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### Formation of Nanofibers with High Water Adhesion by Electrodeposition of Poly(3,4-ethylenedioxypyrrole) and Poly(3,4propylenedioxypyrrole) Films Substituted by Alkyl Chains

Omar Sane,<sup>[a]</sup> Alioune Diouf,<sup>[a]</sup> Samba Yandé Dieng,<sup>[a]</sup> Frédéric Guittard,<sup>[b,c]</sup> Thierry Darmanin\*<sup>[b]</sup>

#### Dedication ((optional))

**Abstract:** Here, in aim to control the surface hydrophobicity and water adhesion, nanofibrous surfaces are prepared by electropolymerization using 3,4-ethylenedioxypyrrole (EDOP) and 3,4-propylenedioxypyrrole (ProDOP) with various alkyl chains (C<sub>3</sub> to C<sub>17</sub>) grafted on the 3,4-alkylenedioxy bridge. The surface properties are very different following the choice of the polymerizable core (EDOP or ProDOP) and the alkyl chain length. The formation of nanofibrous surfaces is much more favored using ProDOP. The alkyl chain length has also a huge influence on the formation of nanofibers and alkyl chains of intermediate length (C<sub>9</sub> and C<sub>11</sub>) give the best results. Apparent contact angle ( $\partial_w$ ) up to 150° are obtained while the water adhesion can also highly change. This work is extremely important and can find many applications where the control of the interaction forces with the media is required such as in oil/water separation membranes or in water harvesting systems.

#### Introduction

The control of the surface wettability is very important for various applications, for example in waterproof textiles, non-stick pans, antifouling paints, microfluidic devices, separation membranes, water purification or in anti-bioadhesion.<sup>[1-4]</sup> Inspired by surfaces present in Nature, the presence of surface structures was found to be fundamental for the control of both surface hydrophobicity and water adhesion.<sup>[5-8]</sup> For example, superhydrophobic properties characterized by high apparent contact angle ( $\theta_w$ ) and low hysteresis are responsible of the self-cleaning properties of

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Lotus leaves, the anti-fogging properties of mosquito eyes or the capacity to walk on water of water striders. Other species having parahydrophobic properties, characterized by high apparent contact angle ( $\theta_w$ ) and high hysteresis, are capable to capture small water droplets even in arid or hot environments.<sup>[9-12]</sup> This is the case of rose petals and gecko foot, for example.

These properties can be explained with the Wenzel and Cassie-Baxter equations, which take into account the effect on the surface roughness on the surface hydrophobicity.[13-17] Hence, two key parameters can highly influence on the surface hydrophobicity and the water adhesion: the surface energy and the surface structuration/roughness. Various processes can be used to control these two parameters including chemical etching, hydrothermal processes, plasma treatment, laser, chemical deposition, vapor anodization, use of nanoparticles/nanocomposites, lithography or templating.[18-22] Conducting polymers can be used to obtain nanostructured materials.<sup>[23]</sup> In particular, the polyaniline was intensively studied for the formation of one-dimensional (1D) structures such as nanofibers thanks to various intra but also intermolecular interactions such as hydrogen bonds, hydrophobic and  $\pi$ stacking.<sup>[24-28]</sup> Indeed, Wang et al. studied the formation of various nanostructures using aniline oligomers (trimers) formed in the first stage of aniline oxidation.<sup>[24]</sup> The asymmetry of this molecule was found to be responsible to the formation of various assemblies such as nanofibers (1D-growth), nanosheets (2Dgrowth) or flower-like and urchin-like structures (3D-growth), depending on the experimental conditions. For example, flowerlike and urchin-like structures can be formed by increasing the acidity and the reaction time.

