

Switchable surfaces from highly hydrophobic to highly hydrophilic using covalent imine bonds

Guilhem Godeau, Thierry Darmanin, Frédéric Guittard

Univ. Nice Sophia Antipolis, CNRS, LPMC, UMR 7336, Nice 06100, France

Correspondence to: F. Guittard (E-mail: guittard@unice.fr)

ABSTRACT: The formation of materials with switchable wettability is extremely important for various applications such as in separation membranes or liquid transportation. Here, we report for the first time the use of imine bonds in order to prepare switchable hydrophobic/hydrophilic surfaces. Based on a poly(3,4-ethylenedioxythiophene) surface bearing amino groups, imination reaction allows for reversible functionalization of surfaces with various carbonyl groups. Here, surfaces functionalization induces high hydrophobic properties while the surface structures are preserved. This reaction can be a choice method to prepare switchable surfaces for a large range of applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43130.

KEYWORDS: nanostructured polymers; stimuli-sensitive polymers; surfaces and interfaces

Received 26 June 2015; accepted 4 November 2015

DOI: 10.1002/app.43130

INTRODUCTION

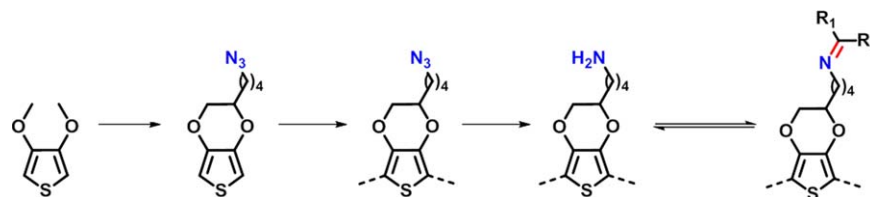
In the past decades, many researches focused on the control of surface hydrophobicity because of a wide range of possible applications such as self-cleaning glasses, waterproof textiles, anti-snow and anti-fog surfaces, sensors/biosensors, or anti-bio adhesion.^{1–3} Several processes have been reported to control surface hydrophobicity and it is now well established that the control of hydrophobicity is linked to different surface parameters. Especially the surface energy and surface morphology are key parameters.^{4–6} Different processes are reported in order to control these parameters. Usually, these strategies can be classified in two categories: the bottom-up approach and the top-down approach. In the top-down strategy an intrinsically hydrophobic substrate is structured, for example using by chemical or plasma etching. In the bottom-up strategy, materials self-assemble or polymerize on a smooth substrate in order to structure it. In that final case, the surface energy is controlled by playing on the hydrophobicity of the starting molecules or can be added using a post-functionalization.

In that work, we focus on electropolymerization, a particular bottom-up approach. Electropolymerization allows for the control of surface morphology and surface energy by playing on monomer or electrochemical parameters and is hence a powerful tool leading to the control of surface hydrophobicity in one step.⁷ Because of unique electrochemical properties (high conductivity, easily and quickly polymerizable), the 3,4-ethylenedioxythiophene derivatives are exceptional candidates for electropolymerization.^{8–11} Various derivatives have been reported in

the literature and lead to highly hydrophobic surfaces with various properties.^{12–14} But in the major case, it is necessary to make modification on monomer to change the surface properties. That approach reported as *ante*-deposition modification requires the synthesis of numerous monomers in order to screen morphologies and properties which is generally difficult and time consuming. Opposite to this strategy, the surface *post*-functionalization is a really attractive method.

Recently, various works have been reported for surfaces *post*-functionalization. This strategy allows for various modifications on only one prepared surfaces. Different chemical ways can be reported for *post*-functionalization. For examples, the thiol-michael reaction, the Staudinger-Vilarassa reaction, and the Huisgen reaction have been extensively studied.^{15–19} All these strategies are efficient but lead to irreversible bonds. The use of reversible bond is a significant advantage in order to prepare smart surfaces able to answer to environmental stress. For example, surfaces with switchable wettability can be prepared by introducing and removing hydrophobic dopant agents playing on electrostatic interactions.^{20,21} However, the properties are not highly stable and only electrochemical stable dopants agents can be introduced. In order to increase the modification stability, covalent but reversible bonds can be used.

