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Ludovic Troian-Gautier, Daniel E. Martinez-Tong, Julie Hubert, François Reniers, Michele Sferrazza, et al.. Controlled Modification of Polymer Surfaces through Grafting of Calix[4]arene-Tetradiazoate Salts. *Journal of Physical Chemistry C*, 2016, 120 (40), pp.22936–22945. 10.1021/acs.jpcc.6b06143 . hal-01395477

HAL Id: hal-01395477

<https://univ-rennes.hal.science/hal-01395477>

Submitted on 5 Jan 2017

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Controlled Modification of Polymer Surfaces Through Grafting of Calix[4]arene-Tetradiazoate Salts

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ABSTRACT: An attractive methodology based on diazonium chemistry has been developed for the surface modification of polymers such as polypropylene (PP), polyethylene terephthalate

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3 (PET) and polystyrene (PS). The grafting procedure involves the *in situ* formation of diazoates in
4 basic aqueous solution. The reactivity of calix[4]arene-tetradiazonium salts and a classical
5 aryldiazonium salt was examined through comparative studies on gold and polymer surfaces.
6 The surfaces were analyzed with a combination of techniques such as AFM, XPS and
7 ellipsometry. The results highlighted the fact that the calix[4]arene molecules are grafted as a
8 robust and uniform monolayer both on gold and polymer surfaces, allowing a fine control over
9 surface modification. Furthermore, the chemical post-functionalization of the grafted calix
10 platforms equipped with carboxylic-pendant groups was successfully performed with either an
11 amine or an alcohol. These results open real possibilities in the controlled immobilization on
12 polymers of a wide variety of molecules of interest such as biomolecules or chromophores and in
13 the tailoring of polymers properties.
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32 Introduction

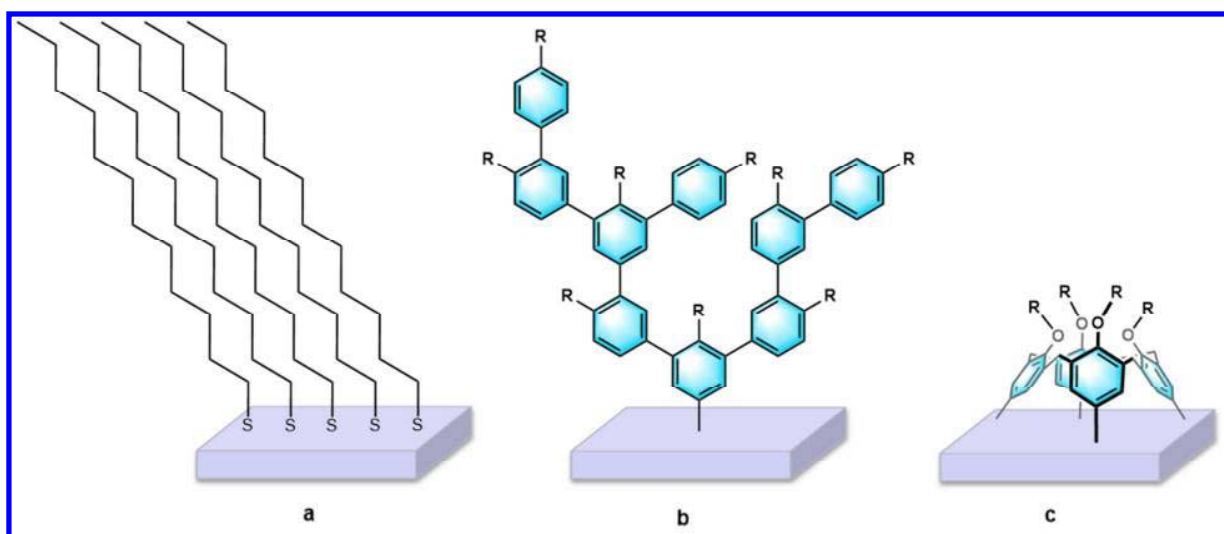
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34 The functionalization of surfaces through reaction with diazonium salts is now a widely
35 recognized method.¹⁻³ It has been successfully implemented in various fields such as sensing,⁴⁻⁷
36 biosensing,^{8, 9} catalysis,^{10, 11} microelectronics,¹² carbon nanotubes modification,¹³⁻¹⁶ batteries,¹⁷⁻¹⁹
37 etc. and could be met nowadays in industrial applications including inks/paints, medical stents or
38 thin layers in microelectronics.²⁰ The attractiveness of the diazonium functionalization is mainly
39 due to the formation of a robust interface and to its great versatility as it can be applied to all
40 forms of carbon (diamond, glassy carbon, HOPG, carbon felts, fullerene, carbon nanotubes,
41 graphene, carbon black), to various metallic surfaces (from noble to industrial metals, Au, Pt, Cu,
42 Ni, Fe, Zn, stainless steel), to semiconductors (Si, SiGe, Ge, GaAs) and to oxides (Indium Tin
43 Oxide, SnO₂, TiO₂, SiO₂, Fe₃O₄ nanoparticles).¹ Aryldiazonium cations can be easily reduced
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3 into the corresponding aryl radicals by loss of nitrogen, and these very reactive aryl radicals are
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5 able to react with a surface, forming a strong surface-carbon bond. The aryl radicals can be
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7 produced by electrochemical reduction at conducting substrates, by chemical reduction with the
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9 use of reducing agents such as H_3PO_2 ,²¹ ascorbic acid,²² or metals such as zinc or iron, combined
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11 with sulfuric or hydrochloric acid²³⁻²⁵ as well as by photochemical reduction in the presence of a
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13 sensitizer.²⁶ Spontaneous reaction with the surface involving solvent-induced homolytic
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15 dediazonation^{27, 28} or aqueous acidic solution for gold modification,²⁹ or involving the substrate
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17 itself in case of reducing metals such as copper,^{30,31} iron³² and nickel³³ have also been described.
18
19 Although rarely reported, an interesting mild route consists in using a basic aqueous solution
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21 (e.g. aqueous sodium hydroxide) for promoting a spontaneous grafting of aryl radicals issued
22
23 from the decomposition of diazoates.³⁴⁻³⁶ Diazonium salts react with strong nucleophiles at the
24
25 terminal nitrogen to give azo adducts, and reaction with hydroxide ions yields transient
26
27 diazohydroxides, which are rapidly deprotonated to diazoates (Ar-N=N-O^-).³⁷ The diazoates
28
29 spontaneously dediazonize to give aryl radicals that were recently shown to react with iron, gold,
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31 Fe_3O_4 or carbon surfaces.³⁴⁻³⁶

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39 The chemical functionalization of polymer surfaces is often required for attaching bioactive
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41 compounds,³⁸ for microfluidics applications^{39,40}, for altering their adhesion,⁴¹ anti-biofouling⁴² or
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43 wetting properties,⁴³ etc. Despite of being easy to process, fast and highly versatile, the
44
45 modification of polymer surfaces by reaction with aryl radical has been little explored:
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47 fluorinated polymers,^{40,44} membranes,^{45,46} polymethylmethacrylate,⁴³ polyvinylchloride,²⁶ cyclic
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49 olefin copolymer,⁴⁷ polyethyleneterephthalate,⁴⁸ have been modified by the reduction of a
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51 diazonium salt. However, in none of these works, the surface grafting was achieved by using the
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53 sodium hydroxide-based process. As far as we know, the reactivity of diazoates toward
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4 polymeric surfaces has never been examined. Yet this route could be of great interest for
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6 polymers, avoiding the use of reducing chemical agents.

