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Electro-catalytic Scission of Carbon-Iodine Bonds. Building of SAMs at Gold Surfaces through Long Chain Primary Radical Adsorption

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Abstract

Primary alkyl iodides (RI) are reduced at smooth gold electrodes in polar organic solvents such as N,N-dimethylformamide (DMF) in the presence of divers tetraalkylammonium salts (TAAX). Beside a main two-electron step currently observed at potential > -2.0 V vs Ag/AgCl, a bell-shaped step appears with all organic iodides within a potential range between -0.6V to -1.2V. This peak does not depend on the organic substrate concentration, its current is proportional to the scan rate in voltammetry; it disappears at the second scan. These features arise form slow adsorption of the RI at gold, followed by an electro-catalytic reduction induced by the metal. It is expected that this (simple) process allows the formation of alkyl radicals readily adsorbed at the metal surface and thus produced layer strongly inhibits the main cathodic step at more negative potentials. With linear chains in C_{10}, C_{12}, C_{16} and C_{18}, the coverage of gold leads to self-assembled monolayers (SAMs). The compactness of this coverage was found to be about 10^{-10} mol cm^{-2}.

Key words: Gold electrodes; Electro-catalysis; Primary alkyl iodides; Grafting onto gold; Reduction of alkyl halides.

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1. Introduction

The discovery of new solid electrodes for achieving specific reactions and/or building new surfaces remains an important goal. Until now, within a broad cathodic range, carbon (graphite or glassy carbon) as well as platinum electrodes are by far the most used [1] with,

however, several important experimental limitations. In the field of the cathodic reduction of alkyl halides, several materials were proposed for specific electro-catalytic reactions [2]. When the use of gold as electrode material is concerned, its successful applications worthy of interest are apparently limited. Its association with palladium permitted to obtain exceptional catalytic gain in the scission of carbon-halogen bonds [3]. Also, let us quote the unexpected reaction of gold with 1,3-dibromopropane and the formation of Au nanoparticles reinforcing the electrocatalytic role of the surface in the overall reduction process [4]. Additionally, the use of Au could strongly influence the cleavage reaction of allylic and propargylic bromides [5] leading to the coverage of Au interface with unsaturated (and therefore reactive) organic layers.

On the other hand, linear alkanes were reported to adsorb at gold; binding energy is 14-81 kJ mol^{-1} [6]. Specific adsorption of alkyl chains at Au(111) [7] occurs with parallel orientation of the C-C-C plane to the surface. Metastable adsorption of MeI at Au(100) [8] also occurs (in first layer) with the C-I bonds parallel to the surface, practically without decomposition, though iodoheptane largely decomposes at Au(111) [9]. A pre-reaction of iodoalkanes with gold was also reported creating Au-C and Au-I bonds [10].

The goal of this contribution is now to specifically renew the interest for gold as electrode material within the field of the cathodic cleavage of primary alkyl iodides RI. As shown in this note, there is preliminary adsorption and further catalytic reduction of RIs within a potential range between -0.7V and -1.2V. A robustly attached alkyl layer concomitantly formed during this process inhibits further electron transfers. With long alkyl chains, SAM building at Au surfaces could occur. Then, dense coverages were established when RIs are marked with redox groups, here ferrocene moieties.

2. Experimental

2.1 Electrochemical procedure; salts and solvents

In this study, the results essentially concern solutions of tetra-*n*-butylammonium and tetramethylammonium tetrafluoroborate ($TBABF_4$ and $TMABF_4$) in dimethylformamide (DMF) purchased from Merck (quality for syntheses). Additionally, solutions of TBAI and $TBAPF_6$ were also tested. The supporting salt concentration was in all cases fixed at 0.1 M. It is worth mentioning that procedures given hereafter do not require extremely dry solutions (water content <1000 ppm). All electrochemical experiments were performed under inert atmosphere bubbling dry argon through the solution.

All potentials are given versus aqueous Ag/AgCl(sat). The electrochemical instrumentation has been previously described [5,11].