For that purpose, the imine strategy can be considered as a good candidate. Amino groups and carbonyl groups spontaneously react in order to form imine bond. That covalent bond can be reversed using hydrolysis or transimination using nucleophilic amines.²² Carbonyl groups like aldehydes or ketones are



Scheme 1. General procedure to obtain surfaces with switchable wettability using imine bonds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

very diverse and provide a great diversity of possible modification for surfaces. In this work, we focus for the first time on alkyl or aryl aldehydes and ketones in order to prepare switchable hydrophobic/hydrophilic surfaces (Scheme 1).

EXPERIMENTAL

Reagent and Material

All starting materials and solvents were obtained from commercial suppliers and were used without further purification. All compounds were characterized using standard analytical and spectroscopic data such as ^1H , ^{13}C NMR spectroscopy (apparatus BRUKER Avance 200 MHz). The NMR chemical shifts are reported in ppm relative to tetramethylsilane using the residual proton of the solvent for ^1H NMR spectra and the carbon atom of the deuterated solvent for ^{13}C NMR spectra (CDCl_3). The ^1H NMR coupling constants J are reported in Hz. Electrochemical polymerization were performed on Gold plates (purchased from Neyco) using an Autolab potentiostat (Metrohm). For surface characterizations the apparent contact angles were measured with a DSA30 goniometer from Krüss using the sessile drop method. The scanning electron microscopy images were obtained using a 6700F microscope of JEOL.

Monomer Synthesis. 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). About 4.6 g of hexan-1,2,6-triol (34.6 mmol) and 665 mg of *para*-toluene-sulfonic 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. The mixture was extracted with NaHCO_3 5% in water (2 X 30 mL) and brine (30 mL), then dried over Na_2SO_4 . The solvents were removed under reduced pressure. **EDOT-OH** was finally purified on column (80/20, cyclohexane/ethyl acetate).

Yield: 1.9 g of slightly yellow oil (51%); *Rf*: 0.5 (5/5, cyclohexane/ethylacetate); ^1H NMR (250 MHz, CDCl_3 , δ): 6.30 (s, 2H), 4.10–4.18 (m, 2H), 3.85–3.91 (m, 1H), 3.64–3.71 (m, 2H), 1.52–1.69 (m, 8H); ^{13}C NMR (50 MHz, CDCl_3 , δ): 142.0, 141.6, 99.3, 73.6, 68.4, 62.6, 32.4, 30.4, 21.3; MS: 213.9.

2-(4-azidobutyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine, **EDOT-N₃**: 1.9 g (8.9 mmol) of **EDOT-OH** were dissolved in dichloromethane (100 mL). About 1.8 g (2 eq, 17.8 mmol) of triethylamine was added. The mixture was cooled at 0°C . About 1.2 g (1.2 eq, 10.6 mmol) of methanesulfonyl chloride was added carefully. 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 ace-

tone (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 was removed under reduced pressure. Dichloromethane (100 mL) was added. The organic layer was washed with water (2 X 30 mL), brine (30 mL) and dried over Na_2SO_4 . The solvents were removed under reduced pressure. **EDOT-N₃** was finally purified on column (95/5, cyclohexane/ethylacetate).

Yield: 1.6 g of colorless oil (75%); *Rf*: 0.66 (8/2, cyclohexane/ethylacetate); ^1H NMR (250 MHz, CDCl_3 , δ): 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, 8H); ^{13}C NMR (50 MHz, CDCl_3 , δ): 141.9, 141.6, 99.4, 73.4, 68.3, 51.2, 30.1, 28.7, 22.3; MS: 239.9.