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8 Unless special conditions or specifically-designed diazonium compounds are used,⁴⁹⁻⁵⁵ the
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10 formation of monolayers with diazonium chemistry remains challenging. Indeed, the aryl units
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12 already grafted can further react with the highly reactive unreacted aryl radicals, leading to
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14 disorganized multilayers structures⁵⁶⁻⁵⁸ rather than to monolayers (**Figure 1b**), in contrast with
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16 the spontaneous adsorption of alkanethiols onto coinage metal (Pt, Au, Ag, Cu), which is known
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18 to form self-assembled monolayers (SAMs) (**Figure 1a**).⁵⁹ In this context, we recently reported
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20 the use of calix[4]arene-tetradiazonium salts to obtain robust monolayers on conducting surfaces
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22 such as gold and carbon (**Figure 1c**).^{60,61} Due to the unique macrocyclic structure of the
23
24 calixarene skeleton, the formation of disorganized multilayers is prevented, and a dense and
25
26 compact monolayer is easily formed. Furthermore, the grafted calix[4]arenes constitute versatile
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28 platforms that can be easily post-functionalized via classical chemical coupling reactions. This
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30 post-functionalization may allow a very accurate spatial control of the immobilization of
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32 chemical species (e.g. DNA, peptides, NPs, etc.) in close proximity to the surface and thus may
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34 afford surfaces exploitable notably in (bio-)sensing and catalysis.
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3 **Figure 1.** Examples of strategies for surface modification: a) self-assembled monolayers of
4 linear alkanethiols, b) “cauliflower” structure obtained with classical aryldiazoniums, c)
5 monolayer obtained with calix[4]arene-tetradiazoniums.
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11 In order to further develop a grafting methodology exhibiting a fine control at the molecular
12 scale that could be applicable on both conducting and insulating materials, we have investigated
13 the grafting of calix[4]arene-tetradiazoate salts on gold and on polymers such as polypropylene
14 (PP). Since the reactivity of diazoates toward polymers is still unknown, the grafting was first
15 examined with gold surfaces as a reference surface material. It is demonstrated that the reported
16 strategy allows the straightforward modification of all type of alkali-resistant surfaces by a
17 robust, uniform and easily post-functionalizable monolayer.
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30 **Experimental**

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32 **Chemicals.** All solvents and reagents were at least of reagent grade quality and were
33 purchased either from Alfa Aesar, Sigma-Aldrich or Acros organics. 4,4,4-trifluorobutylamine
34 97% was purchased from Fluorochem, 4,4,4-trifluoro-1-butanol 98% was purchased from
35 Sigma-Aldrich. Anhydrous DMF and CHCl_3 were obtained from Acros organics. Gold coated
36 silicon wafer (1000 Å layer thickness) and TBAPF_6 (electrochemical grade) were purchased
37 from Sigma-Aldrich. Polypropylene (biaxially oriented, 50 μm), polyethylene terephthalate
38 (optically clear, 36 μm), and polystyrene (crystal transparent amorphous, 1.2 mm) surfaces were
39 purchased from Goodfellow. The typical size of the surfaces reported in this paper was 1 cm^2 .
40 Each grafting experiment was repeated three times to ensure reproducibility. Ultrapure water was
41 obtained via a Millipore Milli-Q system (18.2 $\text{M}\Omega\cdot\text{cm}$). The syntheses of calix[4]arene-
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3 tetraanilines and the corresponding diazonium salts **1** and **2** as well as compound **3** were adapted
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5 from literature (**Figure 2**).^{60, 62, 63}
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8 **Caution!** *Although we have not encountered any problem, it is noted that diazonium salts are*
9
10 *potentially explosive and should be handled with appropriate precautions.*
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13 **Electrochemical grafting.** Gold surfaces were first immersed in a “piranha” solution
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15 (H₂SO₄/H₂O₂ 3:1) and sonicated for 10 minutes. **Caution!** *Piranha solution is a very strong*
16
17 *oxidant and should be handled very carefully.* They were then washed with ultrapure water and
18
19 dried under argon atmosphere. The electrochemical grafting was performed using an Autolab
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21 PGSTAT 100 potentiostat, by applying a constant potential of -0.5 V vs SCE for 5 minutes, in
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23 0.1 M TBAPF₆ anhydrous acetonitrile containing 1 mM solution of compound **2** or **3**. Once the
24
25 grafting was achieved, the surfaces were thoroughly rinsed with acetonitrile, 0.1 M hydrochloric
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27 acid and water. Sonication was applied each time for ten minutes. The surfaces were finally dried
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29 using an argon flow.
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34 **Chemical grafting using sodium hydroxide.** Gold surfaces were first immersed in a
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36 “piranha” solution (H₂SO₄/H₂O₂ 3:1) and sonicated for 10 minutes. Polypropylene, polyethylene
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38 terephthalate, and polystyrene surfaces were cleaned with isopropanol under sonication for 10
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40 minutes, washed with ultrapure water and dried using an argon flow. The surfaces were then
41
42 dipped in a 5 mM solution of the diazonium salt (**1**, **2** or **3**) in aqueous 0.1 M sodium hydroxide
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44 for 16 hours (unless specifically precised), without stirring in order to avoid any mechanical
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46 frictions of the surface with the magnetic stirrer bar (a minimum volume of solution is used).
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48 Once the grafting was achieved, all the surfaces were thoroughly washed with water. Then, those
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50 modified with compound **1** were successively rinsed with acetonitrile, dichloromethane and
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52 toluene, whereas those modified with compound **2** or **3** were rinsed with acetonitrile, 0.1 M
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3 hydrochloric acid and water. Note that the polystyrene surfaces, whether modified or not, were
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hydrochloric acid and water. Note that the polystyrene surfaces, whether modified or not, were rinsed with acetonitrile and hexane as these surfaces are soluble in dichloromethane and toluene. Sonication was applied each time for ten minutes. The surfaces were then dried under argon flow.

