Charge transport through redox active [H₇P₈W₄₈O₁₈₄]³³⁻ polyoxometalate self-assembled onto gold surfaces and gold nanodots.

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SUPPORTING INFORMATION

1. Formation of POM aggregates in the absence of PBS rinsing.









Figure S1. $2x2 \ \mu m$ and $1x1 \ \mu m$ AFM images and height profiles of a slightly rinsed AOT modified gold substrate (without PBS treatment) immersed in a 1 mM solution of H₃[PW₁₂O₄₀] in water. The POMs tend to cling to the physisorbed thiol molecules to form bigger aggregates (around 2.5 nm according to the line profiles recorded on the aggregates).

2. POM incubation

The samples were prepared by incubation of the AOT functionalized gold substrate in a 1 mM POM solution for one hour. We have varied the incubation time from 20 mn to 1h and 24h without observing any significant modification of the layer thickness as follows by ellipsometry. Regarding the POM solution concentration, we have started with 1mM which is the concentration often used. As the 0.8 nm increase of the thickness was slightly lower than expected (POM thickness of about 1.0 nm) we did not try to lower the POM solution concentration but rather we tried to increase it. Unfortunately, we were limited by the low solubility of the POM and longer immersion times (until 24 h) led to exactly the same layer features and significantly more concentrated solutions were not possible to obtain because of the low solubility of the K₂₈Li₅[H₇P₈W₄₈O₁₈₄] in water, even at higher LiCl concentrations.

3. Nanodots

Figure S2 shows the scanning electron microscope images of the nanodot array after the fabrication. We clearly observed a large and regular array of 10 nm in diameter nanodots separated by 100 nm. The fact that only a fraction (around 3 %) of the junctions are electrically active (bright spots in figure 5-a in the main text) may have several origins: nanodots removed during the chemical treatments or removed during the C-AFM measurements (if not well embedded in the Si substrate). We can discard the removal during the C-AFM measurements since we have not observed a significant variation of the number of active NMJs during successive scanning of the samples to measure the current at several voltages as shown in the current histograms (see below figure S3). It is likely that the nanodots were not well embedded onto the substrate for the present case and were removed during the grafting process in solution.



Figure S2. Scanning electron microscope images of the nanodots arrays at two magnifications.



3. Current histograms at different voltages measured on NMJs.

Figure S3. Histograms of the currents measured on NMJs at several voltages (as indicated in the x-axis legend). The black lines are fit with a log-normal distribution. Mean values and standard deviations are given in the table S1.

Applied Voltage (V)	< log l > (log A)	log σ
-0.4	-7.05	0.66
-0.3	-7.41	0.74
-0.2	-7.78	0.64
-0.1	-8.20	0.6
0	-9.59	0.72
0.1	-8.35	1.2
0.2	-7.46	0.90
0.3	-7.29	1.50

Table S1. Mean values and standard deviations of the log-normal distributions fitted onthe histograms of the measured currents shown in Fig. S2.

5. I-V curves adjustment with the Simmons model.

The expression of the tunnel current through a potential barrier is given by Simmons:¹

$$I(V) = S \frac{e}{4\pi h d^2} \left[\left(2\Phi_T - eV \right) \exp\left(-\frac{4\pi d\sqrt{m(2\Phi_T - eV)}}{h} \right) - \left(2\Phi_T + eV \right) \exp\left(-\frac{4\pi d\sqrt{m(2\Phi_T + eV)}}{h} \right) \right]$$
(S1)

with e the electron charge, h the Planck's constant, d the thickness of the tunneling barrier, Φ_T the energy barrier height, V the voltage applied across the junction, m the effective mass of the electron, I the current and S the electrical contact surface area (smaller than the geometrical contact area, due to defects in the SAM and on the substrate, e.g. roughness, grain boundaries,...).²⁻³ The electron effective mass m is $m = m_r m_0$ with m_0 the mass of the electron and m_r the reduced mass.

Adjustments of the measured I-V curves are systematically done for the positive and negative bias. The parameter d corresponding to the total thickness of the monolayer determined by ellipsometry (1.3 nm, see main text) is fixed and the three other parameters (Φ_T , m_r and S) are the fitting parameters.

Figure S4 gives 3 examples of the fits for SAMs on ^{TS}Au surfaces. The histograms for Φ_T , m_r and S are given in Figs. 6 (main text), S5 and S6, respectively. The average S value corresponds to a C-AFM tip electrical contact with a diameter of about 0.45 nm. Albeit the real value of the C-AFM tip contact area is difficult to estimate (it depends on the loading force, Young modulus of the SAM)⁴ this value seems reasonable considering that the tip has a radius of 20 nm and the low loading force (6nN).

