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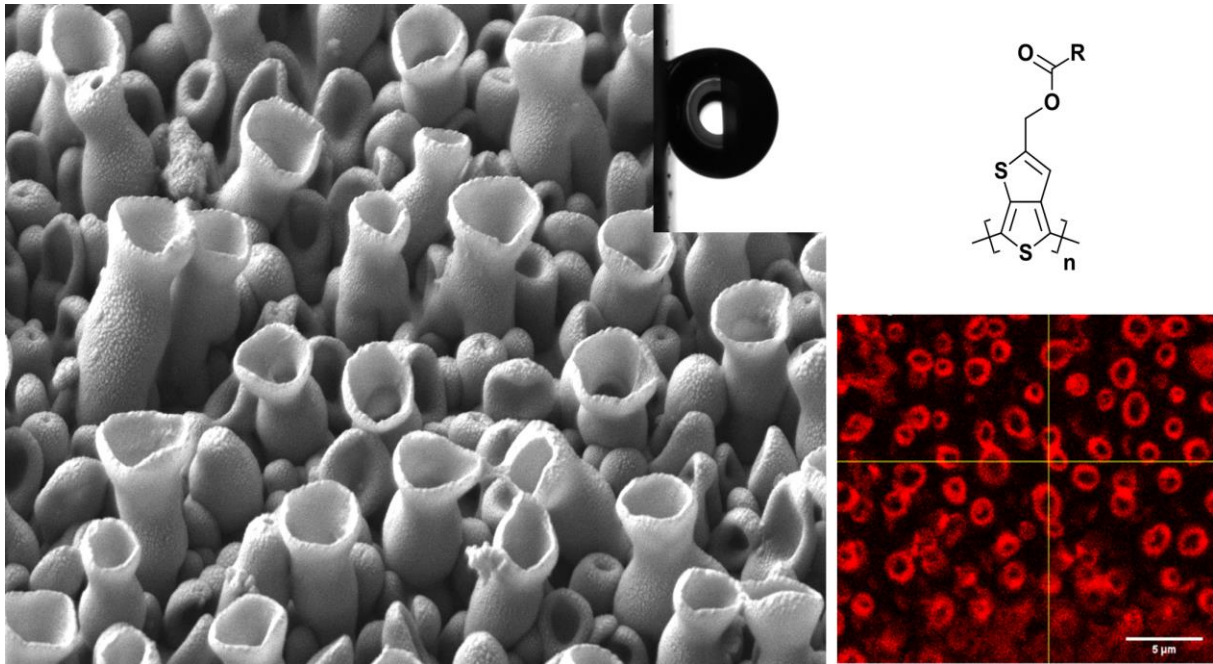
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1 **Graphical Abstract**

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5 **A bioinspired approach to fabricate fluorescent nanotubes with strong**  
6 **water adhesion by soft template electropolymerization and *post-grafting***

7 Ananya Sathanikan<sup>a</sup>, Giacomo Ceccone<sup>b</sup>, Jorge Bañuls-Ciscar<sup>b</sup>, Miaobo Pan,<sup>c</sup> Fadwa Kamal<sup>d</sup>,  
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10

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3

#### 4 **Abstract**

5

##### 6 Hypothesis

7 In this original work, we aim to control both the surface wetting and fluorescence properties  
8 of extremely ordered and porous conducting polymer nanotubes prepared by soft template  
9 electropolymerization and *post-grafting*. For reaching this aim, various substituents of  
10 different hydrophobicity and fluorescence were *post-grafted* and the *post-grafting* yields were  
11 evaluated by surface analyses. We show that the used polymer is already fluorescent before  
12 *post-grafting* while the *post-grafting* yield and as a consequence the surface hydrophobicity  
13 highly depends on the substituent.

14

##### 15 Experiments

16

17 Here, we have chosen to chemically grafting various fluorinated and aromatic  
18 substituents using a *post-grafting* in order to keep the same surface topography. Flat  
19 conducting polymer surfaces with similar properties have been also prepared for determining  
20 the surface energy with the Owens-Wendt equation and estimating the *post-grafting* yield by  
21 X-ray Photoemission Spectroscopy (XPS) and Time of Flight Secondary Emission  
22 Spectrometry (ToF-SIMS). For example, using fluorinated chains of various length (C<sub>4</sub>F<sub>9</sub>,  
23 C<sub>6</sub>F<sub>13</sub> and C<sub>8</sub>F<sub>17</sub>), it is demonstrated that the surface hydrophobicity and oleophobicity do not  
24 increase with the fluorinated chain length due to the different *post-grafting* yields and  
25 because of the presence of nanoroughness after *post-grafting*.

26

##### 27 Findings

28

29 These surfaces have high apparent water contact angle up to 130.5° but also strong water  
30 adhesion, comparable to rose petal effect even if there are no nanotubes on petal surface. XPS  
31 and ToF-SIMS analyses provided a detailed characterisation of the surface chemistry with a  
32 qualitative classification of the grafted surfaces (F6 > F4 > F8). SEM analysis shows that

1 grafting does not alter the surface morphology. Finally, fluorescence analyses show that the  
2 polymer surfaces before *post*-treatment are already nicely fluorescent. Although the main goal  
3 of this paper was and is to understand the role of surface chemistry in tailoring the wetting  
4 properties of these surfaces rather than provide specific application examples, we believe that  
5 the obtained results can help the development of specific nanostructured materials for  
6 potential applications in liquid transport, or in stimuli responsive antimicrobial surfaces.

7

8 **Keywords:** Surface functionalization, Wettability, Hydrophobicity, Surface analysis,  
9 Fluorescence, Conducting polymers, Nanotubes.

10

## 11 **1. Introduction**

12

13 The difficulty in obtaining regular nanoscale structures is a key challenge especially when we  
14 want to find a relationship between unique properties and the shape of these structures [1–6].  
15 In Nature, nanostructures are omnipresent and for example allowing geckos to strongly  
16 adhere and walk to various surfaces [7–10]. In wettability field, the scientific community  
17 focus on vertically aligned nanotubes for their surface-area-to-volume ratio allowing to  
18 control the wetting properties with their dimensions (diameter, height, porosity, shape) [11–  
19 14]. Well-defined vertically aligned nanotubes are often prepared using membranes with the  
20 defined features. One of the most used membrane is anodized aluminium oxide (AAO)  
21 membrane [15–17]. However, one membrane is necessary for each nanotube dimension.

22

23 Alternatively, the nanotube dimensions and even the shape can be easily and fastly tuned by  
24 templateless electropolymerization, which is a soft template electropolymerization. Gas  
25 bubbles play the role of soft template while the polymer electrodeposited around these  
26 bubbles. In the literature, the soft template electropolymerization of pyrrole in water (H<sub>2</sub>O)  
27 has been specifically studied [18–23]. During electropolymerization, H<sub>2</sub>O can be oxidized  
28 and/or reduced to form H<sub>2</sub>/O<sub>2</sub> bubbles following the chosen electropolymerization method  
29 (potentiostatic [18,19] or potentiodynamic methods [20–23]). However, this method needs  
30 water-soluble monomer such as pyrrole while a surfactant is often necessary to stabilize the  
31 gas bubbles.

32 Given the low water solubility of most of the monomers *r*, this process was also tested in  
33 organic solvent (e. g. dichloromethane) and works as soon as trace H<sub>2</sub>O is present in solution.

1 It is even possible to replace surfactant using rigid monomers highly favouring  $\pi$ -stacking  
2 interactions [24–27]. Moreover, very recently it was even clearly demonstrated the presence  
3 of reverse micelles stabilized by the monomer and the electrolyte before  
4 electropolymerization [28]. Although in these works low H<sub>2</sub>O content was used, it was  
5 demonstrated that sometimes it is preferable to saturate CH<sub>2</sub>Cl<sub>2</sub> with H<sub>2</sub>O in order to form a  
6 large number of nanotubes [28].

7 However, for studying the influence of surface energy on nanotubular structures by  
8 electropolymerization, it is preferable to *post*-graft the substituents because they have a huge  
9 influence on the surface structures [29]. In this original work, vertically aligned open  
10 nanotubes with functional hydroxyl groups have been prepared by templateless  
11 electropolymerization of thieno[3,4-*b*]thiophen-2-ylmethanol (**Thieno-OH**) in CH<sub>2</sub>Cl<sub>2</sub>  
12 saturated with H<sub>2</sub>O (CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O) in order to release a very high amount of gas bubbles, to  
13 form densely packed nanotubes and with just with one deposition scan in order to keep the  
14 nanotubes open. Indeed, we already demonstrated with NaphDOT [28] that if the polymer is  
15 intrinsically hydrophilic (Young's angle of PolyNaphDOT  $\theta_w^Y = 63.6^\circ$ ), if we want to highly  
16 increase the water contact angle ( $\theta_w$ ), it is preferable to form densely packed open nanotubes  
17 with a nanometric size (height and diameter). In this work, the formation of densely packed  
18 nanotubes was performed by using the solvent CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O while the formation of open  
19 tubes was done by choosing the cyclic voltammetry as the electropolymerization process  
20 because a much higher of gas bubbles is released with this process compared to deposition at  
21 constant potential, for example. Then, the nanometric size of the nanotubes was possible by  
22 using just one deposition scan.

23 Then, various substituents have been *post*-grafted for changing both the surface wettability  
24 and fluorescent properties by simple esterification reaction (Scheme 1). If the surface *post*-  
25 grafting was already in the literature with different chemical reactions [30,31], here, to our  
26 knowledge, this is the first time we have tried to better explain the wettability results of rough  
27 surfaces by determining the post-grafting yields with each substituent. The main of this paper  
28 is to underline and to understand the role of surface chemistry in tailoring the wetting  
29 properties of these rough surfaces.

30 The influence of the surface tubular structures on the wettability properties has been possible  
31 by preparing smooth surfaces with **Thieno-OH** and *post*-grafted with each substituent. Hence,  
32 with these smooth surfaces, their surface energy has been determined with the Owens-Wendt

1 reaction with three liquid probes while the *post*-grafting yield with each substituent could be  
2 estimated by XPS and ToF-SIMS analyses.

