## CHEMISTRY OF MATERIALS

## Sensitized Photografting of Diazonium Salts by Visible Light.

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**Supporting Information** 

**ABSTRACT:** Visible irradiation of a gold surface dipped into a solution of diversely substituted aryldiazonium salts in the presence of a photosensitizer  $(\text{Ru}(\text{bipy})_3^{2+} \text{ or eosinY})$  leads to a modification of the surface by attached aryl groups. A grafted nanometer thick polyphenylene film is obtained. The reaction is extended to a polyvinylchloride (PVC) surface. The mechanism proposed for the formation of this film involves the formation of an aryl radical that reacts



with the surface and then with the first grafted aryl group. The film is characterized by infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), water contact angles, and ellipsometry.

**KEYWORDS:** surface chemistry, photochemistry, diazonium salts

## I. INTRODUCTION

Surface modification is important both in daily life and in the academic field; for example, industrial processes permit to protect the surface of materials and to improve their aesthetics<sup>1</sup> while a large number of research papers and reviews are found under these headings, covering for example bioanalysis, microelectronics, energy related problems. These surface treatments can be achieved by a variety of physical methods (plasma, physical or chemical vapor deposition (PVD or CVD), atomic layer deposition (ALD)), and also by chemical or electrochemical methods and less commonly by photochemical methods. Contrary to physical methods, chemical methods permit the attachment of complex organic molecules to the surface; they proceed, for example, by silanization,<sup>2</sup> phosphonatation,<sup>3</sup> self-assembling of long alkyl chains (SAMs).<sup>4</sup> In addition to the industrial metal deposition (plating), electrochemical methods permit the attachment of organic molecules to conductive surfaces, either by oxidation (amines,<sup>5</sup> alcohols,<sup>6</sup> carboxylates,<sup>7</sup> Grignard reagents<sup>8</sup>) or by reduction (vinylics,<sup>9</sup> diazonium<sup>10</sup>). UV photochemical grafting of surfaces is more restricted; it has been applied to alkenes,<sup>11</sup> arylazides,<sup>12</sup> and acetonitrile.13

Functionalization of surfaces (carbon, metals, semiconductors, polymers) by homolytic dediazonation of diazonium salts  $(Ar-N_2^+ BF_4^-)$  is currently a well-established method<sup>10</sup> that has led to a variety of applications from analytical and biochemical sensors to microelectronics and biomedical industrial applications. It is easily performed under a variety of conditions:<sup>14</sup> electrochemical or homogeneous reduction in ACN or aqueous media, or ultrasonication and heating. All these methods provide strongly bonded polyaryl layers; the surface-aryl bond has been characterized by different spectroscopic methods<sup>15</sup> as well as by density functional theory (DFT) calculations.<sup>16</sup> A large number of substituents of the aryl group have been used to provide selective properties to the films, from simple groups such as NO<sub>2</sub>, CH<sub>3</sub>, CF<sub>3</sub>, COOH,<sup>10a</sup> C $\equiv$ CH<sup>17</sup> to macromolecules,<sup>18</sup> dendrimers,<sup>19</sup> proteins, and enzymes.<sup>20</sup> The thickness of the bonded films can be tuned from monolayers<sup>21</sup> to micrometric layers.<sup>22</sup> Except for electrochemistry, the methods described above<sup>10</sup> apply to non conductive surfaces such as polymers and inorganic oxides, even if large concentrations of diazonium salts have to be used, for example, in the grafting of polymers under ultrasonication.<sup>14j–1</sup> Patterning surfaces is possible by AFM,<sup>23</sup> by scanning electrochemical microscopy (SECM),<sup>24</sup> with polydimethylsiloxane PDMS stamps or nanoparticles shadowing the surface.<sup>25</sup>

Surprisinly, although photochemical methods (especially using visible light) would be interesting as they could be achieved with a mask above the surface, this approach has rarely been investigated to functionalize surfaces from diazoniums. In this line, the photografting of diazonium salts, either by UV irradiation of the salt or by visible irradiation of a [aryldiazonium cation (0.1 M) - dimethoxybenzene (0.9 M)] charge transfer complex (CTC) has recently been reported and films with up to 50 nm thickness have been obtained.<sup>26</sup> However, because of the poor absorption of visible light of this CTC, this technique requires a large amount of the donor (0.9 M) and the use of a high-power irradiation system (300 W halogen lamp). Since grafting of surfaces by aryl groups

