CHEMISTRY OF MATERIALS

Article

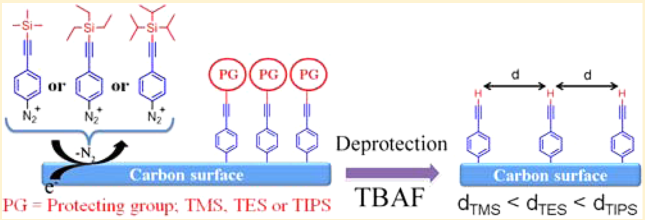
pubs.acs.org/cm

Nanostructured Monolayers on Carbon Substrates Prepared by Electrografting of Protected Aryldiazonium Salts

Yann R. Leroux and Philippe Hapiot*

Institut des Sciences Chimiques de Rennes, Université de Rennes 1, CNRS, UMR 6226 (Equipe MaCSE), Campus de Beaulieu, 35042 Rennes Cedex, France

S Supporting Information



ABSTRACT: The electrogeneration of aryl radicals from protected diazonium salts combined with protection−deprotection steps was evaluated to design functional monolayers on carbon substrates with a well-controlled organization at the nanometric scale. The structure of the obtained monolayer is adjusted by varying the size of the protecting group that is introduced on the precursors (trimethylsilyl, triethylsilyl, and tri(isopropyl)silyl were tested in the present study). After deprotection, a robust ethynylaryl monolayer is obtained whatever the substituent that serves as a platform to attach other functional groups by a specific “click chemistry” coupling step. Electrochemical and structural analyses show that the organization of the attached monolayer is totally governed by the size of the protecting group that leaves a footprint after removal but maintains a total availability of the immobilized functional groups. Properties of the monolayer (charge transfer, permeation of molecules through the layer, density of functional groups) were examined in combination with the performances for postfunctionalization taken with an alkyl-ferrocene derivative as an example of the immobilized species.

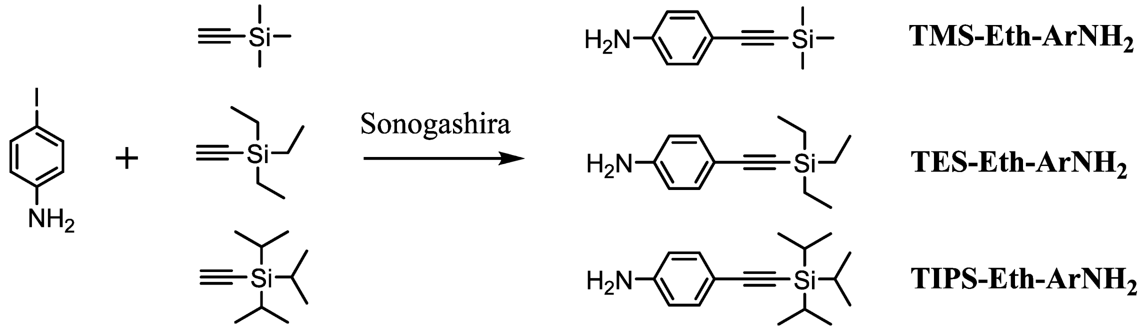
KEYWORDS: *modified organized surfaces, diazonium redox chemistry, carbon materials surfaces*