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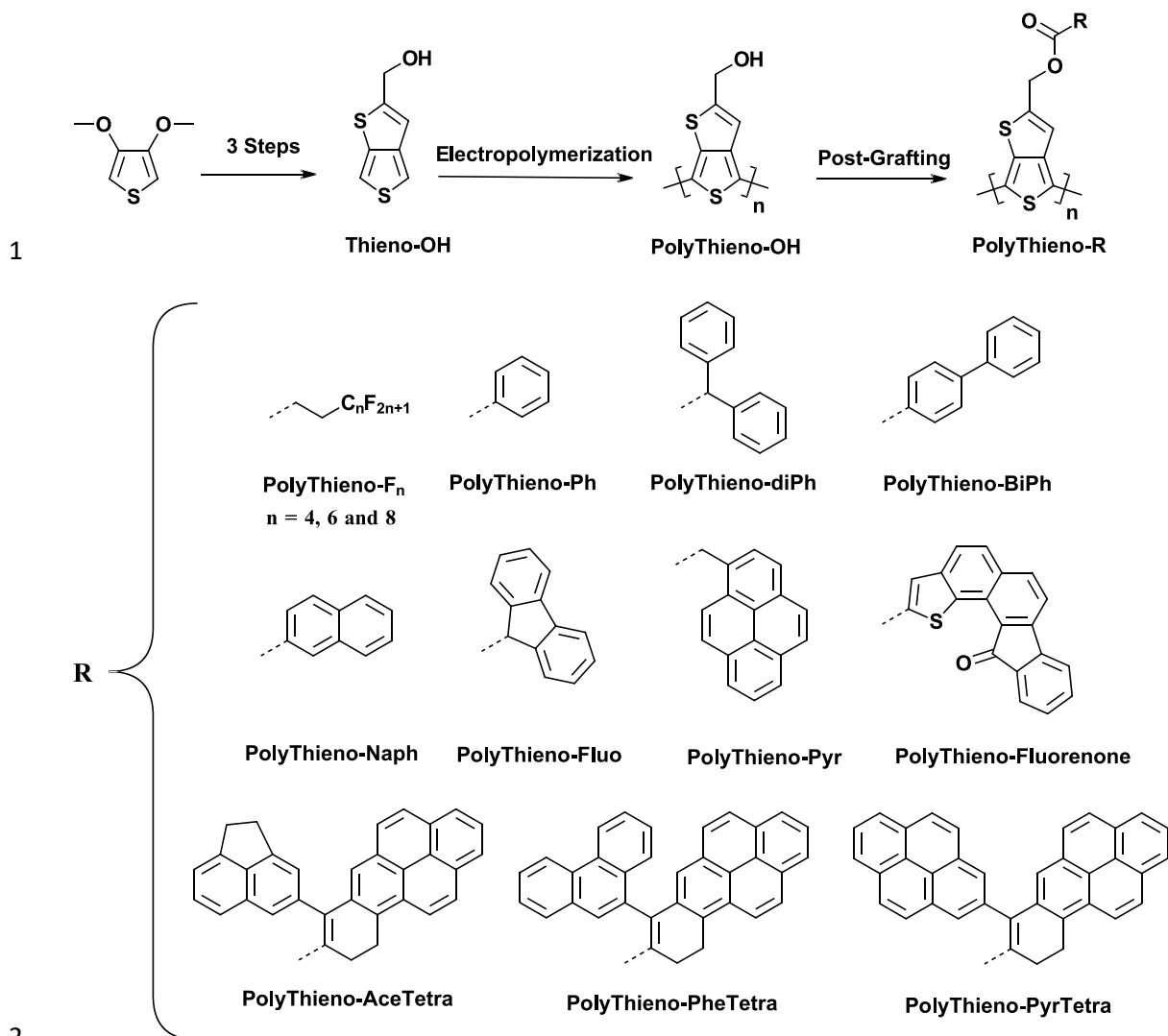
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**Scheme 1.** Strategy used to form conducting polymer nanotubes with various substituents.

## 2. Materials and methods

### 2.1. Formation of nanotubes by soft template electropolymerization

Thieno[3,4-*b*]thiophen-2-ylmethanol (**Thieno-OH**) was synthesized according to a previous work [29]. In order to perform a huge number of nanotubes, CH<sub>2</sub>Cl<sub>2</sub> was saturated with H<sub>2</sub>O (CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O). This solvent was prepared by simply mixing CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O and keeping the organic phase after decantation. 0.1 M of tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) as supporting electrolyte and 0.01 M of **Thieno-OH** as the monomer were added to CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O. For the depositions, a potentiostat (Autolab from Metrohm) *via* three electrode system was used. The electrodes consisted in 2 cm<sup>2</sup> Indium Tin Oxide (ITO)-coated glass as the working electrode, a glassy carbon rod as the counter-electrode and a saturated calomel

1 electrode (SCE) as the reference electrode. Here, ITO was selected especially for the  
2 fluorescence tests. Here, the depositions were performed by cyclic voltammetry in order to  
3 release a high amount a gas necessary to form porous structures (nanotubes) and with just  
4 with 1 deposition scan in order to keep the nanotubes open. More precisely, the formation of  
5 nanotubes was obtained by doing 1 deposition scan from -1 V to the monomer oxidation  
6 potential ( $E^{\text{ox}} = 1.77 \text{ V vs SCE}$ ) at the scan rate of  $20 \text{ mV s}^{-1}$ .

## 8 **2.2. Formation of smooth surfaces by electropolymerization**

9 For the formation of smooth surfaces,  $\text{CH}_2\text{Cl}_2$  was used as the solvent. Here, in order to form  
10 smooth surfaces, the depositions were performed at constant potential ( $E^{\text{ox}} = 1.77 \text{ V vs SCE}$ )  
11 and using an ultra-short deposition charge of  $1 \text{ mC cm}^{-2}$ . However, in order to have the same  
12 polymer that by cyclic voltammetry that means in its reduced state, the polymer was reduced  
13 by cyclic voltammetry but just 1 back scan from  $E^{\text{ox}} = 1.77 \text{ V}$  to -1 V at the scan rate of 20  
14  $\text{mV s}^{-1}$ .

## 16 **2.3. Post-grating**

17 The synthesis of the molecules for *post*-grafting is available in Supporting Information. A  
18 glass flask containing 20 mL of  $\text{CH}_2\text{Cl}_2$  and a large excess of dicyclohexylcarbodiimide  
19 (DCC) (80 mg) and the corresponding acid (80 mg), and a catalytic amount 4-  
20 dimethylaminopyridine (DMAP) is stirred for 30 mn. Then, the coated-substrates were added  
21 and the flask is slightly stirred for 5 days. Finally, the substrates were washed with  $\text{CH}_2\text{Cl}_2$   
22 and slowly dried.

## 24 **2.4. Surface characterization**

25 After metallization, surfaces nanostructures were imaged *via* scanning electron microscopy  
26 (SEM) (6700F microscope from JEOL) with and without surface incination of  $45^\circ$  in order to  
27 better estimate the height of the nanotubes. The surface wettability was characterized *via*  
28 goniometer (DSA30 from Bruker) by placing water droplets on the substrate and measuring  
29 the apparent contact angles with water ( $\theta_w$ ) taken at the triple point ( $n=5$ ). For the contact  
30 angle hysteresis and sliding angles, the substrate was inclined until the droplets moved, using  
31 a procedure described by Amirfazli [32]. The advanced and receding contact angles are taken  
32 in leading edge and trailing edge, respectively, of the droplets just before their moving due to



1 gravity. If the droplets do not move even if the sliding angle is above  $90^\circ$ , the substrate is  
2 highly adhesive and parahydrophobic, as described by Marmur [6].

3

#### 4 **2.5. Surface analysis: XPS and ToF-SIMS**

5 The surface chemistry after functionalization was assessed by X-Ray Photoemission  
6 Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

7 Samples were cleaned in hexane and then mounted on sample holder using a silicon free,  
8 UHV compatible double side Cu tape (3M, USA). The samples were then inserted in a load-  
9 lock for overnight degassing ( $p = 5 \times 10^{-8}$  mbar) and finally in the analysis chamber (base  
10 pressure  $5 \times 10^{-9}$  mbar). XPS analysis was carried out by means of a Axis Ultra-DLD spectrometer  
11 (Kratos Analytical, UK) equipped with a monochromatic Al  $K\alpha$  source ( $h\nu = 1486.6$  eV) operating at  
12 150W. Wide scan spectra were recorded from 0 to 1100 eV binding energy in hybrid mode, “slot”  
13 ( $400 \times 700 \mu\text{m}^2$  analysis area) and FoV2 (100  $\mu\text{m}$  spot) at 80eV and 160 eV pass energy, whereas core  
14 level spectra were recorded in “hybrid” mode using pass energy of 20 eV. The take-off angle (ToA)  
15 respect to the sample normal was  $0^\circ$  for survey and high-resolution (HR) spectra, whilst angle-  
16 resolved XPS analyses (AR-XPS) were performed at ToA =  $30^\circ$ ,  $45^\circ$  and  $70^\circ$ . Operating pressure was  
17  $1.5 \times 10^{-8}$  mbar. Surface charging was compensated using low energy ( $\sim 4$  eV) electrons and adjusted  
18 using the charge balance plate on the instrument. Three different spots were analyzed for each sample.  
19 All the spectra were processed with CasaXPS (ver. 2.3.22). Spectra were calibrated setting  
20 hydrocarbon C1s at 285.0 eV. The surface composition was evaluated from the survey spectra, after  
21 background subtraction, using relative the sensitivity factors provided by the manufacturer. Peak  
22 fitting was performed with no preliminary smoothing. Lorentzian finite functions, LF(a,b,w,n), were  
23 used to approximate the line shapes of the fitting components after a Tougaard U3-type background  
24 subtraction [32,33].

25 ToF-SIMS (ToF IV, IONTOF GmbH, Germany) was also employed to characterize samples'  
26 chemistry. The accelerating voltage of the liquid metal ion gun (LMIG) was 25 keV,  $\text{Bi}_3^+$  was  
27 employed as source of primary ions rastering over an area of  $200 \times 200 \mu\text{m}^2$ . The analyses were  
28 performed in static conditions keeping the ion dose below  $10^{12}$  ions/cm<sup>2</sup>. Acquisition time was 45 s,  
29 with a beam current of 0.5 pA and primary ion beam in pulsed mode. Negative mass spectra were  
30 collected while using an electron flood gun to dissipate surface charging.  $\text{C}^-$ ,  $\text{CH}^-$ ,  $\text{CH}_2^-$ ,  $\text{C}_2\text{H}^-$ ,  $\text{C}_3\text{H}^-$ ,  
31  $\text{C}_4\text{H}^-$  and  $\text{C}_5\text{H}^-$  peaks were used to calibrate the positive spectra and a peak-list was created using the  
32 SurfaceLab software (ver. 6, IONTOF GmbH). Given the large number of peaks and spectra,  
33 Multivariate Analysis (MVA) methods were used to aid in the interpretation of the data. MVA  
34 methods are widely used within the ToF-SIMS community and are designed to reduce the size of large  
35 data sets with a minimal loss of information [34–37]. Normalized intensities of all the peaks selected

1 in the peak-list were loaded into the SimsMVA software [38] where Non-negative Matrix  
2 Factorialization (NMF) and Principal Component Analyses (PCA) were performed, providing  
3 endmembers in the case of NMF and principal components in the case of PCA [39]. Scores and  
4 loadings are the typical outcome of PCA and NMF analysis. The scores describe the relationship  
5 between samples for each principal component/endmember, whereas the loadings provide information  
6 regarding how the variables (peak intensities) relate to each principal component/endmember [35–  
7 40].

8

## 9 **2.6. Fluorescence microscopy on films**

10 Fluorescence images were acquired using Leica TCS SP5-AOBS confocal laser scanning  
11 microscope. The surfaces were submerged in distilled water, and imaged using  $\times 63$ - 1.4  
12 numerical aperture plan apochromat oil immersion objective. The size of the  $xy$  image was  
13  $512 \times 512$  pixels (image sizes:  $49.21 \times 49.21 \mu\text{m}^2$  and  $24.60 \times 24.60 \mu\text{m}^2$ ) recorded on 12  
14 bits. Films were excited at 476 nm or 488 nm and the emission was collected from 500 to 640  
15 nm or 520-700nm. Laser power was usually set around 30% and gain was adjusted in order to  
16 get signal. Each image corresponds to an average of 3 frames.