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from diazonium salts has been previously assigned to the formation of radicals that react with the surface,<sup>27</sup> successful photochemical grafting utilizing a more conventional photoredox sensitizer is expected. Indeed, the formation of aryl radicals from diazonium by sensitized photochemistry ( $\lambda > 410$  nm) has been reported in a series of papers.<sup>28,29</sup>

For example, in the Pschorr cyclization, the stilbenediazonium ion irradiated in ACN in the presence of tris(2,2'bipyridyl)ruthenium(II), Ru(bipy)<sub>3</sub><sup>2+</sup>, leads to the radical through a reductive dediazonation reaction, and this radical cyclizes along a Pschorr reaction with 100% yield and high  $\Phi >$ 0.4 quantum yield (Scheme 1).

Scheme 1. Sensitized Photochemical Pschorr Cyclization



The proposed mechanism (Scheme 2)<sup>30–32</sup> involves the formation of an excited state,  $Ru(bipy)_3^{2+*}$ , that is able to

Scheme 2. Sensitized Photochemical Pschorr Reaction of Stilbene Diazonium



reduce the diazonium salt by transfer of one electron to give an aryl radical and  $\text{Ru(bipy)}_3^{3+}$ . The latter species oxidizes the intermediate cyclohexadienyl ring formed during the cyclization to restore the aromaticity and regenerate  $\text{Ru(bipy)}_3^{2+}$ .

This same reaction<sup>33</sup> was recently used for CH arylation using either  $\text{Ru(bipy)}_{3^{2+}}$  or eosinY as a sensitizer, as shown in Scheme 3.<sup>34</sup>

The mechanism in Scheme 2 is somewhat similar to that described during the grafting of diazonium salts on surfaces.<sup>35</sup> In the latter case, the generated radical reacts with (i) the surface and (ii) the first grafted aryl group to give a cyclohexadienyl moiety that is oxidized to restore the aromaticity, leading to multilayers.

In this paper, we present a different and simple method based on the sensitized photografting of diazonium salts under





visible light, using a conventional LED that permits surface patterning of insulating surfaces and should later on permit obtaining optically addressable selective surface grafting. We describe the photosensitized grafting of diazonium salts on gold and polymers, using 4-nitro (DNO<sub>2</sub>), 4-bromo (DBr), 4carboxy (D-COOH), 4-carboxymethyl (DCH<sub>2</sub>COOH), 3,5bis-trifluoromethyl (D(CF<sub>3</sub>)<sub>2</sub>), and 3,5-dimethoxy (D(OMe)<sub>2</sub>) benzenediazonium tetrafluoroborates. The aryl layers are extensively characterized by infrared reflection absorption spectroscopy (IRRAS), ellipsometry, contact angle measurements, electrochemistry, and X-ray photoelectron spectroscopy (XPS); particularly, XPS allows investigating the lateral homogeneity of the tethered layers.

## **II. MATERIALS AND METHODS**

**Substrates.** Gold coated (100 nm, Aldrich) Si wafer plates were cleaned in concentrated (96%) sulfuric acid, rinsed in ultrapure water and dried. Polyvinylchloride (PVC) was an industrial sample. They were cut into  $\sim 15 \times 15 \text{ mm}^2$  pieces, rinsed with ultrapure water and alcohol.

**Chemicals.** Ru(bipy)<sub>3</sub> (PF<sub>6</sub>)<sub>2</sub> was synthesized along the procedure previously described;<sup>36</sup> eosinY, DNO<sub>2</sub>, and DBr were obtained from Aldrich, and D(CF<sub>3</sub>)<sub>2</sub>, DCOOH, DCH<sub>2</sub>COOH, D(OMe)<sub>2</sub> were prepared from the corresponding anilines in aqueous HBF<sub>4</sub> solution by addition of 1.1 equiv of NaNO<sub>2</sub>.<sup>37</sup> All other chemicals were obtained from Aldrich and used without further purification.

