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SUPPORTING INFORMATION

Electron transfer properties of a monolayer of hybrid polyoxometalates on silicon

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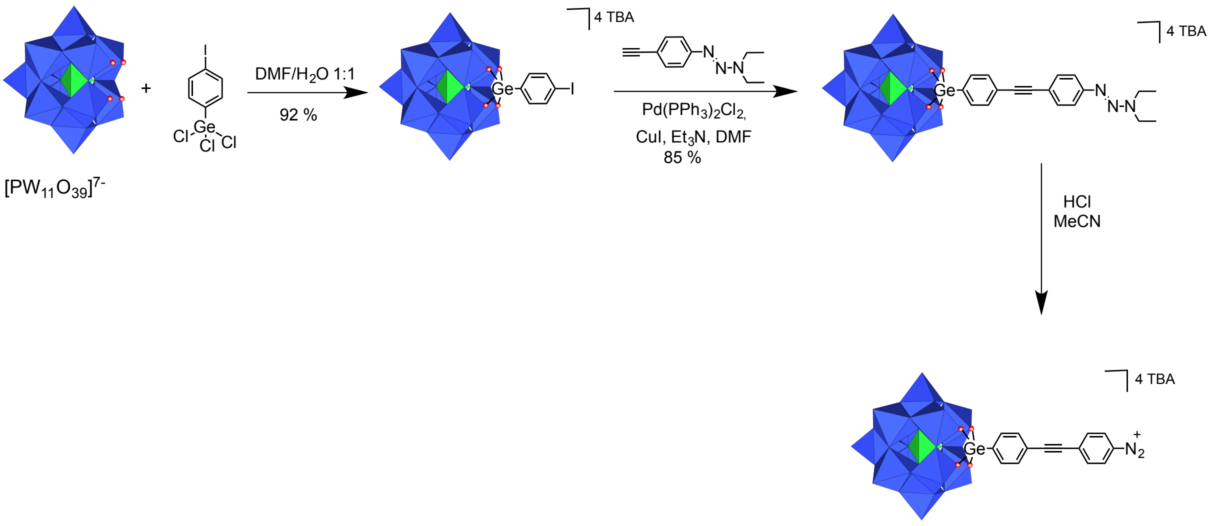
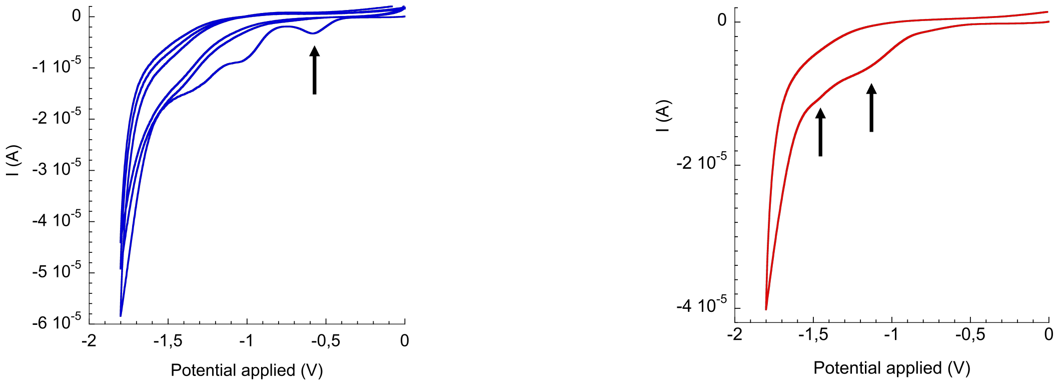
Synthesis steps of the POM-N_2^+ The full synthesis has already been reported in a previous paper.[1]



Scheme S1 The main steps of the synthesis of POM-N_2^+

Physical methods

Cyclic voltammetry



a) b)

Fig. S1 Cyclic voltammograms of a POM modified silicon electrode recorded between 0 and -1,8 V vs SCE at 0.1 $V.s^{-1}$ before (a) and after (b) rinsing with acetonitrile. Electrolyte: TBABr 0.1 M in acetonitrile (ACN). The rinsing induces the disappearing of the wave at -0.5 V vs SCE.

