

## SUPPORTING INFORMATION

### **Electrochemical scanning tunneling spectroscopy of redox active molecules bound by Au-C bonds.**

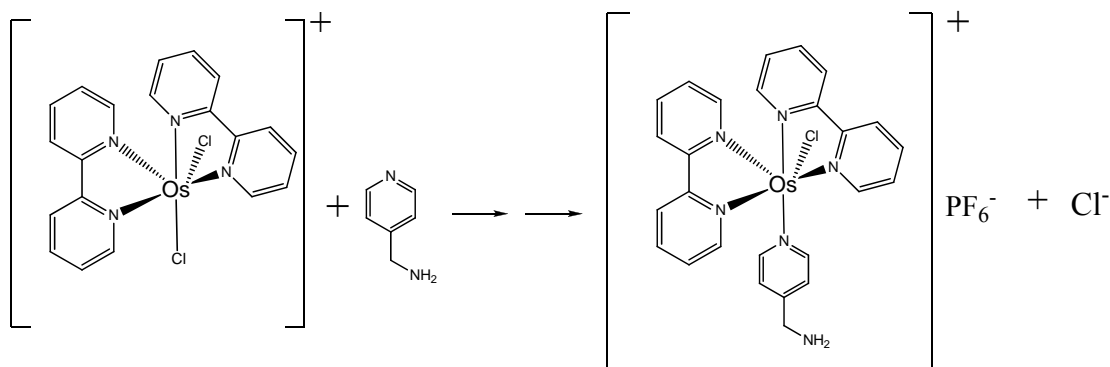
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### Preparation of the amine (-NH<sub>2</sub>) derivatized osmium complex [Os(bpy)<sub>2</sub>Cl(py-CH<sub>2</sub>-NH<sub>2</sub>)]PF<sub>6</sub>

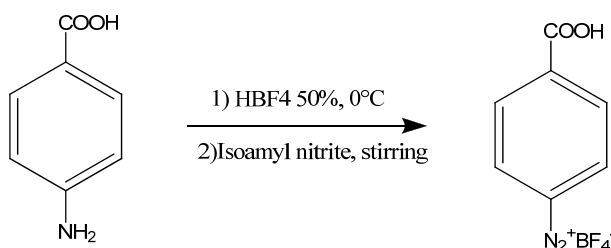
4-aminomethylpyridine (19 mg, 0.178 mmol) and [Os(bpy)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (102 mg, 0.178 mmol) were dissolved in ethylene glycol (2 mL) a Schlenk round-bottom flask. The solution was degassed twice with argon and refluxed for 3 hours under argon. After cooling, a NH<sub>4</sub>PF<sub>6</sub>/H<sub>2</sub>O solution was added (1 mL), the mixture was stirred for 30 minutes and filtrate through a polyamide membrane (Ø 0.45 µm). The precipitate was washed with water and vacuum dried.



### Preparation of the 4-carboxybenzene diazonium tetrafluoroborate

4-aminobenzoic acid (0.4 g, 2.91 mmol) was dissolved in ethanol (1 mL) and aqueous tetrafluoroboric acid solution (50% solution: 0.65 mL, 3.7 mmol); the mixture was then cooled to 0°C. *Isoamyl nitrite* (0.6 mL, 4.5 mmol) was added dropwise to the mixture and stirring was continued for 30 minutes. Dilution of the mixture with diethyl ether (30 mL) led to the precipitation of 4-carboxylbenzene diazonium tetrafluoroborate as light yellow crystals.

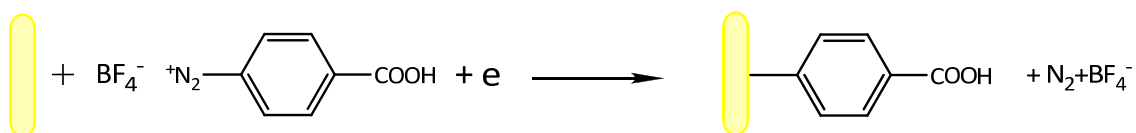
$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3494, 3424, 3093, 3072, 2933, 2651, 2551, 2293, 1725, 1409, 1373, 1311, 1203, 1066, 806.



### Derivatization of gold surfaces

Gold on glass films (Arrandee®) were used as substrates. These were flame-annealed at approximately 800-1000°C with a Bunsen burner immediately prior to use.