**Photografting.** The small gold or polymer plates were placed in a closed deoxygenated cell refrigerated (6 °C (general) or 0 °C  $(D(CF_3)_2$  photografting onto PVC and DNO<sub>2</sub> photografting in aqueous solution), see Supporting Information) to limit the evaporation of the solvent and the spontaneous grafting of the diazonium salt. Visible light irradiation was performed with a LED bulb (4.8 W, 650 lm, cool white, Toshiba).

The irradiation solution was prepared from 2 mL of ACN (99.8%), DMSO (99.9%), DMF ( $\geq$ 99.5%), or ultrapure water, the diazonium salt (c = 0.155, 0.1, 0.05, or 0.01 M) and 0.0025 M Ru(bipy)<sub>3</sub> (PF<sub>6</sub>)<sub>2</sub> or eosinY. It was deposited on the gold plate, and two procedures were used. In procedure A, the maximum possible volume of ACN solution ( $50 \mu$ L/cm<sup>2</sup>) was deposited onto the gold surface, and irradiation was started; after 30 min, the solution was completely evaporated, and irradiation was stopped; with DMF and DMSO, evaporation was negligible. In procedure B, after evaporation of the ACN solution, more solution was added, and the process was repeated for 3 h. After irradiation, the plate was rinsed under ultrasonication for 280 s successively in ACN and ultrapure water and then dried.

**Electrografting.** XPS was used to compare photochemistry to electrochemistry, using a brominated compound (DBr) that presents, on a gold microelectrode, an irreversible voltammogram, with a reduction peak at -0.25 V/(Ag/AgCl) and a prepeak at -0.22 V/(Ag/AgCl). An electrolysis was performed on a gold plate ( $11 \times 11$  mm<sup>2</sup>) in a 10 mM DBr deoxygenated ACN + 0.1 M NBu<sub>4</sub>BF<sub>4</sub> solution at -0.55 V/(Ag/AgCl) for 5 min; the plate was rinsed as above.

**IR Spectra.** IRRAS and ATR spectra were recorded using a JASCO FT/IR-6100 Fourier Transform Infra Red Spectrometer equipped with MCT detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm<sup>-1</sup>. The background recorded before each spectrum was that of a clean substrate.

**XPS Spectra.** X-ray photoelectron spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a microfocused, monochromatic Al K $\alpha$  X-ray source (1486.6 eV) and a magnetic lens, which increases the electron acceptance angle and hence the sensitivity. An X-ray beam of 650  $\mu$ m size was used (15 kV × 200 W) [500  $\mu$ m (15 kV-150 W) for linescans]. The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. The Avantage Software, version 4.67, was used for digital acquisition and data processing. The spectra were calibrated against Au4f<sub>7/2</sub> set at 84 eV. The surface composition was determined using the integrated peak areas, and the corresponding Scofield sensitivity factors were corrected for the analyzer transmission function.

The lateral uniformity of the layers along the main axis of the plate sample was checked for photo- and electro-grafting of the diazonium salt. The conditions are reported in Table 1.

 Table 1. XPS Conditions for Perfoming the Linescan

 Routine Experiment

sample	X-ray spot size (µm)	step size (µm)	no. of points	total distance along X axis (μm)
photografting <sup>a</sup>	500	978	8	6847.5
$electrografting^b$	500	1193	15	16714.9

<sup>*a*</sup>Five survey spectra were accumulated with pass energy = 100 eV; dwell time = 100 ms; step size = 1.0 eV. <sup>*b*</sup>Similar conditions for survey spectra; in addition, high resolution spectra were recorded.

**Ellipsometry.** A Sentech SE 400 ellipsometer was used, with a He–Ne laser  $\lambda = 6328$  Å, angle = 70.00°. The values for ns and ks were measured on a clean gold wafer and then used to determine the thickness of the grafted layer: ambient: n = 1, organic layer:  $n_0 = 1.46$ ,  $k_0 = 0.0$ ; substrate:  $n_s = 0.230$ ,  $k_s = 3.341$ . The thickness was evaluated directly from these data by the ellipsometer software.