Post-functionalization using EDC/NHS. Polypropylene surfaces modified with compound **2** were placed in a sealed tube and covered with 40 mM EDC solution in MES buffer at pH 6.9. After 1 hour, an equal amount of an 8 mM NHS solution in MES buffer at pH 6.9 was added, giving rise to a final concentration of 20 mM EDC and 4 mM NHS in MES buffer. The mixture was allowed to react for 2 hours. After being washed with water and dried under an argon flow, the activated surfaces were then immersed in a 0.2 mM solution of the desired compound (4,4,4-trifluorobutylamine or 4,4,4-trifluoro-1-butanol) in dichloromethane. After 4 hours, the surfaces were rinsed with dichloromethane, acetonitrile and toluene. Sonication was applied each time for 10 minutes. The surfaces were then dried using an argon flow.

Atomic Force Microscopy (AFM). AFM measurements were carried out in a Multimode microscope, equipped with a Nanoscope IIIa controller (Bruker). PPP-NCL-W probes (Nanosensors) were used for all the experiments. The topography characterization of the films was carried out using the tapping protocol, where the probe was driven close to its resonant frequency (about 150 kHz) at an amplitude set-point of 1 V. The thickness characterization of the films was performed adapting a previously reported protocol.⁶⁴ The probe was engaged in contact mode, with a constant deflection set-point of 0.1 V, and a 1 μm^2 area was scanned (for both gold and polymer surfaces). In particular, under these conditions, it was possible to remove the molecular layer without damaging the supporting gold substrate. Afterwards, a 5 μm^2 area was scanned in tapping mode and the mean value of the step between the two different zones

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3 was quantified. The procedure was repeated at different points of the substrate to check the
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5 homogeneity. All the AFM images were analyzed using the Nanoscope Analysis 1.5 software
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7 (Bruker).
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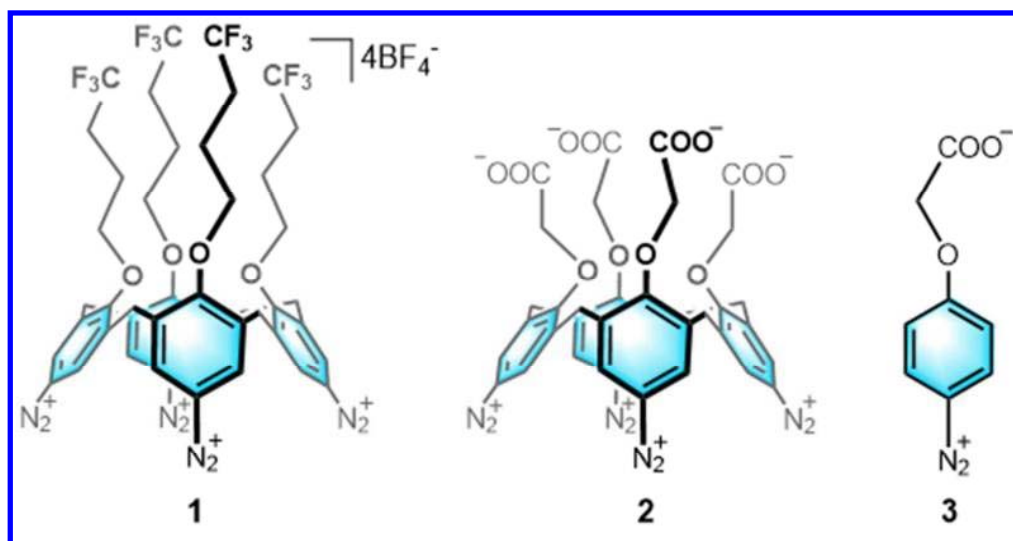
10 **Ellipsometry measurements.** Layers thicknesses on gold were measured in a HS-190
11 spectroscopic ellipsometer, equipped with a VB-250 control module (J. A. Woollam Co Inc). A
12 spectral range from 300 nm to 1200 nm, in steps of 10 nm was scanned at an incident angle of
13 45°. The following values were taken for gold: $n_s = 0.203$, $k_s = 3.431$, while for the molecular
14 layers: $n_s = 1.5$, $k_s = 0$, as previously reported.⁶⁰
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22 **XPS measurements.** XPS analysis was performed on a Physical Electronics PHI-5600
23 photoelectron spectrometer. Survey scans were used to determine the elemental chemical
24 composition of the surface. Narrow-region photoelectron spectra were used for the chemical
25 study of the C1s. The spectra were acquired using the Mg anode (1253.6 eV) operating at 300 W.
26 Wide surveys were acquired at a pass-energy of 187.5 eV with a five-scans accumulation
27 (time/step: 50 ms, eV/step: 0.8) and high-resolution spectra of the C1s peaks were recorded at a
28 pass-energy of 23.5 eV with an accumulation of 5 scans (time/step: 150 ms, eV/step: 0.05).
29 Spectral calibration was determined by setting C1s at 285 eV. The atomic concentration for
30 surface composition was estimated using the integrated peaks areas; the peaks area were
31 normalized by the manufacturer-supplied sensitivity factor ($S_C = 0.205$, $S_F = 1$, $S_O = 0.63$, $S_N =$
32 0.38 , $S_{Si} = 0.17$). The core level C1s spectra were peak-fitted using the CasaXPS software (Casa
33 Software, Ltd., version 2.3.16).
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53 **Results and discussions**

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4 The experiments were conducted with three different diazonium salts **1-3** (Figure 2).
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6 Calix[4]arene-tetradiazonium **1** was used for characterization purpose as the CF₃ group leads to a
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8 very characteristic signal in XPS spectroscopy. Calix[4]arene-tetradiazonium **2** was chosen
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10 because its terminal carboxylic groups allow a post-functionalization of the grafted monolayer.
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12 The grafting of diazonium **3** was investigated for comparison purpose with the related
13
14 tetradiazonium **2**. As previously shown on gold and carbon surfaces,^{60,61} the electrografting of
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16 calix[4]arene-tetradiazonium salts **1** and **2** leads to the formation of dense and compact
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18 monolayers. A study using gold substrates was first undertaken to determine whether similar
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20 results could be obtained from the grafting in aqueous hydroxide solution. Polymers surfaces
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22 were then used as substrates for performing the hydroxide-based grafting of the calix[4]arene
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24 platforms.
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47 **Figure 2.** Diazonium salts 1-3 used for surface modification.