Electrochemical Polymerization

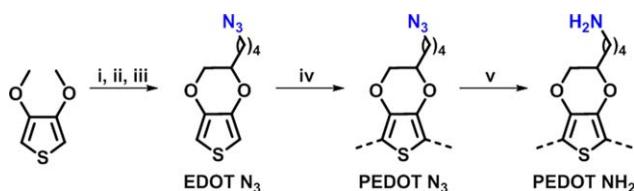
In a glass cell containing 0.1M of tetrabutylammonium perchlorate (Bu_4NClO_4) dissolved in dry acetonitrile, 0.01M of **EDOT-N₃** was inserted. Three electrodes were put inside the solution. Gold plates (purchased from Neyco), glassy carbon rods, and saturated calomel electrodes (SCE) were used respectively as working, counter, and reference electrodes. The three electrodes were connected to an Autolab potentiostat (Metrohm). Before each experiment, the solution was degassed with argon. The depositions were performed by cyclic voltammetry from -1.00 to 1.37 V at a scan rate of 20 mV/s and using different deposition scans (1, 3, and 5). After the deposition, the **PEDOT-N₃** samples were cleaned three times with acetonitrile in order to remove the remaining salts.

Surface Modifications

PEDOT-N₃ To PEDOT-NH₂ Reduction. In a 25 mL vial, 100 mg (0.49 mmol) of tributylphosphine were dissolved in 5 mL of dry THF. The **PEDOT-N₃** on wafer was introduced into the vial. The mixture was shaken 3 hours. The polymer was then successively washed three times with water and three times with ethanol. The polymer on wafer was then dried.

Imine Formation. In a 25 mL vial, 100 mg carbonyl (aldehyde or ketone) were dissolved in 5 mL of dry toluene. Hundred mg (0.99 mmol) of triethylamine and 100 mg (0.83 mmol) of magnesium sulfate were added. The **PEDOT-NH₂** (three scans) on wafer was introduced. The mixture was shaken overnight. The polymer was then successively washed three times with water and three times with ethanol. The polymer on wafer was then dried.

Transimination. In a 25 mL vial, the **PEDOT-imine** was shaken overnight in 5 mL of ethanol amine. The polymer was then successively washed three times with water and three times with ethanol. The polymer on wafer was then dried.



Scheme 2. General procedure for PEDOT-NH₂ surface preparation. i) 1,2,6-hexanetriol (1 eq), 3,4-dimethoxythiophene (0.5 eq), Paratoluenesulfonic acid (0.05 eq), toluene reflux, 36 h. ii) Methanesulfonyl chloride (1.5 eq), triethylamine (3 eq), dichloromethane, rt, 4h. iii) Sodium azide (5 eq), acetone, reflux, overnight. iv) Electropolymerization. v) Tributylphosphine, rt, 3h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Reversibility assay. The cycle “Imine formation followed by transimination reaction” was successively repeated few times as a reversibility cycle.

RESULTS AND DISCUSSION

Synthetic Way to Monomers

Herein we report the first use of imine bond in order to prepare tuneable and smart surfaces. Based on a *post*-deposition modification approach, this study shows the use of reversible bonds for hydrophobic surface preparation. As all *post*-deposition strategies, this work starts with the elaboration of a key tuneable platform. In that work, the starting point is a structured polymers with amino groups. In order to get well-defined nanostructured surfaces, the electropolymerization was chosen. Unfortunately, because of the basicity of amino groups, monomers with amino groups are not suitable for electropolymerization. The first step needs the preparation of monomers with masked amino groups. For this purpose, 3,4-ethylenedioxythiophene (EDOT) containing an azido group separated by a relatively long butyl spacer was synthesized (Scheme 2). A relatively long butyl spacer was chosen to facilitate the electrodeposition and the *post*-treatments.

