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Ante versus post-functionalization to control surface structures with superhydrophobic and superoleophobic properties

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Here, we report the first use of Staudinger-Vilarrasa reaction with perfluorinated surface modification. Based on a 3,4-ethylenedioxythiophene (EDOT) monomer bearing azido groups, we develop *ante* and *post* deposition strategies in order to prepare functionalized surfaces. The Staudinger-Vilarrasa reaction allows to reduce the azido groups into amine functions and the reaction with carboxylic acids leads to amide bounds. Here, the surfaces are investigated for their morphologies and surface properties depending on the side chain length and the modification strategy. This work shows that various wettability properties from hydrophobic to superhydrophobic or oleophilic to superoleophobic can be obtained depending on both modification strategy and nature of the side chain.

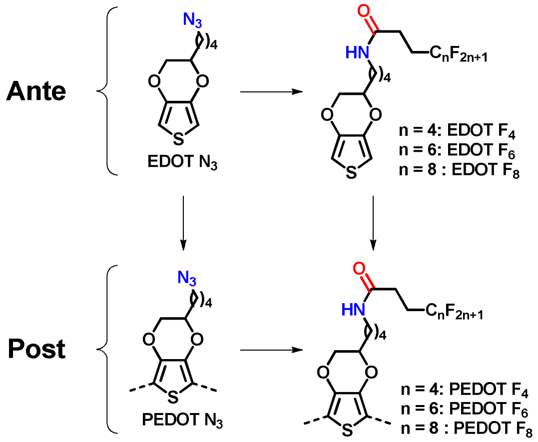
Introduction

On the one hand, superhydrophobic surfaces present a wild range of interest in a theorical point of view and for diverse potential applications such as self-cleaning surfaces, water-proof textiles, antisnow and antifog surfaces, sensors or anti-bioadhesion.[1-5] On the other hand, the liquid-repellency using liquids of lower surface tension than water such oils (usually γ_{LV} < 35 mN/m following the used oil) are more difficult to obtain due to their tendency to spread.[6] The presence of superoleophobic properties is however required for numerous other applications such as in liquid-repellency textiles, microfluidic devices, printing technologies or oil/water separation membranes.[7,8] To prepare superoleophobic properties it is necessary to induce the formation of surface structures.[9,10] Usually, fluorinated materials are used for their high intrinsic oleophobicity while the wetting of oils can be impeded by controlling the geometrical parameters of the surface structures. For example, in the case of surfaces made by lithography, superoleophobic surfaces were fabricated by changing the classical crenelated surface morphology by a re-entrant one.[11-13] Anyway the surface morphology is definitely a key point and need to be controlled.

Due to the possibility to control the surface morphology by several parameters such as electrochemical parameters or the monomer structure,[14,15] the electrodeposition of conducting polymers is a fascinating technique for superhydrophobic or superoleophobic properties. The 3,4-ethylenedioxythiophene (EDOT) derivatives are exceptional candidates for electrodeposition thanks to their unique electrochemical properties (high conductivity, easily and quickly polymerizable) and the possibility to obtain various surface structures such as nanofibers or nanosheets.[16-18] Moreover, it is possible to introduce fluorinated chains to obtain sometimes surfaces with high oleophobic properties. The question here is “What is the best strategy to introduce fluorinated chains?”. The fluorinated chains can be grafted on the monomer before the polymerization (*ante*-functionalization) or can be grafted on the polymer after polymerization (*post*-functionalization).

In this work, in order to compare the effect of the *ante*- or *post*-functionalization on the surface morphology and wettability properties, we have prepared monomers and polymers containing azido groups. Usually, the azido groups can react with alkyne following the Huisgen reaction and click chemistry.[19,20] But the product of the Huisgen 1,3-dipolar cycloaddition is a particular structure, a triazole. However, the basic properties of the triazole make monomers developed by click chemistry not suitable for electrodeposition (*ante*-functionalization).[21,22] A credible alternative to react with azido groups is the Staudinger-Vilarrasa reaction.[23,24] That reaction is described to couple especially azido group and electrophilic activated carboxylic acid in order to make amide bond. Moreover, it was shown that the presence of highly polar linkers such as amide linkers can highly enhance the superoleophobic properties due to high difference polarity between the linkers and oils.[25-27] The Staudinger-Vilarrasa reaction was successfully reported for the modifications on small molecules, macromolecules or even biomolecules.[29] That reaction starts with action of phosphine on azido groups forming *in-situ* reactive aza-ylides. These ylides then react in the same flask with electrophilic carbonyl groups. Various reactions were reported in the literature using different electrophilic carbonyls. Among them carbodiimide activation is a particular interest. That *in-situ* activation allows to use directly any carboxylic acids without particular preparation. The carboxylic acids used for the modification is also a key point, in order to get both hydro and oleophobic properties. Due to their unique properties perfluorinated carboxylic acid are exceptional candidate for that purpose. A single one step reaction for monomer or polymer modification is particularly adapted for this kind of modifications.

