

Research Article

Bioinspired Nanotubular Structures by Soft-Template Electropolymerization: 3,4-(2,3-naphtylenedioxy)Thiophene Monomers Quenched to Form Dimers

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Abstract

Preparing well-ordered nanotubes on materials surface is a great of interest in many applications. Bio-inspired and theoretical approaches show that porous structures such as nanotubes are key parameters for both surface hydrophobicity and water adhesion. Here, a very easy soft-template electropolymerization approach is used to form nanotubular structures, followed by a bioinspired strategy to control the wetting properties. Fully conjugated monomers based on 3,4-(2,3-naphtylenedioxy)thiophene (NaphDOT) core grafted with many rigid aromatic groups such as phenyl, naphthalene, pyrene, pyrrole, were synthesized. Then, electropolymerization is carried out with these monomers, followed by surface and morphologies characterization of corresponding polymers. We show that even if just dimers are formed by electropolymerization, the resulting polymer can be sufficiently insoluble to form structured films. 3,4-(2,3-naphtylenedioxy)thiophene (NaphDOT) is chosen as a judicious example, due to strong π -stacking interactions, and also their capacity to form nanotubular structures by soft template-electropolymerization in the presence of water (H₂O). Here, different substituents, polymerizable or not, are grafted on the 2-position of thiophene. Films are formed with all the studied substituents. Nanotubular structures are especially observed with the following substituents: hydroxyl, pyrene and pyrrole, but in the presence of H₂O. We study also their influence on the surface hydrophobicity.

Keywords

Nanostructures, Nanotubes, Electrochemistry, Wettability, Hydrophobicity

1. Introduction

The bioinspiration is a fascinating to make a breakthrough in a specific field [1-5]. This is particularly true in the wetting field [6-11]. For example, controlling both the surface energy and the surface structures at a micro and/or nanoscale can

induce a huge increase in surface hydrophobicity [12, 13]. The air fraction of rough surfaces being very important as demonstrated by Cassie-Baxter [14], nanotubes were found to be excellent candidates to tune surface hydrophobicity and

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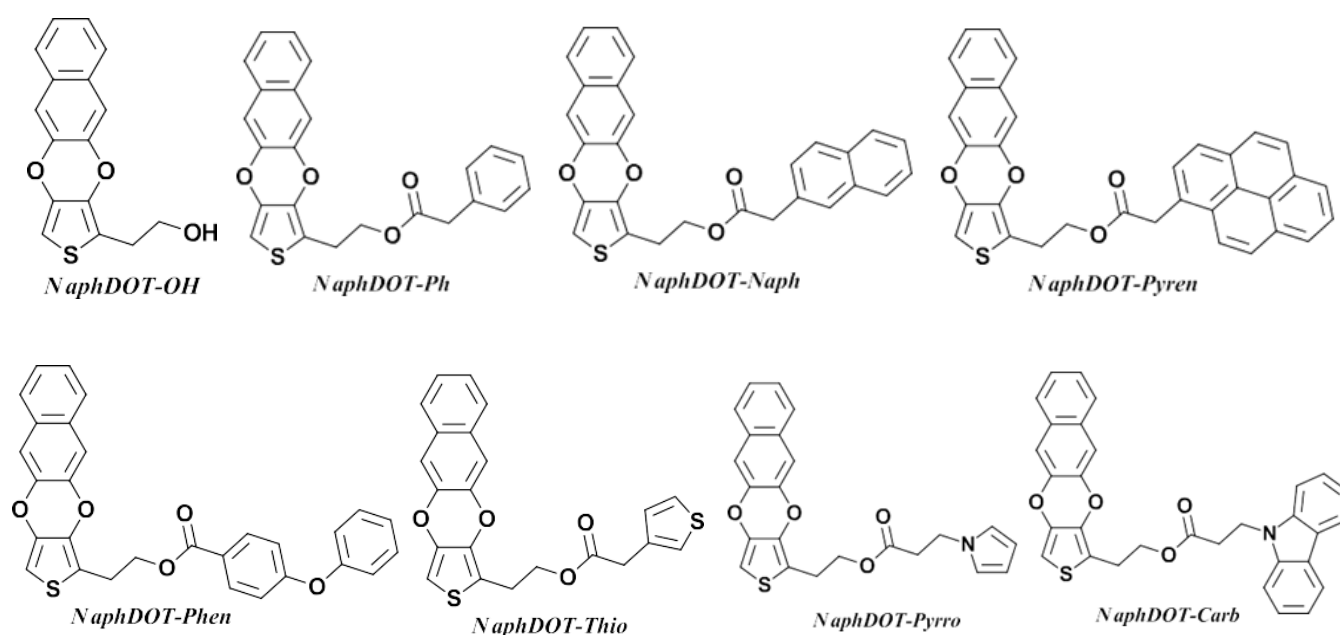
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water adhesion, due to their specific aspect ratio [15-17].

Among the processes for preparing rough surfaces, the electropolymerization has various advantages including the rapidity to implement and the control of surface structures [18]. To obtain porous structures such as nanotubes by electropolymerization, one of the strategies is for inducing the polymer growth around a template [19-21]. It was reported in the literature this possibility using hard templates such as anodized aluminium oxide (AAO) membranes. However, this process is long, multi-step and one membrane is necessary for each variation in the nanotube dimension. This is why processes of templateless or soft-template electropolymerization were recently developed. These processes are possible if soft objects including gas bubbles or micelles are present around a substrate. The case of the electropolymerization of pyrrole directly in H_2O has been particularly studied [22, 23]. During electropolymerization and depending on the electropolymerization method, different gases (dioxygen O_2 and hydrogen H_2) can be generated *in-situ* from H_2O , and leading to various nanotubular structures. However, most of the monomers being not soluble in H_2O , this strategy has been also envisaged in organic solvents such dichloromethane (CH_2Cl_2) or chlo-

roform ($CHCl_3$) [22-28]. Particularly, 3,4-(2,3-naphthylenedioxy)thiophene (NaphDOT) was demonstrated as a model molecule leading to vertically aligned nanotubes with high hydrophobicity and water adhesion [29, 30]. Moreover, it was also demonstrated that this monomer can form micelles in solvents of low water solubility (CH_2Cl_2 or $CHCl_3$, for example) as soon as trace H_2O are present in solution [30].

Previously, we demonstrated using NaphDOT that even if one substituent is positioned in polymerization position (2-position) leading to dimers, the resulting polymer can be sufficiently insoluble to form deposit and use in soft-template electropolymerization [31]. This is mainly due to the strong π -stacking interactions. Here, we want to confirm these preliminary results by designing other NaphDOT derivatives (Scheme 1). We want also to show the influence of the electropolymerizable substituent in the used potential range (naphthalene, pyrene, thiophene, pyrrole, and carbazole) compared to non-electropolymerizable substituents (hydroxyl, phenyl, and phenoxyphenyl). The electropolymerizations were performed in CH_2Cl_2 and CH_2Cl_2 saturated with H_2O ($CH_2Cl_2 + H_2O$ sat.).

