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Electro- and Photografting of Carbon or Metal Surfaces by Alkyl Groups

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Electrografting and photografting of alkyl iodides are achieved on carbon and metals (Fe, Cu, Au, and TiN). An alkyl radical is deemed responsible for this reaction. The attachment of the alkyl layer on the surface is examined by ellipsometry, water contact angle, IR, ToF-SIMS, XPS spectroscopy, and electrochemistry. The layers are strongly bonded to the surface as they resist ultrasonication. Multilayers are formed, indicating that the radicals also react with the first attached layer.

Introduction

Coating a metal with an organic layer permits us to obtain a material that retains the mechanical properties of the metal but evidences the surface properties of the organic layer. These properties can be varied nearly at will due to the flexibility of organic synthesis. One can distinguish two kinds of such composite metal–organic materials. For some of them, the organic coating is only deposited and the bonds between the metal and the organic layer are weak; this is, for example, the case of home appliances where a layer of polymer is deposited on steel and also of cars where the steel body is protected from corrosion by a polymeric layer through a complex process. Other devices require stronger bonds, such as carbon–epoxy composites; in such a case, the carbon fibers undergo an oxidative treatment that improves the bonding to the epoxy matrix.

The formation of stronger bonds between the metal and the organic layer can be achieved either from the metal itself or from surface oxides. The most common process starting from surface oxide is the reaction of trichloro- or trialkoxysilanes with surface OH groups on silica or metals such as iron.^{1,2}

There are a limited number of methods that permit direct bonding of the organic groups to the metal. The self assembled monolayers (SAMs) on gold is certainly the most popular one. It provides true monolayers by simply dipping the gold plate in a solution of thiol. However, the gold–sulfur bond is not very strong and it is even weaker on industrial metals such as iron.³

The electrografting of vinylic compounds directly on metal surfaces was the first process to be discovered in 1982. It permits the establishment of a strong covalent bond between the metal and a thin (5–10 nm) layer of polyvinyl polymer (polyacrylonitrile, polymethacrylate,...). Both the characterization of the layer and the grafting mechanism have been reviewed.⁴ The



Figure 1

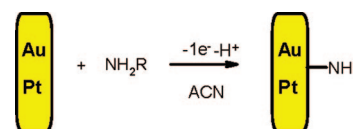


Figure 2

one-electron reduction of the vinylic monomer produces a distonic radical anion. The radical reacts with the surface while the anion starts an anionic polymerization that stabilizes the metal–organic species by pushing the negative charge further and further away from the negatively charged surface (Figure 1).^{4,5}

The second method was first applied to carbon^{6,7} and then to metals.^{8–11} It involves the electrochemical oxidation of a primary amine and leads to a metal–NHR assembly. If neat ethylenediamine is oxidized on platinum, a layer of polyethylenimine is obtained. However, amines are oxidized at rather positive potentials (~1.6 V/Ag/AgCl), much more positive than the open circuit potential of industrial metals, and therefore, only noble metals can be derivatized in this way. The mechanism has been established; it involves the formation of the radical-cation of the amine, the loss of hydrogen from the α -carbon, and finally the migration of hydrogen from the nitrogen to the α -carbon resulting in an aminyl radical that reacts with the surface. More recently,¹¹ it has been shown that the same reaction takes place spontaneously on metals such as Au, Pt, Fe, and Cu (Figure 2).

A third method was first described on carbon¹² and then extended to metals,¹³ metal oxides,^{14,15} semiconductors,¹⁶ and polymers.¹⁷ It was reviewed some time ago.¹⁸ It involves the electrochemical reduction of diazonium salts in aprotic or aqueous medium. It leads to a layer from a few nanometers to a few micrometers thick of a polymer with a polyphenylene structure. The mechanism¹⁹ involves the transfer of one electron concerted with the cleavage of the aryl–N₂ bond to give an aryl radical that reacts with the surface (Figure 3).

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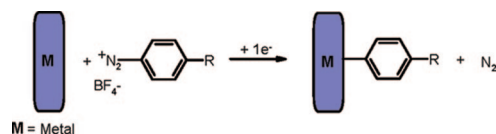


Figure 3

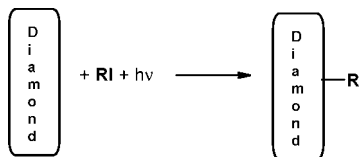


Figure 4

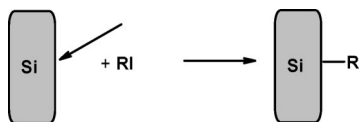


Figure 5

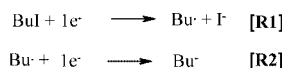


Figure 6

For the three methods described above, electroreductive grafting of vinylics^{20,21} and diazoniums^{22–24} and the electrooxidative grafting of amines,¹¹ it was possible to demonstrate experimentally the existence of a metal–organic bond. In addition, density functional theory (DFT) calculations of carbon and metals surfaces derivatized with diazonium salts support the existence of a covalent bond.^{22,23}

Concerning the reactions of alkylhalides with surfaces, several reactions have been previously reported. The photografting of alkylhalides on diamond surfaces (hydrogenated or not) has been reported using X-ray beams²⁵ or UV irradiation with an Hg arc at $\lambda < 305$ nm (Figure 4).²⁶