Here we report for the first time the comparison of *ante*- and *post*-deposition using Staudiger Vilarrasa reaction in order to prepare superhydrophobic and highly oleophobic surfaces. This work includes *ante*- and *post*-deposition modification for different perfluorinated chain length (C_4F_9, C_6F_{13} and C_8F_{17}) (Scheme 1). The surface morphologies and wettabilities, with water and liquids of lower surface tension (diiodomethane and hexadecane), depending on the modification pathway and chain length are investigated.



Scheme 1: General procedure for surface modifications by *ante* and *post*-deposition.

Experimental

Monomer synthesis

Synthesis of 4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)butan-1-ol, EDOT-OH. 2.5 g of 2,3-dimethoxythiophene (17.3 mmol) were dissolved in toluene (100 mL). 4.6 g of 1,2,6-hexanetriol (34.6 mmol) and 665 mg of *para*-toluenesulfonic acid monohydrate (3.5 mmol) were then added. The mixture was warmed at 110°C over 36 h. The mixture was then cooled at room temperature, extracted with $NaHCO_3$ 5% in water (2 x 30mL) and brine (30 mL), dried over Na_2SO_4. The solvents were removed under reduced pressure. **EDOT-OH** was finally purified on column (8/2, cyclohexane/ethyl acetate).

Yield: 51%; Slightly yellow oil; R*f*: 0.5 (5/5, cyclohexane/ethylacetate); ^{1}H NMR ($CDCl_3$): δ_H(200 MHz, $CDCl_3$, ppm): 6.3 (s, 2H), 4.10-4.18 (m, 2H), 3.64-3.71 (m, 2H), 1.52-1.69 (m, 6H), 3.85-3.91 (m, 1H); δ_C(50 MHz, $CDCl_3$, ppm): 142.0, 141.6, 99.3, 73.6, 68.4, 62.6, 32.4, 30.4, 21.3; MS: 213.9.

Synthesis of 2-(4-azidobutyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine, EDOT-N_3. 1.9 g (8.9 mmol) of **EDOT-OH** was dissolved in dichloromethane (100 mL). 1.8g (2 eq, 17.8 mmol) of triethylamine were added. The mixture was cooled at 0°C and 1.2 g (1.2 eq, 10.6 mmol) of methanesulfonyl chloride were carefully added. The mixture was allowed to warm up at room temperature. After 4 h, 10 mL of methanol were added. The mixture was stirred for 30 additional minutes. All volatiles were removed under reduced pressure. The residual oil was dissolved in acetone (100 mL) and 2.9 g (5 eq, 44.5 mmol) of NaN_3 were added. The mixture was refluxed overnight. The reaction was then allowed to cool at room temperature and most part of the acetone were removed under reduced pressure. Dichloromethane (100 mL) were added. The organic layer was washed with water (2X30mL), brine (30mL) and dried over Na_2SO_4. The solvents were removed under reduced pressure. **EDOT-N_3** is finally purified on column (90/10, cyclohexane/dichloromethane).

Yield: 75%; Colorless oil; R*f*: 0.66 (8/2, cyclohexane/ethyl acetate); δ_H(200 MHz, $CDCl_3$, ppm): 6.3 (s, 2H), 4.11-4.18 (m, 2H), 3.85-3.92 (m, 1H), 3.28-3.35 (m, 2H), 1.56-1.66 (m, 6H); δ_C(50 MHz, $CDCl_3$, ppm): 141.9, 141.6, 99.4, 73.4, 68.3, 51.2, 30.1, 28.7, 22.3; MS: 239.9.

Synthesis of the monomer by Staudinger-Vilarrasa reaction. The corresponding perfluorinated acid (0.63 mmol, 1.5 eq) was dissolved in THF (10 ml). *N*,*N*-dimethylaminopyridine (0.94, 2.2 eq) was added. The mixture was cooled 0°C and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (0.74, 1.8 eq) was added. After 30 min of stirring at room temperature, 100 mg (0.42 mmol) of **EDOT-N_3** were added. The mixture was cooled again at 0°C and 170 mg (2 eq, 0.84 mmol) of tributylphosphine were added. The mixture was stirred at room temperature for three additional hours. All volatiles were removed. The corresponding **EDOT-F_n** was directly purified on column (100/0 to 70/30, cyclohexane/ethyl acetate).

