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# An unusual self-assembly of a deuteroporphyrin 4-aminothiophenol derivative on Au(111) surfaces†

Cite this: DOI: 10.1039/c3nj00118k

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Received (in Porto Alegre, Brazil)
30th January 2013,
Accepted 24th March 2013

DOI: 10.1039/c3nj00118k

**www.rsc.org/njc**

An unexpected ruthenium(II)-deuteroporphyrin 4-aminothiophenol (4-ATP) thiolester derivative (Ru-4ATPP) was obtained by the condensation of 4-ATP with carbonyl[13,17-bis(propanoic acid)-2,7,12,18-tetramethylporphyrinato]ruthenium(II). Ru-4ATPP was self-assembled on Au(111) surfaces through the terminal amino groups, as shown by cyclic voltammetry (CV) and confirmed by X-ray photoelectron spectroscopy (XPS). A slow and incomplete isomerisation process of the self-assembled 4-RuATPP thiolester to its amido analogue was observed, due to the catalytic effect of the gold surface. Consequently, the formed amido isomer of Ru-4ATPP became self-assembled on Au(111) through the resulting terminal thiolate groups, a condition characterized by CV reductive desorption (peak at *ca.* −0.7 eV) and XPS (S2p peaks at 162.1 and 163.3 eV).

## 1. Introduction

Recently we reported a gold electrode modified with a ruthenium(II)-deuteroporphyrin alkyldisulfide derivative ([Ru(Pds)(CO)]). The modified electrode was successfully tested for the electrochemical detection of nitric oxide in aqueous solution.[1] The formed self-assembled monolayer (SAM) of [Ru(Pds)(CO)] was characterized by cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS). The recorded CV reductive desorption peak at −0.92 V indicated the association of the SAM through the thiolate groups after the rupture of the S–S bond.

Self-assembled monolayers have been widely employed to bestow new functionalities of metal surfaces.[2] When metal electrodes are modified with SAMs containing metal ions the presence of aromatic compounds as spacer arms between the latter and the surface is recommended in order to guarantee an efficient electron transfer (ET) process. In this sense, 4-aminothiophenol (4-ATP) constitutes an adequate alternative. 4-ATP has been used for the self-assembly on metal nanoparticles[3–7] and electrodes.[8–11] The rigidity conferred to the monolayer, the delocalized π-electrons of the aromatic ring, as well as the presence of an amino group as a scaffold for further modifications are some of the advantages in the use of such a compound in the formation of SAMs on gold surfaces.[12] SAMs are known to modify the properties of metal surfaces, a process that could catalytically favor different types of reactions. Nevertheless, such studies have received very little attention.

SAMs of 4-ATP on gold surfaces have been characterized by CV,[4,6,8,11–14] XPS,[3,4,6,8,13,15,16] and scanning tunnelling microscopy (STM),[11,13,17] among other techniques. It is well known that in alkali medium, voltammograms of thiolated derivative SAMs can offer a sharp reduction peak as a result of the disruption of Au–SR bonds.[18–23] For SAMs of aromatic thiols on gold, a wide range of values has been reported (−0.6 to −1.5 V) especially for thiophenol and its derivatives.[11,13,24–27] In the particular case of SAMs of 4-ATP and also its 3- and 2-ATP isomers the reductive desorption at low pH gave peaks between 1.51 and −1.45 V.[13] In contrast, the reductive desorption potential of 4-ATP SAMs on gold electrodes employing an alkali solution lied at around −0.73 V.[11]

Here we report the unusual synthesis and self-assembly of a ruthenium(II)-deuteroporphyrin derivative containing 4-ATP as a spacer arm (Ru-4ATPP, Fig. 1), including an isomerization process.

