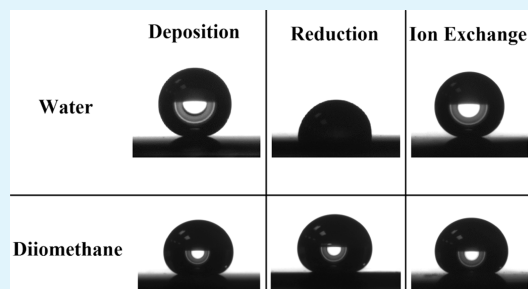


Elaboration of Voltage and Ion Exchange Stimuli-Responsive Conducting Polymers with Selective Switchable Liquid-Repellency

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ABSTRACT: In this work, we report the possibility to selectively switch by voltage and anion exchange the water-repellent properties, in comparison with the oil-repellent properties, of copolymers containing both fluorinated chain (EDOT-F₈) and pyridinium (EDOT-Py⁺) moieties. Here, the fluorinated chains are necessary to reach superhydrophobic properties while the pyridinium moieties allow the switching in the wettability by counterion exchange. Because, conducting polymers can exist in their oxidized and reduced state, here, we report also the switching of their wettability by voltage. The best properties (superhydrophobic properties with low hysteresis and sliding and good oleophobic properties) are obtained for a % of EDOT-Py⁺ of 25 %. Surprisingly, by reducing the polymer by changing the voltage, a selective decrease in the contact angle of water is observed, whereas that of oils (diiodomethane and hexadecane) remain unchanged, making it possible to have higher contact angles with diiodomethane than with water. Here, the switching in the wettability is due to the change of the water droplet from the Cassie–Baxter state to the Wenzel state by changing the voltage. Because of the presence of highly polar pyridinium groups and their perchlorate counterions, the wettability of oil droplets (diiodomethane and hexadecane) is not significantly affected. This effect is confirmed by changing the counterions with highly hydrophobic ones (C₈F₁₇SO₃⁻, Tf₂N⁻, or BF₄⁻). Such materials are excellent candidates for oil/water separation membranes.



KEYWORDS: switchable, smart, conducting polymers, electrochemistry, superhydrophobic

INTRODUCTION

The development of smart materials, especially those with stimuli responsive properties,^{1–6} is experiencing exponential growth for their various potential applications in biomedicine,^{7,8} sensors,⁹ separation membranes,¹⁰ textiles,¹¹ or shape memory materials.¹² To elaborate such materials, it is necessary to introduce some “chemical elements” sensitive to the stimulus we want to apply.

Amongst all materials, conducting polymers are materials with unique intrinsic properties.^{13,14} Beyond their exceptional optical and electronic properties, they can incorporate in their doping state a large amount of doping agents (counterions to stabilize the charges) inside their structures. In a point a view wettability, this capacity allows us to reversibly introduce and remove many hydrophobic or hydrophilic doping agents.¹⁵ This reaction being an oxidation reaction, this capacity can be performed by changing the applied voltage. For example, several authors reported the formation of nanostructured conducting polymer is solution by monomer oxidation and self-assembly. After deposition on a substrate using different strategies (dip-coating, spin-coating, or spray-coating, for example), the authors reported the possibility to change the surface wettability by voltage.^{16–18} To modify the wettability of conducting polymers with dual-responsivity, a substituent responsive to another stimulus can also be grafted to the monomer before polymerization.^{19,20} For example, ammonium groups were introduced to change the wettability by ion-exchange with their counterions.

To obtain superhydrophobic surfaces, it is necessary to render the surface sufficiently structured while the presence of hydrophobic materials at the extreme surface make easier this possibility.^{21–23} Hopefully, conducting polymers can be deposited by electrodeposition to obtain structured surfaces. In this electrochemical deposition process, a system containing two or three electrodes (working electrode, counter-electrode, and reference) is connected to a potentiostat. The working electrode should be conductive and not easily oxidizable (platinum, gold, ITO, titanium, stainless steel, etc.). By applying a potential difference in the range of the monomer oxidation potential, the monomer oxidation leads in one step to its polymerization and its deposition on the working electrode. The electrodeposited film can be smooth or structured. Indeed, this process allows an easy control of the surface morphology and roughness with the electrochemical parameters (nature of solvent, electrolyte, monomer concentration, deposition charge/current, deposition method, etc.) and also with the monomer structure.^{23,24} This last parameter is extremely interesting because it changes the intra- and intermolecular assembly in the polymer structure and leads to various morphologies (for example, cauliflower-like structures, fibers, needles, nanoparticles).

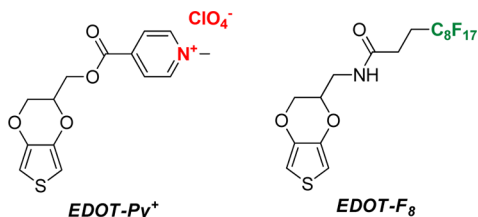
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To obtain stable superhydrophobic properties, a hydrophobic substituent (fluorinated chain, for example) can also be grafted to the monomer.^{25–27} Superhydrophobic with various morphologies were reported with this method as well as superoleophobic (repelling oils) surfaces. Previously, to obtain superhydrophobic polymer with pH and voltage responsivity, carboxylic groups were introduced.²⁸ Here, we report the possibility to reach responsive polymers by voltage and ion-exchange by introducing pyridinium groups. The films were obtained by electrocodeposition using the monomers represented in Scheme 1.