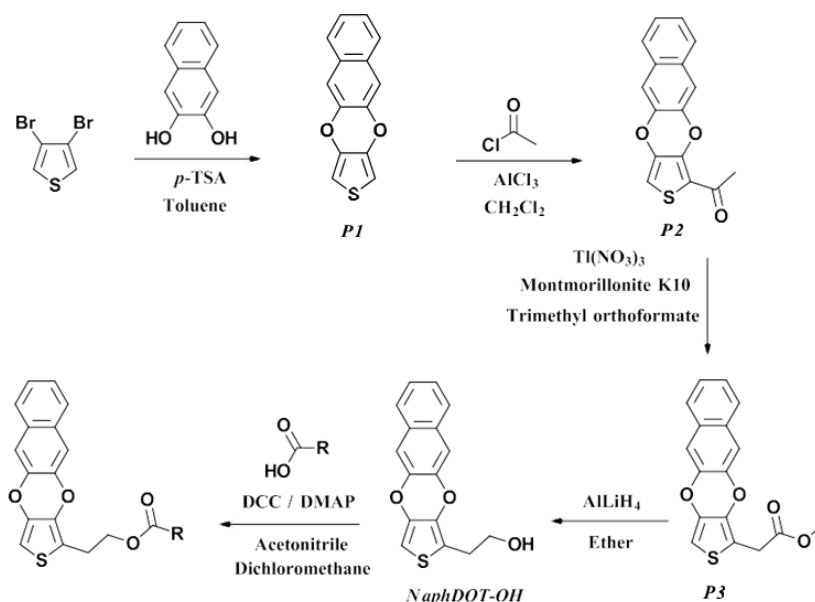


Scheme 1. Original monomers studied in this manuscript.

2. Experimental Section

2.1. Monomer Synthesis

The monomers were synthesized in five steps from 3,4-dibromothiophene, as described in Scheme 2.



Scheme 2. Chemical way to the monomers.

Naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxine (P1) was synthesized as reported in literature [32]. Synthesis of 1-(naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxin-7-yl)ethanone (P2):

Aluminum chloride (2.0 g, 15.1 mmol, 1.5 eq) in 55 mL of anhydrous CH_2Cl_2 was added under argon to NaphDOT (2.4 g, 10.1 mmol, 1 eq) in 200 mL of anhydrous dichloromethane. The mixture was cooled and acetyl chloride (1.60 g, 20.5 mmol, 2 eq) was added dropwise into it under argon flow. The mixture was then stirred at room temperature for a night. Then, hydrochloric acid (50 mL, 1M) was added to quench the solution and the mixture was washed with CH_2Cl_2 , dried on Na_2SO_4 and the solvent evaporated. The product (2) was purified by column chromatography (silica gel; eluent: CH_2Cl_2).

Yield: 63%; Dark brown solid; δH (200 MHz, CDCl_3): 7.70 (2H, m), 7.40 (4H, m), 6.83 (1H, s), 2.69 (3H, s); δC (50 MHz, CDCl_3): 189.11, 140.72, 139.56, 139.43, 138.55, 130.93, 130.37, 126.98, 126.91, 126.00, 125.77, 120.94, 113.21, 112.83, 108.45, 29.31.

Synthesis of methyl 2-(naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxin-7-yl)acetate (P3) [33]:

Thallium (III) nitrate (3.1 g, 7.0 mmol, 1.2 eq) was stirred with trimethoxymethane (7.7g, 72.7 mmol, 12.3 eq) in methanol (10 mL) for 5 min. Montmorillonite K10 (6.6 g) was added and the mixture was stirred for 10 min. The solvent was evaporated, P2 (1.7 g, 6.6 mol, 1 eq) was added in 200 mL of methanol/dichloromethane (1:1). The mixture was stirred at room temperature for 2 days. The product was then purified by column chromatography (silica gel; eluent: CH_2Cl_2).

Yield: 37.2%; Beige solid; δH (200 MHz, CDCl_3): 7.68 (2H, m), 7.35 (4H, m), 6.44 (1H, s), 3.80 (2H, s), 3.77 (3H, s); δC (50 MHz, CDCl_3): 169.59, 140.35, 140.16, 137.98, 137.55,

130.57, 130.40, 126.83, 125.52, 125.46, 112.98, 112.90, 112.67, 101.54, 52.70, 31.04.

Synthesis of 2-(naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxin-7-yl)ethanol (NaphDOT-OH):

To obtain the corresponding alcohol, the ester function was reduced with LiAlH_4 in anhydrous diethyl ether for 1 day and then by performing a basic hydrolysis (4 mg of NaOH in 200 ml of distilled water). The product was then purified by column chromatography (silica gel; eluent: CH_2Cl_2).

Yield: 75%; White powder, $T_f = 126.6^\circ\text{C}$; δH (200 MHz, $\text{DMSO}-d_6$): 7.77 (dd, $J = 6.27\text{ Hz}$, $J = 3.30\text{ Hz}$, 2H), 7.57 (d, $J = 5.7\text{ Hz}$, 2H), 7.39 (m, 2H), 6.82 (s, 1H), 3.64 (t, $J = 6.5\text{ Hz}$, 2H), 3.36 (s, 1H), 2.86 (t, $J = 6.5\text{ Hz}$, 2H); δC (200 MHz, $\text{DMSO}-d_6$): 145.20, 145.15, 142.37, 139.46, 135.33, 135.29, 131.98, 130.63, 121.76, 117.75, 117.62, 104.09, 65.81, 34.29.

Synthesis of the other monomers:

The corresponding acid (1.2 eq) was mixed with dicyclohexylcarbodiimide (DCC) (138 mg, 1.2 eq) and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) in absolute acetonitrile (20 mL). After stirring for 30 min, 1.0 eq. of NaphDOT-OH was added to this mixture. The mixture was stirred at room temperature for 24 h. After a night, the solvents were totally evaporated and the crude product was purified by silica gel column (eluent CH_2Cl_2 : cyclohexane with proportions depending on the monomer).

