

# Time-of-Flight Secondary Ion Mass Spectroscopy Characterization of the Covalent Bonding between a Carbon Surface and Aryl Groups

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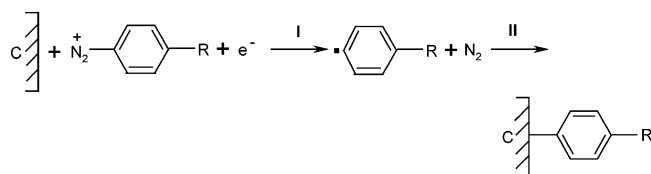
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Grafting of aryl layers derived from aryl diazonium salts onto glassy carbon electrodes is observed by time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The grafting occurs spontaneously when a glassy carbon plate is immersed into a solution of aryl diazonium salt and can be enhanced by biasing the carbon plate at a potential a little more negative than the diazonium salt reduction. C–C and C–O covalent bonding are believed to be responsible for the strong attachment of these layers onto the carbon substrate. Fragments containing aryl dimers, trimers, or tetramers are also observed. A mechanism is proposed to account for the formation of these polymeric chains.

## 1. Introduction

Electrochemical reduction of aryl diazonium salts at a carbon electrode leads to the covalent bonding of the aryl group to the carbon surface according to<sup>1–23</sup>



In step I, the carbon electrode is biased at about 0 V/SCE (saturated calomel electrode) and an aryl radical is

obtained directly, since the electron transfer to the diazonium cation is concerted with C–N bond cleavage.<sup>4</sup> In step II, the aryl radicals are linked to the carbon surface. The reaction can be performed in an aprotic medium such as acetonitrile as well as in acidic water.<sup>2</sup>

Organic layers obtained with diverse diazonium salts have been characterized by different methods such as cyclic voltammetry, X-ray photoelectron spectroscopy (XPS),<sup>1–3,8</sup> vibrational spectroscopy (polarization modulation infrared reflection absorption spectroscopy (PMIRRAS)),<sup>2</sup> Raman spectroscopy,<sup>5–7</sup> and Rutherford backscattering (RBS).<sup>2</sup> In the case of glassy carbon (GC), the influence of such grafted organic layers on electron transfer rates has been measured.<sup>8</sup> Layers grafted on highly oriented pyrolytic graphite (HOPG) have been observed by atomic force<sup>9,10</sup> and scanning tunneling microscopies.<sup>11</sup> These modified surfaces have been used for different applications, among which we can mention the linking of enzymes such as glucose oxidase<sup>12</sup> or avidine–biotin,<sup>13</sup> the bonding of gold nanoparticles,<sup>14</sup> the limitation of protein adsorption,<sup>15</sup> and the functionalization of poly(tetrafluoroethylene) (PTFE) after carbonization.<sup>16</sup> Compact layers of aryl groups can also be grafted on surfaces by the electrochemical reduction of diazonium salts on hydrogenated Si(111)<sup>17–19</sup> or on metals.<sup>20–23</sup>

Grafting of aryl groups derived from diazonium salts has also been obtained directly without electrochemical activation on carbon black to yield materials for the plastics, rubber, and textile industries<sup>24</sup> and also, more recently, on semiconductors and palladium.<sup>25</sup>

Although the presence of an organic layer on top of conductive surfaces (carbon, semiconductor, or metal) has

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been thoroughly characterized, the demonstrations of the existence of a covalent bond between the organic layer and the conductive surface are much more scarce. Until now, the evidence of a strong bond between the surface and the aryl groups has mainly relied on the resistance of the organic layer to sustained ultrasonic rinsing for long periods of time in a variety of solvents. On carbon, McCreery et al. have examined the Raman spectrum of 4-nitroazophenyl groups grafted by reduction of the 4-nitroazophenyl-4'-diazonium salt (NAB) on an especially flat type of carbon (pyrolyzed photoresist film (PPF)). The spectrum showed a weak feature at  $1240\text{ cm}^{-1}$ , which was assigned to the C–C bond between the carbon surface and the C4' carbon atom of the phenyl ring bonded to the surface.<sup>26</sup>

In addition, the spectra of aryl groups derived from NAB on GC or PPF were found to be significantly different from that of nitroazobenzene in solution, implying a strong interaction between the aryl groups and the  $\text{sp}^2$  carbon solid. Previous results from the same group concerning the same species bonded to the edge of ordered graphite also indicated an increase in Raman cross section 2–3 orders of magnitude larger than the parent molecule in solution, reinforcing the hypothesis of a strong interaction between the aryl groups and graphitic carbon.<sup>27</sup> On iron, observation of an XPS peak at the same energy as iron carbide was assigned to the signature of the iron–aryl bond.<sup>23</sup>

As compared, for example, to self-assembled monolayers (SAMs) of thiols on gold, the strength of the aryl–surface bond is one of the distinct features of the process. It is therefore necessary to ascertain unambiguously the nature of this bond. Besides, the presence of a covalent bond between the conducting surface and the organic layer should reduce the contact resistance by 2–3 orders of magnitude, a feature of importance in microelectronic applications.<sup>28–30</sup>

The present paper aims at demonstrating, by time-of-flight secondary ion mass spectroscopy (ToF-SIMS), the existence of the C–C bond between the carbon substrate and the aryl group resulting from the electrochemical grafting of different diazonium salts on glassy carbon. In the static mode, this technique is powerful in the characterization of the chemical structure of self-assembled monolayers<sup>31–33</sup> and thin polymer films.<sup>34</sup> We will show that ToF-SIMS results can also shed some light on the structure and the growth of the organic layer from a monolayer to a multilayer. This is also a characteristic of this process, and the way in which these multilayers are formed is of interest to completely characterize this method of modification.