Scheme 1. Monomers Synthesized for the Co-polymerization and the Formation of Responsive Polymers



We studied the water-repellent properties as well as oil-repellent properties (using diiodomethane and hexadecane) after electrodeposition, polymer reduction by changing the voltage and ion-exchange with various counterions. We show for the first time that the surface properties can be changed from superhydrophobic to hydrophilic while the oil-repellent properties remain unchanged leading to materials with both oleophobic properties (with diiodomethane) and hydrophilic properties.

EXPERIMENTAL SECTION

N-((2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecanamide (EDOT-F₈) was synthesized in three steps from 3,4-dimethoxythiophene, as reported in the literature.²⁹

Synthesis of 4-(((2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methoxy)carbonyl)-1-methylpyridin-1-ium Perchlorate (EDOT-Py⁺). This original monomer was synthesized as following (Scheme 2): 20 mL of dichloromethane containing 0.21 g of 4-carboxy-1-methylpyridinium chloride (1.21 mmol, 1 equiv), 0.30 g of *N,N'*-dicyclohexylcarbodiimide (DCC) (1.45 mmol, 1.2 equiv) and 10 mg of 4-dimethylaminopyridine (DMAP) was stirred for 30 min at room temperature. Then, 250 mg of (2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanol (1.45 mmol, 1.2 equiv) was added and the solution was stirred for 24 h at 50 °C. After, water was added and the product was extracted with dichloromethane. After filtration and solvent evaporation, the product was washed with ethyl acetate. Then, the chloride counterions of the pyridinium functions were changed with chlorate ions using an ion exchange resin Amberlite IRA96. Here, it was necessary to substitute the chloride ions by ions stable in the potential range used for the electrodeposition.

Yield: 75 %; Yellow liquid; δ_{H} (200 MHz, CDCl₃, ppm): 9.73 (d, $^3J_{\text{HH}} = 6.5$ Hz, 2H), 8.42 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 6.35 (s, 2H), 4.84 (s, 3H), 4.31 (m, 2H), 4.11 (m, 1H), 3.82 (d, $^3J_{\text{HH}} = 4.1$ Hz, 2H); δ_{C} (200 MHz,

CDCl₃, ppm): 161.83, 156.96, 141.46, 127.54, 99.63, 94.70, 74.05, 65.81, 61.26, 54.11, 50.59, 49.03, 33.84, 24.87; FTIR (main vibrations): $\nu = 3414, 2935, 2858, 2142, 1738, 1695, 1643, 1486, 1377, 1299, 1187, 1090, 764$; ESI-MS (70 eV): m/z (%): 292 [M⁺].

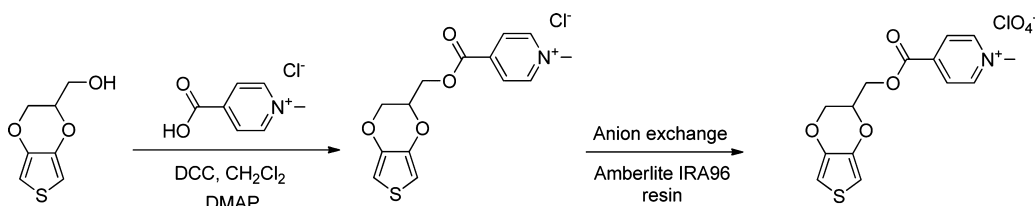
Electrochemical Co-polymerization. EDOT-Py⁺ and EDOT-F₈ (0.01 M in total) were added to a glass cell containing 10 mL of anhydrous acetonitrile and 0.1 M of tetrabutylammonium perchlorate (Bu₄NClO₄) previously degassed with argon. A three-electrode system was inserted inside the solution and connected to an Autolab potentiostat of Metrohm. Gold plates (deposition of 20 nm chromium and 150 nm gold on silicon wafer) were purchased from Neyco and used as working electrode. Glassy carbon rods were purchased from Metrohm and used as counter-electrode. Saturated calomel electrodes (SCE) were purchased from Radiometer analytical and used as reference electrode. To determine the oxidation potential necessary for the deposition (the two monomers have quite the same oxidation potential), we performed a cyclic voltammetry experiment. Here, for the electro-copolymerization it is important to have the same oxidation potential to induce the oxidation and polymerization of the two monomers at the same time. For our two monomers, the oxidation potential is quite the same because the substituents are sufficiently far from EDOT heterocycle. Examples of cyclic voltammograms are given in Figure 1. The oxidation potential was taken slightly before the maximum of the peak. Then, depositions were performed at constant potential and using a deposition charge (Q_{c}) of 100 mC cm⁻², determined as being the best value. The polymers are obtained in their doped state. The molar concentration of EDOT-Py⁺ vs. that of EDOT-F₈ was varied from 0 to 100%.