On porous or monocrystalline hydrogenated Si, the electrochemical reduction of alkyl bromides or iodides leads to the formation of Si–C bonds. The mechanism has been discussed involving either alkyl anions or radicals.²⁷

Alkyl groups have also been grafted on non hydrogenated Si by mechanical scribing the surface in the presence of alkyl halides (iodides, bromides or chlorides) (Figure 5).^{28,29}

It is worth examining the results of the electrochemical reduction of alkyl halides, as it can shed some light on the possibility of electrografting these compounds.³⁰ By cyclic voltametry in dimethylformamide (DMF), *t*-butyliodide³⁰ presents a first monoelectronic wave followed, at more negative potential, by a second of smaller height. The first wave is related to a one electron transfer concerted with the cleavage of the C–I bond, it corresponds to the formation of the *t*-butyl radical according to reaction [R1] (Figure 6), the second wave is related to the reduction of the radical into the *t*-butyl anion [R2]. Therefore, the reduction of *t*-butyliodide at the level of the first wave corresponds to the formation of an alkyl radical that is redox stable.

For *sec*-butyliodide, the second wave is very close to the first one, but for *n*-butyliodide, the authors observe a single two-electron wave indicating that the radical is reduced at a similar or less negative potential than the starting halide. However, by setting the potential at the foot of the wave in the case of *n*-butyliodide, it should be possible to produce *n*-butyl radicals without entirely reducing them to carbanions. With bromides, a single two electron wave is always observed. One could hope

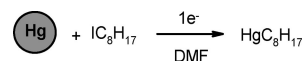


Figure 7

that the redox stable *sec*-butyl or *t*-butyl radicals could react with the surface; however, for steric reasons the reaction should be rather inefficient as shown with the radicals obtained from secondary and tertiary amines.¹¹ Therefore, the best electrografting results should be obtained with primary alkyl iodides or bromides by setting the potential at the foot of the first voltametric wave.

The electrochemical reduction of alkyl halides on mercury has been the subject of many investigations.³¹ The formation of organomercury compounds is nearly always observed.^{31–33} The reduction of 2-bromooctane by Ni(I) salen generated at a Hg electrode gives di-*n*-octylmercury among other products.³⁴ 2-Iodooctane on a mercury electrode in DMF leads to the *sec*-octyl radical stabilized by complexation with mercury, this radical disproportionate to give di-*sec*-octyl mercury (24%).³⁵ Under the same conditions, 1-iododecane leads to large amounts of didecyl mercury. The yield reaches 99% and decrease with the potential along with the reduction of the radical into the carbanion.³⁶ Under similar conditions 1-iodo-5-decyne yields 5-decynylmercury radicals which disproportionate into di-5-decynylmercury.³⁷ These reactions of alkyl radicals with mercury are analogous to the reaction of the same radicals with solid metals. It should be noted that secondary radicals are complexed by mercury (Figure 7).

The reduction of alkyl iodides has also been thoroughly investigated on palladium in aprotic solvents.^{38,39} The first one electron transfer, leading to the alkyl radical, takes place on palladium in DMF at much less negative potential than the two electron transfer on glassy carbon (−1.56 and −2.00 V/SCE, respectively, for 1-iodooctane). Imaging of the surface shows the presence of a polymer and of Pd aggregates. On Cu, Pd electrodes or Cu/Pd electrodes in the presence of iodine the one electron catalytic cleavage of R–Br bonds is also observed.^{40–42} Copper exhibits important catalytic capabilities particularly in the series of α,ω -dibromoalkanes.⁴² The potential of two electron waves shifts to positive values by nearly one volt from glassy carbon to copper. The formation copper–organic complexes has been observed by scanning electron microscopy. Catalytic effects have also been observed on silver electrodes.^{43–45} Passivation of Sn electrodes during the electrochemical reduction of methyl and ethyl halides was also observed.⁴⁶

In all these studies it was shown that the catalytic effect is related to the interaction between the substrate and the catalytic surface, it leads to the formation of radicals interacting with the surface and therefore ready for the attachment to the surface.

The spontaneous reactions of CF₃I with Cu (111) and of diiodomethane on Ni (110) have also been observed under ultrahigh vacuum, leading to surface-bound CF₃ and CF₂I species.^{47,48} In a similar way, on GaAs, under ultrahigh vacuum, CF₃CH₂I and CH₂I₂ lead to the chemisorption of CF₃CH₂ and CH₂ on the surface.^{49,50}

The above results point to the feasibility of electrografting alkyl halides on metal surfaces. The electrochemical reduction of alkyl halides can produce radicals under properly chosen conditions. Radicals (vinylic radical anions,⁴ aminyl,⁶ and aryl radicals¹²) have been previously shown to react with metal surfaces. In addition, alkyl radicals are able to react with mercury and with Pd, Ag, and Sn.

It is the aim of the present paper to describe a method for the electrografting of alkyl groups to metal surfaces through the electrochemical reduction of alkyl halides.