INTRODUCTION

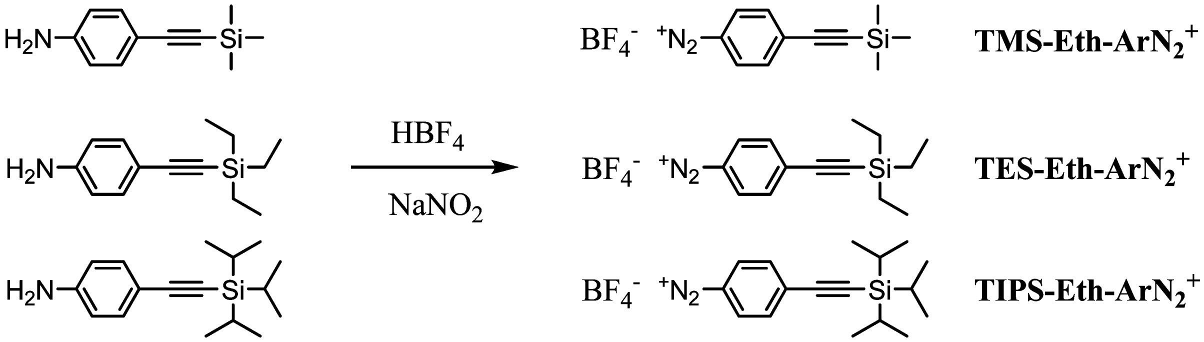
The preparation of robust modified surfaces with a molecular organization remains of primary importance for many applications, for example, in analytical chemistry or molecular electronics.[1] Carbon surfaces are receiving more and more attention because of new possibilities of these materials.[2] If an organized layer could spontaneously be obtained on a gold surface through the adsorption of long chain alkane-thiols,[3] the situation is more problematic when considering carbon materials especially when a robust and organized chemical modification of their surface is desired.[2] The redox chemistry of aryldiazonium salts permits the immobilization of functional groups on almost any carbon materials such as, for example, glassy carbon[4] or graphene sheets.[5] The electrografting method relies on the generation of reactive phenyl radicals that are produced by electrochemical reduction of the corresponding aryl diazonium salts. Such radicals rapidly add on the surface that serves as an electrode.[4] On the basis of this technique, a wide range of functional groups has already been immobilized on carbon substrates.[2,4] On one hand, the advantages of a radical process are its versatility (it could be used with many different materials interfaces) and the robustness of the modification that is linked to the surface through a covalent bond. On the other hand, the major drawback is the difficulty to limit the efficiency of the radical grafting and the resulting disorganization. Without special precautions, electrografting leads to the formation of thick disorganized multilayer films.[4] To circumvent this difficulty, different strategies have been proposed to limit the process to the formation of a single layer. The first approach was the substitution of the aryldiazonium ring with bulky groups[6] or preorganized aromatic units like calyx-arenes[7] that impede the grafting of other radicals onto the already attached aromatic rings. Another approach was the postelimination of the extra-attached materials by breaking a weak bond in the layer after its electrografting.[8] Combining these two strategies, we found that the bulky tri(isopropyl)silyl group introduced on an ethynyl-diazonium salt limits the grafting to the formation of an ultrathin layer.[9] After deprotection, we obtain an active monolayer of ethynylaryl moieties that is covalently linked to the carbon substrate and available for a postfunctionalization using the well-known “click” coupling (Cu(I)-catalyzed Huisgen 1,3-dipolar cyclo-addition).[10] In this process, the deprotection leaves a nanometric footprint on the layer because the protecting trialkylsilyl group is bulkier that the protected entity. A fine control of this phenomenon opens large possibilities to design ordered hierarchical surface modifications. For example, we could imagine building structured monolayers that would be similar to those prepared with alkylthiol/gold surfaces[11] but with the advantages of covalent bonding and the possibility of a much larger diversity of accessible substrates thanks to the radical nature of the grafting reaction. Resulting pinholes could

Received: November 28, 2012
Revised: January 17, 2013
Published: January 18, 2013

Scheme 1. Preparation of the Amine Precursors



Scheme 2. Preparation of the Aryl Diazonium Salt



also be filled with a second functionality for preparing close mixed binary layers.[12,13]

In this paper, we have examined how we could use this effect to tune the molecular arrangement of the produced monolayer. We used different alkylsilyl groups with increasing steric obstructions. Three different substituents were introduced on the ethynyl-aryldiazonium salts: trimethylsilyl (**TMS**), triethylsilyl (**TES**), and tri(isopropyl)silyl (**TIPS**) as protecting groups. The electrochemistry of molecular redox probes in solution was examined to characterize the permeability of the monolayers in combination with the possibility of immobilizing functional groups.

■ EXPERIMENTAL SECTION

Chemicals. Commercially available reagents were used as received without further purification. Aniline precursors were prepared using the Sonogashira coupling reaction (see Scheme 1). All diazonium ions were synthesized from the corresponding aniline using a published procedure (see Scheme 2).[9] 4-((Triisopropylsilyl)ethynyl)-benzenediazonium tetrafluoroborate (**TIPS-Eth-ArN$_2^+$**) was synthesis and purified according to the already published procedure.[9]

General Procedure for the Synthesis of Aniline Derivatives. To a stirring solution of 4-iodoaniline dissolved in a mixture of THF and diisopropylamine was added the corresponding trialkylsilylacetylene (1.1 equiv). After degassing with argon for 30 min, tetrakis-(triphenylphosphine)palladium(0) (5 mol %) was added in one portion. After 5 min, copper(I) iodide (5 mol %) was added, and the solution was stirred at room temperature overnight under Ar. The reaction mixture was filtered and washed with hexane. The combined organic phase was washed with NH_4Cl, brine, and water and dried with $MgSO_4$. Purification was performed on column chromatography using silica gel and hexane:DCM (1:1).

4-((Trimethylsilyl)ethynyl)aniline. According to the general procedure, 4-iodoaniline (1.0 g, 4.6×10^{-3} mol, 1 equiv), trimethylsilylacetylene (0.715 mL, 5.0×10^{-3} mol, 1.1 equiv), tetrakis-(triphenylphosphine)palladium(0) (264 mg, 2.283×10^{-4} mol, 5 mol %), and copper(I) iodide (44 mg, 2.283×10^{-4} mol, 5 mol %) in THF:diisopropylamine (80:20 mL) gave the desired product in 78% yield. NMR data are consistent with the already published procedure.[3] ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.59 Hz, 2H), 6.57 (d, J = 8.59 Hz, 2H), 3.80 (s, 2H), 0.29 (s, 9H).

4-((Triethylsilyl)ethynyl)aniline. According to the general procedure, 4-iodoaniline (1.0 g, 4.6×10^{-3} mol, 1 equiv), triethylsilylacetylene (0.900 mL, 5.0×10^{-3} mol, 1.1 equiv), tetrakis-(triphenylphosphine)palladium(0) (264 mg, 2.283×10^{-4} mol, 5 mol %), and copper(I) iodide (44 mg, 2.283×10^{-4} mol, 5 mol %) in THF:diisopropylamine (80:20 mL) gave the desired product in 79% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 8.56 Hz, 2H), 6.58 (d, J = 8.67 Hz, 2H), 3.78 (s, 2H), 1.03 (t, J = 7.52 Hz, 9H), 0.65 (q, J = 8.01 Hz, 6H).

