

Indirect Grafting of Acetonitrile-Derived Films on Metallic Substrates

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Strongly bonded organic films with amino groups are obtained on gold, copper, and silicon surfaces by reduction of 2,6-dimethyl benzenediazonium in acetonitrile (ACN). The sterically hindered 2,6-dimethylphenyl radical is unable to attach to the surface, but it abstracts an hydrogen atom from ACN to give the cyanomethyl radical (\cdot CH₂CN) that reacts with the surface. A spontaneous reaction is also possible on copper. The film is characterized by IR spectroscopy, scanning electron microscopy, ellipsometry, water contact angles, and cyclic voltammetry. A mechanism is elaborated that accounts for the formation, grafting of the cyanomethyl radical, and finally formation of amino multilayers.

Introduction

The reduction of aryl diazonium¹⁻⁷ and diaryliodonium⁸ salts on various materials provides an easy method to ensure the covalent bonding of aryl layers to surfaces. The key point is the formation of aryl radicals, either by

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Scheme 1



C =Carbon, Met =Metal, SC = Semiconductor, P=Polymer

electrochemistry, or spontaneously^{1b} (through a dissociative electron transfer and N₂ evolution⁹), or in the presence of an added reducing agent.¹⁰ Once produced in aprotic or aqueous media, part of those aryl radicals reacts with carbon,^{2b} metal,^{2h} semiconductor,^{2d} and polymer^{10b} surfaces according to Scheme 1.

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In an ACN solution, the aryl radicals generated from diazonium salts can undergo various reactions that are presented in Scheme 2: (i) electrografting with the surface (k_{surf}) , (ii) dimerization in solution (k_{dim}) , (iii) reaction with another aromatic group (either from an aromatic compound in the solution or already grafted onto the surface) to give dimers or oligomers in solution or attached to the surface $(k_{Ar}, \text{Gomberg-Bachmann}^{11}$ reaction that involves a cyclohexadienyl intermediate), and (iv) abstraction of an hydrogen atom from the solvent, ACN, to give the cyanomethyl radical $\cdot \text{CH}_2\text{CN}(k_{\text{H}})$.¹²

If we consider only the reactions with the surface (i and iii), the reduction of diazonium salts (by electrochemistry, a reducing agent, or a reducing surface) provides aryl radicals that for one part react with the surface, and for the other part attack the first attached aryl groups, leading to the growth of a polyphenylene film.¹³ Previously, we showed that the steric hindrance is one of the parameters that controls the polyphenylene film growth: the two bulky tert-butyl groups of 3,5- di tert-butyl benzenediazonium prevent the growth of the film $(k_{Ar} \approx 0)$ and a monolayer can be obtained;^{14a} the two methyl groups of 2,6-dimethyl benzenediazonium (2,6-DMBD) prevent the attachment of the radical to the surface $(k_{\text{Surf}} \approx 0)$.^{14b} However, these two methyl groups should not prevent the abstraction of an hydrogen atom from the solvent and the formation of the cyanomethyl radical (iv or Scheme 3 [R2]). Besides, such a radical should be stabilized in the medium by the isotopic reaction with ACN itself (Scheme 3 [R3]). This paper deals with the reaction of this radical with the surface and the subsequent formation of an organic

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film of controllable thickness. In this case, an indirect grafting of an easily available solvent takes place through a diazonium salt.

Experimental Section

Chemicals. Anhydrous ACN (99.8%; < 0.05% water) was from Aldrich as well as tetrabutylammonium tetrafluoroborate, which was kept in an oven at 95 °C. Milli-Q water (> 18 M Ω cm) was used for rinsing the samples. 2,6-DMBD was prepared by the standard procedure.^{14b}

Samples. One (or 2) \times 1 cm² gold-coated silicon wafer plates (Aldrich, 1000 Å coating) were cleaned in a "piranha" solution (1/3 v/v H₂O₂/H₂SO₄ for 10 min), and rinsed one time with Milli-Q water under sonication (10 min).

Massive 1 (or 2) \times 1 cm² copper plates were polished with different grades of polishing paper and finally with a 0.04 μ m alumina slurry on a polishing cloth, using a Presi Mecatech 234 polishing machine. After polishing, the plates were rinsed with Milli-Q water, left for 10 min in a 5% aqueous solution of citric acid, rinsed again with Milli Q water, and finally sonicated for 10 min in acetone.