TABLE 1: Samples and Their Preparation

sample	grafted compound	conditions ^g	symbol	thickness/nm
Fe ^a	C ₆ H ₁₃ I 1 (0.1M)	−2.3 V, 30 min	Fe1^{ele}	6.5 ± 0.4 er
Cu ^b	id	−1.5 V, 30 min	Cu1^{ele}	
Au ^c	id	−2.3 V, 30 min	Au1^{ele}	
GC	id	−2.8V, 30 min	C1^{el}	
Fe ^a	I(CH ₂) ₂ C ₈ F ₁₇ 2 (0.01 M)	−2.4 V, 30 min	Fe2^{el}	78.9 ± 2.5
Cu ^b	id	−2.2V, 30 min	Cu2^{el}	
Au ^c	id	−2.6 V, 30 min	Au2^{el}	
GC	id	−2.4V, 30 min	C2^{el}	
Fe ^a	I(CH ₂) ₂ C ₈ F ₁₇ 2^f	phot ^d 150 s	Fe2^{phot}	10.4 ± 1.9
Cu ^b	id	id	Cu2^{phot}	
Au ^c	id	id	Au2^{phot}	

^a Mild steel polished down to 1 μm. ^b Deposited on a Si wafer. ^c Deposited on a Si wafer. ^d 600 W high pressure mercury lamp. ^e Grafting was also achieved at −2.1 and −2.5 V/Ag/AgCl to investigate the effect of potential. ^f Dissolved in acetone that rapidly evaporates under the heat of the lamp. ^g All potentials referred to Ag/AgCl.

The following compounds have been investigated: IC₆H₁₃, **1**; ICH₂CH₂C₈F₁₇I, **2**. Different surfaces have been examined: glassy carbon (GC), a noble metal (gold), industrial metals (iron, copper), and a metal used in microelectronics (TiN). The modified surfaces will be termed by the symbol of the metal followed by that of the alkyl iodide and the method of preparation electrochemical or photochemical, for example, **Fe1^{el}** or **Cu2^{phot}**. When necessary, the conditions of preparation are indicated **Au1^{el}** (−2.3V, 30 min).

Results and Discussion

Electrografted layers and photografted layers were prepared in acetonitrile (ACN + 0.1 M NBu₄BF₄) according to the condition summarized in Table 1. The layers formed in these ways are strongly attached to the metal, as they have all been ultrasonicated for 10 min in acetone (see below).

The thickness of the layers are reported in Table 1. These heights point to the formation of multilayers, for example a fully extended −C₆H₁₃ chain should be close to 0.8 nm and the height of **Cu1^{el}** (−1.5 V, 30 min) would therefore correspond to 8 chains. Similarly a −(CH₂)₂C₈F₁₇ chain is approximately 1.32 nm and **Cu2^{phot}** (40 s) represents also about 8 such groups on top of each other. Therefore the electrografting or photografting of alkyl iodides does not provide monolayers, but rather nanometric thick multilayers.

Water Contact Angle. As could be expected, surfaces become hydrophobic after electrografting by **1** and even more by **2**. This is shown in Table 2. The small variation observed with Fe (both for photochemical and electrochemical grafting) is likely related to the low coverage of the surface. If one compares the two grafting methods, it appears that the layer is more compact on copper and less compact on gold when using photochemistry.

Infrared Characterization. The IRATR spectra of these electrografted and photografted layers have been recorded. Table 3 summarizes the absorptions in the region of CH stretching for samples grafted with **1** (Figure 8) and Table 4 the CF absorptions for samples grafted with **2** (Figure 9). There is a general agreement of the peak positions of **Fe1^{el,phot}**, **Cu1^{el,phot}**, and **Au1^{el}** with that of the starting material C₆H₁₃I but also with that of alkylthiols on gold.⁵¹ This demonstrates the presence and the integrity of the alkyl chains on the surface of the grafted metals. These spectra can also be discussed by comparison with the spectra of alkyl thiols on gold with chains

TABLE 2: Water Contact Angles on Bare and Modified Surfaces

sample	bare surface	modified surface
Cu	37 ± 3 ^a	Cu1^{el} 83 ± 1°
		Cu2^{el} 87 ± 4°
		Cu2^{phot} 98 ± 3°
Au	66 ± 3 ^b	Au1^{el} 80 ± 4°
		Au2^{el} 88 ± 4°
		Au2^{phot} 68 ± 3°
Fe	41 ± 3 ^c	Fe1^{el} 54 ± 4°
		Fe2^{el} 60 ± 4°
		Fe2^{phot} 62 ± 4°
C	64 ± 2 ^c	C1^{el} 87 ± 1°

^a Previously dipped for 30 s in 5% citric acid. ^b Previously rinsed with acetone and ultrapure water. ^c Polished down to 0.04 μm with alumina and rinsed with acetone and ultrapure water.

