A Templateless Electropolymerization Approach to Nanorings using Substituted 3,4-naphthalenedioxythiophene (NaPhDOT) Monomers

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Dedication ((optional))

Abstract: The formation of highly ordered surface structures is fundamental for various applications. Due to their rapidity of implementation and their cost, the templateless processes are extremely interesting alternatives to the use of templates or lithographic processes. In the aim to prepare porous structures such as nanotubes, the templateless electropolymerization was find to be a unique process. Based on previous works, we have synthesized 3,4-naphthalenedioxythiophene (NaPhDOT) monomers substituted with alkyl chains (n = 2 to 10), phenyl and naphthalene substituents. In particular, NaphDOT substituted with naphthalene (NaphDOT-Na) leads for the first time to relatively densely packed nanorings while their internal diameter is controllable with the number of deposition scans. Compared to previous works, which lead to nanotubes from non-substituted NaphDOT and 3,4-phenylenedioxythiophene substituted with naphthalene (PheDOT-Na), with NaphDOT-Na we observed a very important decrease in the polymer growth. As a consequence, only the initial peripherical nucleation around the gas bubbles is possible leading to nanorings while their growth in nanotubes is impeded by their low conductivity.

Introduction

The presence of surface structures is fundamental to enhance the surface properties in various applications such as in surface wettability,[1-3] adhesive systems,[4] catalysis,[5] sensors[6] or in energy systems.[7] In order to investigate the relationship between surface structures and surface properties, it is extremely important to have extremely homogeneous surface structures. For that, two processes are often used: the lithographic processes[8-11] and the use of templates.[12,13] However, these two techniques are often difficult to use and/or expensive.

In particular, nanotubes are exceptional surface structures because an important number of parameters can be varied such as their length, diameter, opening, or their spacing. Anodized aluminum oxide (AAO) membranes are often used to create cylindrical nanopores closed-packed in a hexagonal geometry.[14] For example, these AAO membranes can be filled in *via* solution casting,[15,16] electropolymerization/electrodeposition,[17-24] atomic layer deposition,[25] which are later dissolved in NaOH solution to obtain nanotubes.

As a consequence, the templateless electropolymerization/electrodeposition processes are excellent alternatives to produce very quickly homogenous surface structures. The electropolymerization is an excellent method to prepare very quickly and with a high reproducibility structured conducting polymer films. Depending on the electrochemical parameters and the monomer structure, surface structures of various shapes (for example nanofibers, nanosheets, cauliflower-like structures, flower-like structures) can be obtained.[26-30]

In 2003, Shi et al. reported for the first time the formation of porous structures such as nanotubes or nanocapsules by electropolymerization of pyrrole in aqueous solution containing a surfactant. In the process, gas bubbles (O_2 and/H_2 depending on the electrodeposition method), coming from water, were released from the surface during the electropolymerization process.[31-36] The surfactant was necessary to stabilize the gas bubbles and to induce the polymerization around them. McCarthy et al. acoustically formed emulsions using *N*-(2-cyanoethyl)pyrrole as monomer.[37] In their process, no gas bubbles are present on the surface but adsorbed toluene droplets, present in the emulsion play the role of soft templates. Various micro/ nanotubes were obtained as a function of the electrolyte and the sonication methods.

Very recently, we demonstrated the possibility to prepare arrays of vertically aligned nanotubes in organic solvent (dichloromethane, for example) and without any surfactant.[38-41] Here, trace water present naturally in organic solvent is sufficient to produce gas bubbles.[42] In this process, the role of the monomer is fundamental because it has also to play the role of the surfactant that means it has to stabilize the gas bubbles sufficiently long to allows the polymerization of the polymer around the bubbles. The best results were obtained with naphtho[2,3-*b*]thieno[3,4-*e*]-[1,4]dioxine (NaphDOT).[38] Moreover, the surface displayed extremely high water adhesion due to the presence of these nanotubes. Benzo[*b*]thieno[3,4-*e*][1,4]dioxine (PhEDOT) derivatives with different substituents were also tested in the literature.[43] Exceptional results were obtained with naphthalene moiety.

Here, the results obtained with non-substituted NaphDOT and some substituted PheDOT being exceptional, we have synthesized for the first time substituted NaphDOT and used them to develop nanotubular structures.