**Water Contact Angles.** They were measured with a Krüss DSA3 instrument. Three microliters of Milli-Q water was automatically deposited on the top of the test sample placed in a horizontal position on the instrument stage. At least five measurements were made for each sample. The values of the contact angles were calculated by the tangent method using Drop Shape Analysis software.

**Electrochemistry.** Voltammograms were recorded with an EGG Princeton Applied Research potentiostat 263A and an Echem 4.30 version software. The counter electrode was Pt, and the reference was Ag/AgCl.

#### **III. RESULTS**

Two Different Grafting Procedures on a Gold Substrate. In procedure A, a volume of an ACN solution of  $DNO_2$  is deposited at once on the gold surface and subjected to irradiation for 30 min. In procedure B, the irradiation is maintained for 3 h; during this time, the solution deposited on the surface has to be renewed about every 30 min. At the end of these procedures, the gold plates are carefully rinsed and examined by IRRAS.

**IRRAS Spectra on a Gold Substrate.** The spectra are presented in Figure 1 when using  $\text{Ru(bipy)}_3^{2+}$  as the sensitizer. As expected, the spectrum along procedure B is more intense than along procedure A. On both spectra, the characteristic NO<sub>2</sub> vibrations are observed at 1522 and 1347 cm<sup>-1</sup> as well as the ring vibration at 1599 cm<sup>-1</sup>. The main difference between these spectra is the presence, when procedure B is used, of a band at 2233 cm<sup>-1</sup> that can be assigned to cyano groups; their formation from acetonitrile will be discussed below.

As expected, the optical density of the nitro band (1522 cm<sup>-1</sup>) varies linearly with the concentration of diazonium along procedure A (Supporting Information, Figure S9). Increasing the concentration of Ru(bipy)<sub>3</sub><sup>2+</sup> (PF<sub>6</sub><sup>-</sup>)<sub>2</sub> above 0.0025 M



**Figure 1.** IRRAS spectra of two gold plates modified by irradiating an ACN solution containing 0.1 M DNO<sub>2</sub> and 0.0025 M Ru(bipy)<sub>3</sub><sup>2+</sup> ( $PF_6^-$ )<sub>2</sub>. Gold plate modified along (a) procedure A and (b) procedure B.

would be inefficient as for that concentration the light is completely absorbed in the thin layer of solution, while reducing the concentration of the sensitizer from 0.0025 to 0.001 M decreases the absorbance of the  $-NO_2$  band at 1522 cm<sup>-1</sup> by approximately nine times (Supporting Information, Figure S9, red square).

Other diazonium salts were photografted on gold in ACN and their IR characteristics are gathered in Table 2 (Supporting Information, Figures S2–S8, Table S1). Different solvents were investigated, and photografting was also observed in DMSO (Supporting Information, Figures S3, S4, S6 for DNO<sub>2</sub>, DBr, and DCOOH, respectively), DMF (Supporting Information, Figure S13), and in the presence of eosinY as a sensitizer (Supporting Information, Figures S3 and S14). Interestingly, aqueous solutions (0.1 M DNO<sub>2</sub> and 0.0025 M eosinY) can also be used (Supporting Information, Figure S14). The intensity of the nitro bands does not vary significantly with the solvent.

Since diazonium salts are prone to spontaneous homolytic dediazonation and grafting even on materials of low reactivity such as gold,<sup>40</sup> we have evaluated by IRRAS the importance of spontaneous grafting that always takes place simultaneously with photografting. The corresponding ratio (spontaneous grafting in the absence of irradiation/photochemical grafting under irradiation, Supporting Information, Table S2) amounts to 5% in ACN, 24% in DMSO, 56% in water at pH = 3, and up to 70% in DMF (at 6 °C). This indicates that the photografting reaction is more efficient in ACN but much less in other solvents including water.

**XPS Spectra on a Gold Substrate.** The gold plates modified by the sensitized  $[(Rubipy)_3^{2+}]$  photografting of 4-bromobenzenediazonium (DBr) along procedures A and B in ACN were also examined by XPS. The spectra are presented in Figures 2 and 3.