EDOT-F_4*: *N-(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)butyl)-4,4,5,5,6,6,7,7,7-heptadecafluoroheptanamide. Yield: 54 %; White powder; R*f*: 0.32 (5/5, cyclohexane/ethyl acetate); m.p. 54.2°C; δ_H(200 MHz, $CDCl_3$, ppm): 6.3 (s, 2H), 5.47-5.55 (m, 1H), 4.05-4.18 (m, 2H), 3.81-3.91 (m, 1H), 3.24-3.35 (m, 2H), 2.36-2.58 (m, 4H), 1.42-1.70 (m, 6H); δ_C(50 MHz, $CDCl_3$, ppm): 169.7, 141.9, 141.6, 99.4, 99.3, 73.4, 68.3, 39.5, 30.2, 29.4, 22.3; δ_F(188 MHz, $CDCl_3$, ppm): -81.1, -115.0, -124.6, -126.1; M+H: 487.8.

EDOT-F$_6$:* *N-(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)butyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononanamide. Yield: 34%; White powder; R*f*: 0.36 (5/5, cyclohexane/ethyl acetate); m.p. 86.6°C. δ_H(200 MHz, $CDCl_3$, ppm): 6.29 (s, 2H), 5.70-5.76 (m, 1H), 4.09-4.15 (m, 2H), 3.79-3.81 (m, 1H), 3.24-3.29 (m, 2H), 2.36-2.63 (m, 4H), 1.47-1.59 (m, 6H); δ_C(50 MHz, $CDCl_3$, ppm): 169.8, 141.9, 141.6, 99.4, 99.3, 73.4, 68.3, 39.5, 30.2, 29.4, 22.3; δ_F(188 MHz, $CDCl_3$, ppm): -80.8, -114.7, -122.0, -123.0, -123.6, -126.2; M+H: 587.8.

EDOT-F$_8$:* *N-(4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)butyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanamide. Yield: 62%; White powder; R*f*: 0.54 (5/5, cyclohexane/ethyl acetate); m.p. 80.6°C; δ_H(200 MHz, $CDCl_3$, ppm): 6.3 (AB-system, J_{AB}= 3.4 Hz, 2H), 5.54-5.59 (m, 1H), 4.06-4.16 (m, 2H), 3.81-3.91 (m, 1H), 3.26-3.35 (m, 2H), 2.38-2.60 (m, 4H), 1.42-1.72 (m, 6H); δ_C(50 MHz, $CDCl_3$, ppm): 169.7, 141.9, 141.6, 99.4, 99.3, 73.4, 68.3, 30.2, 29.7, 22.3; δ_F(188 MHz, $CDCl_3$, ppm): -80.8, -114.7, -122.0, -122,8, -123.6, -126.2; M+H: 687.8.

General procedure for post-deposition surface modification

In a 25 mL vial, 100 mg of the corresponding perfluorinated acid were dissolved in 5 mL of dry THF. 100 mg (0.82 mmol) of *N*,*N*-dimethylaminopyridine and 100 mg (0.64 mmol) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide are added. The mixture was shaken for 30 min. The **PEDOT-N$_3$** (3 scans) substrate was introduced followed by 100 mg (0.49 mmol) of tributylphosphine. The mixture was shaken 3 h. The polymer was then successively washed three times with THF and three times with ethanol. The substrate was then dried.

Electrochemical deposition

In a glass cell containing 0.1 M of tetrabutylammonium perchlorate (Bu_4NClO_4) dissolved in dry acetonitrile, 0.01 M of monomer was inserted. Three electrodes were put inside the solution. Gold plate (purchased from Neyco), glassy carbon rods, and saturated calomel electrodes (SCE) were used respectively as working, counter, and reference electrode. The three electrodes were connected to an Autolab potentiostat (Metrohm). Before each experiment, the solution was degassed with argon. After the deposition, the samples were cleaned three times with acetonitrile in order to remove the remaining salts.