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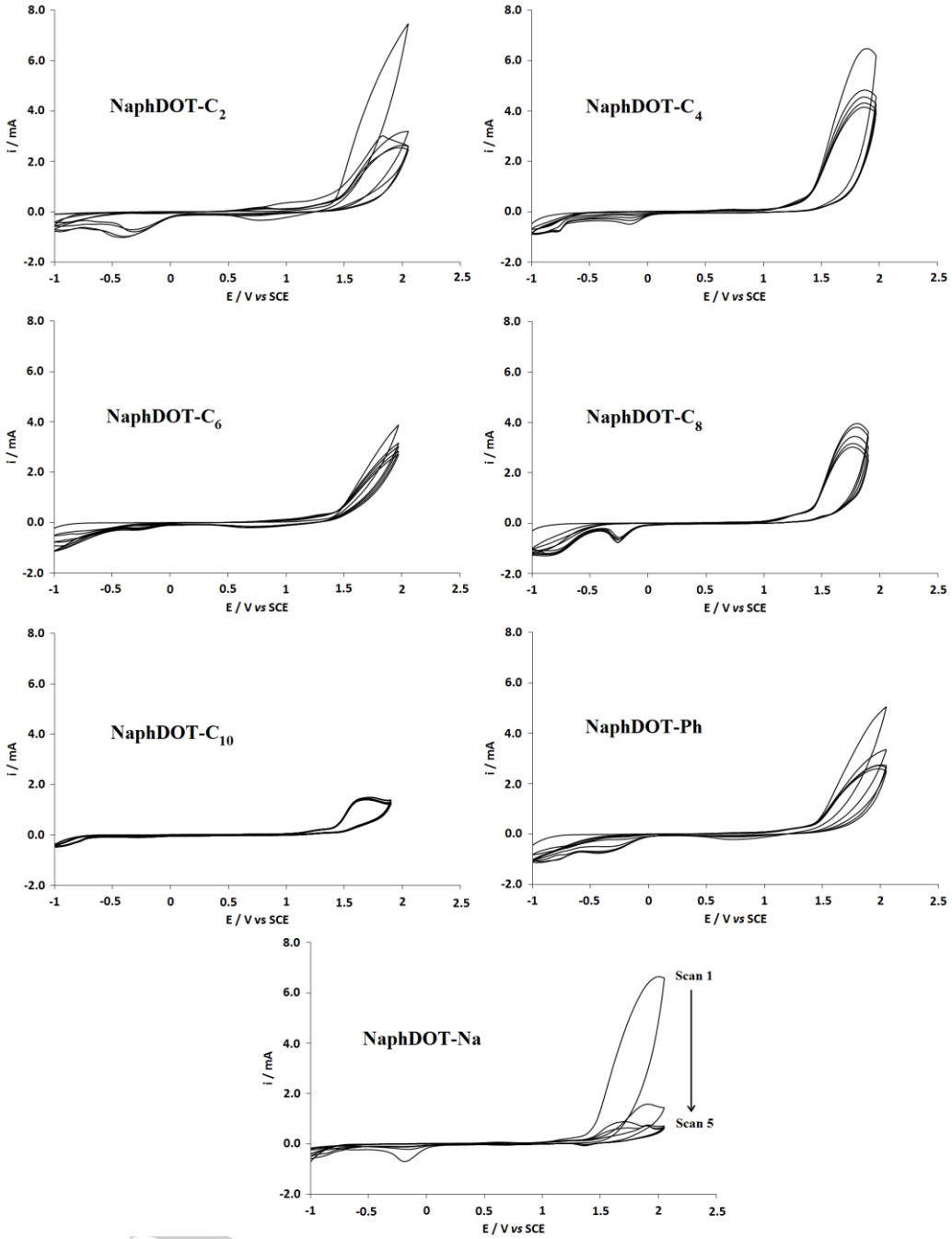
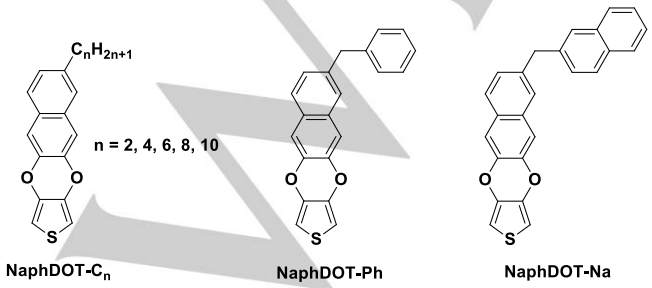


Figure 1. Cyclic voltammograms (5 scans) in Bu_4NClO_4 / dichloromethane of the different monomers (0.01 M); scan rate: 20 mV s^{-1}.



Scheme 1. Original monomers synthesized and used in this manuscript.

This is the first time that the synthesis of substituted NaphDOT is reported in the literature. As shown on Scheme 1, the monomers synthesized contain an alkyl chain of various length (n = 2 to 10), a phenyl or a naphthalene moiety.

Results and Discussion

For the templateless electropolymerization, a solution of dichloromethane with 0.1 M of Bu_4NClO_4 and 0.01 M of monomer was used for electropolymerization. Smooth gold plates (2 cm^2) were used as working electrode. Here, the monomer oxidation was found to be around 2 V vs SCE. Cyclic voltammetry was chosen as polymerization method because a higher amount of gas is expected to be released with this method if a large range of potential is used. Indeed, from trace water both O_2 and H_2 bubbles could be produced at around 2 V and -0.5 V vs SCE, respectively.

As a consequence, the templateless electropolymerization was performed by cyclic voltammetry from -1 V to ≈ 2 V vs SCE (scan rate: 20 mV s^{-1}). The cyclic voltammogram are given in Figure 1. A polymer film was obtained with all monomers. Their thickness is not extremely important and what we observed is especially a high decrease in the polymer thickness as a function of the number of deposition scans (a high decrease in the monomer peak intensity is observed with the number of deposition scans). The higher decrease was observed with NaphDOT-Na.

For NaphDOT-C_{10}, it was also observed the presence of an ultra-thin polymer layer. Indeed, it's known that steric hindrance during electropolymerization are dependent on their size and mobility of the substituent. Here, using NaphDOT-C_{10}, the steric hindrance induces by the $C_{10}H_{21}$ chains is to important and only smooth polymer surfaces are formed.

Surface structures and properties: After washing and drying, the polymer films were characterized. The SEM images of the different polymers are given in Figures 2, 3 and 4.

First of all, the monomers with low alkyl chains (NaPhDOT-C_2 and NaphDOT-C_4) are not highly structured and no porous structures are observed on these surface (Figure 2). Using longer alkyl chains (NaPhDOT-C_6 and NaphDOT-C_8), craters, proof of the presence of gas bubbles, are observed.