2.2. Working electrodes

All the electrodes used in voltammetry had apparent surface area of 0.8 mm^2. Before being used as electrode materials, gold and glassy carbon (GC) surfaces were carefully polished with silicon carbide paper (Struers 500 and 1200) or with Norton polishing paper (type 02 and 03) and rinsed with water, then alcohol and at last with acetone. Finally, each electrode was dried with a hot air flow during about 30 s. Coulometric measurements and electrolyses of alkyl iodides reported in this work were carried out using three-electrode cells with a total catholyte volume of about 5 to 10 mL. A fritted glass separated the two compartments.

2.3. Organic materials

All primary alkyl iodides were purchased from Aldrich and used without any additional purification. Ferrocene derivatives quoted in this article were synthesized according to a previously described method [11].

3. Results

The unexpected behavior of primary RIs at smooth gold electrodes could be summarized through different voltammetric curves displayed in Figure 1, part A. Thus, taking as example a long chain iodide ($C_{12}H_{24}I$, denoted in the following as $C_{12}I$), several scans shown in curves 1 appear to display the reduction step (at -2.6 V!) with a progressive negative shift of the half-peak potential and a tail-crossing of the backward branch. At GC under similar conditions (curve 2), a two-electron wave is observed at much less negative potentials (-2.15 V). Such "anti-catalytic" behavior of gold is surprising since some examples of electro-catalysis by this metal have been already noticed, especially with aliphatic halides. When scrutinizing the first scan displayed in 1 within a potential range between -0.5V and -1.5V, one may discern a subtle peak around -1.2 V. At higher sensitivity, as displayed in curves 3 (first scan), a quite well symmetrical peak becomes clearly seen (E_p = -1.18 V) which is ascribed to the reduction of a compact layer of adsorbed RI molecules. The fact that in second scan this initial current has practically disappeared suggests the reduction of the RI layer followed by the immobilization of $R^{\bullet}$ radicals resulting in a compact surface coverage. Several experiments

were performed in order to specify the nature of this layer and the conditions of its formation: (i) the intensity of the initial layer does depend (after a standby of 2-3 min) on the concentration of RI; (ii) its reduction peak is roughly linear with the scan rate between 20 and 500 mV s^{-1}; (iii) after one scan, the reduction peak of RIs cannot be recovered anymore by stand-by during several minutes attesting chemical stability of the deposit covering gold surface; (iv) inhibiting character of thus formed layer can be checked, which justifies the strong shift of reduction of soluble RI towards more negative potentials (E < -2V); (v) integration of the peak current of the absorbed RI, whatever the conditions (for [RI] > 2 mmol L^{-1} and v = 50 mV s^{-1}), permits to propose an average superficial concentration of fixed alkyl chains, e.g. with C_{16}, as $\Gamma_R = (8\pm2)\times10^{-9}$ mol cm^{-2}. With the surface roughness factor possibly nearing 0.5, these layers were assessed to be close to compact. With C_8 and C_{18}, the values of Γ_R are 4.0×10^{-9} and 6.9×10^{-9} mol cm^{-2}, respectively, coherent with the above value for C_{16}.

A large panel of 1-iodoalkanes was tested (from 1-iodoethane, 1-iodopropane, 1-iodobutane, 1-iodohexane to 1-iodopropybenzene); all of them showing the formation of a robust alkyl layer (see also Figure 1 B). However with alkyl chains shorter than 8 carbon atoms, the peak currents of the adsorbed RIs were found to be larger. This could be explained by partial reduction of $R^{\bullet}$ (then implying a global two-electron reduction of RI) without concomitant adsorption and reduction (possible prominence of the step 3, Scheme 1). As is shown hereafter, this does not impede at all the formation of compact layers and only implies significantly higher amounts of electricity (several scans up to -1.6 V are necessary for the disappearance of the pre-peak).