P-doped silicon samples (Siltronic, resistivity 0.016 Ω cm) were hydrogenated by dipping for 5 min in 3% HF, and then rinsed in Milli-Q water for 5 min under sonication.

The electrodes for cyclic voltammetry were Cu or Au (diameter, 1 mm) wires imbedded in epoxy resin or a small silicon shard. Metallic electrodes were polished and rinsed as the copper plate above.

Electrochemical experiments were performed with an EG&G 263A potentiostat/galvanostat and an Echem 4.30 version software. Electrografting was performed by chronoamperometry in ACN + 0.1 M NBu₄BF₄ solutions with a 10 mM solution of 2,6-DMBD. The reference electrode was Ag/AgCl and the counter electrode a platinum foil. In the case of Si, the modification was achieved by chronopotentiometry at E = -0.9 V/Ag/AgCl for 900 s under light irradiation. The Si sample was scratched and connected in the back with silver conducting polymer and a piece of copper tape.

Spontaneous grafting of the copper plates was carried out by immersing the plates into $ACN+ 0.1 \text{ M } NBu_4BF_4$ solutions in the presence of 10 or 100 mM of 2,6-DMBD for 30 min.

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Scheme 3



IR spectra of the modified samples were recorded using a Jasco FT/IR-6100 Fourier Transform Infra Red Spectrometer equipped with a MCT detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm^{-1} .

TOF-SIMS spectra were obtained with an ION-TOF IV with Au⁺ primary ions at 25 keV. The analyzed zone was 150 μ m², and the acquisition time 75 s. Blank samples were analyzed in the same run as the modified samples. The peak intensity refers to the area of the peak normalized to the total intensity of the spectrum.

Thicknesses of films grafted onto Au and Cu were measured with a mono wavelength ellipsometer Sentech SE400. The following values were taken for gold, $n_s = 0.182$, $k_s = 3.489$; copper, $n_s =$ 0.265, $k_s = 3.108$, and the polymeric layer $n_s = 1.210$, $k_s = 0$. These values were measured on clean surfaces before electrografting, and the thickness was determined from the same plate after electrografting. On Au, the thickness was also measured from the SEM image of the limit of the layer of a tilted sample. Thicknesses of films grafted onto Si were measured by carving a sharp furrow through the film with a sharp tip and measuring the depth of this furrow with an α Step IQ profilometer from KLA Tencor. The length of a chain with multiple CH₂CH(NH₂) groups was calculated with ACD ChemSketch 12 after optimization (11.23 Å for ten groups).

SEM images were obtained using a Zeiss Ultra II electron microscope.

Contact angles were measured by a standard technique, in which the substrate was cooled by a Pelletier element and a drop of a few microliters of water was placed on it, using a microsyringe. A stereomicroscope allowed the droplet image enlargement and the contact angle measurement.



Figure 1. Chronoamperometry of a copper plate in a 10 mM 2,6-DMBD solution in ACN +0.1 M NBu₄BF₄. Electrode biased at E = -0.9 V/Ag/ AgCl for 480 s.

Trifluoroacetylation. A modified gold plate was immersed into 5 mL of THF + 0.5 mL of (CF₃CO)₂O and a few drops of triethylamine and left at room temperature overnight.¹⁵ The plate was then rinsed with acetone and distilled water under sonication.

Results

Electrochemical Measurements. The chronoamperometry of a copper plate ($s = 1 \text{ cm}^2$) in an ACN + 0.1 M NBu₄BF₄ + 10 mM 2,6-DMBD solution is shown in Figure 1. It is very different from the chronoamperogram usually observed with diazonium salts where for t > 5 s, the current is ~0. On the contrary, here, for t > 5 s, the absolute value of the current increases slightly with time, which indicates that the film formed on the electrode through a cathodic reaction is not blocking.^{2m} At the end of the electrolysis, a gray film is observed on the surface. Similar results were observed with gold and hydrogenated silicon and the chronoamperograms are presented in Figures S1 and S2 (see the Supporting Information).