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† Electronic supplementary information (ESI) available: Fig. S1: cyclic voltammograms of Ru-4ATPP SAMs in the anodic region. Fig. S2: reductive desorption CV in the cathodic region of a stored solution of Ru(4-ATPP) on days 2–8 after being prepared. Fig. S3: HMBC spectra in the carbonyl region of Ru-4ATPP in the presence and absence (days 0 and 10) of $AuCl_3$. Fig. S4: HMBC spectra in the carbonyl region of Ru-4ATPP ten days after being prepared. See DOI: 10.1039/c3nj00118k

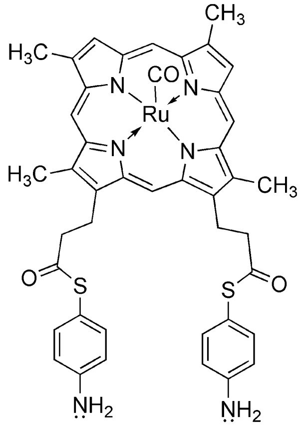

**Fig. 1** Schematic representation of Ru-4ATPP.

## 2. Experimental part

### 2.1. Chemicals

4-Aminothiophenol, 4-ATP (97%), was obtained from Aldrich and used without further purification. Aniline (Ani) (99%) and thiophenol (TP) (95%) were obtained from Acros and Aldrich, respectively, and distilled prior to use. The preparation of the disulphide derivative of 4-ATP (4-ATPds) was performed by a mild oxidation of 4-ATP as described elsewhere.[28] Tetrabutylammonium hexafluorophosphate, TBAHFP (electrochemical grade), and isobutylchloroformate ($ClCO_2iBu$) were purchased from Fluka and used without further purification. $CH_2Cl_2$ (analytical grade) was obtained from Merck, and dried with phosphorous pentoxide, distilled and degassed employing the freeze–pump–thaw cycling. Other solvents were dried using standard methods. Doubly distilled water was always used.

### 2.2. Preparation of the self-assembled monolayer

The gold slides used (200 nm of gold evaporated on glass with a pre-layer of 2–4 nm of chromium; Gold Arrandee) were cleaned before each experiment by immersing in piranha solution for 5 min and then washed with significant amounts of ethanol and water (two times). After cleaning, the slides were flame-annealed in an n-butane-gas flame to produce a flat surface with a predominant Au(111) crystallographic orientation.

The self-assembled monolayers of Ru-4ATPP were formed on Au slides using 1 mM solutions in $CH_2Cl_2$. The immobilization was carried out in a sealed flask (24 hours at RT in the dark) containing both the Ru-4ATPP solution and the gold slide. Once the gold slide was removed from the Ru-4ATPP solution it was rinsed with significant amounts of $CH_2Cl_2$, dried under argon, and stored (if necessary) in sealed flasks. The samples were stored (at RT in the dark) for CV and XPS studies.

### 2.3. Electrochemistry

All glassware was cleaned using a piranha solution followed by rinsing with bi-distilled water ($\lambda \leq 4$ μS). Cyclic voltammetry was performed using a commercial EG&G PAR-384 model equipment. A one compartment Teflon cell, fitted with a Pt foil counter electrode and a Ag/AgCl(sat) reference electrode, was used. The Au(111) slides were clamped against an O-ring, which defined the geometric area of the working electrode as 0.58 $cm^2$. The electrolyte solutions were degassed (30 min) with Ar prior to each experiment.

### 2.4. Spectroscopy

Electronic spectra were recorded using a Varian Cary spectrophotometer interfaced with a microcomputer for data acquisition. IR spectra were recorded using a Perkin-Elmer Paragon 500 FT-IR spectrometer with samples prepared as KBr tablets. $^1H$- and $^{13}C$-NMR spectra were obtained using Bruker DPX-200 and AVANCE DRX-600 MHz spectrometers at 300 K; all chemical shifts were referenced to TMS lock signal. Ru-4ATPP (30 mg) was dissolved in $CD_2Cl_2$ (0.5 mL) + $d^5$-pyridine (5 μL). MS were obtained using a Finnigan MAT 8200 spectrometer [EI (70 eV) and ESI†]. The X-ray photoelectron spectra (XPS) were obtained on Surface Science Instruments X- and M-probe spectrometers using monochromatic Al-Kα X-ray sources ($h\nu$ = 1486.6 eV). The BE scales for the monolayers on gold were referenced by setting the $Au4f_{7/2}$ BE to 84.0 eV. The XPS signals were deconvoluted employing the Voigt function[29] and constraining the customary 1.2 eV peak separations and also the 2 : 1 area ratio of the $S2p_{3/2}$ and $S2p_{1/2}$ components of the sulfur doublet. The binding energies, areas under the curves, and full widths at half-maximum (fwhm) were unconstrained in all the deconvolution procedures.