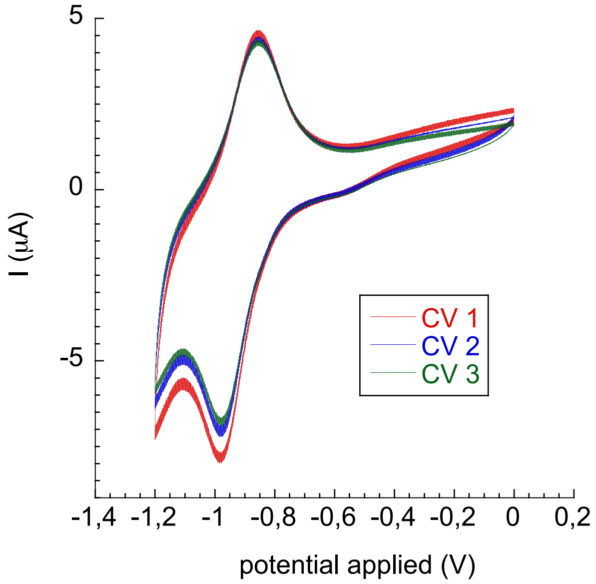


Fig. S2 Cyclic voltammograms of a POM modified silicon electrode recorded between 0 and -1.35 V vs SCE at 0.1 V.s^{-1} after rinsing with acetonitrile. Electrolyte: TBABr 0.1 M in ACN.

Atomic force microscopy

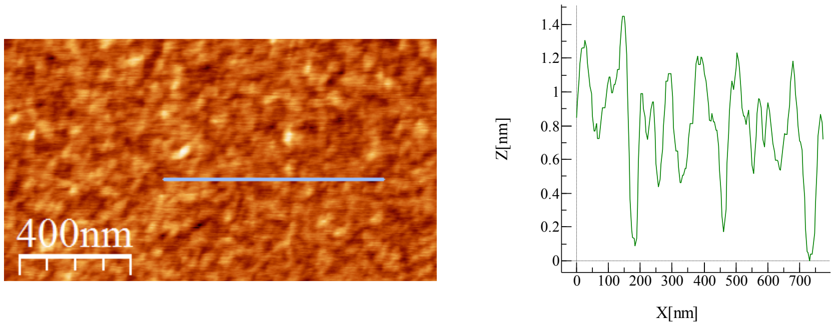


Fig. S3 AFM image (right) and Z profile (left) of the POMs monolayer before rinsing.

