Azidomethyl-EDOT as a Platform for Tunable Surfaces with Nanostructures and Superhydrophobic Properties

Guilhem Godeau, Jessica N'Na, Thierry Darmanin, and Frédéric Guittard*

University Nice Sophia Antipolis, CNRS, LPMC, UMR 7336, 06100 Nice, France

ABSTRACT: We report for the first time the use of click chemistry both to modify the surface morphology and to obtain superhydrophobic properties. Using click chemistry as a postfunctionalization of poly(3,4-ethylenedioxythiophene) nanofibers bearing azido groups, we show that the nanostructures already present on the surface as well as the surface hydrophobicity are highly affected by the used alkyne. These results allow one to envisage widely varied strategies to



modify nanostructured surfaces while introducing various functions, for example to produce biosensors or antibacterial surfaces.

INTRODUCTION

Because of their very special wettability properties, superhydrophobic surfaces (water apparent contact angle $\theta > 150^{\circ}$ and low hysteresis) hold a deep interest for the scientific and industrial communities.^{1,2} The wide range of applications, such as self-cleaning windows, water-proof textiles, antisnow and antifog surfaces, sensors, or antibioadhesion, make these materials very interesting to prepare and study.^{3,4} The fabrication of such materials often needs both low surface energy materials and surface structures.⁵

The electrodeposition of conducting polymers can lead to superhydrophobic properties in one step by a careful control in the electrochemical parameters and the used monomer.^{6–9} For superhydrophobic properties, 3,4-ethylenedioxythiophene (EDOT) and its derivatives are unique candidates because of their exceptional electrochemical properties (high conductivity, easily and quickly polymerizable)^{10,11} and especially their large range of surface morphologies including nanofibers.^{12–15} Indeed, the superhydrophobic properties of surfaces containing nanofibers are highly dependent on the diameter, length, and orientation of the nanofibers.^{16,17} Different derivatives with fluorocarbon or hydrocarbon chains were introduced by grafting on the monomer before polymerization.^{12–15} That strategy focus is on one application, and the focus of the synthesis is on one target. It is a target-oriented surface modification (TOSM).

To introduce various substituents, "click chemistry" can also be used. This strategy allows production of unique compounds bearing a triazole moiety with a modifiable substituent at the 4position.^{18,19} The typical synthesis used, Huisgen 1,3-dipolar cycloaddition between azide and alkyne (Scheme 1), is an efficient way to covalently link two molecules. That chemistry is widely used for postsynthesis modification on a wide range of molecules from biomolecules to materials.^{20–22}

However, the grafting by click chemistry on the monomer before polymerization led to nonpolymerizable monomers because of the basicity of the triazole moiety.²³ Hopefully, monomers with azide groups can polymerize and the click Scheme 1. General Procedure for Huisgen 1,3-Dipolar Cycloaddition; $R = C_4H_9$, C_6H_{13} , C_8H_{17} , $C_{10}H_{21}$ or $C_{12}H_{25}$



chemistry can be performed after polymerization as a posttreatment on the polymer.²⁴⁻²⁷ Even though the use of click chemistry as a post-treatment has already been reported, the post-treatment effect on the surface morphology and wettability has never been investigated. Herein, we report the first use of click chemistry for superhydrophobic surface preparation.

In this work, we focus on the possibility of modifying the surface after electrodeposition. This strategy allows us to prepare a wide variety of surfaces using only one starting monomer with a post deposition modification. Postsynthesis modification is a very interesting way toward use of the diversity-oriented surface modification (DOSM). To investigate the effect on the surface morphology, we used specific electrochemical conditions to induce the formation of PEDOT nanofibers bearing azide groups. Indeed, it is known that polymer nanofibers are highly sensitive nanostructures because of their low stiffness and capillary forces (for example, they can collapse or coalesce).^{28–32} Here, we show that the resulting surface morphology and the hydrophobic surface properties are highly dependent on the used alkyne. We report the results using the following alkynes: 1-hexyne, 1-octyne, 1-decyne, 1-dodecyne, and 1-tetradecyne (Scheme 1).

 Received:
 April 10, 2015

 Revised:
 May 14, 2015

EXPERIMENTAL SECTION

Synthesis. The monomer was obtained in two steps following the procedure shown in Scheme 2.