### 2.5. Preparation of carbonyl[13,17-bis(*S*-(4-aminophenyl)propanedioate-yl))-2,7,12,18-tetramethylporphyrinato]ruthenium(II) [Ru(4-ATPP)(CO)]

Ru(DPdc)(CO)[1] (100 mg, 0.156 mmol) was dissolved under argon in dry THF (50 mL) and freshly distilled triethylamine (1 mL) was added. The resulting dispersion was stirred under cooling (−15 °C) and a solution of isobutylchloroformate (85 mg, 0.624 mmol, 4 eq.) in THF (2 mL) was added. The reaction mixture was stirred for 2 h. The temperature was increased to −10 °C and 2 mL of solution (58 mg, 0.468 mmol, 3 eq.) of 4-aminothiophenol was slowly added. The reaction mixture (under argon) was stirred at RT for 4 h. The resulting reaction mixture was extracted with $CH_2Cl_2$ and washed with saturated solutions of $NaHCO_3$ and NaCl and finally with water. The organic phase was evaporated and the crude brown solid was purified by column chromatography (silica, $CH_2Cl_2$ : MeOH : EtOAc, 10 : 0.4 : 0.4) to yield 99 mg (75%) of a bright orange solid. TLC (silica gel, $CH_2Cl_2$ : MeOH, 10 : 1). Rf = 0.59. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$, nm. $\varepsilon$ ($M^{-1}$ $cm^{-1}$) = 314 nm (13 800), 394 (150 000), 516 (10 500), 546 (14 400). IR (KBr): $\nu$ = 3453, 3367 $cm^{-1}$ (m, $NH_2$), 2920 (s, CH), 2848 (s, CH), 1933 (s, C≡O), 1661 (m, C=O, thiolester), 1591 (m, $\delta(NH_2)$). $^1H$-NMR: (600 MHz, $CD_2Cl_2$ + 5 μL $d^5$-pyridine), $\delta$ = 3.36 (s, 3H, $CH_3$), 3.38 (m, 4H, $CH_2$ α to carbonyl), 3.40 (s, 3H, $CH_3$), 3.48 (s, 3H, $CH_3$), 3.52 (s, 3H, $CH_3$), 4.21 (m, 4H, $CH_2$ β to carbonyl), 5.49 (broad, s, 4H, $NH_2$), 6.43 (m, 4H, CHar), 7.12 (m, 4H, CHar), 8.74 (s, 1H, 8-H), 8.77 (s, 1H, 3-H), 9.64 (s, 1H, 10-H), 9.68 (s, 1H, 5-H), 9.71 (s, 1H, 20-H), 9.77 (s, 1H, 15-H). $^{13}C$-NMR (C=O): 199.7 ppm.

MS (ESI, $CH_2Cl_2$ : MeOH) positive: *m*/*z* 875 $[M + Na]^+$, negative: *m*/*z* 850 $[M - 2H^+]$, *m*/*z* 886 $[M + Cl^-]$.

## 3. Results and discussion

Ru(4-ATPP) was synthesized by the condensation of 4-ATP with carbonyl[13,17-bis(propanoic acid)-2,7,12,18-tetramethylporphyrinato]ruthenium(II).[1] We expected a conjugation between the carboxylic group of the porphyrin derivative and the amino group of 4-ATP. Such a product would leave the thiol of 4-ATP available for the self-assembly on a gold electrode.

The presence of the $\nu$(NH) at 3454 $cm^{-1}$ and 3366 $cm^{-1}$ and the absence of $\nu$(SH) bands at *ca.* 2550 $cm^{-1}$ in the IR spectrum of the product indicated that the thiol group actually participated in the condensation reaction. Additionally, a peak at 199.7 ppm ($^{13}$C-NMR) confirmed the formation of a thiolester group instead of an amido one.[30] Therefore, the unexpected product obtained corresponded to Ru-4ATPP (Fig. 1). The achieved thiolester conjugation is less stable than the expected amido one but kinetically more favored, which should be the reason for the formation of the unexpected product.

The formation of a SAM of Ru-4ATPP on gold surfaces would impose the participation of both of its amino groups. This mode of self-assembly (Au–N), although not usual, has been reported before.[16,31] Nevertheless, this situation required a detailed characterization of the SAM of Ru-4TPP, especially by CV for which no report has been found.