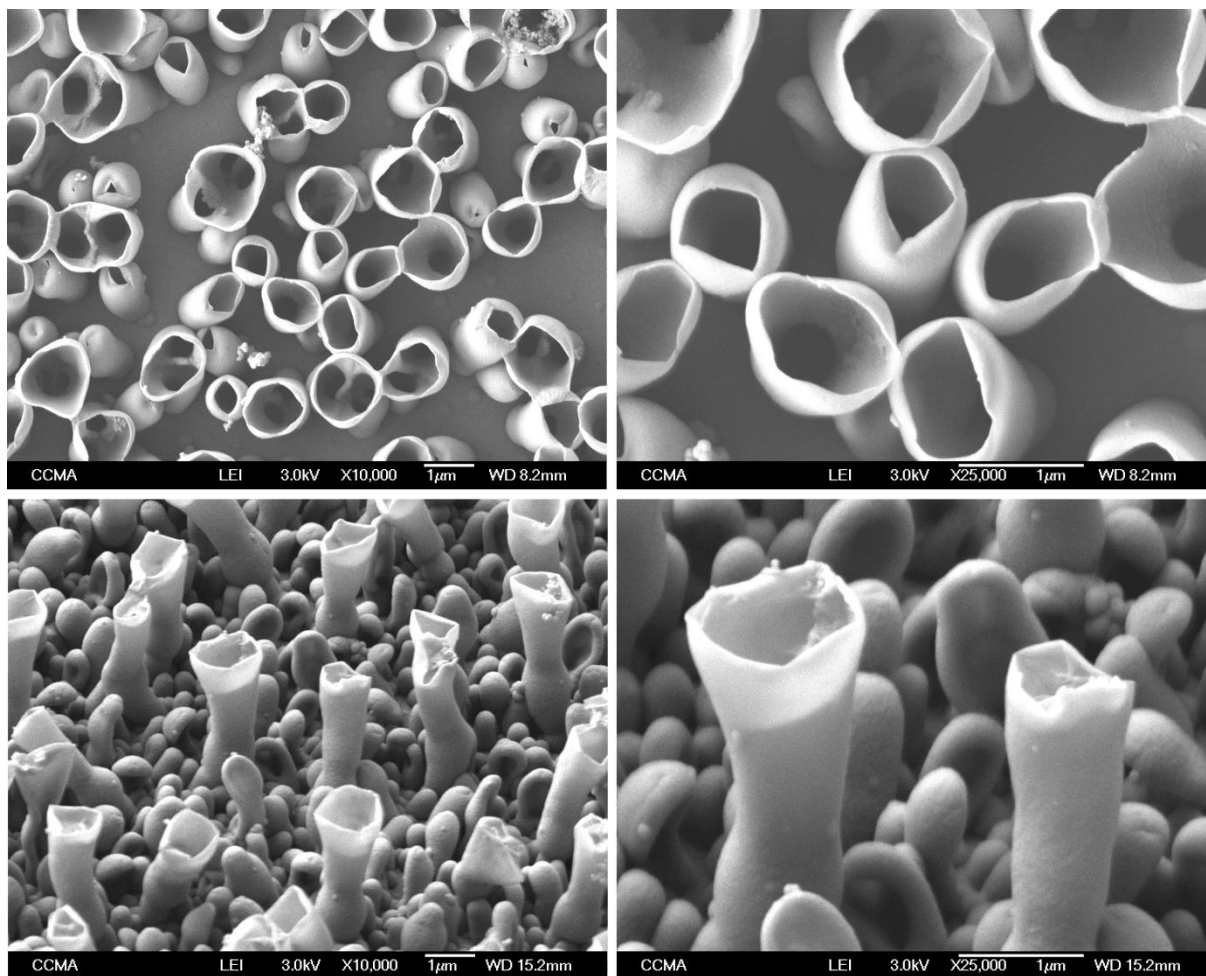
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## 18 **3. Results and discussion**

### 19 **3.1. Formation of nanotubes by soft template electropolymerization and *post-grafting***

20 Thieno-OH was used as monomer for the soft template electropolymerization process, and  
21  $\text{Bu}_4\text{NClO}_4$  as the electrolyte and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) as solvent. In order to release a  
22 high amount of gas bubbles and as a consequence to obtain vertically aligned nanotubes,  
23  $\text{CH}_2\text{Cl}_2$  was saturated with water ( $\text{H}_2\text{O}$ ). The solvent is called here  $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ . The  
24 deposition was performed on ITO substrate by cyclic voltammetry from -1 V to the monomer  
25 oxidation potential ( $E^{\text{ox}} = 1.77 \text{ V vs SCE}$ ) because it allows releasing both  $\text{O}_2$  and  $\text{H}_2$  bubbles.  
26 Only 1 scan at a scan rate of  $20 \text{ mV s}^{-1}$  was selected as optimal parameter to obtain a high  
27 number of open nanotubes. The resulting surfaces was characterized by SEM (Figure 1). The  
28 pictures display the presence of huge open nanotubes with a diameter of roughly  $1 \mu\text{m}$  and a  
29 height of  $3 \mu\text{m}$ . Moreover, the presence of close nanotubes of lower size is also observed. It  
30 should also be noticed that the surface of the tubes is smooth. Then, the surfaces were *post-*  
31 treated with different acids by a simple esterification reaction in order to modify the surface  
32 properties. By *post-treatment* of a modified surface, it is expected that only a part of the  
33 reactive groups would be modified. This point will be discussed in next paragraph.

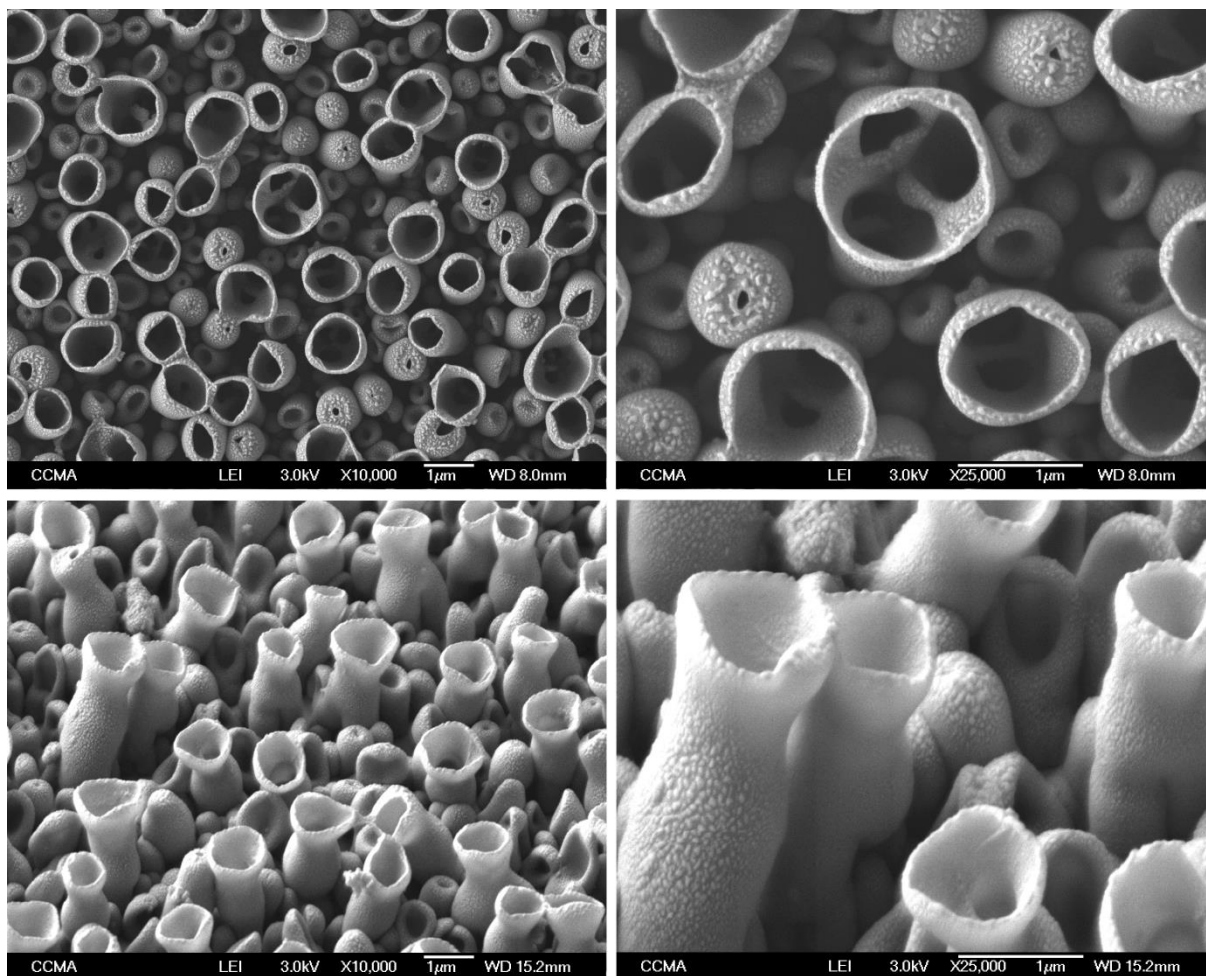
- 1 Representative SEM pictures after *post*-treatment with Fluorenone are presented in Figure 2.
- 2 As expected, surface morphology is maintained but the presence of nano-roughness on the
- 3 nanotube surfaces is observed.
- 4
- 5
- 6



1

2 **Figure 1.** SEM images of the polymer surfaces electrodeposited from the monomer Thieno-  
 3 OH (10 mM) in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> / CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O in potentiodynamic conditions by cyclic  
 4 voltammetry ( $E = -1 / +1.77$  V) after 1 scan. The pictures are taken without (up) and with a  
 5 substrate inclination of 45 ° (down).

6



1

2 **Figure 2.** Representative SEM images of the polymer surfaces after *post*-treatment with  
 3 fluorenone (PolyThieno-Fluorenone). The pictures are taken without (up) and with a substrate  
 4 inclination of 45 ° (down).

