Supporting Information Section.

Nanostructured monolayers on carbon substrates prepared by electrografting of protected aryldiazonium salts.

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1. Electrochemical behaviour of modified GC substrates.

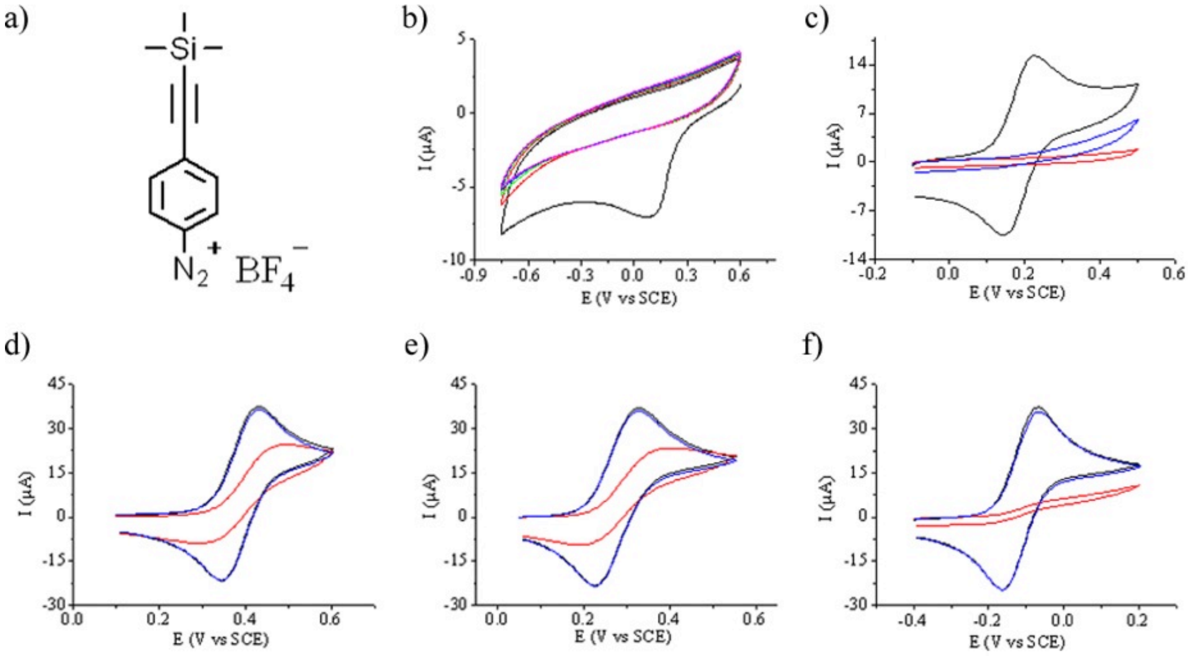


Figure S1. Electrochemical behavior of carbon electrode modified with **TMS-Eth-ArN$_2$$^+$**. a) Drawing of the molecules used during electro-grafting process. b) Electro-reduction of **TMS-Eth-ArN$_2$$^+$** aryl diazonium ion onto glassy carbon using general electro-grafting procedure. Electrochemical behavior of the as prepared modified electrode using (c) ferrocyanide, (d) ferrocene, (e) dimethylferrocene and (f) decamethylferrocene as redox probe. (Black curve) Bare GC electrode, modified-GC electrode (red curves) before and (blue curves) after treatment with nBu$_4$NF. Scan rate 0.1 V.s^{-1}.