### 3.1. Cyclic voltammetric determination

The electrochemical behavior of ruthenium(II)-porphyrin SAMs on gold electrodes is characterized by a reversible redox couple within 0.2 V and 0.8 V that directly involves the metal center.[32,33] The cyclic voltammogram (CV) of gold electrodes modified with Ru-4ATPP in the anodic range presented a reversible redox pair ($\Delta E$ = 36 mV, $E_{1/2}$ = 0.54 V) which corresponds to coordinated ruthenium(II) to the porphyrin macrocycle as a whole (Fig. S1 in ESI†).

The reductive desorption CV (0.5 M KOH) of the Ru-4ATPP SAM immediately after preparation gave a single cathodic peak at −0.87 V (Fig. 2a), which was assigned to the disruption of the Au–N bond in the SAM of Ru-4ATPP (Fig. 1). In order to confirm this assignation we decided to extend the CV reductive desorption studies to free 4-ATP (Fig. 2b) and its aromatic analogues: thiophenol (TP, Fig. 2c), the disulfide analogues of 4-ATP (4-ATPds, Fig. 2d), and aniline (Ani, Fig. 2e). It is necessary to underline that these SAMs were prepared in $CH_2Cl_2$ without the presence of any acid that could favor the protonation of the amino groups.

From a comparative analysis of the cathodic peaks of 4-ATP, TP, Ani and 4-ATPds we observed that:

(a) 4-ATP, with S and N as potential donor atoms, presented an intense peak at −0.71 V, a very weak one at −0.88 V (Fig. 2b). An oxidative peak at −0.60 V was also recorded.

(b) TP, with only S as a possible donor atom, presented one single peak at −0.69 V, also present in 4-ATP.

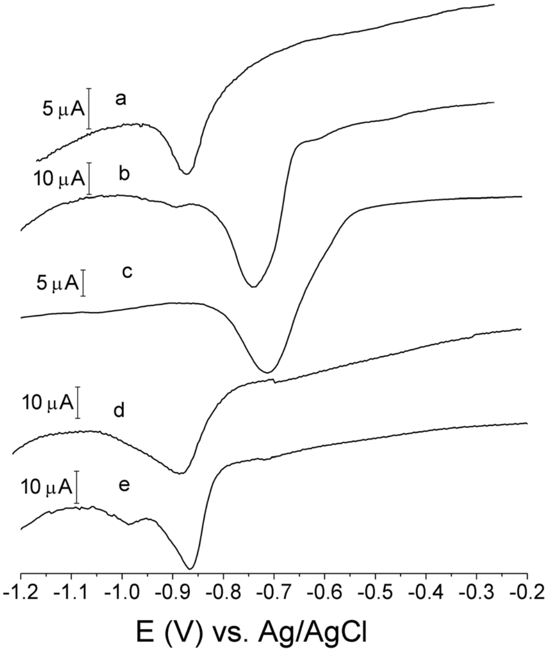

**Fig. 2** Reductive desorption CV in the cathodic region (in KOH 0.5 M) of: (a) Ru-4ATPP; (b) 4-ATP (c) TP (d) 4-ATPds; (e) Ani. Scan rate = 100 mV $s^{-1}$.

(c) 4-ATPds, a chemical analogue of 4-ATP, presented a single peak at −0.87 V.

(d) Ani, with only N as a donor atom, presented two peaks at −0.86 and −0.99 V.

From these observations we assumed the following assignations:

(a) The peak recorded between −0.88 and −0.86 V should correspond to the disruption of the Au–N(amino) bond.

(b) The cathodic peaks at −0.71 and −0.69 should be assigned to the reductive disruption of the Au–S(thiolate) bond. Cathodic peaks at *ca.* −0.70 V have earlier received the same assignation.[11,24,25]

(c) The peak of Ani at −0.99 V was not assignable but could correspond to a highly stable self-assembly of Ani through Au–N(amino) bonds.

Voltammograms of Ru-4ATPP were also recorded over time (1–20 days), as presented in Fig. 3, where significant variations were observed. With only 24 hours after rinsing the gold electrode modified with the Ru-4ATPP SAM (day 1) the CV presented a new reductive desorption peak at −0.69 V assigned to the Au–S(thiolate) bond that increased in intensity in the following days while the initial one at −0.87 V (Au–N(amino) bond) decreased. The peak at −0.87 V not only decreased in intensity but also was shifted to more negative values when compared with the CV at day 0 (Fig. 3), a process that can only be attributed to an increase in the organization of the SAM, something normally expected to happen over time.