Scheme 2. General Synthesis for Azidomethyl-EDOT: (i) *para*-toluenesulfonic acid 10% mol, toluene, 90 °C, 2 days; (ii) sodium azide 5 eq, DMF, 115 °C, 6 h



Compound 1: In a round bottomed flask, 2.5 g of 2,3dimethoxythiophene (17.3 mmol) were dissolved in 250 mL of toluene. Then, 8 g of 3-chloropropan-1,2-diol (72 mmol) and 323 mg of *para*-toluenesulfonic acid (1.7 mmol) were added. The mixture was warmed at 90 °C for 48 h. The mixture was then cooled to room temperature. The toluene phase was extracted twice with 30 mL of NaHCO₃ 5% in water and then washed with 30 mL of brine. The organic layer was then dried on Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The compound was finally purified on column (98/2 to 95/5, cyclohexane/ethyl acetate). Yield: 1.3 g of slightly yellow oil (39%). R_f: 0.67 (9/1, cyclohexane/ethyl acetate). All spectroscopic data agreed with the literature.³³

Compound 2: In a round bottomed flask, 1 g of compound 1 (5.2 mmol) was dissolved in DMF (100 mL). Then, 1.69 g of NaN₃ (26 mmol) was added and the mixture was stirred at 115 °C for 6 h. The mixture was allowed to cool to room temperature. Then, 100 mL of NH₄Cl saturated in water was added and the mixture was extracted three times with 100 mL of ether. The organic layers were combined and washed with 100 mL of brine. The organic phase was dried on Na₂SO₄ and filtered. The solvents were removed under reduced pressure. Compound 2 was finally purified on column (95/5, cyclohexane/ethyl acetate). Yield: 920 mg of colorless oil. R_j: 0.35 (9/1, cyclohexane/ethyl acetate).

 $δ_{\rm H}(200 \text{ MHz}, \text{CDCl}_3, \text{ ppm}): 6.39 (d, {}^{4}J_{HH} = 3.7 \text{ Hz}, 1\text{H}, thiophene hydrogene), 6.36 (d, {}^{4}J_{HH} = 3.7 \text{ Hz}, 1\text{H}, thiophene hydrogene), 4.34 (m, 1\text{H}, ethylenedioxy bridge), 4.20 (dd, {}^{2}J_{HH} = 11.7 \text{ Hz}, {}^{3}J_{HH} = 2.3 \text{ Hz}, 1\text{H}, ethylenedioxy bridge), 4.05 (dd, {}^{2}J_{HH} = 11.7 \text{ Hz}, {}^{3}J_{HH} = 6.8 \text{ Hz}, 1\text{H}, ethylenedioxy bridge), 3.54 (m, 2\text{H}, \text{CH}_2-\text{N}_3). δ_{\rm C}(50 \text{ MHz}, \text{CDCl}_3, \text{ppm}): 141.1 (C thiophene), 140.7 (C thiophene), 100.3 (CH thiophene), 100.1 (CH thiophene), 72.4 (CH–O), 65.8 (CH₂–O), 50.5 (CH₂–N₃). MS (70 eV),$ *m/z*(%): 196.9 (23) [M⁺], 141.0 (37) [C₆H₅O₂S^{+•}], 56.1 (100) [CH₂N₃^{+•}].

General Procedure for Click Chemistry on the Surface. The N_3 surface was immerged in 50/50 water/THF solution (5 mL). Then, 10 mg of CuSO₄ (0.06 mmol), 20 mg of sodium ascorbate (0.1 mmol), and 100 mg of alkyne (from 1.2 to 0.5 mmol depending on the alkyne length) were then added. The mixture was shaken overnight. The polymer was then successively washed three times with water and three times with ethanol. The polymer was then dried.

Electrochemical Deposition. In a glass cell containing 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) dissolved in dry acetonitrile, 0.01 M compound **2** was inserted. Three electrodes were put inside the solution. A gold plate (purchased from Neyco), glassy carbon rods, and saturated calomel

electrodes (SCE) were used as working, counter, and reference electrode, respectively. 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 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 a 6 μ L 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 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.

RESULTS AND DISCUSSION

Monomer Synthesis. The monomer azidomethyl-EDOT (2) was synthesized from 3,4-dimethoxythiophene as represented in Scheme 2. First, 3,4-dimethoxythiophene was reacted with 3-chloropropan-1,2-diol in acidic conditions (10% paratoluenesulfonic acid) over 2 days. That transetherification reaction gave the chloromethyl-EDOT (1) with a 39% yield. The second step was the substitution of the chlorine from compound 1 by an azido group. That reaction was carried out with sodium azide in DMF at 115 °C for 6 h. That second step provided azidomethyl-EDOT (2) with 89% yield.

