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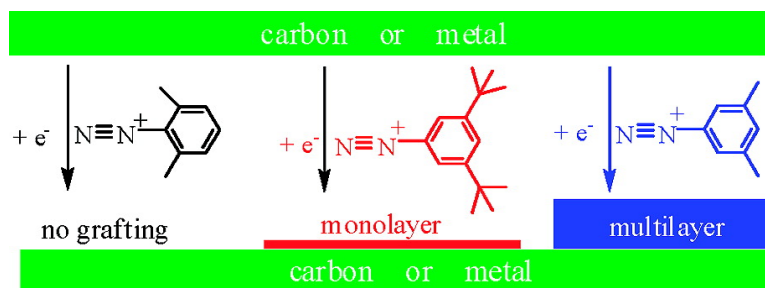University of Prishtina
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Steric Effects in the Reaction of Aryl Radicals on Surfaces

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Steric effects are investigated in the reaction of aryl radicals with surfaces. The electrochemical reduction of 2-, 3-, 4-methyl, 2-methoxy, 2-ethyl, 2,6-, 2,4-, and 3,5-dimethyl, 4-*tert*-butyl, 3,5-bis-*tert*-butyl benzenediazonium, 3,5-bis(trifluoromethyl), and pentafluoro benzenediazonium tetrafluoroborates is examined in acetonitrile solutions. It leads to the formation of grafted layers only if the steric hindrance at the 2- or 2,6-position(s) is small. When the 3,5-positions are crowded with *tert*-butyl groups, the growth of the organic layer is limited by steric effects and a monolayer is formed. The efficiency of the grafting process is assessed by cyclic voltammetry, X-ray photoelectron spectroscopy, infrared, and ellipsometry. These experiments, together with density functional computations of bonding energies of substituted phenyl groups on a copper surface, are discussed in terms of the reactivity of aryl radicals in the electrografting reaction and in the growth of the polyaryl layer.

1. Introduction

Besides their always increasing interest in organic chemistry,[1,2] radicals are the key species in a material chemistry reaction: the electrografting of surfaces.[3] In this reaction, a radical produced from the oxidation of amines,[4] carboxylates,[5] Grignard reagents,[6] or from the reduction of vinylic monomers[7] or diazonium salts,[3] reacts with carbon, metallic, or semiconductive surfaces to provide a covalently bonded organic layer. Among these methods, the electrochemical grafting of aryldiazonium salts in aprotic or aqueous solutions onto carbon surfaces is particularly efficient; it leads to the covalent attachment of polyphenylene layers to the carbon surfaces.[8–14] This method also applies to metals,[15–20]

Scheme 1
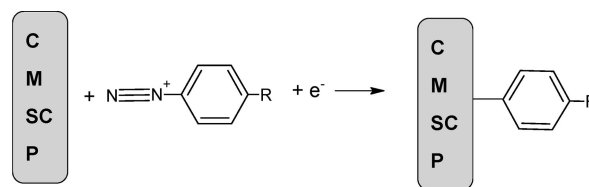
C = carbon, **M** = metal, **SC** = semiconductor and **P** = polymer

semiconductors,[21–24] oxides,[25] and polymers (Scheme 1).[26] It is now used industrially for the production of inks[27] and drug-eluting stents.[28]

The spontaneous chemical grafting of aryldiazonium salts is another possibility to modify conductor[29–33] and semiconductor surfaces;[30] it works by simple dipping of the substrate into a solution of the diazonium salt.

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Whether the reaction is spontaneous or electrochemical, the same aryl radical, obtained from the concerted electron transfer−bond cleavage of the diazonium ion, is involved.[34] This radical reacts with the surface but also with an already attached aryl group. Unlike the case for thiolate self-assembled monolayers (SAMs) on gold, electrografting of diazonium salts does not routinely produces monolayers. The thickness of organic layers obtained by reduction (chemical or electrochemical) of diazonium salts varies from an organized monolayer on Si[23] to thin layers (a few nanometers thick on atomically flat pyrolized photoresist−PPF)[13,35] and up to 2 μm thick layer of polyphenylene on iron, starting from benzenediazonium cation.[38]
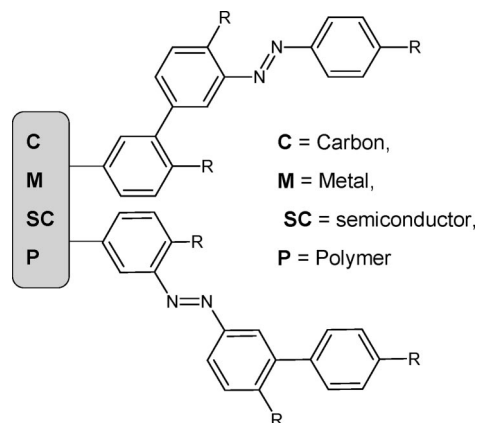
When grafting takes place spontaneously (chemically) by simple dipping of the surface into a solution of the diazonium salt or by electrochemistry, the parameters controlling the thickness of the layer are the concentration of the solution and the immersion time. For example, in the case of 4-nitropolyphenylene, the layer increases from 2.8 nm (after 1 min) to 9.7 nm (after 360 min) during the spontaneous grafting of iron by 4-nitrobenzene diazonium cation[31] (10 mM solution in ACN). In the case of electrografting, the same parameters are operative: the thickness of the layer obtained from 4-nitroazobenzene diazonium cation increases rapidly for 200 s and then reaches a plateau of 6.2 nm when this salt is electrografted to PPF[36] in ACN (150 mV negative to the voltammetric peak). But the potential is an additional parameter: this is exemplified[35] by the height of the layer obtained after a single voltammetric scan to −0.2, −0.3, −0.4, and −0.6 V/(Ag/Ag$^+$) that gives layers with increasing thickness of 1.9, 2.0, 2.3, and 2.6 nm, respectively (1 mM 4-nitroazobenzene diazonium salt). Controlling the potential and the time is equivalent to controlling the charge: a careful control of the charge during electrografting has permitted monolayer formation on Si.[23]