However, the best results are clearly obtained with aromatic substituents. Very nice and packed tubular structures are obtained with NaPhDOT-Ph (Figure 3) but most of the structures have their top in part close. Here, unique results are obtained with the naphthalene substituents (NaPhDOT-Na) (Figure 4). For the very first time, we obtain relatively densely packed nanorings with very low height. Moreover, by performing different numbers of scans, no change in the number of nanorings or in their height is observed but a clear increase in their diameter is obtained.

These results are very different than the results non-substituted NaphDOT[34] or with PheDOT substituted with a naphthalene substituent (PheDOT-Na) (Figure 5).[43] Indeed, nanotubes of very high height or length were obtained with these two monomers. Here, the low height obtained with NaPhDOT-Na and as a consequence the formation of nanorings could be explained by the high decrease in conductivity observed as a function of the polymer thickness. That means with NaPhDOT-Na only initial peripherical nucleation around the gas bubbles is possible because the polymer conductivity decreases quickly while with NaphDOT and PheDOT-Na the growth of hollow tubes is possible from this initial peripherical nucleation.

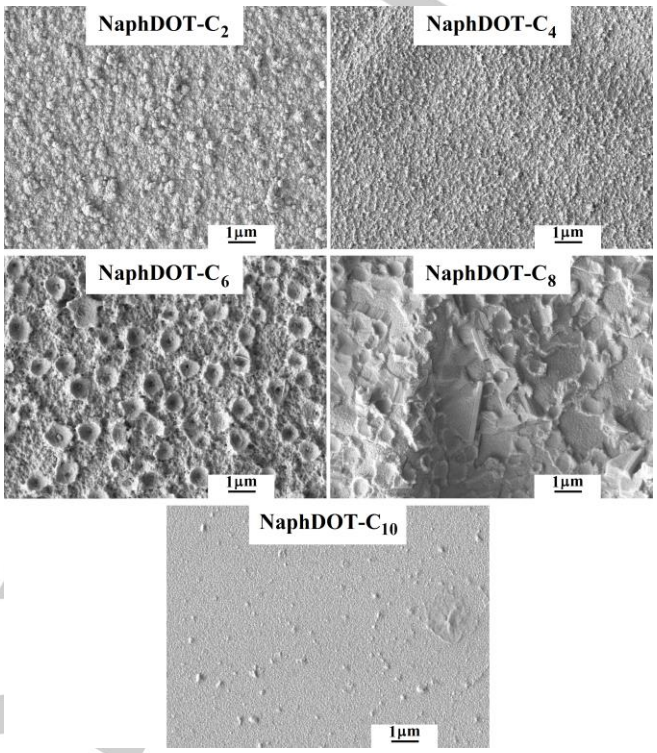


Figure 2. SEM images of the surface obtained from NaphDOT substituted with alkyl chains; 5 scans.

To confirm this, cross-section images were performed as shown In Figure 6. We observed that the thickness of the film was about 320 nm after 1 scan, 420 nm after 3 scans and 520 nm after 5 scans. Hence, the polymer thickness was 320 nm after 1 scan and increased of only 50 nm after each scan.

It is known that the necessary charge for the conducting polymer (semi-conducting polymers) growth increases with the thickness because the electron diffusion inside the polymer needs energy. Compared to 3,4-ethylenedioxythiophene (EDOT), the decrease in polymer thickness is drastic but can be easily explained by the extremely high electron withdrawing effect (mesomeric effect) of the naphthalene moiety close to the two oxygen atoms,[29,44] even if the naphthalene rigidity favors the polymer conductivity. Moreover, the substituent also affects the polymer conductivity by steric hindrance.

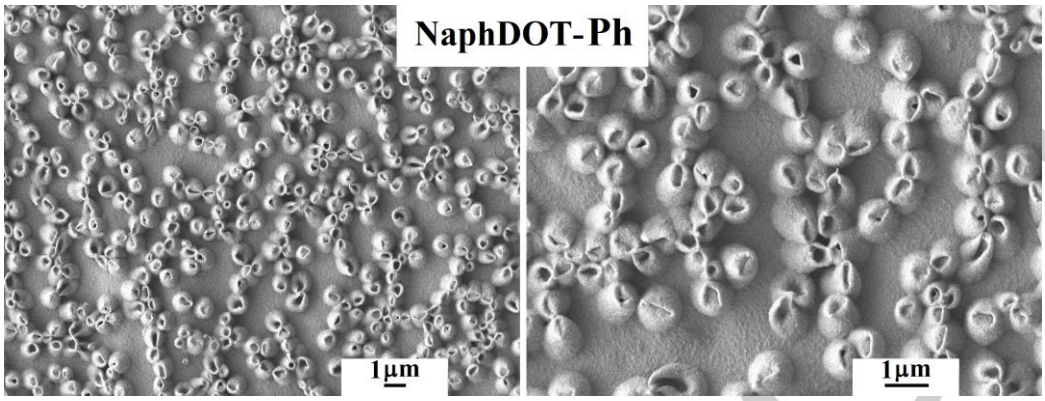


Figure 3. SEM images of the surface obtained from NaphDOT-Ph at two different magnifications; 5 scans.