Electrodeposition. Azidomethyl-EDOT was then electropolymerized on a gold-covered wafer as working electrode using a cyclic voltammetry procedure. The electropolymerization was carried out in 0.1 M tetrabutylammonium perchlorate in anhydrous acetonitrile (CH₃CN). The monomer oxidation potential for compound **2** was measured at 1.49 V vs saturated calomel electrode (SCE). To obtain highly homogeneous and adherent films, the cyclic voltammetry chosen was electrodeposition method. The electrodepositions were performed from -1 to 1.43 V at a scan rate of 20 mV/s and using different deposition scans (1, 3, and 5). The cyclic voltammogram after 5 deposition scans is given in Figure 1.



Figure 1. Cyclic voltammogram of compound 2 (0.01 M) on a Pt electrode recorded in 0.1 M tetrabutylammonium perchlorate/ CH_3CN .

Post-Treatment by Click Chemistry. These clickable surfaces could be finally modified using a post-treatment (Scheme 1) by immersion in solution of copper sulfate (CuSO₄) and sodium ascorbate, following procedures previously reported in the literature.²¹ Various alkynes have been used, from 1-hexyne to 1-tetradecyne. All the surfaces were then studied to investigate their surface wettabilities and morphologies.

Surface Characterization. The wettability results are given in Figure 2. All the surfaces after post-treatment displayed water



Figure 2. Water contact angle for nonmodified and modified surfaces.

apparent contact angle (θ) much higher than that of the polymer films with azido groups ($\theta = 117^{\circ}$), indicating that the post-treatment reactions were realized. Surpringely, the θ of the surfaces after post-treatment did not increase as the alkyl chain length of the used alkyne. This could be explained by a change in the surface morphology. Indeed, using 1-hexyne, $\theta = 156.5^{\circ}$ while dynamic contact angle measurements revealed a hysteresis $H = 21^{\circ}$ and a sliding angle $\alpha = 14.9^{\circ}$, proving that the surface was very close to having superhydrophobic properties ("Cassie-Baxter state").³⁴ As the alkyl chain length increased from 1-hexyne to 1-decyne, a large decrease in θ was observed as well as a large increase in the water adhesion. On these surfaces, a water droplet put on them remained completely stuck even after surface inclination of 90°. In the literature, such surface properties are called parahydrophobic³⁵ and are responsible for the water adhesion of red roses and gecko feet,^{36,37} for example. Using very long alkyl chains (1dodecyne or 1-tetradecyne), the surfaces were superhydrophobic and H and α were very low.

To understand these results, it was necessary to examine the surface morphology after each post-treatment. The scanning electron microscopy (SEM) images of the surface show a very nice evolution before and after modification (Figure 3). The clickable azido surface shows a well-defined fibrillar assembly (Figure 3 A). The fibrillary assembly is three-dimensional with a high porosity, explaining the high θ of 117° of these surfaces. The formation of the nanofibers can be explained by a unidirectional polymer growth. The growth on the surface usually occurred by formation of polymer nanoparticles or seeds followed by a preferential growth on these seeds.^{38,39} Usually, to induce unidirectional growth, it is necessary to have high intermolecular interactions as observed in the formation of polyamide fibers because of the presence of amide functions introducing hydrogen bonds. Hence, because of the presence of hydrogen bonds, the polyaniline $^{38-41}$ and polypyrrole 42,43 are the most employed conducting polymers for the formation of nanofibers. If there were no hydrogen bonds in the PEDOT structure, highly polar interactions were observed in this polymer, making it another choice polymer for the formation of nanofibers.^{10,11}



Article

Figure 3. SEM images of nonmodified and modified surface (scale bar: 1 μ m). Nonmodified surface (A) and modified surfaces with hexyne (B), octyne (C), decyne (D), dodecyne (E), and tetradecyne (F).