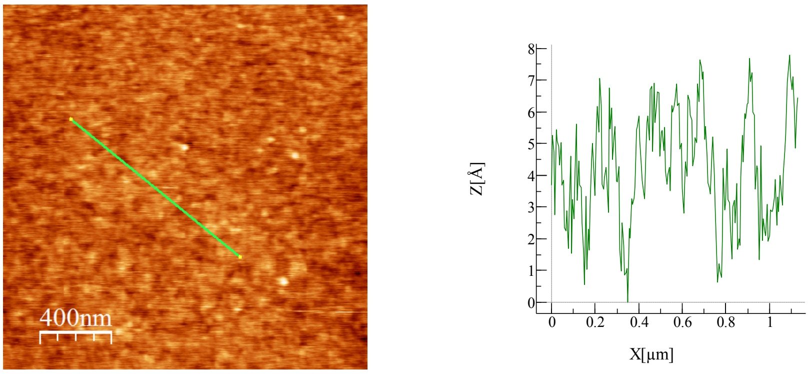


Fig. S4 AFM image (right) and Z profile (left) of a bare silicon substrate

X-ray Photoelectron Spectroscopy

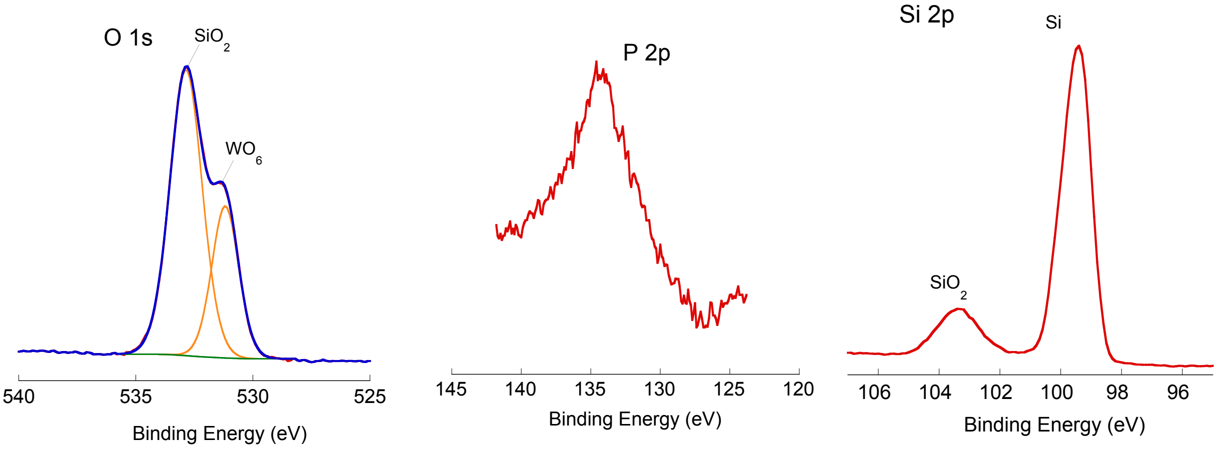
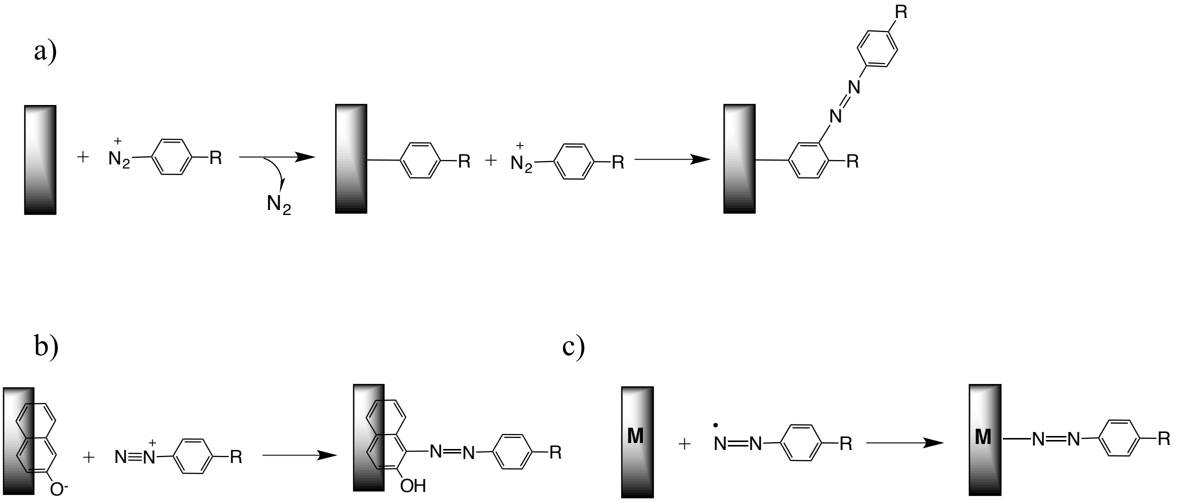


Fig. S5 O1s, P2p and Si2p X-ray photoelectron spectra of the grafted POM monolayer registered after one month guarded in an Ar purged pill-box.