The growth of nanostructured conducting polymers is also possible directly on substrate using different techniques including electropolymerization.<sup>[23,29-32]</sup> This technique also a fast growth of conducting polymer films while the control in the surface structuration is possible with electrochemical parameters and also the monomer chemical structure. By contrast, the control in the surface energy is possible by grafting hydrophobic substituents, for example. Among the multiple possibilities, monomers of the 3,4-alkylenedioxypyrrole (XDOP) family such 3,4-ethylenedioxypyrrole (EDOP) and 3,4as propylenedioxypyrrole (ProDOP) are exceptional monomers for their ultra-low exceptional potential and leading to polymers with unique opto-electronic properties including high conductivity, multicolor cathodic and anodic electrochromism, and rapid redox switching.<sup>[33-37]</sup> In order to obtain nanofibers using XDOP with high hydrophobicity, it is preferable to put the substituent on the bridge (not on the nitrogen) in order to keep the NH group free, and as a consequence favor the formation of nanofibers with hydrogen bonds.<sup>[38-40]</sup> Previously, it was found a way to obtain EDOP and ProDOP derivatives with hydroxyl groups on the bridge using epibromohydrin.<sup>[38]</sup> The formation of nanofibers was studied using fluorinated chains.



Scheme 1. Monomers studied in this manuscript ( $C_n = C_n H_{2n+1}$  with n = 3 to 17).

Here, we investigate the formation of nanofibers using EDOP and ProDOP with alkyl chains on the bridge, and the resulting surface hydrophobicity (Scheme 1). Contrary to other works in the literature for example using polyaniline,<sup>[24-28]</sup> this strategic has other advantages. The NH should be kept free for the formation of nanofibers but various substituents can be easily grafted. The surface morphology and properties can be easily controlled by electrochemical parameters but also the substituent nature. Here, we study the influence of the monomer (EDOP or ProDOP) as well as the alkyl chain length on the formation of nanofibers and the resulting surface hydrophobicity.



#### **Results and Discussion**

*Electrochemical characterization:* The electrodepositions were performed in optimal electrolyte consisting in anhydrous acetonitrile with 0.1 M of tetrabutylammonium perchlorate ( $Bu_4NCIO_4$ ). The role of the electrolyte ( $Bu_4NCIO_4$ ) is to enhance the solution conductivity. It is also necessary to stabilize the conducting polymers formed in their doped state. The monomer oxidation potentials were first determined by cyclic voltammetry and were found to be about 0.9 V vs SCE for the EDOP derivatives and 1.1 V for the ProDOP derivatives. Their oxidation potentials are in agreement with previous works report in the literature. The alkyl chain length has not, here, a significant influence on the monomer oxidation potential because they are far from the polymerizable sites.

In order to study the polymer growth, cyclic voltammogram (10 scans at a scan rate of 20 mV s<sup>-1</sup>) were performed with each monomer. The cyclic voltammograms confirm the exceptional polymerization capacity of these ProDOP and EDOP derivatives. Indeed, a constant increase in the polymer oxidation and reduction peaks after scans is observed after each scan. Significant steric hindrances are observed only with ProDOP-C7 and EDOP-C<sub>5</sub>. With them, a shift in the high potential is observed after each scan, as known in the literature.[41,42] Moreover, the polymer oxidation and reduction potentials are extremely low (most of the time lower than 0 V vs SCE) showing that the polymer chain lengths are extremely high, which is extremely important in electrodeposition. Here, this is in part due to the presence of 3,4-alkylenedioxybridge, which have high electro-donating effect and also avoid the polymerization at  $\beta$ positions of pyrrole.[34-37]

As the alkyl chain length increases, it is observed both an increase in the polymer oxidation and reduction potentials and a reduction in their intensity.

Surface properties: First of all, the surface properties obtained with the ProDOP derivatives are very different from that obtained with the EDOP ones. Using ProDOP as polymerizable core, a change in the surface morphology from small nanofibers to huge spherical structures are observed when the alkyl chain length increases. More precisely, both microdomes and nanofibers are obtained with short alkyl chains ( $C_3$  to  $C_7$ ), which induce an increase in the surface hydrophobicity even if the surface is intrinsically hydrophilic.

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Figure 4. SEM images of the polymer films obtained with the ProDOP-C<sub>9</sub> with a deposition charge of 100 and 200 mC cm<sup>-2</sup>.

