

Some Evidence for the Formation of an Azo Bond during the Electroreduction of Diazonium Salts on Au Substrates

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Molecular films obtained by electrochemical reduction of diazonium tetrafluoroborate salts [4-carboxybenzene (PhCOOH) and 4-amino-(2,3,5,6-tetrafluoro)-carboxybenzene (PhF₄COOH)] on Au substrates and post-functionalization with an osmium pyridil-bipyridine complex are studied by a combination of X-ray photoelectron (XPS) and polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS). The spectroscopic evidence suggests the formation of N=N bonds tether-

ing the complexes to Au. The surface coverage of the azo-bonded osmium complexes strongly depends on the electrode potential. The resulting tethered osmium redox centres were characterized by cyclic voltammetry and impedance spectroscopy. Similar electron transfer-rate constants were measured for both fluorinated and non fluorinated benzene-linked Os complexes.

1. Introduction

Materials surfaces can be chemically functionalized in order to achieve special chemical and physical properties which differ from the bulk material. Functional surfaces can therefore be designed to respond to changes in certain environmental conditions or to improve their performance for a given process.

Progress in this field has been driven by a large variety of applications, such as electrocatalysis,^[1–8] electrochromics, smart windows^[9,10] and displays, corrosion protection,^[11,12] superhydrophobicity, antibacterial coatings, sensors and biosensors, molecular electronics,^[13,14] and so forth.

Finally, there is a growing interest in molecular electronic devices that mimic diodes, transistors and electrical networks.^[15–19] In particular, electrode modification with redox species has opened the possibility of studying in great detail electron-transfer processes that take place between acceptor or donor molecules and the electrode surface.^[20–24]

Several strategies can be employed to modify different material surfaces with molecular mono- or multilayers.^[25] Molecular species can be covalently bonded to surfaces through spontaneous or electrochemical reduction of organic moieties containing diazonium functionalities.^[26] Electroreduction of diazonium salts has gained some prominence during recent years, since it is an easy technique to implement and it generates strong adsorbate–substrate bonds.^[27]

The accepted mechanism for this reaction has been demonstrated using a wide variety of substituted aryl diazonium salts. It involves the generation of an aryl radical with further formation of a covalent bond to a surface species. Thus, organic molecules containing diazonium functionalities have been covalently bonded to a great variety of materials,^[26,28–30] forming molecular films that are more stable than those obtained by thiol self-assembly^[31] and that could be used to study charge-transport phenomena through a carbon-substrate bond.^[32–35]

Diazonium salts yield different types of chemisorbed layers depending on the potential or charge applied during electro-

duction. When highly reductive potentials are applied, multilayers are formed on the electrode surface, whereas when the reduction is carried out at potentials close to the equilibrium one, thin layers or monolayers can be deposited.^[30,32,36,37] Multilayers result from aryl radical attack on molecules already attached to the surface with branching at 3- and 5- positions of the aromatic ring.

However, monolayers can be achieved by several strategies. For example, the charge can be regulated during deposition^[38] or the chemical potential can be controlled.^[37] Secondly, Pinson and co-workers demonstrated that hindrance to the 3- and 5-positions on phenyl ring results in monolayers,^[39] as does the use of bulky cleavable protecting groups, such as Boc^[40] or hydrazone protected benzene diazonium salts in *para* position of the phenyl ring.^[41]

On the other hand, the presence of nitrogen has been observed by X-ray photoelectron spectroscopy (XPS) in films obtained by this method and has been attributed to 1) the direct reaction of the diazonium cation with surface functional groups or to 2) the formation of an azophenyl radical after diazonium salt reduction and its direct bond to the electrode or to an aromatic ring already attached to it.^[36] Belanger was the first to claim the presence of azo groups in the surface layers.^[42] This last scenario is more likely to occur when electroreduction takes place at gold substrates. However, there has not been any direct experimental evidence confirming the formation of Au-N=N-C bonds in deposited films, but only the

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presence of azo bonds inside the films (i.e. C–N=N–C bonds) forming multilayer surface films.^[43]

Herein, we studied molecular films obtained by electroreduction of 4-amino carboxybenzene, (PhCOOH) and 4-amino-(2,3,5,6-tetrafluoro)-carboxybenzene (PhF₄COOH) diazonium tetrafluoroborate salts on gold substrates. Note that for the all-fluorine substituted diazonium salt multilayer formation is not expected even under the strongest reductive conditions. We used a combination of XPS and polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) to study the chemical nature of the different surface species formed by cyclic voltammetry as a function of the applied potential.

From electrochemical experiments, cyclic voltammetry, and electrochemical impedance spectroscopy we characterized the surface coverage and interactions of tethered molecules, while the role of electron transfer was assessed by impedance.

2. Results and Discussion

XPS measurements were performed on derivatized gold substrates obtained after electroreduction of non-substituted and F-substituted diazonium salts at different potentials. In both cases we observed signals corresponding to the C1s, O1s, N1s, and Au4f core-level photoemission,^[36] but only in the second case we also observed the F1s signal confirming the molecular modification of the gold substrate. In principle, electroreduction of the diazonium salt should result in N₂ (g) elimination, and therefore no N1s signal should be present in the XPS spectra. However, as discussed in the literature,^[43] electroreduction could result in the formation of an azophenyl radical that could form a direct bond to an adsorbed aromatic ring. Figure 1 shows the N1s level spectral regions for Au/PhCOOH (obtained at 0.3 and –0.7 V) and for Au/PhF₄COOH (obtained at 0, –0.2 and –0.7 V). Both systems present an N1s peak at

400 eV that becomes more intense as the applied potential during the reduction becomes more negative. Similar findings at 400 eV have been reported before and been ascribed to the formation of azo bonds.^[31,36,42–46] Trapping acetonitrile in a compact surface layer would also result in an excess N signal in the XPS experiment, however, the N1s signal for acetonitrile has been reported at 397–398 eV^[47] and the electrodes in the present study have been thoroughly rinsed with distilled water and exposed to ultrahigh vacuum (UHV) in the XPS chamber. Furthermore, IR spectroscopy failed to detect the characteristic mode for acetonitrile at 2270 cm^{–1}.