Interpretation of the N 1s spectrum

The presence of a peak at 400 eV on the N1s spectrum is not an unknown issue in the field of diazonium surface chemistry.[2-10] Various scenarii have been claimed and if it cannot be attributed to the partial reduction of a nitro function to an amine function[2] or to the presence of nitrogen impurities,[3] the formation of azo functions has been proposed. The origin of the azo groups can be explained by (i) the reaction between an outer aromatic ring grafted on the substrate and a diazonium ion in solution[4-7] (Scheme S2a) (ii) the attack of a diazonium ion directly on the substrate and formation of an azo link (Scheme S2b,c).[4, 8-10]

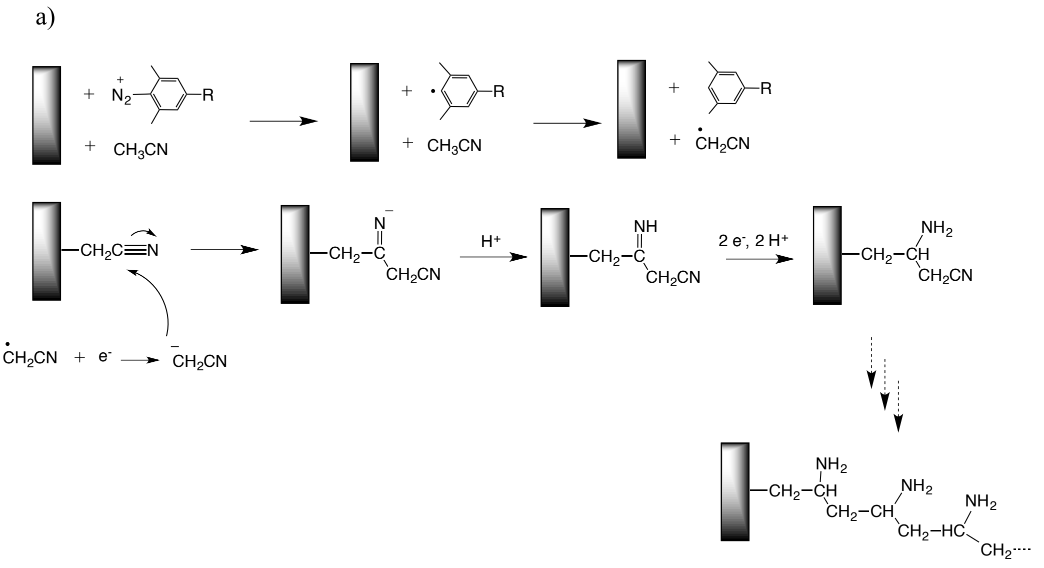


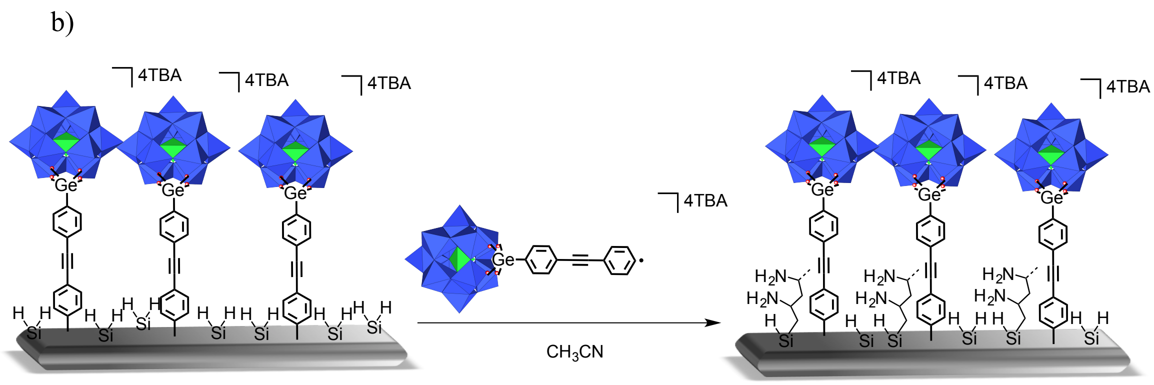
Scheme S2 Possible origins for the presence of azo bonds on a surface functionalized with diazonium salts: the reaction between an outer aromatic ring grafted on the substate and a diazonium ion in solution (a); the attack of a diazonium ion directly on the surface for a carbon substrate[4] (b), a metallic substrate[9] (c).