After the click reaction, that organization evolved differently depending on the length of the alkyne used for the click reaction. Using short alkyl chains (1-hexyne and 1-octyne), the fibrillar assembly collapsed to form needle mats (Figure 3B,C). The collapsing caused drastic changes in the surface roughness and porosities, explaining the differences observed in the surface hydrophobicity. Such structures are relatively close to that reported for anodized aluminum and more precisely using relatively long anodization time.⁴⁴ To have extremely high θ using short alkyl chains (1-hexyne) means that the surface morphology highly favors the Cassie-Baxter state.³⁴ Indeed, it is known that fibrous nanostructures are extremely interesting for reaching superhydrophobic and even superoleophobic properties because these structures possess re-entrant curvatures limiting the liquid penetration.^{45,46} Using longer alkyl chains (1-decyne to 1-tetradecyne), the surface morphology was modified but the fibrillar assembly of the polymer was preserved (the porous network is preserved). The organization became more and more rough with the increase of the chain length (Figure 3D–F). To have a decrease in θ between C₈ and C_{10} means that the surface morphology of C_{10} induces less reentrant curvatures due probably to the high porosity.

CONCLUSION

We have shown for the first time the possibility of using click chemistry both to modify surface morphology and to obtain superhydrophobic properties. By modifying PEDOT nanofibers with azido groups, we showed that the nanofibers are affected by the used alkyne leading to various hydrophobic or superhydrophobic properties. This work reveals widely varied strategies for modifying nanostructured surfaces while introducing various functions.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Frederic.Guittard@unice.fr. Tel: (+33)4 92 07 61 59.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Jean-Pierre Laugier of the Centre Commun de Microscopie Appliquée (CCMA, Université Nice Sophia Antipolis) for the realization of the SEM images.

REFERENCES

(1) Tian, Y.; Su, B.; Jiang, L. Interfacial Material System Exhibiting Superwettability. *Adv. Mater.* **2014**, *26*, 6872–6897.

(2) Bellanger, H.; Darmanin, T.; Taffin de Givenchy, E.; Guittard, F. Chemical and Physical Pathways for the Preparation of Superoleophobic Surfaces and Related Wetting Theories. *Chem. Rev.* **2014**, *114*, 2694–2716.

(3) Darmanin, T.; Guittard, F. Recent Advances in the Potential Applications of Bioinspired Superhydrophobic Materials. *J. Mater. Chem. A* **2014**, *2*, 16319–16359.

(4) Si, Y.; Guo, Z. Superhydrophobic Nanocoatings: From Materials to Fabrications and to Applications. *Nanoscale* **2015**, *7*, 5922–5946.

(5) Erbil, H. Y.; Demirel, A. L.; Avcı, Y.; Mert, O. Transformation of a Simple Plastic into a Superhydrophobic Surface. *Science* **2003**, *299*, 1377–1380.

(6) Long, Y.-Z.; Li, M.-M.; Gu, C.; Wan, M.; Duvail, J.-L.; Liu, Z.; Fan, Z. Recent Advances in Synthesis, Physical Properties and Applications of Conducting Polymer Nanotubes and Nanofibers. *Prog. Polym. Sci.* **2011**, *36*, 1415–1442.

(7) Darmanin, T.; Guittard, F. Wettability of Conducting Polymers: From Superhydrophilicity to Superoleophobicity. *Prog. Polym. Sci.* **2014**, *39*, 656–682.

(8) Li, C.; Bai, H.; Shi, G. Conducting Polymer Nanomaterials: Electrosynthesis and Applications. *Chem. Soc. Rev.* **2009**, *38*, 2397–2409.

(9) Beaujuge, P. M.; Reynolds, J. R. Color Control in π -Conjugated Organic Polymers for Use in Electrochromic Devices. *Chem. Rev.* **2010**, 110, 268–320.

(10) Turbiez, M.; Frere, P.; Allain, M.; Gallego-Planas, N.; Roncali, J. Effect of Structural Factor on the Electropolymerization of Bithiophenic Precursors Containing a 3,4-Ethylenedisulfanylthiophene Unit. *Macromolecules* **2005**, *38*, 6806–6812.

(11) Raimundo, J.-M.; Blanchard, P.; Frère, P.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. Push–Pull Chromophores Based on 2,2′-bi(3,4-ethylenedioxythiophene) (BEDOT) π -Conjugating Spacer. *Tetrahedron Lett.* **2001**, 42, 1507–1510.

(12) Darmanin, T.; Guittard, F. Superhydrophobic Fiber Mats by Electrodeposition of Fluorinated Poly(3,4-ethyleneoxythiathiophene). *J. Am. Chem. Soc.* **2011**, *133*, 15627–15634.