IRRAS Measurements. The IR spectrum of a 2 cm² copper plate submitted to a constant potential of -0.9 V/ Ag/AgCl for 480 s is presented in Figure 2a. The main features of this spectrum are the absence of a $-C \equiv N$ stretching band¹⁶ (2254 cm⁻¹ for ACN itself) and the presence of bands corresponding to grafted amine groups at 1595 cm⁻¹ (NH deformation) and at 3243 cm⁻¹ (-NH stretching). A band at 1397 cm⁻¹ (CH₂ scissoring) is also observed.¹⁷

The IR spectrum of a 2 cm² copper plate submitted to a lower potential (E = -0.45 V/Ag/AgCl) for 480 s is presented in Figure 2b. The latter amino bands at 3260 and 1595 cm⁻¹ are still observed, although smaller, and a new strong C=O band is present at 1693 cm⁻¹. This indicates that changing the potential for electrografting results in a different structure for the grafted film.

Grafting on copper was also achieved under the same conditions as for Figure 2a except that ACN contained 1% H₂O. The main IR bands of the plate modified under these conditions are shown in the insert of Figure 2c together with the corresponding bands under dry conditions (Figure 2a). The IR bands have decreased by $\sim 40\%$.

The electrochemical modification of a gold plate at E = -0.9 V/Ag/AgCl for 480 s is also possible as shown by IRRAS in Figure 3a. The IRRAS spectrum is similar to that obtained on copper (Figure 2a); however, the band at 1397 cm⁻¹ is absent.

To ascertain the presence of amino groups on the surface, a gold plate modified with ACN was treated with trifluoroacetic anhydride (5% solution in THF) overnight to transform primary amine groups into trifluoroacetamide functions $(-NH_2+(CF_3C=O)_2O \leftrightarrow -NHC(O)CF_3)$. The IR spectrum of Figure 3b shows that the NH deformation at 1617 cm⁻¹ has disappeared and the band at 3243 cm⁻¹ has decreased; it now corresponds to the NH stretching of amide functions. The presence of CF₃(CO) groups in the film is evidenced by the C=O band at 1785 cm⁻¹ and the CF₃ stretching bands at 1210 and 1170 cm⁻¹ (~3350, 3200, 1705, 1200, 1155 cm⁻¹ for trifluoroacetamide, CF₃C(=O)NH₂).

An ACN-derived film can also be grafted on copper and iron electrodes by spontaneous reduction of 2,6-DMBD in an ACN solution (without supporting electrolyte). Figure 4 shows the presence of amino bands at 3300 and 1600 cm⁻¹ and also of a strong C=O band at 1693 cm⁻¹ as in the case of the electrochemical grafting at E = -0.45 V/Ag/AgCl. For such a spontaneous grafting, the intensity of the IR bands increases with the concentration of 2,6-DMBD (from 10 to 100 mM) (compare Figures 4 a and b).

ToF-SIMS. We have recorded the Tof-SIMS spectrum of a copper plate spontaneously grafted in ACN + 100 mM 2,6-DMBD for 30 min (without any supporting electrolyte). The main features of this spectrum are summarized in Table 1 and some significant peaks are presented in Figure 5.

Thickness of the Films. They were measured by ellipsometry, profilometry, or SEM and are gathered in Table 2.

The thickness of the layers corresponds to a quite large number of $-CH_2-CH(NH_2)-$ groups (see below). Because the size of this group is 1.1 Å along the chain axis, there should be ~500 of such groups on both gold and copper, indicating a very efficient process for the growth of the layer.

SEM Results. The acetonitrile derived films grafted electrochemically on gold or copper surfaces via 2,6-dimethyl phenyl radicals were observed by SEM (Figures 6a, b and c, d for gold and copper respectively). Figure 6b shows the interface between the film and the unmodified gold surface. Other images are given in the Supporting Information (see Figures S3–S5). The films are homogeneous and dense. On gold (Figure 6a,b), the surface is rather homogeneous with some bumps, and on copper a clear structure is visible, the origin of which is still unclear (Figures 6c,d and S5).

Contact Angle Measurements. The water contact angle measurements before and after treatment are gathered in

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⁽¹⁶⁾ The nitrile band of acetonitrile is located at 2254 cm⁻¹. This position is very close to that of residual CO₂, but careful examination of the spectra before CO₂ correction indicates that, in any case, the CN band should not exceed the background noise.