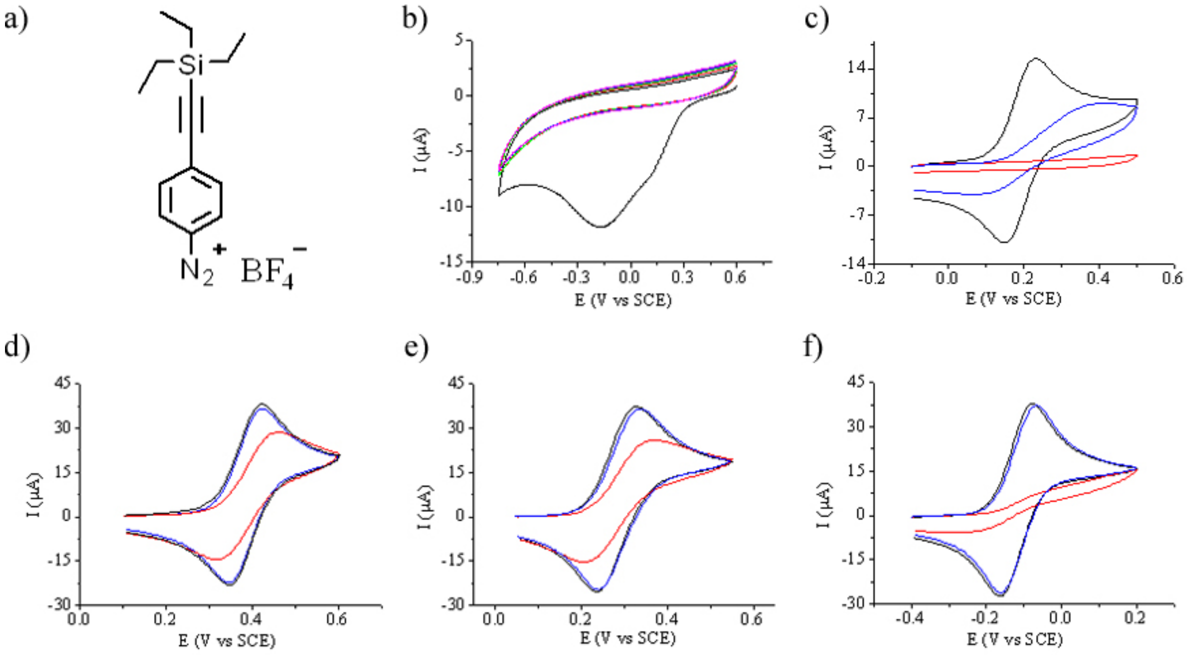


Figure S2. Electrochemical behavior of carbon electrode modified with **TES-Eth-ArN$_2^+$**. a) Drawing of the molecules used during electro-grafting process. b) Electro-reduction of **TES-Eth-ArN$_2^+$** aryl diazonium ion onto glassy carbon using general electro-grafting procedure. Electrochemical behavior of the as prepared modified electrode using (c) ferrocyanide, (d) ferrocene, (e) dimethylferrocene and (f) decamethylferrocene as redox probe. (Black curve) Bare GC electrode, modified-GC electrode (red curves) before and (blue curves) after treatment with nBu$_4$NF. Scan rate 0.1 V s^{-1}.

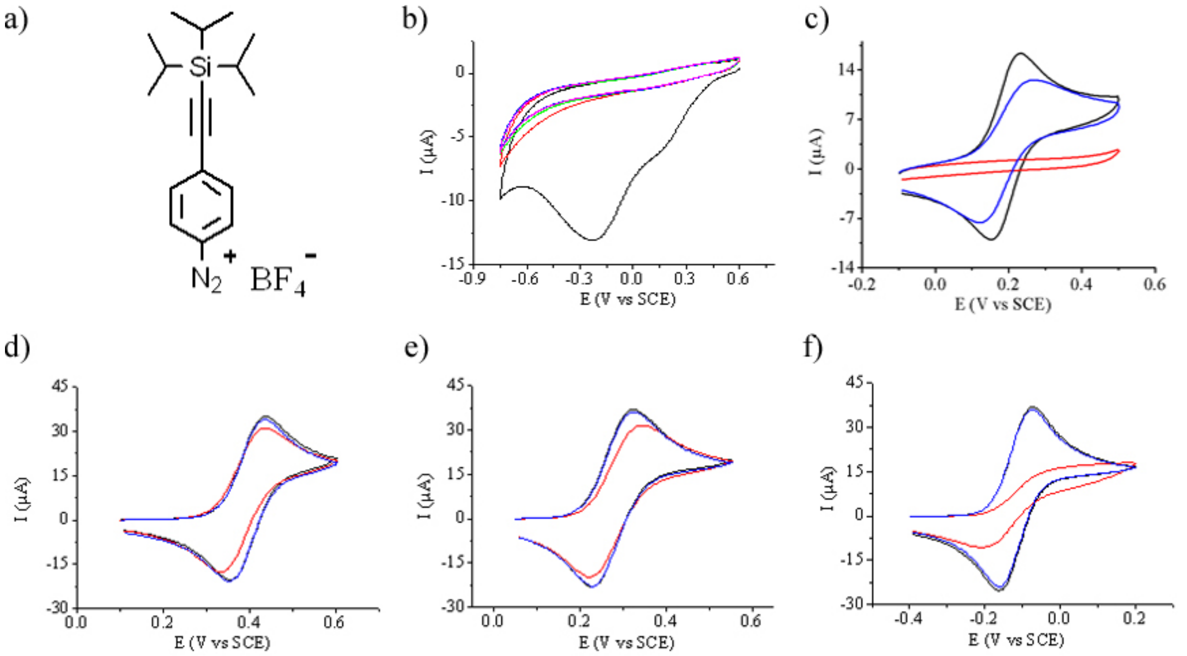


Figure S3. Electrochemical behavior of carbon electrode modified with **TIPS-Eth-ArN$_2^+$**. a) Drawing of the molecules used during electro-grafting process. b) Electro-reduction of **TIPS-Eth-ArN$_2^+$** aryl diazonium ion onto glassy carbon using general electro-grafting procedure. Electrochemical behavior of the as prepared modified electrode using (c) ferrocyanide, (d) ferrocene, (e) dimethylferrocene and (f) decamethylferrocene as redox probe. (Black curve) Bare GC electrode, modified-GC electrode (red curves) before and (blue curves) after treatment with nBu$_4$NF. Scan rate 0.1 V s^{-1}.