The stability of the films was also studied by cyclic voltammogram. For example, Figure 2 shows two examples of cyclic voltammogram (10 scans at 20 mV s⁻¹) of the copolymer with 50% mol EDOT-Py⁺ vs EDOT-F₈ after electrodeposition and ion exchange with Tf₂N⁻. Here, we observed a higher stability after electrodeposition than after ion exchange with Tf₂N⁻, which is due to a loss of small polymer fraction after each scan. However, it is expected that the stability should increase with the decrease in EDOT-Py⁺ because the solvent is highly polar (water).

Switchability of the Polymers. After deposition at constant potential, the polymers were in their doping (oxidized) state, which means that they contained positive charges and counterions of the electrolyte (here ClO₄⁻) to stabilize them. Because the polymers contain perchlorate anions in their doped state, it was first necessary to reduce the polymer (voltage-switchability) before to investigate the anion exchanges thanks to the pyridinium moieties. Hence, the polymers were reduced at a constant potential of -1 V vs. SCE for 30 min and in an aqueous solution of sodium perchlorate (NaClO₄). Then, the anion exchanges were realized by immersing the substrate in 0.1 mol of solution of Milli-Q water to change the ClO₄⁻ anions with BF₄⁻, Tf₂N⁻, and 0.1 mol solution of MeOH for C₈F₁₇SO₃⁻.

Surface Analyses. The surfaces were analyzed by apparent and dynamic contact angle measurements with water ($\gamma_{\text{L}} = 72.8$ mN m⁻¹) and hexadecane ($\gamma_{\text{L}} = 27.6$ mN m⁻¹) to determine the surface hydrophobicity and oleophobicity. Diiodomethane was also used as probe liquid of intermediate surface tension ($\gamma_{\text{L}} = 50.0$ mN m⁻¹). The sessile drop method was used to determine the apparent contact angles. The tilted-drop was used to determine the dynamic contact angles. After deposition of a droplet and surface inclination, the advanced and receding contact angles and as a consequence the hysteresis were taken

Scheme 2. Synthetic Way to the Synthesis of an EDOT Derivative with a Pyridinium Moiety



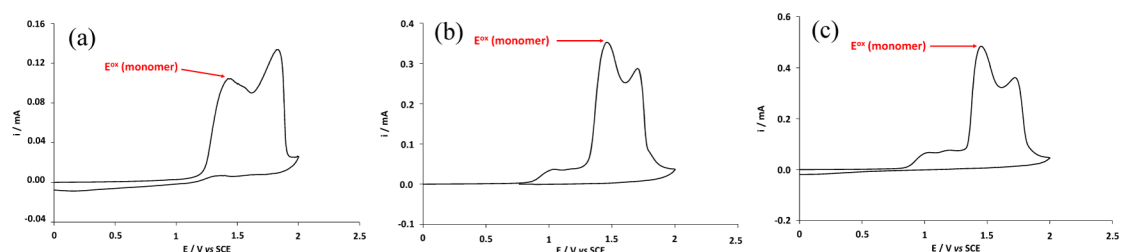


Figure 1. Cyclic voltammogram (1 scan) as a function of % mol EDOT-Py⁺ vs EDOT-F₈: (a) 0, (b) 50, and (c) 100%.

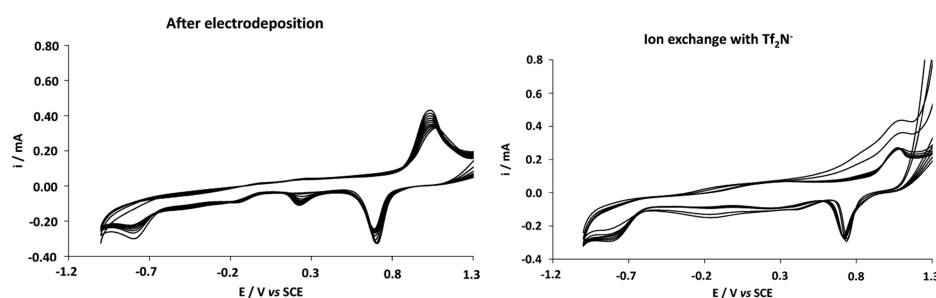


Figure 2. Cyclic voltammogram (10 scans at 20 mV s⁻¹) for the copolymer with 50% mol EDOT-Py⁺ vs. EDOT-F₈ after electrodeposition (in 0.1 M NaClO₄ aqueous solution) and ion exchange with Tf₂N⁻ (in 0.1 M LiTf₂N aqueous solution).