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Figure 2. IRRAS spectra of a copper plate after electrolysis in an ACN solution of 10 mM 2,6-DMBD. Plate biased at E = (a) - 0.90 and (b) - 0.45 V/Ag/ AgCl for 480 s under dry conditions; inset (c) in the presence of 1% H₂O. IR assignments in cm⁻¹: 3243, NH stretching; 1595, NH deformation; 1693, C=O stretching.



Figure 3. IRRAS spectra of a gold plate after electrolysis in a 10 mM 2,6-DMBD ACN solution. Plate biased at E = -0.9 V/Ag/AgCl for 480 s (a) before and (b) after reaction overnight with trifluoroacetic anhydride (CF₃C=O)₂O in a THF solution. IR assignments in cm⁻¹: 3243, NH stretching; 1597, NH deformation; 1170 and 1210, CF₃ stretching.

Table 3 for gold and copper. They indicate that the surface has been modified by the treatment into a more hydrophobic one.

Discussion

The 2,6-DMBD salt is electrochemically reduced^{14b} at $E_p = -0.25$ V/Ag/AgCl (gold electrode, 10 mM solution in ACN + 0.1 M NBu₄BF₄, scan rate v = 100 mV s⁻¹; see Figure S6 in the Supporting Information). In the above experiments, the electrolyses were performed at -0.9 or -0.45 V/Ag/AgCl to reduce the aryldiazonium salt into the aryl radical. We showed

previously that, when using a 4 mM solution of 2,6-DMBD, the radical obtained does not attach to metal surfaces.^{14b}

Besides, when diazonium salts are grafted to a metal, the structure of the film does not change with the grafting potential;¹ this is not the case with the ACN film presented above, as the IRRAS spectra are different when the grafting is performed at -0.45 or -0.90 V (Figure 2). In addition, in the case of spontaneous grafting, ACN is the only compound present in the solution besides the diazonium salt. Therefore, the observed grafted organic film should originate from ACN.



Figure 4. IRRAS spectra of a copper plate dipped for 30 min in (a) 10 and (b) 100 mM 2,6-DMBD in an ACN solution. IR assignments in cm⁻¹: 3250, NH stretching; 1595, NH deformation; 1693, C=O stretching.

Table 1. Tof-SIMS Spectrum of a Copper Plate Modified in ACN + 2,6-DMBD (positive fragments)

m/z	assignment	intensity on bare Cu	intensity on modified Cu
62.93	⁶³ Cu	5034	766
64.93	⁶⁵ Cu	2229	336
77.04	C ₆ H ₅	289	1423
78.04	C_6H_6	63	390
91.05	$C_6H_4-CH_3$	223	751
105.07	CH ₃ -C ₆ H ₄ -CH ₃	120	1514
115.05	$(CH_3)_2C_6H_4-CH$	70	620
146.10	CH ₂ -C ₆ H ₄ -CH-CH-NH ₂	14	950
267.17	$[C_6H_4(CH_3)\text{-}CH\text{-}CH(NH_2)]_2$	12	254

In addition, the spectra do not indicate the presence of nitrile groups, alternatively they clearly present the signature of amine groups, and this is confirmed by the trifluoroacetylation reported above. Tof-SIMS spectra also present nitrogen containing fragments that can be assigned to amino groups. To account for these observations, we propose the mechanism reported in Scheme 3.

After its formation [R1], the 2,6-dimethylphenyl radical can dimerize in solution but the abstraction of an hydrogen atom from the solvent [R2] is favored by the large concentration of ACN (17 M) and by the fast rate of hydrogen atom abstraction (the pseudo first order rate constant of the reaction of the cyanophenyl radical measured in ACN¹² is $k_{\rm H} = 4 \times 10^7 \, {\rm s}^{-1}$). Once formed, the cyanomethyl radical is stabilized by the isotopic reaction [R3]¹⁸ and reacts with the surface in reaction [R4]. However, the IR spectra do not show any significant −C≡N bands but present strong amino bands. To rationalize this fact, we propose that the surface-CH₂CN be attacked by the cyanomethyl anion as in reaction [R8]. When the reaction is performed electrochemically, this anion can be obtained in two ways: by reduction of the radical or by deprotonation of ACN. The redox potential $E^{\circ}(\cdot CH_2CN/^{-}CH_2CN) = -0.69 \text{ V/SCE that is } -0.66 \text{ V/}$ Ag/AgCl has been measured by Gennaro;¹⁹ therefore, at the electrolysis potential of -0.9 V, the cyanomethyl radical should be reduced to its anion by the electrode [R5]. At this potential, the 2,6-dimethyl phenyl radical should also be reduced to its anion $[R6]^{20}$ and this aryl anion should also be able to deprotonate ACN [R7].²¹