In order to determine the nature of the nitrogen species detected by XPS, PM-IRRAS analysis was performed in all cases and the results are shown in Figure 2. It shows the spectra obtained after reducing 4-carboxybenzene diazonium tetrafluoroborate (i.e. Au/PhCOOH) at 0.3 V and –0.7 V for 5 min on Au substrates.

The PM-IRRAS spectra obtained by electroreduction of 4-(2,3,5,6-tetrafluoro)-carboxybenzene diazonium tetrafluoroborate at three different potentials (0, –0.2 and –0.7 V), that is Au/PhF₄COOH, showed the same features, therefore only the spectrum obtained after reduction at –0.2 V is shown in Figure 2.

All spectra in Figure 2 show a broad band centered at ~1720 cm^{–1} that can be attributed to the stretching mode of the carboxylic acid group (ν_a C=O). The bands at ~1483 and ~1550 cm^{–1} can be attributed to the symmetric and asymmetric stretching modes of carboxylate, ν_{sCO_2} and ν_{aCO_2} , respectively. In addition, the bands corresponding to collective ring modes are also observed at ~1605 cm^{–1} (ν_q Ph, quadrant stretching mode) and at ~1409 cm^{–1} (ν_{sc} Ph, aromatic ring semicircular stretching mode). These bands shift slightly in the spectra of the fluorinated compound. Additionally, all three PM-IRRAS spectra exhibit a band at ~1380 cm^{–1} that can be assigned to an azo-group stretching mode ($\nu_{N=N}$). Usually N=N stretching modes appear at higher frequencies, but shift to lower wave numbers upon conjugation. In fact, *trans* azobenzenes are reported to have a N=N stretch frequency at 1463–1380 cm^{–1}^[48] and in the case of *p*-phenyl azobenzoic acid (a compound with a conjugation similar to our system) in the solid state the peak at 1380 cm^{–1} can be assigned to the N=N stretching mode.^[48] Magnussen et al.^[49] have reported 1377, 1403, and 1439 cm^{–1} for *trans* N=N vibrations in azobenzene adlayers by Raman spectroscopy. In addition to these bands, the Au/PhF₄COOH system also shows bands at 1273 cm^{–1} and 1203 cm^{–1} that correspond to the stretching modes associated with the C–F bonds (ν_{C-F}).^[50,51] These signals are summarized in Table 1. The measurements show that the molecules retain their chemical identity and confirm the formation of azo bonds during diazonium salt reduction on gold substrates.

We noticed a slight difference in peak position for both fluorinated molecules (i.e. 1377 cm^{–1} in Figures 2a and b) with respect to the non-fluorinated one (i.e. 1392 cm^{–1} in Figure 2c), which may be an in-

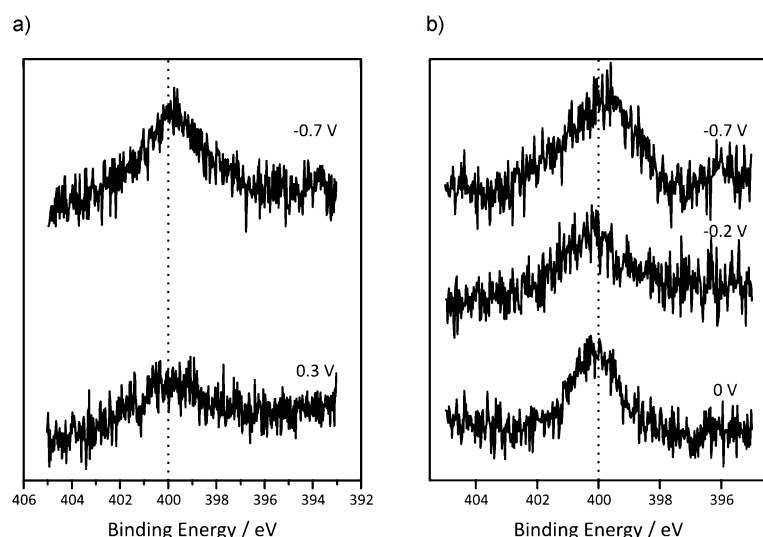


Figure 1. N1s level XPS spectra of gold substrates derivatized by electroreduction of a) 4-carboxybenzene-diazonium tetrafluoroborate and b) 4-amino-(2,3,5,6-tetrafluoro)-carboxybenzene diazonium tetrafluoroborate. The applied potentials during reduction are indicated for each spectrum.