ranging from C₃ to C₂₁. The ν_a(CH₂) mode has been previously⁵¹ used as an indicator of the lateral interaction of polymethylene chains. The corresponding peak of a crystalline polymethylene chain (2920 cm^{−1}) is 8 cm^{−1} lower than for the liquid state (2928 cm^{−1}), whereas the ν_s(CH₂) is 6 cm^{−1} lower in the crystalline (2850 cm^{−1}) sample than in the liquid (2856 cm^{−1}). No such trend is observed when comparing neat liquid IC₆H₁₃ with the spectra of **Fe1^{el,phot}**, **Cu1^{el,phot}**, and **Au1^{el}**. This indicates that there is no organization of the layer as in short alkyl thiols on gold (**AuS(CH₂)₅or7 CH₃**) but at the difference of long chain thiols (**AuS(CH₂)_{15,17,or21} CH₃**) on gold. The long (n = 15–21) alkyl chains of thiols on the surface of gold are tilted 20–30° from the surface normal, this results in the decrease of the νsCH₂ peak intensity by comparison with a bulk-phase thiol. Such variation is a consequence of the selection rules for surface-bound chains.⁵² Comparison of the spectra of neat IC₆H₁₃ with **Fe1^{el}** or **Cu1^{el}** does not indicate an overall orientation of the chains.

The intensity of the band at 2962 cm^{−1} (0, 1, and 0.34 relative values) was recorded after grafting iron at −2.1 and −2.3 and −2.5 V/Ag/AgCl, respectively. These relative values indicate that (i) at −2.1 V/Ag/AgCl the iodo compound **1** is not reduced and (ii) at more negative potentials −2.5 V/Ag/AgCl electrografting is less efficient, in line with the findings of Peters³⁶ who found a lesser amount of organomercuric compound at more negative potential.

The spectra of the metals electro or photografted with **2** are reported in Table 4. Figures 9 and 10 present, respectively, the spectra of **Au2^{el}** (−2.2 V, 30 min) and **Au2^{phot}** (150 s). The general agreement of the position and intensity of the spectra of **2**, **Au2^{el}** (−2.2 V, 30 min) and **Au2^{phot}** (150 s) demonstrates the grafting of the (CH₂)₂C₈F₁₇ chains on the metals. In addition to the bands reported in Table 4 two bands are present at 2991 cm^{−1} (weak) (CH stretching) that is related to the presence of the (CH₂)₂ group in the grafted molecule. A similar spectrum is observed on iron **Fe2^{el}** and copper **Cu2^{el}**. The spectra of the photografted surfaces **Fe2^{phot}** (150 s), **Cu2^{phot}** (150 s), and **Au2^{phot}** (150 s) are also presented in Table 4; they reflect the photografting of these surfaces. The spectrum of a SAM of HS(CH₂)₂C₈F₁₇ on gold has been carefully investigated by Porter.⁵³ He calculated a spectrum representative of what is expected for a randomly oriented monolayer. From the comparison of the observed and calculated spectra, he concluded that the chains are tilted ~20° to the surface normal. The qualitative similarity of the spectrum of **Au2^{el}**, of that of the starting material **2** (Figure 9) and of the spectrum calculated by Porter (ref 53, see Figure 7) clearly indicates that the copper surface has been modified by a −(CH₂)₂C₈F₁₇ group. In addition,

TABLE 3: IR Spectra of Attached Hexyl Groups. Wavelength in cm^{-1} .

$\text{C}_6\text{H}_{13}\text{I}_{\text{neat}}$	$\text{AuS}(\text{CH}_2)_{20}\text{CH}_3^a$	$\text{AuS}(\text{CH}_2)_7\text{CH}_3^a$	Fe1^{el}	Fe1^{phot}	Cu1^{el}	Cu1^{phot}	$\text{Au1}^{\text{el } c}$
2956	2965 $\nu_{\text{a}}(\text{CH}_3)$	2966	2962	2963	2962	2964	2962
	2937 $\nu_{\text{s}}(\text{CH}_3) + \text{FR}^b$	2939					
2924	2918 $\nu_{\text{a}}(\text{CH}_2)$	2921	2928	2921	2925	2920	2923
2854	2850 $\nu_{\text{s}}(\text{CH}_2)$	2852	2861	2850	2854	2854	2851

^a From ref 48. ^b Fermi resonance. ^c The spectrum is very weak, and no significant spectrum was obtained by photografting.

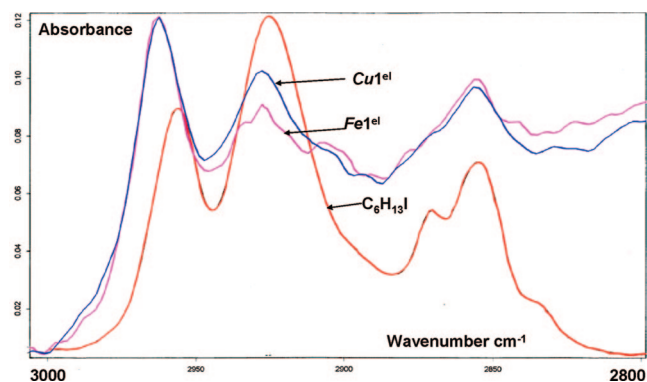


Figure 8. ATR IR spectrum of (a) neat $\text{C}_6\text{H}_{13}\text{I}$ and of (b) Fe1^{el} an iron plate electrografted with $\text{C}_6\text{H}_{13}\text{I}$ at -2.3 V/Ag/AgCl in $\text{ACN} + \text{NBu}_4\text{BF}_4$. (c) Cu1^{el} a copper plate electrografted with $\text{C}_6\text{H}_{13}\text{I}$ at -1.5 V/Ag/AgCl in $\text{ACN} + \text{NBu}_4\text{BF}_4$. The absorbance scale is different for both cases.