2-(naphtho[2,3-*b*]thieno[3,4-*e*][1,4]dioxin-7-yl)ethyl 2-phenylacetate: Yield: 95 %; yellow powder, $T_f = 72.6^\circ\text{C}$; δH (400 MHz, CDCl_3): 7.65 (m, 2H), 7.34 (dd, $J = 3.24\text{ Hz}$, $J = 6.3\text{ Hz}$, 2H), 7.30 (m, 3H), 7.27 (d, 1.0Hz, 1H), 7.22 (m, 1H), 7.15 (d, $J = 1.5\text{ Hz}$, 1H), 7.13 (s, 1H), 6.34 (s, 1H), 4.33 (t, $J = 6.6\text{ Hz}$, 2H), 3.64 (s, 2H), 3.07 (t, $J = 6.6\text{ Hz}$, 2H); δC (400 MHz, CDCl_3): 170.39, 139.51, 137.19, 134.59, 132.96, 132.79, 129.41, 128.48, 127.69, 127.51, 126.06, 125.76, 124.28,

113.14, 111.58, 111.49, 97.15, 62.78, 40.35, 24.41.

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-naphtalenacetate: Yield: 79 %; T_f = 89.5 °C, White powder; δ H(400 MHz, CDCl₃): 7.74 (m, 4H), 7.68 (s, 1H), 7.62 (m, 2H), 7.40 (m, 2H), 7.26 (d, J = 2.2 Hz, 2H), 7.23 (s, 1H), 7.28 (s, 1H), 6.34 (s, 1H), 4.34 (t, J = 6.6 Hz, 2H), 3.78 (s, 2H), 3.05 (t, J = 6.6 Hz, 2H); δ C(400 MHz, CDCl₃): 170.36, 139.49, 137.17, 134.6, 132.37, 132.42, 130.26, 129.40, 127.39, 127.32, 127.17, 127, 126.66, 126.59, 126.48, 126.31, 125.76, 125.21, 125.06, 124.85, 124.71, 124.25, 111.55, 97.11, 62.81, 40.55, 24.43.

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-pyrenacetate: Yield: 95 %; T_f = 151.5 °C, Yellow powder; δ H(400 MHz, CDCl₃): 8.19 (s, 1H), 8.14 (m, 1H), 8.1 (d, J = 1.4 Hz, 2H), 8.06 (d, J = 1.4 Hz, 1H), 8.02 (d, J = 2.0 Hz, 2H), 7.99 (d, J = 1.3 Hz, 1H), 7.95 (d, J = 1.0 Hz, 2H), 7.9 (m, 2H), 7.57 (m, 2H), 7.32 (m, 2H), 7.13 (d, J = 5.1 Hz, 2H), 6.12 (s, 1H), 4.41 (t, J = 6.36 Hz, 2H), 4.37 (s, 2H), 3 (t, J = 6.4 Hz, 2H); δ C(400 MHz, CDCl₃): 171.44, 140.25, 137.99, 131.22, 130.77, 130.32, 129.41, 128.35, 127.86, 127.29, 127.018, 126.75, 126, 125.88, 125.18, 125.05, 124.88, 124.64, 123.17, 113.97, 112.37, 97.91, 63.77, 39.63, 25.44.

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethylcarbazole: Yield: 99 % T_f = 135.9 °C; White powder; δ H(400 MHz, CDCl₃): 7.93 (d, J = 1.0 Hz, 1H), 7.89 (d, J = 1.0 Hz, 1H), 7.49 (m, 2H), 7.26 (m, 4H), 7.15 (m, 4H), 7.05 (m, 2H), 6.15 (s, 1H), 4.48 (t, J = 7.1 Hz, 2H), 4.11 (t, J = 6.6 Hz, 2H), 2.81 (t, J = 6.6 Hz, 2H), 2.72 (t, J = 7.4 Hz, 2H); δ C(400 MHz, CDCl₃): 171.23, 140.53, 140.50, 139.96, 138.24, 135.62, 130.47, 126.81, 125.81, 125.36, 123.11, 120.43, 119.23, 113.97, 112.61, 108.57, 98.26, 63.87, 38.7, 33.56, 25.3;

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-thiophenacetate: Yield: 86 % T_f = 60.5 °C; White powder; δ H(400 MHz, CDCl₃): 7.65 (m, 2H), 7.34 (dd, J = 3.2 Hz, J = 6.3 Hz, 2H), 7.30 (m, 3H), 7.27 (d, 1.0 Hz, 1H), 7.22 (m, 1H), 7.15 (d, J = 1.5 Hz, 1H), 7.13 (s, 1H), 6.34 (s, 1H), 4.33 (t, J = 6.6 Hz, 2H), 3.64 (s, 2H), 3.07 (t, J = 6.6 Hz, 2H); δ C(400 MHz, CDCl₃): 169.91, 139.51, 137.22, 134.63, 132.58, 132.34, 129.42, 127.47, 125.78, 124.97, 124.67, 124.3, 122.06, 121.93, 113.13, 111.58, 97.18, 62.84, 42.38, 34.83, 24.43.

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl phenoxyphenylacetate: Yield: 55 %; T_f = 98.8 °C; δ H(200 MHz, CDCl₃): 7.97 (dd, J = 6.9 Hz, J = 2.1 Hz, 2H), 7.54 (m, 2H), 7.30 (m, 3H), 7.22 (m, 4H), 7.11 (m, 2H), 6.87 (m, 4H), 6.27 (s, 1H), 4.44 (t, J = 6.3 Hz, 2H), 3.11 (t, J = 6.3 Hz, 2H); δ C(200 MHz, CDCl₃): 161.97, 140.5, 131.86, 130.42, 130.02, 126.8, 125.33, 124.54, 124.31, 120.19, 117.17, 114.51, 112.58, 112.51, 98.22, 64.07, 25.68.

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-pyrrolate: Yield: 68 %; T_f = 109.8 °C; δ H(400 MHz, CDCl₃): 7.68 (dd, J = 3.29 Hz, J = 6.2 Hz, 2H), 7.36 (m, 4H), 6.64 (t, J = 2.1 Hz, 2H), 6.37 (s, 1H), 6.12 (t, J = Hz, 2H), 4.34

(t, J = 6.6 Hz, 2H), 4.21 (t, J = 7.0 Hz, 2H), 3.07 (t, J = 6.58 Hz, 2H), 2.81 (t, J = 7.0 Hz, 2H); δ C(400 MHz, CDCl₃): 169.84, 139.51, 137.27, 134.65, 129.44, 125.77, 124.33, 119.5, 112.97, 111.58, 111.55, 107.45, 97.23, 62.81, 43.77, 35.55, 24.39.