The survey spectrum of a gold plate modified along procedure B (3 h irradiation, Figure 2a) evidences the presence of Br3d (as a doublet at 69.6 and 70.7 eV in the  $\sim$ 3:2 peak area ratio, Figure 2b), Br3p (183–187 eV) and C1s (284.8 eV, close to the value of 285.10 eV reported for bromobenzene<sup>41</sup>), indicating that the bromophenyl group has been attached to the surface. This is confirmed by the presence of a shakeup satellite peak at 291 eV along procedure A in DMSO (Figure 2e). Note the absence of the XPS signature of Ru, indicating that the aryl radical does not attack the pyridine rings of the sensitizer, in

Table 2. IRRAS	Spectra of	Gold Plates	Photografted	in ACN	with	Different	Diazonium	Salts
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$Ar-N_2^+$	IR-ATR of $Ar-N_2^+$	IR of Ar–H	IRRAS of modified gold plates	
	wavenumber (cm <sup>-1</sup> )	wavenumber (cm <sup>-1</sup> )	wavenumber (cm <sup>-1</sup> )	assignment
DNO <sub>2</sub>			2233 <sup>b</sup>	CN
	2303			N≡N
	1612 1615 1574	1689, 1620, 1607	1599 <sup><i>a</i>,<i>b</i></sup>	ring vibration
	1539, 1352	1521, 1347	1522, 1347 <sup><i>a,b</i></sup>	NO <sub>2</sub> as and s
	856, 738	855, 739 <sup>38</sup>	857 <sup><i>a,b</i></sup>	CH out of plane
DBr			2204 <sup>b</sup>	CN
	2285			N≡N
	1554, 1464, 1414	1579, 1476, 1443	1568, 1484, 1445	ring vibration
	1123, 1030	1075–1065 <sup>39</sup>	1074, 1060	C-Br combination
	828,762	812, 735	811	CH out of plane
$D(CF_3)_2$			2233	CN
	2154		/	N≡N
	1594		1563	ring vibration
	1353, 1277, 1208, 1153,1135, 1108	1345–1265, 1190–1130, 1165–1105 <sup>39</sup>	1377, 1277, 1246, 1198, 1143	CF <sub>3</sub>
DCO <sub>2</sub> H	centered at 3117	3073-2965	3366	СООН
	2265			N≡N
	1706	1689	1745	C=0
	1589, 1509	1605,1585,1464 <sup>38</sup>	1585, 1526	ring vibration
DCH <sub>2</sub> CO <sub>2</sub> H	3105		3246	СООН
	2285			N≡N
	1706		1708	C=0
	1589, 1419		1599, 1498	ring vibration
$D(OMe)_2$	3105	3093,3070 <sup>38</sup>		aromatic C–H stretching
	2950, 2846	2959, 2942, 2836		CH <sub>3</sub>
	2303			N≡N
	1633, 1547,1471	1606, 1593, 1548, 1494	1606	ring vibration
<sup><i>a</i></sup> Procedure A.	<sup>b</sup> Procedure B.			

agreement with the IR spectra that do not exhibit the sensitizer signature (Supporting Information, Figure S1).

The presence of  $Au4f_{7/2}$  (84 eV) and  $Au4d_{5/2}$  (335 eV) indicates that the organic layer is rather thin (<5–10 nm). It does not completely shield the Au plate and does not retain the inelastically scattered electrons, as attested by the intense inelastic background beyond Au4f. The difference between procedures A and B is evidenced in Table 3.