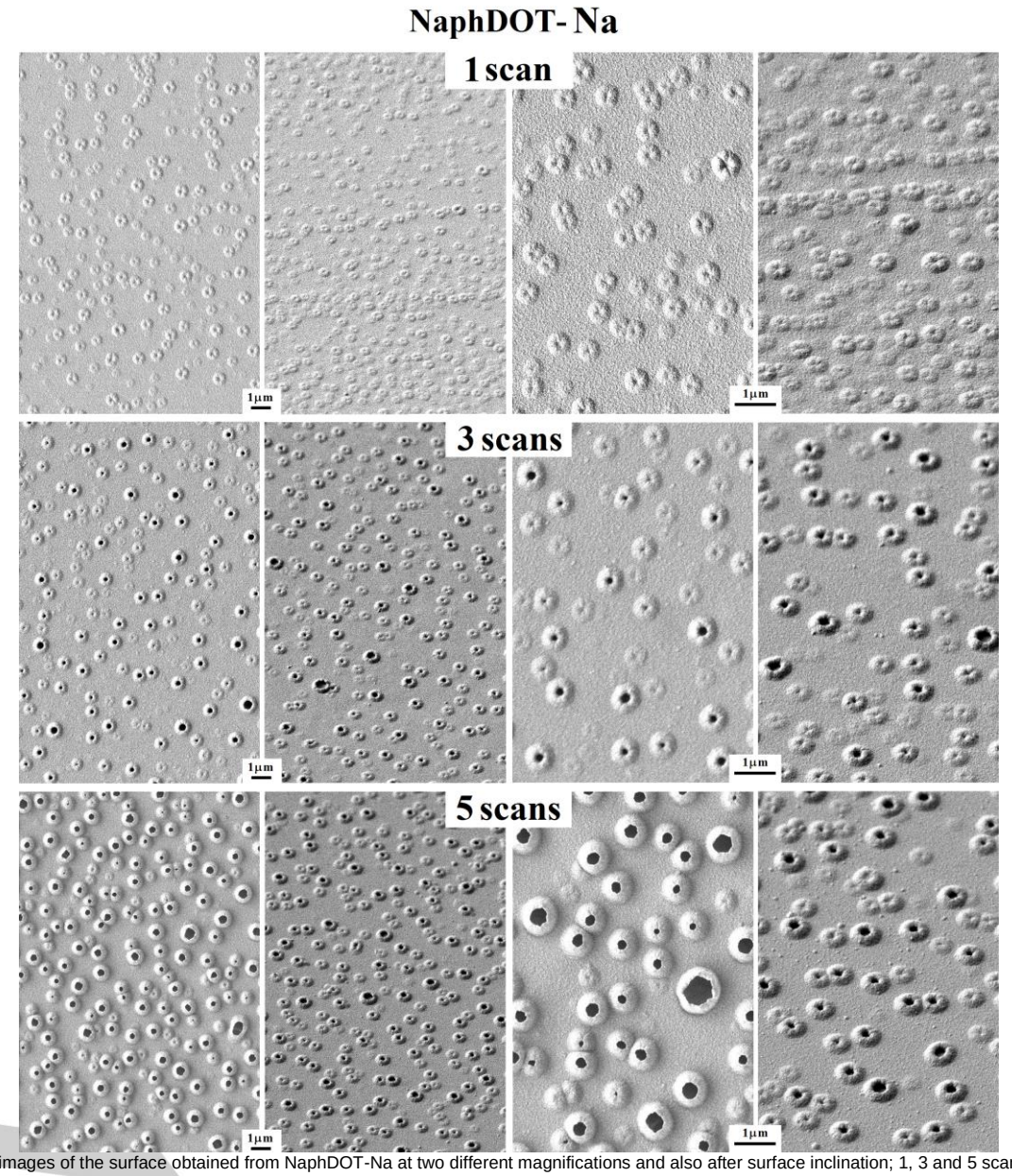


Figure 4. SEM images of the surface obtained from NaphDOT-Na at two different magnifications and also after surface inclination; 1, 3 and 5 scans.

Table 1. Surface roughness and hydrophobicity of the different polymers as a function of the number of deposition scan.

Polymer	Number of scans	Ra (nm)	Rq (nm)	θ_w (deg)
NaphDOT-C_2	1	16 ± 3	20 ± 3	95 ± 3
	3	18 ± 2	35 ± 4	80 ± 6
	5	730 ± 15	900 ± 50	50 ± 6
NaphDOT-C_4	1	20 ± 5	40 ± 8	95 ± 2
	3	130 ± 25	200 ± 17	109 ± 3
	5	310 ± 17	500 ± 30	92 ± 7
NaphDOT-C_6	1	45 ± 10	70 ± 20	58 ± 1
	3	450 ± 15	710 ± 40	57 ± 6
	5	900 ± 80	1290 ± 110	76 ± 5
NaphDOT-C_8	1	55 ± 20	85 ± 30	87 ± 7
	3	280 ± 60	440 ± 140	80 ± 5
	5	680 ± 150	1160 ± 200	72 ± 7
NaphDOT-C_{10}	1	10 ± 1	13 ± 2	87 ± 2
	3	10 ± 1	13 ± 2	85 ± 1
	5	16 ± 5	33 ± 10	90 ± 1
NaphDOT-Ph	1	90 ± 2	115 ± 5	36 ± 3
	3	840 ± 25	1230 ± 45	81 ± 8
	5	850 ± 90	1170 ± 120	76 ± 10
NaphDOT-Na	1	23 ± 8	30 ± 10	77 ± 2
	3	20 ± 9	25 ± 10	88 ± 2
	5	100 ± 25	240 ± 75	90 ± 2