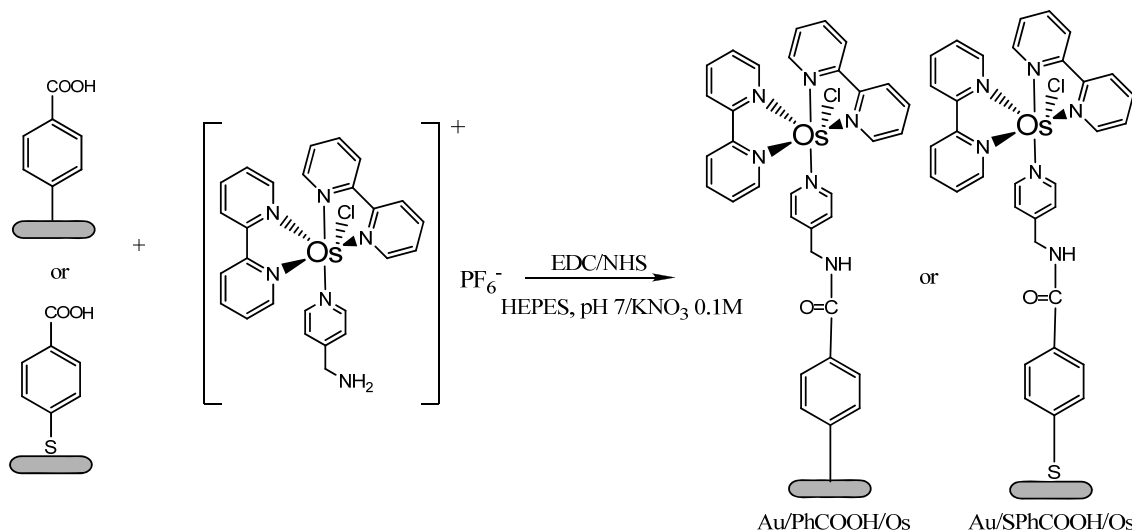
*Electroreduction of the diazonium salt:* A glass electrochemical cell with a Pt counter electrode and a saturated calomel reference electrode (SCE) was employed, and electrode potentials are reported with respect to this reference scale. Benzoic acid was attached to gold surfaces by electrochemical reduction of the corresponding diazonium salt using chronoamperometry (0.32 V, 5 minutes in 5mM of the 4-carboxybenzene diazonium tetrafluoroborate with 0.1M tetrabutylammonium tetrafluoroborate/acetonitrile).



*Derivatization with 4-mercaptobenzoic acid:* The gold substrates were immersed in a 1mM ethanolic solution of 4-mercaptobenzoic acid for 1 hour.

### Post-functionalization of gold substrates<sup>1</sup>

The surfaces modified with benzoic and 4-mercaptobenzoic acid were incubated in 40 mM 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC)/ 10 mM N-hydroxysuccinimide (NHS) solution for 1 hour and then they were immersed in 0.25 mM  $[\text{Os}(\text{bpy})_2\text{Cl}(\text{py-CH}_2\text{NH}_2)]^+\text{PF}_6^-$ /0.05M HEPES buffer (N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid) pH=7.3, I= 0.1 M KNO<sub>3</sub> for 24 hours. This resulted in an amide bond being formed between the amino group in the complex and the acid group on the surface. We will refer to these systems as Au(111)/SPhCOOH/Os and Au(111)/PhCOOH/Os.



### Electrochemical STM spectroscopy

A Pico2000 system (Molecular Imaging) STM using the PicoScan 4.19 software was employed throughout this study. Gold STM tips were prepared by etching in an HCl/ethanol (1:1) solution. The custom made three-electrode cell was equipped with Au wires as counter and reference electrodes, the later calibrated against SCE electrode. KClO<sub>4</sub> (0.1M) was employed as the electrolyte.