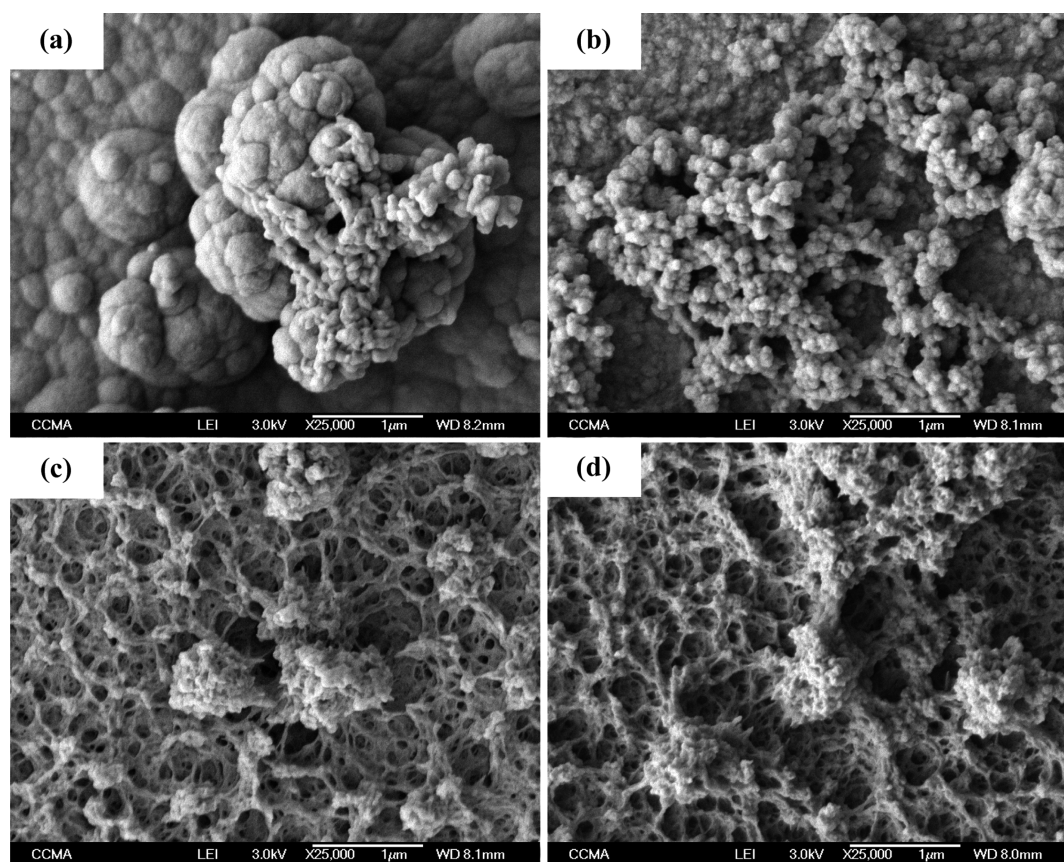


Figure 3. SEM images of the copolymers as a function of % mol EDOT-Py⁺ vs EDOT-F₈: (a) 0, (b) 25, (c) 75, and (d) 100%; magnification: ×25000.

just before the droplet rolled off the surface. The maximum surface inclination is called sliding angle (α).

The surface morphologies were investigated by scanning electron microscopy images using a 6700F microscope of JEOL. The surfaces were metallized before analyzed to have images of exceptional resolution at extremely high magnification.

RESULTS AND DISCUSSION

Surface Morphologies. The SEM images as a function of the molar percentage (% mol) of each monomer is given in Figure 3. The homopolymer PEDOT-F₈ film (Figure 3a) was composed especially of large cauliflower-like structures and contain also some

small particles. On the opposite, the homopolymer PEDOT-Py⁺ (Figure 3d) was especially composed of small nanofibers forming a porous structures. By varying the proportion of EDOT-Py⁺ vs. EDOT-F₈, a change from cauliflower-like structures to porous structures. For example, the copolymer with 25 % of EDOT-Py⁺ (Figure 3b) contained especially small nanoparticles with the appearance of porosity was observed from 37.5 % of EDOT-Py⁺. To explain, these changes in the surface morphology, it is important to mention a work in the literature,³⁰ in which the authors showed that the surface morphology of electrodeposited films is highly affected by the solubility of the oligomers formed in the first instances. Here, the introduction of EDOT-Py⁺ in PEDOT-F₈ induces an increase in the polymer hydrophilicity. Because the solvent for the electrodeposition is highly polar (acetonitrile), the addition of EDOT-Py⁺ also increases the solubility of the oligomers formed in the first instances.

The mean arithmetic (R_a) and quadratic (R_q) surface roughness are given in Table 1. Interestingly, it was observed

Table 1. Roughness Parameters (R_a and R_q) as a Function of % mol EDOT-Py⁺ vs. EDOT-F₈

	% mol EDOT-Py ⁺						
	0	25	37.5	50	62.5	75	100
R_a	165	90	65	45	45	55	140
R_q	300	160	130	90	90	110	230

that the surfaces with the highest surface roughness are the homopolymers PEDOT-F₈ and PEDOT-Py⁺. Then, the introduction of EDOT-Py⁺ in PEDOT-F₈ or reversely induced a decrease in the surface roughness until to reach a minimal value ($R_a \approx 45$ nm) for proportion of EDOT-Py⁺ vs. EDOT-F₈ of 50–62.5%.