## 2. Experimental Section

The following diazonium salts were used:  $^+\text{N}_2\text{Ar BF}_4^-$ , with  $\text{Ar} = \text{C}_6\text{F}_{13}\text{--Ph}$  (1),  $\text{Br--Ph}$  (2),  $\text{NO}_2\text{--Ph}$  (3),  $\text{HO}_2\text{C--Ph}$  (4), Phen (5), and Anth (6), with Ph = phenyl ( $\text{C}_6\text{H}_5$ ), Phen = phenanthrenyl, and Anth = anthracenyl.

The synthesis of diazonium salts has been described in previous publications.<sup>2,21</sup> Glassy carbon plates ( $1 \times 1 \times 0.1\text{ cm}^3$ , Tokai, Japan) were polished first on polishing cloth (DP-Nap, Struers, Denmark) with  $1\text{ }\mu\text{m}$  diamond paste and second with  $0.02\text{ }\mu\text{m}$  alumina slurry (Presi, France) in Nanopure water to avoid organic contaminants on the electrodes.<sup>6</sup> Then, they were rinsed in acetone under sonication for 5 min and dried in an oven ( $80\text{ }^\circ\text{C}$ , overnight). Grafting was performed in a solution of  $10\text{ mL}$  of acetonitrile containing  $2\text{ mM}$  diazonium salt and  $0.1\text{ M}$   $\text{NBu}_4\text{--BF}_4$  (supporting electrolyte). The latter was synthesized from ammonium tetrafluoroborate and tetrabutylammonium chloride (Fluka, France) and recrystallized in petroleum ether.<sup>35</sup> The other chemical reagents were purchased from Aldrich (Saint-Quentin Fallavier, France) and used as received.

The counter electrode was a platinum wire (radius  $0.5\text{ mm}$ ) and the reference an anodized  $\text{Ag/AgCl}$  wire (radius  $0.5\text{ mm}$ ) without any reference compartment. The working electrode was biased at  $-0.5\text{ V/Ag/AgCl}$  for 5 min and then ultrasonicated in ultrapure acetone for 10 min to remove any species adsorbed on the surface.

ToF-SIMS analyses were carried out with an ION-TOF ToF-SIMS IV spectrometer. Surface analysis was performed in a static mode. A  $0.8\text{ pA}$   $\text{Ga}^+$  ion beam was used, that was rastered on a  $100 \times 100\text{ }\mu\text{m}^2$  surface area. The ion density, which reaches the surface, was  $\sim 5 \times 10^{10}\text{ ions s}^{-1}\text{ cm}^{-2}$ . The mass peak resolution was  $\sim 0.007\text{ amu}$ .

To observe the consequence of the grafting, we have focused on the high mass domain ( $m/z > 150$ ). A contamination peak at  $m/z = 242.28$  was observed on all spectra. It corresponds to  $\text{NBu}_4^+$  and is due to the previous use of the glassy carbon plates.<sup>36,37</sup>

We have analyzed glassy carbon surfaces submitted to (i) the grafting procedure (G samples), (ii) the grafting procedure without applying the potential (S samples), and (iii) rinsing only (blank, denoted B). These experiments are summarized in Table 1.

## 3. Results

The results obtained for 1–5 are summarized in Table 2.

**3.1. 4-Perfluorohexylphenyl Diazonium (1).** Parts a, b, and c of Figure 1 present, respectively, the positive ToF-SIMS spectra of the blank (B),  $\text{S}_1$ , and  $\text{G}_1$  in the mass region of the perfluorohexylphenyl moiety. No signal was detected on B. A peak was observed on  $\text{S}_1$  at  $m/z \sim 395$ . The latter was about 10 times higher for  $\text{G}_1$ , and other different peaks were also present on the  $\text{G}_1$  spectrum.

Let  $[\text{M}_1]^+$  be the fragment corresponding to  $m/z \sim 395$ ; it should correspond to  $[\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$ . The peaks at  $m/z \sim 409$  and  $407$  can be interpreted, respectively, as  $[\text{M}_1\text{--CH}_2]^+$  and its parent at  $m/z - 2$ . The intense peak at  $m/z \sim 423$  (with parent peaks) should correspond either to  $[\text{M}_1\text{--CH}_2\text{CH}_2]^+$  or to  $[\text{M}_1\text{--OC}]^+$ . To discriminate between these two possibilities, we have fitted the experimental peak to two Gaussian curves centered on the theoretical  $m/z$  values for  $\text{OCC}_6\text{H}_4\text{C}_6\text{F}_{13}$  ( $m/z = 423.01$ ) and  $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}$  ( $m/z = 423.04$ ). The intensities of the two peaks are in the proportions 2.5:1.

The peak at  $m/z = 439.01$  could be due to  $[\text{M}_1\text{--C}_2\text{HF}]^+$  and that at  $m/z 439.05$  to  $[\text{M}_1\text{--C}_3\text{H}_3]^+$  (distinction between both is difficult in Figure 1c). In higher mass spectra, dimeric fragments could be responsible for the peak observed at  $m/z \sim 817$   $[\text{M}_1\text{--C}_6\text{H}_3[\text{C}_6\text{F}_{13}]\text{OC}]^+$  or  $[\text{M}_1\text{--C}_6\text{H}_3\text{--C}_6\text{F}_{13}\text{--CH}_2\text{--CH}_2]^+$  and parents. We have fitted, as

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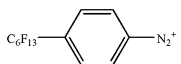
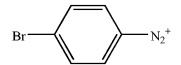
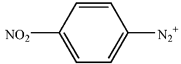
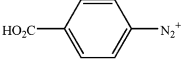
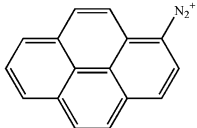
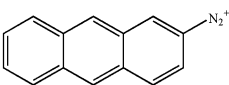
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**Table 1. Experimental Conditions for the Analysis of Glassy Carbon Surfaces**

Diazonium $\text{ArN}_2^+$	Experimental conditions	
	Potential = -0.5 V/Ag/AgCl	no potential applied
 <b>1</b>	G <sub>1</sub>	S <sub>1</sub>
 <b>2</b>	G <sub>2</sub>	S <sub>2</sub>
 <b>3</b>	G <sub>3</sub>	
 <b>4</b>	G <sub>4</sub>	
 <b>5</b>	G <sub>5</sub>	
 <b>6</b>	G <sub>6</sub>	

was mentioned previously, the experimental peak to two Gaussian curves, and the intensities of the two peaks are again in the proportions 2.5:1.