(13) Darmanin, T.; Mortier, C.; Eastoe, J.; Sagisaka, M.; Guittard, F. Sticky Superhydrophobic Hard Nanofibers from Soft Matter. *RSC Adv.* **2014**, *4*, 35708–35716.

(14) Darmanin, T.; Guittard, F. Homogeneous Growth of Conducting Polymer Nanofibers by Electrodeposition for Superhydrophobic and Superoleophilic Stainless Steel Meshes. *RSC Adv.* **2014**, *4*, 50401–50405.

(15) Luo, S.-C.; Sekine, J.; Zhu, B.; Zhao, H.; Nakao, A.; Yu, H.-h. Polydioxythiophene Nanodots, Nonowires, Nano-Networks, and Tubular Structures: The Effect of Functional Groups and Temperature in Template-Free Electropolymerization. *ACS Nano* **2012**, *6*, 3018–3026.

(16) Zhu, H.; Guo, Z.; Liu, W. Adhesion Behaviors on Superhydrophobic Surfaces. *Chem. Commun.* **2014**, *50*, 3900–3913.

(17) Cheng, Z.; Gao, J.; Jiang, L. Tip Geometry Controls Adhesive States of Superhydrophobic Surfaces. *Langmuir* **2010**, *26*, 8233–8238.

(18) Huisgen, R. In 1,3-Dipolar Cycloaddition Chemistry; Wiley: New York, 1984; pp 1–176.

(19) Tornøe, C. W.; Christensen, C.; Meldal, M. Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides. *J. Org. Chem.* **2002**, *67*, 3057–3064.

(20) Michinobu, T. Adapting Semiconducting Polymer Doping Techniques to Create New Types of Click Postfunctionalization. *Chem. Soc. Rev.* **2011**, *4*, 2306–2316.

(21) Godeau, G.; Arnion, H.; Brun, C.; Staedel, C.; Barthelemy, P. Fluorocarbon Oligonucleotide Conjugates for Nucleic Acids Delivery. *MedChemComm* **2010**, *1*, 76–78.

(22) Rao, H.; Sawant, A. A.; Tanpure, A. A.; Srivatsan, S. G. Posttranscriptional Chemical Functionalization of Azide-Modified Oligoribonucleotides by Bioorthogonal Click and Staudinger Reactions. *Chem. Commun.* **2012**, *48*, 498–500.

(23) Bu, H.-B.; Goetz, G.; Reinold, E.; Vogt, A.; Schmid, S.; Blanco, R.; Segura, J. L.; Baeuerle, P. "Click"-Functionalization of Conducting Poly(3,4-ethylenedioxythiophene) (PEDOT). *Chem. Commun.* **2008**, 1320–1322.

(24) Bu, H.-B.; Goetz, G.; Reinold, E.; Vogt, A.; Azumi, R.; Segura, J. L.; Baeuerle, P. "Click"-Modification of a Functionalized Poly(3,4-ethylenedioxythiophene) (PEDOT) Soluble in Organic Solvents. *Chem. Commun.* **2012**, *48*, 2677–2679.

(25) Sinha, J.; Sahoo, R.; Kumar, A. Processable, Regioregular, and "Click"able Monomer and Polymers Based on 3,4-Propylenedioxythiophene with Tunable Solubility. *Macromolecules* **2009**, *42*, 2015–2022.

(26) Scavetta, E.; Mazzoni, R.; Mariani, F.; Margutta, R. G.; Bonfiglio, A.; Demelas, M.; Fiorilli, S.; Marzocchi, M.; Fraboni, B. Dopamine Amperometric Detection at a Ferrocene Clicked PEDOT:PSS Coated Electrode. *J. Mater. Chem. B* **2014**, *2*, 2861–2867.

(27) Xu, J.; Tian, Y.; Peng, R.; Xian, Y.; Ran, Q.; Jin, L. Ferrocene Clicked Poly(3,4-ethylenedioxythiophene) Conducting Polymer: Characterization, Electrochemical and Electrochromic Properties. *Electrochem. Commun.* **2009**, *11*, 1972–1975.

(28) Chandra, D.; Yang, S. Stability of High-Aspect-Ratio Micropillar Arrays against Adhesive and Capillary Forces. *Acc. Chem. Res.* **2010**, *43*, 1080–1091.