Wetting properties. The influence of the % of EDOT-Py⁺ vs. EDOT-F₈ on the apparent contact angle (θ) of water, diiodomethane and hexadecane is represented in Figure 4. Surprisingly, the highest θ were not obtained with homopolymer PEDOT-F₈ but the introduction of 25% of EDOT-Py⁺ (a hydrophilic and oleophilic molecule as shown in Figure 3a for 100% of EDOT-Py⁺) induced an increase of θ for each probe liquid. Moreover, superhydrophobic surfaces with low hysteresis (H) and sliding angle (α) were obtained only for this proportion. Indeed, for 25% of EDOT-Py⁺, $\theta_{\text{water}} = 155.1^\circ$, $H = 1.9^\circ$, and $\alpha = 1.8^\circ$. Hence, the highest superhydrophobic properties were not obtained with the rougher surfaces.

This effect can be explain with Wenzel ($\cos \theta = r \cos \theta^Y$ with r a roughness parameter and θ^Y the Young's angle) and Cassie–Baxter ($\cos \theta = f \cos \theta^Y + f - 1$ with f the solid fraction and $(1 - f)$ the air fraction) equations, which give the possibility to reach superhydrophobic properties in certain conditions.^{31,32} In these equation, the Young's angle³³ correspond to the apparent contact angle of the same materials but smooth (without surface structures). In the Wenzel state,³¹ the interface of the water droplet fully follows that of the surface roughness. As a consequence, it is possible to reach superhydrophobic surfaces but only with high H and α . Moreover, this possibility is allowed only if the materials is intrinsically hydrophobic ($\theta^Y_{\text{water}} > 90^\circ$). In the Cassie–Baxter state,³² the droplet sits on top of surface roughness and on air trapped between the surface and the droplet. The presence of this air can allow to reach superhydrophobic surfaces with extremely low H and α and even if the materials are intrinsically hydrophilic ($\theta^Y_{\text{water}} < 90^\circ$). This last case is possible is the three-phase contact line is highly pinned by the surface structures.^{34,35} Hence, the fact that the rougher surface do not correspond to the highest water-repellent properties can be explained by the fact that the roughness is an important parameter when the droplet is in the Wenzel state but not in the Cassie–Baxter state, for which the amount of air trapped below the droplet is more important.

Hence, it was first necessary to determine θ^Y for the three probe liquids and for each proportion of EDOT-Py⁺ vs EDOT-F₈. Figure 4b gives this effect. Smooth surfaces were, here, produced by depositing an extremely thin polymer layer (1 mC.cm^{-2}) because only a smooth thin layer is produced in the first instance while the formation of surface structures appear a little after. As expected, Figure 4b shows that θ^Y for each liquid with the % of EDOT-Py⁺ and also with the surface tension of the liquid probe ($\theta^Y_{\text{water}} > \theta^Y_{\text{diiodomethane}} > \theta^Y_{\text{hexadecane}}$). Moreover, the copolymers are intrinsically hydrophobic ($\theta^Y_{\text{water}} > 90^\circ$) for a % of EDOT-Py⁺ < 50 % and intrinsically oleophilic ($\theta^Y_{\text{diiodomethane}}$ and $\theta^Y_{\text{hexadecane}} < 90^\circ$) whatever the % of EDOT-Py⁺.

As a consequence, the increase in θ for 25% of EDOT-Py⁺ was not due to an increase in θ^Y and as consequence was due to a change in the surface morphology. Here, the change from large cauliflower-like structure (Figure 3a) to small nanoparticles (Figure 3b) induced this effect because the presence of small nanoparticles favored the Cassie–Baxter state for each liquid probe.

Wetting Properties after Changing the Voltage (Reduction). To study the effect of the voltage, the conducting polymers were reduced at a negative potential of -1 V vs SCE for

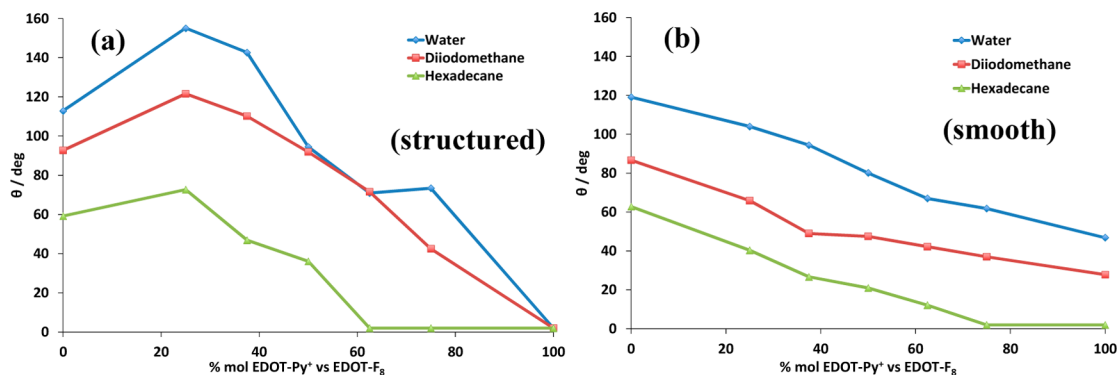


Figure 4. Apparent contact angle (θ) of water, diiodomethane, and hexadecane as a function of the % mol of EDOT-Py⁺ vs. EDOT-F₈ for (a) the structured films ($Q_s = 100 \text{ mC cm}^{-2}$) and (b) the smooth corresponding films ($Q_s = 1 \text{ mC cm}^{-2}$).