6. Transition voltage spectroscopy (TVS).

The I–V curves are analyzed by the TVS method.⁵⁻⁷ In brief, the I– V data are plotted as Ln(I/V²) vs. 1/V. A minimum in this curve corresponds to a transition from a direct tunneling electron transport through the molecules to a resonant tunneling via a frontier molecular orbital (LUMO or HOMO). The energy position ϵ of the orbital involved in the transport mechanism with respect to the Fermi energy of the metal electrode is given by :

$$\varepsilon = 2 \frac{e |V_{T+}V_{T-}|}{\sqrt{V_{T+}^2 + 10 |V_{T+}V_{T-}| / 3 + V_{T-}^2}}$$
(S2)

with e the electron charge, V_{T+} and V_{T-} the voltage of the minima of the TVS plot at positive and negative voltages, respectively.⁸ Eq. S2 reduces to:

$$\boldsymbol{\varepsilon} = 0.86 \text{ eV}_{\mathrm{T}} \tag{S3}$$

when the I-V curves are symmetric with respect of the applied voltages (our case here) and $V_{T+}{=}V_{T-}$

Figure S4 shows 3 examples of TVS plots (on the same IV curves fitted with the Simmons equation). The corresponding histograms of ϵ are given in Fig. 6 (main text).

7. Molecular single energy level model.

A simple analytical model to describe electron transport through a molecular junction is the single energy level model.⁹⁻¹³ This model is based on the following assumptions: (i) the transport is phase coherent (tunneling mechanism),

(ii) the current is dominated by a single energy level, ε_0 , of the molecule (HOMO or LUMO) in the voltage range considered to fit the experimental I-V curves, and (iii) the voltage drops exclusively over the contacts which are described by the coupling constants g_1 and g_2 .

$$I(V) = N \frac{8e}{h} \frac{g_1 g_2}{g_1 + g_2} \left[\arctan\left(\frac{2\varepsilon + eV \frac{g_1 - g_2}{g_1 + g_2} + eV}{2(g_1 + g_2)}\right) - \arctan\left(\frac{2\varepsilon + eV \frac{g_1 - g_2}{g_1 + g_2} - eV}{2(g_1 + g_2)}\right) \right]$$
(S4)

with h the Planck's constant and N the number of molecules in the junctions. The fitting parameters are ε , g_1 and g_2 . Since the exact number of molecules in the junction is not known (albeit weak, e.g. <25 in the NMJs, see main text) we fixed N=1, but we have observed that the exact value of N does not have a drastic influence on ε , only on the coupling parameters g_1 et g_2 . Albeit the obtained values seem reasonable (in the range 0.1 - few tens of meV), it is known that these fitting parameters are also very sensitive to the I-V curve "quality" (e.g. noise, sudden jumps in the IV,...)¹³ while the value of ε is not, consequently we have not discussed these values in more detail.

Figure S4 shows 3 examples of these fits on the same IVs (SAMs on ^{TS}Au) also analyzed with the Simmons equation and the TVS method. The corresponding histogram of ε_0 is shown in Fig. 6 (main text).



Figure S4. Typical examples of the fit (Simmons and molecular models) of 3 different I-V curves measured by C-AFM on the SAM on ^{TS}Au substrates (left), and corresponding plot of the TVS method (right).



Figure S5. Histograms of the effective reduced mass from Simmons model fitted on I-V curves measured for POM SAMs on ^{TS}Au electrodes. Black curve: Gaussian fit.



Figure S6. Histograms of the electrical contact area from Simmons model fitted on I-V curves measured for POM SAMs on ^{TS}Au electrodes. Black curve: Gaussian fit.

8. Application of the Simmons and molecular models on I-V measured on NMJs.

Figure S7 shows a typical example of the Simmons model and molecular model fitted on the same I-V curve measured on NMJ. For the Simmons model, the thickness was fixed at 1.3 nm as for SAM on ^{TS}Au since it is not easy to measure the POM thickness on the Au nanodots.¹⁴



Figure S7. I-V curve (same data as in Fig. 5-c, mean current vs. voltages from histograms in Fig. S2) measured on POM NMJ, and fits with Simmons equation and molecular model.

9. Characterization of [H₇P₈W₄₈O₁₈₄]³³⁻



Figure S8. Cyclic voltammogram of $K_{28}Li_5[H_7P_8W_{48}O_{184}]$ (10⁻⁴ M) in CH₃COOH/CH₃COOLi 0.1M in water at a scan rate 10 mV.s⁻¹. Working electrode = glassy carbon, reference = calomel saturated electrode (SCE), counter-electrode = platinum wire. It is compliant with those published in by Keita et al.¹⁵







Figure S10. ³¹P (121 MHz) NMR spectrum of $K_{28}Li_5[H_7P_8W_{48}O_{184}]$ in LiCl 1M / D_2O

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