The intensities of the peaks assigned to the Au–N(amino) and Au–S(thiolate) bonds were compared when referred to the sum of the areas of both peaks. Already on the 7th day the area of the new peak at *ca.* −0.7 V (Au–S(thiolate) bond) constituted

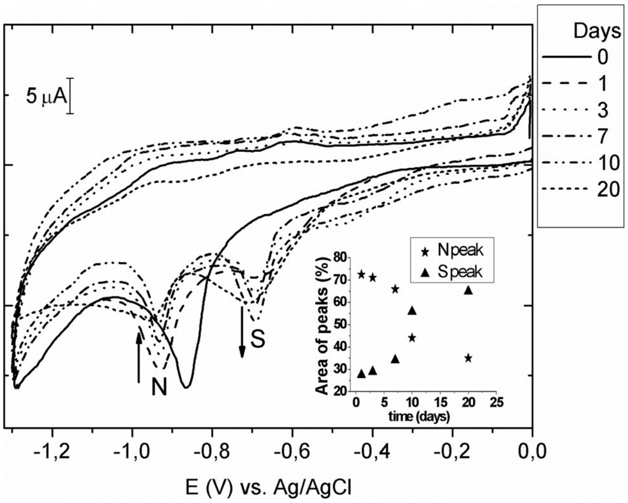

**Fig. 3** Reductive desorption CV of Ru-4ATPP recorded at different days after the formation of the SAM.

34% of the sum of the areas of both peaks, while on the 20th day this value increased to 65% (Fig. 3, inset).

The observed variations in intensity of the Au–N (amino) peak and the additional presence of a peak assigned to the Au–S(thiolate) bond could be interpreted as a slow isomerization of self-assembled Ru-4ATPP from its thiolester form to the corresponding amido isomer.

The proposed isomerization of Ru-4ATPP should be attributed to the catalytic role of the gold surface since when its solution was prepared and stored for CV determination for eight days no significant variation was observed. This study was performed by only putting in contact the Ru-4ATPP solution with the gold electrode for each CV determination (days 2, 4, 6 and 8) (Fig. S2 in ESI†). Therefore, the isomerization process should not be attributed to the hydrolysis of the thiolester group since it only occurs in the presence of the gold surface.

### 3.2. XPS determination

In order to confirm the variations observed in the voltammograms recorded over time, a XPS study of the gold surface modified with a SAM of Ru-4ATPP was performed.

XPS determination of SAMs of 4-ATP on gold indicated that the formation of Au–N[4,16,31] bonds or free amine[34,35] is characterized by a N1s peak at *ca.* 399 eV. On the other hand, associated thiolate groups present a pair of S2p peaks at around 161–163 eV, while when free, both peaks are shifted to higher energies.[36]

The XPS spectrum in the N1s region of a gold surface modified on the 7th day with a SAM of Ru-4ATPP was resolved into three peaks (Fig. 4a). The assignations were made mainly considering an earlier report on the angle-resolved XPS study of 4-ATP self-assembled on gold electrodes, where the peak at 400.1 eV was assigned to the free amino group when a Au–S(thiolate) bond was formed, while the peak at 399.1 eV was assigned to the associated amino group (Au–N(amino) bond).[16]