In addition, the thickness of the layer depends on the diazonium salt to be grafted. Under identical conditions, 1.36, 1.90, 1.75, and 1.83 equivalent monolayers are obtained for, respectively, biphenyl, terphenyl, nitrobiphenyl, and nitroazobenzene diazonium salts (single voltammetric scan to −0.6 V/Ag/AgCl, 1 mM solution in ACN).[37]
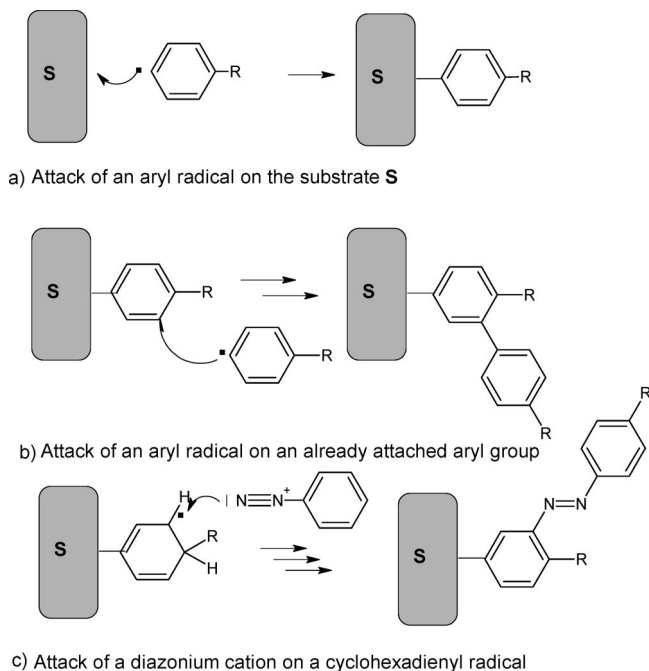
Changing the surface to be modified also influences the thickness of the organic layer. On iron, 2 μm films are obtained, whereas under identical conditions the height only reaches 0.33 μm on a resistive TaN/Ta substrate.[38]

There is, in addition, another parameter that could be used to control the growth and the structure of polyphenylene: the steric hindrance of the radical that is responsible at the same time for the grafting of the aryl group to the surface and for the growth of the organic layer. The structure of the layer can be schematically represented as shown in Scheme 2.[39] It results from the attack of[14,39] (a) an aryl radical on the surface, (b) an aryl radical on an already attached aryl group, (c) a diazonium cation on a cyclohexadienyl radical. These radical reactions are shown in Scheme 3. The effect of steric hindrance ortho to the diazonium function should be strong for reactions a and b, but somewhat alleviated for reaction c, as the attacking nitrogen is further away from the ortho substituents. Crowding the para and meta positions

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Scheme 2

C = Carbon,

M = Metal,

SC = semiconductor,

P = Polymer

Scheme 3

a) Attack of an aryl radical on the substrate **S**

b) Attack of an aryl radical on an already attached aryl group

c) Attack of a diazonium cation on a cyclohexadienyl radical

to the diazonium function should slow down reactions b and c, thereby limiting the growth of the layers. Modifying the steric hindrance of the diazonium salt, therefore, offers a way to investigate the reactivity of radicals on surfaces.

It is the purpose of the present paper to investigate these steric effects and their influence on the thickness and the structure of the organic layer. It is, of course, difficult to separate steric effects from electronic ones; this is why we mainly compare diazoniums salts with similar substituents (isomers of methyl- or isomers of dimethyl-benzenediazonium ions) or with substituents that are known for their important steric effect (*t*-Bu). By looking at the first and second voltammograms, that is, at the very beginning of the grafting process, we try to estimate the steric effect during the grafting process, whereas by measuring the thickness of the layer under identical conditions we compare the rate at which the layers grow.

We have investigated the electrografting of 2-, 3-, 4-methyl (2-, 3-, 4-MBD); 2-ethyl (2-EBD); 2-methoxy (2-MeOBD); 2,6-, 3,5-, and 2,4-dimethyl (2,6-, 3,5-, and 2,4-DMBD); 4-*tert*-butyl (4-*t*-BuBD), 3,5-bis-*tert*-butyl (3,5-D-*t*-BuBD); 3,5-bis(trifluoromethyl) (3,5-DCF$_3$BD), and pentafluoro (F$_5$-BD) benzenediazoniums. The modified surfaces will be termed by the symbol of the surface material followed by that of the aryl group, for

Table 1. Cyclic Voltammetry of Benzenediazoniums

diazonium	Ep^a
2-MBD	−0.20
3-MBD	−0.17
4-MBD	−0.21
2-EBD	−0.32
2-MeOBD	−0.24
2,4-DMBD	−0.35
2,6-DMBD	−0.22
3,5-DMBD	−0.32
4-*t*-BuBD	−0.14
3,5-D-*t*-BuBD	−0.88
3,5-DCF$_3$BD	0.08
F$_5$-BD	0.07

^{a} Glassy carbon electrode, 4 mM solution in ACN + 0.1 M NBu$_4$BF$_4$, scan rate $v = 100$ mV s^{-1}, Ag/AgCl reference.

example, Cu−2-MBD for a copper plate grafted by 2-methyl benzenediazonium tetrafluoroborate.

