



Superhydrophobic (low adhesion) and parahydrophobic (high adhesion) surfaces with micro/nanostructures or nanofilaments

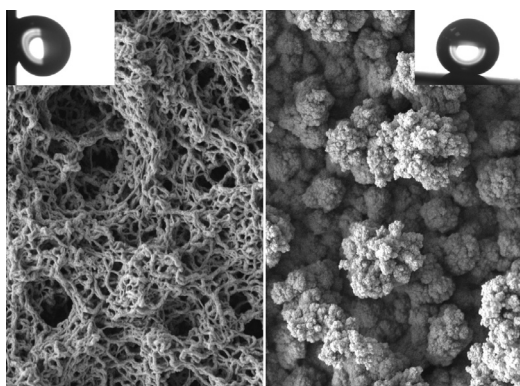


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GRAPHICAL ABSTRACT



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ABSTRACT

Controlling the water adhesion is extremely important for various applications such as for water harvesting. Here, superhydrophobic (low adhesion) and parahydrophobic (high adhesion) substrates are both obtained from hydrophilic polymers. We show in the work that a judicious choice in the monomer structure used for electropolymerization can lead to these two properties. Using a phenyl group, parahydrophobic properties are reached due to the formation of nanofilaments. By contrast, using a naphthalene or a biphenyl group, superhydrophobic properties are obtained due the formation of both micro- and nanostructures.

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1. Introduction

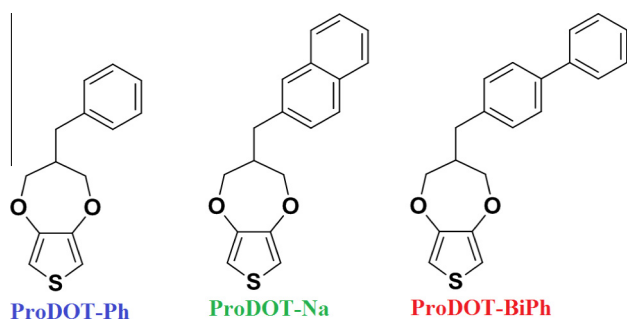
Extremely various applications are dependent on the surface wetting properties. Among these applications, we can cite cookware coatings, self-cleaning textiles, anti-fingerprint optical devices, drag reduction and microfluidic devices, water harvesting,

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separation membranes, anti-corrosion and anti-bacteria coatings, cell/protein adhesion, sensors, solar cells, batteries and catalysis [1–4]. Whatever the surface chemistry, the apparent contact angle of a water droplet put on a smooth substrate, also called Young angle (θ_w^y) [5], is limited to about 125–130° [6,7]. To exceed this chemical limit, the presence of surface roughness is necessary. The effect of surface roughness on the surface hydrophobicity can have different effects [8–10]. For example, it can lead to superhydrophobic properties characterized by apparent water contact

angle (θ_w) > 150° and low adhesion, as observed in Nature on lotus leaves [11,12]. It is also possible to have $\theta_w > \theta_w^Y$ but with high adhesion. Such surface properties are called parahydrophobic [8] and are responsible of the high adhesion of gecko leaves or red roses, for example [13,14]. Hence, it is extremely important to find a strategy to control the adhesion of hydrophobic materials [15]. The water adhesion is extremely dependent on the shape of the surface structures [16–20]. For example, Jiang et al. showed that the adhesion of aligned polystyrene (PS) nanopillars can be controlled with the geometry of their tips [16]. More precisely, PS nanopillars with flat and concave tips exhibited high adhesion while nanotubes exhibited low adhesion. Otherwise, the water adhesion can also be controlled by applying an external energy (electric, luminous, thermal, or mechanical). For example, Jiang et al. changed the underwater oil adhesion of ZnO nanorods by UV irradiation [21]. The authors determined the adhesive forces with liquid droplet versus distance curves on different substrates using a microelectromechanical balance system.

Because conducting polymers [22] can also lead to various nanostructures [23–25], they can be used to control the water adhesion. Different nanostructures such as nanofibers, nanotubes, nanosheets can be produced in solution. Because of the presence of hydrogen bonds, polyaniline is probably the most studied conducting polymer to obtain nanostructured materials [26–28]. For the other conducting polymers, hard and soft templates are very often used [29–32]. To induce the growth of nanostructures directly on substrates and without template, the electropolymerization can be employed [33]. This fast process allows the control on the surface nanostructures by adjusting the electrochemical parameters but the shape of the nanostructures is also highly dependent on the used monomer. For example, the monomers derived from 3,4-ethylenedioxythiophene (EDOT) or 3,4-propylenedioxythiophene (ProDOT) can induce the formation of various nanostructures including nanofibers, nanosheets, flower-like structures or cauliflower-like structure [34–38]. Moreover, the surface hydrophobicity can also be tuned by introducing hydrophobic substituents in order to modify the θ_w^Y [38]. Fluorocarbon and hydrocarbon chains were investigated in the literature but their use often led to superhydrophobic properties with low adhesion. In order to induce a high increase in the water adhesion, it is necessary to reduce the θ_w^Y while keeping the nanostructures. Previously, this possibility was performed by introducing branching in hydrophobic chains [39]. In this work, we investigate their replacing by using aromatic cycles having lower θ_w^Y than linear hydrocarbon chains. Moreover, the rigidity of the aromatic rings facilitates the electrodeposition process. We report the surface properties of electrodeposited films obtained using the three ProDOT derived monomers bearing a phenyl, a naphthalene and a biphenyl group, as shown in Scheme 1.