This increase is not possible using the Wenzel equation because the polymers are intrinsically hydrophilic, but can be explained with the Cassie-Baxter equation indicating of the presence of air inside the surface structures. Extremely long fibers are obtained with intermediate lengths (C9 to C11). Using ProDOP-C<sub>9</sub>, extremely well-defined fibers are observed but only using a deposition charge up to 200 mC cm<sup>-2</sup>. The presence of the fibers induced a huge increase in surface hydrophobicity with  $\theta_w$  up to 136°. However, the surfaces are completely sticky (parahydrophobic as observed on rose petals),<sup>[9-12]</sup> that means water droplets remain completely stuck on the surface even if the surface is inclined to 90°. Nanofibers are also observed with ProDOP-C<sub>11</sub> but  $\theta_w$  is up to 150° for Qs = 400 mC cm<sup>-2</sup> and with a much lower water adhesion. The sliding angle ( $\alpha$ ) is 20°, and the advancing contact angle ( $\theta_{adv}$ ) is 154° and receding contact angle ( $\theta_{\text{rec}}$ ) is 127° that mean the hysteresis is 27° (Figure 5). Hence, the surface is not superhydrophobic but relatively close to this state. Using long alkyl chains ( $C_{13}$  to  $C_{17}$ ), the surface morphology changes into spherical particles with an increase in the size of the particles as the alkyl chain length increases.



Figure 5. Picture of a water droplet on a surface obtained with ProDOP-C<sub>11</sub> and with a deposition charge of 400 mC cm<sup>-2</sup>, and just before the water droplets rolls off the surface.

Table	1.	Surface	roughness	and	apparent	contact	angle	of	the	different
PProD	OP	polymers	s as a functi	on of	the numbe	er of depo	osition	sca	ns.	

Monomer	Deposition charge [mC cm <sup>-2</sup> ]	Ra [nm]	Rq [nm]	$\theta_{\rm w}$ [deg]
ProDOP-C <sub>3</sub>	12.5	25	32	55
	25	23	34	51
	50	29	43	54

	100	74	96	56
	200	108	144	76
	400	1400	1900	86
ProDOP-C₅	12.5	33	40	87
	25	27	34	81
	50	42	52	78
	100	112	156	72
	200	232	292	70
	400	1200	2610	58
ProDOP-C7	12.5	22	29	73
	25	24	30	87
	50	51	65	92
	100	110	142	87
ProDOP-C <sub>9</sub>	12.5	38	55	86
	25	46	72	77
	50	63	100	100
	100	127	170	125
	200	217	283	136
	400	2290	3475	77
ProDOP-C <sub>11</sub>	12.5	25	32	96
	25	36	47	96
	50	28	36	95
	100	126	160	120
	200	145	192	110
	400	200	265	150
ProDOP-C <sub>13</sub>	12.5	8	12	94
	25	10	14	95
	50	40	58	93
	100	37	55	118
	200	95	122	96
	400	152	220	122
ProDOP-C <sub>15</sub>	12.5	7	10	98
	25	7	9	94
	50	9	12	100
	100	29	39	100
	200	136	178	100
	400	214	272	114
ProDOP-C <sub>17</sub>	12.5	8	12	95
	25	7	8	96
2	50	12	23	97
	100	58	73	98
	200	203	365	106
	400	315	416	94

Using EDOP as polymerizable core, a change in the surface morphology from smooth to huge spherical structures is observed when the alkyl chain length increases (Figure 5). The formation of fibrous structures is much rarer with EDOP derivatives and was observed only with EDOP-C<sub>9</sub>. The fibers are relatively small but extremely high hydrophobicity with  $\theta_w$  up to 147° is reached because the surface is also extremely rough and porous. However, the surface is completely sticky (parahydrophobic)<sup>[9-12]</sup> as shown in Figure 6.

It should also be noticed that high hydrophobicity is reached with spherical nanoparticles using EDOP- $C_{11}$  and EDOP- $C_{13}$ .



Figure 5. SEM images of the polymer films obtained with the PEDOP derivatives with a deposition charge of 400 mC cm<sup>-2</sup>.