2. Electrochemical Simulations – Evaluation of the Fractional Coverage.

A semi-analytical model for charge transfer at partially blocked electrode has been proposed by C. Amatore *et al.* at the beginning of the 80's.[5] As a main result, when the fractional coverage of the electrode θ is close to unity, the equation that describes the response of the electrode is formally identical to the expression that would be obtained at an unblocked electrode with a CEC mechanism (chemical-electrochemical-chemical) mechanism:

$$I \underset{k_2}{\overset{k_1}{\rightleftarrows}} A \qquad K = k_1/k_2$$

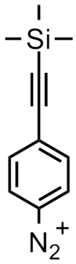
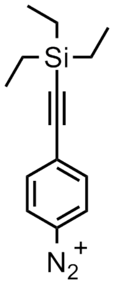
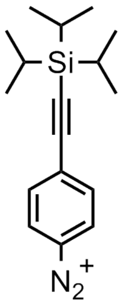
$$A + e^- \rightleftarrows B \qquad (E°, \alpha, k_s)$$

$$B \underset{k_1}{\overset{k_2}{\rightleftarrows}} J \qquad K = k_1/k_2$$

This model has been largely used in many examples of partially blocked electrode for evaluating the coverage and pinhole radius. However, it must be highlighted that such analysis supposes that the size of the pinhole is much larger than the size of the molecule probe, which is not the case in our situation. It results an overestimation of the pinhole radius, but the model is sufficient to establish the occurrence of the permeation of the molecular probe through the layer instead of charge tunneling. Notice that in a "perfect" situation *i.e;* without effect due to the size or interaction of the probe, θ and the density of active sites Γ should vary monotonously. CEC mechanism was solved using a difference finite method as implanted in the Digielch Software Version 4.0.[2] Parameters used in the simulations are gathered in Table S2.The CEC system could be described by two parameters $K\lambda^{1/2}$ and $\Lambda K/(1+K)$ where $\lambda=(k_1+k_2)$ (RT/Fv) with R is the gas constant, T the absolute temperature, F the faraday number and v the scan rate. The fractional coverage is derived as $\theta_{CEC} = 1/(1+K)$.

The method also allows an estimation of the pinhole radius. This part of the analogy was not used here considering the previous remark about the probe size and the pinhole radius.

Table S1. Parameters used in the simulation of voltamograms of Figure 4.

Diazonium Precursor	Λ	λ	K	θ_{CEC}
	1.99	25300	0.002	0.998
	1.99	644	0.02	0.98
	1.99	1.77	0.4	0.714

$\Lambda = k_s/D^{1/2}\,(RT/Fv)^{1/2}$; $\lambda = (k_1+k_2)\,(RT/Fv)$.

3. Atomic force Microscopy (AFM). Film Thickness estimation.

All atomic force microscopy (AFM) experiments were carried out with a Pico plus (Molecular Imaging) in tapping mode. A classic NCH acoustic probe was employed for imaging. Experiments were performed in order to estimate the thickness of the organic layers by the McCreery AFM “scratch” procedure.[3] The term "AFM scratching" is used here to describe intentional damage to a modification layer on a relatively hard substrate. If the applied force is sufficient to disrupt the organic layer but not to damage the substrate, it is possible to "carve out" a rectangular trench in the deposit layer. On modified-PPF surface, a 0.4 × 2 µm scratch was made by moving the tip in contact mode with a set-point voltage around 3 V. Note that careful examination confirmed that scratching of the underlying PPF substrate did not occur. Loose debris from the scratch often created AFM tip-surface tracking problems, but these could be overcome by gentle air convection near the AFM tip to remove most of the debris. The images shown were acquired in tapping mode after "scratching", and representative line profiles through each scratch are also shown.