In the present case, the reaction between an outer aromatic ring and a diazonium ion is not possible since it would lead to multilayer and would be detected by ellipsometry and cyclic voltammetry. As attested in the main text of this article, the steric hindrance of the POMs and their counter cations on top layer prevent from extra attacks by the diazonium ions on the grafted species.

The presence of azo bonds directly on the surface is still controversial. It is well understood in the case of carbon surfaces,[4, 8] since oxygen functions are present on the surface, they can be chemically modified in many ways, and such “activated” phenyl groups on the surface can react easily with diazonium salts (Scheme S2b). In the case of metallic substrates, the presence of surface bonded azo groups was highlighted but under negative potentials conditions, permitting the formation of a diazenyl radical, which directly bonds to the surface (scheme 1c).[9, 10] In the present case, spontaneous grafting is performed on a silicon substrate, and at such a low driving force, the diazenyl radical cannot be an intermediate.[11] As a matter of fact, the formation of a silicon bonded azo group has never been discussed in the literature.[12, 13] This hypothesis is thus very unlikely to explain the peak at 400 eV.

The most probable explanation is finally provided by recent studies reported by Podvorica and coll.:[14, 15] they highlighted the possible attack of the acetonitrile solvent on the surface by using a hindered diazonium salt, unable to attach to the surface. They propose that the aryl radicals react with acetonitrile molecules to form cyanomethyl radicals that attack the surface and polymerize to finally form amine multilayers (Scheme S3a). In the present case, there are large free areas below the POM spheres. The excess of POM-aryl radicals in solution can react with the solvent molecules and the formed cyanomethyl radicals may attack the free oxidized silicon surface. Thus, polymerization occurs around the organic tether of the grafted hybrid POMs, leading to the formation of amine groups on the substrate (Scheme S3b). This is probably the most plausible interpretation for the characteristic peak at 400 eV on the X-ray photoelectron N1s spectrum.





Scheme S3 a) Main steps of the mechanism for the polymerization of acetonitrile molecules on a silicon surface; b) proposed polymerization of acetonitrile on the POM modified silicon surface.

Scanning Electrochemical Microscopy

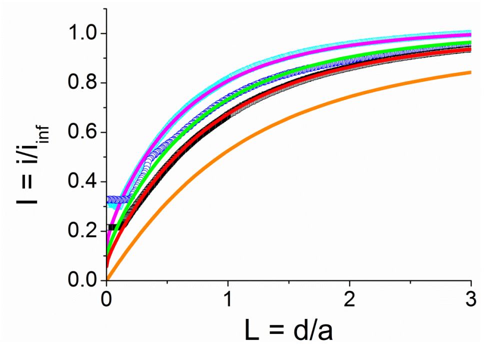


Fig. S6 SECM approach curves recorded at three different bare Si substrates before modification with a 25 µm radius Pt microelectrode in a solution of DMF containing 0,1 M NBu$_4$BF$_4$ and 4 mM 3NX. Lines are the theoretical curves using an electrode with Rg =8. Insulating behaviour (orange line), κ = 0.05 (red line), κ = 0.08 (green line), κ = 0.13 (pink line).