Surface characterization

The apparent and dynamic contact angles were obtained with a DSA30 goniometer from Krüss. While the apparent contact angles were measured using the sessile drop method, the dynamic ones were obtained with the tilted-drop method. In this last method, a surface, on which an 8-μL water droplet was deposed, is inclined until the water droplet rolls off the surface. The maximum surface inclination is called sliding or tilting angle (α). The advanced and receding contact angles and, as a consequence, the hysteresis are taken just before the droplet rolls off the surface. Indeed, the droplet is deformed by the gravity when the surface is inclined. The angle in the moving direction is the advanced contact angle and that in the opposite direction is the receding contact angle.

The roughness measurements were performed with a WYKO NT 1100 Optical Profiling System from Veeco.

Synthesis

Reaction on azido groups were very studied for the last decades. Particularly Huisgen reaction and Sharpless modification of Huisgen reaction were center of interest for great number of researchers.[19,20] Some other reactions can also be noticed, among them the Staudinger reactions and particularly the Staudinger-Vilarrasa reaction are full of interest.[23,24] That reaction allows to create in one step amide bonds between azido groups and electrophilic activated carboxylic acid derivatives. In this work, we focus on the use of Staudinger-Vilarrasa reaction to covalently link perfluorinated chain to monomers or polymer surfaces in order to create hydro and oleophobic surface properties. The Staudinger-Vilarrasa reaction is a one pot reaction (Fig. 1), first the azido group reacts with trialkylphosphine in order to form intermediate aza-ylide and N_2.

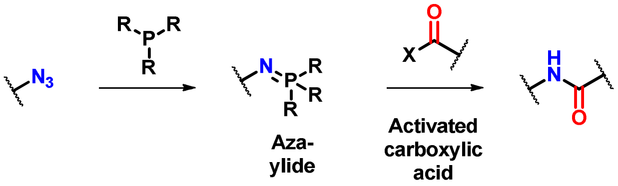


Fig. 1 General principle for Staudinger-Vilarrasa reaction.

The aza-ylide reacts with electrophilic center like carbodiimide activated carboxylic acid and forms amide bond and phosphine oxide. The efficiency and selectivity of that reaction allow us to functionalize monomer but also to *post*-functionalize azido-surface in just three hours.

The key starting material in this work is the monomer bearing an azido group. That monomer will allow us to prepare functionalized monomer using *ante*-deposition modification strategy or to prepare azido surface for *post*-deposition modification strategy. In order to have a nice availability of the reactive group (N_3), we decide to separate it from the polymerizable unit using C_4H_8 spacer. The used monomer is the (4-azidobutyl)-EDOT (**EDOT-N$_3$**). **EDOT-N$_3$** can be prepared in three steps starting with 3,4-dimethoxythiophene (Fig. 2).