this spectrum is characteristic of perfluoroalkyl chains essentially lacking of ordered orientation. The 1147 and 1116 cm^{-1} absorption bands have been assigned to a $\nu_{\text{as}}\text{CF}_2$ vibration with E1 symmetry perpendicular to the chain. Based on "IR surface selection rules" which gives rise to a preferential excitation of vibrational modes with dipole normal to the highly reflecting metallic surface one would expect a very small band at 1147 and 1116 cm^{-1} if the chains were oriented perpendicular to the surface. This band is of similar relative intensity on the spectrum of **2** and Au2^{el} pointing to the disordered arrangement of the perfluoroalkylated chains. This conclusion is also supported by the large qualitative difference between the spectrum of ordered monolayers of $\text{HS}(\text{CH}_2)_2\text{C}_8\text{F}_{17}$ ⁵³ and that of Au2^{el} .

XPS. We also examined the electrografting of **2** on TiN: TiN2^{el} . TiN is a material used in the micro electronic industry as a barrier to the diffusion of copper into silicon. TiN itself shows a complex signal of Ti (22.4%) between 452.7 and 466.9 eV including contributions from $\text{Ti2p}_{1/2}$ and the doublet of $\text{Ti2p}_{3/2}$. Nitrogen (24.4%) is observed is observed between 396.9 and 403.6 eV ; the high binding energy side energy contribution to corresponds the signal of nitrides. Oxygen is present at 529.8 eV (21.4%). In addition to these contributions from the substrate, the surface shows the presence of carbon (31.7%). After electrografting at -2.6 V/Ag/AgCl (a potential necessary to compensate the large ohmic drop of this highly resistive material) for 300 s in a 5 mM solution of **2** one observes on the survey spectrum, in addition to Ti2p (18.7%), N1s (21.1%), C1s (31.9%), O1s (19.2%) and a contamination by K2p (0.22%) the presence of fluorine at 689.3 eV (8.8%). The signal of fluorine includes two components the largest one at 689 eV corresponding to the CF_2 groups and a smaller one at 684 eV which corresponds to some fluorine (probably some contaminations by the supporting electrolyte NBu_4BF_4). This indicates that even on this very resistive material electrografting is possible on all the surface of the sample ($\sim 1 \text{ cm}^2$).

ToF-SIMS (Time of Flight-Secondary Ion Mass Spectrometry). The spectrum of Cu1^{el} is particularly demonstrating of the electrografting of alkyl iodide ($\text{C}_6\text{H}_{13}\text{I}$) on metals. The

spectrum is summarized in Table 5. The fragments represent not only the alkyl chain, but also copper atoms bonded to methylene groups from the alkyl chain, therefore testifying for the covalent bonding of the alkyl chain to the copper substrate. The presence of iodine can be detected on the surface, albeit in very low amounts (for example its intensity is only one-fourth of that of $\text{Cu}(\text{CH}_2)_2$). It is likely related to the grafting of some iodine radicals that may result from the oxidation of iodide at the unseparated anode). Finally, the presence of Cu_2OH represents some oxidation of the surface in spite of the care taken to prevent it.

Table 6 shows the spectrum of Cu2^{el} . It evidence the total perfluoroalkyl chain (up to $(\text{CF}_2)_5\text{CF}_3$), some iodine as above, but also a fragment bonded to the surface $(\text{CF}_3(\text{CF}_2)_2\text{CH}_2\text{CN}^-)$ that represent the attack of the solvent (CH_3CN) by the radical resulting from the cleavage of iodine. The involvement of the solvent in the cleavage of halo compounds has already been observed in the case of aromatic halides.⁵⁵ However, it is not clear how the resulting species binds to the surface. The spectrum of Cu2^{phot} is similar although the perfluoroalkyl fragments are shorter and the surface of copper is oxidized during irradiation in the presence of air.

On TiN, (the surface of which was previously treated by dipping 10 s in $1\% \text{ HF}$), **2** (10 mM in ACN) has been electrografted either under potentiostatic conditions at -3 V/Ag/AgCl (a very negative potential necessary to compensate for the ohmic drop of this highly resistive material) or by scanning repetitively (between -1 and -3 V/Ag/AgCl at 5 mVs^{-1}). The coupons of TiN2^{el} have been examined by ToF-SIMS; the spectrum of Table 7 unambiguously confirms the presence of the perfluoro molecule on the TiN surface. Fragments corresponding to $(\text{CF}_2)_n\text{CF}_3^-$ and $\text{C}_2(\text{CF}_2)_n\text{CF}_3^-$ are likely obtained by fragmentation of the grafted $(\text{CH}_2)_2\text{C}_8\text{F}_{17}$ chain. In the $(\text{CF}_2)_n\text{NH}_3^+$ fragments, the nitrogen probably comes from the TiN surface.

Cyclic Voltammetry. The peak potentials of **1** and **2** and the number of electrons are summarized in Table 8.