(29) Grinthal, A.; Kang, S. H.; Epstein, A. K.; Aizenberg, M.; Khan, M.; Aizenberg, J. Steering Nanofibers: An Integrative Approach to Bio-Inspired Fiber Fabrication and Assembly. *Nano Today* **2011**, *7*, 35–52.

(30) Guenthner, A. J.; Khombhongse, S.; Liu, W.; Dayal, P.; Reneker, D. H.; Kyu, T. Dynamics of Hollow Nanofiber Formation During Solidification Subjected to Solvent Evaporation. *Macromol. Theory Simul.* **2006**, *15*, 87–93.

(31) Wu, X.-F.; Dzenis, Y. A. Collapse Analysis of Nanofibres. Nanotechnology **2007**, 18, 285702/1–285702/6.

(32) Kustandi, T. S.; Samper, V. D.; Yi, D. K.; Ng, W. S.; Neuzil, P.; Sun, W. Self-Assembled Nanoparticles Based Fabrication of Gecko Foot-Hair-Inspired Polymer Nanofibers. *Adv. Funct. Mater.* **2007**, *17*, 2211–2218.

(33) Segura, J. L.; Gómez, R.; Reinold, E.; Baeuerle, P. Synthesis and Electropolymerization of a Perylenebisimide-Functionalized 3,4-Ethylenedioxythiophene (EDOT) Derivative. *Org. Lett.* **2005**, *7*, 2345–2348.

(34) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–551.

(35) Marmur, A. Hydro- Hygro- Oleo- Omni-Phobic? Terminology of Wettability Classification. *Soft Matter* **2012**, *8*, 6867–6870.

(36) Koch, K.; Bhushan, B.; Barthlott, W. Diversity of Structure, Morphology and Wetting of Plant Surfaces. *Soft Matter* **2008**, *4*, 1943–1963.

(37) Liu, K.; Du, J.; Wu, J.; Jiang, L. Superhydrophobic Gecko Feet with High Adhesive Forces towards Water and their Bio-Inspired Materials. *Nanoscale* **2012**, *4*, 768–772.

(38) Liang, L.; Liu, J.; Windisch, C. F., Jr.; Exarhos, G. J.; Lin, Y. Direct Assembly of Large Arrays of Oriented Conducting Polymer Nanowires. *Angew. Chem., Int. Ed.* **2002**, *41*, 3665–3668.

(39) Huang, J.; Kaner, R. B. A General Chemical Route to Polyaniline Nanofibers. J. Am. Chem. Soc. 2004, 126, 851–855.

(40) Zhu, Y.; Li, J.; Wan, M.; Jiang, L. Superhydrophobic 3D Microstructures Assembled from 1D Nanofibers of Polyaniline. *Macromol. Rapid Commun.* **2008**, *29*, 239–243.

(41) Xu, L.; Chen, Z.; Chen, W.; Mulchandani, A.; Yan, Y. Electrochemical Synthesis of Perfluorinated Ion Doped Conducting Polyaniline Films Consisting of Helical Fibers and their Reversible Switching between Superhydrophobicity and Superhydrophilicity. *Macromol. Rapid Commun.* **2008**, *29*, 832–838.

(42) Zang, J.; Li, C. M.; Bao, S.-J.; Cui, X.; Bao, Q.; Sun, C. Q. Template-Free Electrochemical Synthesis of Superhydrophilic Polypyrrole Nanofiber Network. *Macromolecules* **2008**, *41*, 7053–7057.

(43) Zhong, W.; Liu, S.; Chen, X.; Wang, Y.; Yang, W. High-Yield Synthesis of Superhydrophilic Polypyrrole Nanowire Networks. *Macromolecules* **2006**, *39*, 3224–3230.

(44) Jeong, C.; Choi, C.-H. Single-Step Direct Fabrication of Pillaron-Pore Hybrid Nanostructures in Anodizing Aluminum for Superior Superhydrophobic Efficiency. *ACS Appl. Mater. Interfaces* **2012**, *4*, 842–848.

(45) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. Designing Superoleophobic Surfaces. *Science* **2007**, *318*, 1618–1622.

(46) Darmanin, T.; Guittard, G. Superoleophobic Surfaces with Short Fluorinated Chains? *Soft Matter* **2013**, *9*, 5982–5990.