2. Results

We have used cyclic voltammetry, IR, X-ray photoelectron spectroscopy (XPS), and ellipsometry to characterize the extent of electrografting by the different diazonium salts. When electrografting takes place, the surface is covered by an organic layer, which inhibits the electron transfer. Therefore, observation of this blocking effect allows the qualitative observation of the reactivity of the different radicals. IR and XPS permit us to confirm the presence or the absence of the organic layer and its relative thickness, whereas ellipsometry gives access to the thickness of all the obtained layers.

2.1. Cyclic Voltammetry of the Different Diazonium Salts. The peak potentials of the investigated compounds are reported in Table 1.

The voltammograms of the diazonium salts investigated in this paper can be classified into three categories. The first category is represented by the 2-, 3-, and 4-MBD, 2,4- and 3,5-DMBD, 2-MeOBD, 4-*t*-BuBD, 3,5-DCF$_3$BD, and F$_5$-BD. On a glassy carbon electrode, the typical voltammograms of 2,4- and 3,5-DMBD ($c = 4$ mM) present during the first scan a broad irreversible wave (Figure 1, parts A and B). These waves are assigned to the formation of dimethylphenyl radicals obtained from the diazonium precursor by loss of dinitrogen concerted with the electron transfer.[3,34] A similar voltammogram is obtained with 2-MBD (Figure 1C). During the second scan, the first wave of 3,5-DMBD is strongly attenuated and disappears upon successive scans, but one should notice that the decrease of this wave is slower for 2-MBD than 2,4-DMBD and the fastest for 3,5-DMBD.

The behavior of 3,5-DMBD is usually observed with diazonium salts.[3] It indicates that aryl radicals are formed close to the electrode surface. They graft to the carbon surface, which produces an organic layer that finally blocks the electrode. The wave decrease at the second and successive scans is faster if the concentration increases. The similar voltammograms of F$_5$-BD (on glassy carbon), 2-MeOBD, 2-, 3-, and 4-MBD (on platinum) are presented in Figures S1−S5 (Supporting Information).

Very different irreversible voltammograms are observed on glassy carbon with the second category made of 2,6-DMBD and 2-EBD, as reported in, respectively, Figure 2, parts A and B. Upon repetitive scanning (Figure 2A, curves a, b, and c, after, respectively, 1, 2, and 10 cycles without stirring the solution between the cycles), the wave remains of nearly constant height (the small decrease can be assigned to the depletion of the starting compound in the vicinity of the electrode as usually observed for irreversible waves). These voltammograms are characteristic
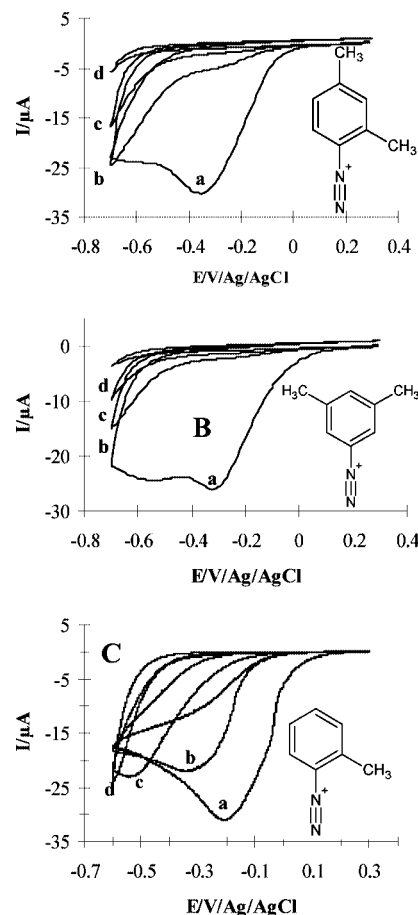

Figure 1. Cyclic voltammetry in ACN + 0.1 M NBu$_4$BF$_4$ on a glassy carbon electrode (diameter = 2 mm) of (A) 4 mM 2,4-dimethylbenzene diazonium tetrafluoroborate; (B) 4 mM 3,5-dimethylbenzene diazonium tetrafluoroborate, and (C) 4 mM 2-methyl benzenediazonium tetrafluoroborate: (a) first, (b) second, (c) third, and (d) fourth scan. Scan rate = 0.1 V s^{-1}. Reference Ag/AgCl.

of an electron transfer followed by an irreversible chemical reaction without any surface involvement. This indicates that the reduction of these diazonium salts does not modify the surface of the electrode. It should, however, be noted that a somewhat similar voltammogram has been observed with the benzenediazonium salt, which forms conducting micrometric thick films onto metals,[38] but in the latter case, one could observe the film with the naked eye; this does not occur with 2,6-DMBD or 2-EBD. In the case of benzenediazonium tetrafluoroborate, we have shown in a previous paper that the chronoamperometric response exhibited a current decrease for the first 3 s followed by an increase for the next 200 s assigned to the formation of a conducting film via a nucleation mechanism.[38] We have not observed this behavior with 2,6-DMBD or 2-EBD.