### 5 **3.2. Wetting properties**

6 The apparent contact angles ( $\theta$ ) of the different surfaces are reported in Table 1. Surprisingly,  
 7 even if the polymer has polar hydroxyl groups, PolyThieno-OH is slightly hydrophobic with a  
 8 water contact angle of  $\theta_{\text{water}} = 92.1^\circ$ , indicating that the surface structures/roughness have an  
 9 effect on contact angle. After *post*-treatment, the surfaces modified with fluorinated  
 10 PolyThieno-F<sub>8</sub> have the highest hydrophobicity ( $\theta_{\text{water}}$  up to  $130.5^\circ$ ) and oleophobicity  
 11 characters but these properties do not increase with the fluorinated chains length. Moreover,  
 12 in order to have more information about the water adhesion of these substrates, we tried to  
 13 determine the advancing ( $\theta_{\text{adv}}$ ) and receding ( $\theta_{\text{rec}}$ ) contact angles and as a consequence the  
 14 contact angle hysteresis  $H = \theta_{\text{adv}} - \theta_{\text{rec}}$ . First, we tested the sessile drop method [41], that  
 15 means by increasing and reducing the droplet volume but unfortunately it was not possible to  
 16 determine the  $\theta_{\text{rec}}$  because, due to the strong water adhesion, the triple-point line did not move

1 when the was sucked off. Then, the tilted-drop method was also tested [32], even if  
2 Krasovitski and Marmur demonstrated that the measured angles with this method did not  
3 exactly corresponded to  $\theta_{adv}$  and  $\theta_{rec}$  [42,43]. As shown in Figure 3, water droplets on these  
4 surfaces remained stuck even if the surfaces are inclined at 90° indication also of strong water  
5 adhesion but it was not possible to determine the  $\theta_{adv}$  and the  $\theta_{rec}$ . The strong adhesion of  
6 these surfaces is comparable to rose petals or gecko foot [8-10, 44-46]. Moreover, we tested  
7 water droplets from 1  $\mu$ L to 50  $\mu$ L and observed the sliding of the droplets only for droplets  
8 above 25  $\mu$ L. These surfaces could be applied in the future in water harvesting systems  
9 because with these surfaces it is possible to collect small water droplet due to the high water  
10 adhesion while it would be possible to release the water droplet when their size increases [47].  
11

12 In order to determine if the water droplet on these surfaces are in Wenzel state [48], Cassie-  
13 Baxter state [49] or intermediate states between the Wenzel and Cassie-Baxter, it was first  
14 necessary to determine the Young's angle [50] of these surfaces, that means the same surfaces  
15 but smooth. However, the droplets are not in the Cassie-Baxter state because it is admitted  
16 that the contact angle hysteresis has to be ultra-low that means only for truly  
17 superhydrophobic surfaces (lotus effect). It is also important to notice that to explain the  
18 strong water adhesion of rose petals, Bhushan and Nosonovsky demonstrated that several  
19 wetting regimes can coexist with the Wenzel, Cassie, lotus and petal [45]. Here, we use the  
20 term "intermediate states between the Wenzel and Cassie-Baxter" because we do not know  
21 exactly in which regime we are.  
22

23 The Young equation [50] being dependent on the surface energy  $\gamma_{sv}$ , it was first necessary to  
24 determine  $\gamma_{sv}$  of the starting polymer (PolyThieno-OH) and after each *post*-treatment.  
25 Moreover, since the Young equation is valid only for smooth surfaces,  $\gamma_{sv}$  can be determined  
26 also only on smooth surfaces using the Owens-Wendt equation [51]. For this, smooth surfaces  
27 were prepared as described in the experimental section. These surfaces revealed very  
28 interesting properties (Table 2). In particular, as expected, PolyThieno-OH is clearly the most  
29 hydrophilic ( $\theta_{water}^Y = 49.4^\circ$ ) due to the presence of hydroxyl groups and has the highest  $\gamma_{sv} =$   
30  $52.8 \text{ mN m}^{-1}$ . As expected, the polymers modified with fluorinated chains are intrinsically  
31 hydrophobic ( $\theta_{water}^Y > 90^\circ$ ) have the highest hydrophobic and oleophobic character but  
32 surprisingly the lowest  $\gamma_{sv} = 22.7 \text{ mN m}^{-1}$  is obtained with PolyThieno-F<sub>6</sub> and not  
33 PolyThieno-F<sub>8</sub>. These results will be explained below by different *post*-grafting yields. The

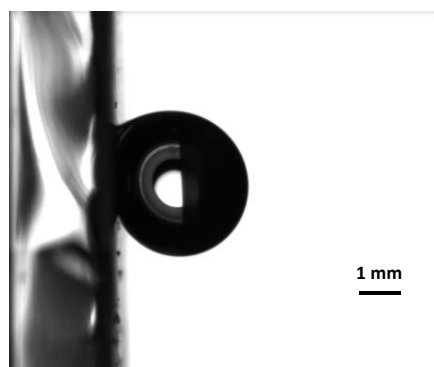
1 polymers modified with aromatic groups have  $\gamma_{sv}$  between PolyThieno-OH and PolyThieno-  
2 F<sub>n</sub>. The highest  $\gamma_{sv} = 47.3 \text{ mN m}^{-1}$  is obtained with PolyThieno-Ph and the lowest  $\gamma_{sv} = 38.0$   
3  $\text{mN m}^{-1}$  is obtained with PolyThieno-Fluorenone, which has  $\theta_{\text{water}}^Y \approx 90^\circ$  if we take into  
4 account the standard deviation. Hence, because only the fluorinated polymers being  
5 intrinsically hydrophobic ( $\theta_{\text{water}}^Y > 90^\circ$ ), only these surfaces may be in the Wenzel state  
6 otherwise it would be observed an increase of the surface hydrophilicity. For the same reason,  
7 except with PolyThieno-PheTetra for which  $\theta_{\text{water}} \approx \theta_{\text{water}}^Y$ , all the other surfaces are really in  
8 intermediate state between the Wenzel and Cassie-Baxter state because it is observed an  
9 increase of  $\theta_{\text{water}}$  whereas  $\theta_{\text{water}}^Y < 90^\circ$ . This may be due because water wet only the external  
10 part of the nanotubes but not the inner part [25]. It is also surprising to observe that the *post*-  
11 treatment with aromatic groups can induce sometimes an increase and sometimes a decrease  
12 of  $\theta$  compare with PolyThieno-OH.

13  
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17 **Table 1.** Apparent contact angles ( $\theta$ ) with different probe liquids of different nantubular  
18 surfaces.

Polymer	$\theta_{\text{water}}$ [deg]	$\theta_{\text{diiodo}}$ [deg]	$\theta_{\text{hexa}}$ [deg]
PolyThieno-OH	$92.1 \pm 7.1$	0	0
PolyThieno-F <sub>4</sub>	$129.0 \pm 4.6$	$117.0 \pm 5.5$	$30.5 \pm 6.8$
PolyThieno-F <sub>6</sub>	$122.7 \pm 4.6$	$130.8 \pm 0.9$	$83.4 \pm 2.1$
PolyThieno-F <sub>8</sub>	$130.5 \pm 3.8$	$125.0 \pm 4.9$	$90.7 \pm 3.5$
PolyThieno-Ph	$98.6 \pm 5.5$	0	0
PolyThieno-diPh	$115.0 \pm 5.4$	0	0
PolyThieno-BiPh	$112.6 \pm 3.5$	0	0
PolyThieno-Naph	$92.2 \pm 5.8$	0	0
PolyThieno-Fluo	$98.4 \pm 6.0$	0	0
PolyThieno-Pyr	$92.4 \pm 6.4$	0	0
PolyThieno-Fluorenone	$112.0 \pm 2.4$	0	0
PolyThieno-AceTetra	$85.8 \pm 4.9$	0	0
PolyThieno-PheTetra	$79.8 \pm 6.6$	0	0
PolyThieno-PyrTetra	$106.2 \pm 2.3$	0	0

1



2

3 **Figure 3.** Picture of a water droplet on the polymer surfaces after *post*-treatment with F<sub>6</sub>  
 4 (PolyThieno-F<sub>6</sub>) with a substrate inclination of 90°.

5

6

7 **Table 2.** Apparent contact angles ( $\theta$ ) with different probe liquids as well as the surface energy  
 8 of the corresponding smooth surfaces ( $\gamma_{sv}$ ) and the dispersive ( $\gamma_{sv}^D$ ) and polar ( $\gamma_{sv}^P$ ) parts.

Polymer	$\theta_{\text{water}}^Y$ [deg]	$\theta_{\text{diiodo}}^Y$ [deg]	$\theta_{\text{hexa}}^Y$ [deg]	$\gamma_{sv}$ [mN m <sup>-1</sup> ]	$\gamma_{sv}^D$ [mN m <sup>-1</sup> ]	$\gamma_{sv}^P$ [mN m <sup>-1</sup> ]
PolyThieno-OH	49.4 ± 3.0	36.8 ± 5.1	0	52.8	28.1	24.7
PolyThieno-F <sub>4</sub>	95.3 ± 2.7	62.4 ± 1.5	33.1 ± 1.6	26.2	24.2	2.0
PolyThieno-F <sub>6</sub>	101.4 ± 2.4	68.5 ± 2.1	42.8 ± 4.4	22.7	21.6	1.1
PolyThieno-F <sub>8</sub>	100.4 ± 2.5	65.5 ± 1.5	35.7 ± 3.3	24.5	23.4	1.1
PolyThieno-Ph	61.6 ± 1.7	19.8 ± 4.8	0	47.3	32.6	14.7
PolyThieno-diPh	81.9 ± 2.8	20.5 ± 2.4	0	38.8	34.6	4.1
PolyThieno-BiPh	82.3 ± 2.6	17.8 ± 3.0	0	38.9	35.0	3.9
PolyThieno-Naph	78.2 ± 1.3	16.5 ± 2.9	0	40.2	34.7	5.5
PolyThieno-Fluo	69.5 ± 5.0	15.0 ± 3.9	0	43.7	33.9	9.8
PolyThieno-Pyr	78.5 ± 1.8	15.1 ± 5.5	0	40.3	34.9	5.4
PolyThieno-Fluorenone	90.7 ± 2.7	11.9 ± 1.9	0	38.0	36.7	1.3
PolyThieno-AceTetra	77.5 ± 0.4	12.9 ± 1.3	0	40.6	34.3	6.3
PolyThieno-PheTetra	76.9 ± 2.9	19.5 ± 5.0	0	39.8	35.0	4.8
PolyThieno-PyrTetra	79.9 ± 2.9	13.0 ± 2.6	0	40.3	36.7	1.3

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### 1 3.3. Surface characterization by XPS and ToF-SIMS

2 In order to better understand these results, XPS and ToF-SIMS analyses were performed,  
3 especially for determining the *post*-grafting yield obtained with each substituent. Here, these  
4 techniques were chosen rather than infrared (IR) spectroscopy because ITO-coated glass  
5 absorbs IR.

6 In Table 3 the surface compositions of the samples are reported, whilst the correspondent  
7 survey spectra are illustrated in Figure S1. The theoretical compositions (excluding H) of the  
8 different compounds are reported in Table 4 and in Figure 4 the C1s core level spectra of the  
9 samples functionalized with the  $C_nF_{2n+1}$  SAMS are illustrated. As expected the intensities of  
10 the elements of ITO, namely In and Sn, together with the sulfur signal decrease in all samples  
11 after functionalization with all the molecules tested indicating a successful surface  
12 functionalization. The data related to the Indium Tin Oxide (ITO) substrate reveal the  
13 presence of a relatively high amount of carbon contamination routinely found on surfaces  
14 exposed to air (Figure 4a and Figure S2, supporting information), together with In, Sn and O  
15 peaks related to ITO. In particular, the C 1s spectrum can be fitted with three components  
16 corresponding to CC/CH (C1 285.00 eV, Figure 4a), C-O (C2 285.4 eV) and C=O, COOR  
17 (C3 288.9 eV). Analysis of In3d and Sn3d core level spectra reveals the presence of both  
18  $In_2O_3$  (In 3d 5/2 at 444.27 eV) and  $In(OH)_3$  (In 3d 5/2 at 445.08 eV, indicative of the  
19 presence of hydroxyl groups at the surface, whilst the Sn is present as  $SnO_2$  (Sn 3d 5/2 at  
20 486.7 eV), (Figure S2)) [52–54]. The O 1s core level spectrum of ITO can be fitted with three  
21 components corresponding to  $In_2O_3$  (O1 at about 530 eV),  $SnO_2$  and COOR (O2 at about  
22 531.5 eV) and C-O/ $In(OH)_3$  (O3 at about 532.3 eV) (Figure S2). After the functionalization  
23 with the Poly-Thieno-OH the surface composition changed drastically. A clear S 2p signal  
24 related to C-S appears at about 164 eV, whereas In and Sn concentrations decreased  
25 drastically. Moreover, C and O contents are also slightly reduced. The analysis of the S 2p  
26 core level reveals the presence of a of two separate doublets (Figure S3): the major doublet at  
27 164.05 eV with a spin-orbit splitting of 1.16 eV is attributable to C-S bonds present in the  
28 Poly-Thieno compounds whilst the smaller doublet at 168 eV and spin orbit splitting of 1.25  
29 eV is likely attributable to oxidized sulfur due to Thieno degradation during the reaction  
30 [55,56]. Finally, the C1s core level spectrum is largely different respect to that of ITO (Figure  
31 4 b). It is noticed a slight shift ( $\sim 0.3$  eV to lower binding energies) and intensity increase of  
32 the component C2 (286.5 eV) related to the C-O bonds and the C3 ( $\sim 288$  eV, O-  
33 C=O/COOR), while two additional components C4 and C5, attributable to aromatic satellites  
34 are also observed [57]. The O 1s core level spectrum is also affected by the presence of the

1 Thione-OH molecules: as illustrated in figure S3. In particular, the intensity component O1 is  
 2 strongly reduced indicating the coverage of the ITO substrate, while the O2 is shifted toward  
 3 higher binding energies because of the presence of C-O moieties; finally the O3 is also shifted  
 4 toward higher binding energy and strongly reduced in intensities.