 Table 2. Surface roughness and apparent contact angle of the different

 PEDOP polymers as a function of the number of deposition scans.

Monomer	Deposition charge [mC cm <sup>-2</sup> ]	Ra [nm]	Rq [nm]	$ heta_{w}$ [deg]
EDOP-C <sub>3</sub>	12.5	28	55	46
	25	25	42	44

	50	24	32	50
	100	20	26	69
	200	158	200	73
	400	248	330	57
EDOP-C₅	12.5	24	39	51
	25	23	30	75
	50	24	33	68
	100	22	31	86
	200	120	155	75
	400	258	325	77
EDOP-C7	12.5	27	35	69
	25	24	30	64
	50	22	30	68
	100	115	160	102
	200	208	280	100
	400	426	550	94
EDOP-C <sub>9</sub>	12.5	30	43	79
	25	25	37	68
	50	56	100	80
	100	170	219	113
	200	200	257	147
	400	2400	3970	140
EDOP-C <sub>11</sub>	12.5	9	12	91
	25	6	8	101
	50	10	14	96
	100	34	44	102
	200	190	235	126
	400	160	200	149
EDOP-C <sub>13</sub>	12.5	8	11	99
	25	19	40	99
	50	10	13	97
	100	32	55	109
	200	127	181	111
	400	220	317	139
EDOP-C <sub>15</sub>	12.5	12	16	92
	25	24	44	92
	50	12	17	95
	100	24	39	94
	200	200	276	84
	400	312	480	88
EDOP-C <sub>17</sub>	12.5	8	14	99
	25	15	21	94
	50	28	44	88

100	96	129	121
200	232	290	111
400	1600	2220	106



Figure 6. Picture of a water droplet on a surface inclined to  $90^{\circ}$ , obtained with EDOP-C<sub>9</sub> and with a deposition charge of 200 mC cm<sup>-2</sup>.

#### Conclusions

Here, we demonstrated the huge influence on the polymerizable core (EDOP or ProDOP) and the alky chain length on the formation of nanofibrous surfaces with high hydrophobicity by electropolymerization. We show that the formation of nanofibrous surfaces was much more favored using ProDOP as polymerizable core and with alkyl chains of intermediate length (C<sub>9</sub> and C<sub>11</sub>). Apparent contact angle ( $\theta_w$ ) up to 150° were obtained with various water adhesion. This is work is extremely important and open new doors for applications in oil/water separation membranes or in water harvesting systems, for example.

#### **Experimental Section**

*Monomer synthesis*: The monomers were synthesized according to publications in the literature.<sup>[38]</sup> The key intermediates were ProDOP-OH and EDOP-OH obtained in eight steps from iminodiacetic acid (Scheme 2). Then, alkyl chains were grafted by simple esterification reaction. For that, 1.2 equiv. of the corresponding acid, 0.31 g of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC) (0.0015 mol, 1.2 equiv.) and 20 mg of *N*,*N*-dimethylaminopyridine (DMAP) were added to 20 mL of absolute dichloromethane. After stirring for 30 min, the mixture was added to 20 mL of absolute acetonitrile containing 0.2 g of ProDOP-OH or EDOP-OH (0.0013 mol, 1 equiv.). After 1 day, the products were purified by column chromatography using tetrahydrofuran/petroleum ether 60:40 as eluent. Here, it was also extremely important to add 10% of triethylamine in the silica gel and in the eluent because of the product sensitivity.

# ProDOP-C<sub>3</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl butyrate

Yield 56%;Crystalline solid; m.p. 106.6°C;  $\delta_H$ (200 MHz, CDCl<sub>3</sub>): 7.19 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.19 (m, 1H), 4.22 (dd, J = 12.4 Hz, J =4.9 Hz, 2H), 4.06 (dd, J =12.4 Hz, J =2.7 Hz, 2H), 2.39 (t, J = 7.4 Hz, 2H), 1.68 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H);  $\delta_C$ (200 MHz, CDCl<sub>3</sub>): 172.99, 138.89, 103.10, 72.66, 72.57, 36.10, 18.44, 13.58; [MH]<sup>+</sup> = 226.00.