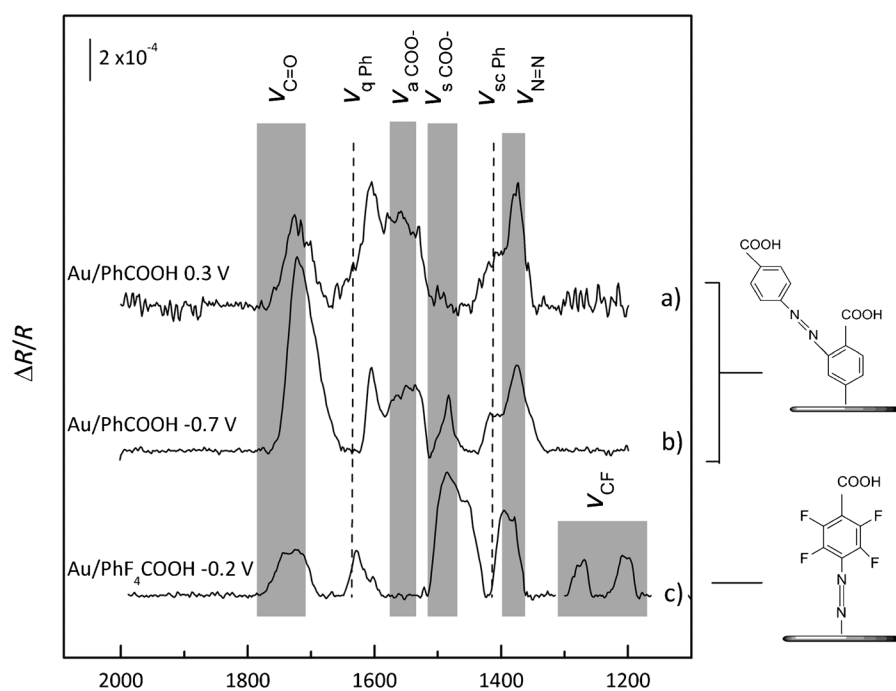


Figure 2. PM-IRRAS spectra of organic films deposited on gold substrates from 4-carboxybenzenediazonium tetrafluoroborate electroreduction at a) 0.3 V and b) -0.7 V. c) PM-IRRAS spectrum of a gold substrate derivatized with 2,3,5,6-tetra-fluorobenzoic acid by reduction at -0.2 V.

Au/PhCOOH (0.3 V)	Au/PhCOO (-0.7 V)	Au/PhF ₄ COOH (0, -0.2 and -0.7 V)	Assignment
1720	1720	1720	$\nu_{\text{a C=O}}$
1605	1605	1630	$\nu_{\text{q Ph}}$
1550	1550	–	$\nu_{\text{a COO}^-}$
–	1483	1485	$\nu_{\text{s COO}^-}$
1409	1409	1396	$\nu_{\text{sc Ph}}$
1377	1377	1392	$\nu_{\text{N=N}}$
–	–	1273-1203	ν_{CF}

dication for different N=N bonds as expected for branching and terminal bonds to Au.

In Figure 2, the broad shape of the band corresponding to the $\nu_{\text{a C=O}}$ can be ascribed to a partial dimer formation of the carboxylic groups, while others remain as monomers.^[40] This has been observed both for aliphatic and aromatic carboxylic acids chemisorbed on surfaces and may be due to the presence of dimer structures found in lateral hydrogen-bonded acid groups in ordered monolayers,^[52] or intra-monolayer hydrogen bonding with the carboxylic groups facing toward each other.^[53] Symmetric and asymmetric COO^- broad bands are observed as well, which can be ascribed to different environments for this functional group.

As stated before, Figure 2 shows that all spectra exhibit essentially the same bands although a difference in relative intensities can be observed among them. Interestingly, a very important feature in the spectra is the absence of the asym-

metric stretching peak of the carboxylate group ($\sim 1550 \text{ cm}^{-1}$) in the Au/PhF₄COOH system (Figure 2c). According to the surface selection rules^[54] the absence of a peak indicates that the dipole moment of that particular vibration is parallel to the surface. In this case, it means that the carboxylate group has a preferential orientation on the surface and that the C–O bonds are tilted 30° with respect to the normal to the surface,^[54,55] since the estimated direction of the transition dipole moment for the $\nu_{\text{a COO}^-}$ is perpendicular to the C–COO[–] bond and in the O–C–O plane. This implies that a highly organized monolayer is formed. On the other hand, for the Au/PhCOOH systems (Figures 2a–b), the peak corresponding to $\nu_{\text{a COO}^-}$ is present indicating ramification and therefore multilayer formation. In line with this, for the spectrum shown in Fig-

ure 2c (Au/PhF₄COOH), a very large band is observed for $\nu_{\text{s COO}^-}$. This particular vibration has a dipole moment that would be perpendicular to the surface in the proposed ordered monolayer, and consequently, according to the surface selection rules,^[54] its relative intensity would increase. Interestingly, this peak is not observed in the spectrum of Au/PhCOOH obtained under mild reducing conditions (Figure 2a), probably due to its low extinction coefficient,^[51] while it can be observed in Au/PhCOOH obtained under higher reducing potentials (Figure 2b). This is probably because branching is enhanced and more product is formed on the surface.

Briefly, from the comparison of these spectra it can be concluded that Au/PhF₄COOH forms ordered monolayers, while ramification is always observed in the Au/PhCOOH system, and the extent of ramification depends on the conditions of the diazonium salt reduction.

Furthermore, it must be borne in mind that in this system (Au/PhF₄COOH) the presence of the fluorine substituents on the ring prevents radical attack of any kind from taking place. Therefore, the presence of nitrogen in these systems may be due to the binding of the organic molecule to the metallic substrate through a Au–N=N–C bond forming an azo carboxybenzene-modified electrode surface. In conclusion, combined XPS and PM-IRRAS analysis confirm that N=N bonds are formed during the diazonium salt reduction and that this reaction is favoured when higher reductive potentials are applied.