Formation of Polymer Films by Electropolymerization

This monomer was electropolymerized to form PEDOT nanofibers with azido groups (PEDOT-N₃). The electropolymeriza-

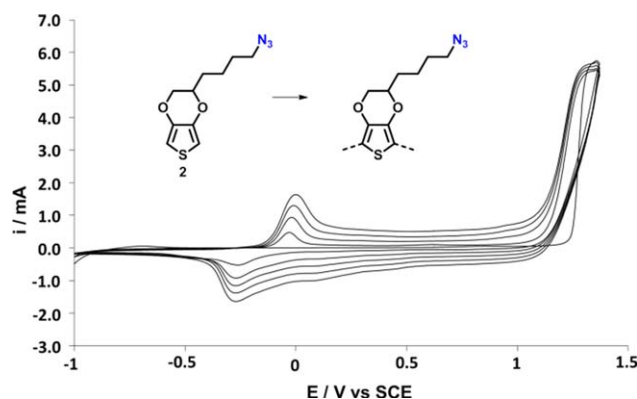


Figure 1. Cyclic voltammogram of compound 2 (0.01M) on gold plate recorded in 0.1M tetrabutylammonium perchlorate/CH₃CN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

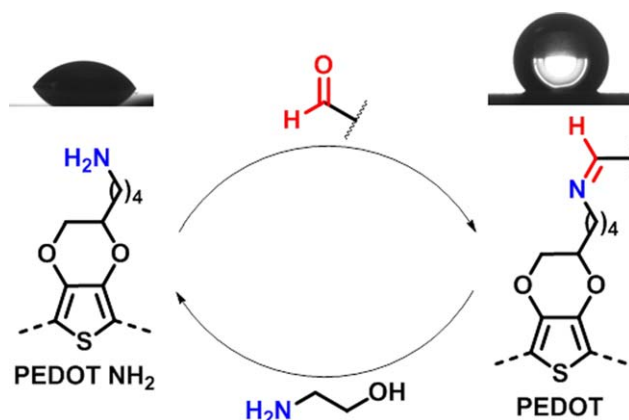


Figure 2. General concept for switchable *post*-functionalization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion experiments were performed on gold-covered wafer as working electrode using a cyclic voltammetry procedure. The deposition was done in 0.1M tetrabutylammonium perchlorate in anhydrous acetonitrile (CH₃CN). The oxidation potential for EDOT-N₃ was measured vs saturated calomel electrode (SCE) and was 1.43 V. In order to obtain highly homogeneous and adherent films, the cyclic voltammetry was chosen as electrodeposition method. The deposition was performed from -1.00 to 1.37 V at a scan rate of 20 mV/s and using different deposition scans (1, 3, and 5). The voltammogram after five deposition scans is shown in Figure 1. We observed that EDOT-N₃ electrochemically polymerized perfectly and gave extremely well-defined cyclic voltammograms.

Switchable Surfaces by Formation of Imine Bonds

These surfaces were reduced in order to get amino surfaces (PEDOT-NH₂) using Staudinger reduction (Scheme 2). The reaction was performed with tributylphosphine for 3 h in order to free the amino groups. The reduction of PEDOT-N₃ into PEDOT-NH₂ induces an important switch on surface wettability. The water apparent contact angle (θ_w) decreases from 120° for PEDOT-N₃ to 53° for PEDOT-NH₂. This change is very consistent with the formation of hydrophilic amino groups.

On these surfaces, *post*-functionalization was performed by imination with different carbonyl groups including aldehydes and ketones. Different modifications were performed and studied for their reversibility (Figure 2). This work includes studies on surface wettability and morphologies.