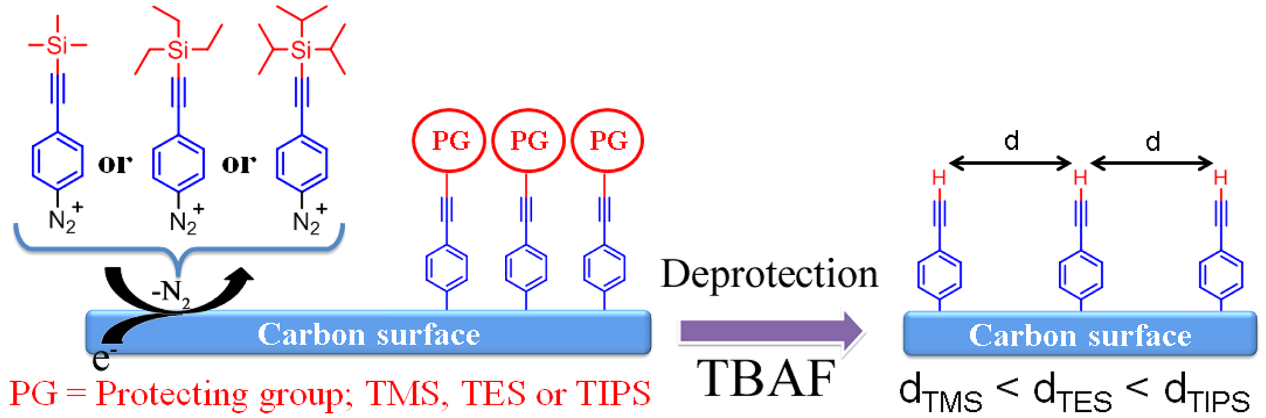
4-((Trimethylsilyl)ethynyl)benzenediazonium Tetrafluoroborate (TMS-Eth-ArN$_2^+$). Aryl diazonium ion **TMS-Eth-ArN$_2^+$** was produced from **TMS-Eth-ArNH$_2$**. ^1H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, J = 8.87 Hz, 2H), 7.77 (d, J = 9.10 Hz, 2H), 0.29 (s, 9H).

4-((Triethylsilyl)ethynyl)benzenediazonium Tetrafluoroborate (TES-Eth-ArN$_2^+$). Aryl diazonium ion **TES-Eth-ArN$_2^+$** was produced from **TES-Eth-ArNH$_2$**. ^1H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, J = 8.76 Hz, 2H), 7.74 (d, J = 8.67 Hz, 2H), 1.03 (t, J = 7.91 Hz, 9H), 0.69 (q, J = 7.91 Hz, 6H).

(11-Azidoundecyl)ferrocene. (11-Azidoundecyl)ferrocene was synthesized according published procedure.[14] Tetrabutylammonium fluoride, dimethylferrocene, ferrocene, decamethylferrocene, and ferrocyanide were purchased from Alfa Aesar. Acetonitrile was 99.8% anhydrous from Aldrich as well as tetrabutylammonium hexafluorophosphate.

Electrochemical Setup and Surface Modification Procedures. All electrochemical measurements were performed with an Autolab PGSTAT 12 (Metrohm) and a conventional three-electrode system, comprising the modified substrate as working electrode, a platinum foil as the auxiliary electrode, and SCE electrode (Metrohm) as reference. The GC electrodes were purchased from CH Instruments, Inc. (TX, USA) as 2-mm-diameter rods. The electrodes were polished successively with 1.0, 0.3, and 0.05 μm alumina slurry made from dry alumina powder and Milli-Q water on microcloth pads (CH Instruments, Inc., TX, USA). The electrodes were thoroughly rinsed with Milli-Q water, acetone, and ethanol. Before derivatization,

Scheme 3. Modification Procedure of the Carbon Surfaces Using Different Protecting Group Sizes