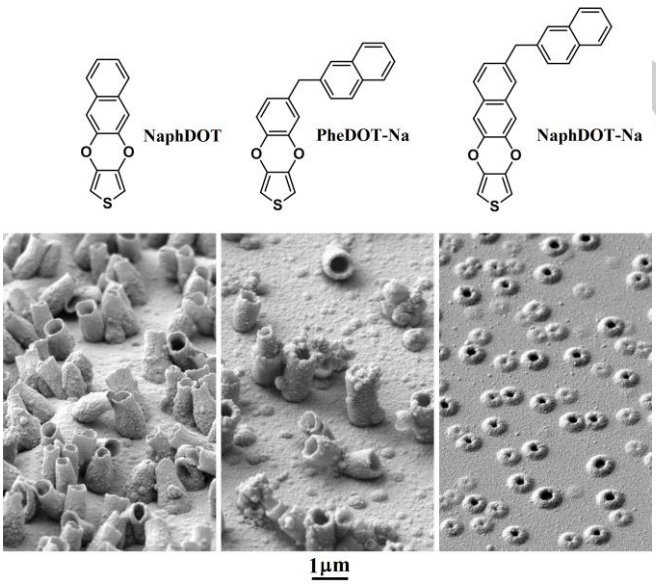


Figure 5. SEM images of the surface obtained from NaphDOT-DOT, PheDOT-Na and NaphDOT-Na after surface inclination (magnification: 10000x); 5 scans.

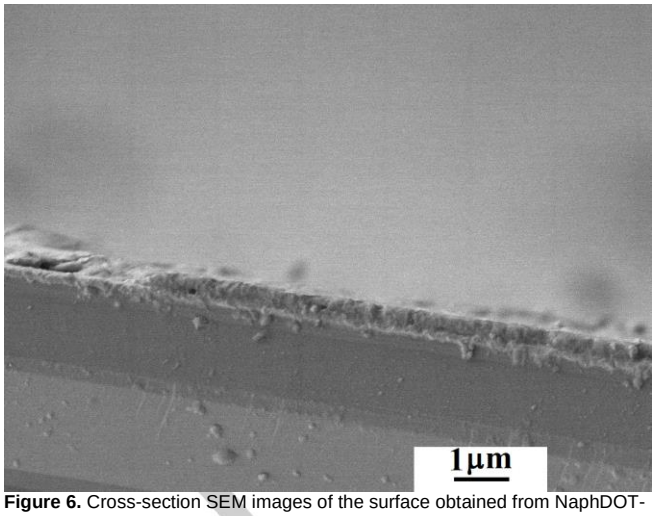


Figure 6. Cross-section SEM images of the surface obtained from NaphDOT-Na; 1 scans.

The results of relatively close to the results obtained McCarthy et al. but using a completely different method: electropolymerization of *N*-(2-cyanoethyl)-pyrrole using an acoustically formed emulsion.[37] In their process, the formation of hollow structures was obtained thanks to adsorbed toluene droplets while in our process trace water induces for the formation of gas bubbles. But our results are quite similar. Indeed, they observed that the tubular structures can be controlled by sonication method and also with the electrolyte. In particular, they observed that the presence of HPO_4^{2-} or $H_2PO_4^-$ anions induce a vertical growth by acting as a scaffolding agent through H bonding between polypyrrole chains. This is similar to ours results except that the naphthalene substituent play the role of HPO_4^{2-} or $H_2PO_4^-$ anions but especially by π-stacking interactions.

In our work, the monomer used plays a fundamental role in the polymerization rapidity, the polymer conductivity, the polymer rigidity while the presence of naphthalene as substituent was found to be also crucial for the growth of vertical structures by π-stacking interactions with the aromatic polymer chains. Indeed, different authors used naphthalenesulfonic acid as electrolyte for the formation of polypyrrole nanotubes in water.[32,45]

The hydrophobicity of these surfaces was also investigated (Table 1). The water apparent contact angle (θ_w) shows that none of these surfaces is highly hydrophobic. Here, the surface structures can induce an increase or a decrease in the contact angle. In fact, it is possible only if the contact angle of smooth surfaces (Young angle θ^Y)[46] is lower than 90°C that means for intrinsically hydrophilic surfaces, which is the case here for all our polymer except maybe with the longest alkyl chains. If θ^Y < 90°, the contact angle can decrease if that follows the Wenzel equation[47] or increase if that follows the Cassie-Baxter equation.[48] Hence, the contact angle of intrinsically hydrophilic materials can increase only if air is trapped between the surface and the droplet.

However, the presence of nanorings induces an increase in θ_w up to 90°, which is not bad because the naphthalene substituent

has not a high intrinsic hydrophobicity such as long hydrocarbon chains.

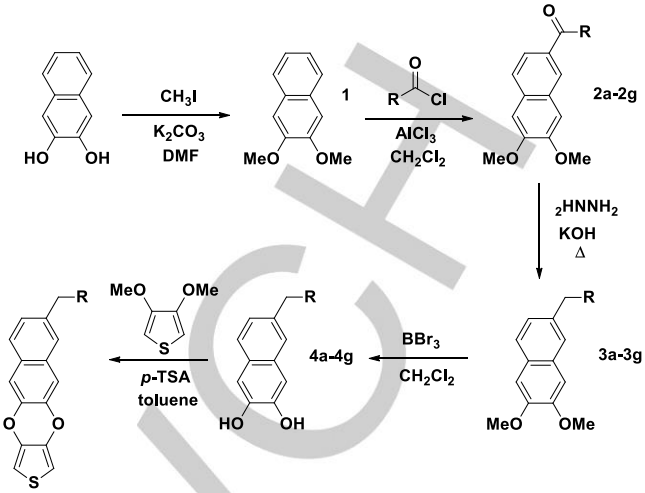
Conclusions

Here, in the aim to prepare porous structures using a templateless electropolymerization, we synthesized NaPhDOT monomers substituted with alkyl chains (n = 2 to 10), phenyl and naphthalene substituents. In particular, we observed that NaphDOT substituted with naphthalene (NaphDOT-Na) leads to relatively densely packed nanorings while their internal diameter was adjustable with the number of deposition scans. The results were compared our previous works for which we observed the formation of nanotubes from non-substituted NaphDOT and 3,4-phenylenedioxythiophene substituted with naphthalene (PheDOT-Na). With NaphDOT-Na we observed a huge decrease in the polymer growth. As a consequence, only the initial peripherical nucleation around the gas bubbles was possible leading to nanorings while their growth in nanotubes was impeded by their low conductivity. This works is extremely important for the preparation of extremely homogeneous surface structures with unique morphology using templateless processes. These materials could also be used for various application in catalysis, sensors or in water harvesting systems.