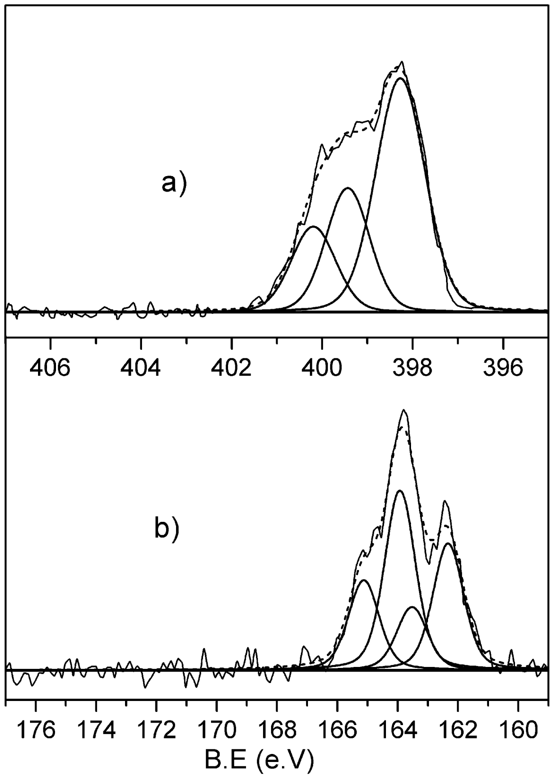

**Fig. 4** XPS spectra of Ru-4ATPP SAM in: (a) N1s region and (b) S2p region.

The more intense peak at 398.3 eV should correspond to the four equivalent nitrogen atoms of the porphyrin macrocycle.[1] The peak at 399.4 eV was assigned to the nitrogen atoms of the amino groups associated to gold.[16] The third and less intense peak at 400.2 eV could be attributed to unassociated nitrogen (amino group) atoms. The presence of the three N1s peaks could be interpreted as due to the formation of a mixed SAM of Ru-4ATPP associated in two different forms: (a) through the terminal amino group of the thiolester isomer and (b) through the thiolate group of its amido isomer.

The analysis of the XPS spectrum in the S2p region (Fig. 2b) also offered indications of the isomerization process of Ru-4ATPP. Two pairs of peaks were recorded. One pair of S2p peaks was observed at 162.1 and 163.3 eV, which should be assigned to self-assembled sulfur atoms of the thiolester group. The other pair of S2p peaks was recorded at 163.9 and 165.1 eV which should correspond to unassociated sulfur atoms.[36,37] In this sense it is important to point out that Ashwell *et al* reported the S2p peaks of 4-ATP at 161.9 and 163.1 eV when a Au–S(thiolate) bond was formed, while the free thiol group (Au–N bond) was recorded at 163.6 and 164.8 eV.[16]

It is important to underline that the S : N atomic ratio determined by XPS (1 : 2.98), in a high concordance with the theoretical ratio (1 : 3), indicates that no decomposition took place during the self-assembly and isomerization process.

The percentage of the peaks corresponding to each isomer was determined with respect to the sum of the areas of them for each element. In the case of the N1s peaks at 399.4 and 400.2 eV, the sum of both areas was considered as 100% of the nitrogen contained in the 4-ATP residue. 41% corresponded to the peak at 400.2 eV (Au–S(thiolate) bond), while the rest (59%) was covered by the N1s peak at 399.4 eV (Au–N(amino) bond). A similar result was obtained when comparing the intensities of the S2p peaks. The intensity of the $S2p_{3/2}$ peak, corresponding to the Au–S bond (at 162.1 eV), represented *ca.* 39% of the total area while the peak at 163.9 eV (Au–N bond) covered 61%. These results are in agreement with those obtained by reductive desorption CV for the same period of time, where the area of the peak corresponding to the Au–S(thiolate) bond constituted 34% of the sum of the areas of both peaks.

The formation of a mixed SAM could also be interpreted by the presence of Ru-4ATPP only in its thiolester form but associated both through the terminal amino group and through the thiolester group in a bent position of the spacer arm.

The catalytic participation of a capped Au(111) surface is an unusual result but has not been excluded before. In this sense, it is interesting to mention an earlier report on the role of a SAM of 4-ATP on gold in the electrochemical polymerization of aniline.[8]

Additionally, we decided to perform *ab initio* calculations of the simplest system: 4-ATP. The delocalized π system of the aromatic ring is extended over the amino group but does not include the thiol. This favors a high negative density on the nitrogen atom, an important factor when considering a nucleophilic attack on the carbonyl group of the thiolester isomer as represented in Fig. 5.

The presence of terraces and adatoms on the Au(111) surface should have favored the necessary vicinity between the carbonyl and the amino groups of self-assembled Ru-4ATPP in order to carry out the nucleophilic attack. Although a sulfur atom in a thiolester moiety cannot provoke a high partial positive charge over the carbon (C=O) atom the relatively weak S–C(=O) bond would favor the proposed nucleophilic attack by the electronically rich amino groups.