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50 **Grafting on gold surfaces.** The grafting of diazonium salts **2** and **3** (dediazonized either by
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52 electrochemical reduction or in aqueous hydroxide solution) was performed on gold surfaces for
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54 comparison purposes. The electrochemical grafting was achieved by applying a constant
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56 potential of -0.5 V vs SCE during 5 minutes. The grafting promoted by sodium hydroxide was
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3 realized by immersing the surfaces in an alkaline solution (pH = 13) of the desired diazonium
4 compound. In all cases, the modified gold surfaces were thoroughly rinsed with acetonitrile, 0.1
5 M hydrochloric acid and water (sonication was applied each time for 10 minutes). The surfaces
6 were then analyzed using atomic force microscopy and ellipsometry to estimate the thickness of
7 the deposited layer.
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15 **Figures 3** and **4** show AFM topography images of gold substrates grafted with compounds **2**
16 and **3** respectively, through electrochemical reduction (**Figures 3b** and **4b**) and by using sodium
17 hydroxide (**Figures 3c** and **4c**). The AFM height images of bare gold surfaces are also
18 represented for comparison purposes (**Figures 3a** and **4a**). A granular surface with a mean
19 roughness value close to 1.4 nm can be observed for the bare gold surface. After grafting with
20 compounds **2** or **3**, the surfaces roughness mean values evolved little (less than 20 %), showing
21 that the grafted layer fits the morphology of the bare gold substrates, indicating hence the
22 formation of a thin layer. In all cases, one can observe the formation of a uniform layer as no
23 important material accumulation or depletion zones are observed. The AFM images after
24 scratching a 1 μm^2 area as well as the corresponding surface profiles are represented in **Figures**
25 **3b-c** and **4b-c**, respectively. Using the height difference among both areas of the surface profile,
26 a similar thickness value of 1.5 ± 0.3 nm could be estimated for the surfaces modified with
27 compound **2** through both electrochemical and sodium hydroxide promoted dediazonization
28 (**Figures 3b-c**). Ellipsometry measurements also lead, within experimental errors, to an identical
29 thickness value of 1.9 ± 0.5 nm in both cases. Considering the height of calix[4]arene **2** (0.74
30 nm^{65}) plus the length of the gold-carbon bond (c.a. 0.2 nm^{66}) on the one hand and the similar
31 values found in both grafting methodologies on the other hand, these thickness estimations show
32 that a monolayer of calix[4]arene is obtained from the hydroxide-based process, as demonstrated
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3 in our earlier work using electrochemical reduction of calix[4]arene-tetradiazonium. Worth is
4 noting that the specific structure of the calix[4]arene moiety presents no available sites for the
5 formation of a multilayer. To further support this conclusion, the compound **3** that can produce
6 multilayered films as the ortho position is available for reaction,¹ was also grafted using the two
7 strategies. For the surfaces modified with compound **3**, the height difference calculated from the
8 surface profile gives a thickness estimated value of 3.5 ± 0.5 nm, for both grafting procedures.
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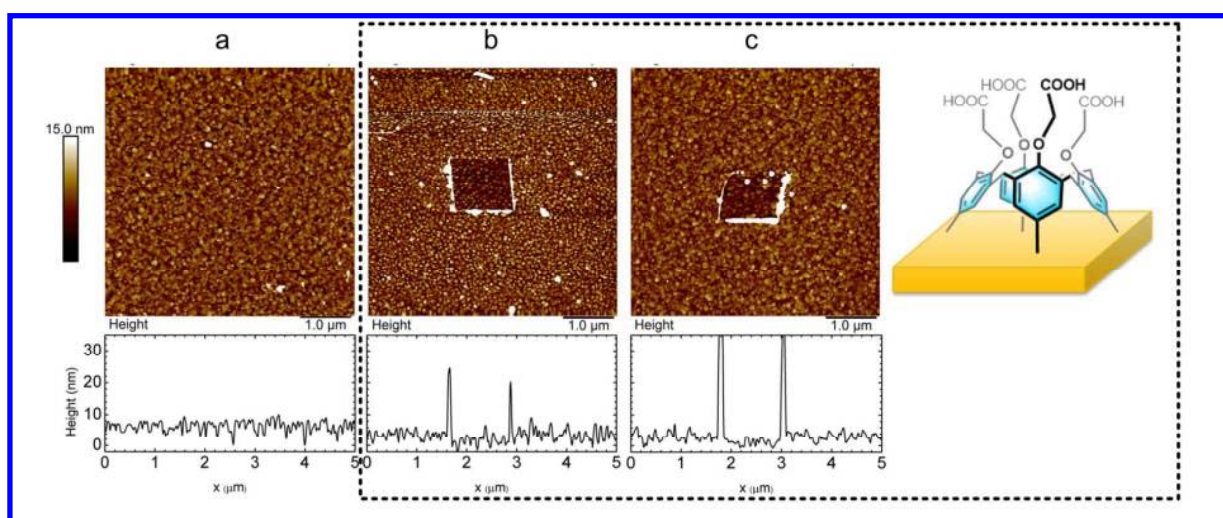


Figure 3. AFM images of a) the bare gold surface after scratching a $1 \mu\text{m}^2$ area b) compound **2** grafted on gold by electrochemistry and c) compound **2** grafted on gold using sodium hydroxide. b) and c) also include the scratching of a $1 \mu\text{m}^2$ area as well as the corresponding surface height profile.

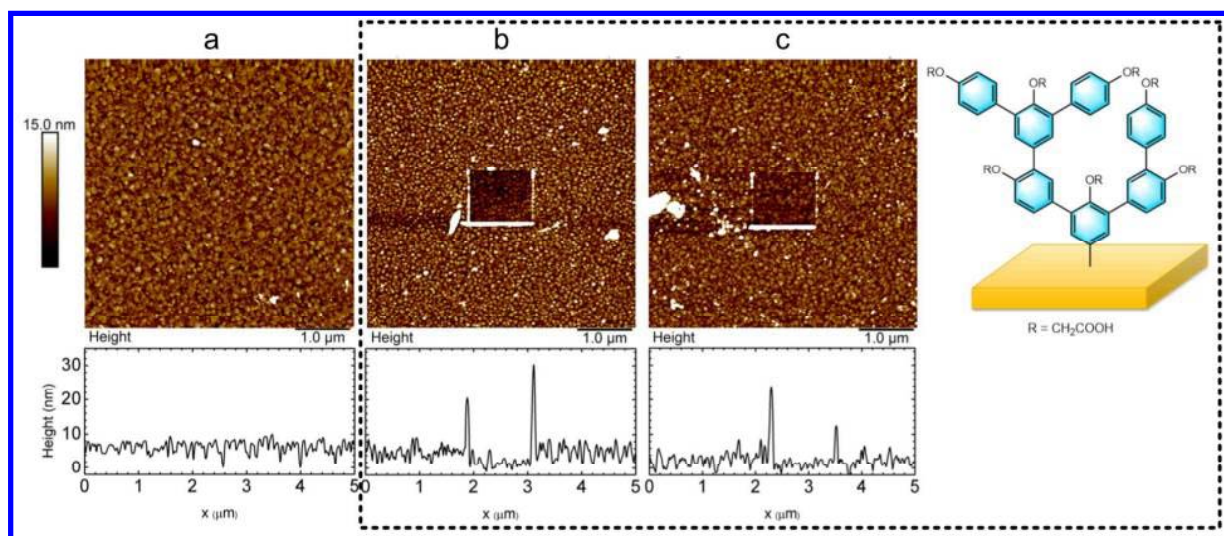


Figure 4. AFM images of a) the bare gold surface after scratching a $1 \mu\text{m}^2$ area b) compound **3** grafted on gold by electrochemistry and c) compound **3** grafted on gold using sodium hydroxide. b) and c) also include the scratching of a $1 \mu\text{m}^2$ area as well as the corresponding surface height profile.