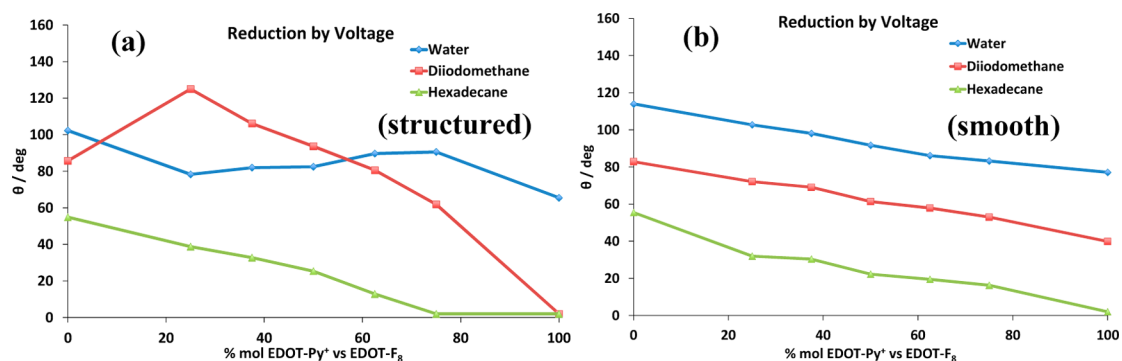


Figure 5. Apparent contact angle (θ) of water, diiodomethane, and hexadecane after reduction as a function of the % mol of EDOT-Py⁺ vs. EDOT-F₈ for (a) the structured films ($Q_s = 100 \text{ mC cm}^{-2}$) and (b) the smooth corresponding films ($Q_s = 1 \text{ mC.cm}^{-2}$).