Electrochemical STM spectroscopy measurements were performed in the following manner: with the osmium complex tethered to the surface, the STM tip was approached to a set-point current of 1 nA and the bias potential between tip and substrate, ( $E_{bias} = E_T - E_S$ ), was kept constant. When the tip was fully retracted from the surface, a background electrochemical current of 0.01 nA was observed. The initial substrate electrochemical potential ( $E_{S,i}$ ) was set suitably away from the equilibrium redox potential of the complex ( $E^o$ ). At this point the feedback loop was switched off, and the substrate potential ( $E_S$ ) scanned at 50 mVs<sup>-1</sup> by 0.45 V, wide enough to pass  $E^o$  with both sample potential ( $E_S$ ) and tip potential ( $E_T$ ), while monitoring tunnelling current ( $i_T$ ). Figure 2 in the manuscript depicts typical  $i_T$  vs. ( $E_S - E^o$ ) curves for the Os complex tethered to the Au surface by Au-C (Fig.2a) and Au-S bonds (Fig.2b), respectively, both recorded at a bias potential  $E_{bias} = +0.05$  V. The curves in the positive going potential scan exhibit  $i_T$  maxima at  $E_{max} = 0.04$  V and 0.1 V for the Au-C and Au-S bonded adsorbates, respectively. For comparison, the cyclic voltammograms of the substrate Au(111) chemically modified by Au-C and Au-S osmium complex is shown in the respective figures, showing  $E_{max}$  close to the equilibrium redox potential of the complex. Notice that approximately the same initial  $i_T$  is reached at ( $E_S - E^o$ ) = 0.2 V indicating close to constant tip-sample height during the full  $E_S$  sweep.

### Coverage of the surfaces with the osmium complexes

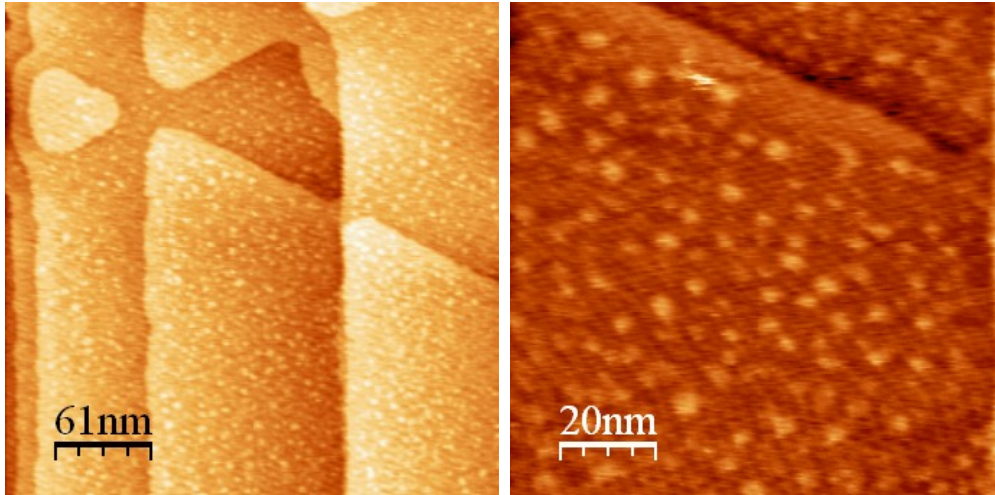
The equilibrium redox potentials of the surface bound Os-complexes ( $E^\circ$ ) were estimated from cyclic voltammetry by taking the mid-point between anodic and cathodic waves for the surface redox wave. The corresponding values measured for Au/PhCOOH/Os and Au/SPhCOOH/Os are 0.23-0.26 V vs. SCE. In Figure 2 of the manuscript the substrate potential is conveniently shown with respect to the equilibrium redox potentials; i.e.  $i_T$  is plotted versus ( $E_S - E^\circ$ ).

The redox charge determined from cyclic voltammograms of the immobilized Os complexes was 3 and 11  $\mu\text{C cm}^{-2}$  respectively for Au-S and Au-C tethered Os complex. In the first case, the surface coverage is lower than a maximum coverage of 13  $\mu\text{C cm}^{-2}$  (138  $\text{pmol cm}^{-2}$ ) for a close packed structure on the basis of the molecular projection of 120  $\text{\AA}^2$  for an upright standing molecule.

**Table S 1 Electrochemical characterization of Au/PhCOOH/Os and Au/SPhCOOH/Os**

	$E_{1/2}$ vs. SCE / V	Q / $\mu\text{C cm}^{-2}$	% of monolayer
<b>Au/PhCOOH/Os</b>	0.3	11	87
<b>Au/SPhCOOH/Os</b>	0.27	3	24

Even though both these systems contain the Os(II)/Os(III) couple, they show different  $E^\circ$ . This is because the surroundings of the osmium center in each case are not identical. The attachment of the osmium complex to the surface implies the formation of an amide bond between the amino group of the complex and the acid groups on the surface. However, not all of the acid groups react with the complex, with the degree of surface functionalisation being different for the two systems as is apparent from Table 1. For instance, a lower surface coverage of osmium centers leads to less electrostatic interactions between them and this spatial separation means that oxidation of the osmium in the layer is more facile, since it is then easier to add positive charge to the surface. So, in the case of Au-C linked monolayers, the  $E^\circ$  value is more positive since the surface coverage of the complex is larger making it more difficult to oxidize the osmium.