# EDOP-C<sub>3</sub>: (3,6-dihydro-2H-[1,4]dioxino[2,3-*c*]pyrrol-2-yl)methyl butyrate

Yield 56%; Liquid;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ : 7.03 (s, 1H), 6.14 (m, 2H), 4.26 (m, 3H), 4.15 (dd, J = 11.5 Hz, J = 1.8 Hz, 1H), 3.96 (dd, J = 11.5 Hz, J = 6.6 Hz, 1H), 2.28 (t, J = 7.4 Hz, 2H), 1.58 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ : 173.32, 132.18, 131.97, 98.69, 98.47, 72.24, 66.64, 62.44, 35.92, 18.36, 13.62; Mass: [MH]<sup>+</sup> = 226.00.

# ProDOP-C<sub>5</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl hexanoate

Yield 75%; Crystalline solid; m.p. 60.6°C;  $\delta_H$ (200 MHz, CDCl<sub>3</sub>): 7.23 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.18 (m, 1H), 4.22 (dd, J = 12.4 Hz, J =4.9 Hz, 2H), 4.06 (dd, J =12.4 Hz, J =2.7 Hz, 2H), 2.40 (t, J = 7.3Hz, 2H), 1.66 (m, 2H), 1.33 (m, 4H), 0.89 (t, J = 6.7Hz, 3H);  $\delta_C$ (200 MHz, CDCl<sub>3</sub>): 173.19, 138.86, 103.09, 72.66, 72.65, 72.57, 34.20, 31.23, 30.30, 24.59, 22.26, 13.87; [MH]<sup>+</sup> = 254.07.

## EDOP-C<sub>5</sub>: (3,6-dihydro-2H-[1,4]dioxino[2,3-*c*]pyrrol-2-yl)methyl hexanoate

Yield 62%; Liquid;  $\delta_{H}(200 \text{ MHz}, \text{ CDCl}_3)$ : 7.03 (s, 1H), 6.14 (m, 2H), 4.26 (m, 3H), 4.14 (dd, J = 11.5 Hz, J = 1.8 Hz, 1H), 3.96 (dd, J = 11.5 Hz, J = 6.6 Hz, 1H), 2.28 (t, J = 7.5 Hz, 2H), 1.57 (m, 2H), 1.24 (m, 4H), 0.82 (t, J = 6.6 Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{ CDCl}_3)$ : 173.51, 132.18, 131.97, 98.68, 98.46, 72.24, 66.64, 62.46, 34.03, 31.24, 24.55, 22.27, 13.87; [MH]<sup>+</sup> = 254.00.

## ProDOP-C7: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl octanoate

Yield 71%; Crystalline solid; m.p. 59.9°C;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ : 7.21 (s, 1H), 6.31 (d, J = 3.4 Hz, 2H), 5.18 (m, 1H), 4.22 (dd, J = 12.4 Hz, J = 4.9 Hz, 2H), 4.06 (dd, J = 12.4 Hz, J = 2.7 Hz, 2H), 2.40 (t, J = 7.3 Hz, 2H), 1.65 (m, 2H),1.28 (m, 8H), 0.87 (t, J = 6.3 Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ : 173.19, 138.87, 103.09, 72.65, 72.57, 34.25, 31.62, 29.02, 28.87, 24.92, 22.56, 14.03; [MH]<sup>+</sup> = 282.07.

# EDOP-C<sub>7</sub>: (3,6-dihydro-2H-[1,4]dioxino[2,3-*c*]pyrrol-2-yl)methyl octanoate

Yield 61%; Liquid;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ ; 7.08 (s, 1H), 6.21 (m, 2H),4.33(m, 3H), 4.21(dd, J = 11.4Hz, J = 1.5Hz, 1H), 4.03 (dd, J = 11.4Hz, J = 6.4Hz, 1H),2.36(t, J = 7.4 Hz, 2H), 163 (m, 2H),1.27 (m, 8H),0.87 (t, J = 6.6Hz, 3H); $\delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ ; 173.52, 132.19, 131.98, 98.68, 98.47, 72.25, 66.65, 62.46, 34.07, 31.62, 29.05, 28.88, 24.87, 22.57, 14.04; [MH]<sup>+</sup> = 282.07.