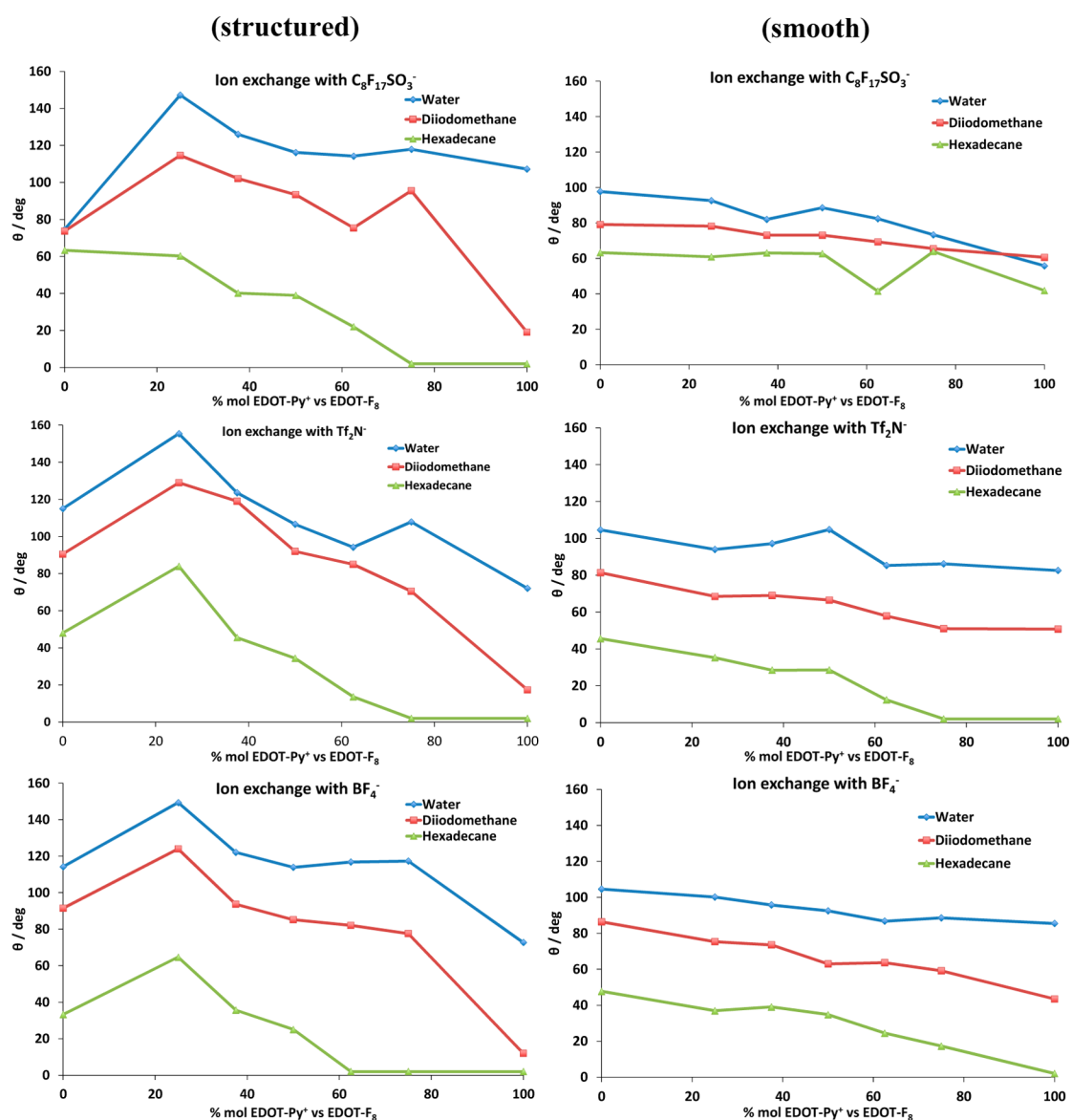


Figure 6. Apparent contact angle (θ) of water, diiodomethane, and hexadecane after reduction and ion exchange (C₈F₁₇SO₃⁻, Tf₂N⁻ or BF₄⁻) as a function of the % mol of EDOT-Py⁺ vs. EDOT-F₈ and for the structured films ($Q_s = 100 \text{ mC cm}^{-2}$) and the smooth corresponding films ($Q_s = 1 \text{ mC cm}^{-2}$).

30 min. Here, the dedoping allows to reduce the polymers and as a consequence also to remove the perchlorate anions being present inside the polymer to stabilize it.

The θ after reduction are represented in Figure 5. Surprisingly, the reduction induced a high decrease of θ_{water} at low % of EDOT-Py⁺ and a high increase of θ_{water} at high % of EDOT-Py⁺,

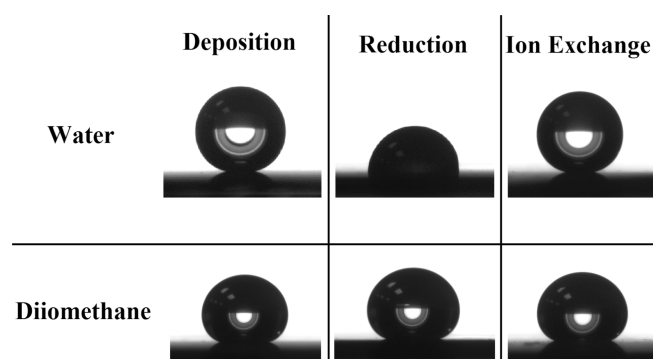


Figure 7. Pictures of water and diiodomethane droplets after electrodeposition, reduction by changing the voltage and ion exchange with hydrophobic TF_2N^- ions (here, the copolymer contains 25 % of EDOT- Py^+).

whereas $\theta_{\text{diiodomethane}}$ and $\theta_{\text{hexadecane}}$ remained quite unchanged. As a consequence, it was possible for a % of $25\% \leq \text{EDOT-}\text{Py}^+ \leq 50\%$ to obtain $\theta_{\text{diiodomethane}} > \theta_{\text{water}}$. This possible is extremely rare in the literature but, as in this report, it was reported in works with materials containing both hydrophobic/oleophobic (fluorinated

chains, for example) and hydrophilic/oleophilic (charged species, for example) parts.^{36–41} Indeed, several works reported the possibility to obtain hydrophilic and “underwater” superoleophobic properties,^{42–47} superoleophobic both in air and water,⁴⁸ switchable underwater superoleophobic surfaces,⁴⁹ or switchable superoleophobic surfaces,^{50,51} but there are very works reporting higher oleophobicity than hydrophobicity when the media is air.^{36–41}

In fact, this effect can be explained by the change in a water droplet from a Cassie–Baxter state³⁰ to a Wenzel state.³¹ Because the polymer contains highly polar groups due to the presence pyridinium groups and the perchlorate counterions only wettability of a water droplet was highly effected. Moreover, the amide connectors between the polymer and the fluorinated chains may also be attracted when a polar liquid (water) is present on the surface and reduce the presence of the fluorinated chains at the extreme surface (surface rearrangements).

Wetting Properties after Ion Exchange. To verify if the effect induced by the reduction is due to the pyridinium moieties, the polar ClO_4^- counterions of the moieties were replaced with highly apolar $\text{C}_8\text{F}_{17}\text{SO}_3^-$, TF_2N^- and BF_4^- . As shown in Figure 6, this change allowed to obtain again superhydrophobic properties