**Figure S 1:** STM images of Au/SPhCOOH/Os under mesitylene.

Typical STM images of the osmium complex covalently attached to 4-mercaptobenzoic acid SAM onto flame annealed Au. These STM experiments were recorded under mesitylene with a setpoint of 1 nA and  $E_{\text{bias}} = 1$  V. Gold step and terrace structures are observed typical of the Au (111) substrate. Overlying this structure is a patchwork of bright spots. Line cross sections show heights of  $\approx 0.8$  nm which would correspond to the height of the osmium complex.

#### Calculation of tunneling current for different values of $\xi$ and $\gamma$

In the communication we have employed  $\xi = 1$  and  $\gamma = 1$  following the work Albrecht *et. al.* which used related Os complexes<sup>2</sup>. However, recent work has shown that these parameters should be considered within theoretical frameworks as dependent parameters<sup>3</sup>. For example, by considering this theoretical dependence of  $\xi$  and  $\gamma$ , a value of  $\gamma = 0.5$  and  $z/L = 0.5$  yields  $\xi = 0$ . Equations describing  $\gamma(z, L_d)$  and  $\xi(z)$  and their interdependence are:

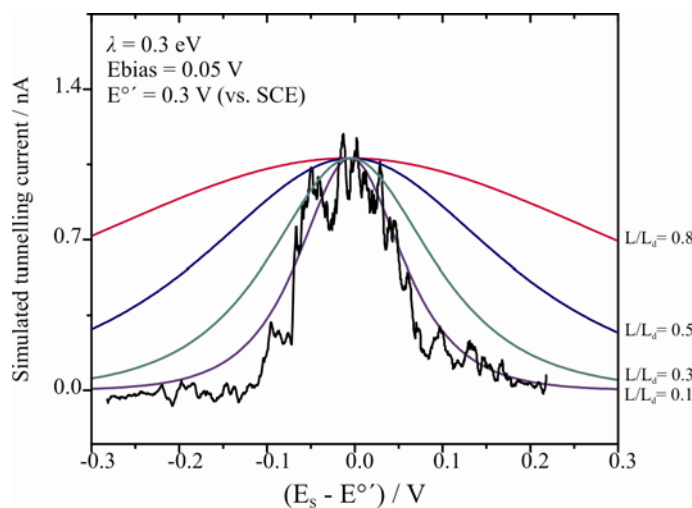
$$\gamma(z; L_d) = \frac{\exp(z / L_d) - \exp(-z / L_d)}{\exp(L / L_d) - \exp(-L / L_d)} \quad (1)$$

$$\xi(z) = 1 - \gamma(L - z, L_d) - \gamma(z, L_d); \quad \gamma(z) = \gamma(z, L_d) \quad (2)$$

Where  $z$  is the position of the redox center in the tunneling gap,  $L_d$  is the Debye length and  $L$  is the width of the tunneling gap (between tip and substrate electrodes). With these equations we calculated the dependence of the tunneling current (normalized to the maximum fitted value in Figure 2 of the communication) on the overpotential for

$\lambda = 0.3$  eV,  $E_{bias} = 0.05$  V and  $E^{\circ'} = 0.3$  V (see Table S 2). Figure S 2 shows the results for different ratios of  $L/L_d$  and  $z/L = 0.5$ ; the closest curve to the experimental data results from  $\xi = 0.99$  and  $\gamma = 0.01$ . However, these values are unrealistic since one expects  $\gamma > 0.5$  because  $E_{max}$  shifts positive when  $E_{bias}$  is negative (Figure 2 of the manuscript paper).