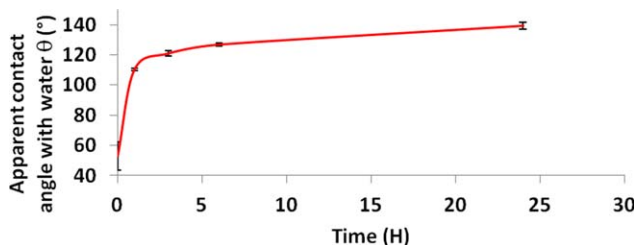


Figure 3. Kinetic for surface imination. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

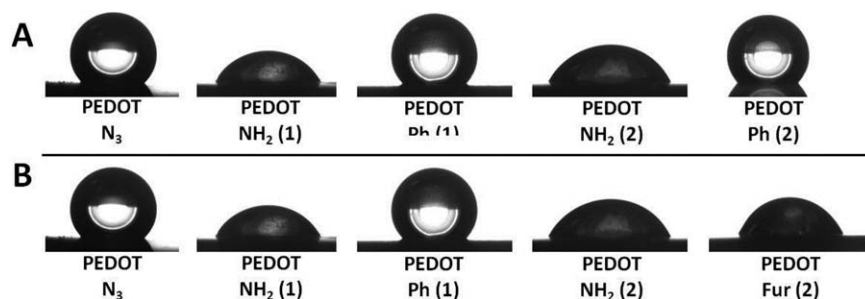
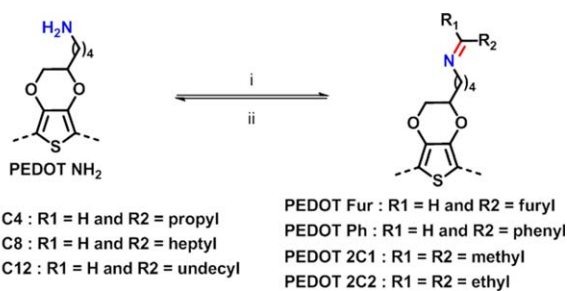


Figure 4. Water drop profile for different modification cycle. (A) With benzaldehyde for all cycle. (B) Modification with benzaldehyde (first cycle) and furfural (second cycle).

The imine bond is very interesting for its selectivity and reversibility. In order to first study the reaction, the kinetic and reversibility of the reaction were investigated. For that purpose, the surface wettability was observed depending on the reaction time between octanal and PEDOT-NH₂ (Figure 3). The results show that after 6 h most of the reaction is complete, but still slightly evolves until 24 h. For the subsequent functionalization, the reaction time was 16 h in order to get a good ratio reaction/time. The formed imine bond is stable in these experimental conditions, and can be immersed overnight in 1M HCl ethanol solution or 34% ammonia in water without any change of the surface properties. The PEDOT-NH₂ surface can be released using a transimination reaction with an excess of etha-

nolamine. The released PEDOT-NH₂ can be engaged in a new round of functionalization. This cycle has been repeated few times without change in surface properties for different cycle of the same modification [Figure 4(A)]. The aldehyde can be changed for each cycle, in that final case the surface properties



Scheme 3. General procedure for post-functionalization. i) Carbonyl, triethylamine, magnesium sulphate, toluene, rt, overnight. ii) Ethanolamine, rt, overnight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

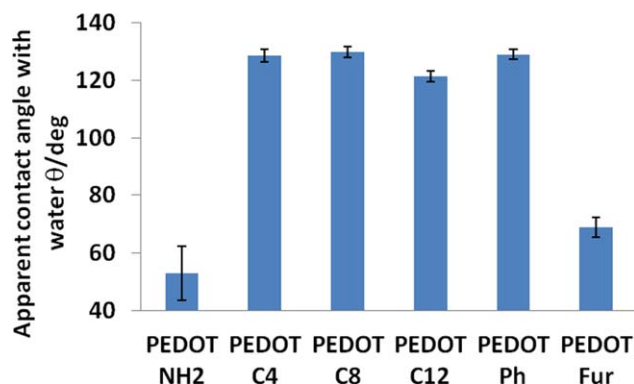


Figure 5. Water apparent contact angle of modified and unmodified surfaces using aldehydes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