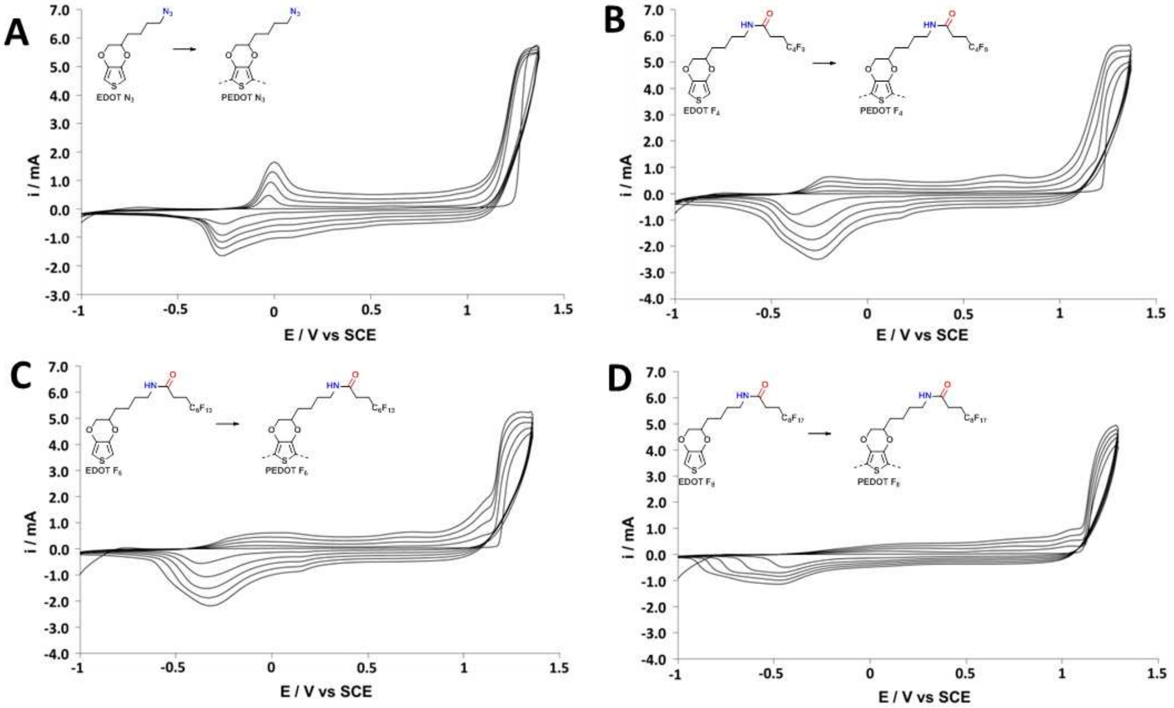


Fig. 3 Example of voltagramms for **PEDOT-F$_n$** 5 scans deposition.

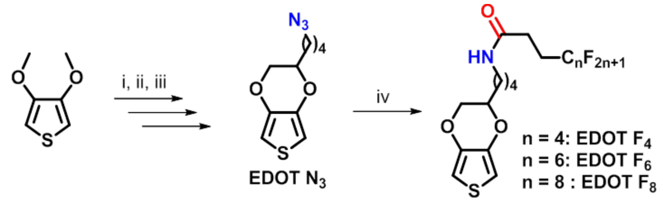


Fig. 2 Global synthesis for EDOT-F$_n$ monomers.: i) 1,2,6-hexanetriol (1 eq), 3,4-dimethoxythiophene (0.5 eq), *Para*-toluenesulfonic acid (0.05 eq), toluene reflux, 36 h. ii) Methanesulfonyl chloride (1.5 eq), triethylamine (3 eq), dichloromethane, rt, 4 h. iii) Sodium azide (5 eq), acetone, reflux, overnight. iv) perfluorinated carboxylic acid, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, N,N-dimethylaminopyridine, tributylphosphine, THF, rt, 3 h.

In the first step, 1,2,6-hexanetriol and 3,4-dimethoxythiophene reacted using acid as catalyst. The mixture was refluxed 36 h in toluene. The transetherification gave the (4-hydroxybutyl)-EDOT (**EDOT-OH**) with 53% yield. The second step was the mesylation of the hydroxyl groups. That reaction was performed in dichloromethane with methanesulfonyl chloride in basic conditions (triethylamine). After 4 h, all the volatiles were removed and the compound was used without further purification for the next step.

The final step was the nucleophilic substitution of the mesyl by an azido groups. That reaction was performed with sodium azide in acetone. The mixture was then refluxed overnight to give the final **EDOT-N$_3$** with 75% yield.

The synthetized **EDOT-N$_3$** is suitable for electrodeposition and will be used for the post-deposition strategies. The *ante*-deposition strategy needs the preparation of other fluorinated monomers. These monomers were prepared with the Staudinger-Villarrasa reaction. The carboxylic acid was first activated using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and *N*,*N*-dimethylaminopyridine. EDOT-N$_3$ was added and then the phosphine in order to form in-situ the reactive aza-ylide. The formed aza-ylide reacted with activated carboxylic group and formed the wanted perfluorinated **EDOT** after 3 h. The aimed monomers were obtained with yield between and 34 and 62% (Fig. 2).

Electrochemical properties

The monomers were electropolymerized on gold covered wafers as working electrode using a cyclic voltammetry procedure. The electropolymerization was carried out in tetrabutylammonium perchlorate (Bu$_4$NClO$_4$) acetonitrile solution. All the monomer oxidation potential were measured *vs* saturated calomel electrode (SCE). The values for monomers **EDOT-F$_4$**, **F$_6$** and **F$_8$** are respectively 1.37, 1.43 and 1.44 V. Then, a cyclic voltammetry deposition process was chosen to obtain highly homogeneous and adherent films. The electrodepositions were performed for monomers **EDOT-F$_4$**, **F$_6$** and **F$_8$** from -1 V to a potential close from the monomer oxidation potential, respectively 1.29, 1.36 and 1.37 V at a scan rate of 20 mV/s. For the *ante*-strategy, in order to study the influence of the polymer growth on surface properties different number of scans were performed (1, 3 and 5). The cyclic voltammograms after 5 deposition scans are given in Fig. 3. As shown on the voltammograms, both compounds polymerized perfectly and gave extremely well-defined cyclic voltammograms.