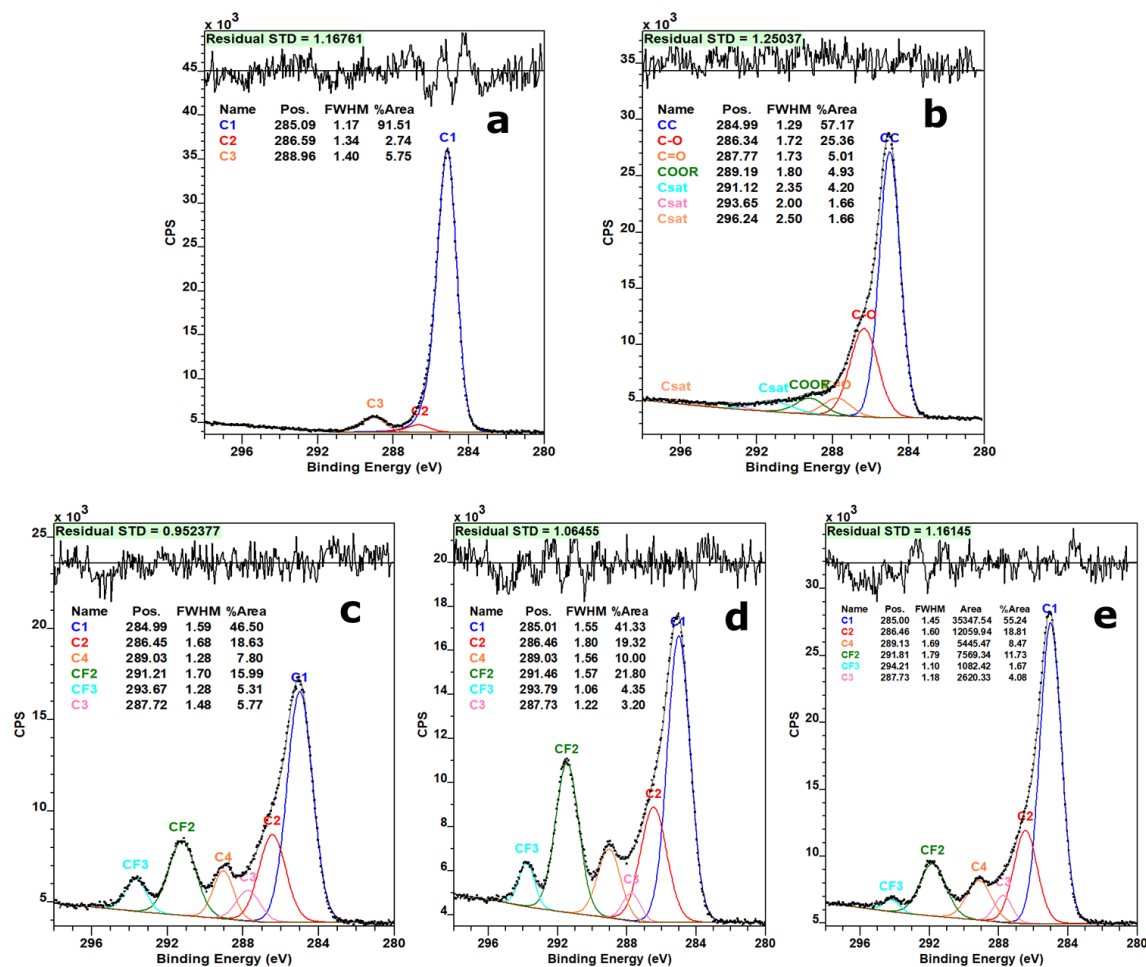
5 After functionalization with  $C_nF_{2n}$  compounds, the appearance of F 1s peak at about 688 eV  
 6 (Figure S1) is a clear indication of the grafting of the hydrophobic molecules onto the ITO  
 7 surface supporting the results of CA measurements (Table 1). Looking at the theoretical  
 8 compositions of the functionalizing compounds presented in Table 4 one should expect an  
 9 increase of F concentration when going from PolyThieno-F<sub>4</sub> to F<sub>8</sub> with a correspondent  
 10 decreases of In, Sn and S signals. However, the F/C ratios are lower than the theoretical ones  
 11 expected in case of full functionalization (Table 3 and 4). Furthermore, the fluorine  
 12 concentration is lower in the case of PolyThieno-F<sub>8</sub> sample indicating a less degree of  
 13 functionalization. This is supported by the higher content of indium, sulfur and oxygen  
 14 compared to the PolyThieno-F<sub>6</sub> sample. These data are also supported by the analysis of the C  
 15 1s core level spectra illustrated in Figure 4. The functionalization with the Poly-Thieno-F<sub>n</sub> is  
 16 reflected in the appearance of the components at about 291 (CF<sub>2</sub>) and 293 eV (CF<sub>3</sub>), Figure 4  
 17 c-e. The ratios between these components are in agreement with the  $C_nF_{2n+1}$  theoretical  
 18 compositions [58,59]. However, it is evident that the intensities of the  $C_nF_{2n+1}$  component are  
 19 as follows  $F_6 > F_4 > F_8$  supporting the conclusion of a different degree of grafting.

20

21 **Table 3.** Surface compositions obtained from XPS survey spectra.

Sample ID	Concentration (at%)						
	C1s	O1s	F1s	S2p	In3d	Sn3d	Rest Si, Ca,N, Cl
ITO	67.57 (4.51)	20.35 (2.04)	--	--	9.65 (2.43)	1.33 (0.17)	<2
PolyThieno-OH	61.43 (2.10)	17.91 (1.60)	--	13.73 (1.76)	4.23 (1.81)	0.50 (0.28)	<1
PolyThieno-F <sub>4</sub>	47.43 (0.73)	20.03 (1.03)	20.17 (0.99)	6.26 (0.36)	4.22 (0.69)	0.82 (0.05)	<1

PolyThieno-F <sub>6</sub>	48.64 (1.76)	14.28 (0.71)	28.58 (1.34)	6.28 (0.29)	0.71 (0.55)	0.37 (0.06)	<1
PolyThieno-F <sub>8</sub>	55.44 (1.69)	18.76 (1.99)	15.59 (1.59)	7.47 (1.42)	1.42 (0.47)	0.37 (0.05)	<1
PolyThieno-Ph	66.27 (1.77)	23.14 (1.42)		7.70 (1.259)	1.29 (0.17)	0.17 (0.02)	0.97 (0.40)
PolyThieno-diPh	78.64 (0.65)	11.77 (0.83)	--	7.94 (0.43)	0.69 (0.22))	0.07 (0.04)	0.6 (0.42)
PolyThieno-BiPh	71.22 (0.75)	18.51 (0.80)	--	8.04 (0.18)	0.93 (0.10)	0.15 (0.02)	(1.20) (0.32)
PolyThieno-Naph	76.49 (0.51)	13.45 (0.91)	--	7.21 (0.79)	0.83 (0.10)	0.15 (0.03)	0.94 (0.47)
PolyThieno-Fluo	75.44 (2.32)	12.85 (0.35)		7.62 (1.00)	0.83 (0.34)	0.11 (0.08)	2.58 (1.46)
PolyThieno-Pyr	80.81 (0.41)	10.78 (0.07)	--	6.49 (0.65)	0.74 (0.24)	0.14 (0.01)	1.04 (0.29)



1  
 2 **Figure 4.** C 1s core level spectra of the ITO substrate (a ), after PolyThieno-OH (b), after  
 3 Poly-Thieno-F<sub>n</sub> grafting: C<sub>4</sub>F<sub>9</sub> (c), C<sub>6</sub>F<sub>13</sub>(d) and C<sub>8</sub>F<sub>17</sub> (e). (note: intensity in Counts per  
 4 Second, CPS).

5 **Table 4.** Theoretical compositions of the compounds used in this study (excluding H) and  
 6 normalized aromatic content.

Sample	Composition (at%)				Formula (excluding H)	Normalized aromatic content
	C	O	S	F		
PolyThieno-OH	70.0	10.0	20.0	--	C <sub>7</sub> S <sub>2</sub> O	--