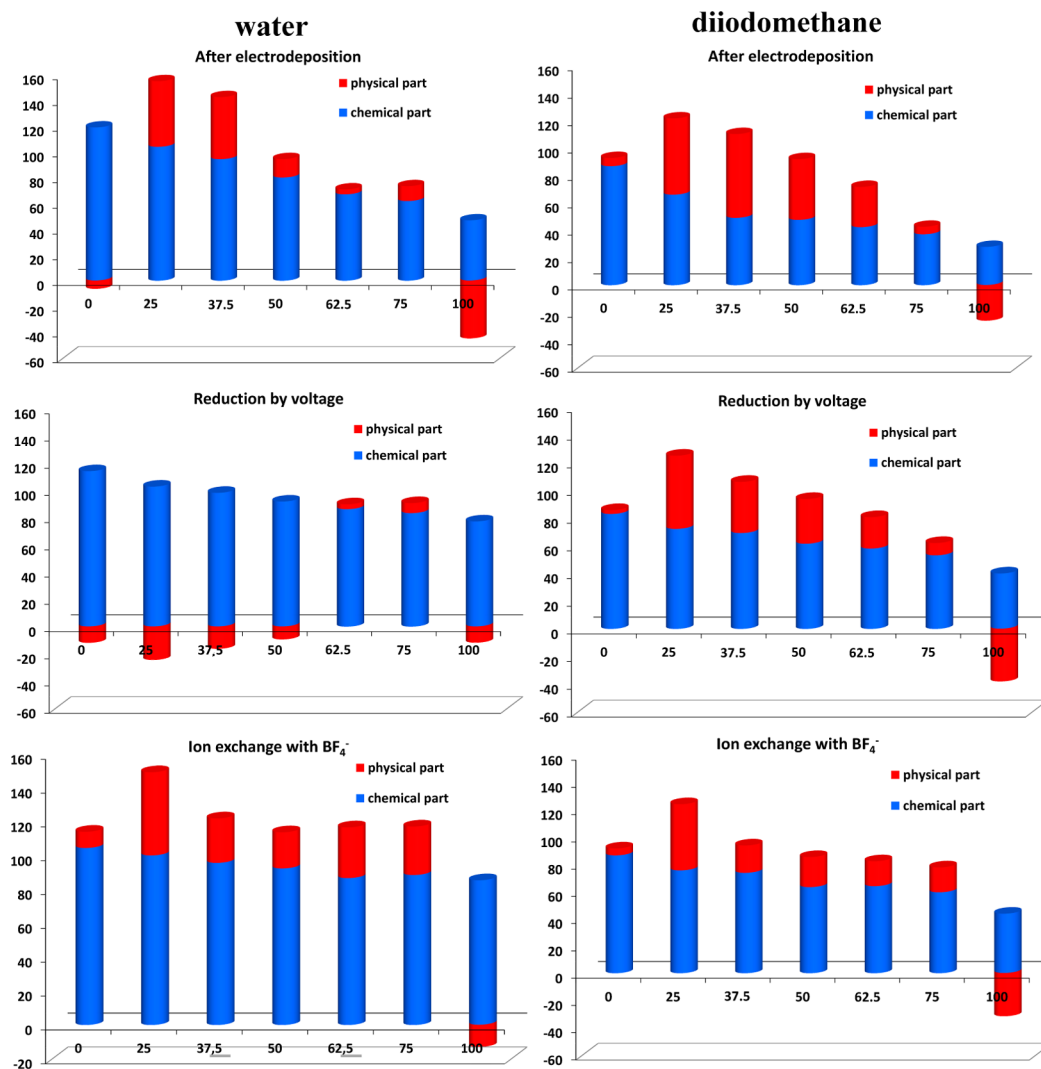


Figure 8. Schematic representation of the effect of the surface structures (physical part) and the intrinsic liquid repellency (chemical part) on the apparent contact angles of water and diiodomethane after each treatment.

for 25% of EDOT-Py⁺, confirming the effect of the pyridinium moieties and their counterions in the decrease in only the water-repellency after the polymer reduction. Figure 7 gathers images of water and diiodomethane after each treatment. Moreover, the change of the counterions of the pyridinium moieties with highly apolar ones allowed also to highly increase the surface hydrophobicity even for high percentages of EDOT-Py⁺.

To better visualize the effect of the surface structures (physical part) and that on the intrinsic liquid-repellent properties (chemical part) on the apparent contact angle, we calculated these two parts after each treatment. The chemical part corresponds θ^Y and the physical part to the difference $\theta - \theta^Y$. Figure 8 shows these effects for water and diiodomethane. It can be deduced that the treatments have no significant effect for the contact angles of diiodomethane (both chemical and physical parts). However, for water, the effects are drastic. For example, for a % of EDOT-Py⁺ between 25 and 50%, the effect of the surface structures is positive after electrodeposition, negative after reduction, and become again positive after ion exchange.

CONCLUSIONS

Here, we have reported the elaboration of electrodeposited conducting polymers containing fluorinated chains (EDOT-F₈) and pyridinium (EDOT-Py⁺) moieties with selective liquid-repellent properties by voltage and ion-exchange. Superhydrophobic properties with low hysteresis and sliding and good oleophobic properties were obtained with a percentage of EDOT-Py⁺ of 25%. By switching the voltage to reduce the polymer, a selective decrease in the contact angle of water was observed in comparison with that of oils (diiodomethane and hexadecane) making possible to have higher oil-repellent properties than water-repellent properties. We have shown that the switching is due to the change of the water droplet from the Cassie–Baxter state to the Wenzel and that the oils are not affected because of the presence of highly polar pyridinium groups and their perchlorate counterions. We have confirmed this effect by changing the counterions with highly hydrophobic ones (C₈F₁₇SO₃⁻, Tf₂N⁻, or BF₄⁻). Such materials can be used for oil/water separation membranes.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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