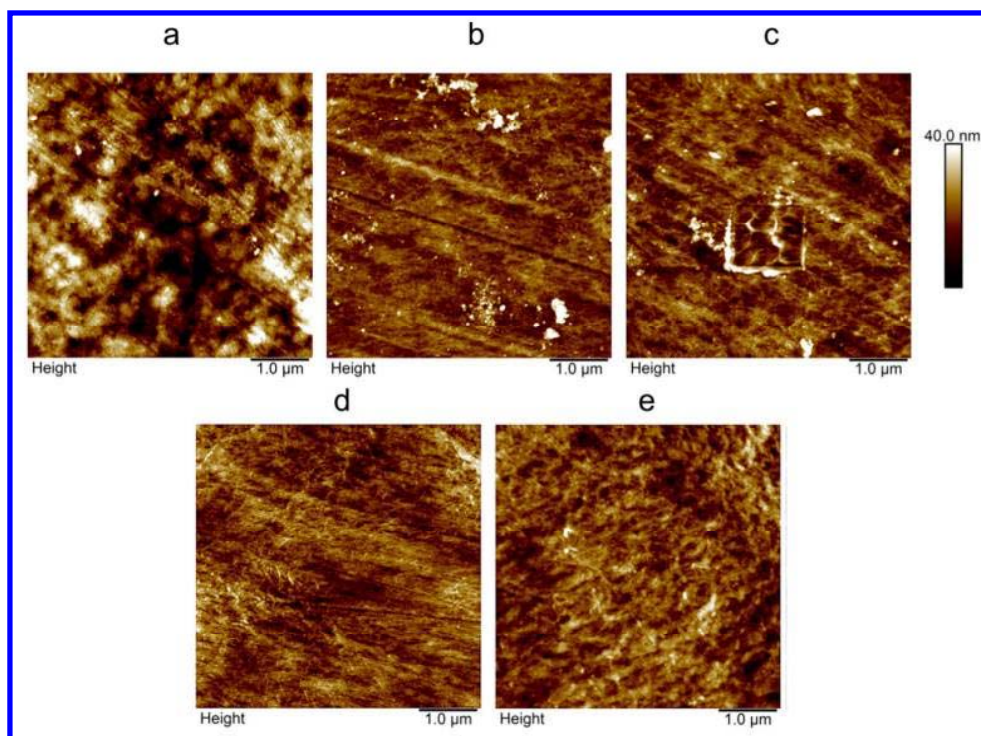
These results clearly indicate that the grafting by electrochemistry as well as by using sodium hydroxide allows the formation of a compact, uniform, robust layer on gold substrate. In agreement with previously reported results,^{1,60,61} a monolayer is obtained by grafting compound **2** whereas compound **3** leads to a multilayer. The grafting procedure using sodium hydroxide being validated on gold, we next moved to the modification of polymers.

Grafting on polypropylene surfaces. Grafting of compounds **1-3** on polypropylene surfaces was achieved by immersing the polymer surface in an aqueous 0.1 M sodium hydroxide solution containing 5 mM of the desired diazonium salt. The surfaces modified from compounds **2** and **3** were then thoroughly rinsed with acetonitrile, 0.1 M hydrochloric acid and water whereas surfaces modified from compound **1** were washed with water and thoroughly rinsed with