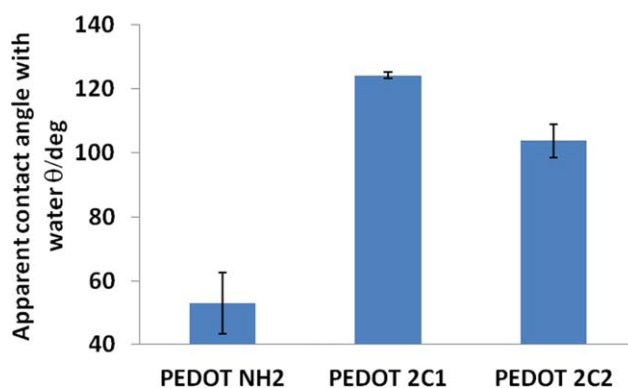


Figure 6. Water apparent contact angle of modified and unmodified surfaces using ketones. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

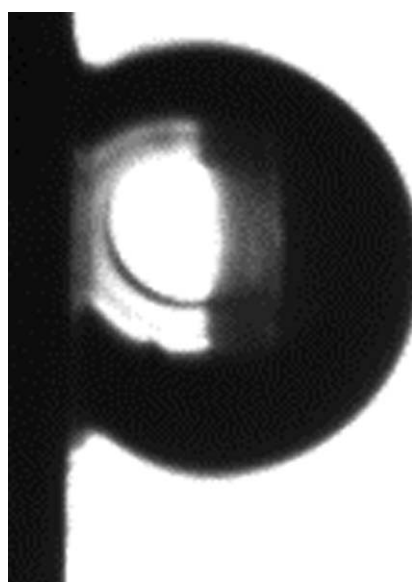


Figure 7. Example of parahydrophobic properties for surfaces tilted at 90° for PEDOT-C₈ (B).