Although the presence of N atoms in films formed through the electroreduction of diazonium salts has already been observed by XPS by other authors,^[36,43,46,56,57] this study provides the first direct experimental FTIR evidence of the formation of

the azo bond between the organic moiety and the metal substrate, that is Au-N=N-C bonds.

The F 1s core-level spectral region was measured after the reduction of the F-substituted diazonium salt at 0, -0.2 and -0.7 V (Figure 3 a). In all three cases we observed a peak cen-

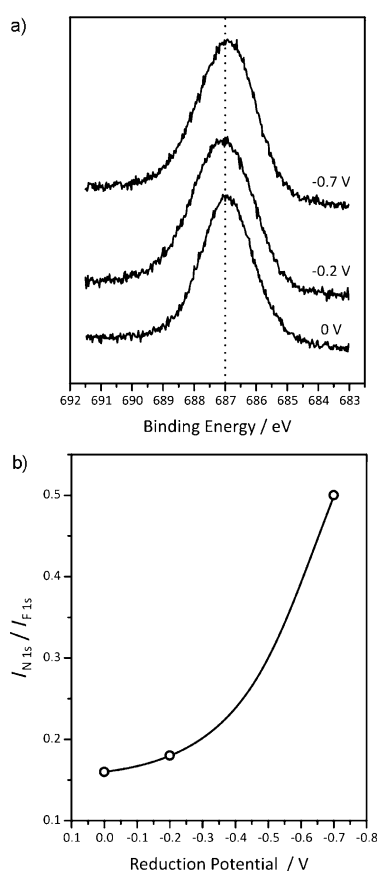


Figure 3. a) F1s level XPS spectra of gold substrates derivatized by electro-reduction of 4-amino-(2,3,5,6-tetrafluoro)-carboxybenzenediazonium tetrafluoro-borate at 0, -0.2 and -0.7 V, respectively. b) Intensity ratio of F 1s and N 1s signals observed in the XPS spectra of these samples. The line is a guide to the eye.

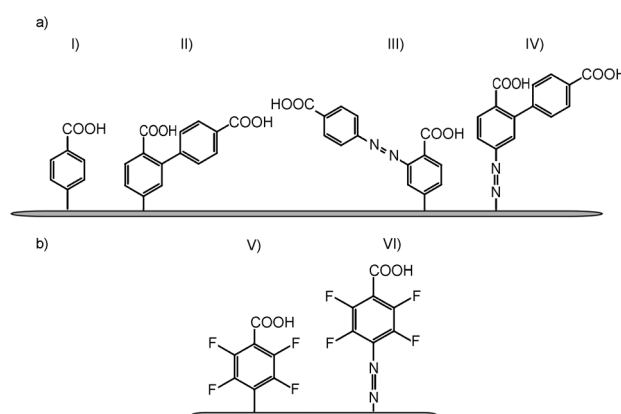
tered at 687 eV indicating the presence of fluorine on the Au surface. In particular, it was possible to estimate the molecular surface coverage from the XPS spectra taking into account the intensity of this signal. The surface coverage was estimated to be $\approx 4.5 \times 10^{-10} \text{ mol cm}^{-2}$ for all reduction potentials. This value is in agreement with the one expected for a compact monolayer of 2,3,5,6-tetrafluorobenzoic acid ($\approx 5 \times 10^{-10} \text{ mol cm}^{-2}$). Therefore, using this diazonium salt, in which all aromatic ring positions are blocked by fluorine substituents, it is possible to deposit molecular monolayers by electroreduction at highly negative potentials.

Interestingly, the amount of XPS N1s present in these monolayers changes with the diazonium salt reduction potential. This is shown in Figure 3b, where the intensity ratio of N1s to F1s peaks is plotted as a function of the electrode potential. From this Figure it can be seen that the formation of N=N bonds increases sharply for highly reductive conditions, indi-

cating an increment in the fraction of molecules tethered to the surface by an N=N-Au bond. If all molecules were attached to the surface through a N=N group, then the ratio of signal intensities N1s/F1s in an XPS spectrum would be 0.5.

Figure 3b shows that this value is reached under the most reducing conditions, whereas it remains close to 0.1–0.2 for the other two samples. Potentials lower than -0.25 V result in 35% of the PhF₄COOH molecules bound to the surface through an azo bond, whereas highly reductive potentials (-0.7 V) result in a compact monolayer of molecules bound in 100% of the cases through an azo bond. This would indicate that the applied potential during the diazonium salt reduction does not only determine the nature of the layer deposited (monolayer vs. multilayer when the molecular structure allows it to take place), but also determines the type of bond between molecules and the surface.

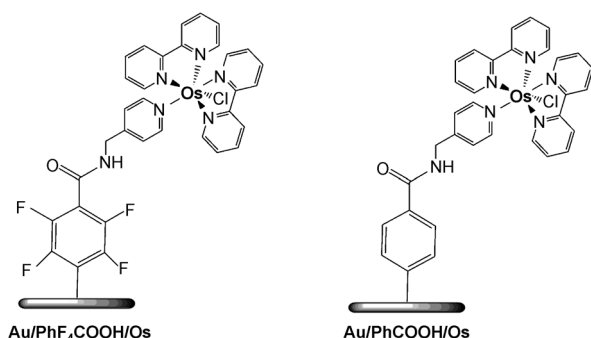
From the preceding analysis different species can be expected to be found in these films for each of the diazonium salts employed in this work, depending primarily on the potential applied during electroreduction and the chemical nature of the substituent present in the benzene ring. Scheme 1 summarizes the surface chemistry described. In the case of the Au/PhCOOH system we always observed some ramification even