With 3,5-D-*t*-BBD, a third behavior is observed:[40] on copper or gold, upon repetitive scanning, the voltammogram of 3,5-D-*t*-BuBD presents a slow decrease (Figure S6, Supporting Information).[40]

2.2. Redox Probes. In order to confirm the origin of these differences we have examined the behavior of redox probes on tentatively modified electrodes. These experiments are intended to evidence the barrier properties of the electrografted layers on the platinum electrode using the outer-sphere inorganic [Fe(CN)$_6$]$^{3-}$ redox system. This multicharged probe is very

(40) Combellas, C.; Kanoufi, F.; Pinson, J.; Podvorica, F. I. *J. Am. Chem. Soc.* **2008**, *130*, 8576.
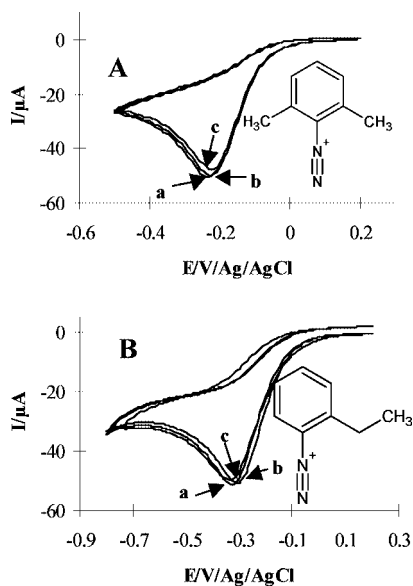
Figure 2. Cyclic voltammetry in ACN + 0.1 M NBu$_4$BF$_4$ on a glassy carbon electrode (diameter = 2 mm) of (A) 4 mM 2,6-dimethylbenzene diazonium tetrafluoroborate, (a) first, (b) second, and (c) 10th scan, and (B) 4 mM 2-ethyl benzenediazonium tetrafluoroborate, (a) first, (b) second, and (c) fourth scan. Scan rate = 0.1 V s^{-1}. Reference Ag/AgCl.

efficiently blocked by polyphenylene layers, but the blocking efficiency depends on the chemical structure of the layer. For example, the charge-transfer resistance of a carboxyphenyl modified electrode in the presence of [Fe(CN)$_6$]$^{3-}$ increases with pH.[41] However, in the present case, the layers are not charged or ionizable and they are of similar structure (polyalkylphenylene). Therefore, the effect observed with the redox probes can reasonably be related to the presence or absence of the layer.

The electrografted glassy carbon electrodes with 3,5- and 2,4-DMBD (five cycles between 0.2 and −0.7 V/Ag/AgCl in a 4 mM solution in ACN + 0.1 M NBu$_4$BF$_4$, v = 0.1 V s^{-1}) were carefully rinsed in acetone in an ultrasonic bath for 10 min and transferred into a new aqueous solution containing 0.1 M KCl + 4 mM K$_3$[Fe(CN)$_6$] (Figure 3A); the characteristic reversible reduction/oxidation system does not appear on the modified electrodes suggesting the presence of an insulating layer on the platinum surface. The behavior is quite different with 2,6-dimethyl and 2-ethyl benzenediazonium tetrafluoroborates. By comparison with the voltammogram of a bare glassy carbon and platinum electrode, the voltammogram of the redox probe is not much affected by the preceding treatment, as observed for 2,6-DMBD in Figure 3B (glassy carbon) and Figure S7 (Supporting Information, platinum). This confirms that, in the latter case, there is no organic layer attached to the carbon surface. Other examples of redox probes are given in Figures S8−S12 (Supporting Information) for, respectively, 2-MeOBD, F$_5$BD, 2-, 3-, and 4-MBD with K$_3$[Fe(CN)$_6$] and in Figures S13 and S14 (Supporting Information) for 2,4- and 2,6-DMBD with ferrocene; they confirm the above conclusions.

2.3. Cyclic Voltammetry of Methyl Benzenediazonium Tetrafluoroborates. Cyclic voltammetry was also performed at lower concentrations; 1 mM solutions exhibit interesting differences in the rate at which the waves decrease. Figure 4, parts A, B, and C, which present the cyclic voltammograms of 1 mM solutions of, respectively, 2-, 3-, and 4-MBD, shows that the wave decreases more slowly for the 2-MBD than for the 4-MBD isomer; the fastest decrease is observed for the 3-MBD isomer.
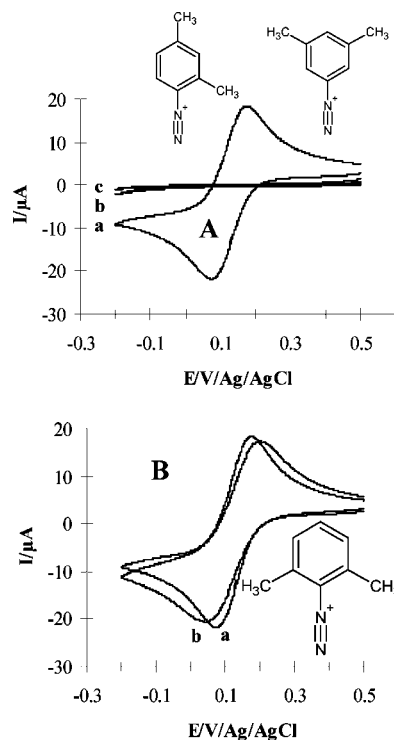

Figure 3. Cyclic voltammetry of a glassy carbon electrode (diameter = 2 mm) in aqueous 0.1 M KCl + 4 mM K$_3$[Fe(CN)$_6$] solution: (A) (a) bare electrode and after treatment with (b) 3,5-dimethyl benzene-diazonium tetrafluoroborate and (c) 2,4-dimethyl benzenediazonium tetrafluoroborate; (B) (a) bare electrode and (b) after treatment with 2,6-dimethylbenzene diazonium tetrafluoroborate (10 cycles to −0.7 V/Ag/AgCl in a 4 mM solution in ACN + 0.1 M NBu$_4$BF$_4$, v = 0.1 V s^{-1}). Scan rate = 0.1 V s^{-1}. Reference Ag/AgCl.

The ratios of the peak intensities at the second and first scans are reported in Table 2.