As the irradiation time increases from procedure A to procedure B, the Au signal is more shielded by the organic layer and the Br/Au and C/Au atomic ratios increase. In DMSO, the ratios are higher than in ACN partly because of the spontaneous reaction evidenced above. The N/C atomic ratio is 0.03, both in DMSO and after electrografting in ACN; it is due partly to contamination and partly to the -N=N- groups that are formed during the growth of multilayers by attack of a diazonium group on a cyclohexadienyl radical.<sup>35</sup> During photografting by procedure A, the N/C atomic ratio in ACN is 0.06; it increases to 0.10 during procedure B, which is consistent with the appearance of CN bands on the IR spectra. The location of the N1s peak at 399.6 eV is similar to that given for polyacrylonitrile  $(399.6 \text{ and } 399.2 \text{ eV})^{42}$  and valeronitrile on Ni (399.7 eV).<sup>43</sup> On tilting the specimen from 90° to 40° (relative to the surface), the Br/N ratio (direct experimental ratio) increases slightly from 1.6 to 1.8, suggesting that the outermost layer of the coating is aryl-rich (Br is a unique elemental marker for the diazonium salt) whereas the electrode-organic layer interface is nitrogen- and thus "acetonitrile"-rich. We also checked the absence of (i) S2p in the layers prepared in DMSO, indicating that during procedure A, the solvent has not been involved in the photografting process and (ii) F1s indicating that no  $BF_4^-$  anion has been trapped in the film and also that no Balz–Schiemann reaction occurred that would have furnished fluorobenzene from benzenediazonium.<sup>44</sup>

A linescan was performed to check the homogeneity of the photo and electrografting. This experiment, presented in Figure 3, indicates that photografting provides homogeneous films regarding the spot size of the X-ray beam (see also in Supporting Information, Figure S17).

**Ellipsometry on a Gold Substrate.** In agreement with the XPS and IR results, ellipsometry shows that, except for DBr upon 90 min irradiation, the films are rather thin with thicknesses always less than 5 nm (Table 4). For example, the film obtained with DNO<sub>2</sub> in the presence of  $[Ru(bipy)_3^{2+}]$  along procedure A in ACN is  $1.8 \pm 0.6$  nm thick; such film corresponds to a tetraphenyl group (~ 1.7 nm), as shown in Scheme 4. The films are hydrophobic and thinner than those obtained by irradiation of charge transfer complexes.<sup>26</sup>

Water Contact Angles on a Gold Substrate. The values for the contact angles can be compared with those reported in the literature for grafted surfaces: Au- $C_6H_4$ - $C(=O)C_6H_5$ : ~ 70°,<sup>45</sup> C-C<sub>6</sub>H<sub>4</sub>-COOH: from ~45 to ~10° depending on pH,<sup>46</sup> C-C<sub>6</sub>H<sub>4</sub>-CF<sub>3</sub>: 82° and C-C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>H: 63°,<sup>47</sup> Au-C<sub>6</sub>H<sub>4</sub>-C(=O)C<sub>6</sub>H<sub>4</sub>-Polystyrene: 78°, Au-C<sub>6</sub>H<sub>4</sub>-C(=O)-C<sub>6</sub>H<sub>4</sub>-polyhydroxyethylmethacrylate: 44.5°, Au-C<sub>6</sub>H<sub>4</sub>-C(=O)-C<sub>6</sub>H<sub>4</sub>-polymethyl methacrylate: 57°.<sup>48</sup> The layers prepared by photochemistry (Table 4) are quite hydrophobic. The value obtained for the CF<sub>3</sub> substituted film, Au-C<sub>6</sub>H<sub>3</sub>-(CF<sub>3</sub>)<sub>2</sub>: 87° is in reasonable agreement with that in the literature for C-C<sub>6</sub>H<sub>4</sub>-CF<sub>3</sub>: 82°.

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**Figure 2.** XPS Spectra of a gold plate modified by photografting DBr in the presence of 0.0025 M  $\text{Ru}(\text{bipy})_3^{2+}$  (a,b,c) in ACN along procedure B; (d) in ACN along procedure A; (e) in DMSO along procedure A; (a) survey spectrum, (b) Br3d, (c, d) N1s, (e) C1s.



**Figure 3.** XPS linescan along a gold plate modified by photografting of DBr (c = 0.1 M) in ACN in the presence of 0.0025 M Ru(bipy)<sub>3</sub><sup>2+</sup> (PF<sub>6</sub><sup>-</sup>)<sub>2</sub> along procedure B.