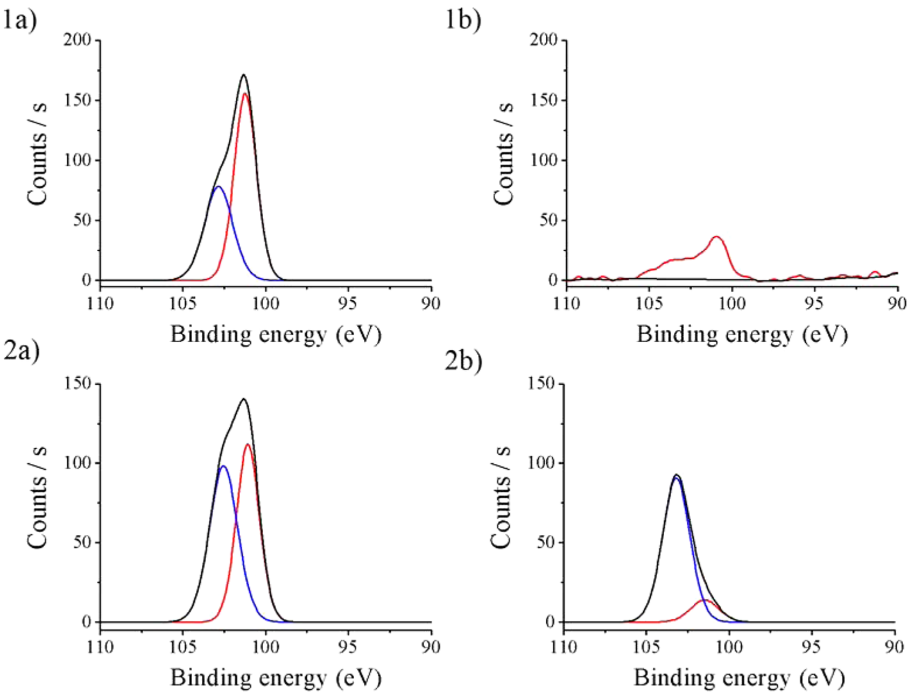


Figure 1. Si 2p XPS spectra of PPF carbon substrate modified with (1) **TMS-Eth-ArN$_2^+$** and (2) **TES-Eth-ArN$_2^+$** (a) before and (b) after deprotection with nBu$_4$NF solution.

the electrodes were dried with an argon gas stream. The preparation of pyrolyzed photoresist film (PPF) followed methods described previously.[15] The PPF substrates were a gift from Prof. Alison Downard (University of Canterbury, Christchurch, NZ) and were squares of 15 × 15 mm^2. Different carbon substrates (glassy carbon (GC) and pyrolyzed photoresist film (PPF)) were considered as test materials for the modification. PPF layers and GC present similar reactivities, but PPF is more suitable for AFM experiments because of a low roughness.[2] Surface modification was performed in a solution of 10^{-2} mol L^{-1} aryldiazonium salt and 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in acetonitrile (ACN) using cyclic voltammetry with a scan rate of 50 mV s^{-1} for five cycles between +0.60 and −0.75 V. The electrodes were rinsed with a copious amount of ACN and acetone, stirred 20 min in THF solution, and dried under a stream of argon. The deprotection step consists of stirring the modified surface 20 min in a THF solution containing 0.1 mol L^{-1} tetrabutylammonium fluoride (Bu$_4$NF) as deprotecting agent. The deprotection step is followed by a last cleaning of the sample.

Modelization. The diameters *d* of the disk representing the protecting group were evaluated by computing the molecular volume of the corresponding tri(alkyl)silyl-acetylene representing the protecting group moieties. The molecular volume is defined as the volume inside a contour of 0.001 electrons/Bohr^3 density without additional correction. The conformation of the molecule was optimized using DFT calculations at the B3LYP/6-31G* level. All calculations were performed using the Gaussian 03 package with the default parameters.[16]

■ RESULTS AND DISCUSSION

Electrografting of Carbon Surfaces. Scheme 3 presents the general principle of the modification process. Briefly, the carbon sample is used as an electrode and dipped in a solution containing the protected aryldiazonium salt. The electrode potential is cycled around the reduction threshold of the aryldiazonium salts. After a careful cleaning, the sample is treated using a solution of Bu$_4$NF in THF to remove the protecting group. In these conditions, the electrografting is a self-inhibited process as the film blocks the electrode. The interest is to provide well reproducible deposited layers. XPS experiments were first made in order to confirm the effective

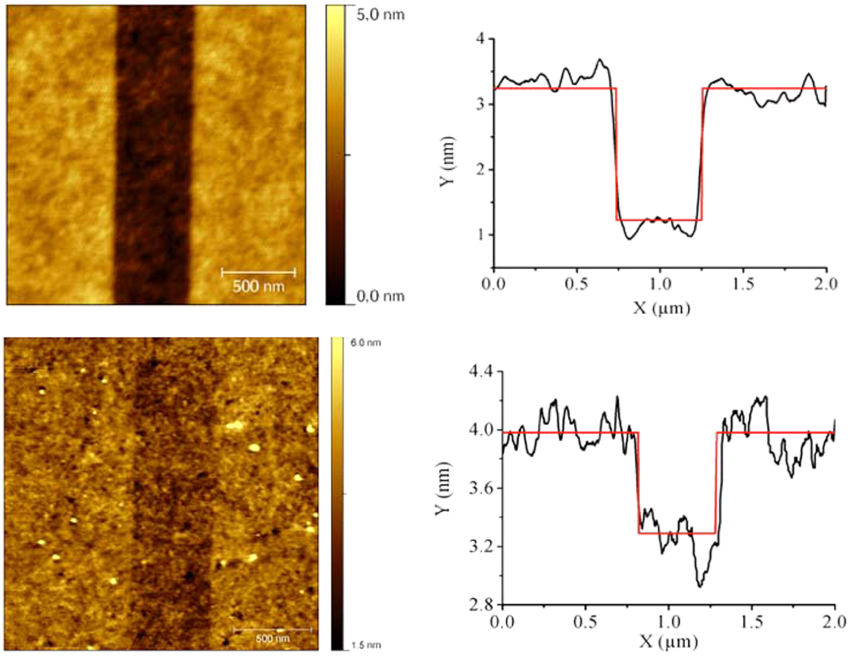


Figure 2. 2 × 2 μm topographic picture of PPF substrate modified with **TES-Eth-ArN$_2^+$** showing a 0.4 × 2 μm scratch, after deprotection step and line (black) and adjustment curve (red) of the AFM picture before (top) and after deprotection (bottom).