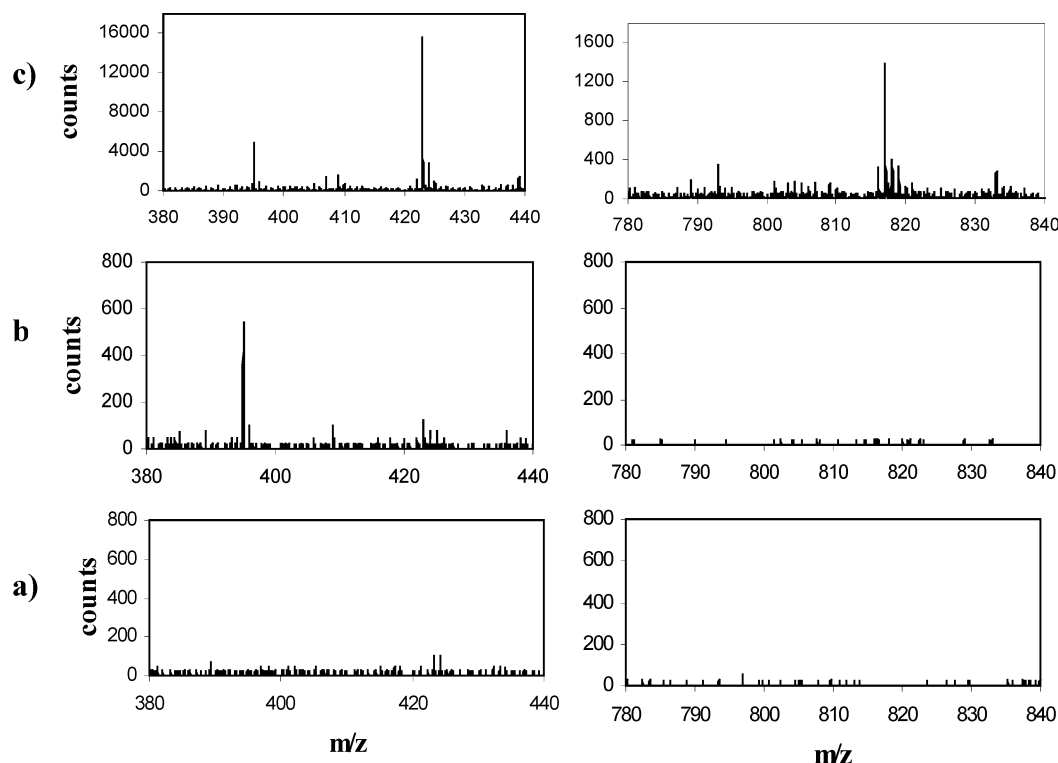
Negative ToF-SIMS spectra of the blank (B), S<sub>1</sub>, and G<sub>1</sub> are represented, respectively, in parts a, b, and c of Figure 2. When no potential was applied to the substrate (S<sub>1</sub>), the same peaks were observed, as in the case of the sample submitted to grafting (G<sub>1</sub>), but their intensity was lower. The peak at  $m/z = 411.01$  (Figure 2c) could be attributed to  $[\text{M}_1-\text{O}]^-$ , that at  $m/z = 419.00$ , to  $[\text{M}_1-\text{C}\equiv\text{C}]^-$ , and that at  $m/z = 805.00$ , to  $[\text{M}_1-\text{C}_6\text{H}_3-\text{C}_6\text{F}_{13}-\text{O}]^-$ .

The spectra for G<sub>1</sub> and S<sub>1</sub> in the lower mass region presented fragments characteristic of polyfluorinated surfaces such as that of a PTFE surface ( $[\text{CF}]^+$ ,  $[\text{CF}_2]^+$ ,  $[\text{CF}_3]^+$ ,  $[\text{C}_2\text{F}_4]^+$ , ..., and  $[\text{C}_6\text{F}_{13}]^+$  and also  $[\text{F}]^-$ ,  $[\text{F}_2]^-$ ,  $[\text{CF}_3]^-$ ,  $[\text{C}_2\text{F}_3]^-$ ,  $[\text{C}_2\text{F}_5]^-$ , and  $[\text{C}_6\text{F}_9]^-$ ). The peak intensities were at least 10 times higher for G<sub>1</sub> than for S<sub>1</sub>, and none of those fragments were observed for the blank (B). Moreover, the fingerprint signature of the carbon region ( $[\text{C}]^+$ ,  $[\text{CH}]^+$ ,  $[\text{CH}_2]^+$ , and  $[\text{CH}_3]^+$ ) for G<sub>1</sub>, S<sub>1</sub>, and B represents the extent of grafting of fluorinated moieties onto the surface (Figure 3). This signature is characteristic of a hydrocarbon surface for B, while it resembles that of a fluorinated surface such as that of PTFE for G<sub>1</sub> and S<sub>1</sub>.<sup>38</sup> The extent of fluorination of the carbon surface is less important for S<sub>1</sub> than for G<sub>1</sub>.