In the case of spontaneous reactions, the problem is more complicated, the only reducing agent in the experiment is copper. The open circuit potential measured for a copper plate in a 100 mM ACN solution of 2,6-DMBD is -0.44 V/Ag/AgCl; therefore, reduction of the cyanomethyl radical should be possible, at least in part. The cyanomethyl anion should attack the first grafted cyanomethyl group in the same [R8] reaction as in electrochemistry. The attack of the grafted cyanomethyl group by the cyanomethyl anion is known as the Thorpe reaction,²² a reaction analogous to the aldol reaction. In both caseselectrochemical or spontaneous-one obtains an iminium ion that should be protonated by the very small amount of residual water or by abstraction of a proton from ACN,

⁽¹⁸⁾ The increase in the current observed during the chronopotentiometry is most likely related to the increasing concentration of the cyanomethyl radical in the solution .

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^{(20) (}a) The reduction potential of the phenyl radical to its anion was measured by Andrieux,^{20b} $E_p = -0.64$ V/SCE, and Vase,^{20c} $E_p = -0.95$ V/SCE. The reduction potential of the 2,6-dimethyl phenyl radical should be slightly more negative because of the effect of the methyl groups. (b) Andrieux, C. P.; Pinson, J. J. Am. Chem. Soc. 2003, 125, 14801. (c) Vase, K. Ph.D. Thesis, University of Aarhus, Aarhus, Denmark, 2007.

 ^{(21) (}a) The pKa of acetonitrile is 31.3^{21b} and that of phenyllitium is about 43,^{21c} therefore, the 2,6-dimethylbezene anion should be able to deprotonate acetonitrile to give the cyanomethyl anion. (b) Rossi, L.; Feroci, M.; Inesi, A. Mini-Rev. Org. Chem. 2005, 2, 79. (c) Smith, M. B.; March, J. March's Advanced Organic Chemistry, 5th ed.; Wiley Interscience: New York, 2001; p 331. (22) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*,

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Figure 5. Some characteristic ToF-SIMS peaks.

Table 2. Thickness of the Layers Prepared by Reduction of 2,6-DMBD in ACN at E = -0.90 V/Ag/AgCl for 480 s

Au ^a	Cu^b	Si ^c
$56 \pm 1 \text{ nm}$	$49 \pm 3 \text{ nm}$	$9\pm4~\mathrm{nm}$

^{*a*}Measured by SEM. ^{*b*}Measured by ellipsometry. ^{*c*}Measured by profilometry. [2,6-DMBD] = (a,b) 100 mM.

regenerating the cyanomethyl anion [R9]. Imines are known to be reducible,²³ leading to amines via [R10] that are characterized through their IR spectra and their transformation into trifluoroacetamide. However, during the spontaneous reaction, the potential is less negative than during the electrochemical reaction and only part of the imines is reduced. As imines are known to be very easily hydrolyzed,²⁴ the unreduced part is transformed to ketones [R11], most probably during the rinsing of the samples as the experiments were performed under dry conditions. This is in agreement with the IR spectra that show the formation of both amines and ketones. The absence of IR bands corresponding to the terminal nitrile group is a consequence of the low proportion of nitrile groups compared to $-CH_2CH(NH_2)-$ groups (1 for 500).

In addition, the ToF–SIMS spectra indicate that the aryl radical is able to react with the polymeric chain obtained from acetonitrile, in agreement with some fragments presented in Table 1. Such reaction, if sufficiently effective, should also be observed by a less sensitive method such as IR. Then bands similar to those of 2,6-dimethylaniline could be expected, such as CH₃ stretching at 2967 and 2921 cm⁻¹ and ring vibrations at 1622 and 1480 cm⁻¹; on the spectrum of Figure 2, the 2967, 2921, and 1480 cm⁻¹ bands are clearly absent. The

bands at 848 and 770 cm⁻¹ can be attributed to aromatic groups, but the 848 cm⁻¹ signal could also correspond to an aliphatic amine (strong 856 cm⁻¹ band for isopropylamine). This indicates that the number of aryl groups attached to the chain is limited or small. Indeed, once formed the 2,6-dimethylphenyl radical can react either with acetonitrile (17 M) or with the thin organic layer present on the surface; in view of the relative concentrations, the reaction with ACN is favored.