It is now well-established[3] that the phenomenon responsible for the decrease of the wave is the formation of an organic layer bonded to the electrode. This is, however, a complicated phenomenon that implies both the compactness of the layer, its conductivity, and the presence of defects. In the following, we compare the first two scans of the voltammograms of isomers of methyl benzene diazonium; that is, the very beginning of the process. The layer starts to form during the first scan and the height of the second scan gives an indication of the blocking effect of the layer that has been formed during the first scan. The microbalance measurements obtained by Laforgue et al. support this statement.[42] These authors observe simultaneously the voltammogram and the mass of the layer that is deposited (Figure 1 recorded at 5 mM concentration); they notice that a change in the slope of the mass versus time occurs at the end of the first scan. This indicates that the first slope corresponds to the grafting of aryl radicals on the surface and the second slope to the growth of the layer. It is reasonable to assume that at lower concentration (1 mM), the growth of the layer takes place later, and this is even more true when grafting is sterically hindered.

The higher ratios obtained with 2-MBD are therefore indicative of a slower coverage of the surface by 2-MBD, after a single scan, which in turn reflects the lower reactivity of the 2-methyl phenyl radical with the surface by reference to its 3-analogue. At higher concentration (4 mM, on platinum) but otherwise identical conditions (Figures S3 and S4, Supporting Information), grafting is more efficient and the wave of 3-MBD comes close

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(42) Laforgue, A.; Addou, T.; Belanger, D. *Langmuir* **2005**, *21*, 6855.
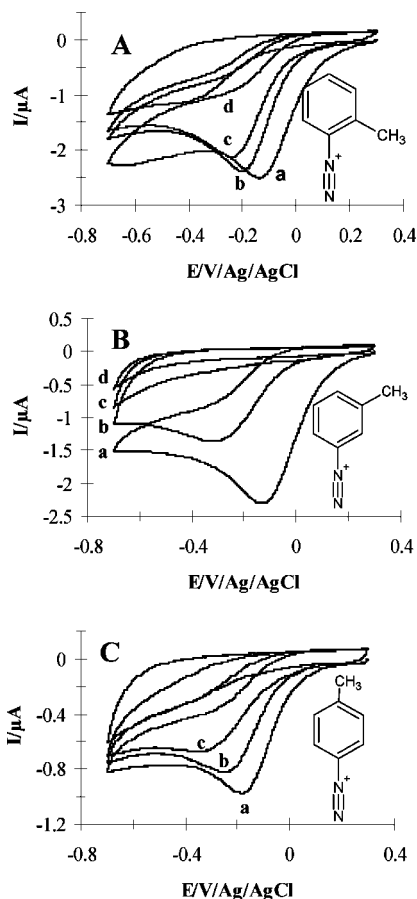
Figure 4. Cyclic voltammetry of a platinum electrode ($d = 1$ mm) in ACN + 0.1 M NBu$_4$BF$_4$ + (A) 1 mM 2-methyl benzenediazonium tetrafluoroborate, (B) 1 mM 3-methyl benzenediazonium tetrafluoroborate, and (C) 1 mM 4-methyl benzenediazonium tetrafluoroborate: (a) first, (b) second, (c) third, and (d) fourth scan. Scan rate = 0.1 V s^{-1}. Reference. Ag/AgCl.

Table 2. Intensity of the Reduction Wave during Repetitive Scanning[a]

	2-MBD	3-MBD	4-MBD
ip (second cycle)/ip (first cycle)	0.93	0.71	0.85

[a] 1 mM solution of methyl benzenediazonium in ACN + 0.1 M NBu$_4$BF$_4$, glassy carbon electrode, $v = 0.1$ V s^{-1}.

to the background; however, with 2-MBD the wave, albeit small, is still visible. This is also observed on a glassy carbon electrode (Figure 1C). These experiments indicate the lower reactivity of the 2-methyl phenyl radical toward the surface by comparison with its 3- and 4-isomers. Along the same lines, the electrografting on a glassy carbon electrode is little affected by F$_5$-BD, likely due to the low steric hindrance of the two fluorine atoms. On the contrary the formation of the layer is very fast with 4-*t*-BuBD (not shown). The effect of the 2-methyl group is not so surprising considering, for example, in a very different mechanism, the ortho/para ratio for the nitration of toluene (0.72).

2.4. IR Confirmation of the Modification of Surfaces. IR confirmation of the modification of surfaces. The above electrochemical results indicate that electrografting occurs with most diazonium salts but is prevented in two cases (2-EBD, 2,6-DMBD) by steric hindrance. To confirm these results, we examined copper and gold surfaces submitted to the same electrografting process by IR and XPS. The main features of the IR spectra are summarized in Table S1 and discussed along in the Supporting Information. The most interesting conclusion is the absence of signal after reduction of 2-EBD and 2,6-DMBD.

This confirms the absence of grafting due to the steric hindrance of the radical.

2.5. XPS Confirmation of the Modification of Surfaces. Survey spectra before and after modification of gold surfaces treated with different diazonium salts are presented in Figure 5A. The spectrum of a bare gold electrode presents the characteristic features of Au[4f$_{7/2}$] and Au[4f$_{5/2}$], Au[4d$_{5/2}$], and Au[4d$_{3/2}$] at, respectively, ~84 and 88, 335, and 352 eV (Figure 5A). Small peaks relative to carbon and oxygen are also detected; they result from the adsorption of organic contaminants during and after the cleaning process.[20] After the electrochemical reduction of 3,5-DMBD (five scans by cyclic voltammetry between 0.2 and −0.7 V/Ag/AgCl in ACN) and of 2,4-DMBD (100 s by chronoamperometry at −0.7 V/Ag/AgCl in ACN), the intensities of the Au peaks decrease significantly especially for Au−3,5-DMB and Au−2,4-DMB (Figure 5A, curves d and e). In addition, the presence of a film in the case of, respectively, Au−3,5-DMB and Au−2,4-DMB is confirmed by the increase of inelastic scattering of photoelectrons due to the grafted layer that screens gold. Following modification, the carbon peak at 285 eV increases significantly and a peak relative to N1s appears at 400 eV (Figure S15, N1s core level on gold, Supporting Information). These spectral changes confirm the presence of organic moieties derived from the corresponding diazonium salts at the gold surface. In the case of 2-EBD and 2,6-DMB (Figure 5A, curves b and c) there is no difference between the spectrum of a bare gold electrode and that of an electrode treated with the diazonium salts; this confirms the absence of electrografting.