Our scanning tunneling spectroscopy data were obtained in 0.1 M 1:1 base electrolyte, therefore  $\kappa^{-1} = 0.96$  nm. Estimating the molecule length as 1.6 nm we tried several values of  $z$  for  $L = 1.6$  nm,  $L/L_d = 1.67$  as shown in the Table S 3, but for  $\gamma > 0.5$  they give a very poor fit (see Figure S 3) while for  $\gamma = 1$  and  $\xi = 1$  the fit is much better. For this reason we have retained the fitting presented in the main manuscript with  $\xi$  and  $\gamma$  as independent parameters (both unity). Fitting of electrochemical spectroscopy responses with  $\xi$  and  $\gamma$  as dependent parameters described in the recent theoretical works needs to be addressed in future works with aptly chosen model experimental systems.



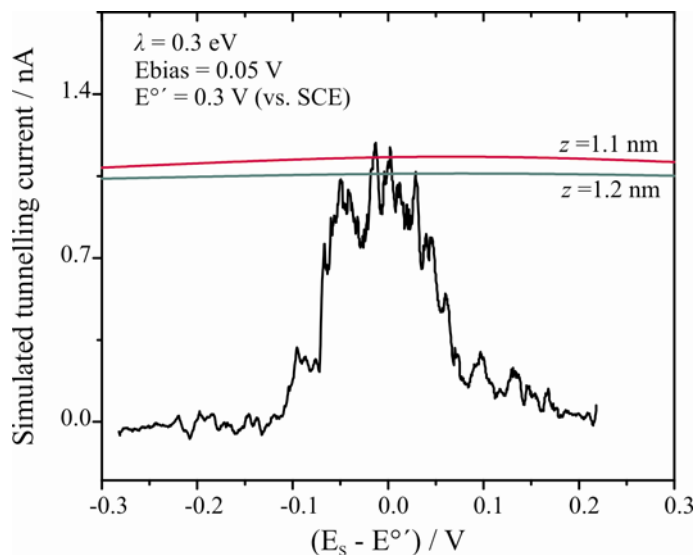
**Figure S 2:** Fitting of experimental data using equations (1) and (2) for different values of  $L/L_d$ .

**Table S 2: Different values of  $\gamma$  and  $\xi$  obtained for different  $L/L_d$  using equations (1) and (2) – see text.**

$L/L_d$	$\gamma$	$\xi$
0.05	0	1
0.1	0.01	0.99
0.3	0.18	0.64
0.5	0.32	0.35
0.8	0.42	0.17

**Table S 3: Different values of  $\gamma$  and  $\xi$  obtained with  $L_d = 0.96$  nm and different values of  $z$  (see text).**

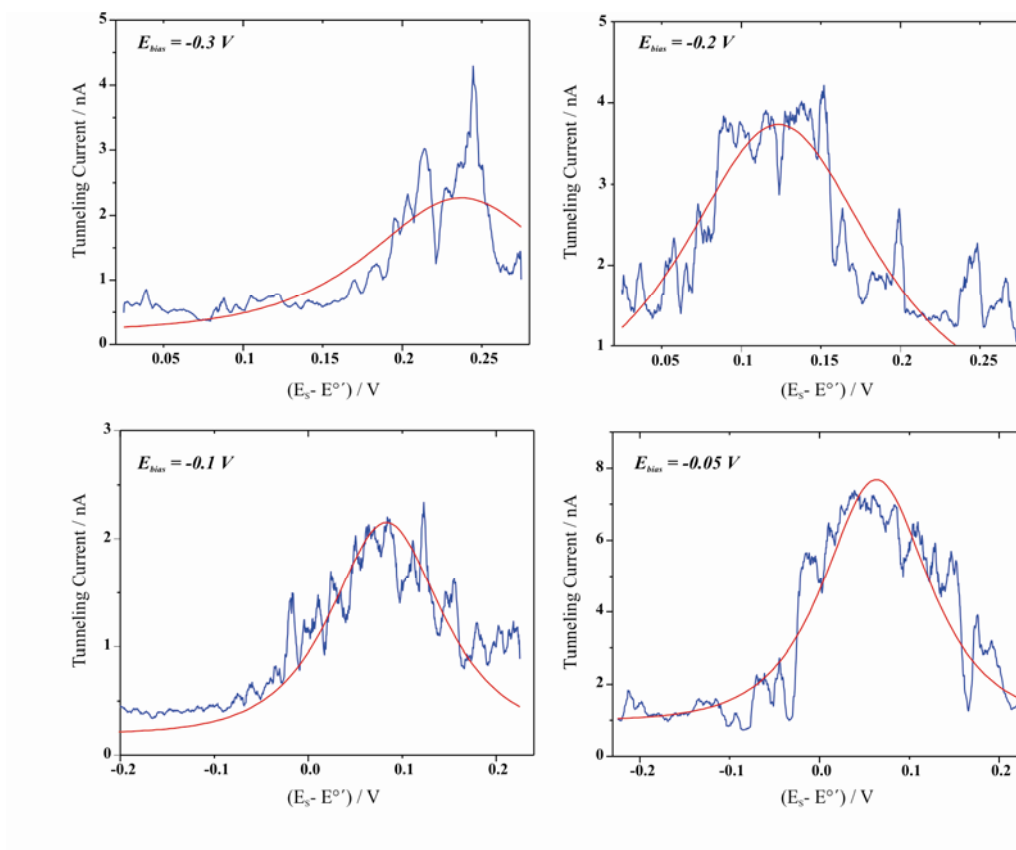
$z$	$\gamma$	$\xi$
0.2	0.08	0.11
0.7	0.31	0.22
1.1	0.55	0.23
1.2	0.63	0.2