Post-deposition surface modification

For the *post*-deposition strategy, Staudinger-Vilarrasa reaction was also used. After a carbodiimide activation of the perfluorinated carboxylic acid, the gold supported **PEDOT-N$_3$** (3 scans) was introduced followed by the phosphine. The vial was shaken 3 h at room temperature giving the corresponding **PEDOT-F$_n$** (Fig. 4).

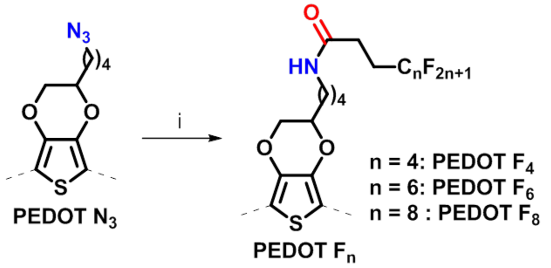


Fig. 4 General procedure for *post*-deposition modification. i) perfluorinated carboxylic acid, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, *N*,*N*-dimethylaminopyridine, tributylphosphine, THF, rt, 3 h.

Wettability

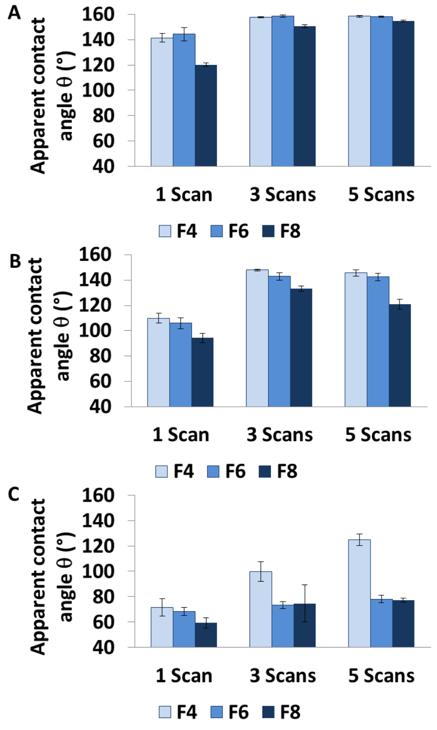


Fig. 5 Apparent contact angles for *ante*-deposition **PEDOT-F$_4$**, **F$_6$** and **F$_8$** with different probe liquids: A) water, B) diiodomethane and C) hexadecane.

Apparent contact angles were measured for different solvents including water, diiodomethane and hexadecane in order to investigate the surface hydrophobic and oleophobic. These measurements were carried out on **PEDOT-F$_4$**, **F$_6$** and **F$_8$** for both *post* and *ante*-deposition strategies. The result for *ante*- and *Post*-deposition modification are presented respectively Fig. 5 and Fig. 6.

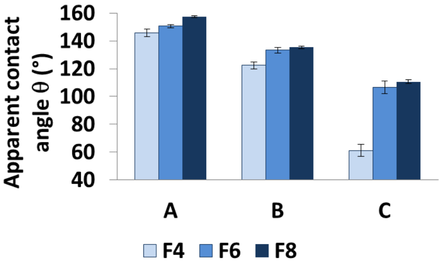


Fig. 6 Apparent contact angles for *post*-deposition modified **PEDOT-F$_4$**, **F$_6$** and **F$_8$** with different probe liquids: A) water, B) diiodomethane and C) hexadecane.

Globally, the measured values can by classified as same range. High hydrophobicity for all chain length and mild oleophobicity. But the very interesting point here, is that we observe an increase of both the surface hydrophobicity and oleophobicity as the fluorinated chain length increases, which is the reverse of the wettability results obtained with the *ante*-deposition strategy. The wettability study shows high hydrophobic properties, some polymers can be described as superhydrophobic with low hysteresis (H) and roll off angle (α) values (Table 1).
The study also show mild oleophobic properties. But the more interesting result is that both *post* and *ante* strategies which are supposed to give the same polymer provide different behavior and evolution. An investigation of their surface morphology is needed to explain these results.

Table 1. Hysteresis (H) measurement with water for ante and post deposition modified **PEDOT-F$_n$**.