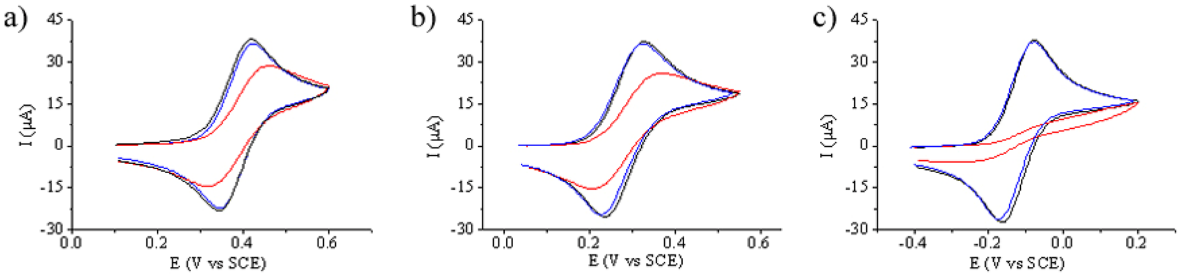


Figure 3. Cyclic voltammetry of ferrocene derivatives (10^{-3} mol L^{-1}) in ACN (+0.1 mol L^{-1} NBu$_4$PF$_6$). Ferrocene (a), dimethylferrocene (b), and decamethylferrocene (c) recorded on a blank GC electrode (black), after electrografting with **TES-Eth-ArN$_2^+$** (red), and after deprotection (blue). Scan rate = 0.1 V s^{-1}.

deprotection of the different silyl protecting groups using Bu$_4$NF solution. Figure 1 shows Si 2p XPS spectra of a PPF carbon substrates modified with aryl diazonium **TMS-Eth-ArN$_2^+$** and **TES-Eth-ArN$_2^+$** before and after deprotection. In Figure 1, two peaks could be identified at 101 and 102.5 eV. The peak located at 101 eV is related to Si−C bonds and ascribed to silicon in **TMS** and **TES** protection groups.[17] No particular precaution against O$_2$ was taken explaining the contribution at 102.5 eV in the Si 2p signal, due to the formation of oxidized species. After deprotection, (Figure 1-1b), the signal related to Si 2p (at 101 and 102.5 eV) is considerably decreased. In Figure 1-2b, the signal at 101 eV attributed to Si−C bonds is no longer visible. A contribution at 102.5 eV is still visible showing the presence of Si−O−C bonds, which is probably due to fragments trapped in the organic layer after the deprotection step.

Thicknesses of the layers were measured by AFM scratching before and after the deprotection step[18] (see Figure 2 for sample modified with **TES-Eth-ArN$_2^+$** and Supporting Information). To avoid possible bias, a statistical procedure was devised to average the layer thickness over a large fraction of the scratch area. At least 10 profile lines were taken to calculate an average layer thickness. After electrografting, film thicknesses range from 0.8 to 2 nm based on repetitive experiments.[19] We noticed that at this step of the procedure, the measured thickness depends on the cleaning of the surface. It suggests the presence of loosely attached materials that also limits the layer growing during the electrografting step. However, after the deprotection step, all layers present similar thicknesses (around 0.6 nm) with an excellent reproducibility over several measurements and different samples. As seen in Figure 2, the roughness of the modified sample was that of the original PPF substrate. Such value agrees well with the thickness expected for an ethynylaryl monolayer (around 0.66 nm)[9] and is not dependent on the size of the used protecting group. Interest in the deprotection is thus not only to reveal the active ethynylaryl group but also to eliminate all loosely attached materials. It is remarkable that a **TMS** group is large enough to inhibit the attack of aryl radicals as we have observed for the bulkier **TIPS** groups.[9]

To complete characterizations of the as-prepared layers, permeation of molecules through the deposited layer was investigated by examining the modifications of the electrochemical response of different redox probes in solution on the modified surfaces. The voltammogram characteristics, such as the shape or the variations of the peak current intensities,