Scheme 1. Possible structures formed by the deposition of a) benzoic acid (I–IV) and b) 2,3,5,6-tetrafluorobenzoic acid (V and VI) on gold electrodes from the electro-reduction of the corresponding diazonium salts.

for low coverage. Furthermore we also observed azo-bond formation possibly between the Au substrate and the organic molecule and between organic molecules in the film. However, in the case of the Au/PhF₄COOH system we only observed the formation of compact monolayers. The nature of the bond between the organic molecule and the Au substrate depends on the reductive potential employed. At low potentials the Au–C bond dominates, whereas at high reductive potentials we only observed evidence of azo bonds, Au-N=N-C.

We used the controlled surface modification of Au substrates with -COOH groups in order to covalently attach an osmium complex through the formation of an amide bond (Scheme 2). We used this complex as a redox probe to measure electron-transfer rate constants. Both systems, Au/PhCOOH/Os and Au/PhF₄COOH/Os, were characterized by XPS



Scheme 2. Idealized structures of the systems obtained by post-functionalization of the films prepared by electroreduction of the diazonium salts.

(Figure 4). In both cases we observed XPS signals corresponding to the elements present in both samples (Au 4f, C 1s, O 1s, N 1s, Cl 2p, and Os 4f).^[58] In the second case, the F 1s signal was also observed.

The ratio Os:N was 1:16 for both systems, which is smaller than the expected 1:6 for the original monolayers of PhCOOH and PhF₄COOH and can be explained by the N=N bond formation as discussed above. In the particular case of the fluorinated system, the ratio of intensities Os:F was 1:8. This ratio indicates that not all of the carboxylic functions were post-functionalized but only half of them reacted with the osmium complex. We would have expected an Os:F ratio of 1:4 if all molecules had been bound the Os complex. Finally, the Os:Cl ratio was 1:1 in both cases, as expected. The surface coverage of the complex was roughly estimated from the Os4f signal intensity and was equal to 2.6×10^{-10} and 1.44×10^{-10} mol cm⁻² for Au/PhCOOH/Os and Au/PhF₄COOH/Os, respectively. These measurements showed that the osmium complex retains its chemical integrity during the post-functionalization reaction, that approximately half of the carboxylic acid functions are modified with the osmium complex, and finally that the osmium molecules assemble in a compact array, as a compact monolayer would have an Os coverage of approximately 1.38×10^{-10} mol cm⁻².

Both systems were also characterized by cyclic voltammetry in a 0.1 M NaNO₃ solution (scan rate 0.1 V s⁻¹). Figure 5 depicts the voltammograms obtained in each case.

The formal redox potential (E°) was determined as the average of the anodic and cathodic peak positions. The Os complex surface coverage (Γ_{Os}) was estimated from the electrochemical charge involved in the oxidation-reduction of the redox couple, taking the ratio between the average area below the anodic and cathodic peaks and the scan rate. In both cases, the roughness of the gold substrates was considered in these calculations. Finally, the full widths at half maximum (FWHM) were also obtained. This information is summarized in Table 2.

The voltammetry curves in Figure 5 have the characteristic shape of an electroactive species tethered to the electrode surface. In both cases a linear relationship between the peak current and the scan rate was observed, indicating that the redox couple is attached to the surface.^[59] Moreover, the anodic and cathodic charge was almost equal suggesting that the osmium

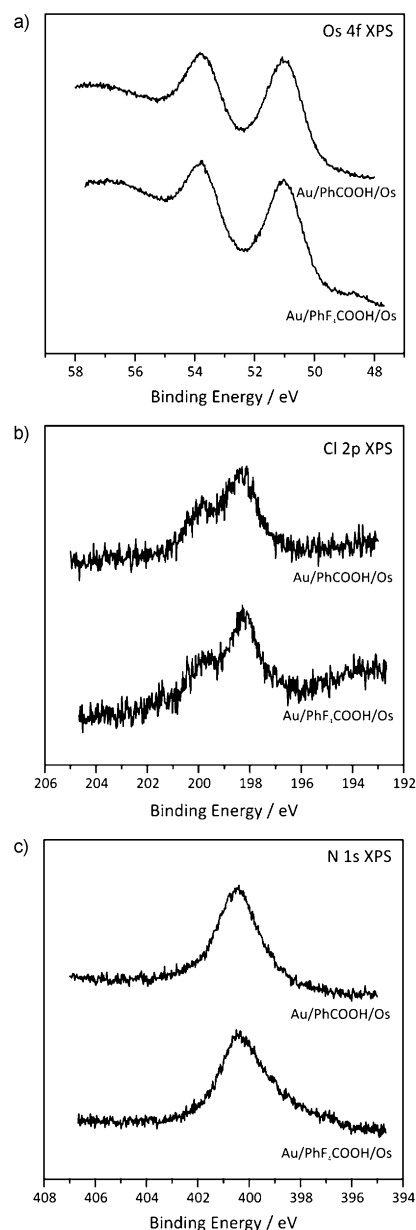


Figure 4. XPS spectra of Au/PhCOOH/Os and Au/PhF₄COOH/Os. For both systems a) Os 4f, b) Cl 2p, and c) N 1s spectral regions are shown.

complex can be completely oxidized and reduced under these conditions. The formal potential in both cases was ≈ 0.30 V in good agreement with the reported values for this and similar Os complexes adsorbed on electrode surfaces.^[60–62] The voltammetric traces in Figure 5 are not ideal for surface species.^[62] A peak separation of $\Delta E_p > 0$ is observed, even for low scan rates, and the FWHM is larger than the value expected for an ideal one-electron redox process, (≈ 90.6 mV), indicating the existence of repulsive interactions between redox centres confined to the surface. Note however, that for the PhF₄COOH system the redox peaks are narrow compared to the PhCOOH modified surface, where multilayer formation is expected. The Os complex surface coverage obtained from the redox charge is approximately 1×10^{-10} mol cm⁻² in both systems (Table 2).