Figure 1C depicts Nyquist plots for the reduction of 1,2,4,5-tetracyanobenzene (TCB) in CH_3CN/0.1 M Bu_4NPF_6 at Au electrodes modified with C_8, C_{12} and C_{16} chains by means of constant potential electrolyses of the corresponding alkyl iodides ($\approx 3\times10^{-2}$ mol L^{-1}) at -1.0 V until nil current (amount of electricity 0.5×10^{-3} C). Charge transfer resistances R_{CT} of the layers formed with C_8, C_{12} and C_{16} (41.6, 87 and 198 kohm, respectively) are particularly coherent and underline the robustness of these organic layers.

Furthermore, in order to calculate superficial concentrations of immobilized alkyl chains at smooth Au, the RIs (in C_6 and C_{12}) labelled with ferrocene moieties were used as displayed in Figure 2. With the hexyl chain, the compactness was obtained after several scans (shown in curve 3). The average coverage (obtained from curves A4 and B3) found for the hexyl chain is $\Gamma_6 = (10\pm2)\times10^{-10}$ mol cm^{-2} while the value for a SAM (grafting of C_{12} chains) is quite similar, $\Gamma_{12} = (8\pm2)\times10^{-10}$ mol cm^{-2}. These amounts are significantly smaller than those

obtained from the integration of pre-peaks directly from the voltammograms of RIs but are quite perfectly coherent with the values reported for long chains thiols adsorbed onto Au. Thus, a theoretical surface coverage for a compact layer of alkyl ferrocene, based on the assumption that ferrocene species can be represented as a sphere of 6.6 Å in diameter, is available (4.8×10^{-10} mol cm^{-2} [12]); this value has been confirmed by the experiment (5×10^{-10} mol cm^{-2} for a planar Au electrode [13]).

4. Conclusion

This work bears out two closely associated features of smooth gold: to adsorb and to catalytically reduce primary alkyl iodides within a potential range where electro-generated free radicals are not yet reduced. As a result, alkyl layers are easily formed on the metal interface. Such organic coverage can be made compact ($\Gamma \cong 10^{-10}$-10^{-9} mol cm^{-2}) by means of repetitive scans (chains shorter than C_8) or by fixed potential deposits at potentials ca. -1V. Such deposits appear to be robustly attached to the metal albeit can suffer from the contact with air and from sonication. The reported process looks quite akin to the arylation [14] of carbons by means of aryl-diazonium salts (primary adsorption state followed by an *in situ* electron transfer). This preliminary electrochemical approach opens new perspectives for a diverse decoration of gold using substituted alkyl iodides of the type FG-C_n-I with a large palette of organic and organometallic functions (FG) that are cathodically inactive at E > -1.2V. Lastly, let us mention that secondary and tertiary alkyl iodides exhibit comparable features.