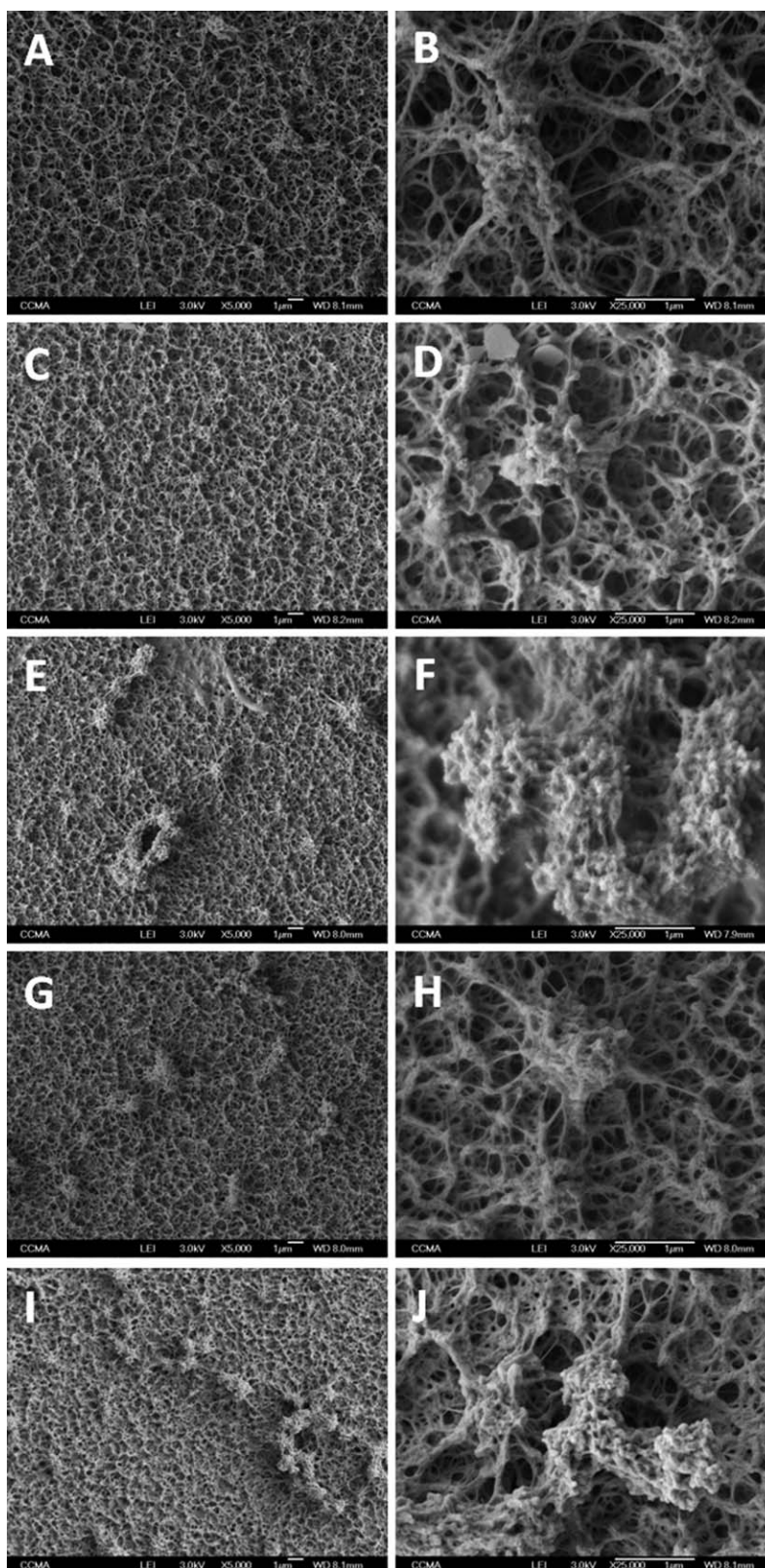


Figure 8. Examples of SEM images at two different magnifications ($\times 5k$ and $\times 25k$, scale bar = 1 μm) obtained for PEDOT. (A,B) PEDOT-N₃, (C,D) PEDOT-NH₂, (E,F) PEDOT-C₈, (G,H) PEDOT-Ph, and (I,J) PEDOT-C₁.

will depend only on the last used aldehyde. It is necessary to note that after four cycles, because of the great number of washing and deeping steps, the polymer started to detach from the gold surfaces.

In order to get different surface properties, the amine surface was *post*-functionalized with various aldehydes and ketones. To get good hydrophobic properties, alkyl and aryl aldehydes as well as ketones were selected: butanal (C₄), octanal (C₈), dodecanal (C₁₂), benzaldehyde (Ph), furfural (Fur), propan-2-one (2C₁), and pentan-3-one (2C₂) (Scheme 3).

θ_w of modified surfaces was evaluated and the results are shown in Figures 5 and 6. As expected, the starting PEDOT-NH₂ surface presents a low θ_w of 53°. All the PEDOT formed with alkyl aldehydes show hydrophobic properties confirming the *post*-functionalization. Interestingly, if the wettability is the same for PEDOT C₄ ($\theta_w = 128^\circ$) and PEDOT C₈ ($\theta_w = 130^\circ$), PEDOT C₁₂ presents a little lower hydrophobicity ($\theta_w = 121^\circ$). That result can probably be correlated to the increase of the steric hindrance and a lower level of functionalization. Aromatic aldehydes such as benzaldehyde show high hydrophobicity ($\theta_w = 129^\circ$); not surprisingly, more polar furfural gives lower contact angle and gives hydrophilic surface ($\theta_w = 69^\circ$). Even if their electrophilic properties are a little lower than aldehydes, ketones were also investigated. The surface *post*-functionalized with ketones give little lower contact angle. Similar results were obtained (Figure 6) for PEDOT-2C₁ ($\theta_w = 124^\circ$) and PEDOT-2C₂ ($\theta_w = 103^\circ$).