Process	Side chain	Scans	α (°)	H (°)
Ante	F4	1		Sticky
		3	2.7	1.5
		5	2.3	0.7
	F6	1		Sticky
		3	2.8	1.2
		5	1.9	0.8
	F8	1		Sticky
		3	1.9	2.3
		5	10.2	9.0
Post	F4	3		Sticky
	F6	3	1.7	1.6
	F8	3	2.3	2.5

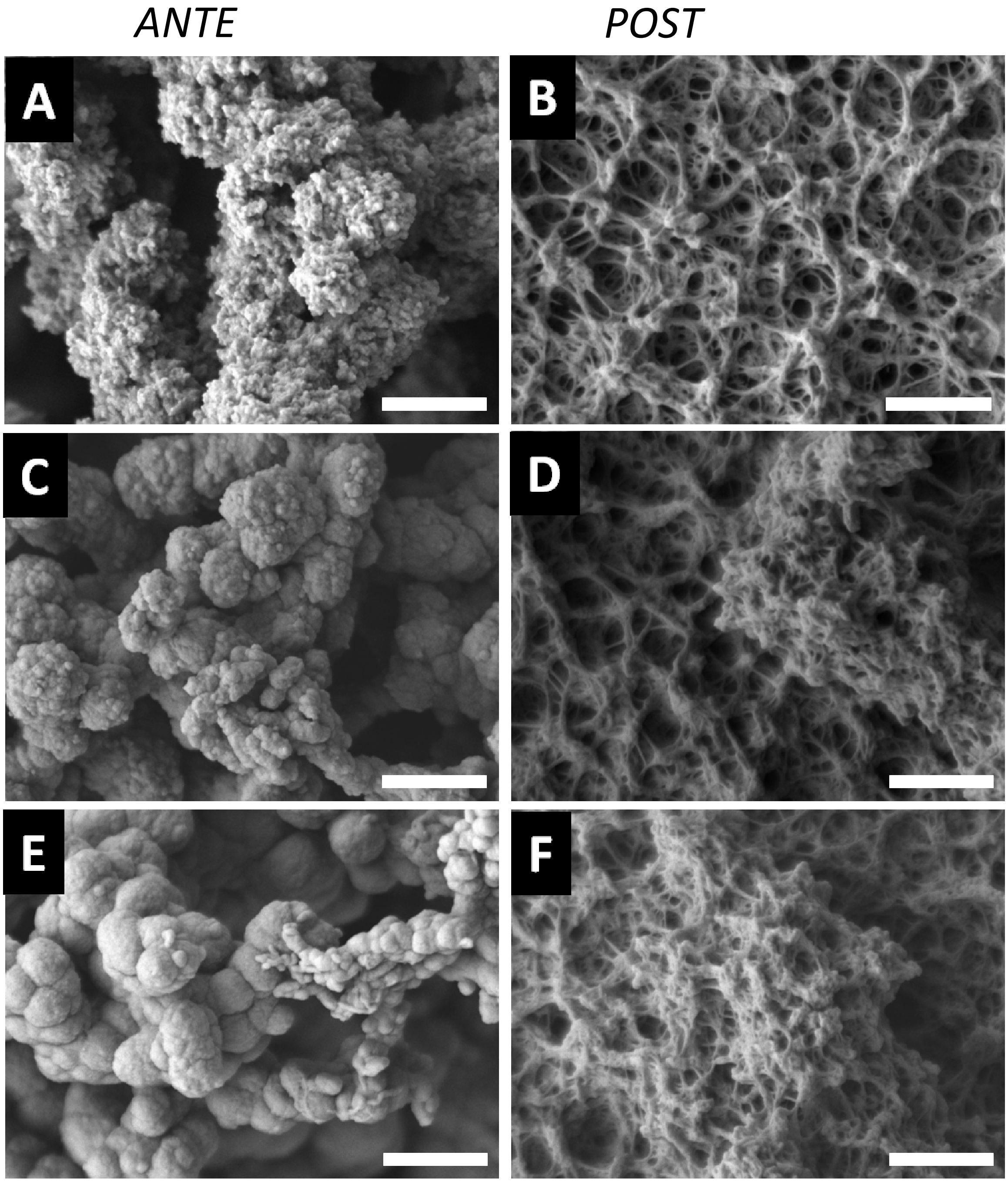


Fig. 7 SEM images of ante and post deposition modified surfaces (Scale bar = 1 µm). *Ante* modified surfaces: A) **PEDOT- F$_4$**, C) **PEDOT F$_6$** and E) **PEDOT-F$_8$**. *Post* modified surfaces: B) **PEDOT-F$_4$**, D) **PEDOT F$_6$** and F) **PEDOT-F$_8$**.

Surface morphology

The surface morphologies were studied on **PEDOT-F$_n$** for both two strategies. The pictures are given Fig. 7.