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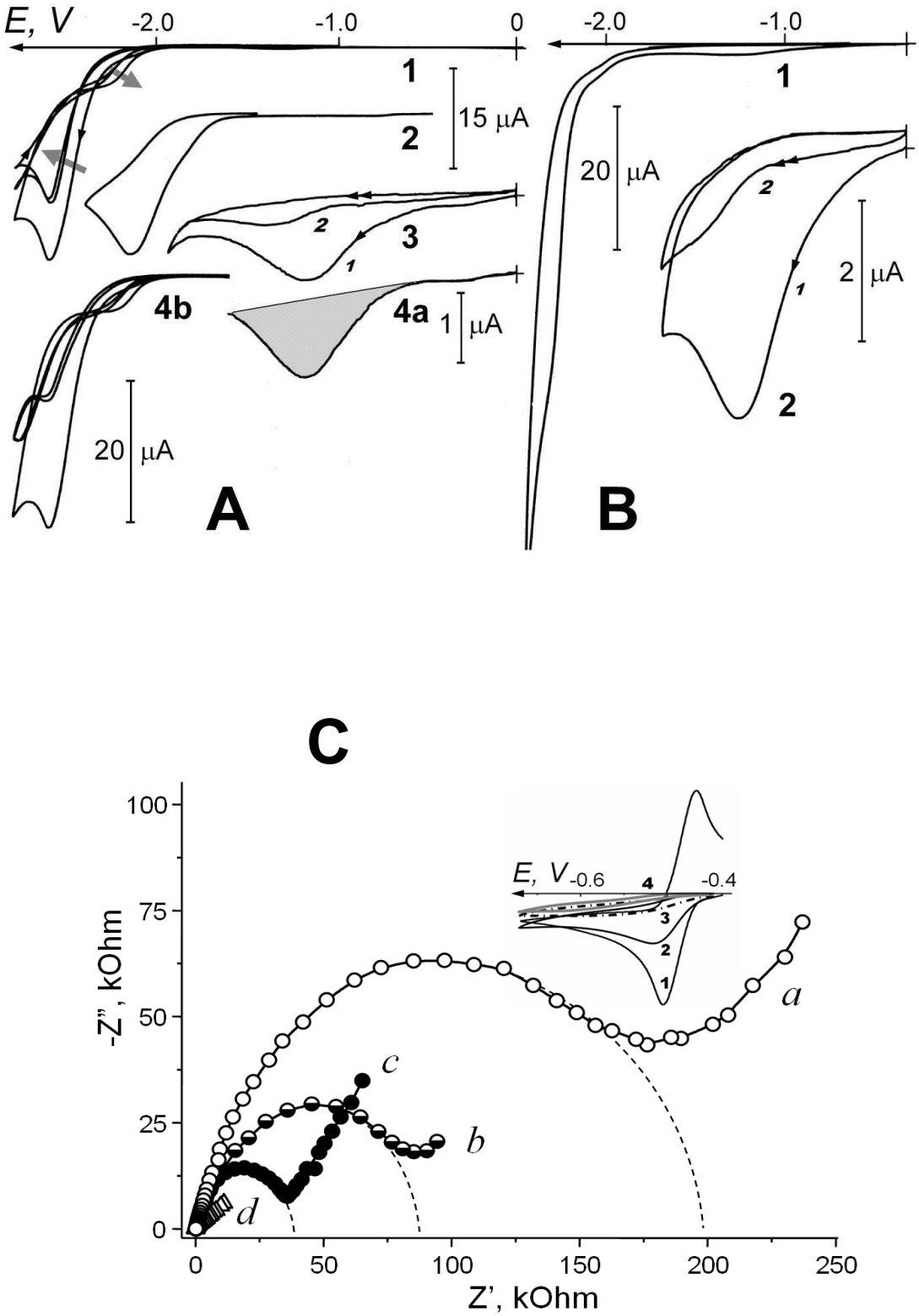
Figure Captions

Figure 1



Voltammetry of long chain primary RIs at smooth Au and GC electrodes in DMF + $TBABF_4$. Electrode surface area: 0.8 mm^2. Polishing with silicon carbide (Struers 1200) papers.

A) 1-Iodohexadecane (14.2 mmol L^{-1}). Scan rate: 50 mV $s^{-1.}$

1) Multiple scans at Au.

2) Voltammetry at GC.

3) Gold electrode: scans between 0V and -1.9 V. Standby at 0V for about 2 min.

4) Voltammetry showing the catalytic pre-wave obtained after a hold of 2 min at -1.6 V and evidencing an inhibited reduction of the RI at potentials < -2.5V. Beware the change of intensity scale before and after -1.6V.

B) Voltammetry of 1-iodododecane (5.2 mmol L^{-1}) in DMT + $TBABF_4$. Global curve in 1 (scan rate 50 mV s^{-1}) and the focus on the branch up to -1.7 V (100 mV s^{-1}).

C) Nyquist plots for the reduction of 1,2,4,5-tetracyanobenzene (TCB) in CH_3CN/0.1 M Bu_4NPF_6 at Au electrodes modified with: (*a*) C_{16}; (*b*) C_{12}; (*c*) C_8. (*d*) Same electrode after removal of the grafted layer. E = -0.45 V. ΔE = 10 mV. Frequency range: from 1 MHz to 0.01 Hz. In the inset: Voltammograms of reduction of TCB at these electrodes: (1) bare Au (1); with grafted C_8 (2), C_{12} (3) and C_{16} (4), respectively.