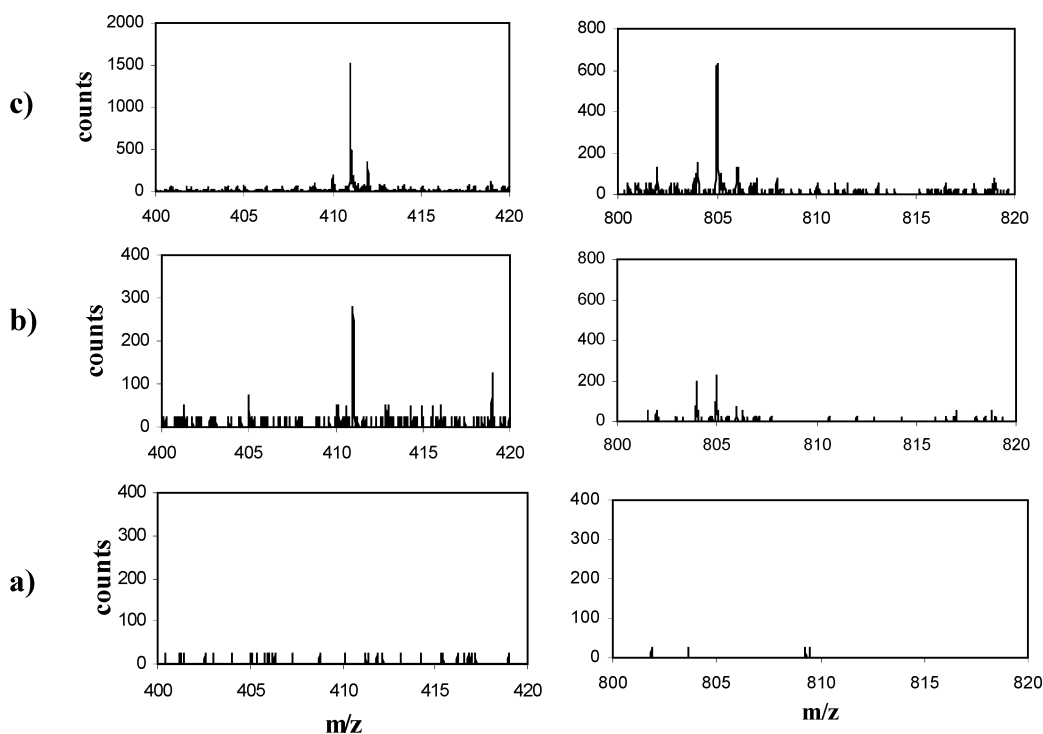
**3.2. 4-Bromophenyl Diazonium (2).** The following similar features were observed on the positive ToF-SIMS spectra of S<sub>2</sub> and G<sub>2</sub>: (i) existence of fragment peaks on both surfaces, with higher intensities on G<sub>2</sub> than on S<sub>2</sub>, and (ii) peaks at  $m/z \sim 155$  and  $157$  ( $[\text{M}_2 = \text{C}_6\text{H}_4-\text{Br}]^+$ ),  $169$  and  $171$  ( $[\text{M}_2-\text{CH}_2]^+$ ), and  $183$  and  $185$  ( $[\text{M}_2-\text{CH}_2-\text{CH}_2]^+$  and  $[\text{M}_2-\text{CO}]^+$ ). Dimeric fragments were also observed at  $m/z = 229.98$ ,  $231.98$  [ $\text{C}_6\text{H}_3-\text{C}_6\text{H}_4\text{Br}^+$ ]. These results are summarized in Table 2. Brominated ions were also observed in both the positive and negative spectra, indicating the presence of bromine atoms on the surface.

**Table 2. Possible Ions for G<sub>1</sub>-G<sub>5</sub> with the Corresponding Experimental ToF-SIMS  $m/z$  and Counts**

sample	ion formula	mass ( $m/z$ )	counts
G <sub>1</sub>	$[\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$	395	6025
	$[\text{CH}_2-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$	409	1500
	$[\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$ and $[\text{COC}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$	423	18075
	$[\text{CHCF}-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$ and $[\text{C}_3\text{H}_8-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$	439	1275
	$[\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_3\text{C}_6\text{F}_{13}-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$	817	1725
	$[\text{O}-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^-$	411	1525
	$[\text{C}\equiv\text{CC}_6\text{H}_4\text{C}_6\text{F}_{13}]^-$	419	125
	$[\text{O}-\text{C}_6\text{H}_3\text{C}_6\text{F}_{13}-\text{C}_6\text{H}_4\text{C}_6\text{F}_{13}]^-$	805	625
	$[\text{C}_6\text{H}_4\text{Br}]^+$	155, 157	5450, 6675
	$[\text{CH}_2\text{C}_6\text{H}_4\text{Br}]^+$	169, 171	1225, 1500
G <sub>2</sub>	$[\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Br}]^+$ and $[\text{COC}_6\text{H}_4\text{Br}]^+$	183, 185	5800, 6625
	$[\text{C}_6\text{H}_3\text{C}_6\text{H}_4\text{Br}]^+$	230, 232	1075, 1075
	$[\text{C}_6\text{H}_4\text{NO}_2]^-$	122	1750
G <sub>3</sub>	$[\text{OC}_6\text{H}_4\text{NO}_2]^-$	138	3950
	$[\text{CCC}_6\text{H}_4\text{NO}_2]^-$	146	2125
	$[\text{O}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	154	400
	$[\text{C}_3\text{H}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	160	450
	$[\text{C}_3\text{H}_3\text{C}_6\text{H}_4\text{NO}_2]^-$	161	1825
	$[\text{CCOC}_6\text{H}_4\text{NO}_2]^-$	162	2875
	$[\text{CHC}_6\text{H}_5\text{NO}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	258	850
	$[\text{OC}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	259	650
	$[\text{CCC}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	267	175
	$[\text{CHC}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_5\text{NO}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	379	350
	$[\text{CHC}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_5\text{NO}_2\text{C}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	500	50
	$[\text{OC}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_3\text{NO}_2\text{C}_6\text{H}_4\text{NO}_2]^-$	501	75
	$[\text{C}_6\text{H}_5\text{CO}_2]^-$	121	375
	$[\text{OC}_6\text{H}_3\text{CO}_2]^-$	135	1725
G <sub>4</sub>	$[\text{OCC}_6\text{H}_3\text{CO}_2]^-$	147	1500
	$[\text{O}_2\text{CC}_6\text{H}_3\text{CO}_2]^-$	163	225
	$[\text{OCCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{COOH}]^-$	177	10875
	$[\text{C}_{20}\text{H}_{13}\text{O}_5]^-$	333	300
	$[\text{C}_2\text{C}_{16}\text{H}_9]^-$	225	225
	$[\text{O}_2\text{C}_{16}\text{H}_9]^-$	233	1250
G <sub>5</sub>	$[\text{C}_{16}\text{H}_8\text{C}_{16}\text{H}_8]^-$	400	300
	$[\text{CC}_{16}\text{H}_8\text{C}_{16}\text{H}_9]^-$	413	375
	$[\text{C}_{16}\text{H}_9]^+$	201	700
	$[\text{C}_{17}\text{H}_9]^+$	213	450
	$[\text{C}_2\text{HC}_{16}\text{H}_9]^+$	226	475



