565*, 148718. <https://doi.org/10.1016/j.electacta.2026.148718>.
- (52) Amatore, C.; Maisonhaute, E.; Schöllhorn, B.; Wadhawan, J. Ultrafast Voltammetry for Probing Interfacial Electron Transfer in Molecular Wires. *ChemPhysChem* **2007**, *8* (9), 1321–1329. <https://doi.org/10.1002/cphc.200600774>.
- (53) Amatore, C.; Lefrou, C. New Concept for a Potentiostat for On-Line Ohmic Drop Compensation in Cyclic Voltammetry above 300 kV S⁻¹. *Journal of Electroanalytical Chemistry* **1992**, *324* (1–2), 33–58. [https://doi.org/10.1016/0022-0728\(92\)80034-2](https://doi.org/10.1016/0022-0728(92)80034-2).
- (54) Mulas, A.; Hervault, Y.-M.; He, X.; Di Piazza, E.; Norel, L.; Rigaut, S.; Lagrost, C. Fast Electron Transfer Exchange at Self-Assembled Monolayers of Organometallic Ruthenium(II) σ -Arylacetylide Complexes. *Langmuir* **2015**, *31* (25), 7138–7147. <https://doi.org/10.1021/acs.langmuir.5b01629>.
- (55) Laviron, E. General Expression of the Linear Potential Sweep Voltammogram in the Case of Diffusionless Electrochemical Systems. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1979**, *101* (1), 19–28. [https://doi.org/10.1016/S0022-0728\(79\)80075-3](https://doi.org/10.1016/S0022-0728(79)80075-3).
- (56) Laviron, E. The Use of Linear Potential Sweep Voltammetry and of a.c. Voltammetry for the Study of the Surface Electrochemical Reaction of Strongly Adsorbed Systems and of Redox Modified Electrodes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1979**, *100* (1–2), 263–270. [https://doi.org/10.1016/S0022-0728\(79\)80167-9](https://doi.org/10.1016/S0022-0728(79)80167-9).
- (57) Eckermann, A. L.; Feld, D. J.; Shaw, J. A.; Meade, T. J. Electrochemistry of Redox-Active Self-Assembled Monolayers. *Coordination Chemistry Reviews* **2010**, *254* (15–16), 1769–1802. <https://doi.org/10.1016/j.ccr.2009.12.023>.
- (58) Robinson, D. B.; Chidsey, C. E. D. Submicrosecond Electron Transfer to Monolayer-Bound Redox Species on Gold Electrodes at Large Overpotentials. *J. Phys. Chem. B* **2002**, *106* (41), 10706–10713. <https://doi.org/10.1021/jp026195+>.
- (59) Busche, C.; Vilà-Nadal, L.; Yan, J.; Miras, H. N.; Long, D.-L.; Georgiev, V. P.; Asenov, A.; Pedersen, R. H.; Gadegaard, N.; Mirza, M. M.; Paul, D. J.; Poblet, J. M.; Cronin, L. Design and Fabrication of Memory Devices Based on Nanoscale Polyoxometalate Clusters. *Nature* **2014**, *515* (7528), 545–549. <https://doi.org/10.1038/nature13951>.
- (60) Hu, B.; Wang, C.; Wang, J.; Gao, J.; Wang, K.; Wu, J.; Zhang, G.; Cheng, W.; Venkateswarlu, B.; Wang, M.; Lee, P. S.; Zhang, Q. Inorganic–Organic Hybrid Polymer with Multiple Redox for High-Density Data Storage. *Chem. Sci.* **2014**, *5* (9), 3404–3408. <https://doi.org/10.1039/C4SC00823E>.