Figure 5B presents Au[4f] core level spectra for gold before (Figure 5B, curve a), and after modification by 2-EBD, 2,6-, 3,5-, and 2,4-DMBD (Figure 5B, curves b−e). As observed on the survey spectra, gold surface modification by 3,5-DMBD and 2,4-DMBD (Figures 5B, curves d and e) (i) leads to a decrease of the intensity of the Au4f signals as noticed by Laforgue et al.[42] and (ii) this decrease is larger for 2,4-DMBD as observed on the survey spectra. This indicates that the thickness of the grafted layer is larger for 2,4-DMBD than for 3,5-DMBD. Conversely, the Au spectra of 2-EBD and 2,6-DMBD are not modified upon electrografting conditions. These results are in agreement with the electrochemical data for redox probes and suggest that 3,5- and 2,4-DMBD are able to modify the gold surface, whereas 2-EBD and 2,6-DMBD are not.

XPS spectra were also recorded for the same compounds on copper plates (Figures S16−S18, Supporting Information). These spectra confirm the grafting of 2,4- and 3,5-dimethyl and 2-methoxy benzenediazonium reagents on copper; the intensities of the XPS spectra are summarized in Table 3. Upon electrografting, a clear decrease of the Cu[2p] signal is observed, larger for 3,5-DMBD than for its 2,4-isomer. This variation is correlated with the increase of the carbon percent. As concerns nitrogen, no significant variation can be observed.

2.6. Thickness of the Polyphenylene Layers. As discussed above, cyclic voltammetry permits estimation of the reactivity of the aryl radicals on the surface. Alternatively, the measure of the layer thickness gives access to the relative reactivity of radicals during the formation of the layer. Table 4 gathers the thickness of the layers obtained on deoxidized copper from the different diazonium tetrafluoroborates investigated; they were prepared by chronoamperometry at Ep −400 mV for 30 s for a 4 mM concentration in ACN + 0.1 M NBu$_4$BF$_4$.

Ellipsometric measurements confirm the absence of electrografting with Cu−2-EBD and Cu−2,6-DMBD, in good agreement with the preceding results. Although cyclic voltammetry indicates that electrografting of 2-MBD is somewhat more difficult than
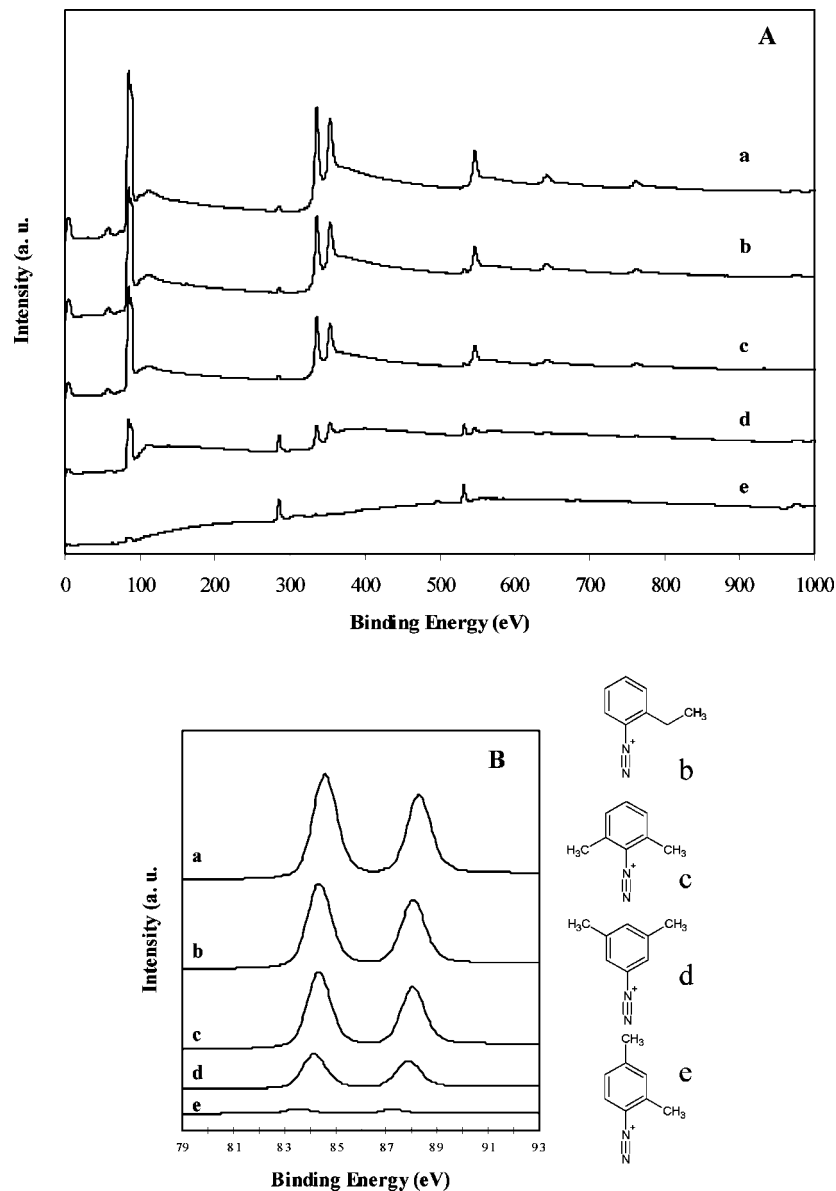
Figure 5. XPS analysis of gold: (A) survey spectra; (B) Au4f core level (a) before and following treatment with (b) 2-ethyl benzenediazonium tetrafluoroborate, (c) 2,6-, (d) 3,5-, and (e) 2,4-dimethyl benzenediazonium tetrafluoroborate. (b–d) Cyclic voltammetry is used to reduce the diazonium salt in ACN (five scans at 0.2 V s^{-1} between 0.2 and −0.7 V/Ag/AgCl). (e) Chronoamperometry is used to reduce the diazonium tetrafluoroborate for 100 s at −0.7 V/Ag/AgCl.