The results described here can be compared with the reaction observed when hydrogenated diamond is treated with peroxides in ACN.²⁵ The mechanism, which is shown in Scheme 4, involves the formation of the peroxy radical that abstracts an hydrogen atom from the diamond surface; the diamond radical also abstracts an hydrogen from ACN and recombination of a diamond radical with the cyanomethyl radical provides a surface that is functionalized with -CH₂CN groups. The presence of the $-C \equiv N$ group is observed through its vibration at 2271 cm⁻¹ that increases with time. But the IR spectrum²⁵ does not show any signal corresponding to an amine. Even if the grafted radical is the same, the layer is quite different from that observed here; this is due to the absence of an anion that could attack the first grafted cyano group.

This reaction can also be compared with that described by Deniau et al. who were able to form composite polynitrophenylene-polyvinyl films by simultaneous reduction of the 4-nitrobenzenediazonium salt and a vinylic compound.²⁶ In this case, the nitrophenyl radicals initiate the radical polymerization of vinylic monomers under protic conditions. This reaction has been called SEEP (surface electroinitiated emulsion polymerization). The main difference with our procedure is that the 2,6-DMBD

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Figure 6. SEM of (a, b) gold and (c, d) copper plates immersed into a 100 mM 2,6-DMBD + 0.1 M NBu₄BF₄ ACN solution for (a, b) 900 s at E = -0.9 V/Ag/AgCl, (c, d) 1800 s without electrochemical assistance. Scale bars: (a) 100 nm, (b) 10 μ m (c) 200 nm, (d) 1 μ m. Secondary electron analysis.

Table 3.	Water	Contact	Angles
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	Au (deg)	Cu (deg)	
bare surface modified surface	$\begin{array}{c} 44\pm2\\ 53\pm4\end{array}$	$\begin{array}{c} 35\pm2\\ 52\pm4 \end{array}$	

Scheme 4. Grafting of the Cyanomethyl Radical on Hydrogenated Diamond Surfaces²⁵

<i>Diamond</i> -H + C ₆ H ₅ COO•	>	<i>Diamond</i> [●] + C ₆ H ₅ COOH
<i>Diamond</i> [●] + CH ₃ CN	>	<i>Diamond</i> -H + [•] CH ₂ CN
<i>Diamond</i> • + • CH₂CN	>	Diamond-CH ₂ CN

radical itself is not grafted on the electrode surface, but is able to provide radicals from the solvent by hydrogen atom abstraction. A film derived from acetonitrile is formed, but in our case, aryl radicals are not incorporated into the film, at least, to a large extent.

Conclusion

Under electrochemical or spontaneous grafting conditions, the 2,6-dimethyl benzenediazonium salt does not lead to the modification of the surface by 2,6-dimethylphenyl groups. This is related to the steric hindrance in the positions ortho to the nitrogen atom. The 2,6-dimethyl phenyl radical is formed but instead of reacting with the surface, it abstracts an hydrogen atom from ACN to give the cyanomethyl radical, that reacts with the surface. The reaction is triggered by electrochemistry or started spontaneously with reducing metals such as copper. It should also be triggered by other reducing metals, such as iron, nickel, zinc, etc. The growth of the layer results from the further attack of the cyanomethyl anion on the first grafted cyanomethyl group. This provides a surface containing amino groups and, in some cases, keto groups. A mechanism is proposed to account for the formation of such grafted surfaces.

As both amino and keto groups are very reactive, this method provides surfaces that can be easily further derivatized, for example, for controlled protein immobilization.²⁷ The method can be extended to other molecules (RH) that can transfer an hydrogen atom to the 2,6-dimethylphenyl radical to give a new radical ($\mathbf{R} \cdot$) able to react with a surface. Work is in progress to explore new grafting reactions along these lines.

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Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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