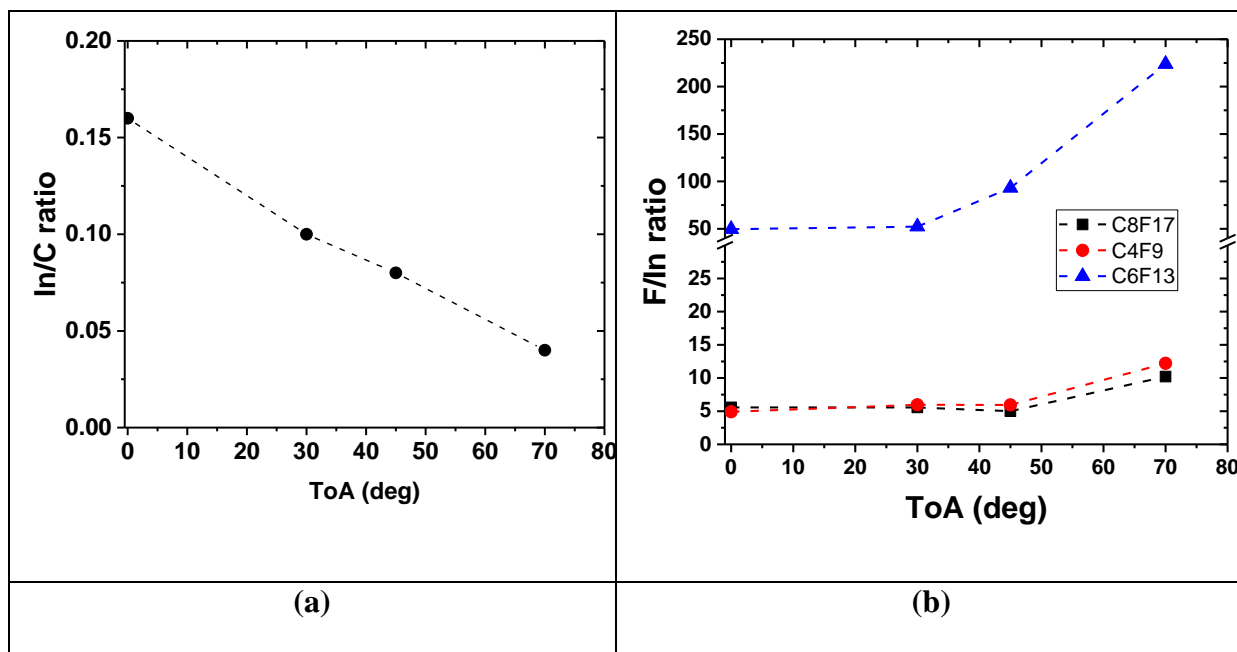
PolyThieno-F <sub>4</sub>	51.8	7.4	7.4	33.3	C <sub>14</sub> O <sub>2</sub> S <sub>2</sub> F <sub>9</sub>	--
PolyThieno-F <sub>6</sub>	48.5	6	6	39.4	C <sub>16</sub> O <sub>2</sub> S <sub>2</sub> F <sub>13</sub>	--
PolyThieno-F <sub>8</sub>	46.1	5.1	5.1	43.6	C <sub>18</sub> O <sub>2</sub> S <sub>2</sub> F <sub>17</sub>	--
PolyThieno-Ph	77.8	11.1	11.1	--	C <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	0.28
PolyThieno-diPh	84	8.0	8.0	--	C <sub>21</sub> O <sub>2</sub> S <sub>2</sub>	0.35
PolyThieno-Naph	81.8	9.1	9.1	--	C <sub>18</sub> O <sub>2</sub> S <sub>2</sub>	0.33
PolyThieno-BiPh	83.3	8.3	8,3	-	C <sub>20</sub> O <sub>2</sub> S <sub>2</sub>	0.33
PolyThieno-Pyr	85.7	7.1	7.1	--	C <sub>24</sub> O <sub>2</sub> S <sub>2</sub>	0.40
PolyThieno-Fluor	84	8.0	8.0	--	C <sub>21</sub> O <sub>2</sub> S <sub>2</sub>	0.25

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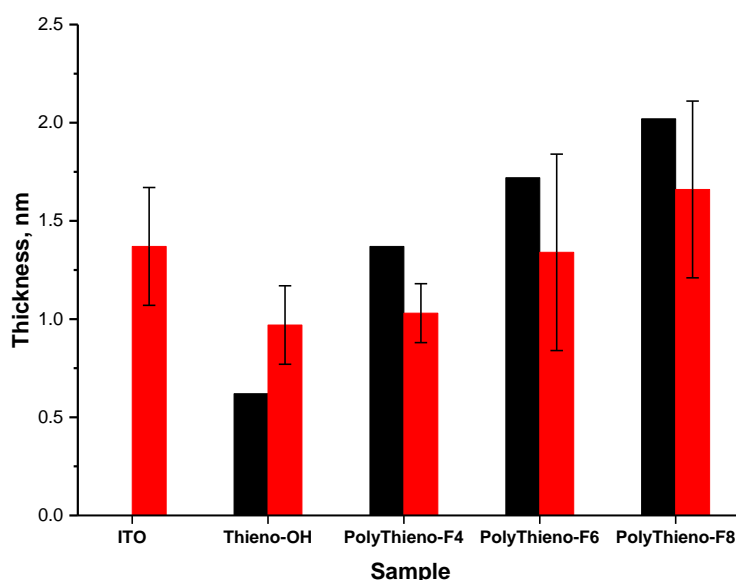
3 Further information can be inferred from the AR-XPS data. Figure 5 (a) illustrates the In/C  
4 signal ratio of the ITO substrate as a function of the Take off Angle (ToA). As can be seen the  
5 In/C ratio drops almost linearly when decreasing the analysis depth. This indicates the  
6 presence of a relatively large carbon overlayer, the presence of which is confirmed by the  
7 estimation of the overlayer thickness using the so-called “Thickogram” method and using the  
8 Inelastic Mean Free Path (IMFP) from the Seah formula [59,60]. In fact, an hydrocarbon layer  
9 of about 1.4 nm in thickness is present on the as received ITO substrate (Figure 6). After the  
10 reaction with the Poly-Thieno-OH the estimated thickness is 0.97 nm not far from the  
11 theoretical thickness of 0.6 nm calculated on the base of geometrical bond considerations and  
12 assuming a dense packed monolayer.

13 Figure 5 (b) shows the F/In signal evolution as a function of the ToA for the three Poly-  
14 Thieno-F<sub>n</sub> samples. As can be seen, the signal is almost constant until the 70 ° ToA. This  
15 indicates that the Poly-Thieno-F<sub>n</sub> are almost parallel to the ITO substrate, supporting the idea  
16 that the grafted molecules are not straight packed respect to the ITO surface, but more likely  
17 randomly distributed onto the nanotubular structures.



1 **Figure 5.** (a) In/C signal ratio as a function of ToA in ITO sample; (b) F/In signal ratios of the  
 2 Poly-Thieno-F<sub>n</sub> samples.

3 Although the theoretical thicknesses were estimated by simple geometrical considerations and  
 4 that all samples show a hydrocarbon contamination the results are supporting the conclusions  
 5 obtained by considering the surface compositions (Table 2) and ARXPS data presented in  
 6 Figure 5.

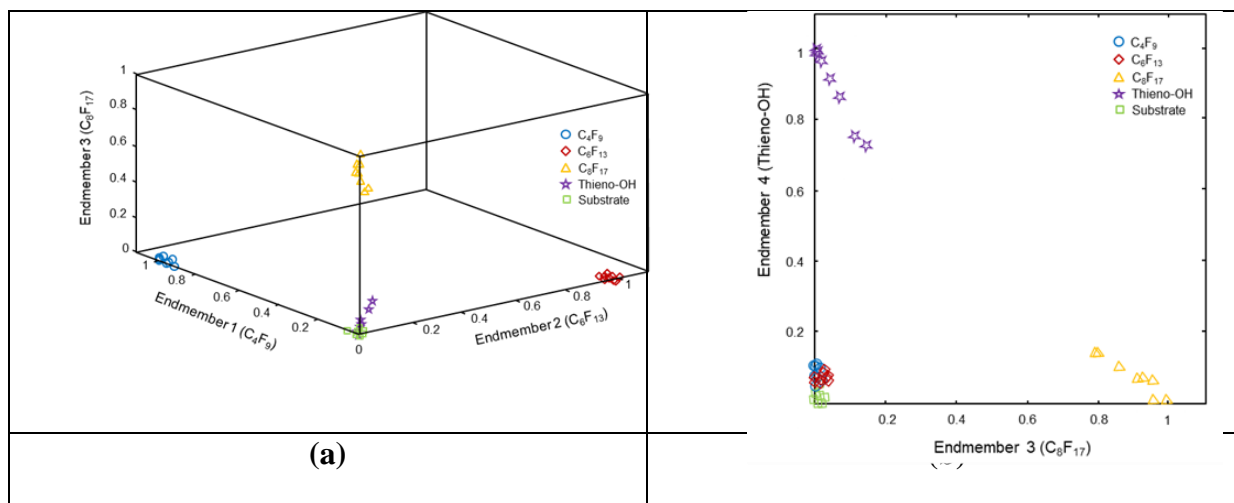


7  
 8 **Figure 6.** Theoretical (black film thicknesses from XPS data.

9  
 10 Apart the Thieno-OH, all the measured overlayer thicknesses are lower than the theoretical  
 11 ones (Figure 6). This together with the presence of the hydrocarbon contamination layer as

1 discussed above, indicates that PolyThieno- $F_n$  are not forming a vertical close packed  
2 structure on the substrate, but most likely a structure where the PolyThieno- $F_n$  form a low  
3 angle with the ITO substrate. However, it should be also noticed that, given the  
4 nanostructured nature and large roughness of the substrate, the thicknesses of the PolyThieno-  
5  $F_n$  can vary largely within the sample, making the overlayer estimation not very precise.  
6 Interestingly, there is no correlation between the contact angle (Table 1) and degree of  
7 chemical functionalization of the PolyThieno- $F_n$  surfaces. In fact, the larger content of  $CF_n$  is  
8 observed in the PolyThieno- $F_6$ , the PolyThieno- $F_8$  shows the higher water CA. this result  
9 indicates that the roughness effects is predominant in determine the surface response.

10 ToF-SIMS analyses of ITO, Thieno-OH and the PolyThieno- $F_n$  were also performed. Eight  
11 negative spectra were acquired for each specimen and processed using the simsMVA software  
12 and Five NMF EMs (endmembers) were obtained. Figure 7 (a) reports the NMF scores for the  
13 first three EMs showing successful grouping of samples belonging to the same specimen,  
14 whilst Figure 7 (b) illustrates the NMF scoring for the EMs 3 and 4. Samples from fluorinated  
15 SAMs,  $C_4F_9$ ,  $C_6F_{13}$  and  $C_8F_{17}$ , scored high in EM 1, 2 and 3 respectively. The loadings of all  
16 EMs obtained by the NMF analysis are shown in Figure S44. The loadings provide  
17 information about which peaks are responsible for the score of the samples in the NMF space.  
18 Peaks comprised in the loadings for a certain EM are correlated with samples scoring high for  
19 the same EM. EMs 1, 2 and 3 contained characteristic peaks of the PolyThieno- $F_n$ . All of  
20 them shared similar low mass peaks (up to 150 u) which is not surprising according to the  
21 similar constitutional structure of the SAMs,  $C_nF_{2n+1}$ . The main differences were found at  
22 higher mass where the peaks are more characteristic. Main fragments for EM 1 ( $C_4F_9$ ), 2  
23 ( $C_6F_{13}$ ) and 3 ( $C_8F_{17}$ ) were  $C_3F_6OH^-$  ( $m/z = 166.99$ ),  $C_5F_{10}OH^-$  ( $m/z = 266.99$ ) and  $C_7F_{14}OH^-$   
24 ( $m/z = 366.99$ ) respectively. Interestingly, the difference among these peaks is exactly  $\pm C_2F_4$   
25 which is the difference in carbon and fluorine atoms among the PolyThieno- $F_n$  supporting the  
26 peak assignments. EM 4 and 5 were related to Thieno-OH and ITO respectively, with  
27 loadings containing high intensity peaks for fragments containing sulfur for EM 4 and  
28 fragments containing In, Sn as well as  $C_xH_yO_z$  (contaminants) for EM 5. These results  
29 confirm the successful attachment of the three different SAMs components to the Thieno-OH  
30 surface.



1 **Figure 7.** NMF scores of (a) EM1, 2, 3 and (b) EM 3, 4.