Compound **1** is reduced along an irreversible bielectronic wave at quite negative potentials, on gold and GC but the peak potential on Cu shifts to a more positive value and the number of electron is equal to one indicating electrochemical catalysis by copper. Such catalytic phenomena have already been described on palladized surfaces, and on copper and silver electrodes.^{38,45} As indicated in the introduction, observation of the bielectronic wave indicates that the radical is reduced to the anion; in the spite of that, grafting of **1** on GC or Au is possible at very negative potentials. This is likely related to the concertedness of the electron transfer and the bond cleavage. The radical is formed "on the surface" of the electrode and reacts with it before being reduced. One could also hypothesize that the bond formation is concerted with the cleavage of the C–I bond. The wave of **2** is always monoelectronic indicating that the radical is surprisingly difficult to reduce. This can be related to the observation by Peters of the formation of

TABLE 4: IR Spectra of Attached (CH₂)₂C₈F₁₇ Groups^a

PFO ^b KBr	PFO ^c Ag	PFT ^d	2 ^a neat	Cu2 ^{el}	Fe2 ^{el}	Au2 ^{el}	Cu2 ^{phot}	Fe2 ^{phot}	Au2 ^{phot}	assignment
1366	1365	1372	1357	1369	1362	1362	1362	1362	1362	$\nu_s(\text{CF}_2, \text{A}_1)$
1330	1321	1335	1332	1330	1339	1338	1339	1339	1339	$\nu_s(\text{CF}_2, \text{E}_2)$
1295	1293	1295	1304		1305					$\nu_s(\text{CC}, \text{E}_1)$
1237	1251	1246	1228	1244	1233	1232	1242	1242	1242	$\nu_s(\text{CF}_3, \text{E}_1)$
1204	1216		1197	1208	1194	1206	1206	1209	1209	$\nu_a(\text{CF}_2, \text{A}_2) + \nu(\text{CF}_3)$
1146	1151	1150	1145	1151	1149	1150	1151	1151	1151	$\nu_s(\text{CF}_2, \text{E}_1)$

^a In cm⁻¹. ^b Perfluorooctanoic acid, KBr pellet.⁵⁴ ^c Perfluorooctanoic acid adsorbed on Ag.⁵⁴ ^d CF₃(CF₂)₇(CH₂₂)SH on Au (111).⁵³ ^e ATR spectrum.

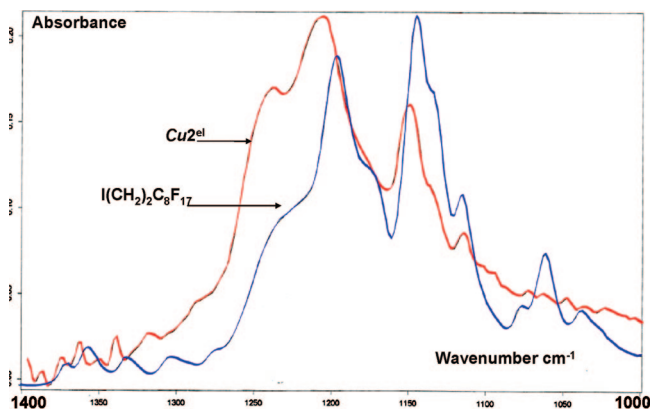


Figure 9. ATR IR spectrum of neat I(CH₂)₂C₈F₁₇ and of Au2^{el}, a copper plate electrografted with I(CH₂)₂C₈F₁₇ at -2.2 V/Ag/AgCl in ACN + NBu₄BF₄.

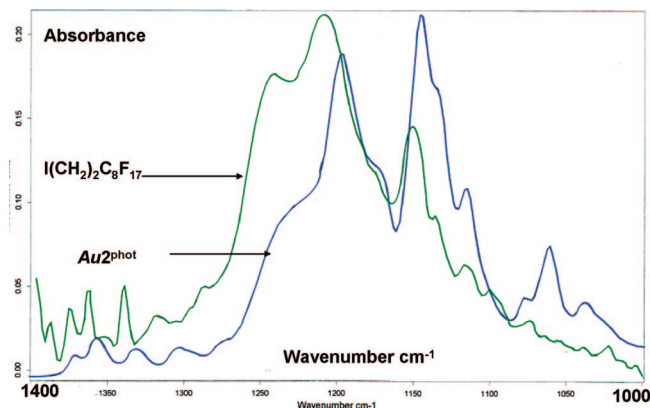


Figure 10. ATR IR spectrum of neat I(CH₂)₂C₈F₁₇ and of Au2^{phot} a gold plate photografted with I(CH₂)₂C₈F₁₇.

TABLE 5: ToF-SIMS Spectrum of Cu1^{el}

m/z^a	assignment
29.039	CH ₂ CH ₃ ⁺
43.055	(CH ₂) ₃ CH ₃ ⁺
57.070	(CH ₂) ₄ CH ₃ ⁺
71.086	(CH ₂) ₄ CH ₄ ⁺
62.940, 64.928	Cu ⁺
91.661, 92.959	Cu(CH ₂) ₂ ⁺
104.987, 106.975	Cu(CH ₂) ₃ ⁺
119.002, 120.990	Cu(CH ₂) ₄ ⁺
126.904	I ⁻
142.882, 144.870, 146.858	Cu ₂ OH ⁺

^a Calculated exact mass.

organomercuric compounds.^{31–37} The radical may be stabilized and more difficult to reduce by complexation with the surface.