**Figure 1.** Positive ToF-SIMS spectra of the blank (B) (a),  $S_1$  (b), and  $G_1$  (c).



**Figure 2.** Negative ToF-SIMS spectra of the blank (B) (a),  $S_1$  (b), and  $G_1$  (c).

**3.3. 4-Nitrophenyl (3), 4-Carboxyphenyl (4), 1-Phenanthrenyl (5), and 2-Anthracenyl (6) Diazonium Salts.** In the case of **3**, the peaks at  $m/z \sim 122$ , 146, 160, and 161 could be interpreted by monomer grafting, while those at  $m/z \sim 258$ , 259, 267, 379, and 500 correspond to dimers, trimers, and tetramers (see Table 2). Oxygenated

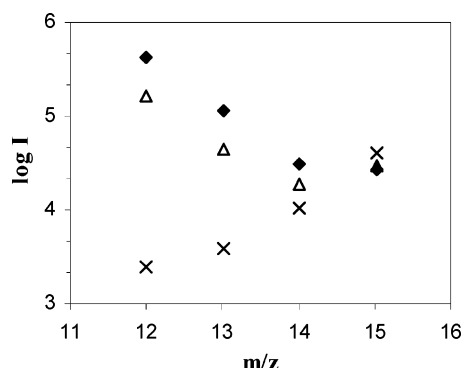
fragments were also observed at  $m/z \sim 138$ , 154, 259, and 501.

In the case of **4**, negative fragments that could correspond to  $[\text{C}_6\text{H}_5\text{CO}_2]^-$ ,  $[\text{OC}_6\text{H}_3\text{CO}_2]^-$ ,  $[\text{OCC}_6\text{H}_3\text{CO}_2]^-$ ,  $[\text{O}_2\text{CC}_6\text{H}_3\text{CO}_2]^-$ ,  $[\text{OCCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{COOH}]^-$ , and  $[\text{C}_{20}\text{H}_{13}\text{O}_5]^-$  were observed, respectively, for  $m/z \sim 121$ , 135, 147, 163, 177, and 333 and no higher mass fragments were observed.

In the case of **5**, negative fragments that could be attributed to monomers ( $m/z \sim 225$ ,  $[\text{C}_2\text{C}_{16}\text{H}_9]^-$ ;  $m/z \sim$

(38) *Handbook of Static Secondary Ion Mass Spectrometry*; Briggs, D., Brown, A., Vickerman, J. C., Eds.; Wiley & Sons, Inc.: London, 1989.





**Figure 3.** Logarithm of the intensity for detection of  $[C]^+$ ,  $[CH]^+$ ,  $[CH_2]^+$ , and  $[CH_3]^+$  expelled from B (x), S<sub>1</sub> (Δ), and G<sub>1</sub> (♦).

233,  $[O_2C_{16}H_9]^-$  or dimers ( $m/z \sim 400$ ,  $[C_{16}H_8C_{16}H_8]^-$ ;  $m/z \sim 413$ ,  $[CC_{16}H_8C_{16}H_9]^-$ ) have been observed. The presence of the monomeric fragments was confirmed on the positive spectra by peaks at  $m/z = 201.07$  ( $[C_{16}H_9]^+$ ),  $m/z = 213.07$  ( $[C_{17}H_9]^+$ ), and  $m/z = 226.08$  ( $[C_2HC_{16}H_9]^+$ ) and their parents.

In the case of **6**, the signals observed on both the negative and positive spectra were of very low intensity and nearly no difference was observed between the spectra of G<sub>6</sub> and the blank (B).

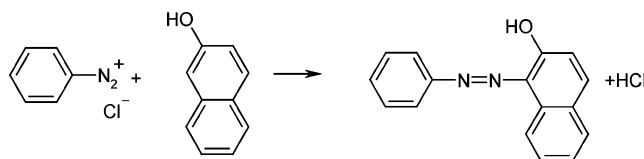
#### 4. Discussion

Several important features of the carbon–organic-layer assembly can be deduced from the above spectra.