Table 3. XPS Spectra of Derivatized Copper Plates[a]

sample	Cu[2p3]/%	C[1s]/%	N[1s]/%
Cu	30.2	42.2	0.9
Cu−2,4-DMB	17.3	52.5	2.7
Cu−3,5-DMB	2.4	77.7	2.2
Cu−2-MeOB	6.4	67.5	2.5

[a] Chronoamperometry at $E = -0.8$ V/Ag/AgCl, for 50 s, $c = 6$ mM in ACN + NBu$_4$BF$_4$.

for its 3- and 4-isomers, the Cu−2-MBD is the thickest methylphenyl layer indicating that the steric hindrance ortho to the radical does not prevent the growth of the layer. On copper, the smaller value obtained for the thickness of Cu−2,4-DMBD by comparison with Cu−3,5-DMBD is in agreement with the XPS results of Table 3, which indicate a larger attenuation of copper for the latter layer. XPS on gold indicates that the Cu−2,4-DMBD layer is thicker than the Cu−3,5-DMBD, this results from the different experimental conditions for the grafting: 2,4-DMBD *is* reduced by chronoamperometry for 100 s at −0.7

V/Ag/AgCl, whereas 3,5-DMBD is reduced by cyclic voltammetry for five scans at 0.2 V s^{-1} between 0.2 and −0.7 V/Ag/AgCl).

The 4-*tert*-butyl substituent, although bulky, does not prevent the growth of the layer; it gives the thickest layer of all the diazonium tetrafluoroborates investigated. But the two *tert*-butyl substituents of 3,5-D-*t*-BuBD permit electrografting of the radical but prevent the growth of the layer and give a monolayer as we shall see below. Conversely, the two CF$_3$ groups of 3,5-DCF$_3$BD or the five fluorine atoms on the five positions of the aromatic ring do not provide any hindrance to the growth of the layer. In the case of the two CF$_3$ groups of 3,5-DCF$_3$BD the thickness of the grafted layer is lower than for 3,5-DMBD, indicating higher steric effect for the growth of the layer.

With Cu−F$_5$-BD the growth of the layer should involve the attack of a radical on a carbon bearing a fluorine atom. Such homolytic aromatic substitution of fluorine atoms has been described previ-

Table 4. Thickness of the Different Layers Obtained by Electrografting of Diazonium Salts at (Ep −400) mV for 30 s for a 4 mM Concentration in ACN + 0.1 M NBu$_4$BF$_4$

sample	Cu−2-MBD	Cu−3-MBD	Cu−4-MBD	Cu−2-EBD
thickness (nm)	25 ± 0.2	12 ± 0.3	16 ± 0.2	not measurable
sample	Cu−2-MeOBD	Cu−2,6-DMBD	Cu−2,4-DMBD	Cu−3,5-DMBD
thickness (nm)	20.3 ± 0.4	not measurable	16.5 ± 0.3^a	33.0 ± 0.4^b
sample	Cu−4-*t*-BuBD	Cu−3,5-D-*t*-BuBD	Cu−3,5-DCF$_3$BD	Cu−F$_5$-BD
thickness (nm)	47.7 ± 1.0^c	1.50 ± 0.1	16.2 ± 0.7	16.8 ± 0.1

^{a} 22.2 ± 0.6 nm after 100 s. ^{b} 37.9 ± 0.5 nm after 100 s. ^{c} 16.2 ± 0.7 nm for E = Ep for 30 s.

Table 5. Bonding Energy (BE) of Phenyl Radicals on Cu(111) and Off-Surface Displacement of the Cu Atom Connected to Carbon

	phenyl	2-methylphenyl	2,6-dimethylphenyl
BE (eV)^a	1.14	1.05	0.52
Cu displacement (Å)	0.21	0.33	0.63

^{a} BE = $E_{Cu(111)}$ + E_{Phenyl} − $E_{Phenyl−Cu(111)}$.

ously;[43] it leads, at least in part, to dimers. In the context of this paper, this reaction would lead to the growth of the layer.