Experimental Section

Monomer synthesis: The strategy used here to obtained substituted NaphDOT was inspired than that reported for substituted PheDOT.[41-43] The monomers were obtained in five steps from 2,3-naphthalenediol. First, the two hydroxy groups were protected (Scheme 2). Then, (C=O)-R groups were introduced using a Friedel-Craft acylation. After reduction of the ketone and releasing of the two hydroxy groups, the monomers were obtained *via* a *trans*-etherification with 3,4-dimethoxythiophene.

Here, the global yield is only about 5%. However, only the yield of the last reaction is very low because we observed an important amount of polymerization/oligomerization rather than the formation of the product. Indeed, this reaction often needs high temperature 130°C and high amount of *p*-toluenesulfonic acid. These conditions were chosen according to previous works on substituted PhEDOT.[43,49,50] Here, the aim was to obtain the monomers and this last reaction was not optimized. In the future, it will be necessary to optimize this last reaction to obtain higher amount of monomers.



Scheme 2. Synthetic pathway to the substituted NaphDOT monomers.

15 g (90 mmol, 1 eq.) of naphthalenediol, 38 g of iodomethane (270 mmol, 3 eq.) and 37 g of K_2CO_3 (270 mmol, 3 eq.) were added to 500 mL of *N*,*N*-dimethylformamide (DMF). After stirring for 2 days at 80°C, the solution was poured in an aqueous solution and extracted with diethyl ether. The solution was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified on chromatographic column (silica gel; eluent: dichloromethane) to yield to 1.

2,3-dimethoxynaphthalene (1).

Yield 96 %; δ_H(200 MHz, $CDCl_3$): 7.69 (m, 2H), 7.34 (m, 2H), 7.13 (s, 2H).

8.1 g (40 mmol, 1 eq.) of 2,3-dimethoxynaphthalene and 1 eq. of the corresponding acyl chloride or placed in 250 mL of anhydrous dichloromethane. The solution was cooled using an ice bath, and a solution of aluminum trichloride 5.9 g, (44 mmol, 1.1 eq.) in 100 mL of anhydrous dichloromethane is added dropwise. The mixture is refluxed for 24 h under nitrogen. The solution then undergoes hydrolysis, through the drop-wise addition of 180 mL of 6 M HCl solution. Afterwards, the resulting aqueous phase was extracted twice with dichloromethane. The organic phase was washed with 150 mL of a saturated solution of K_2CO_3. The solution was dried over Na_2SO_4 and the solvent was evaporated. The product was purified on chromatographic column (silica gel; eluent: dichloromethane) to yield to 2a-2g.

1-(6,7-dimethoxynaphthalen-2-yl)ethanone (2a).

Yield 71 %; δ_H(200 MHz, $CDCl_3$): 8.34 (d, *J* = 1.4 Hz, 1H), 7.90 (dd, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 16.3 Hz, 2H), 4.02 (m, 6H), 2.69 (s, 3H).

1-(6,7-dimethoxynaphthalen-2-yl)butan-1-one (2b).

Yield 54 %; δ_H(200 MHz, $CDCl_3$): 8.34 (d, *J* 1.4, 1H), 7.90 (dd, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 17.0 Hz, 2H), 4.03 (m, 6H), 3.05 (t, *J* = 7.3 Hz, 2H), 1.82 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

1-(6,7-dimethoxynaphthalen-2-yl)hexan-1-one (2c).

Yield 82 %; δ_H(200 MHz, $CDCl_3$): 8.34 (d, *J* = 1.4 Hz, 1H), 7.90 (dd, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.16 (d, *J* = 17.1 Hz, 2H), 4.02 (m, 6H), 3.05 (t, *J* = 7.4 Hz, 2H), 1.78 (m, 2H), 1.40 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H).

1-(6,7-dimethoxynaphthalen-2-yl)octan-1-one (2d).

Yield 93 %; δ_H(200 MHz, $CDCl_3$): 8.33 (d, *J* = 1.4 Hz, 1H), 7.90 (dd, *J* = 8.5 Hz, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 17.1 Hz,

2H), 4.00 (m, 6H), 3.06 (t, *J* = 7.4 Hz, 2H), 1.78 (m, 2H), 1.30 (m, 8H), 0.85 (t, *J* = 6.5 Hz, 3H).

1 eq. of 2a-2g was dissolved in 130 mL of diethylene glycol, and 3 g of hydrazine hydrate (60 mmol, 2.15 eq.) was added. The solution was stired under ambient conditions for 30 min. After, 7 g of KOH (126 mmol, 4.5 eq.) was added and the solution was brought to 120°C for 1 h 30. The temperature was then gradually increased to distil all low boiling point materials (especially water) until the solution temperature reached 215°C, and and the solution was kept to this temperature for 3 hr. Then, the solution was cooled to room temperature. The solution was then acidified with HCl until pH 2. The aqueous phase was extracted with diethyl ether. The organic phase was washed with water. The solution was dried over Na_2SO_4 and the solvent was evaporated. The product was purified on chromatographic column (silica gel; eluent: dichloromethane) to yield to 3a-3g.
During this step, it was observed that a part of the methoxy groups became deprotected but it was not a problem since the next reaction involved the complete deprotection of these groups.