In spite of the success of the process on gold, it cannot be applied for the modification of oxidizable substrates. For example, a 150 nm layer of copper on Si completely disappears under the same experimental conditions; this is likely due to the oxidation of copper by the oxidizing  $\text{Ru}(\text{bipy})_3^{3+}$  ( $E_{1/2} = 1.35$  V/SCE). A distinctive characteristic of photografting, by comparison with electrochemistry, is the possibility of using

# Table 3. Surface Chemical Composition $^a$ of the Modified Gold Plates

atomic ratios	ACN procedure A	DMSO procedure A	ACN procedure B	ACN electrochemistry
Br/Au	0.068	0.114	0.455	3.33
C/Au	1.05	2.17	4.55	16.7
N/C	0.06	0.03	0.10	0.03
<sup><i>a</i></sup> In atomi	c ratios.			

## Table 4. Films Thicknesses Measured by Ellipsometry and Water Contact Angles

diazonium salt [sensitizer]	solvent (procedure)	thickness (nm)	water contact angles (degrees)
none	bare g	57 ± 4	
$DNO_2 [Ru(bipy)_3^{2+}]$	ACN (A)	$1.8 \pm 0.3$	$75 \pm 1$
	DMF (A)	$3.9 \pm 0.6$	
	DMSO (A)	$1.3 \pm 0.1$	
	ACN (B)	$3.2 \pm 0.5$	$80 \pm 3$
DNO <sub>2</sub> [EosinY]	water, pH = 3 (A)	2.1 ± 0.4	86 ± 2
DBr $[Ru(bipy)_3^{2+}]$	ACN (A)	$3.1 \pm 0.4$	84 ± 3
	DMSO (A)	$3.3 \pm 0.7$	87 ± 4
	ACN (B)	$15.0\pm1.8$	81 ± 2
$D(CF_{3})_{2} [Ru(bipy)_{3}^{2+}]$	ACN (B)	$3.1 \pm 0.9$	87 ± 2
$D(OMe)_2 [Ru(bipy)_3^{2+}]$	ACN (A)	$1.7 \pm 0.4$	$80 \pm 3$

Scheme 4. Schematic Representation of the Film Formed with DNO<sub>2</sub> in ACN along Procedure A



nonconducting substrates. We therefore investigated the grafting of PVC as an example of polymer.

**PVC Substrate.** A DNO<sub>2</sub> solution (c = 0.1 M) and eosinY (c = 0.0025M) in ACN was deposited on PVC and subjected to irradiation for 1 h at 0 °C. The bands of the nitrophenyl group clearly appear at 1525 and 1347 cm<sup>-1</sup>, as shown in Figure 4, and a blank experiment in the dark does not present any NO<sub>2</sub> band.

Irradiation allows to localize the grafting, as shown in Figure 5 that presents the image of ~4 mm grafted spots obtained after 1 h irradiation of droplets containing  $D(CF_3)_2$  and  $Ru(bipy)_3^{2+}$ . An IRRAS spectrum recorded on a 100 × 100  $\mu$ m<sup>2</sup> surface inside the spot presents the same bands as those in Figure 4, and the water drop angle inside the spots is 107 ± 4° while it is only 84 ± 3° outside the spots on unmodified PVC.



**Figure 4.** IRRAS spectrum of PVC modified by photografting  $DNO_2$  (c = 0.1 M) and eosinY (c = 0.025 M) for 1 h at 0 °C.



**Figure 5.** Optical image of a PVC surface  $(15 \times 20 \text{ mm}^2)$  patterned with  $PVC-C_6H_4$ - $(CF_3)_2$  spots (~ 4 mm).

#### **IV. DISCUSSION**

IRRAS (for example, characteristic bands of the nitrophenyl group), XPS (Br3d peaks and change in the survey spectra background), electrochemistry (characteristic nitrophenyl reduction peak), and water contact angles (hydrophobic surface obtained with  $D(CF_3)_2$ ) indicate that the substituted phenyl groups are attached to the surface. The film resistance to ultrasonic rinsing, as for electrografted films for which the existence of a bond between the surface and the aryl group has been demonstrated,<sup>15</sup> indicates the existence of a strong bonding. The films are rather thin, generally less than 5 nm, even for long irradiation times.

The mechanism we propose for the formation of these films is given in Schemes 5 and 6. It is similar to that operating during electrografting.