Figure 2

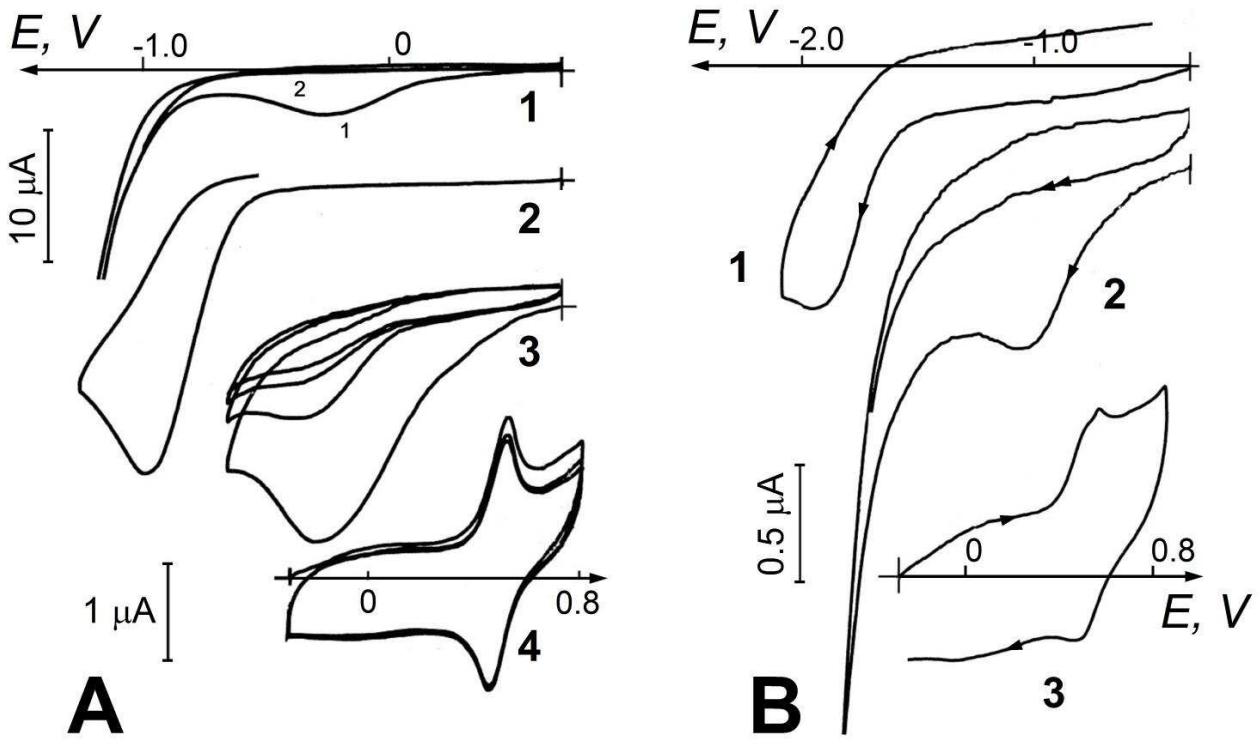


Figure 2 Au RI 13

Voltammetry of α,ω-iodo-*n*-alkylferrocenes in DMF/$TBABF_4$ at solid electrodes. Surface area: 0.8 mm^2.