**4.1. C–C Bonding between the Aryl Groups and the Glassy Carbon Surface.** The comparison of the ToF-SIMS spectra obtained for (i) the blank carbon plate and (ii) the samples submitted to grafting in solutions of **1** or **2** confirms the presence of the aryl moiety derived from the diazonium salt on the carbon plate.<sup>3–12</sup> Fragments corresponding to perfluorophenyl (G<sub>1</sub>) and bromophenyl (G<sub>2</sub>) groups were observed.

The presence of fluorinated fragments of high intensity and the fingerprint signature of the carbon region are in favor of high density of grafting of the perfluorohexyl moiety on the glassy carbon surface.<sup>31</sup> The comparison of G<sub>1</sub> and S<sub>1</sub> shows that perfluorohexyl moieties are also grafted onto carbon for S<sub>1</sub> but to a lesser extent than for G<sub>1</sub>. Grafting occurs spontaneously without electrochemical assistance, but it is more efficient when the carbon plate is biased on the reduction plateau of the diazonium salt. These results have been confirmed for the other salts (**3–5**) under electrochemical assistance both for positive (**1**, **2**, and **5**) and negative (**1** and **3–5**) spectra: fragments corresponding to nitrophenyl (G<sub>3</sub>), carboxyphenyl (G<sub>4</sub>), and phenanthryl (G<sub>5</sub>) groups are observed. In the case of the anthracenyl diazonium salt (**6**), no significant difference was observed between the spectra of the sample submitted to grafting (G<sub>6</sub>) and the blank (B). This can be explained by the different CH structures of the glassy carbon surface itself, among which polyaromatics have already been described.<sup>6,39</sup> The latter impede the detection of anthracenyl grafting using ToF-SIMS, which is not a quantitative method. However, grafting of anthracenyl monolayers onto pyrolyzed photoresist films has already been observed by atomic force microscopy (AFM).<sup>40,41</sup>

#### Scheme 1. Reaction of Diazonium Salts with Phenols



The second result obtained from this ToF-SIMS study is the detection of C–aryl fragments, which should result from C–C bonding between the carbon plate and the aryl moiety. In this respect, the fragments  $CCC_6H_4NO_2$  (G<sub>3</sub>),  $CCC_6H_3NO_2C_6H_4NO_2$  (G<sub>3</sub>), and  $CCC_{16}H_9$  (G<sub>5</sub>) are particularly significant, but the fragments such as  $CH_2-CH_2C_6H_4Br$  may include surface carbons. In the ToF-SIMS spectrum of an untreated carbon plate, one can observe peaks at  $m/z \sim 14$ , 15, 26, and 27 corresponding to  $CH_2$ ,  $CH_3$ ,  $C_2H_2$ , and  $C_2H_3$ , indicating that the carbons and the hydrogens of the C–C and  $CH_2CH_2$  groups originate from the surface. Therefore, the presence of these fragments provides a direct support to the claim that the reduction of diazonium salts leads to a covalent carbon–aryl bond.

However, the presence of O–aryl fragments indicates that C–C bonding is not the unique way of bonding to the surface but that part of the bonding occurs to oxygenated functions. Such functions as phenols, carbonyls, carboxylic groups, lactones, and quinones are always present at the surface of carbon, mostly after polishing (as shown by XPS and Raman spectroscopy).<sup>26</sup> Conventionally polished GC surfaces were found to have 1–5% C=O groups coverage, with an increase to about 10% upon electrochemical oxidation, with also various functional groups and surface impurities. When the glassy carbon surface is grafted by aryl groups derived from diazonium salts, the concentration of surface phenyl groups does not change when the oxygen proportion decreases.<sup>5,42</sup> Diazonium salts are known to react with phenols<sup>43,44</sup> to give azo dyes with  $-N=N-$  functionalities, as shown in Scheme 1. In this case, there is no formation of O–C bonds. In addition, diazonium salts do not react with carboxylic or keto groups. Therefore, the O–aryl fragments should not be obtained from the reaction of diazonium salts on the phenolic groups of the carbon surface but rather from reaction of the aryl radical with surface oxygens. In addition, McCreery et al. have observed the reaction of phenyl radicals with surface oxygens on copper oxide.<sup>45</sup>

As suggested by a referee, some peaks could also be interpreted by nitrogen coupling. The peak at  $m/z \sim 14$  could be due in part to nitrogen and the peak at  $m/z \sim 28$  to  $N_2$ . The peaks at  $m/z \sim 409$  and 423 in the spectrum of G<sub>1</sub> could also be assigned to  $[N-C_6H_4C_6F_{13}]^+$  and  $[N=N-C_6H_4C_6F_{13}]^+$ . The latter species would be obtained by reaction of diazonium salts with oxygenated phenolic functions (Scheme 1). The same possibility stands for the peaks at 183 and 185 in G<sub>2</sub>  $[N=N-C_6H_4Br]^+$ . It should be noted that such species are not observed during the grafting of nitrophenyl groups. The formation of  $-N=N-$  groups (i) at the surface of carbon and (ii) inside the layer has already been proposed by Belanger<sup>8</sup> and McCreery<sup>40</sup> in order to account for the XPS peak at 400 eV. However,

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the peak at 400 eV could also be due to the reduction of the nitro group under the XPS beam.<sup>46</sup>