It can be assumed that the desorbed Ru-4ATPP, in equilibrium with the associated form, does not completely separate from the gold surface, achieving a position in which the free amino group could interact with the thiolester carbonyl group and provoke its substitution (Fig. 5). This criterion is based on the characteristics of the CV of Ru-4ATPP (Fig. 2) where the oxidative reabsorption peaks are of very low intensity. Moreover, the desorbed Ru-4ATPP could present strong intramolecular interactions (mainly π–π stacking) with the remaining self-assembled molecules present in the formed SAM.

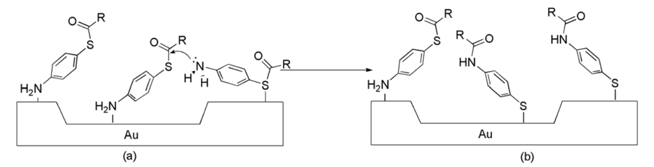

**Fig. 5** Schematic representation of the possible mechanism for the isomerization of self-assembled Ru-4ATPP: (a) the nucleophilic attack of a free amino group and the direct weakening interaction of the sulfur atoms of the thiolester with the gold surface are represented; (b) the formed amido isomer. Individual spacer arms were represented for the sake of simplicity, where R represents the porphyrin and the second chain.

A direct interaction of the sulfur atoms of the thiolester group with gold, a process that weakens the S–C(=O) bond, should have played an important role in the isomerization process. Considering this possibility, an additional experiment was carried out. Ru-4ATPP was set to interact with $AuCl_3$ and the resulting product was characterized by a $^{13}C$–$^{1}H$ Heteronuclear Multiple Bond Correlation (HMBC) experiment (Fig. S3 in ESI†). The HMBC spectrum of Ru-4ATPP (in DMSO-$d^6$) presented a signal at 199.7 ppm corresponding to the carbon of the thiolester group. This carbonyl group showed cross peaks with the aliphatic protons at 3.38 and 4.21 ppm, which are two and three bonds away, respectively (see S3 in ESI†). No other carbonyl signal was recorded. When the same experiment was repeated for ten days after preparing the Ru-4ATPP solution no variation was observed (Fig. S4 in ESI†). The corresponding HMBC experiment for an equimolar mixture of Ru-4ATPP and $AuCl_3$ (in DMSO-$d^6$) gave a signal at 174.5 ppm (no signal at 199.7 ppm) that showed cross peaks with the protons mentioned before (Fig. S3 in ESI†). This result suggests the complete isomerization of the thiolester isomer into the amido one, a process that should have been favored by the high mobility and accessibility between both reagents in solution. The isomerization process should have been induced by the strong interaction between two "soft" atoms: Au(III) and S.

The determination by HMBC of a unique species, the amido isomer of Ru-4ATPP, indicates that the only interpretation possible for the formation of a mixed SAM on gold is the isomerization process. The differences between Au(III) and metallic gold, being both soft, permit us to make such comparison. We took into consideration that when a sulfur donor atom interacts with gold, at any oxidation state, a Au(I)–S bond is expected to be formed. The complete isomerization in the presence of $AuCl_3$ should be attributed to the absence of the steric impediments that are present when the process occurs on a gold surface.

The unavoidable irregularities of the gold surface due to the presence of terraces and adatoms should have also favored the interactions with the sulfur atoms weakening the thiolester bond.

## 4. Conclusions

A thiolester derivative was obtained when 4-ATP was condensed to carbonyl [13,17-bis(propanoic acid)-2,7,12,18-tetramethylporphyrinato]ruthenium(II). The resulting Ru-4ATPP was self-assembled on gold surfaces initially through its two free amino groups according to CV determination. Over time, a slow isomerization took place to give its amido isomer, a process that has been attributed to the catalytic effect of gold. In this isomerization the strong interaction between two soft elements (Au and S) should have played an important role, since a complete isomerization was observed when Ru-4ATPP was set to interact with $AuCl_3$ in solution.

We have observed that the self-assembly of amino groups on gold is a stable and thermodynamically favored process, a fact first reported by us based on CV determination.

Self-assembled monolayers can change the work function of gold surfaces in such a way that they could catalytically favor different types of reactions. More reports in this direction should be expected in the near future. At present we are studying other catalytic processes of sulfur-containing SAM on gold surfaces, a novel topic with perspective applications.[38]

## Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support of the project MO 274/24-1. Dr Ana Lilian Montero Alejo and Joel Mieres for the theoretical calculations and Johanes Stelten for the NMR determination are also acknowledged.

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