First, for the polymers obtained by *post*-deposition, the surface morphology is not affected by the *post*-treatment. The surface morphology (porous and fibrillar network) is the same whatever the fluorinated chain length is and is also the same than the morphology of the starting polymer PEDOT-N$_3$. That explains the increase in both the surface hydrophobicity and oleophobicity as the fluorinated chain length increases.

For the polymers obtained with the *ante*-deposition strategy, the surface morphology changes as the fluorinated chain length changes. A change from cauliflower-like structures for C_8F_{17} to micro/ and nanostructures for C_4F_9 is observed. This change is due to an increase in the solubility of the oligomers formed in the first instances of the electropolymerization as the alkyl chain length decreases, as already reported in the literature.[14,15] This change explains the increase in both the surface hydrophobicity and oleophobicity as the fluorinated chain length decreases. Indeed, the presence of micro/ and nanostructures in PEDOT-F_4 allows to induce a high increase with the three probe liquids because the micro/ and nanostructures of PEDOT-F_4 possess a high amount of re-entrant curvatures limiting the liquid penetration, as explained in the literature.[11-13] In order to complete the morphology study roughness measurements were performed. The results are presented Fig 8 and show very different for *ante*- and *post*-deposition modifications.

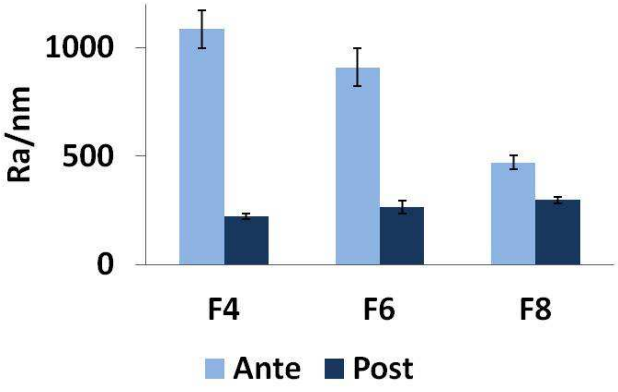


Fig. 8 Average roughness measurements for ante and post deposition modified surfaces.

Globally, *ante*-deposition modification presents higher roughness than *post*. That result is not surprising because the change on the monomer structure with *ante*-deposition modification induces modification on the surface structures. On the opposite, the *post*-deposition modification induces only surface modification on a preformed polymer. The results for *ante*-deposition modifications show important decrease of the roughness average (Ra) from 1085 to 472 nm while the fluorinated chain increases it from F_4 to F_8. In comparison, the *post*-deposition modification shows a slight increase of the Ra from 224 to 298 nm for fluorinated chains from F_4 to F_8.

Conclusion

In this work, we presented for the first time the use of Staudinger-Vilarrasa in order to prepare perfluorinated surfaces. *Ante* and *post*-deposition surface modifications were developed. The surfaces properties and morphologies were investigated for both two strategies with different chain lengths. The two developed strategies showed nicely the impact of morphologies and chain length on surface properties. The *ante*-deposition strategy showed that if the morphology changes, the surface properties are not necessarily linked to the hydrophobicity/oleophobicity of the substituent. The *post*-deposition strategy showed that in this case, the morphology did not change and that the surface properties were dependent on the hydrophobicity/oleophobicity of the substituent. Here, in order to obtain superoleophobic properties, the *ante*-deposition strategy gave better results.

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Notes

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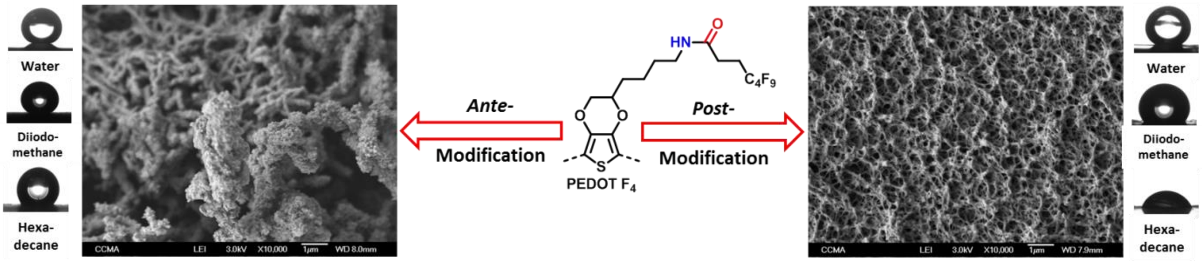
SYNOPSIS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Ante-
Modification
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O
O
S
PEDOT F4
Post-
Modification
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Water
Diiodo-methane
Hexa-decane