# ProDOP-C<sub>9</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl decanoate

Yield 84%; Crystalline solid; m.p. 44.3°C;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ : 7.21 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.19 (m, 1H), 4.22 (dd, J = 12.4 Hz, J = 4.9 Hz, 2H), 4.06(dd, <math>J = 12.4 Hz, J = 2.7 Hz, 2H), 2.40 (t, J = 7.3 Hz, 2H), 1.63 (m, 2H), 1.25 (m, 16H), 0.87 (t,  $J = 6.1\text{Hz}, 3\text{H}); \delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ : 173.19, 138.88, 103.09, 72.65, 72.57, 34.25, 31.83, 29.38, 29.22, 29.07, 24.92, 22.64, 14.08; [MH]<sup>+</sup> = 310.07.

EDOP-C<sub>9</sub>:(3,6-dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl decanoate

Yield 55%; Liquid;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ : 7.07 (s, 1H), 6.20 (m, 2H), 4.33 (m, 3H), 4.21 (dd, J = 11.5 Hz, J = 1.8 Hz, 1H), 4.03 (dd, J = 11.5 Hz, J = 6.5 Hz, 1H), 2.35 (t, J = 7.4 Hz, 2H), 1.63 (m, 2H), 1.26 (m, 12H),0.87 (t, J = 6.1 Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ : 173.52, 132.20, 131.98, 98.68, 98.47, 72.25, 66.64, 62.46, 34.07, 31.83, 29.38, 29.23, 29.09, 24.87, 22.64, 14.08; [MH]<sup>+</sup> = 310.13.

# ProDOP-C<sub>11</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl dodecanoate

Yield 83%; Crystalline solid; m.p. 56.6°C;  $\delta_H$ (200 MHz, CDCl<sub>3</sub>): 7.19 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.19 (m, 1H), 4.22 (dd, J = 12.4 Hz, J =4.9 Hz, 2H), 4.06 (dd, J =12.4 Hz, J =2.8 Hz, 2H),2.40(t, J= 7.3Hz, 2H), 1.63(m, 2H), 1.25(m, 16H), 0.89(t, J= 6.1Hz, 3H);  $\delta_C$ (200 MHz, CDCl<sub>3</sub>): 173.19, 138.89, 103.09, 72.66, 72.56, 34.25, 31.89, 30.31, 29.57, 29.43, 29.31, 29.22, 29.08, 24.92, 22.66, 14.10; [MH]<sup>+</sup> = 338.07.

#### EDOP-C<sub>11</sub>: (3,6-dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2yl)methyldodecanoate

Yield 99%; Crystalline solid; m.p. 30.6°C;  $\delta_{H}(200 \text{ MHz}, \text{CDCI}_3)$ ;7.09 (s, 1H), 6.21 (m, 2H), 4.34(m, 3H),4.21(dd, J = 11.5Hz, J = 1.7Hz, 1H), 4.03(dd, J = 11.5Hz, J = 6.7Hz, 1H), 2.36 (t, J = 7.1Hz, 2H), 1.63 (m, 2H),1.25(m, 16H), 0.88 (t, J = 6.1Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{CDCI}_3)$ : 173.52, 132.18, 131.97, 98.68, 98.45, 72.24, 66.64, 62.46, 34.07, 31.89, 29.57, 29.43, 29.31, 29.23, 29.09, 24.87, 22.66, 14.09; [MH]^+ = 338.13.

## ProDOP-C<sub>13</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl tetradecanoate

Yield 54%; Crystalline solid; m.p. 50.2°C;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ : 7.20 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.18 (m, 1H), 4.22 (dd, J = 12.4 Hz, J = 4.9 Hz, 2H), 4.06 (dd, J = 12.4 Hz, J = 2.7 Hz, 2H), 2.40 (t, J = 7.3Hz, 2H), 1.68 (m, 2H), 1.25(m, 20H), 0.88 (t, J = 6.1Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ : 173.12, 138.88, 103.08, 72.66, 72.56, 34.25, 31.90, 30.30, 29.65, 29.62, 29.57, 29.43, 29.33, 29.22, 29.08, 24.92, 22.67, 14.10; [MH]<sup>+</sup> = 366.00.