2.2. Soft-Template Electropolymerization

Here, in order to study the influence of H₂O in soft-template electropolymerization, two solvents were used: CH₂Cl₂ and CH₂Cl₂ saturated with H₂O (CH₂Cl₂ + H₂O sat.). CH₂Cl₂ + H₂O sat. was very easily prepared by mixing CH₂Cl₂ with H₂O and after discarding the aqueous phase. The electrodepositions were performed with an Autolab potentiostat (Metrohm). Gold-coated silicon wafer was used as the working electrode, a carbon rod as the counter-electrode, a saturated calomel electrode (SCE) as the reference electrode. In the solvent, were added the monomer (0.01 M) and the electrolyte (0.1 M of tetrabutylammonium perchlorate). After determining the monomer oxidation potentials (E^{ox} ≈ 2 V vs SCE) by 1) cyclic voltammetry, the electrodepositions were performed using two processes: by cyclic voltammetry (E = -1 V to E^{ox}) with a scan rate of 10 mV s⁻¹ and different number of scans, and 2) at constant potential (E = E^{ox}) with different charges.

2.3. Surface Characterization

The surface structures were explored by scanning electron microscopy (SEM). The surface roughness by optical profilometry. For the surface wetting properties, apparent contact angle measurements were performed with three liquids of different surface tension (γ_L): water γ_L = 72.8 mN/m, diiodomethane γ_L = 50.8 mN/m and hexadecane γ_L = 27.6 mN/m.

3. Results and Discussion

All monomers were electropolymerized by soft-template electropolymerization. In order to determine the effect of H₂O in the formation of porous structures, two solvents were used CH₂Cl₂ and CH₂Cl₂ + H₂O sat. The monomers having oxidation potential (E^{ox}) close to 2 V vs SCE, they were electro-deposited by cyclic voltammetry from -1 V to E^{ox} in order to have also H₂O reduction at around -0.5 V (2H₂O + 2e⁻ → H₂ + 2OH⁻) and as a consequence release of H₂ bubbles. Examples of cyclic voltammograms are given on Figure 1. All the monomers give polymer films even if non-polymerizable substituents are used such as NaphDOT-OH, NaphDOT-Ph or NaphDOT-Phen, that means only dimers are formed as represented in Scheme 3.

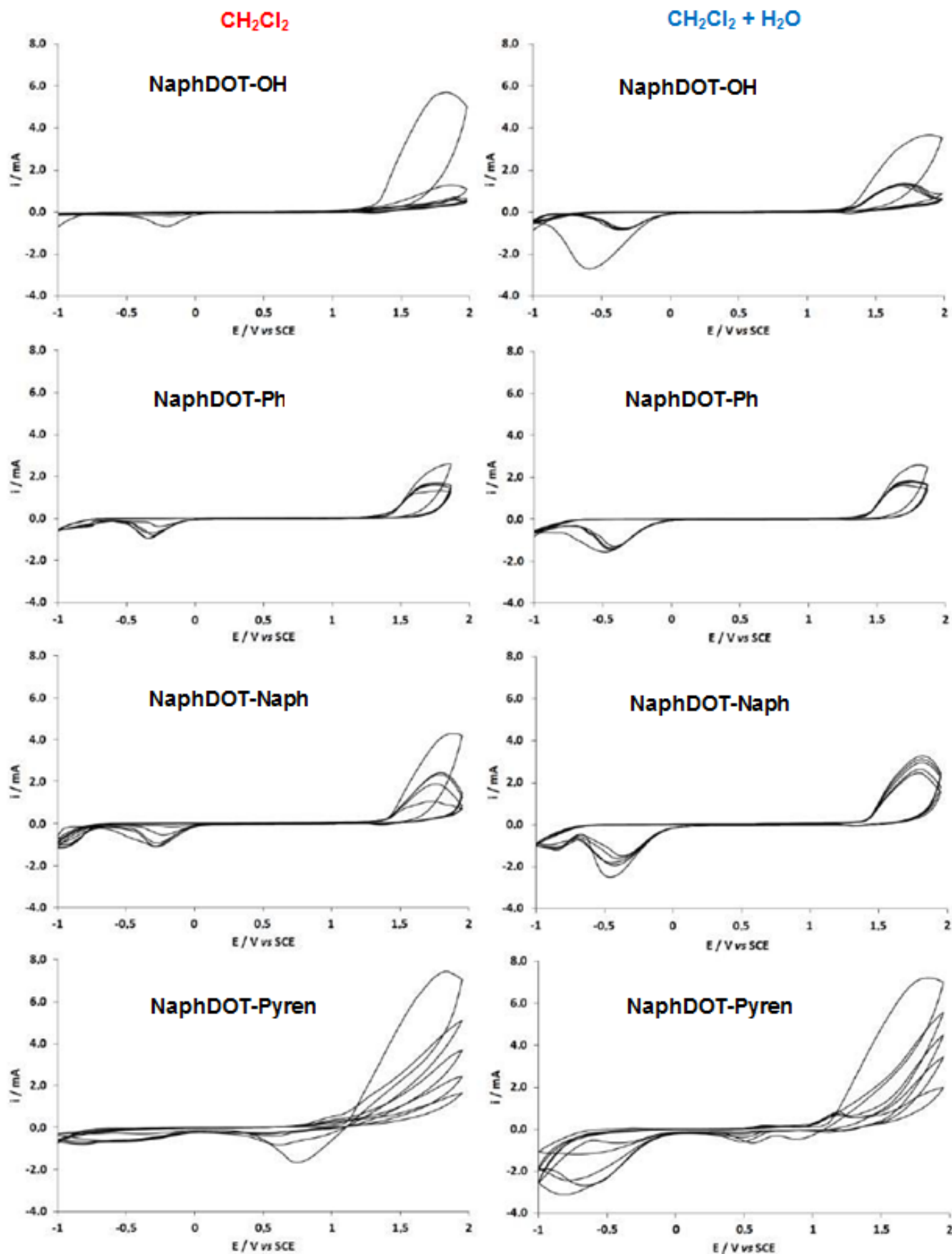
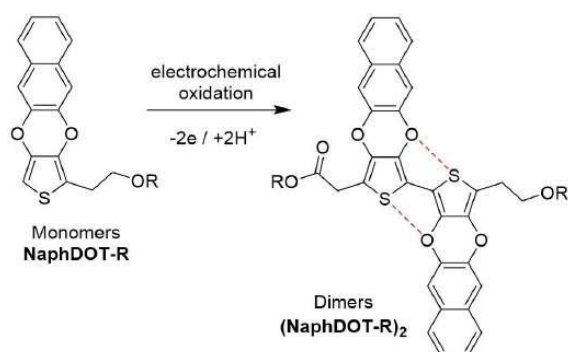


Figure 1. Examples of cyclic voltammogram in CH_2Cl_2 and $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$. The monomer concentration was 0.01 M, the electrolyte Bu_4NClO_4 was 0.1 M, the potential range between -1 V and E^{ox} , and the scan rate 10 mV s^{-1} . The number of scan was five.