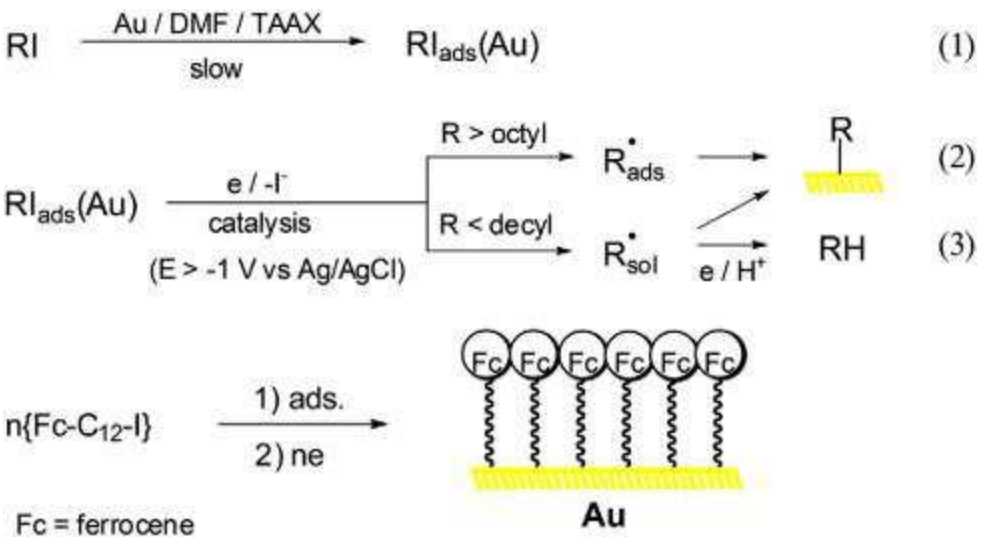
A) I-C_6-Fc (12 mmol L^{-1}).

1) At Au. 2) At GC. 3) Multiple scans at gold between -0.3 and -1.6 V. Scan rate: 50 mV s^{-1}. 4) Oxidation of the deposit obtained in 3. Scan rate: 200 mV s^{-1}.

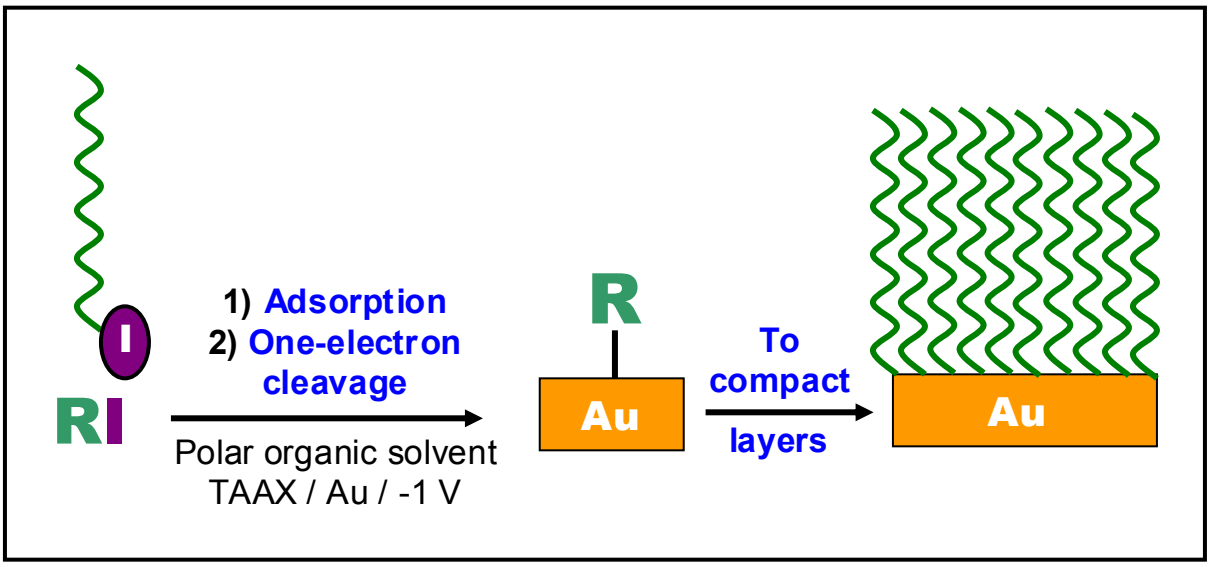
B) I-C_{12}-Fc (3.4 mmol L^{-1}).

1) Voltammetry at GC. 2) At Au, scan rate: 100 mV s^{-1}. 3) Oxidation of the deposit obtained from two sweeps shown in 2. Scan rate: 200 mV s^{-1}.

Scheme 1



Scheme 1
Proposed mechanism for the coverage of smooth gold surface with alkyl chains under electron transfer at E < -1.2 V.



Graphical Abstract