#### EDOP-C<sub>13</sub>: (3,6-dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2yl)methyltetradecanoate

Yield 70%; Crystalline solid; m.p. 45.2°C;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ ; 7.11 (s, 1H), 6.20 (m, 2H), 4.33 (m, 3H), 4.21 (dd, J = 11.5 Hz, J = 1.8 Hz, 1H), 4.03 (dd, J = 11.5 Hz, J = 6.6 Hz, 1H), 2.35 (m, J = 7.3 Hz, 2H), 1.25 (m, 25H), 0.88 (t, J = 6.1 Hz, 3H);  $\delta_{C}(200 \text{ MHz}, \text{CDCl}_3)$ ; 173.52, 132.17, 131.95, 98.67, 98.46, 72.24, 66.63, 34.06, 31.89, 29.64, 29.62, 29.57, 29.42, 29.33, 29.22, 29.09, 24.86, 22.66, 14.09; [MH]\* = 366.20.

# ProDOP-C<sub>15</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-c]pyrrol-3-yl palmitate

Yield 98%; Crystalline solid; m.p. 69.4°C;  $\delta_H(200 \text{ MHz}, \text{CDCl}_3)$ : 7.19 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.19 (m, 1H), 4.22 (dd, J = 12.4 Hz, J = 4.9 Hz, 2H), 4.06 (dd, J = 12.4 Hz, J = 2.7 Hz, 2H), 2.40 (t, J = 7.3Hz, 2H), 1.65 (m, 2H), 1.25(m, 24H), 0.88 (t, J = 6.1Hz, 3H);  $\delta_C(200 \text{ MHz}, \text{CDCl}_3)$ : 173.19, 138.89, 103.08, 72.66, 72.56, 34.25, 31.91, 30.31, 29.67, 29.64, 29.58, 29.44, 29.34, 29.22, 29.09, 24.93, 22.68, 14.10; [MH]<sup>+</sup> = 394.27.



ProDOP1

Scheme 2 Synthesis way to the monomers ( $C_n = C_nH_{2n+1}$  with n = 3 to 17).

#### EDOP-C<sub>15</sub>:(3,6-dihydro-2H-[1,4]dioxino[2,3-*c*]pyrrol-2yl)methylpalmitate

Yield 78%; Crystalline solid; m.p. 53.7°C;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ ; 7.10 (s, 1H), 6.21 (m, 2H), 4.33 (m, 3H), 4.21 (dd, J = 11.5 Hz, J = 1.8 Hz, 1H), 4.03 (dd, J = 11.5 Hz, J = 6.6 Hz, 1H), 2.35 (t, J = 7.3 Hz, 2H), 1.61 (m, 2H), 1.25 (m. 24H) 0.89 (t, J = 6.9Hz, 3H);  $\delta_{C}(100 \text{ MHz}, \text{CDCl}_3)$ : 173.52, 132.18, 131.96, 98.68, 98.46, 72.24, 66.64, 62.46, 34.07, 31.91, 29.67, 29.64, 29.58, 29.43, 29.34, 29.23, 29.10, 24.87, 22.67, 14.10; [M-H]<sup>+</sup> = 395.13.

## ProDOP-C<sub>17</sub>: 2,3,4,7-tetrahydro-[1,4]dioxepino[2,3-*c*]pyrrol-3-yl stearate

Yield 98%; Crystalline solid; m.p. 72.1°C;  $\delta_H$ (200 MHz, CDCl<sub>3</sub>): 7.19 (s, 1H), 6.31 (d, J = 3.3 Hz, 2H), 5.19 (m, 1H), 4.22 (dd, J = 12.4 Hz, J =4.9 Hz, 2H), 4.06 (dd, J =12.4 Hz, J =2.7 Hz, 2H), 2.40 (t, J = 7.3Hz, 2H), 1.64 (m, 2H), 1.25(m, 28H), 0.88 (t, J = 6.1Hz, 3H);  $\delta_C$ (200 MHz, CDCl<sub>3</sub>): 173.19, 138.89, 103.08, 72.66, 72.56, 34.26, 31.91, 30.31, 29.68, 29.68, 29.58, 29.44, 29.35, 29.23, 29.09, 24.93, 22.68, 14.10; [MH]<sup>+</sup> = 422.27.