Scheme 3. Electrochemical dimerization of 2-substituted NaphDOT monomers. Red dashed line shows attractive S··O contacts which planarize the dimers (NaphDOT-R)₂.

Then, the polymer films were investigated by cyclic voltammetry in free-monomer solution. In most of the CV curves of the electrodeposited polymer films (Figure 2), there is only one oxidation and reduction peak confirming that the substituent does not highly participate to the polymerization. A peak of low intensity is observed with phenyl, pyrrole and carbazole substituents. By contrast, a huge peak is present with a pyrene substituent at around 1 V vs SCE in a typical region for CV response of electrochemically prepared pyrene polymers.

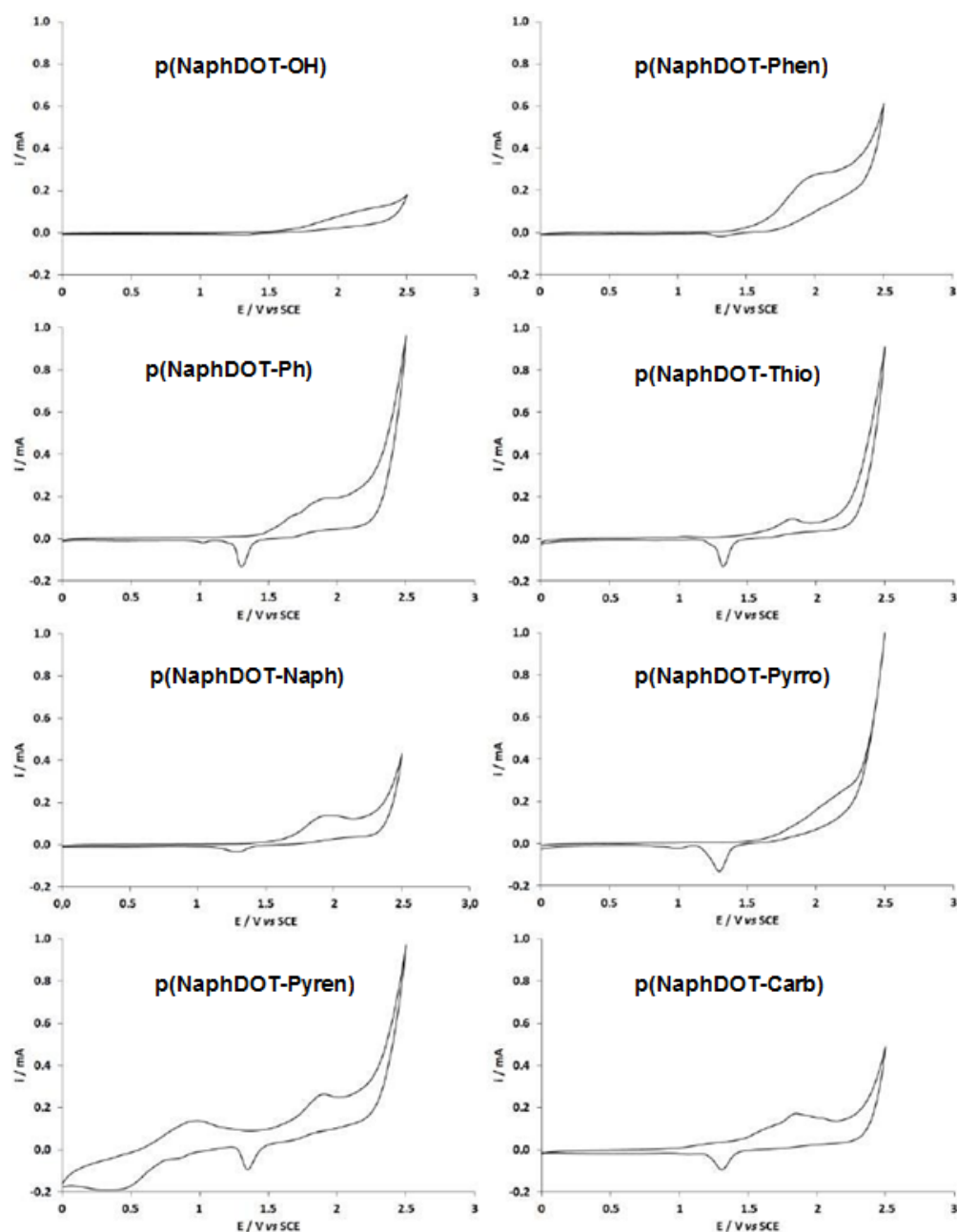


Figure 2. Cyclic voltammograms of the electrodeposited films in CH₂Cl₂. The electrolyte Bu₄NClO₄ was 0.1 M, the potential range between 0 V and 2.5 V, and the scan rate 10 mV s⁻¹. The number of scan was one.

The different surface structures are gathered in Figure 3 and Figure 4. The SEM analyses show first that the surfaces obtained in CH_2Cl_2 are relatively smooth. The surface obtained from NaphDOT-Pyren has non-porous spherical particles and from NaphDOT-Thio some tubular structures. In $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$, a huge number of nanotubes of very small size are observed especially with NaphDOT-OH and NaphDOT-Pyrro. Unique results are obtained with NaphDOT-Pyren, which leads to very huge open structures. These results can be explained by π -stacking interactions known between pyrene moieties, and the participation to polymerization.