- (61) Chen, X.; Huang, P.; Zhu, X.; Zhuang, S.; Zhu, H.; Fu, J.; Nissimagoudar, A. S.; Li, W.; Zhang, X.; Zhou, L.; Wang, Y.; Lv, Z.; Zhou, Y.; Han, S.-T. Keggin-Type Polyoxometalate Cluster as an Active Component for Redox-Based Nonvolatile Memory. *Nanoscale Horizons* **2019**, *4* (3), 697–704. <https://doi.org/10.1039/C8NH00366A>.
- (62) Yin, P.; Li, D.; Liu, T. Solution Behaviors and Self-Assembly of Polyoxometalates as Models of Macroions and Amphiphilic Polyoxometalate–Organic Hybrids as Novel Surfactants. *Chem. Soc. Rev.* **2012**, *41* (22), 7368. <https://doi.org/10.1039/c2cs35176e>.
- (63) Linnenberg, O.; Moors, M.; Solé-Daura, A.; López, X.; Bäumer, C.; Kentzinger, E.; Pyckhout-Hintzen, W.; Monakhov, K. Yu. Molecular Characteristics of a Mixed-Valence Polyoxovanadate $\{V^{IV/V}_{18}O_{42}\}$ in Solution and at the Liquid–Surface Interface. *J. Phys. Chem. C* **2017**, *121* (19), 10419–10429. <https://doi.org/10.1021/acs.jpcc.7b02138>.
- (64) Balliou, A.; Douvas, A. M.; Normand, P.; Tsikritzis, D.; Kennou, S.; Argitis, P.; Glezos, N. Tungsten Polyoxometalate Molecules as Active Nodes for Dynamic Carrier Exchange in Hybrid Molecular/Semiconductor Capacitors. *Journal of Applied Physics* **2014**, *116* (14), 143703. <https://doi.org/10.1063/1.4897397>.
- (65) Balliou, A.; Bouroushian, M.; Douvas, A. M.; Skoulatakis, G.; Kennou, S.; Glezos, N. Size-Dependent Single Electron Transfer and Semi-Metal-to-Insulator Transitions in Molecular Metal Oxide Electronics. *Nanotechnology* **2018**, *29* (27), 275204. <https://doi.org/10.1088/1361-6528/aabdc3>.
- (66) Huez, C.; Guérin, D.; Lenfant, S.; Volatron, F.; Calame, M.; Perrin, M. L.; Proust, A.; Vuillaume, D. Redox-Controlled Conductance of Polyoxometalate Molecular Junctions. *Nanoscale* **2022**, *14* (37), 13790–13800. <https://doi.org/10.1039/D2NR03457C>.
- (67) Huez, C.; Renaudineau, S.; Volatron, F.; Proust, A.; Vuillaume, D. Experimental Observation of the Role of Counteranions in Modulating the Electrical Conductance of Preyssler-Type Polyoxometalate Nanodevices. *Nanoscale* **2023**, *15* (25), 10634–10641. <https://doi.org/10.1039/D3NR02035E>.
- (68) Prabhakaran, V.; Mehdi, B. L.; Ditto, J. J.; Engelhard, M. H.; Wang, B.; Gunaratne, K. D. D.; Johnson, D. C.; Browning, N. D.; Johnson, G. E.; Laskin, J. Rational Design of Efficient Electrode–Electrolyte Interfaces for Solid-State Energy Storage Using Ion Soft Landing. *Nat Commun* **2016**, *7* (1), 11399. <https://doi.org/10.1038/ncomms11399>.
- (69) Das, A.; Samayoa-Oviedo, H. Y.; Mohapatra, M.; Basu, S.; Laskin, J. Enhancing Energy Storage Capacity of 3D Carbon Electrodes Using Soft Landing of Molecular Redox Mediators. *Small* **2024**, 2311585. <https://doi.org/10.1002/smll.202311585>.
- (70) Huder, L.; Rinfrey, C.; Rouchon, D.; Benayad, A.; Baraket, M.; Izzet, G.; Lipp-Bregolin, F.; Lapertot, G.; Dubois, L.; Proust, A.; Jansen, L.; Duclairoir, F. Evidence for Charge Transfer at the Interface between Hybrid Phosphomolybdate and Epitaxial Graphene. *Langmuir* **2016**, *32* (19), 4774–4783. <https://doi.org/10.1021/acs.langmuir.6b00870>.
- (71) Errington, R. J.; Petkar, S. S.; Horrocks, B. R.; Houlton, A.; Lie, L. H.; Patole, S. N. Covalent Immobilization of a TiW_5 Polyoxometalate on Derivatized Silicon Surfaces. *Angew Chem Int Ed* **2005**, *44* (8), 1254–1257. <https://doi.org/10.1002/anie.200461065>.
- (72) Volatron, F.; Izzet, G.; Vuillaume, D.; Proust, A. Unveiling Polyoxometalate Redox Properties at the Nanoscale. *Comptes Rendus. Chimie* **2024**, *27* (G1), 255–268. <https://doi.org/10.5802/crchim.344>.
- (73) Makrygenni, O.; Brouri, D.; Proust, A.; Launay, F.; Villanneau, R. Immobilization of Polyoxometalate Hybrid Catalysts onto Mesoporous Silica Supports Using Phenylene Diisothiocyanate as a Cross-Linking Agent. *Microporous and Mesoporous Materials* **2019**, *278*, 314–321. <https://doi.org/10.1016/j.micromeso.2018.11.036>.
- (74) Zhou, X.-S.; Liu, L.; Fortgang, P.; Lefevre, A.-S.; Serra-Muns, A.; Raouafi, N.; Amatore, C.; Mao, B.-W.; Maisonhaute, E.; Schöllhorn, B. Do Molecular Conductances Correlate with Electrochemical Rate Constants? Experimental Insights. *J. Am. Chem. Soc.* **2011**, *133* (19), 7509–7516. <https://doi.org/10.1021/ja201042h>.
- (75) Terada, K.; Nakamura, H.; Kanaizuka, K.; Haga, M.; Asai, Y. Long-Range Electron Transport of Ruthenium-Centered Multilayer Films via a Stepping-Stone Mechanism. *ACS Nano* **2012**, *6* (3), 1988–1999. <https://doi.org/10.1021/nn300126m>.
- (76) McCreery, R. L. The Merger of Electrochemistry and Molecular Electronics. *The Chemical Record* **2012**, *12* (1), 149–163. <https://doi.org/10.1002/tcr.201100006>.
- (77) Nitzan, A. A Relationship between Electron-Transfer Rates and Molecular Conduction. *J. Phys. Chem. A* **2001**, *105* (12), 2677–2679. <https://doi.org/10.1021/jp003884h>.
- (78) Sowa, J. K.; Mol, J. A.; Briggs, G. A. D.; Gauger, E. M. Beyond Marcus Theory and the Landauer–Büttiker Approach in Molecular Junctions: A Unified Framework. *The Journal of Chemical Physics* **2018**, *149* (15), 154112. <https://doi.org/10.1063/1.5049537>.
- (79) Leary, E.; Higgins, S. J.; Van Zalinge, H.; Haiss, W.; Nichols, R. J.; Nygaard, S.; Jeppesen, J. O.; Ulstrup, J. Structure–Property Relationships in Redox-Gated Single Molecule Junctions – A Comparison of Pyrrolo-

- Tetrathiafulvalene and Viologen Redox Groups. *J. Am. Chem. Soc.* **2008**, *130* (37), 12204–12205. <https://doi.org/10.1021/ja8014605>.
- (80) Scofield, J. H. Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV. *Journal of Electron Spectroscopy and Related Phenomena* **1976**, *8* (2), 129–137. [https://doi.org/10.1016/0368-2048\(76\)80015-1](https://doi.org/10.1016/0368-2048(76)80015-1).

Just Accepted