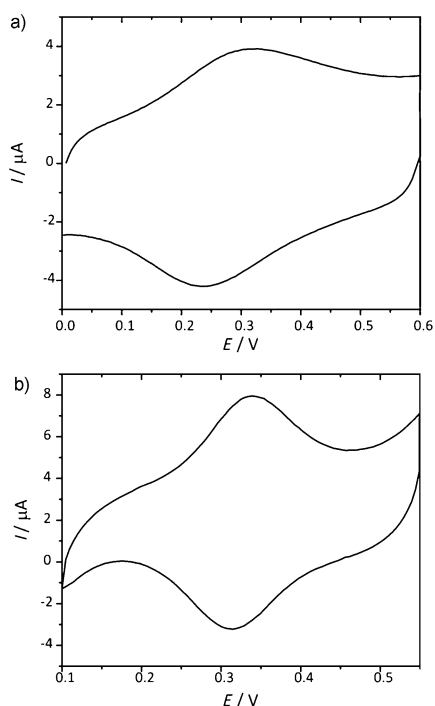


Figure 5. Cyclic voltammetry of a gold electrode modified with a) PhCOOH/Os and b) PhF₄COOH/Os in 0.1 M NaNO₃ at 0.1 V s⁻¹.

Table 2. Electrochemical data obtained by cyclic voltammetry in 0.1 NaNO ₃ M at 0.1 V s ⁻¹ and electrochemical impedance spectroscopy.		
	Au/PhCOOH/Os	Au/PhF ₄ COOH/Os
$E^{0'}$ [V]	0.30	0.32
ΔE_p [V]	0.06	0.02
Q [$\mu\text{C cm}^{-2}$]	1.0	0.79
Γ_{Os}^+ [$\times 10^{-10}$ mol cm ⁻²]	1.04	0.82
FWHM [V]	0.16	0.11
k^0 [s ⁻¹]	$(1.4 \pm 1.4) \times 10^5$	$(3.0 \pm 1.4) \times 10^5$
C_{ads} [$\times 10^{-6}$ F]	0.4 ± 0.1	0.4 ± 0.2
$R_s C_{\text{dl}}$ [s]	9×10^{-9}	1×10^{-8}

These values are in relatively good agreement with the values calculated from the XPS signals.

Electron-transfer kinetic constants were measured for both systems by a method proposed by Creager et al.^[63] This method is recommended for fast electron-transfer reactions where the Laviron^[64] trumpet plot analysis fails. Electrochemical impedance spectroscopy was employed and impedance spectra ($Z_{\text{Re}} + jZ_{\text{Im}}$ vs. f) were measured at different potentials chosen in a window centred around the Os couple formal potential (i.e. $0 \leq E^{0'} \leq 0.5$ V). At each potential the impedance spectra were obtained at 25 different frequencies ranging between 106 and 1 Hz. From these spectra the cell impedance was measured at each potential and each frequency, and the variation of the cell admittance (Y) was analyzed as a function of potential for every frequency. In this way the cell admittances at the formal potential (Y_{peak}) and away from it (Y_{bkg}) were obtained and the ratio ($\xi = Y_{\text{peak}}/Y_{\text{bkg}}$) was plotted against $\log(f)$.

The electron-transfer kinetics were derived from these plots using the Randles equivalent circuit to model the electrochemical cell, and the experimental data were fitted to Equation (1):

$$\xi = \frac{(Y_{\text{peak}}/Y_{\text{bkg}} - 1)}{[(Y_{\text{peak}}/Y_{\text{bkg}})_{\text{max}} - 1]} \quad (1)$$

employing as parameters the standard electron-transfer kinetic constant, k^0 , and the electroactive film capacitance, C_{ads} .^[63]

Figure 6 shows and compares for both systems the results of normalized admittances in Equation (1) and the fitted parameters are shown in Table 2. Furthermore, the cell time constant, which limits the measuring technique, was estimated

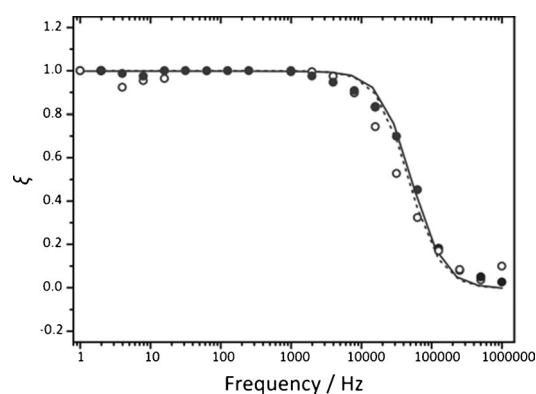


Figure 6. ξ variation as a function of the excitation frequency for both systems. The dots correspond to experimental data: Au/PhF₄COOH/Os (○) and Au/PhCOOH/Os (●) and the continuous and dashed lines are the best fit to the Randles equivalent circuit of each set of data.

from the values of uncompensated resistance R_s and double layer capacitance C_{dl} obtained respectively from the real and imaginary components of the complex high-frequency cell impedance as shown in Table 2 for both systems ($R_s C_{\text{dl}} \ll 1/k^0$).