3. Discussion

From the above results we can discuss the effect of steric hindrance on the first step of the process: the electrografting of aryl radicals on metallic surfaces, but also on the subsequent growth of the layer, which involves the attack of aryl radicals on aryl groups.[14,39]

The above results indicate that two hydrogen atoms on the ortho substituents do not hinder the grafting reaction: 3,5-DMB as the many diazonium salts previously investigated (4-nitro,[8] 4-bromo,[8] 4-dodecyl,.[32] ..) attach to the surface upon electrochemical reduction. It should also be noticed that two fluorine atoms on the ortho positions (F$_5$-BD) permit the grafting of the pentafluorobenzene moiety. One methyl or one methoxy group on the ortho position does not prevent electrografting (2-MBD, 2-MeOBD, 2,4-DMBD). However, cyclic voltammetry indicates that the 2-methyl substituent makes electrografting somewhat more difficult. An ortho bulkier ethyl group (2-EBD) or two ortho methyl groups (2,6-DMBD) completely prevent the attachment of the radical to the surface, as shown by the convergent measurements performed in this study. This indicates that the reaction of the radical with the surface (Scheme 3a) is quite sensitive to steric hindrance.

Jiang and co-workers[44,45] have calculated the structure of bonded phenyl groups on metals and carbon. They have shown that there is a bond between the phenyl carbon and another carbon of the graphene sheet or a gold or copper atom from the surface. To compare briefly the substituent effect, we have employed the same method of periodic density functional theory with plane wave bases and computed the binding energy and structure of 2-methylphenyl and 2,6-dimethylphenyl radicals on the Cu(111) surface, in comparison with those of the unsubstituted phenyl. Table 5 and Figure 6 show the binding energies and structures of the three radicals on the Cu(111) surface. Here, we have only considered one most stable configuration of the aryl radical attachment, namely, the atop attachment of the aryl radical carbon atom to a Cu atom on the surface. We have found that 2-methyl substitution decreases the binding energy slightly (∼9%) and causes the phenyl ring to tilt toward the unsubstituted side, whereas 2,6-dimethyl substitution dramatically decreases the binding energy (>50%) and causes the Cu atom connected to carbon to move out of the surface by as much as 0.6 Å. These computational results show that the thermodynamics driving force for phenyl attachment is greatly reduced for 2,6-dimethylphenyl, but only
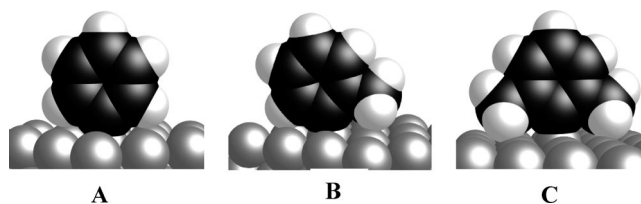

Figure 6. DFT-optimized structures of atop attachment of (A) phenyl, (B) 2-methylphenyl, and (C) 2,6-dimethylphenyl on Cu(111). Radii used for C (black), H (light gray), and Cu (dark gray) are 1.7, 1.2, and 1.3 Å, respectively.

mildly affected for 2-methylphenyl, in agreement with our experimental observation that electrografting is realized for 2-MBD, but not for 2,6-DMBD.

Another factor of steric hindrance due to methyl substitution is the kinetic effect, that is, there may be a kinetic barrier for the attachment of a phenyl radical onto the Cu surface that slows down the grafting reaction. Inspection of the structures in Figure 6 indicates that this barrier is likely small for phenyl and 2-methylphenyl, but substantial for 2,6-dimethylphenyl, given the large displacement of the Cu atom connected to carbon, due to repulsion between methyl groups and the Cu surface. This large barrier, together with greatly weakened thermodynamics driving force, may be the reason for the prevention of electrografting with 2,6-DMBD. Computational determination of reaction barriers is time-consuming and planned for the future to further explain our experimental observations.

Concerning the growth of the organic layer, the steric hindrance is alleviated in the attack of an aryl group by ortho-substituted aryl radicals: Cu−2-MBD, Cu−2-MeOBD, Cu−2,4-DMBD, F$_5$-BD present a thickness that is of the same order as that of the 2-unsubstituted diazoniums. However, the Cu−2,4-DMBD layer is somewhat thinner than that of its 3,5-analogue; this could indicate some steric effect. The possible reaction of an ortho-substituted aryl radical with an already grafted aryl group (Scheme 3b) is probably related to the fact that the two aryl groups are not coplanar during the attack. However, if the 3- and 5-positions are substituted with very bulky *tert*-butyl groups,[40] the attack of the radical becomes very difficult and a monolayer is easily obtained. In this case, the aryl radical probably reacts with the solvent; this is a major route for the evolution of aryl radicals.[46]

Finally, one can discuss the effect of steric hindrance on the attack of an aryl diazonium on a grafted aryl group (Scheme 3c). The N[1s]% presented in Table 3 do not evidence any effect of the 2-substituent as could be expected from the larger distance between the two aryl groups.

4. Conclusion

The above results and discussion constitute an approach to understand the effect of steric hindrance on the reactivity of aryl radicals with surfaces such as carbon or metals. Substitution of one or two ortho substituents (2-ethyl, 2,6-dimethyl) readily

prevents any reaction with the surface. The other substituents investigated (2-, 3-, 4-methyl, 2-methoxy, 3,5- and 2,4-dimethyl, 4-*tert*-butyl, 3,5-bis(trifluoromethyl), and pentafluoro) lead to the formation of multilayers. Blocking the growth of the polyphenylene layer is much more difficult; it necessitates two bulky 3,5-*tert*-butyl groups to limit the layer to a monolayer. A possible development of such an investigation would be the formation of ordered polyphenylene layers. By adjusting the steric hindrance on the aromatic ring, it should be possible to observe the growth from a single position and the formation of more ordered layers.

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Supporting Information Available: Experimental section, cyclic voltammetry of selected diazonium salts and redox probes, IR main features, XPS high-resolution spectra of N1s on Au, Cu3d and C on Cu, and wide scan of a Cu plate. This material is available free of charge via the Internet at http://pubs.acs.org.

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