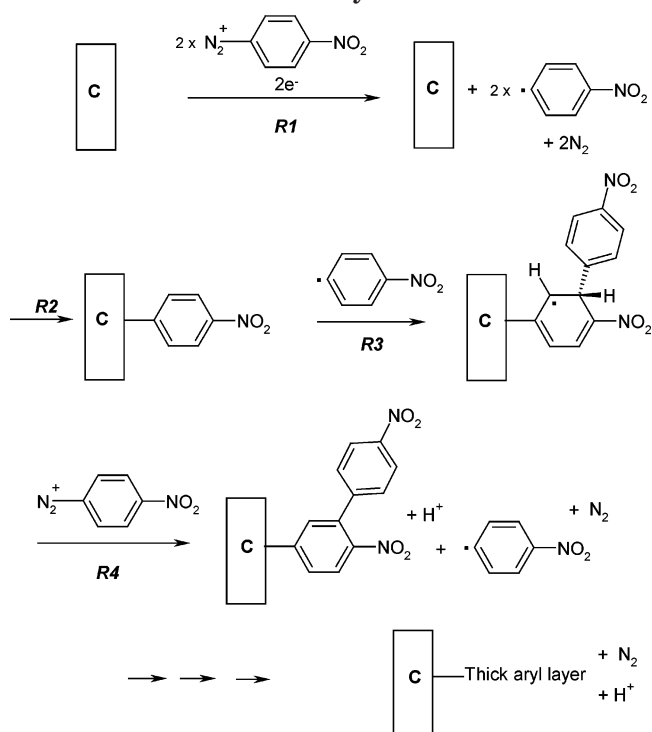
**4.2. Organic Multilayer Formation on Glassy Carbon.** These results also shed some insight on the structure of the organic layer through the observation of fragments including several aryl groups (for example,  $[\text{CH}_2\text{--CH}_2\text{--C}_6\text{H}_3\text{C}_6\text{F}_{13}\text{--C}_6\text{H}_4\text{C}_6\text{F}_{13}]^+$ ,  $[\text{C}_6\text{H}_3\text{C}_6\text{H}_4\text{Br}]^+$ ,  $[\text{CH--C}_6\text{H}_3\text{NO}_2\text{--C}_6\text{H}_5\text{NO}_2\text{--C}_6\text{H}_4\text{NO}_2]^-$ , and  $[\text{CC}_{16}\text{H}_8\text{--C}_{16}\text{H}_9]^-$ ). These polymeric fragments can originate from (i) recombination after the fragmentation of secondary ions extracted from a dense layer or (ii) direct extraction of polymeric fragments grafted on the surface. It would be rather unlikely that a tetramer as observed in G<sub>3</sub> would be formed under high vacuum, even in a dense medium such as a compact assembled monolayer. Therefore, the polymeric fragments could stem from a polymeric layer on top of the carbon surface. The growth of the grafted phase has already been observed by AFM on GC and HOPG<sup>9,10</sup> but also on metals,<sup>22</sup> and layers up to 100 nm have been produced provided the potential is negative enough.<sup>47</sup>

As stated above, it is possible to obtain rather thick layers in the range 5–15 nm both on carbon<sup>9,10</sup> and on metals.<sup>22</sup> However, integration of the voltammograms of nitrophenyl reporting groups always gives a number of nitro groups lower or at most equal to that of a close-packed monolayer.<sup>2,8,42,43</sup> These different studies have been performed under different conditions (substrate, potential, and time), which renders comparisons difficult.

To solve this discrepancy, Downard et al. investigated carefully the aryl layers obtained by the reduction of 4-nitrophenyl diazonium salt on PPF.<sup>48</sup> The potential of the electrode was set 150 mV more negative than the peak of the 4-nitrophenyl diazonium salt in acetonitrile, and integration of the voltammograms of the nitro groups attached to the grafted carbon surface provided the surface concentration of nitrophenyl groups. The surface concentration of these groups increased with time up to 600 s to reach the concentration of a compact close-packed monolayer ( $12 \times 10^{-10}$  mol cm<sup>-2</sup>). The thickness of layers obtained in this way was measured by AFM. The average thickness of the film corresponded approximately to four layers. These results attest that the compactness of the film was 21% of that which can be calculated for an ideal close-packed monolayer of nitrophenyl groups. It is however somewhat surprising that, whatever the conditions,<sup>2,48–50</sup> the integration of the phenyl groups corresponds to the surface concentration of a close-packed monolayer. If one expands this result to 5–15 nm thick multilayers, the compactness of the multilayer should decrease with its thickness in order to give a number of nitro groups of about that of a close-packed multilayer. This seems unlikely.

Different interpretations of the above results are possible. The compactness would be higher than that measured above if some nitro groups were lost in the grafting process. This would lower the surface concentration measured experimentally. We have searched unsuccessfully in the grafting solution for the presence of bromide or nitrite ions, in the case of, respectively, **2** or **3**, which would be present if bromo or nitro groups were lost in the grafting process (see the Supporting Informa-

**Scheme 2. Multilayer Formation**



tion). This is also clearly confirmed by the ToF-SIMS observation of fragments with up to four nitro groups.

Another possibility would be that some of the nitro groups do not respond at the potential of the nitrophenyl group. A discussion concerning the mechanism of multilayer formation is then required to further our present understanding. The mechanism of the electrochemical attachment of aryl groups to carbon or metallic surfaces has been assigned to the reaction of an aryl radical produced concertedly with the electron transfer to the diazonium salt<sup>4</sup> and further reaction of this radical with the carbon surface (**R1** + **R2** in Scheme 2). The transfer of a second electron to another diazonium salt would lead to the formation of dinitrogen and a new radical, which would attack the first grafted nitrophenyl group to give a cyclohexadienyl radical along reaction **R3** (Scheme 2). This reaction is the well-known S<sub>H</sub> homolytic substitution<sup>51–54</sup> (the Gomberg reaction<sup>55,56</sup>) which gives dimers and quadrimers by attack of an arene by an aryl radical. The rate constant for the reaction of the nitrophenyl radical on nitrophenyl is close to the rate constant for the reaction of the phenyl radical on benzene.<sup>52</sup> The latter, which has been measured as  $10.3 \times 10^5$  L mol<sup>-1</sup> s<sup>-1</sup>,<sup>54</sup> can be taken as an estimate for reaction **R3**. In order for the layer to grow, this radical must be reoxidized (and this is a key step in this demonstration). In the same way, to obtain fully polyaromatic compounds, the Gomberg mixtures must also be reoxidized, for example, by high potential