Similar rate constants, in the 10^5 s⁻¹ range, were found for both fluorinated and non-fluorinated benzene linkers of the osmium complex, and therefore we were unable to distinguish with the techniques available any differences in the electron-transfer rates between the two configurations.

We also overcame the instability of the fluorinated diazonium salt by in situ diazotization and reduction close to the electrode surface. From the XPS and PM-IRRAS analysis it was demonstrated that when all the ring positions are blocked, monolayers can be formed even at strong reducing potentials. Furthermore, both techniques showed the presence of azo bonds in the surface film structure and demonstrated that their formation is favoured under strong reducing conditions.

In fact, high reductive potentials would result in a compact monolayer with the molecules bonded to the Au substrate through an azo bond.

We suggest that these results provide the first experimental evidence for the binding of organic molecules to metal surfaces through an azo bond generated by the electroreduction of a diazonium salt. The same analysis with non-fluorinated 4-car-

boxybenzene diazonium tetrafluoroborate showed the formation of a thin layer with some branching even when the diazonium salt was reduced under mild reducing conditions, whereas multilayers containing nitrogen due to azo-bond formation were detected by XPS and PM-IRRAS analysis for strongly reducing conditions.

Finally we showed that electroreduction of diazonium salts could serve as a good means to covalently modify Au surfaces with carboxylic functional groups.

These groups were employed to bind an Os redox center through an amide bond forming a compact layer. Electron-transfer rate constants were determined not to be influenced by the nature of the substituents in the aromatic ring.

3. Conclusions

Molecular films formed by electrochemical reduction of diazonium salts on Au form different structures on the electrode surface depending on the applied potential. It has been shown that under strongly reducing conditions multilayers are formed, due to radical attack on the free positions of the aromatic rings of those aromatic molecules already attached to the surface. When fluorine substituents are blocking all of the phenyl-ring positions, this attack is no longer possible and monolayer formation can be easily achieved. The surface coverage of redox groups obtained by XPS analysis and integrated redox charge confirmed the formation of monolayers for the fluorinated molecules.

The spectroscopic evidence suggested the formation of N=N bonds either between phenyl rings or to the Au surface, since the phenyl rings may tether the complex to the gold surface either through a direct C–Au or through a C–N=N–Au bond. In the case of the tetrafluorinated phenyl ring, however, branching through radical attack on other aromatic rings was not possible. New experimental evidence of combined 400 eV XPS N1s peak and the 1392 cm⁻¹ IR peak assigned to the N=N stretching mode for the 4-amino-(2,3,5,6-tetrafluoro)-carboxybenzene suggested the formation of an Au–N=N bond, the population of which strongly depends on the electrode potential.

Experimental Section

Chemicals: The following chemicals were used as received: tetrafluoroborate tetrabutylammonium (Fluka), 4-aminobenzoic acid (Sigma–Aldrich), 4-amino-2,3,5,6-tetrafluoro-benzoic acid (Sigma–Aldrich), iso-amyle nitrite (Sigma–Aldrich), sodium fluoroborate (Sigma–Aldrich), acetonitrile (Sintorgan, Buenos Aires, Argentina), tetrafluoroboric acid (50% solution, Riedel de Haën), ethyl ether (Sintorgan), 1-ethyl-3-(3-dimethylamino-propyl)-carbodiimide (Sigma–Aldrich), N-hydroxysuccinimide (Sigma–Aldrich), 4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid (HEPES) (Sigma–Aldrich), potassium nitrate (Merck), absolute ethanol (Sintorgan, Buenos Aires, Argentina), sodium nitrate (Biopack)

Preparation of Au substrates: Silicon(100) substrates were coated with a 20 nm titanium and 20 nm palladium adhesion layer and a 200 nm gold layer, thermally evaporated with an Edwards Auto 306 vacuum coating system at P < 10⁻⁸ bar, and employed as elec-

trodes. Before surface modification, the electrode potential was cycled in 2 M sulfuric acid between 0 and 1.6 V at 0.1 V s⁻¹ to check for surface contamination. Electrochemically active areas were calculated from the reduction peak of gold oxide. The surface roughness was calculated as the ratio of surface area to geometric area and was always in the range between 1.5–2.

Electroreduction of diazonium salts: The synthesis of 4-carboxybenzene-diazonium tetrafluoroborate has been described elsewhere.^[65] The derivatization was carried out in a three-electrode cell with the gold substrate to be modified acting as the working electrode. A 5 mm 4-carboxybenzenediazonium tetrafluoroborate and a 0.1 M in tetrabutylammonium tetrafluoroborate (supporting electrolyte) solution in acetonitrile were used. Two different potentials were applied (0.3 and –0.7 V) during 5 min, in order to carry out the reduction in different conditions. After modification, the substrate was washed with acetonitrile and water and dried under a N₂ stream. We refer to this system as Au/PhCOOH. The synthesis of 4-(2,3,5,6-tetrafluoro)-carboxybenzenediazonium tetrafluoroborate was performed in situ simultaneously with its reduction, because the fluoride substituents strongly withdraw the electron density from the aromatic ring destabilizing the diazonium group and making it very reactive. Therefore, an ethanol solution of tetrafluoroboric acid was prepared (50%, 0.01 mol) and isoamyle nitrite was added (6 μL, 0.045 mmol). This solution was introduced in a three-electrode cell with the gold substrate to be modified acting as the working electrode. A reductive potential was applied and 1.5 mL of an ethanol solution of 1-amino-(2,3,5,6-tetrafluoro)-benzoic acid (0.02 mmol) were added. The potential was applied for 5 min, then the substrate was washed with ethanol and water and dried under a N₂ stream. This derivatization was carried out with three different potentials (–0.7 V, –0.2 V and 0 V) in order to perform the reduction of the diazonium salt in different conditions. This system is referred to as Au/PhF₄COOH.