Upon irradiation with visible light, the excited state of  $Ru(bipy)_3^{2+}$  is formed (**R1**, Scheme 5) that reduces the diazonium salt to give the aryl radical (**R2**); this radical reacts







with the surface to give a surface bonded aryl group (**R3**).<sup>35</sup> In a second step, another aryl radical attacks the first attached aryl group to give a cyclohexadienyl radical (**R4**); this radical can be reoxidized to a biaryl by  $\text{Ru}(\text{bipy})_3^{3+}$  (**R5**) or by the starting diazonium itself. Since  $\text{Ru}(\text{bipy})_3^{3+}$  is a much stronger oxidizing species [ $E^{\circ}$  ( $\text{Ru}^{3+}/\text{Ru}^{2+}$ ) = 1.30 V/SCE] than diazonium salts [ $E^{\circ}(^+\text{N}_2\text{C}_6\text{H}_5/\text{C}_6\text{H}_5^{\bullet})$  = 0.05 V/SCE], the Ru species should be much more efficient for the oxidation of the cyclohexadienyl radical than the diazonium salt (**R5**). We have not attempted to characterize some possible remaining  $\text{Ru}(\text{bipy})_3^{3+}$  as the amount of solution used was too small.

For longer irradiation times, cyano groups are observed by IR and through the increase of %N in XPS, the location of the peak being in agreement with published values for cyano groups. This observation can be compared with previously published results concerning the 2,6-dimethylbenzenediazonium salt. When the latter is reduced electrochemically, the ensuing sterically hindered radical cannot react with the surface, but it is able to abstract a hydrogen atom from acetonitrile to give the cyanomethyl radical ( $\cdot$ CH<sub>2</sub>CN). The latter reacts with the surface to give *Surface*-CH<sub>2</sub>CN, and it further attacks the already grafted nitrile group to give *Surface*-CH<sub>2</sub>(NH<sub>2</sub>)-[CH<sub>2</sub>(NH<sub>2</sub>)]<sub>n</sub>-CH<sub>2</sub>-CN.<sup>49</sup>

The formation of cyanomethyl radicals likely also occurs in the present experiments along reaction (R6, Scheme 6). The issue is to know where they react; they do not form  $-[CH_2(NH_2)_n]$ - chains as previously observed,<sup>49</sup> since in such a case, the-CN bands would have disappeared from the IR spectra and strong NH deformation bands would have appeared at  $\sim 1600$  cm<sup>-1</sup>. Therefore, they either react with the surface, in competition with the aryl radicals, or they react on attached aryl groups along a S<sub>H</sub> homolytic aromatic substitution. Such a substitution requires a further oxidation step (similar to **R5**) that can be performed by  $Ru(bipy)_3^{3+}$ . We have shown above that when the sample is tilted from 90 to  $40^{\circ}$ (relative to the surface), the N1s signal decreases slightly, indicating that the nitrogen atoms are close to the gold surface, and Br/N increases, indicating that the CH<sub>2</sub>CN groups are closer to the gold surface than the bromoaryl groups. These observations fit reaction (R9). Therefore, for long reaction times, a mixed aryl/CH<sub>2</sub>CN surface seems the most likely structure (R9, Scheme 6).

## **Chemistry of Materials**

## V. CONCLUSION

Visible light sensitized photografting of aryldiazonium salts provides homogeneous thin oligoaryl films that have been characterized by IR, XPS, ellipsometry, and water contact angles. Such strategy should be amenable to a large set of substituted aryl groups. Unlike electrografting, photografting allows the surface modification of non conducting substrates such as polymers (PVC in this paper). Moreover, unlike irradiation of charge transfer complexes,<sup>26</sup> this process does not require large amounts of the complexing species, and it provides thinner films close to a monolayer. Besides, patterned grafting can be obtained by localized deposition of the reacting solution or through the use of masks. Therefore, this process should be useful for the fabrication of sensors, the thin localized aryl films serving as the anchoring place for the biosensing molecule.

## ASSOCIATED CONTENT

### **S** Supporting Information

IR spectra of the sensitizers and of the surfaces modified by different diazonium salts; rinsing procedures; blank experiments, electrochemical, and XPS experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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