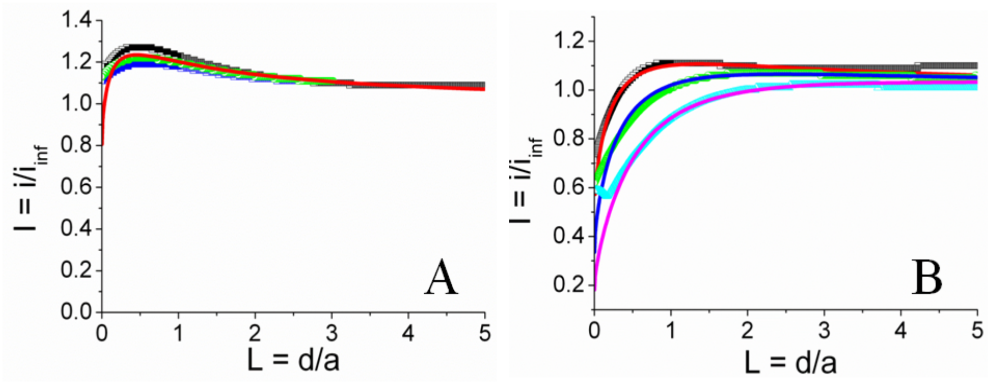


Fig. S7 SECM approach curves recorded at different spots of a Si substrate modified by a POM A) monolayer, B) bilayer with a 25 µm radius Pt microelectrode in a solution of DMF containing 0,1 M NBu$_4$BF$_4$ and 4 mM

3NX. Lines are the theoretical curves using an electrode with Rg =8. (A) $\kappa = 1$ (red line). (B) 1st approach curve $\kappa = 0.6$ (red line), 2nd approach curve $\kappa = 0.4$ (blue line), 3rd Approach curve $\kappa = 0.2$ (pink line).

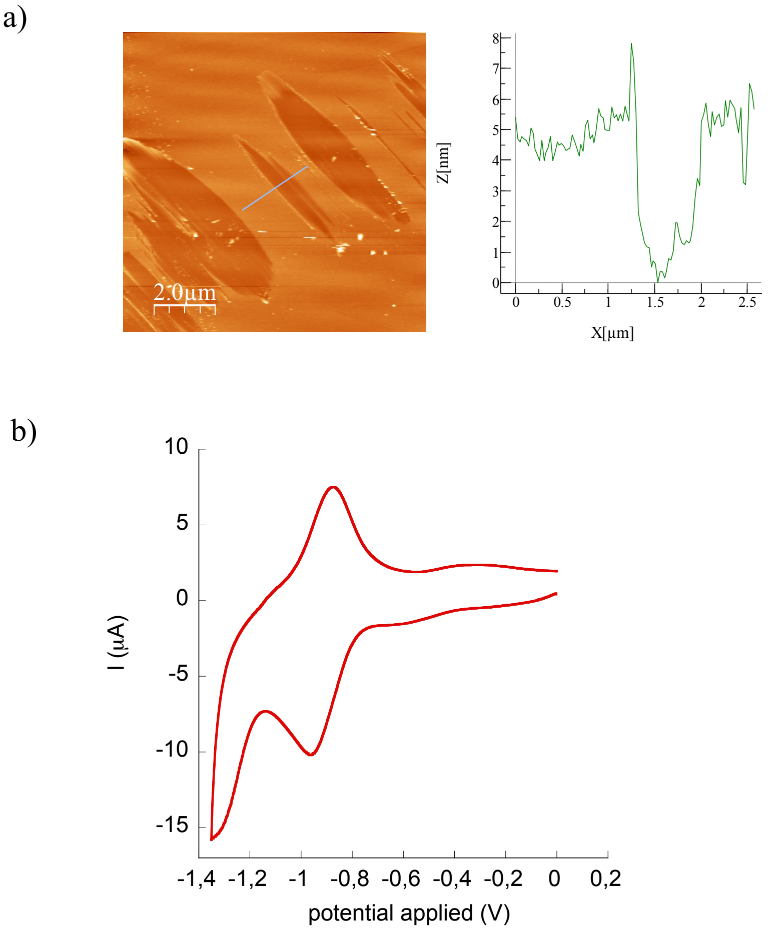


Fig. S8 Characterization of the grafted POM bilayer: a) AFM image and height profile through a chance pliers scratch. A 5.5 nm thickness is measured for the POM film, which corroborates the ellipsometry results. On the homogeneous parts, the RMS roughness is equal to 1.02 nm. b) CV recorded on the bilayer modified silicon electrode, the immersed surface of which is 0.42 cm^2. The surface density calculated from the integration of the cathodic peak is 2.4×10^{-10} $mol.cm^{-2}$ (1.8×10^{-10} $mol.cm^{-2}$ is expected for a bilayer).

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