After 10 scans (and homogenization of the solution) in a 10 mM solution of **1** and **2** on Au, Cu and GC the waves decrease significantly (Figures 11, 12, S1, and S2). However, this

TABLE 6: ToF-SIMS Spectrum of Cu2^{el} and Cu2^{phot}

m/z^a	sample	assignment
18.998	Cu2 ^{el} , Cu2 ^{phot}	F ⁻
30.998	Cu2 ^{el} , Cu2 ^{phot}	CF ⁺
37.997	Cu2 ^{el} , Cu2 ^{phot}	F ₂ ⁻
39.048	Cu2 ^{el} , Cu2 ^{phot}	HF ₂ ⁻
49.997	Cu2 ^{el} , Cu2 ^{phot}	CF ₂ ⁺
68.995	Cu2 ^{el} , Cu2 ^{phot}	CF ₃ ⁺ and -
62.940, 64.928	Cu2 ^{el} , Cu2 ^{phot}	Cu ⁺
78.028	Cu2 ^{el}	CH ₂ CH ₂ CF ₂ ⁺
99.994	Cu2 ^{el} , Cu2 ^{phot}	(CF ₂) ₂ ⁺
118.991	Cu2 ^{el} , Cu2 ^{phot}	CF ₂ CF ₃ ⁺ and -
126.904	Cu2 ^{el} , Cu2 ^{phot}	I ⁻
130.992	Cu2 ^{el} , Cu2 ^{phot}	C ₃ F ₅ ⁺
142.921, 144.990, 149.858	Cu2 ^{el}	Cu ₂ OH ⁺
168.989	Cu2 ^{phot}	(CF ₂) ₂ CF ₃ ⁺ and -
204.873, ^b ...	Cu2 ^{el} , Cu2 ^{phot}	Cu ₃ O ⁺
209.007	Cu2 ^{el}	CF ₃ (CF ₂) ₂ CH ₂ CN ⁻
218.985	Cu2 ^{phot}	(CF ₂) ₃ CF ₃ ⁻
221, 876, ^b ...	Cu2 ^{el}	Cu ₃ O ₂ H
268.982	Cu2 ^{el}	(CF ₂) ₄ CF ₃ ⁻
292.982	Cu2 ^{el}	C ₇ F ₁₁ ⁻
319.045	Cu2 ^{el}	(CF ₂) ₅ CF ₃ ⁻
368.976	Cu2 ^{el}	(CF ₂) ₆ CF ₃ ⁻

^a Calculated exact mass. ^b And other isotopes.

TABLE 7: ToF-SIMS Spectrum of TiN2^{el} Electrografted on TiN

m/z	assignment
18.998	F ⁻
30.998	CF ⁻
37.997	F ₂ ⁻
67.038	CF ₂ NH ₃ ⁻
68.995	CF ₃ ⁻
101.001	CHFCF ₃ ⁻
117.020	CF ₂ CF ₂ NH ₃ ⁻
118.991	CF ₂ CF ₃ ⁻
167.024	(CF ₂) ₃ NH ₃ ⁻
168.989	(CF ₂) ₂ CF ₃ ⁻
192.998	C ₂ (CF ₂)CF ₃ ⁻
217.014	(CF ₂) ₄ NH ₃ ⁻
243.985	C ₂ (CF ₂) ₃ CF ₃ ⁻
267.011	(CF ₂) ₅ NH ₃ ⁻
317.007	(CF ₂) ₆ NH ₃ ⁻
367.004	(CF ₂) ₇ NH ₃ ⁻
391.004	C ₂ (CF ₂) ₆ CF ₃ ⁻
417.001	(CF ₂) ₈ NH ₃ ⁻

decrease is much slower than with diazonium salts; in this last case, the wave nearly disappears on the second scan. This is confirmed by the chronoamperograms (Figures S5–S8) where the current decreases very slowly indicating (i) that electrografting is not very fast and (ii) that the layer is not very compact as the current continues to flow after at least 900s (Figures S5–S7). On copper in a C₈F₁₇(CH₂)₂I solution the curve (Figure S8) is quite different as the current comes close to zero after about 200 s, in this case a thickness of 78.9 nm was measured

TABLE 8: Peak Potentials of 1 and 2^a and Number of Electrons Transferred

	1 C ₆ H ₁₃ I	2 C ₈ F ₁₇ (CH ₂) ₂ I
GC	−2.3 (<i>n</i> = 2)	−2.1 (<i>n</i> = 1)
Au	−2.5 (<i>n</i> > 2) ^b	−2.0 (<i>n</i> = 1)
Cu	−1.3 (<i>n</i> = 1)	−1.8 (<i>n</i> = 1)

^a Vs Ag/AgCl. ^b The height of the wave on gold is difficult to measure as it is close to the background.