Post-functionalization with [Os(2,2'-bpy)₂ClPyCH₂NH₂]₂PF₆: The synthesis of the osmium complex and its attachment to the surface have been described elsewhere.^[66] Briefly, after initial derivatization by reduction of the diazonium salts, the gold surfaces were incubated in a 40 mM 1-ethyl-3-(3-dimethyl-amino-propyl)-carbodiimide (EDC)/10 mM N-hydroxysuccinimide (NHS) solution for 1 h, and dipped in a 0.25 mM [Os(bpy)₂Cl(py-CH₂-NH₂)]PF₆/0.05 M HEPES buffer [(N-2-hydroxyethyl-piperazine-N'-2-ethanesulfonic acid) pH 7.3, I = 0.1 M KNO₃] for 12 h. We refer to the systems obtained with this post-functionalization as Au/PhF₄COOH/Os and Au/PhCOOH/Os, respectively.

IR Measurements: PM-IRRAS experiments were performed on a Thermo Nicolet 8700 (Nicolet, Madison, WI) spectrometer equipped with a custom-made external tabletop optical mount, a MCT-A detector (Nicolet), a photo elastic modulator, PEM (PM-90 with II/Zs50 ZnSe 50 kHz optical head, Hinds Instrument, Hillsboro, OR), and synchronous sampling demodulator, SSD, (GWC Instruments, Madison, WI). The IR spectra were acquired with the PEM set for a half wave retardation at λ₀ = 1500 cm⁻¹ (aromatic region, C–H bending and stretching modes associated with the COOH group), and at λ₀ = 1200 cm⁻¹ (C–F stretching modes). The angle of incidence was set at 80°, which gives the maximum of mean square electric field strength for the air/gold interface. The demodulation technique developed by Corn^[67,68] was used in this work. The signal was corrected by the PEM response using the method described by Frey et al.^[69] Typically 1000 scans were performed and the resolution was set for 4 cm⁻¹.

X-ray Photoelectron Spectroscopy measurements: XPS was performed under UHV conditions (base pressure $<5.10^{-10}$ mbar) in a SPECS UHV spectrometer system equipped with a 150 mm mean radius hemispherical electron energy analyzer and a nine channeltron detector. XPS spectra were acquired at a constant pass energy of 20 eV using an un-monochromated $Mg_{K\alpha}$ (1253.6 eV) source operated at 12.5 kV and 20 mA and a detection angle of 30° with respect to the sample normal on grounded conducting substrates. Quoted binding energies refer to the Au $4f_{7/2}$ emission at 84 eV. Atomic ratios and surface concentrations were calculated from the integrated intensities of core levels after instrumental and photoionization cross-section corrections.

Electrochemical measurements were carried out with an Autolab V 30 system (Eco Chemie, Utrecht, the Netherlands) controlled by a General Purpose Electrochemical Software (GPES) or FRA Software. This potentiostat is equipped with 750 kHz bandwidth ADC750 fast sampling module and scangen analog sweep module. All experiments were carried out at room temperature ($20 \pm 2^\circ\text{C}$). Cyclic voltammetry experiments were performed in a purpose-built, three-electrode Teflon cell, with an electrode exposed area of approximately 0.28 cm^2 delimited by an inert "o" ring. A Pt counter electrode and an Ag/AgCl, 3 M KCl reference electrode were employed, and potentials herein are reported with respect to this reference. Electrochemical impedance spectroscopy experiments implemented a frequency response analyzer (FRA 2) and excitation frequency ranged between 106 and 1 Hz. The amplitude of the excitation signals was 10 mV. The electron transfer kinetic measurements were carried out with spherical gold working electrodes prepared by melting the end of a $150\text{ }\mu\text{m}$ -diameter gold wire in a flame to form a sphere of approximately $400\text{ }\mu\text{m}$ in diameter. The low values for the cell time constants of these electrodes (Table 2), needed to measure fast kinetics, is the result of a small electrode size (small double layer capacitance) and low uncompensated resistance in highly concentrated electrolyte.

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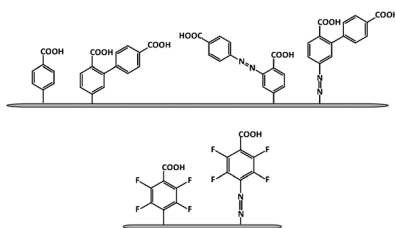
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ARTICLES

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Some Evidence for the Formation of an Azo Bond during the Electroreduction of Diazonium Salts on Au Substrates



Azo tether: Molecular films obtained by electrochemical reduction of diazonium tetrafluoroborate salts of 4-carboxy benzene and 4-amino-(2,3,5,6-tetrafluoro)-carboxy benzene on Au substrates are studied by a combination of X-ray photoelectron and polarization-modulation infrared reflection absorption spectroscopy. The spectroscopic evidence demonstrates the formation of N=N bonds tethering the complexes to Au (see picture).