Scheme 1. Monomers investigated in this work.

2. Materials and methods

2.1. Monomer synthesis

The monomers were synthesized in three steps from diethylmalonate by adjusting a procedure reported in the literature (Scheme 2) [40,41]. This synthetic way is very advantageous because it can lead in three steps to various ProDOT derivatives with one and even two substituents in the 3-position. The three steps consists in the C-alkylation of diethylmalonate in the presence of potassium carbonate (K_2CO_3) and the corresponding bromide. Then, the two ester groups are reduced into alcohols and the resulting 1,3-diols are used in a transesterification reaction with 3,4-dimethoxythiophene. More precisely, 10 g of diethylmalonate (1 eq., 62.5 mmol), the corresponding bromide (1.5 eq., 93.7 mmol) and 25.8 g of K_2CO_3 (3 eq., 187.5 mmol) were mixed to 100 mL of acetonitrile. After stirring for 72 h at 70 °C, the solvent was removed and the resulting products (**1a–c**) were distilled under vacuum.

2.1.1. Diethyl 2-benzylmalonate (**1a**)

Yield 80%; δ_H (200 MHz, $CDCl_3$): 7.22 (5 H, m), 4.16 (4 H, q, J 7.2), 3.64 (1 H, t, J 7.9), 3.21 (2 H, d, J 7.9), 1.20 (6 H, t, J 7.2).

2.1.2. Diethyl 2-(naphthalen-2-ylmethyl)malonate (**1b**)

Yield 80%; δ_H (200 MHz, $CDCl_3$): 7.84 (4 H, m), 7.49 (3 H, m), 4.15 (4 H, q, J 7.1), 3.75 (1 H, t, J 7.8), 3.38 (2 H, d, J 7.8), 1.19 (6 H, t, J 7.1).

2.1.3. Diethyl 2-([1,1'-biphenyl]-4-ylmethyl)malonate (**1c**)

Yield 72%; δ_H (200 MHz, $CDCl_3$): 7.47 (9 H, m), 4.19 (4 H, q, J 7.1), 3.69 (1 H, t, J 7.8), 3.27 (2 H, d, J 7.8), 1.23 (6 H, t, J 7.1).

In 20 mL of anhydrous tetrahydrofuran (THF) containing 26.3 mmol of **1a–c** were carefully 2.5 g of lithium aluminum hydride ($LiAlH_4$) (65.7 mmol). After stirring for 24 h at 80 °C, an aqueous solution of sulfuric acid (H_2SO_4) (10%) was added dropwise until all the aluminum complexes were hydrolyzed. Then, the THF was removed and the products were extracted by ethyl acetate. The solution was dried on sodium sulfate (Na_2SO_4), the solvent was evaporated to yield after distillation under vacuum the products (**2a–c**).

2.1.4. 2-benzylpropane-1,3-diol (**2a**)

Yield 70%; δ_H (200 MHz, $CDCl_3$): 7.26 (5 H, m), 3.82 (2 H, dd, J 10.6, J 3.9), 3.68 (2 H, dd, J 10.6, J 6.8), 2.63 (2 H, d, J 7.5), 2.08 (1 H, m).

2.1.5. 2-(naphthalen-2-ylmethyl)propane-1,3-diol (**2b**)

Yield 69%; δ_H (200 MHz, CD_3OD): 7.78 (4 H, m), 7.40 (3 H, m), 3.59 (4 H, d, J 5.7), 2.82 (2 H, d, J 7.3), 2.04 (1 H, m).

2.1.6. 2-([1,1'-biphenyl]-4-ylmethyl)propane-1,3-diol (**2c**)

Yield 77%; δ_H (200 MHz, $CDCl_3$): 7.42 (9 H, m), 3.83 (2 H, dd, J 10.6, J 3.9), 3.68 (2 H, dd, J 10.6, J 6.7), 2.68 (2 H, d, J 7.1), 2.08 (1 H, m).

2.5 g of 3,4-dimethoxythiophene (1 eq., 17.4 mmol), **2a–c** (1.5 eq., 26.1 mmol) and 200 mg of *para*-toluenesulfonic acid (*p*-TSA) were introduced in 200 mL of toluene. After stirring for 24 h at 95 °C, 100 mL of water were added and the products were extracted by ethyl acetate. The solution was dried on Na_2SO_4 and the solvent was evaporated to yield after chromatography column (stationary phase: silica gel; eluent: cyclohexane/diethyl ether 75:25) the monomers.

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