1 eq. of 3a-3g was dissolved in 300 mL of anhydrous dichloromethane. 9.5 mL of BBr_3 (100 mmol, 4 eq.) in anhydrous dichloromethane was dropped into the solution. The mixture was stirred for 3 hours and after which 900 g of cold water was added to the solution. After 45 min of stirring, the solution was saturated with NaCl. The aqueous phase was extracted with dichloromethane. The organic phase was washed with a saturated solution of NaCl. The solution was dried over Na_2SO_4 and the solvent was evaporated. The product was purified on chromatographic column (silica gel; eluent: cyclohexane/ dichloromethane (3 : 7)) to yield to 4a-4g.
The solvent is evaporated from the products
6-ethylnaphthalene-2,3-diol (4a).
Yield 99 %; δ_H(200 MHz, CD_3OD): 7.45 (d, *J* = 8.3 Hz, 1H), 7.32 (s, 1H), 7.06 (m, 3H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).
6-butylnaphthalene-2,3-diol (4b).
Yield 95 %; δ_H(200 MHz, CD_3OD): 7.45 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.05 (m, 3H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.63 (2 H, m), 1.36 (2 H, m), 1.26 (t, *J* = 7.2 Hz, 3H).
6-hexylnaphthalene-2,3-diol (4c).
Yield 86 %; δ_H(200 MHz, CD_3OD): 7.45 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.06 (m, 3H), 2.66 (t, *J* = 7.5 Hz, 1H), 1.67 (2 H, m), 1.35 (6 H, m), 0.89 (t, *J* = 6.7 Hz, 3H).
6-octylnaphthalene-2,3-diol (4d).
Yield 83 %; δ_H(200 MHz, CD_3OD): 7.44 (d, *J* = 8.4 Hz, 1H), 7.29 (s, 1H), 7.05 (m, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.63 (m, 2H), 1.29 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H).
6-decylnaphthalene-2,3-diol (4e).
Yield 82 %; δ_H(200 MHz, CD_3OD): 7.45 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.05 (m, 3H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.65 (m, 2H), 1.27 (m, 14H), 0.89 (t, *J* = 6.4 Hz, 3H).
6-benzylnaphthalene-2,3-diol (4f).
Yield 56 %; δ_H(200 MHz, CD_3OD): 7.45 (d, *J* = 8.4 Hz, 1H), 7.33 (s, 1H), 7.16 (m, 8H), 4.01 (s, 2H).
6-(naphthalen-2-ylmethyl)naphthalene-2,3-diol (4g).
Yield 67 %; δ_H(200 MHz, CD_3OD): 7.72 (m, 4H), 7.39 (m, 5H), 7.07 (m, 3H), 4.17 (s, 2H).