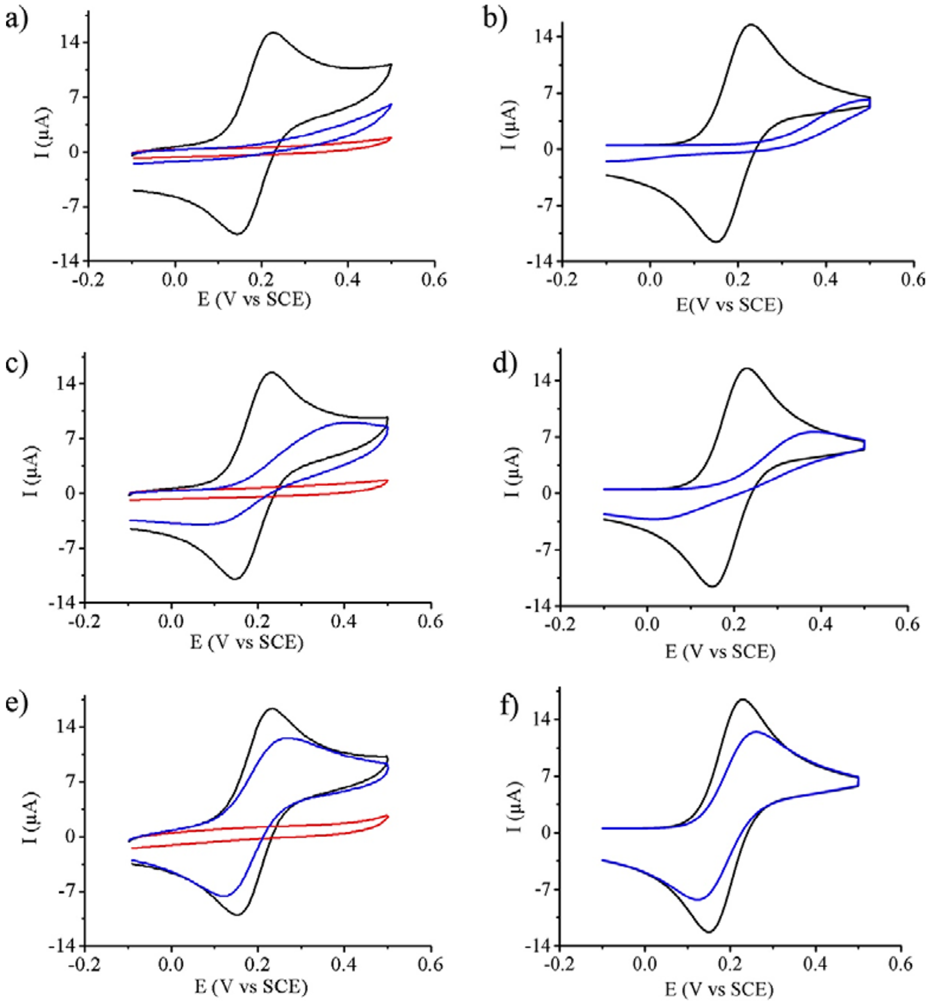


Figure 4. Cyclic voltammetry of 10^{-3} mol L^{-1} $Fe(CN)_6^{4-}$ in H_2O (+0.1 mol L^{-1} KCl) on a bare GC surface (black) and after modifications with **TMS-Eth-ArN$_2^+$** (a,b), **TES-Eth-ArN$_2^+$** (c,d), and **TIPS-Eth-ArN$_2^+$** (e,f); before (red) and after deprotection (blue). Experimental (a,c,d) and CEC simulations (b,d,f). Scan rate = 0.1 V s^{-1}.

provide valuable information about the global charge transfer process (notably to discriminate between charge transfer by tunneling through the layer or permeation through pinholes).[20] A series of ferrocene derivatives with increasing sizes were first considered (see Figure 3). Similar trends were observed for all modified surfaces. Upon electrografting and after cleaning the sample, the peak current becomes broader and its intensity decreases showing a partial blockage of the electrode. The inhibition increases with the size of the probe illustrating by an S-shape voltammogram for the bulkiest ferrocene indicative of a diffusion of the redox probe through pinholes.[20]

After deprotection and for all the ferrocene derivatives, the voltammogram turns out to be indiscernible from that obtained on the blanked carbon surface suggesting that the charge transfer occurs through different pathways (via pinholes and tunneling through the layer).[20,21] This observation falls in line with the AFM scratching data that conclude about a subnanometric deposit layer allowing an efficient tunneling of the charge besides permeation. Thus, ferrocene and its derivatives are not sensitive enough to detect permeation and the ferrocyanide/ferricyanide couple was chosen instead. As discussed before, its inner sphere character permits the observation of structural differences even for very thin modified surfaces.[11,22] After the electrografting step and for all modified surfaces, ferrocyanide oxidation is totally inhibited (Figure 4, red lines). After deprotection of the layer, ferrocyanide oxidation reappears for the **TES**- and **TIPS**- prepared surfaces (Figure 4c,e, blue lines) but remains inhibited for the **TMS**-one (Figure 4a). The curves display a larger peak-to-peak potential separation and a global decrease of the current associated with a strong "S-shape" character. The voltammograms were compared with simulations assuming a model of interacting pinholes (interacting diffusing channels treated by the CEC analogy).[20a] The experimental tendency is well reproduced in the simulations confirming that the electrochemical response is for this probe governed by diffusion channels. Notice that the blockage follows the size of the protecting group used during the electro-grafting process; inhibition is more pronounced for the **TES**- prepared surface than for the **TIPS**- one, the oxidation of ferrocyanide on the **TMS**- surface being totally inhibited.