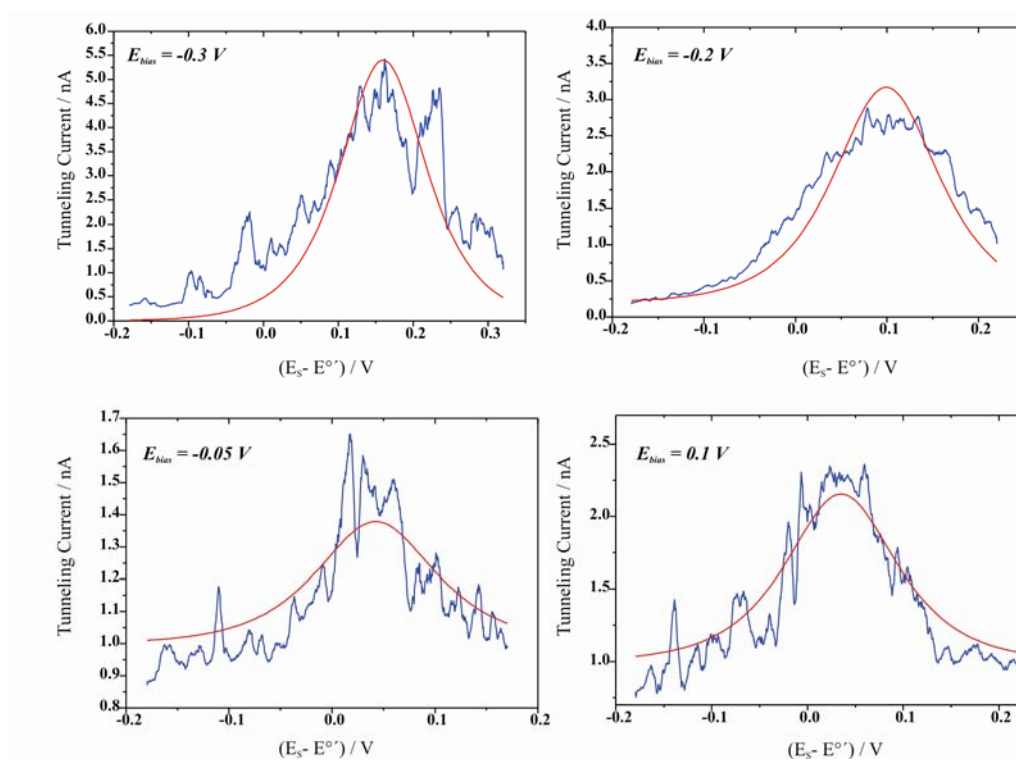
**Figure S 3** Fitting of experimental data using equations (1) and (2) for two different values of  $z$  and  $L_d = 0.96$  nm and  $L = 1.6$  nm.



## Tunneling Current vs. Sample Potential Measurements



**Figure S 4** STS curves with electrochemical control of Au/SPhCOOH/Os using  $E_{bias} = -0.3$ ,  $-0.2$ ,  $0.1$  and  $-0.05 V$ , respectively.



**Figure S 5** STS curves with electrochemical control of Au/PhCOOH/Os using  $E_{bias} = -0.3$ ,  $-0.2$ ,  $-0.05$  and  $0.1 V$ , respectively.

## References

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- (3) Kuznetsov, A. M.;Medvedev, I. G.;Ulstrup, J. *J. Chem. Phys.* 2000, *127*, 104708.