2 It is interesting to note that data from specimens PolyThieno-F<sub>8</sub> and Thieno-OH showed to be  
 3 more dispersed toward a particular direction. This dispersion can be observed clearly by  
 4 plotting EM 4 against EM 3 as reported in Figure 7 (b). Data from the PolyThieno-F<sub>8</sub> are  
 5 dispersed towards Thieno-OH samples indicating a small but significant contribution of EM 4  
 6 characteristic peaks in the specimen surface. This might be due to a low surface grafting yield,  
 7 which would explain the results obtained by XPS where it was found that PolyThieno-F<sub>8</sub> was  
 8 the component with lower atomic concentration of fluorine, and the results regarding the  
 9 surface energy, where the lowest  $\gamma_{SV}$  was surprisingly obtained with PolyThieno-F<sub>6</sub> instead of  
 10 PolyThieno-F<sub>8</sub>. In fact, looking at the loadings of EM 1, 2 and 3, it is evident that the  
 11 fragments containing sulfur, which are related to the Thieno-OH, are more intense in EM 3  
 12 supporting the hypothesis of a low grafting yield for the PolyThieno-F<sub>8</sub>.

13 XPS analysis of the different aromatic molecules grafted onto the ITO-PolyThieno-OH  
 14 surfaces reveal a relative high level of functionalization as can be seen from the decrease of  
 15 the In 3d, Sn 3d and S 2p intensities illustrated in Table 3 and the correspondent increase of  
 16 the Carbon signal. However, it should be noticed that in all samples a relatively large amount  
 17 surface contaminants such as Si, Na, Cl and Ca is also detected. This surface contamination  
 18 can be partially explained both with sample preparation (Cl and Na) and also with sample  
 19 handling (Si), whilst the presence of Ca was also observed on the starting ITO surface.

20 The C 1s core level spectra recorded after functionalization show very similar features in all  
 21 samples as illustrated in Figure 8 for the case of Poly-Thieno-diPh. As can be seen beside the  
 22 aliphatic hydrocarbon component (C1-AL ~ 285 eV), the aromatic component (C1-AR) at  
 23 about 284.5 eV is also observed supporting the quantitative analysis [61,62]. Furthermore,  
 24 components related to C-OH (C3 at about 286.5), COO(H) (C4 ~ 289.2 eV) are clearly

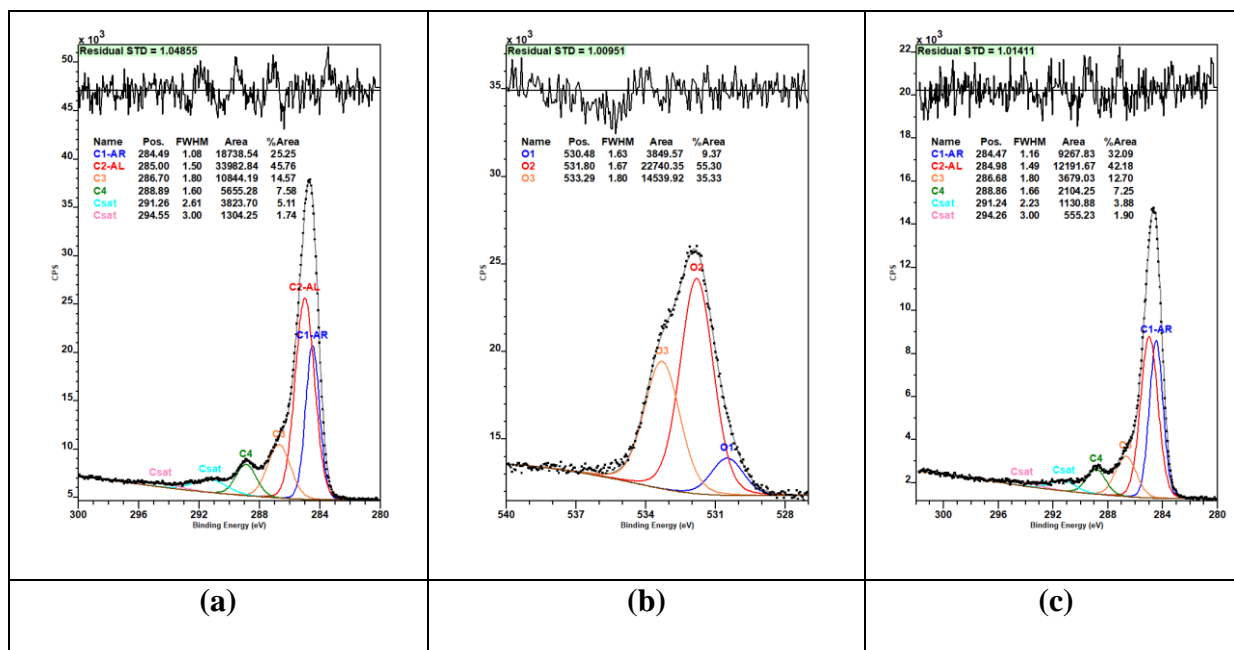


1 detected. Finally, components at higher binding energies (291-195 eV) attributable to  
2 aromatic satellites are also detected (Figure 8 and Figure S5). ARXPS data provided further  
3 support to the successful functionalization; in fact the C 1s spectrum recorded at 70 ° ToA  
4 reveals an increase of the aromatic component (C1-AR in Figure 8c). This is expected in case  
5 of successful functionalization because of the higher surface sensitivity at glancing detection  
6 angles. The O 1s core level spectrum is presented in Figure 8 (b) and can be fitted with three  
7 components related to In<sub>2</sub>O<sub>3</sub> (O1 ~ 530.5 eV), a second one attributable to O-C=O moieties  
8 (O2 ~ 531.8 eV) and a third one related to C-O bonds and In(OH)<sub>3</sub> (O3 ~ 533.3 eV).  
9 Comparing this result with that of Figure S 2 (bare ITO) it can be noticed a strong decrease of  
10 component O1, as expected and a corresponding increase of the component O2 due to the post  
11 grafting process. These data are in agreement with the quantitative results further vouching  
12 the success of the surface functionalization process.

13 Similar type of core level spectra are also observed in the case of the other aromatic  
14 molecules (Figure S 5). However, based on the analysis of the quantitative data and the C 1s  
15 core level fittings a sort of qualitative ranking related to the level of functionalization can be  
16 attempted. In particular, by normalizing the aromatic component intensity to the theoretical  
17 carbon content (Table 4), the best functionalization is obtained with Poly-Thieno-Pyr  
18 followed by Poly-Thieno-Diph, whilst Poly-Thieno-Phen is the less effective. Finally, the  
19 same level of functionalization is achieved when using Poly-Thieno-Naph and Poly-Thieno-  
20 Biph molecules.

21 As in the case of CF<sub>n</sub> functionalization, no specific link between the functionalization level  
22 and the wettability properties reported in Table 1 were observed. In fact, while lower contact  
23 angles (less than 70 °) are measured in samples with low aromatic content (< 0.30), increasing  
24 the functionalization level did not result in a systematic increase of the water contact angle.  
25 This indicates that, beside the functionalization level, (nano)structural character of the surface  
26 is playing a paramount role in defining the wettability properties of these surfaces making  
27 difficult the evaluation of the surface chemistry contribute.

28 The S 2p core level spectra (Figure S6 in supporting information) are similar to those  
29 observed in the samples functionalized with PolyThione-F<sub>n</sub> molecules and consist of two  
30 doublets related to C-S moieties and some oxidized sulfur likely related to the Thieno-OH  
31 degradation during sample preparation and aging.



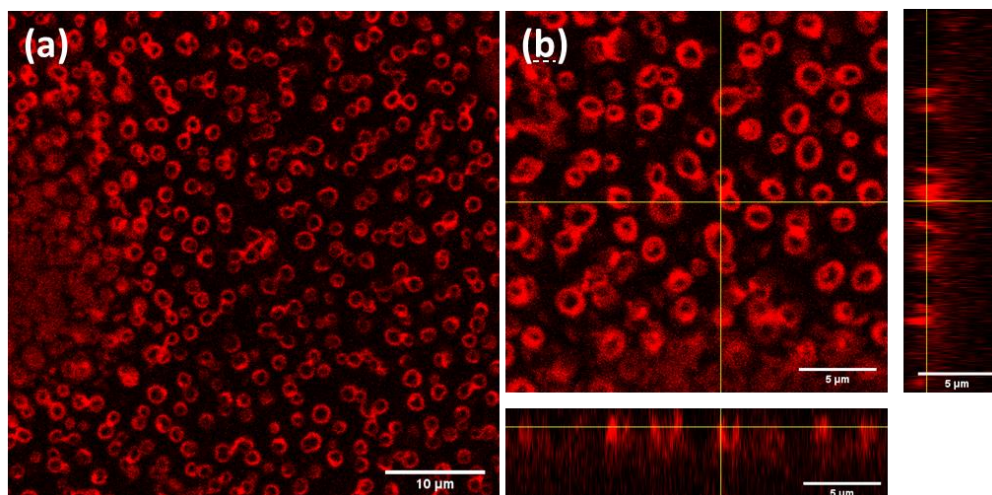
1 **Figure 8.** Photoelectron core level spectra of the PolyThieno-diPh: C 1s and O 1s recorded at  
 2 0° ToA, (a), (b) at 70° ToA (c).

3

#### 4 **3.4. Fluorescence of surfaces**

5 For the fluorescence properties of surfaces, it was not possible to measure absorption and  
 6 emission spectra on any ITO films with a standard steady-state equipment due to high  
 7 absorption (dark grey to black colour) and diffusion of any surface. More precisely, it was not  
 8 possible to measure any quantum efficiency and the spectra were already terribly difficult to  
 9 record. This is probably due to the fact that starting polymer (PolyThieno-OH) being already  
 10 fluorescent, the polydispersity in size of this polymer made the fluorescence analyses  
 11 difficult, as already observed in electropolymerized polyfluorenes, for example [63].  
 12 Nevertheless, we were able to perform fluorescence microscopy imaging in order to compare  
 13 topography and luminescence signal. PolyThieno-OH and any PolyThieno-postgrafted films  
 14 are nicely luminescent (Figure 9 and ESI). Different substructures can be observed. The  
 15 fluorescence images correlate well with the SEM images: showing bright rings corresponding  
 16 well to the tops of the tubular shapes. The 3D-reconstruction (z-scan on Figure 8b) clearly  
 17 shows a similar thickness of films (less than 5 micrometres) but with different surface  
 18 coverage. Using similar illumination, it seems that PolyThieno-postgrafted films with  
 19 polyaromatics are brighter than parent PolyThieno-OH (ESI), this might come from the  
 20 intrinsic chromophore luminescence.

1



2

3 **Figure 9.** Fluorescence imaging and orthogonal view of PolyThieno-BiPh, ( $\lambda_{\text{exc}}$ : 488nm  $\lambda_{\text{em}}$ :  
4 510-650nm). The surrounding medium is distilled water.

5

## 6 **4. Conclusions**

7 Here, we tried to investigate or confirm [11] how surface nanostructures with nanotubular  
8 shape give exceptional properties. We studied not only the adhesive but also the fluorescence  
9 properties of conducting polymer nanotubes made by soft template electropolymerization and  
10 *post*-grafting. Different substituents were studied such a fluorinated chains and aromatic  
11 groups, in order to tune these surface properties. For example, XPS and ToF-SIMS analyses  
12 demonstrated that using fluorinated chains of various length ( $\text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$  and  $\text{C}_8\text{F}_{17}$ ), the  
13 surface hydrophobicity and oleophobicity did not increase with the fluorinated chain length  
14 because the *post*-grafting yields are not the same and also because of the presence of  
15 nanoroughness after *post*-grafting. These surfaces also displayed strong water adhesion  
16 known as the petal effect [42] and responsible of the gecko's foot adhesion [8]. They were  
17 also nicely fluorescent before and after *post*-grafting. We would like to underline that the  
18 main goal of this paper was to understand the role of the chemical functionalization of  
19 nanostructured surfaces on their wetting properties. However, we believe this work could  
20 find many practical applications, in the future, such as in liquid transport for water and oil  
21 harvesting systems [65,66], as well as in stimuli responsive antibacterial surfaces [67].