Moreover, modified surfaces become hydrophobic but show strong adhesion with water. The water droplet did not roll off even when the surface is tilted at 90° (Figure 7). Such kind of functionalized surfaces can be described as parahydrophobic.⁶

The scanning electronic microscopy (SEM) images performed on starting PEDOT-N₃, PEDOT-NH₂ and *post*-modified surfaces show that the *post*-deposition imination perfectly preserves the morphology of the starting surfaces (Figure 8). Each surface is nicely defined and shows a highly fibrillary structure. The conservation of surface morphology can be very important for applications where the surface morphology as to be preserved.

CONCLUSIONS

Here, we reported the first use of imine as a covalent link for *post*-deposition surface modification. This reaction allowed to prepare switchable hydrophilic/hydrophobic surfaces with possible reversibility. The use of very common functional groups such as aldehydes or ketones allows to use this reversible ligation for a wide range of applications from biomedical engineering to smart materials.

ACKNOWLEDGMENTS

The group thanks Jean-Pierre Laugier (CCMA, Univ. Nice Sophia Antipolis) for the SEM analyses. The group thanks Emilie Charles for her kind English checking.

REFERENCES

1. Darmanin, T.; Guittard, F. *J. Mater. Chem. A* **2014**, *2*, 16319.
2. Yan, Y. Y.; Gao, N.; Barthlott, W. *Adv. Colloid Interface Sci.* **2011**, *169*, 80.
3. Yao, X.; Song, Y.; Jiang, L. *Adv. Mater.* **2011**, *23*, 719.
4. Nagappan, S.; Ha, C. S. *J. Mater. Chem. A* **2015**, *3*, 3224.
5. Marmur, A. *Soft Matter* **2013**, *9*, 7900.
6. Marmur, A. *Soft Matter* **2012**, *8*, 6867.
7. Darmanin, T.; Guittard, F. *Prog. Polym. Sci.* **2014**, *39*, 656.
8. Turbiez, M.; Frere, P.; Allain, M.; Gallego-Planas, N.; Roncali, J. *Macromolecules* **2005**, *38*, 6806.
9. Gaupp, C. L.; Welsh, D. M.; Reynolds, J. R. *Macromol. Rapid Commun.* **2002**, *23*, 885.
10. Kerszulis, J. A.; Amb, C. M.; Dyer, A. L.; Reynolds, J. R. *Macromolecules* **2014**, *47*, 5462.
11. Amb, C. M.; Kerszulis, J. A.; Thompson, E. J.; Dyer, A. L.; Reynolds, J. R. *Polym. Chem.* **2011**, *2*, 812.
12. El-Maiss, J.; Darmanin, T.; Guittard, F. *J. Colloid Interface Sci.* **2015**, *447*, 167.
13. Lamy, M.; Darmanin, T.; Guittard, F. *Colloid Polym. Sci.* **2015**, *293*, 933.
14. Luo, S.-C.; Sekine, J.; Zhu, B.; Zhao, H.; Nakao, A.; Yu, H.-H. *ACS Nano* **2012**, *6*, 3018.
15. Wei, B.; Ouyang, L.; Liu, J.; Martin, D. C. *J. Mater. Chem. B* **2015**, *3*, 5028.
16. Feldman, K. E.; Martin, D. C. *Biosensors* **2012**, *2*, 305.
17. Molino, P. J.; Wallace, G. G.; Hanks, T. W. *Synth. Met.* **2012**, *162*, 1464.
18. Bu, H. B.; Goetz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segura, J. L.; Baeuerle, P. *Chem. Commun.* **2008**, 1320.
19. Bu, H. B.; Goetz, G.; Reinold, E.; Vogt, A.; Azumi, R.; Segura, J. L.; Baeuerle, P. *Chem. Commun.* **2012**, *48*, 2677.
20. Xu, L.; Chen, W.; Mulchandani, A.; Yan, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 6009.
21. Chang, J. H.; Hunter, I. W. *Macromol. Rapid Commun.* **2011**, *32*, 718.
22. Mäkelä, M. J.; Korpela, T. K. *Chem. Soc. Rev.* **1983**, *12*, 309.