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4 acetonitrile, dichloromethane and toluene. Sonication was applied each time for ten minutes. The
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6 surfaces were then analyzed using atomic force microscopy, ellipsometry and X-ray
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8 photoelectron spectroscopy.
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10 **Figure 5** shows AFM height images of grafted polypropylene surfaces using compounds **1**, **2**
11 and **3** and the sodium hydroxide-based procedures. For comparison, an AFM image of a bare PP
12 surface which was only treated with sodium hydroxide is also shown (**Figure 5a**). It is worth
13 noting that the relatively soft bare PP surfaces display a large roughness (rms \approx 8-9 nm). The
14 ungrafted PP surface shows grooves. After grafting, a continuous surface was observed and no
15 signs of agglomeration neither depletion were found. The grooves were still visible but the
16 blurred aspect qualitatively suggests the formation of a thin organic film at the polymer surfaces.
17 The modified surfaces from compounds **1**, **2** and **3** show mean roughness values of 3.7, 4.0 and
18 3.5 nm, respectively, that correspond to a decrease of almost 45% in comparison to the bare
19 polypropylene substrate, indicating that the organic molecules were indeed grafted on
20 polypropylene surfaces. The modified polypropylene surfaces were then scratched using the
21 same protocol than that used for the gold modified surfaces. It should be emphasized that
22 scratching experiments are particularly difficult to carry out and we systematically damaged the
23 surface, even by drastically lowering the deflection set-point. It was literally impossible to
24 perform analyzable scratching experiments with surfaces modified with compounds **1** and **2**.
25 However, for surfaces modified with compound **3**, the procedure caused weaker damages on the
26 supporting PP than for the other modified surfaces. This allows to measure the height profile for
27 surfaces modified with compound **3** equal to 9 ± 2 nm (**Figure 5c** and **Figure S9**). This thickness
28 value is about 3 times that found for the corresponding modified gold surface. Importantly, this
29 measurement is only a coarse estimation because i) of the high roughness of the bare PP, and ii)
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4 even if the supporting substrate is less strongly scratched than for surfaces modified with
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6 compounds **1** or **2**, it could be modified down to a few nanometers. The fact that the thickness of
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8 the layers deposited on PP cannot be quantified, in the case of the grafting from **1** and **2** deserves
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10 being further commented. Indeed, when scratching with the AFM probe, the polypropylene
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12 substrate was heavily damaged, even at the lowest possible deflection set-point (thus the lowest
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14 possible applied force), indicating that the grafted organic layer is probably very thin. As a result,
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16 the thickness of the organic layer cannot be determined by this technique. Unfortunately, the
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18 ellipsometry technique that requires a flat reflective surface cannot be applied to measure the
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20 thickness of the film deposited onto the PP surfaces. Nevertheless, the qualitative observations
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22 made by the AFM techniques point to the formation of very thin films in the case of PP modified
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24 with the hydroxide-based grafting of compounds **1** and **2**.
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3 **Figure 5.** AFM topography images of polypropylene surfaces a) bare, treated with sodium
4 hydroxide only; b) modified by compound **3**; c) modified by compound **3** and after scratching a 1
5 μm^2 ; d) modified by compound **1**; e) modified by compound **2**
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11 Further evidence of the grafting of calix[4]arene-tetradiazonium salts on PP was obtained by
12 X-ray photoelectron spectroscopy (XPS) (**Figure 6**). The compound **1** was specifically used to
13 assess the success of the surface modification, the CF_3 group being used as a chemical tag (see
14 also **Tables S1** and **S2**). The survey spectrum shows the presence of carbon C1s (280-296 eV, 75
15 % atom), oxygen O1s (533 eV, 9 % atom), fluorine F1s (688.5 eV, 13 % atom) and a small
16 amount of nitrogen at 400 eV that might either be due to the formation of a small proportion of
17 azo groups derived from the diazonium salts or to contamination, as already reported in the
18 literature.^{30, 66-69} The absence of peaks at 403.8 eV indicates that no diazonium compounds
19 remain adsorbed at the surface. The presence of the F1s photoelectron peak obviously suggests
20 the grafting of the calix[4]arene with CF_3 *termini* at the PP surface. The C1s core level spectrum
21 could be decomposed into different components (**Figure 6** right, **Table S2**). The main
22 component centered at 285 eV can be attributed to the carbon atoms of the calix[4]arene core as
23 well as the carbon atoms from the PP substrate. The component at 286.3 eV is mostly assigned to
24 the ether links present in the calix[4]arene core. Also, this component partly contributes to
25 oxidized contamination species, as well as the component at 287.3 eV; these components were
26 detected on the bare PP substrate, being soaked or not in the hydroxide solution prior to analysis
27 (see SI). The component at 293 eV corresponds to the CF_3 groups and further confirms the
28 grafting of compound **1** on PP surface.
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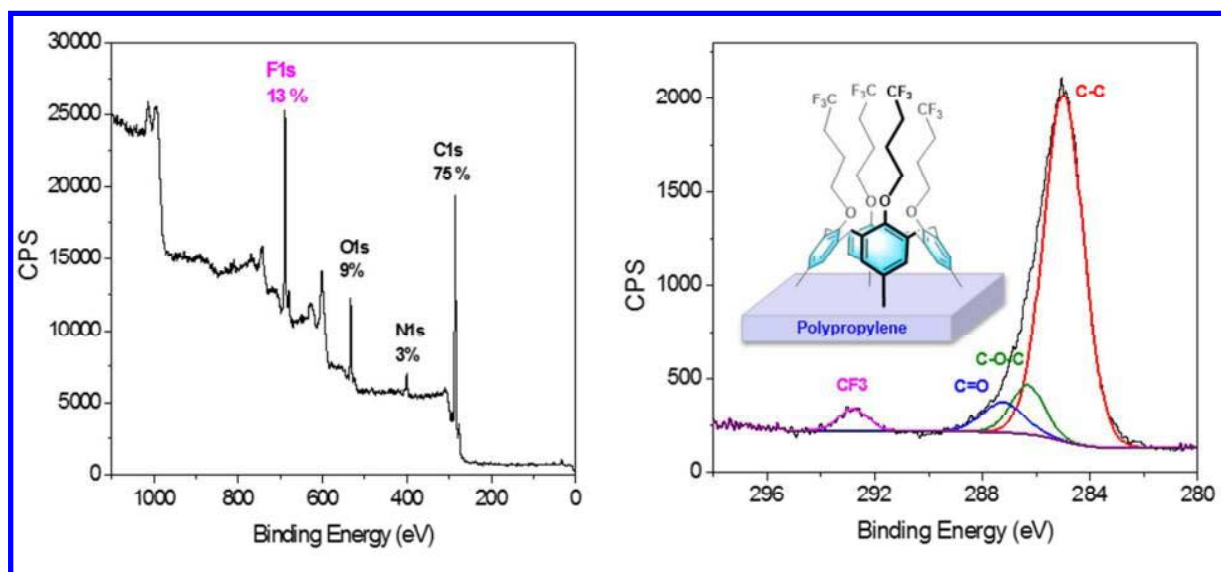


Figure 6. XPS spectra of (left) polypropylene modified with compound **1** and (right) corresponding C1s core level spectrum.

The AFM observations combined to the XPS measurements suggest that a monolayer of calixarenes is deposited on the surface of polypropylene through the spontaneous dediazonization of the calix[4]arene-tetradiazonium cations in the hydroxide solution. Yet, the diazoate species are rather unstable and their radical decomposition are reported to be fast^{34,35,70,71}. It was then of interest to check if the functionalization of the PP surface could occur over shorter times than 16h, i.e. whether functionalization process could indeed occur from dediazonization of diazoate. The hydroxide-based chemical grafting with compound **1** was also performed by soaking the surface for 1h or 4h. After a thorough rinsing, the resulting surfaces were characterized by XPS spectroscopy. In both cases, elemental species C, O and F are detected (see **Figure S8**). The atomic ratio (%) are close to those found for PP modified for 16h (**Table S3**). An immersion time of 1h is sufficient to allow for the functionalization of the PP surfaces, which is highly consistent with the relatively short lifetime of diazoates.

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4 **Post-functionalization of the modified polypropylene surfaces.** The PP surfaces modified
5 with compound **2** could undergo a chemical post-functionalization reaction by using the reactive
6 carboxylic terminal groups. As a proof of concept, such a post-functionalization was investigated
7 with CF₃-containing compounds in order to allow the straightforward XPS characterization of
8 the post-functionalized PP surfaces. The pendant carboxylic groups were first converted into the
9 corresponding activated esters by EDC/NHS in MES buffer at a pH of 6.9 (**Figure 7**). The
10 resulting activated surfaces were then engaged in a reaction either with 4,4,4-trifluorobutylamine
11 or with 4,4,4-trifluoro-1-butanol. Prior to their spectroscopic analyses, the surfaces were
12 thoroughly rinsed with acetonitrile, dichloromethane and toluene (sonication was applied each
13 time for 10 minutes).