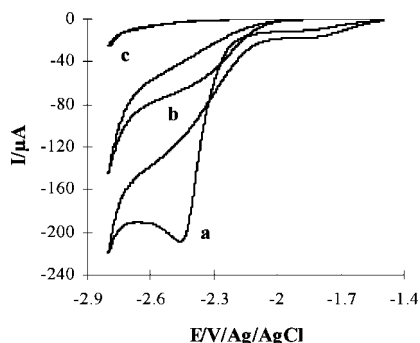


Figure 11. Cyclic voltammetry on a gold electrode (*d* = 1 mm) in an ACN + 0.1 M NBu₄BF₄ solution after addition of **1**, IC₆H₁₃ (*c* = 10 mM) (a) 1st scan; (b) 10th scan, and (c) in absence of **1**. Reference Ag/AgCl, *v* = 0.1 V s^{−1}.

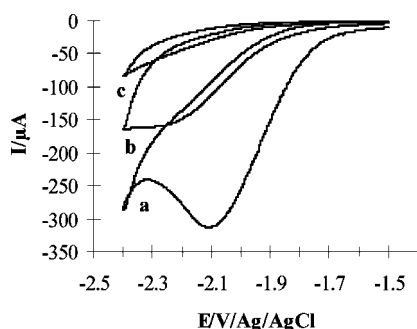


Figure 12. Cyclic voltammetry on a GC electrode (*d* = 3 mm) in ACN + 0.1 M NBu₄BF₄ of **2** I(CH₂)₂C₈F₁₇ (*c* = 10 mM), (a) first; (b) second; and (c) third scans. Reference Ag/AgCl, *v* = 0.1 V s^{−1}.

by ellipsometry. This is likely related to the formation of a thick layer of organocopper as observed with different compounds by Simonet.⁴¹

On TiN, it was possible to observe (with millimetric electrodes) a small wave of **2** at *E*_p ≈ −1.8 V/Ag/AgCl which disappeared on the next scan.

The decrease of the voltammetric waves upon repetitive scanning is also observed during other electrografting reactions due to the blocking of the electrodes.^{6,18} It is a clear indication that grafting also occurs during the reduction of alkyl halides.

Stability of the Layers. It was checked by recording the IR spectrum of **Fe1^{el}**, **Cu1^{el}**, **Au1^{el}**, **Fe2^{el}**, **Cu2^{el}**, and **Au2^{el}** before and after ultrasonication for 10 min in a commercial bath (350 W); the two spectra are superimposable. The stability was also tested with redox probes, the reversible voltammogram of [Fe(CN)₆]^{3−} observed on Au and GC electrodes, disappears when the electrodes are modified by **2** (**Au2^{el}** and **C2^{el}**) (Figures S9 and S10). Upon sonication as above there is no change in the voltammogram: the waves of voltammogram of [Fe(CN)₆]^{3−} does not reappear. Both of these experiments indicate a good stability of the layer.

Conclusion

The formation of an organic layer on top of different metals (Fe, Cu, Au, TiN) has been ascertained by ellipsometry, water

contact angle, IR spectroscopy, XPS and ToF-SIMS. Water contact angle indicate the formation of quite dense hydrophobic surfaces as could be expected from **1** and **2**. Ellipsometry indicates the formation of multilayers. In the case of C₆H₁₃I **1**, they are probably obtained by hydrogen atom abstraction (from a grafted chain by a radical in solution) and radical recombination (between a grafted and a solution radical, this reaction being favored by the rather high concentration of **1**). As concerns ICH₂CH₂C₈F₁₇I **2** the reduction takes place at quite negative potentials and in spite of the fact that the consumption of only one electron is measured by cyclic voltammetry, some reduction of C–F bonds is possible. This would lead to carbon radicals that would be reduced to carbanions giving finally rise to C=C double bonds. Attack of this double bond by a radical in solution would permit the growth of the layer. More studies are necessary to confirm the mechanism of these reactions, for example: if the multilayers result from radical recombination or radical attack on double bonds, it should be possible to obtain monolayers by decreasing the concentration, we are presently investigating this possibility. The layer obtained from copper is particularly thick, this can be related to the formation of organo-copper⁵⁶ layers observed by Simonet starting from 1,3-dibromopropane.⁴² Infrared spectroscopy and ToF-SIMS indicate that the integrity of the chains is maintained during the grafting process.

The presence of ⁺Cu(CH₂)_{2–4} from **Cu1^{el}** clearly point to the existence of a covalent bond between the metal and the organic layer. The surface coverage of this layers remains to be determined, attaching a redox reporter group to the end of the chain is a possibility but if multilayers are formed this can lead to erroneous results (as it has been observed with diazonium salts),⁵⁷ in the same way XPS ratios such as F/Au for the grafting of **2** depend on the thickness of the layer and its structure as the thicker the layer the smaller the percentage of Au.

Adding the formation of organomercury^{31–37} and organopaladium compounds^{38–45} described in the introduction to the results presented in this paper and to the mechanical grafting of silicon,^{28,29} it appears that alkyl halides can be used to attach alkyl groups on many materials and probably nearly any metal.

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Supporting Information Available: Experimental section, cyclic voltammograms, chronoamperograms, and redox probes experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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