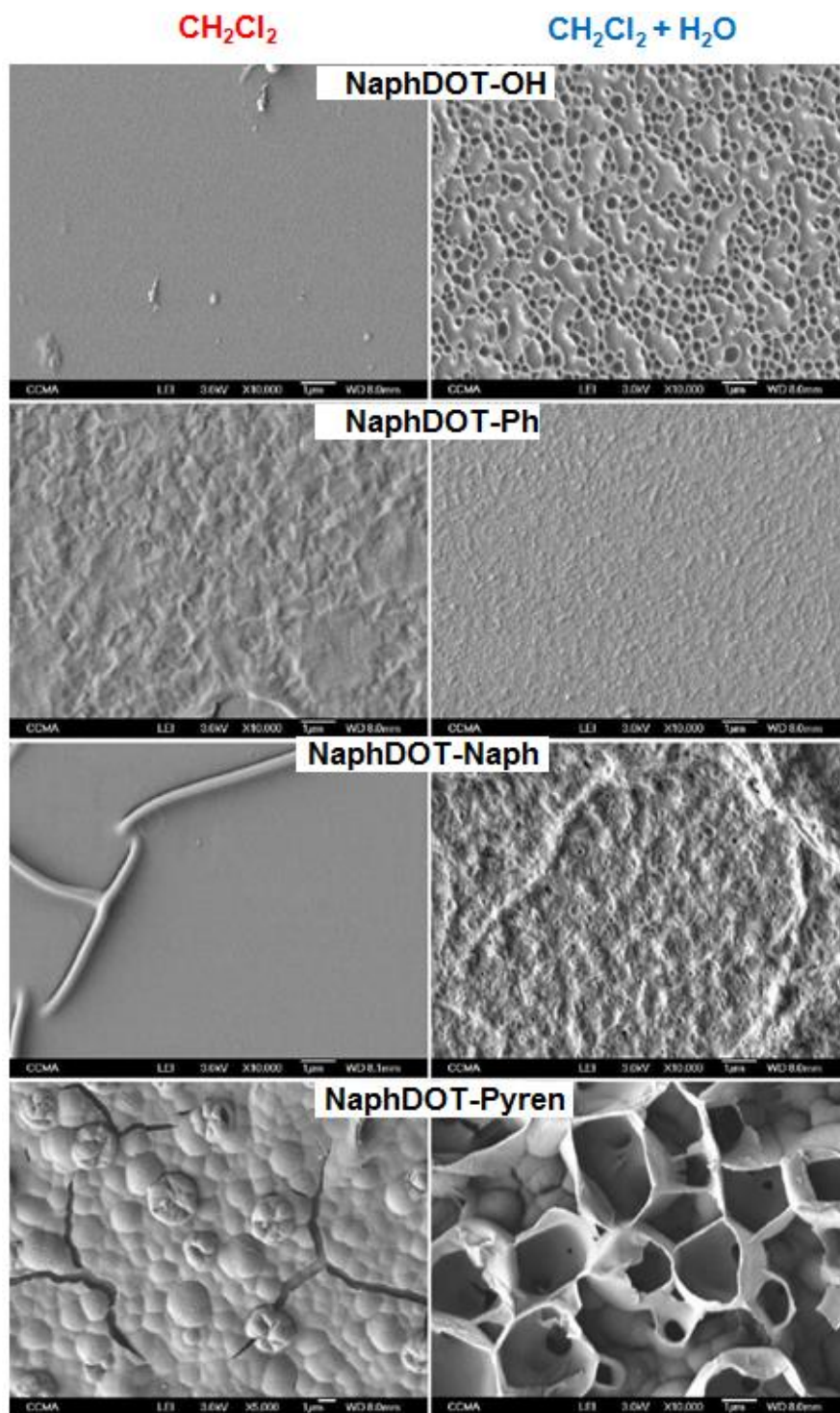


Figure 3. SEM images of the electrodeposited films from NaphDOT-OH, NaphDOT-Ph, NaphDOT-Naph and NaphDOT-Pyren in CH_2Cl_2 and $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$. The electrolyte Bu_4NClO_4 was 0.1 M, the potential range between -1 V and E^{ox} , and the scan rate 10 mV s^{-1} . The number of scan was three.

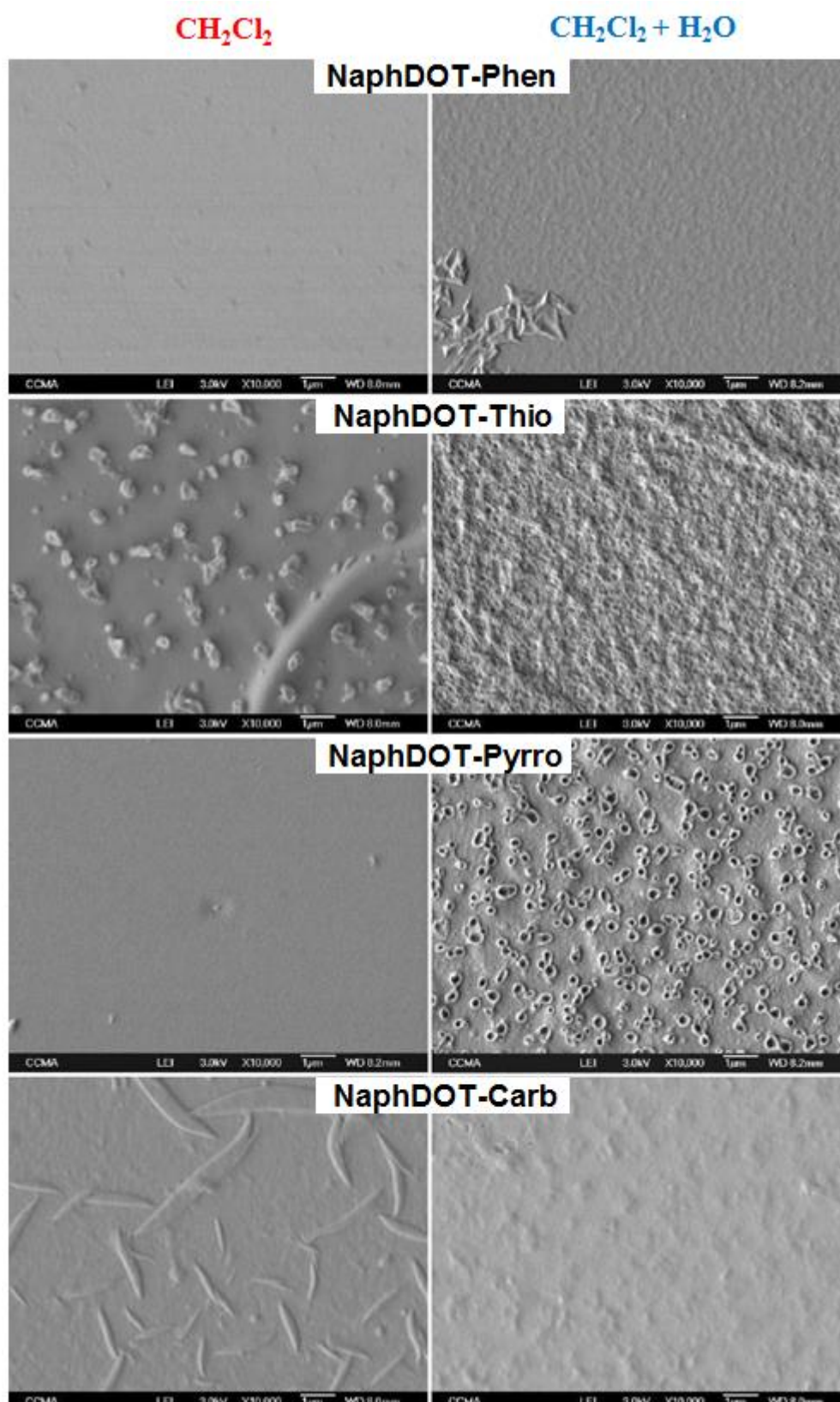


Figure 4. SEM images of the electrodeposited films from NaphDOT-Phen, NaphDOT-Thio, NaphDOT-Pyrro and NaphDOT-Carb in CH_2Cl_2 and $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$. The electrolyte Bu_4NClO_4 was 0.1 M, the potential range between -1 V and E^{ox} , and the scan rate 10 mV s^{-1} . The number of scan was three.