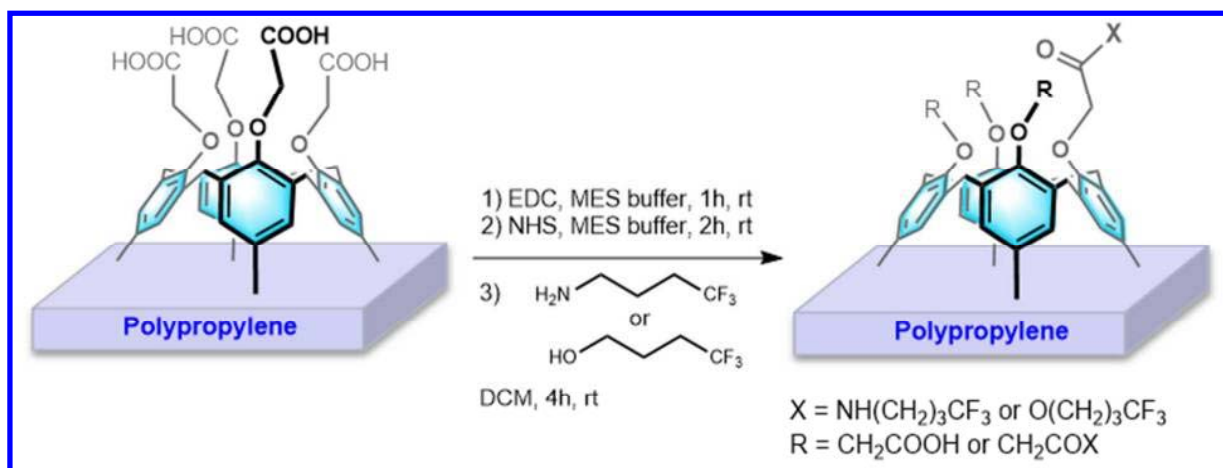


Figure 7. Post-functionalization of polypropylene surfaces modified with compound **2**.

The survey spectra of the post-functionalized PP surfaces show main peaks attributed to C, O and F elemental species (see SI). In both cases, the presence of F1s photoelectron peaks at 688.5 eV is a clear indication that the post-functionalization reactions at the PP surfaces were successful. This conclusion is strengthened by the decomposition of the C1s core level spectrum showing a component at 293 eV, characteristic of CF₃ groups (**Figure 8**). In the C1s peak, the main contribution at 285 eV can be attributed to the aliphatic and aromatic carbon atoms of

calix[4]arene **2** coupled with the trifluorobutyl compounds as well as the carbon atoms from the PP substrate. The C-O-C contribution at 286.3 eV corresponds to the ether groups in the calixarene core but also to contaminant species that are also associated to the C=O contribution at 287.3 eV, as detected on bare PP samples (see SI). As a result, the atomic ratio of C in C-O-C/C in CF₃ is somewhat higher than the expected theoretical value on the basis of the sole calixarene structure (4/4 = 1) (see **Table 1**).

Table 1. Atomic ratio evaluated in the C1s decomposition fit for the two post-functionalized surfaces.

Samples PP-2	Ratio	Ratio	Ratio	Ratio	Ratio
coupled to	<i>C-O-C/C-C</i>	<i>C=O/C-C</i>	<i>CF₃/C-C</i>	<i>C-O-C/CF₃</i>	<i>O-C=O/CF₃ or N-C=O /CF₃</i>
trifluorobutanol	0.15	0.085	0.05	3	1
trifluorobutylamine	0.12	0.048	0.033	3.6	0.7

A component at 289.2-289.4 eV corresponds to the carbon atoms in amide or ester groups formed after the coupling reaction with the trifluorobutyl compounds or, possibly, to unreacted carboxylic groups. Interestingly, the atomic ratio of C in this component to C in CF₃ is found to be 1 for the coupling with 4,4,4-trifluoro-1-butanol and equal to 0.7 with 4,4,4-trifluorobutylamine. This shows that the chemical coupling is highly efficient, involving 3 to 4 of the reactive carboxylic *termini* in the same calix platform. This result evidences the possibility to introduce molecular species with a fine spatial control that is imposed by the geometry of the calixarene small rim.

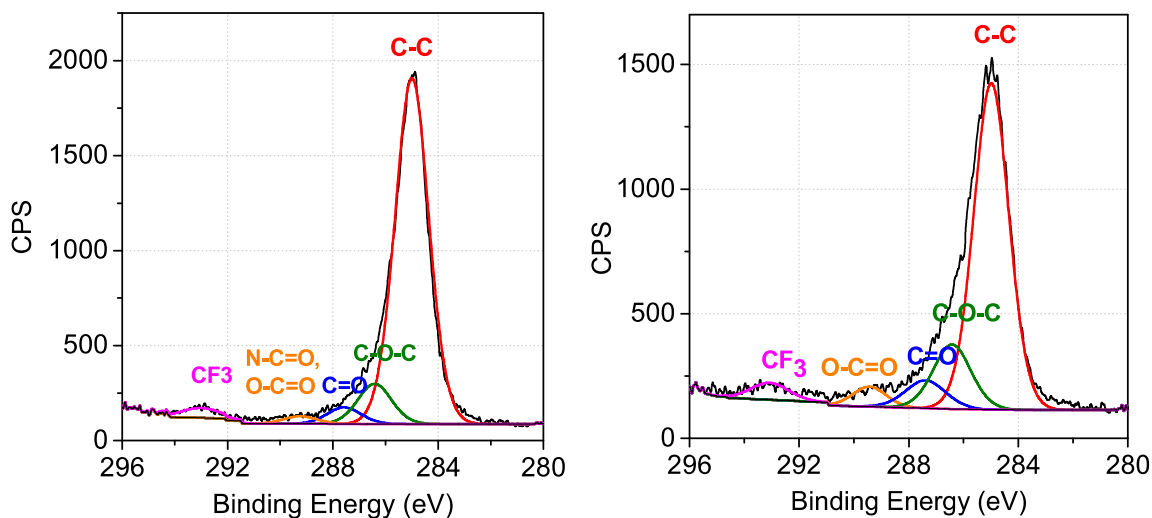
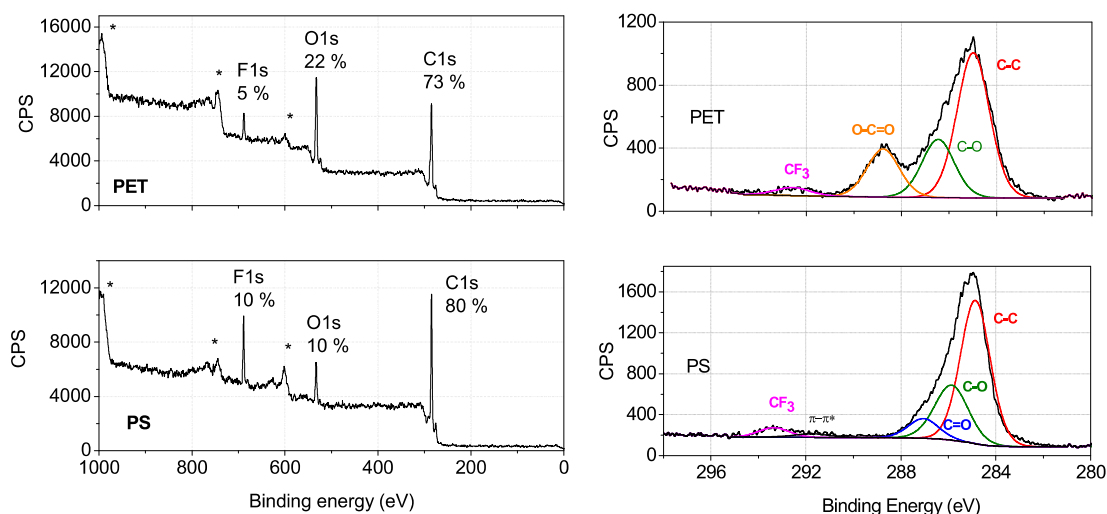


Figure 8. High resolution C1s spectra with insets showing survey spectra of (left) 4,4,4-trifluorobutylamine modified surface and (right) 4,4,4-trifluoro-1-butanol modified surface.