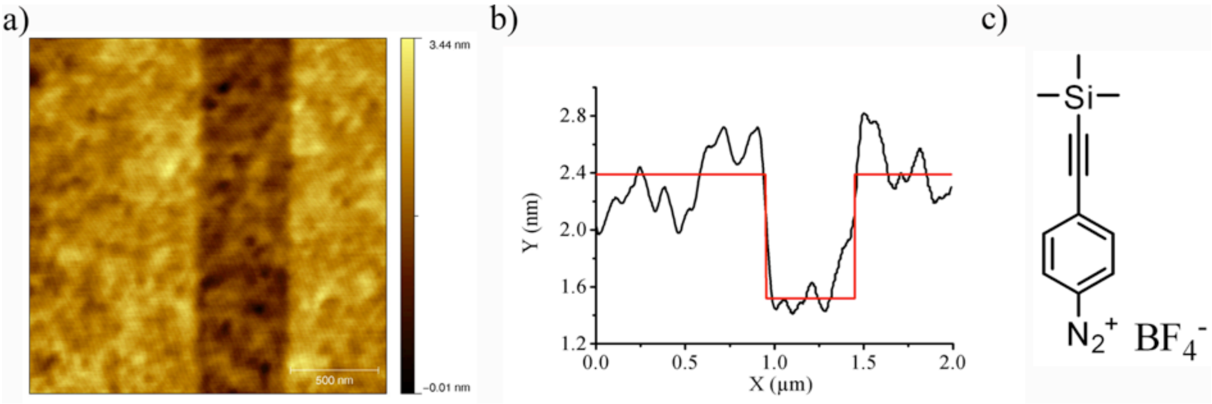


Figure S4. a) 2 x 2 µm topographic picture of PPF substrate modified with **TMS–Eth-ArN$_2^+$** showing a 0.4 x 2 µm scratch. b) Line profile (black) and adjustment curve (red) of the AFM image. c) Scheme of the aryl diazonium used for electro-deposition.

As shown in Figures S4, S5, a square image is recorded, which includes both scratched and unscratched regions. Lines were defined arbitrarily across this square. Gwyddion software[4] was used to determine adjustment curve (red curves) fitting to experimental ones. This software also allows us to determine the thickness of the layer, using the difference between the highest part and the lowest part of the adjustment curves. 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.

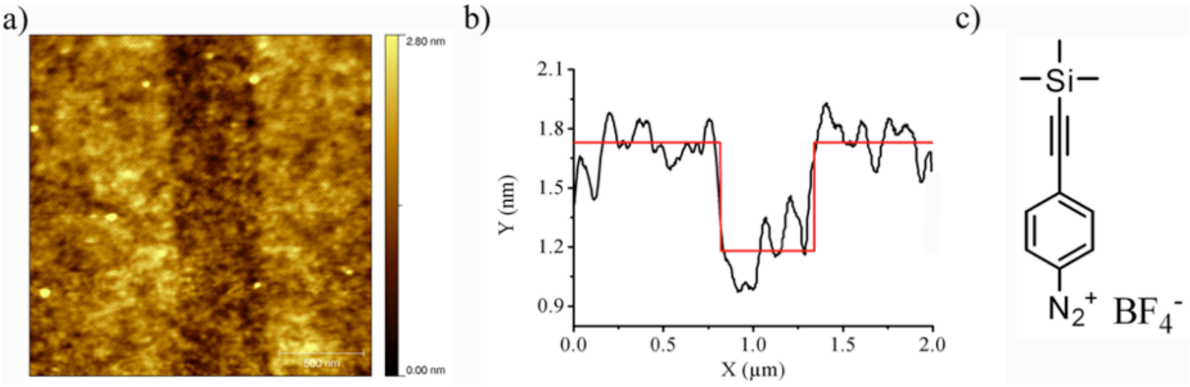


Figure S5 a) 2 x 2 µm topographic picture of PPF substrate modified with **TMS–Eth-ArN$_2^+$** showing a 0.4 x 2 µm scratch, after deprotection step. b) Line profile (black) and adjustment curve (red) of the AFM image. c) Scheme of the aryl diazonium used for electro-deposition.

Table S2 reports all the measurements perform using AFM scratching experiments in order to estimate the layer thickness of carbon substrate modified by electro-grafting of aryl diazonium **TMS–Eth-ArN$_2^+$**, **TES–Eth-ArN$_2^+$** and **TIPS–Eth-ArN$_2^+$** before and after deprotection step. After treatment with nBu_4NF, to remove silyl protecting group onto the modified PPF surface, the obtained layer thickness is now very thin and corresponds to a monolayer of ethynylbenzene deposited onto the surface, which is not possible using direct electro-reduction of ethynylbenzenediazonium ion.

Table S2.

Aryl diazonium ion used for electro-deposition	Layer thickness before TBAF treatment	Layer thickness after TBAF treatment
TMS–Eth-ArN$_2^+$	0.87 ± 0.16 nm	0.53 ± 0.13 nm
TES–Eth-ArN$_2^+$	2.07 ± 0.25 nm	0.69 ± 0.15 nm
TIPS–Eth-ArN$_2^+$	0.92 ± 0.17 nm [a]	0.65 ± 0.18 nm [a]

[a] value taken from reference 9.

References:

(1) Amatore, C.; Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1983**, *147*, 39.

(2) Digielech 4.0 http://www.elchsoft.com/digielch/digielch4/Default.aspx

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

(4) Gwyddion is Free and Open Source software, covered by the GNU General Public License. http://gwyddion.net/