The surface wettability was evaluated by measuring apparent contact angles (θ) with three liquids of very different surface tension: water ($\gamma_L = 72.8 \text{ mN/m}$) to demonstrate the hydrophobicity and diiodomethane ($\gamma_L = 50.0 \text{ mN/m}$) and hexadecane ($\gamma_L =$

27.6 mN/m) for the oleophobicity. The results are gathered in Table 1. The surface roughness was also determined by optical profilometry (Table 2). These data are just for information because there is direct relationship between these values and the contact angles.

Table 1. Wettability data with water, diiodomethane and hexadecane for the polymer films obtained by cyclic voltammetry in 0.1 M Bu_4NClO_4 / CH_2Cl_2 or $CH_2Cl_2 + H_2O$ in potentiodynamic conditions by cyclic voltammetry ($E = -1 / +E^{ox}$ V).

Monomer	Number of CV	θ_w [deg]		θ_{diiodo} [deg]		θ_{hexa} [deg]	
	Scans	CH_2Cl_2	$CH_2Cl_2 + H_2O$	CH_2Cl_2	$CH_2Cl_2 + H_2O$	CH_2Cl_2	$CH_2Cl_2 + H_2O$
NaphDOT-OH	1	91.3	98.1	<10	<10	<10	<10
	3	90.3	117.7	<10	<10	<10	<10
	5	86.1	102.7	<10	<10	<10	<10
NaphDOT-Ph	1	48.6	51.3	55.0	45.3	36.5	<10
	3	40.4	52.9	45.0	44.8	12.9	12.6
	5	44.8	53.3	47.2	39.7	21.2	<10
NaphDOT-Naph	1	56.8	44.0	40.6	49.7	16.4	21.6
	3	48.3	68.0	49.0	41.8	<10	<10
	5	74.1	69.9	42.8	37.7	<10	<10
NaphDOT-Pyren	1	83.7	71.9	31.1	39.3	<10	<10
	3	79.0	92.2	24.9	39.7	<10	<10
	5	101.6	113.9	21.3	<10	<10	<10
NaphDOT-Carb	1	48.2	58.2	37.5	44.2	17.3	15.3
	3	87.1	73.7	31.6	45.5	<10	12.2
	5	64.5	69.7	44.8	36.2	13.6	<10
NaphDOT-Thio	1	75.0	49.6	33.3	45.2	<10	14.2
	3	78.0	50.8	24.4	47.6	<10	<10
	5	65.5	76.0		30.2	<10	<10
NaphDOT-Phen	1	40.1	57.7	37.9	57.7	<10	<10
	3	62.2	72.7	39.1	72.7	<10	<10
	5	55.0	67.6	47.1	67.6	14.4	<10
NaphDOT-Pyrro	1	70.8	97.1	19.2	13.7	29.9	<10
	3	54.4	100.3	14.0	24.5	28.6	<10
	5	93.6	95.4	34.2	<10	17.9	<10

Table 2. Arithmetic and quadratic roughness (R_a and R_q) for the polymer films obtained by cyclic voltammetry in 0.1 M Bu_4NClO_4 / CH_2Cl_2 or $CH_2Cl_2 + H_2O$ and in potentiodynamic conditions by cyclic voltammetry ($E = -1 / +E^{ox}$ V).

Monomers	Solvents	CH_2Cl_2		$CH_2Cl_2 + H_2O$	
	Number of scans	R_a [nm]	R_q [nm]	R_a [nm]	R_q [nm]
NaphDOT-OH	1	48	57	28	35

Monomers	Solvents	CH ₂ Cl ₂		CH ₂ Cl ₂ +H ₂ O	
	Number of scans	Ra [nm]	Rq [nm]	Ra [nm]	Rq [nm]
NaphDOT-Ph	3	62	69	86	109
	5	52	62	95	136
	1	24	29	27	32
	3	25	31	27	32
	5	22	27	23	27
NaphDOT-Naph	1	53	75	38	47
	3	39	51	47	61
	5	66	80	80	102
NaphDOT-Pyren	1	59	75	29	35
	3	38	51	31	44
	5	25	31	57	61
NaphDOT-Carb	1	40	48	25	31
	3	38	46	23	27
	5	75	95	54	69
NaphDOT-Thio	1	44	53	53	62
	3	50	64	53	65
	5	70	93	70	89
NaphDOT-Phen	1	48	59	43	68
	3	42	48	37	41
	5	48	59	28	37
NaphDOT-Pyrro	1	29	35	46	59
	3	41	51	52	69
	5	53	6	83	88

Here, as already reported in the literature, conducting polymers with hydrophilic or aromatic groups are expected to be intrinsically hydrophilic with water Young' angle $\theta_w < 90^\circ$. As a consequence, if the water droplets completely wet rough surface, as described by Wenzel [34], it is expected an increase of surface hydrophilicity that means a decrease of θ_w . However, sometimes it is observed a high increase of θ_w even above 90° but only for the polymer films with nanotubular structures. The highest angles are obtained after three CV scans in CH₂Cl₂ + H₂O for NaphDOT-OH ($\theta_w = 113.9^\circ$), after five CV scans in CH₂Cl₂+H₂O for NaphDOT-Pyren ($\theta_w = 117.7^\circ$), and after three CV scans in CH₂Cl₂ + H₂O for NaphDOT-Pyrro ($\theta_w = 100.3^\circ$). These θ_w can be explained only with the Cassie-Baxter equation [14], demonstrating hence also the presence of air between the water droplet and

these nanotubular surfaces.

After these preliminary tests, NaphDOT-OH, NaphDOT-Pyren and NaphDOT-Pyrro were selected for further experiments only in CH₂Cl₂ + H₂O but at constant potential (Figure 5 and Table 3). The surface structures obtained here are relatively similar than that previously obtained by CV even if with NaphDOT-Pyren the size of the structures is smaller. For the wetting properties, these surfaces are less hydrophobic. However, it is observed sometimes higher oleophobicity with diiodomethane than with water. This is possible when we have polymers which are both hydrophilic and oleophobic [35]. However, all the surfaces are superoleophilic with hexadecane because the surface tension of it is too low compared to the two other liquids used here.