All these XPS data demonstrate that the polymer surface could be efficiently post-functionalized thanks to the calixarene platform. These results show the versatility of the approach for tailoring the PP polymeric surfaces.

Functionalization of other polymeric substrates. Preliminary work was undertaken with other polymeric substrates such as polyethylene terephthalate (PET) and polystyrene (PS) in order to evaluate the generalization of the approach. The different polymer surfaces were modified with calixarene **1**, allowing a straightforward characterization from XPS measurements (**Figure 9, Tables S1 and S2**). The characteristic peak for F1s photoelectrons at 688.5 eV can be clearly observed in the survey spectra for all modified polymers. The decomposition of the C1s core level spectra shows the presence of a peak corresponding to CF₃ (293 eV, 3.4 % of C1s for PET; 293.3 eV, 4 % of C1s for PS). This observation clearly indicates that calix[4]arene **1** was grafted onto these polymeric surfaces. As discussed in the former sections, the main components

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4 at 285 eV can be attributed to the carbon atoms of the grafted calix[4]arene molecules but also to
5 the aliphatic or aromatic carbon atoms (C-C) from the substrates. The C-O component (286.3
6 eV) is due partly to the grafted calixarene compound and to the polymer substrates, as identified
7 onto the bare polymer surfaces (see SI). The higher binding energy components correspond to
8 carbon atoms in the polymer substrates (probably contaminants for PS). Especially, the XPS C1s
9 spectrum of PET (bare) surface gives a characteristic signal, with a relative composition of peaks
10 for C-C, C-O-C and O-C=O corresponding to the chemical structure of the PET polymer. Note
11 that a treatment in hydroxide solution prior to analysis does not modify the XPS spectra
12 signature (see Table S1 and S2). After grafting the calixarene platform onto the PET surface, the
13 typical spectrum of PET is still observed, showing that the grafted calixarene layer is necessarily
14 thin. This observation is fully consistent with the AFM study.⁷²



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Figure 9. Survey spectra (left) and high resolution C1s spectra (right) of polymers (PS and PET) modified with calix[4]arene **1**. * denotes Auger peaks.

Conclusion

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3 We have reported here a systematic study of the sodium hydroxide-based grafting of
4 diazonium salts on gold and polymer surfaces, producing the corresponding reactive diazoate
5 salt. Two different calix[4]arene-tetradiazonium salts **1** and **2** as well as a classical aryldiazonium
6 salt **3** were used to evaluate the efficiency of this approach. Being rarely employed, this grafting
7 method was first validated on gold substrates from comparison with the well-known
8 electrografting procedure. AFM and ellipsometry measurements indicate that a compact
9 monolayer of calix[4]arenes is obtained, in agreement with our previous study based on the
10 electrochemical procedure. In contrast, the diazonium salt **3** has led to the formation of a
11 multilayered film on gold, as expected. We then transposed this sodium hydroxide-based grafting
12 procedure on insulating polymers, focusing mainly on polypropylene. Polypropylene surface was
13 successfully modified with the diazonium salt **3** in a multilayer fashion as indicated by atomic
14 force microscopy (AFM), while the calix[4]arenes compounds **1** and **2** were shown to produce
15 thinner films at the polymer surface. The hydroxide-based grafting of the calix[4]arene-
16 tetradiazonium salts on polypropylene was further confirmed by X-ray photoelectron
17 spectroscopy (XPS) measurements. The strategy was successfully extended to other polymer
18 substrates including polystyrene and polyethylene terephthalate. Finally, as a proof of concept,
19 the post-functionalization of the polypropylene surfaces modified by the calix[4]arene decorated
20 with carboxylic appending arms was easily achieved. These results highlight the powerful
21 technique that is the grafting of diazonium in sodium hydroxide for the modification of
22 polymers. This method is particularly simple to operate and does not require complex and costly
23 equipment like, for instance, for plasma methods. It indeed only necessitates dipping polymer
24 samples in a solution containing the diazonium salts. Using this technique, we have gained
25 further access and understanding of the modification and post-functionalization of insulating
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3 materials. The use of the calix[4]arene platform permits a further fine molecular control of the
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5 polymeric surface modification, allowing to i) modify surface properties of polymers without
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7 drastic modifications of their bulk properties, ii) introduce a large range of chemical objects
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9 (including biomolecules, chromophores, nanoparticles, ...). These results open real possibilities
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11 in the tailoring of polymers properties.
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18 ASSOCIATED CONTENT

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21 **Supporting Information.** Ellipsometry measurements on gold, XPS measurements of bare
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23 polymeric surfaces and post-functionalized polypropylene surfaces, XPS data tables for all the
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25 polymer surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.
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47 **Author Contributions**

48
49 The manuscript was written through contributions of all authors. All authors have given approval
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51 to the final version of the manuscript.
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55 ACKNOWLEDGMENT

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3 The authors would like to thank Pascale Blond for the generous gift of compound **3** and
4 Delphine Merche for performing control XPS measurements. JH thanks the FNRS (Belgian
5 National Fund for Scientific Research) for an “Aspirant Grant”. FR and JH also thank the
6 Belgian Federal Office for Science Policy (BELSPO) for financial support to the I.A.P
7 (Interuniversity Attraction Pole) programs “PSI _ Physical Chemistry of Plasma Surface
8 Interactions -IAP-VII/12, P7/34-. AM and LTG thank the Région Wallonne for financial support
9 to the “FIRST Spin-off MONOCAL” grant.
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29 homolytic pathway⁷⁰, with an apparent kinetic rate constant $k_{\text{obs}} \approx 5 \times 10^{-3} \text{ s}^{-1}$ at 60°C (in
30 20% EtOH/H₂O). This could roughly correspond to $k_{\text{obs}} \approx 3\text{-}4 \times 10^{-4} \text{ s}^{-1}$ at 20°C (considering
31 an activation energy of 60 kJ mol⁻¹, which is a reasonable average value for this kind of
32 reaction). An half-time decay equal to 1730-2300 s for the diazoate could be deduced from
33 this value
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41 (72) Similar observations could be drawn from the comparison of XPS spectra of bare PP or
42 PS and the functionalized surfaces. However, the corresponding C1s signals for these
43 polymers are much less characteristic, making it difficult to get a clear cut conclusion.
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TOC Graphic