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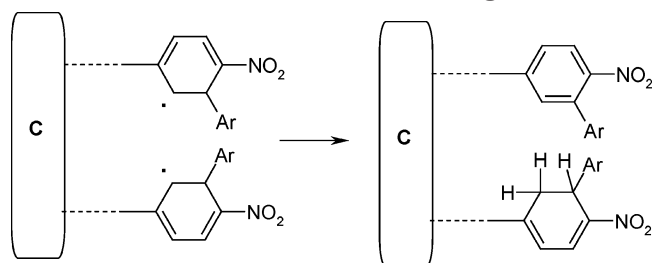
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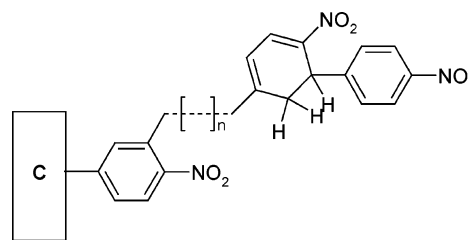
**Scheme 3. One Possible Terminating Reaction**

quinones.<sup>52,57</sup> In our case, this can be achieved by electron transfer with another nitrophenyl diazonium cation along reaction **R4** (Scheme 2).

Cyclohexadienyl radicals are prone to oxidation, for example, by oxygen<sup>58</sup> or metal ions.<sup>59,60</sup> It has already been observed that the growth of the layer was somewhat impeded in the presence of dioxygen,<sup>25</sup> which is in favor of termination reactions by oxidation. For instance, the hydroxycyclohexadienyl radical is oxidized by  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  ( $E^\circ = +0.239$  V/SCE) with a rate of  $1.30 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  and the cyclohexadienyl radicals deriving from 3-methylfluorene-9-one are oxidized in the presence of an excess of hexa-aquacopper(II) with a rate constant  $> 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ .<sup>59,60</sup> The comparison of the standard redox potentials reported above compared to that for the reduction of 4-nitrophenyl diazonium,  $E_p = 0.20$  V/SCE,<sup>2</sup> gives confidence in the existence of reaction **R4**. The products of this reaction are a dimer attached to the surface, an aryl radical, which can continue the growth process, and a proton. Indeed, one observes an increased acidity of the solution at the end of the reaction (see the Supporting Information). The reaction consumes two electrons per chain of polymer attached to the electrode, and the growth of the layer would be a purely chemical radical reaction (an electrochemically catalyzed homolytic aromatic substitution), which could explain the observation of dimers in  $\text{S}_2$ .

The chain terminating reaction is likely to be a hydrogen atom transfer from the solvent to the chain bearing the aryl radical; it should occur with a rate constant of  $\sim 10^7 \text{ s}^{-1}$ .<sup>54,61,62</sup> A hydrogen atom transfer can also occur from the solvent to the cyclohexadienyl radical,<sup>63</sup> leading to a cyclohexadiene cycle imbedded in the chain.

A disproportionation between two cyclohexadienyl radicals (which should be spatially close to each other, as they cannot diffuse away) would also terminate the reaction leading to a chain including a cyclohexadiene, as shown in Scheme 3, and another entirely aromatic chain. Finally, a dimerization of the propagating radical could also terminate the chain to give dimers, as in the Gomberg reaction. There is therefore a definite possibility that

**Scheme 4. Final Material**

cyclohexadiene groups can be included in the polymeric chain. Some of the hydrogens found in the fragments may possibly stem from a cyclohexadiene included in the chains; for example, in the case of **3**, the fragment at  $m/z = 379$  can be written as  $[\text{CH}-\text{C}_6\text{H}_3\text{NO}_2-\text{C}_6\text{H}_5\text{NO}_2-\text{C}_6\text{H}_4\text{NO}_2]^-$ , where C would be a carbon from the surface and  $\text{C}_6\text{H}_5\text{NO}_2$  a cyclohexadienyl group.

The presence of cyclohexadienyl groups in the chain allows an explanation of the growth of the chain. Such groups, which have lost their aromaticity, are not reduced at the potential of the nitrophenyl groups. Therefore, they are not accounted in the measurement of the surface concentration of the reporting groups by voltammetry. In addition, they interrupt the conjugation of the polymeric layer, as shown in Scheme 2. The final material is indicated in Scheme 4.

Finally, it should be mentioned that Bélanger et al. have proposed a different structure for the organic layer obtained from diazonium salts: the grafting mechanism would be operative for a few layers, and the remainder of the film would be the result of the adsorption of reaction products coming from the reduction of the diazonium salt (dimers or oligomers).<sup>64</sup> The present results would rather favor the model of Scheme 1 involving chains of six-membered rings, some being aromatic and some being cyclohexadienyl.

## 5. Conclusions

ToF-SIMS experiments performed on aryl layers derived from aryl diazonium salts and glassy carbon support grafting of these layers at the surface carbon. Grafting was spontaneous when a glassy carbon plate was immersed in a solution of aryl diazonium salt, but it was enhanced when the carbon plate was biased at a potential a little more negative than that of the diazonium salt reduction. These experiments suggest a C–C and C–O covalent bonding between the aryl groups and the carbon surface, which can explain the strong attachment of these layers to the carbon substrate. The fragments containing aryl dimers, trimers, or tetramers observed are indicative of the structure of these layers. A mechanism is proposed to account for the formation of these polymeric chains.

**Acknowledgment.** ToF-SIMS measurements were carried out by T. Cretin and J.-M. Berquier in collaboration with A. Huignard at the Saint-Gobain research center, Aubervilliers, France.

**Supporting Information Available:** Discussion on the analysis of the grafting solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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