22

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## 11 **6. Author contributions**

12 Ananya Sathanikan did post-grafting and surface wetting properties, Giacomo Ceccone and  
13 Jorge Bañuls-Ciscar did the XPS and Tof-SIMS analyses, Miaobo Pan and Rachel Méallet-  
14 Renault did the fluorescence analyses, Fadwa Kamal, Talia Bsaibess, Anne Gaucher and  
15 Damien Prim did the chemical syntheses, Thierry Darmanin did the electropolymerization and  
16 SEM images, Pascal Colpo, Sonia Amigoni and Frédéric Guittard worked on the discussion  
17 part.

18

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## Figures captions

**Scheme 1.** Strategy used to form conducting polymer nanotubes with various substituents.

**Figure 1.** SEM images of the polymer surfaces electrodeposited from the monomer Thieno-OH (10 mM) in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> / CH<sub>2</sub>Cl<sub>2</sub> + H<sub>2</sub>O in potentiodynamic conditions by cyclic voltammetry ( $E = -1 / +1.77$  V) after 1 scan. The pictures are taken without (up) and with a substrate inclination of 45 ° (down).

**Figure 2.** Representative SEM images of the polymer surfaces after *post*-treatment with fluorenone (PolyThieno-Fluorenone). The pictures are taken without (up) and with a substrate inclination of 45 ° (down).

**Figure 3.** Picture of a water droplet on the polymer surfaces after *post*-treatment with F<sub>6</sub> (PolyThieno-F<sub>6</sub>) with a substrate inclination of 90°.

**Figure 4.** C 1s core level spectra of the ITO substrate (a ), after PolyThieno-OH (b), after Poly-Thieno-F<sub>n</sub> grafting: C<sub>4</sub>F<sub>9</sub> (c), C<sub>6</sub>F<sub>13</sub>(d) and C<sub>8</sub>F<sub>17</sub> (e). (note: intensity in Counts per Second, CPS).

**Figure 5.** (a) In/C signal ratio as a function of ToA in ITO sample; (b) F/In signal ratios of the Poly-Thieno-F<sub>n</sub> samples.

**Figure 6.** Theoretical (black film thicknesses from XPS data).

**Figure 7.** NMF scores of (a) EM1, 2, 3 and (b) EM 3, 4.

**Figure 8.** Photoelectron core level spectra of the PolyThieno-diPh: C 1s and O 1s recorded at 0 ° ToA, (a), (b) at 70 ° ToA (c).

1 **Figure 9.** Fluorescence imaging and orthogonal view of PolyThieno-BiPh, ( $\lambda_{ex}$ : 488nm  $\lambda_{em}$ :  
2 510-650nm). The surrounding medium is distilled water.

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1 **Table 1.** Apparent contact angles ( $\theta$ ) with different probe liquids of different nanotubular  
 2 surfaces.

Polymer	$\theta_{\text{water}}$ [deg]	$\theta_{\text{diiodo}}$ [deg]	$\theta_{\text{hexa}}$ [deg]
PolyThieno-OH	$92.1 \pm 7.1$	0	0
PolyThieno-F <sub>4</sub>	$129.0 \pm 4.6$	$117.0 \pm 5.5$	$30.5 \pm 6.8$
PolyThieno-F <sub>6</sub>	$122.7 \pm 4.6$	$130.8 \pm 0.9$	$83.4 \pm 2.1$
PolyThieno-F <sub>8</sub>	$130.5 \pm 3.8$	$125.0 \pm 4.9$	$90.7 \pm 3.5$
PolyThieno-Ph	$98.6 \pm 5.5$	0	0
PolyThieno-diPh	$115.0 \pm 5.4$	0	0
PolyThieno-BiPh	$112.6 \pm 3.5$	0	0
PolyThieno-Naph	$92.2 \pm 5.8$	0	0
PolyThieno-Fluo	$98.4 \pm 6.0$	0	0
PolyThieno-Pyr	$92.4 \pm 6.4$	0	0
PolyThieno-Fluorenone	$112.0 \pm 2.4$	0	0
PolyThieno-AceTetra	$85.8 \pm 4.9$	0	0
PolyThieno-PheTetra	$79.8 \pm 6.6$	0	0
PolyThieno-PyrTetra	$106.2 \pm 2.3$	0	0

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 4 **Table 2.** Apparent contact angles ( $\theta$ ) with different probe liquids as well as the surface energy  
 5 of the corresponding smooth surfaces ( $\gamma_{sv}$ ) and the dispersive ( $\gamma_{sv}^D$ ) and polar ( $\gamma_{sv}^P$ ) parts.

Polymer	$\theta_{\text{water}}^Y$ [deg]	$\theta_{\text{diiodo}}^Y$ [deg]	$\theta_{\text{hexa}}^Y$ [deg]	$\gamma_{sv}$ [mN m <sup>-1</sup> ]	$\gamma_{sv}^D$ [mN m <sup>-1</sup> ]	$\gamma_{sv}^P$ [mN m <sup>-1</sup> ]
PolyThieno-OH	$49.4 \pm 3.0$	$36.8 \pm 5.1$	0	52.8	28.1	24.7
PolyThieno-F <sub>4</sub>	$95.3 \pm 2.7$	$62.4 \pm 1.5$	$33.1 \pm 1.6$	26.2	24.2	2.0
PolyThieno-F <sub>6</sub>	$101.4 \pm 2.4$	$68.5 \pm 2.1$	$42.8 \pm 4.4$	22.7	21.6	1.1
PolyThieno-F <sub>8</sub>	$100.4 \pm 2.5$	$65.5 \pm 1.5$	$35.7 \pm 3.3$	24.5	23.4	1.1
PolyThieno-Ph	$61.6 \pm 1.7$	$19.8 \pm 4.8$	0	47.3	32.6	14.7
PolyThieno-diPh	$81.9 \pm 2.8$	$20.5 \pm 2.4$	0	38.8	34.6	4.1
PolyThieno-BiPh	$82.3 \pm 2.6$	$17.8 \pm 3.0$	0	38.9	35.0	3.9
PolyThieno-Naph	$78.2 \pm 1.3$	$16.5 \pm 2.9$	0	40.2	34.7	5.5
PolyThieno-Fluo	$69.5 \pm 5.0$	$15.0 \pm 3.9$	0	43.7	33.9	9.8
PolyThieno-Pyr	$78.5 \pm 1.8$	$15.1 \pm 5.5$	0	40.3	34.9	5.4
PolyThieno-Fluorenone	$90.7 \pm 2.7$	$11.9 \pm 1.9$	0	38.0	36.7	1.3

PolyThieno-AceTetra	77.5 ± 0.4	12.9 ± 1.3	0	40.6	34.3	6.3
PolyThieno-PheTetra	76.9 ± 2.9	19.5 ± 5.0	0	39.8	35.0	4.8
PolyThieno-PyrTetra	79.9 ± 2.9	13.0 ± 2.6	0	40.3	36.7	1.3

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2 **Table 3.** Surface compositions obtained from XPS survey spectra.

Sample ID	Concentration (at%)						
	C1s	O1s	F1s	S2p	In3d	Sn3d	Rest Si, Ca,N, Cl
ITO	67.57 (4.51)	20.35 (2.04)	--	--	9.65 (2.43)	1.33 (0.17)	<2
PolyThieno-OH	61.43 (2.10)	17.91 (1.60)	--	13.73 (1.76)	4.23 (1.81)	0.50 (0.28)	<1
PolyThieno-F <sub>4</sub>	47.43 (0.73)	20.03 (1.03)	20.17 (0.99)	6.26 (0.36)	4.22 (0.69)	0.82 (0.05)	<1
PolyThieno-F <sub>6</sub>	48.64 (1.76)	14.28 (0.71)	28.58 (1.34)	6.28 (0.29)	0.71 (0.55)	0.37 (0.06)	<1
PolyThieno-F <sub>8</sub>	55.44 (1.69)	18.76 (1.99)	15.59 (1.59)	7.47 (1.42)	1.42 (0.47)	0.37 (0.05)	<1
PolyThieno-Ph	66.27 (1.77)	23.14 (1.42)		7.70 (1.259)	1.29 (0.17)	0.17 (0.02)	0.97 (0.40)
PolyThieno-diPh	78.64 (0.65)	11.77 (0.83)	--	7.94 (0.43)	0.69 (0.22))	0.07 (0.04)	0.6 (0.42)
PolyThieno-BiPh	71.22 (0.75)	18.51 (0.80)	--	8.04 (0.18)	0.93 (0.10)	0.15 (0.02)	(1.20) (0.32)
PolyThieno-Naph	76.49 (0.51)	13.45 (0.91)	--	7.21 (0.79)	0.83 (0.10)	0.15 (0.03)	0.94 (0.47)

PolyThieno-Fluo	75.44 (2.32)	12.85 (0.35)		7.62 (1.00)	0.83 (0.34)	0.11 (0.08)	2.58 (1.46)
PolyThieno-Pyr	80.81 (0.41)	10.78 (0.07)	--	6.49 (0.65)	0.74 (0.24)	0.14 (0.01)	1.04 (0.29)

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2 **Table 4.** Theoretical compositions of the compounds used in this study (excluding H) and  
3 normalized aromatic content.

Sample	Composition (at%)				Formula (excluding H)	Normalized aromatic content
	C	O	S	F		
PolyThieno-OH	70.0	10.0	20.0	--	C <sub>7</sub> S <sub>2</sub> O	--
PolyThieno-F <sub>4</sub>	51.8	7.4	7.4	33.3	C <sub>14</sub> O <sub>2</sub> S <sub>2</sub> F <sub>9</sub>	--
PolyThieno-F <sub>6</sub>	48.5	6	6	39.4	C <sub>16</sub> O <sub>2</sub> S <sub>2</sub> F <sub>13</sub>	--
PolyThieno-F <sub>8</sub>	46.1	5.1	5.1	43.6	C <sub>18</sub> O <sub>2</sub> S <sub>2</sub> F <sub>17</sub>	--
PolyThieno-Ph	77.8	11.1	11.1	--	C <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	0.28
PolyThieno-diPh	84	8.0	8.0	--	C <sub>21</sub> O <sub>2</sub> S <sub>2</sub>	0.35
PolyThieno-Naph	81.8	9.1	9.1	--	C <sub>18</sub> O <sub>2</sub> S <sub>2</sub>	0.33
PolyThieno-BiPh	83.3	8.3	8,3	-	C <sub>20</sub> O <sub>2</sub> S <sub>2</sub>	0.33
PolyThieno-Pyr	85.7	7.1	7.1	--	C <sub>24</sub> O <sub>2</sub> S <sub>2</sub>	0.40
PolyThieno-Fluor	84	8.0	8.0	--	C <sub>21</sub> O <sub>2</sub> S <sub>2</sub>	0.25

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