Postfunctionalization Procedures. The "click" chemistry reaction (Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition) is nowadays often used to functionalize a wide range of surfaces and is used here to verify the reactivity of the deprotected acetylene moieties. The coupling was performed for each modified and deprotected substrate with (11-azidoundecyl)-ferrocene as a test system. The redox group serves as a

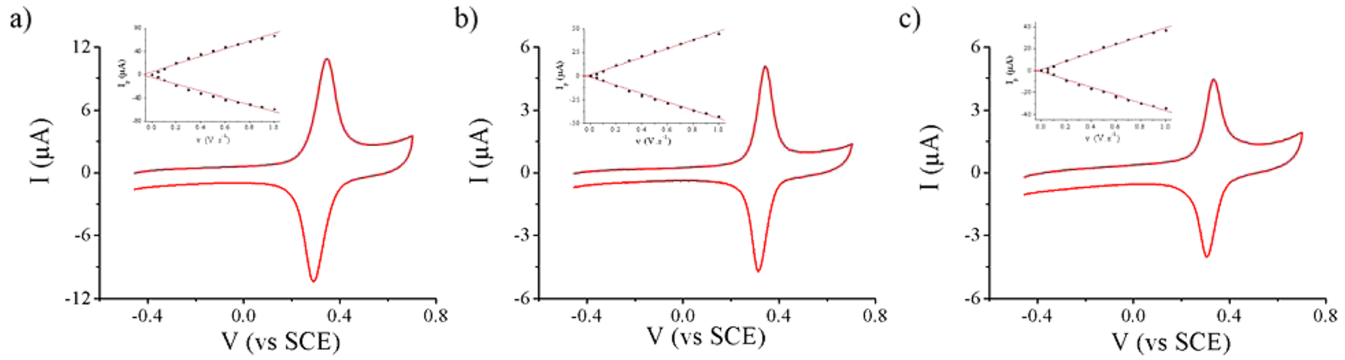


Figure 5. Cyclic voltammogram in ethanol + 0.1 mol L^{-1} LiClO$_4$ of modified-GC electrode after postfunctionalization with (11-azidoundecyl)ferrocene using click chemistry coupling method on modified-GC electrode with (a) **TMS-Eth-ArN$_2$$^+$**, (b) with **TES-Eth-ArN$_2$$^+$**, and (c) with **TIPS-Eth-ArN$_2$$^+$**. Scan rate 0.1 V s^{-1}. Inset: Variation of the anodic and cathodic peak current with the scan rate.

convenient label for measuring the initial amount of ethynylaryl moieties. In a typical click chemistry procedure, a 1:1 water:THF solution of $CuSO_4$ (10^{-2} mol L^{-1}) and L(+)-ascorbic acid (2×10^{-2} mol L^{-1}) was stirred in the presence of (11-azidoundecyl)ferrocene[9] (10^{-5} mol L^{-1}) and the modified substrate. Figure 5 shows the electro-activity of the modified electrode in a blank ethanolic solution containing only 0.1 mol L^{-1} $LiClO_4$ as supporting electrolyte.

The surface concentrations of active ferrocene centers (Γ) were derived from these experiments using the slope of the linear variation of the peak current I_p vs scan rate v according to $\Gamma = 4aRT/F^2S$. F is the Faraday constant, a the slope of I_p vs v variation, and S the surface area of the sample. The surface S is corrected from the roughness factor (S/S_{geom}, where S_{geom} is the geometric surface area) taken as 2.48 for a glassy carbon substrate. As seen in Table 1, all Γ values are on the order of several 10^{-10} mol cm^{-2} corresponding for a monolayer to high densities of active ethynylaryl groups.[9] Notice that Γ considerably decreases when the size of the protecting group increases. Γ values for the **TES-** and **TIPS-** prepared layers are 0.73 and 0.61 times lower than that of the **TMS-** one. Assuming that the deposited aryl moieties are arranged in a hexagonal close packing lattice (the optimal way to stack n discs of diameter d), the surface concentration Γ in mol cm^{-2} could be estimated using the following relation $\Gamma = 1.92 \times 10^{-8}/d^2$ where d is in Å.[9] The diameter d of the disk representing the protecting group was evaluated by computing the molecular volume of the corresponding tri(alkyl)silyl-acetylene representing the protecting group moieties. We obtained d = 0.758, 0.84, and 0.92 nm respectively for the **TMS**, **TES**, and **TIPS** protecting groups leading to the theoretical Γ shown in Table 1. It is remarkable that the experimental surface concentrations show a good agreement with the calculated predictions that assume control of the active function density by the size of the used protecting group. Finally, we could compare Γ variations with the permeability seen by a ferro-/ferricyanide probe (Figure 2) that is quantified by the apparent fractional coverage ratio θ_{CEC} where θ_{CEC} is the value derived from the CEC analogy.[20a] It illustrates that the porosity decreases suddenly when passing from the **TIPS-** to the **TES-** layer. This behavior is similar to what was observed for a nanostructured alkylthiol monolayer on a gold surface.[11] It was estimated that the passage of the ferrocyanide couple is blocked when pinholes have diameter lower than 0.5 nm, a value that is in good agreement with our observations.