#### EDOP-C<sub>17</sub>: (3,6-dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2yl)methylstearate

Yield 40%; Crystalline solid; m.p.  $60.5^{\circ}$ C;  $\delta_{H}(200 \text{ MHz}, \text{CDCl}_3)$ : 7.08 (s, 1H), 6.21 (m, 2H), 4.34 (m, 3H), 4.21 (dd, J = 11.5 Hz, J = 1.8 Hz, 1H), 4.03 (dd, J = 11.5 Hz, J = 6.6 Hz, 1H), 2.28 (t, J = 7.3 Hz, 2H), 1.63 (m, 2H), 1.25 (m, 28H), 0.89 (t, J = 6.2 Hz, 3H);  $\delta_C(200 \text{ MHz}, \text{CDCl}_3)$ : 173.52, 132.20, 131.99, 98.69, 98.47, 72.25, 66.65, 62.46, 34.07, 31.91, 29.68, 29.58, 29.44, 29.35, 29.24, 29.11, 24.87, 22.68, 14.11; [MH]<sup>+</sup> = 422.20.

*Electropolymerization:* For each deposition, 10 mL of anhydrous was placed in an electrochemical cell. 0.01 M of monomer and 0.1 M of

tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) were added. The solution was degassed under argon before each experiment. Three electrodes were connected to the electrochemical cell. A glassy carbon rod and a saturated calomel electrode (SCE) were used as the counter-electrode and the reference electrode, respectively. A platinum tip was first used as the working electrode in order to study the electrochemical characterization and a 2 cm<sup>2</sup> gold plate was used for surface characterization. The three electrodes were connected to an Autolab potentiostat from Metrohm with the GPES software.

Surface characterization: Scanning electron microscopy (SEM) images were performed with a 6700F microscope from JEOL. The arithmetic (Ra) and quadratic (Rq) roughness were obtained with a WYKO NT1100 optical profiling system from Bruker using the working mode High Mag Phase Shift Interference (PSI), the objective 20X, and the field of view 0.5X. The surface hydrophobicity was characterized with a DSA30 goniometer from Krüss. The water apparent contact angles ( $\theta_w$ ) were obtained using the sessile drop method using 2 µL water droplets. For that, the water droplets were placed on the surface and the  $\theta_w$  were taken at the triple point. For the dynamic contact angles, the tilted-drop method was used using 6 µL water droplets. For that, the water droplets were placed on the surface and the surface was inclined until the droplet moves. The advanced and receding contact angle and as a consequence the hysteresis were taken just before the droplet moves. If the droplets do not move whatever the surface inclination, the surface is called sticky.

#### **Conflict of Interests**

There are no conflict of interests to declare.

Keywords: Hydrophobic • Adhesion • Nanostructures • Electropolymerization • Conducting Polymers

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#### **Entry for the Table of Contents**

Layout 1:

### FULL PAPER

#### **Controlled Nanofibrous Structures:**

Electropolymerization of 3,4ethylenedioxypyrrole (EDOP) and 3,4propylenedioxypyrrole (ProDOP) with alkyl chain leads to various surface structures. The presence of nanofibers highly increases the surface hydrophobicity.



Omar Sane, Alioune Diouf, Samba Yandé Dieng, Frédéric Guittard, Thierry Darmanin\*

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Formation of Nanofibers with High Water Adhesion by Electrodeposition of Poly(3,4-ethylenedioxypyrrole) and Poly(3,4-propylenedioxypyrrole) Films Substituted by Alkyl Chains