1 eq. of 4a-4 and 3.6 g of 3,4-dimethoxythiophene (25 mmol, 1 eq.) are dissolved in 120 mL
of toluene. 0.7 g of *p*-toluenesulfonic acid (4 mmol, 0.16 eq.) was added to the solution, which is then heated at 140°C for 24 h. Then, 0.7 g of *p*-toluenesulfonic acid (4 mmol, 0.16 eq.) was added again and the solution was heated at 140°C for 24 h. The resulting product was purified on chromatographic column (silica gel; eluent: cyclohexane/ dichloromethane (1 : 1)) to yield to the monomers.
7-ethylnaphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-C_2).
Yield 10 %; δ_H(200 MHz, $CDCl_3$): 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.19 (2 H, d, *J* = 5.1 Hz), 7.15 (1 H, dd, *J* 8.5 = Hz, *J* 1.7 = Hz), 6.43 (m, 2H), 2.68 (2 H, q, *J* = 7.6 Hz), 1.23 (3 H, t, *J* = 7.6 Hz); δ_C(50 MHz, $CDCl_3$): 141.31, 140.60, 139.98, 138.85, 138.82, 130.71, 128.80, 126.72, 126.60, 124.52, 112.34, 112.11, 100.92, 100.88, 28.90, 15.42; MS (70 eV): m/z 268 (M^+, 90), 253 ($C_{15}H_9O_2S^{+\bullet}$, 100).
7-butylnaphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-C_4).
Yield 5 %; δ_H(200 MHz, $CDCl_3$): 7.58 (1 H, d, *J* = 8.4 Hz), 7.44 (s, 1H), 7.26 (d, *J* = 5.9 Hz, 2H), 7.21 (dd, *J* 8.4 Hz, *J* = 1.7 Hz, 1H), 6.51 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.69 (m, 2H), 1.41 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); δ_C(50 MHz, $CDCl_3$): 140.59, 140.00, 139.97, 138.86, 138.83, 130.66, 128.79, 126.99, 126.64, 125.25, 112.33, 112.08, 100.92, 100.88, 35.68, 33.45, 22.39, 13.97; MS (70 eV): m/z 296 (M^+, 72), 253 ($C_{15}H_9O_2S^{+\bullet}$, 100).
7-hexylnaphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-C_6).
Yield 5 %; δ_H(200 MHz, $CDCl_3$): 7.59 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.26 (2 H, d, *J* 5.7 Hz), 7.21 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 6.51 (m, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.68 (m, 2H), 1.33 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H); δ_C(50 MHz, $CDCl_3$): 140.57, 140.00, 138.85, 138.82, 130.66, 128.79, 126.98, 126.64, 125.23, 112.33, 112.08, 100.91, 100.87, 35.99, 31.73, 31.28, 29.02, 22.60, 14.09; MS (70 eV): m/z 324 (M^+, 85), 253 ($C_{15}H_9O_2S^{+\bullet}$, 100).
7-octylnaphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-C_8).
Yield 4 %; δ_H(200 MHz, $CDCl_3$): 7.55 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H), 7.22 (d, *J* 5.7 Hz, 2H), 7.18 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 6.50 (m, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.63 (m, 2H), 1.25 (m, 10H), 0.87 (t, *J* = 6.4 Hz, 3H); δ_C(50 MHz, $CDCl_3$): 140.58, 140.05, 138.86, 138.83, 130.66, 128.79, 126.98, 126.63, 125.31, 112.33, 112.08, 100.91, 100.87, 36.00, 31.87, 31.32, 29.48, 29.35, 29.25, 22.65, 14.09; MS (70 eV): m/z 352 (M^+, 95), 253 ($C_{15}H_9O_2S^{+\bullet}$, 100).
7-decylnaphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-C_{10}).
Yield 4 %; δ_H(200 MHz, $CDCl_3$): 7.58 (d, *J* = 8.5 Hz, 1H), 7.44 (s, 1H), 7.24 (d, *J* = 5.7 Hz, 2H), 7.20 (dd, *J* = 8.5 Hz, *J* = 1.6 Hz, 1H), 6.51 (m, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.66 (m, 2H), 1.25 (m, 14H), 0.88 (t, *J* = 6.2 Hz, 3H); δ_C(50 MHz, $CDCl_3$): 140.59, 140.06, 138.87, 138.83, 130.66, 128.80, 126.99, 126.64, 125.23, 112.34, 112.09, 100.92, 100.88, 36.00, 31.89, 31.32, 29.70, 29.61, 29.59, 29.52, 29.32, 22.685, 14.11.
7-benzylnaphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-Ph).
Yield 5 %; δ_H(200 MHz, $CDCl_3$): 7.51 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.20 (m, 8H), 6.43 (m, 2H), 4.01 (s, 2H); δ_C(50 MHz, $CDCl_3$): 140.83, 140.72, 140.23, 138.78, 138.76, 138.20, 130.64, 128.98, 128.51, 127.15, 126.99, 126.18, 126.01, 112.37, 112.28, 101.00, 100.95, 41.97; MS (70 eV): m/z 330 (M^+, 100), 253 ($C_{15}H_9O_2S^{+\bullet}$, 10).
7-(naphthalen-2-ylmethyl)naphtho[2,3-b]thieno[3,4-e][1,4]dioxine (NaphDOT-Na).
Yield 5 %; δ_H(200 MHz, $CDCl_3$): 7.70 (m, 5H), 7.30 (m, 7H), 6.51 (m, 2H), 4.25 (s, 2H); δ_C(50 MHz, $CDCl_3$): 140.28, 140.24, 138.78, 138.30, 138.07,

133.60, 129.06, 128.15, 127.63, 127.56, 127.21, 127.03, 126.14, 126.03, 125.42, 112.40, 112.30, 101.01, 100.96, 42.14.

Electrochemical experiments: The electropolymerization experiments were performed with an Autolab potentiostat of Metrohm using a three-electrode system. A 2 cm^2 gold-coated silicon wafer was used as working electrode, a glassy carbon rod was used as counter-electrode and a saturated calomel electrode (SCE) was used as reference electrode. The three-electrode system was connected to an electrochemical cell containing 10 mL of dichloromethane with 0.1 M of tetrabutylammonium perchlorate (Bu_4NClO_4) and 0.01 M of monomer. The solutions were degassed over argon before use.

Surface Characterization: Scanning electron microscopy (SEM) images were recorded with a 6700F microscope of JEOL. The arithmetic (Ra) and quadratic (Rq) surface roughness were obtained with a WYKO NT1100 optical profiling system from Bruker. For these measurements, the working mode High Mag Phase Shift Interference (PSI), the objective 50×, and the field of view 0.5× were used. The hydrophobicity was determined by contact angle measurements using a DSA30 goniometer of Krüss using 2 μL deionized water (γ_L =72.8 mN m^{-1}) droplets. (γ_L = 27.6 mN m^{-1}).

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Keywords: Nanotubes • Nanostructures • Parahydrophobic • Wettability • Conducting polymers

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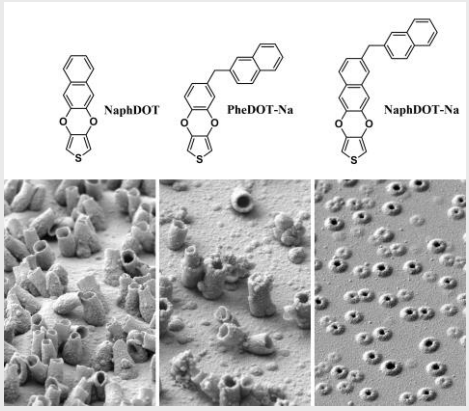
Entry for the Table of Contents

Layout 1:

FULL PAPER

Homogeneous arrays of nanorings are obtained using a templateless electropolymerization of substituted NaphDOT. Exceptional results are obtained with a naphthalene substituent.



*André Gbilimou, Thierry Darmanin, Guilhem Godeau and Frédéric Guittard**

Page No. – Page No.

A Templateless Electropolymerization Approach to Nanorings using Substituted 3,4-naphthalenedioxythiophene (NaPhDOT) Monomers