Table 1. Characteristics of the Deprotected Monolayers

layer	$\Gamma_{labeling}$[a,b] (relative to TMS-)	$\Gamma_{Theoretical}$[a,c] (relative to TMS-)	θ_{CEC}[d]
TMS-	3.3 (1)	3.3 (1)	0.995
TES-	2.5 (0.77)	2.7 (0.82)	0.98
TIPS-	2.0 (0.62)	2.3 (0.68)	0.72

[a] Γ in 10^{-10} mol cm^2. [b] Taking 2.48 as roughness factor for a glassy carbon surface. [c] Estimated from the diameter of the equivalent sphere of the protecting group **TMS**: 0.75 nm, **TES**: 0.84 nm, **TIPS**: 0.92 nm and hexagonal compact packing. [d] Using the CEC analogy.[20a]

■ CONCLUSION

The electrografting of protected aryldiazonium salts is an efficient process for the preparation of controlled structured monolayers. It is noticeable that a trimethylsylil group is bulky enough to protect the already attached aromatic groups from the attack of aryl radicals and thus ensures the formation of functional monolayer with high density of active sites. However, the monolayer keeps a memory of the protecting groups after its removal leading to the formation of molecular pinholes. A thin control of this phenomenon opens large possibilities to design ordered hierarchical surface modifications at the molecular scale. Changing the size of the protecting group controls the size of the pinhole as it could be demonstrated by examining the permeation properties and the density of immobilized active functions. Taking advantage of the "click chemistry", the layer could serve as a versatile platform for immobilizing many functional entities with a controlled spatial arrangement (density, spacing). Notice that the procedure could easily be extended to different materials substrates thanks to the radical nature of the electrografting process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional electrochemical and AFM experimental data and details about calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: philippe.hapiot@univ-rennes1.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by the Agence Nationale de la Recherche. Contract ANR10-BLAN-714, Cavity-zyme(Cu) project). Prof A.J. Downard (University of Canterbury, Christchurch, NZ) is warmly thanked for providing us the sample of PPF substrates. Dr. Fei Hui is thanked for his help in the AFM scratching measurements.

■ REFERENCES

(1) See for example: Devadoss, A.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2007**, *129*, 5371 and references therein.

(2) McCreery, R. L. *Chem. Rev.* **2008**, *108*, 2646.

(3) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.

(4) (a) Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883. (b) Pinson, J.; Podvorica, F. I. *Chem. Soc. Rev.* **2005**, *34*, 429. (c) Bélanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995.

(5) Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C. *J. Am. Chem. Soc.* **2009**, *131*, 1336.

(6) Combellas, C.; Jiang, D.; Kanoufi, F.; Pinson, J.; Podvorica, F. *Langmuir* **2009**, *25*, 286.

(7) Mattiuzzi, A.; Jabin, I.; Mangeney, C.; Roux, C.; Reinaud, O.; Santos, L.; Bergamini, J.-F.; Hapiot, P.; Lagrost, C. *Nat. Commun.* **2012**, *3*, 1130.

(8) Malmos, K.; Dong, M.; Pillai, S.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2009**, *131*, 4928.

(9) Leroux, Y. R.; Fei, H.; Noël, J.-M.; Roux, C.; Hapiot, P. *J. Am. Chem. Soc.* **2010**, *132*, 14039.

(10) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew.Chem., Int. Ed.* **2002**, *41*, 2596. (b) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057.

(11) Chailapakul, O.; Crooks, R. M. *Langmuir* **1995**, *11*, 1329.

(12) A strategy for the preparation of binary layer based on the formation of guess−host complexes (cyclodextrin and bithiophene-aryl diazonium salt) was recently proposed: Santos, L.; Ghilane, J.; Lacroix, J.-C. *J. Am. Chem.* **2012**, *134*, 5476.

(13) Leroux, Y. R.; Hui, F.; Noël, J.-M.; Roux, C.; Downard, A. J.; Hapiot, P. *Langmuir* **2011**, *27*, 11222.

(14) Niskala, J. R.; Rice, W. C.; Bruce, R. C.; Merkel, T. J.; Tsui, F.; You, W. *J. Am. Chem. Soc.* **2008**, *130*, 9763.

(15) Brooksby, P. A.; Downard, A. J. *Langmuir* **2004**, *20*, 5038−5045.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.1; Gaussian, Inc.: Wallingford CT, 2009.

(17) Avila, A.; Montero, I.; Galan, L.; Ripalda, J.-M.; Levy, R. *J. Appl. Phys.* **2001**, *1*, 212.

(18) Anariba, F.; DuVall, S. H.; McCreery, R. L. *Anal. Chem.* **2003**, *75*, 3837.

(19) For TMS-Eth-Ar and TIPS-Eth-Ar layers, AFM scratching measurements are consistent with monolayer formation. For the TES-Eth-Ar layer, the measured thickness is larger than that expected for a monolayer. This is more likely ascribed to the difficulty of removing all adsorbed and loosely attached species during the rinsing process. Another possible explanation could be that the aryl radicals slowly attack (by H atom abstraction) the alkyl groups of the protecting groups.

(20) (a) Amatore, C.; Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1983**, *147*, 39. (b) Compton, R. G.; Menshykau, D. *Langmuir* **2009**, *25*, 2519.

(21) Outsphere redox probe like ferrocene are almost insensitive to the presence of monolayer coverage. See for example: Lhenry, S.; Leroux, Y. R.; Hapiot, P. *Anal. Chem.* **2012**, *84*, 7518 and references therein.

(22) Chen, P.; McCreery, R. L. *Anal. Chem.* **1996**, *68*, 3958.