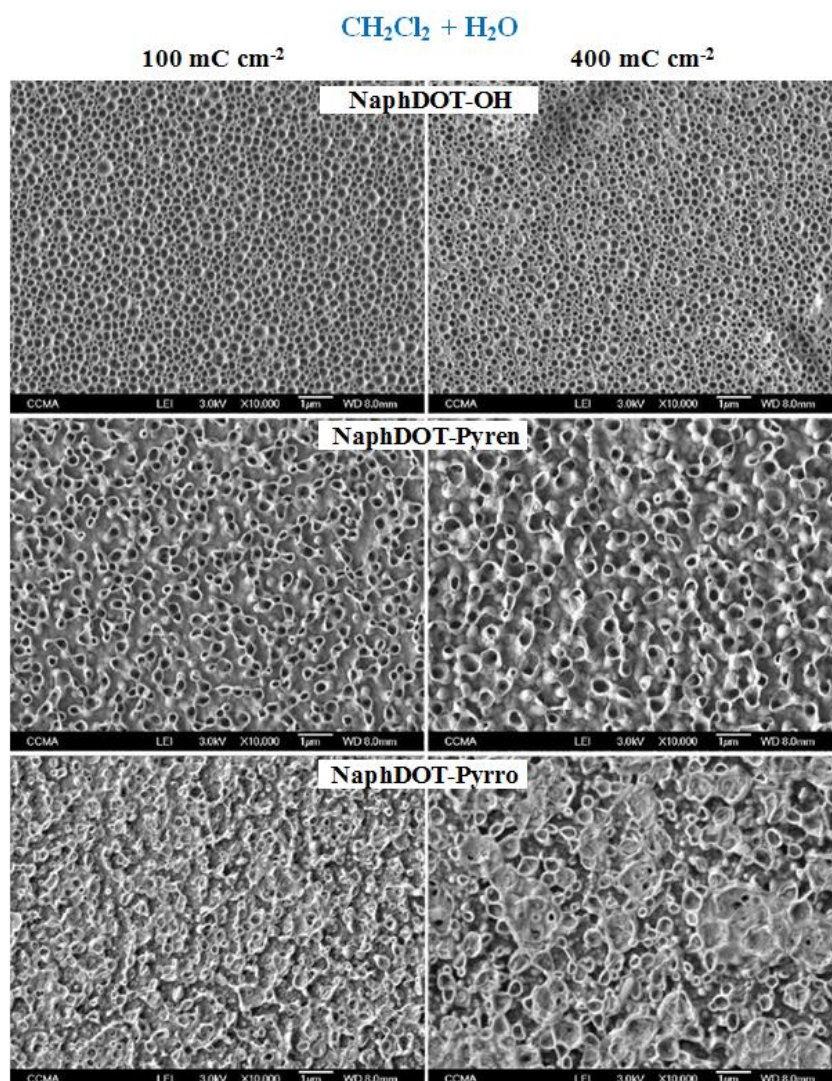


Figure 5. SEM images of the electrodeposited films from NaphDOT-OH, NaphDOT-Pyren and NaphDOT-Pyrro in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$. The electrolyte Bu_4NClO_4 was 0.1 M, the potential was kept constant at E^{ox} . The deposition charge was 100 and 400 mC cm^{-2} .

Table 3. Wettability data with water, hexadecane and diiodomethane for the polymer films obtained by cyclic voltammetry in 0.1 M $\text{Bu}_4\text{NClO}_4 / \text{CH}_2\text{Cl}_2$ and $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ in potentiostatic conditions at constant potential ($E = +E^{\text{ox}}$ V).

Monomer	Number of deposition charge [mC cm^{-2}]	θ_w [deg] in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$	θ_{diiodo} [deg] in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$	θ_{hexa} [deg] in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$
NaphDOT-OH	12.5	54.0	42.0	<10
	25	51.3	36.4	<10
	50	53.6	50.5	<10
	100	34.6	33.5	<10
	200	<10	38.3	<10
	400	46.1	38.5	<10
NaphDOT-Pyren	12.5	62.6	35.0	<10
	25	50.0	11.6	<10
	50	51.1	43.3	<10
	100	47.9	38.6	<10

Monomer	Number of deposition charge [mC cm ⁻²]	θ_w [deg] in CH ₂ Cl ₂ +H ₂ O	θ_{diiodo} [deg] in CH ₂ Cl ₂ +H ₂ O	θ_{hexa} [deg] in CH ₂ Cl ₂ +H ₂ O
NaphDOT-Pyrro	200	<10	34.0	<10
	400	<10	36.6	<10
	12.5	37.4	38.1	<10
	25	52.0	53.1	<10
	50	<10	40.0	<10
	100	46.0	60.7	<10
	200	63.1	64.6	<10
	400	0	60.6	<10

4. Conclusion

We demonstrated that even if dimers are formed by electropolymerization, polymer films can be obtained. NaphDOT monomers substituted at the 2-position of thiophene with various substituents were synthesized and used studied by soft template-electropolymerization. Nanotubular structures were particularly formed with hydroxyl group, pyrene and pyrrole, and in the presence of H₂O. We study also their influence on the surface hydrophobicity and found sometimes a high increase with these nanotubular structures. These surfaces could be used in the future in water-harvesting systems, for instance.

Abbreviations

γ_L : Surface tension Liquid
 θ_w : Static water contact angle
 Bu₄NClO₄: Tetrabutylammonium perchlorate
 CDCl₃: Deuterated chloroform
 CH₂Cl₂: Dichloromethane
 CV: Cyclic voltammetry
 H₂O: Water
 NaphDOT: Naphtho[2,3-b]thieno[3,4-e][1,4]dioxine
 NaphDOT-Carb: 2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethylcarbazole
 NaohDOT-Naph 2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-naphthalenacetate
 NaphDOT-OH: 2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethanol
 NaphDOT-Ph: 2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-phenylacetate
 NaphDOT-Phen: 2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl phe-noxyphenylacetate

NaphDOT-Pyr:

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-pyrenacetate

NaphDOT-Pyrro:

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-pyrrolate

NaphDOT-Thio:

2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethyl 2-thiophenacetate

P1: Naphtho[2,3-b]thieno[3,4-e][1,4]dioxine

P2: 1-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)ethanone

P3: 2-(naphtho[2,3-b]thieno[3,4-e][1,4]dioxin-7-yl)acetate

Ra: arithmetic Roughness

Rq: quadratic Roughness

SCE: Saturated Calomel Electrode

SEM: Scanning Electron Microscopy

Author Contributions

Fatoumata Sow: Conceptualization, Formal Analysis, Methodology

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Aboubacary Sene: Data curation, Visualization

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Thierry Darmanin: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Software, Validation, Visualization

Data Availability Statement

Not applicable for this manuscript.

Conflicts of Interest

The author declares no conflicts of interest.

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