Semicrystalline polythiophene-based nanoparticles deposited from water on flexible PET/ITO substrates as a sustainable approach towards long-lasting solid-state electrochromic devices

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I. Synthesis

General. 3-hexylthiophene, N-bromosuccinimide, sodium bicarbonate, 1,1’-bis(diphenylphosphino)ferrocene palladium(II)chloride dichloromethane complex (PdCl$_2$dppf), 3-methoxythiophene, 2-ethyl-1-hexanol, p-Toluenesulfonic acid (p-TSA), bis(pinacolato)diboron, Hexafluoro-2-propanol (HFIP), [Hydroxy(tosyloxy)iodo]benzene (HTIB), FeCl$_3$, Bromotrimethylsilane (TMSBr) and 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) were purchased from Sigma-Aldrich Co. Microwave experiments were carried out in a Milestone Microsynth Labstation operating at 2450 MHz monitored by a proprietary control unit. The oven was equipped with magnetic stirring, pressure and temperature sensors. Reactions were performed in a glass vessel (capacity 10 mL) sealed with a septum. The microwave method was power controlled (100 W maximum power input) and the samples were irradiated with the required power output (setting at the maximum power) to achieve the desired temperature (80°C). All $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Mercury-400/500 spectrometer equipped with a 5-mm probe. Chemical shifts were calibrated using the internal CDCl$_3$ or benzene-$d_6$ resonance which were referenced to TMS. Mass spectra were collected on a Finningan Mat GCQ spectrometer. UV-Vis spectra were recorded using a Perkin Elmer Lambda 20 spectrometer. Photoluminescence spectra were collected on a Perkin Elmer LS50 spectrofluorometer. Fluorescence measurements were performed using an excitation wavelength corresponding to the maximum absorption lambda.
Synthesis of Poly(4-(3,4′-bis((2-ethylhexyl)oxy)-[2,2′-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole), POR

Scheme S1 – Synthetic scheme of POR polymer.  

i. HTIB, TMSBr, HFIP  
ii. NBS (1 or 2 eq), CH₂Cl₂;  
iii. 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole, NaHCO₃, Pd(dppf)Cl₂, MW, 80°C.

3-((2-ethylhexyl)oxy)thiophene (1). A solution of 3-methoxythiophene (1 mmol), 2-ethyl-1-hexanol (2 mmol) and p-TSA (0.1 mmol) in Toluene was refluxed for 17 h. The reaction mixture was brought to room temperature and the product was extracted with DCM. The combined organic layers were dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. The residue was isolated by flash chromatography (100% cyclohexane). → Yield 93%. Pale yellow oil; El-MS m/z 212 (M⁺); ¹H NMR (500 MHz, CDCl₃, TMS/ppm): δ 7.17 (dd, J = 5.2 Hz; J = 3.1 Hz, 1H), 6.76 (dd, J = 5.2 Hz; J = 1.1 Hz, 1H), 6.23 (d, J = 2.9 Hz; 1.3 Hz, 1H), 3.84 (d, J = 5.8 Hz, 2H), 1.76-1.66 (m, 1H), 1.58-1.28 (m, 8H), 0.98-0.87 (m, 6H); ¹³C NMR (500 MHz, CDCl₃): δ 158.3, 124.4, 119.7, 96.8, 72.8, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1.

3,4′-bis((2-ethylhexyl)oxy)-2,2′-bithiophene (2). To a solution of 3-((2-ethylhexyl)oxy)thiophene (1) (1 mmol) in HFIP (2 ml) at room temperature, HTIB (0.5 mmol) and TMSBr (1 mmol) were added. After 3 h, a saturated solution of NaHCO₃ was added and the product extracted with DCM. The organic solvent was removed, and the products were purified by flash chromatography. The residue was isolated by flash chromatography cyclohexane/DCM (9:1, v/v) → Yield 69%. Yellow oil; El-MS m/z 422 (M⁺); ¹H NMR (400 MHz, CDCl₃, TMS/ppm): δ 7.04 (d, ³J = 5.5 Hz, 1H), 6.89 (d, ⁴J = 1.6 Hz, 1H), 6.83 (d, ³J = 5.6 Hz, 1H), 6.11 (d, ⁴J = 1.6 Hz, 1H), 4.00 (d, ³J = 5.4 Hz, 2H), 3.84 (d, ³J = 5.6 Hz, 2H), 1.79-1.67 (m, 2H), 1.62-1.27 (m, 16H), 0.99-0.88 (m, 12H); ¹³C NMR (400 MHz, CDCl₃): δ 157.4, 153.1, 133.9, 121.3, 117.1, 115.0, 114.5, 95.3, 73.9, 72.5, 39.8, 39.4, 30.5, 30.4, 29.1, 23.9, 23.8, 23.1, 23.0, 14.1, 11.2, 11.1.
**5,5'-dibromo-3,4'-bis((2-ethylhexyl)oxy)-2,2'-bithiophene (3).** To a solution of 2 (1 mmol) in DMF at 0 °C, 2 mmol of NBS were added. The reaction mixture was brought to room temperature and reacted overnight. The solvent was removed, and the products were purified by flash chromatography. The residue was isolated by flash chromatography cyclohexane/DCM (9:1, v/v) → Yield 70%. Yellow oil; EI-MS \( m/z \) 580(M⁺); \(^1\)H NMR (400 MHz, CDCl₃, TMS/ppm): δ 6.84 (s, 1H), 6.71 (s, 1H), 3.96 (d, \(^3\)J = 5.5 Hz, 2H), 3.91 (d, \(^3\)J = 5.8 Hz, 2H), 1.77-1.66 (m, 2H), 1.60-1.26 (m, 16H), 0.98-0.88 (m, 12H); \(^{13}\)C NMR (400 MHz, CDCl₃): δ 154.1, 151.9, 132.5, 120.4, 116.1, 111.7, 109.2, 90.0, 74.7, 74.4, 39.7, 39.6, 30.4, 30.3, 29.03, 29.02, 23.8, 23.7, 23.1, 23.0, 14.1, 11.1.

**Poly(4-(3,4'-bis((2-ethylhexyl)oxy)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) POR (4).** A mixture of 5,5'-dibromo-3,4'-bis((2-ethylhexyl)oxy)-2,2'-bithiophene (3) (2 mmol), 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (1 mmol), Pd(dppf)Cl₂ (0.1 mmol) and NaHCO₃ (6 mmol) in THF/water 2:1 (3 mL) was irradiated with microwaves at 80°C for 20 min. The reaction mixture was brought to room temperature and the solvent was evaporated under reduced pressure. The residue was washed with MeOH, acetone and diethyl ether to remove the low molecular weight polymer fractions. → Yield 50%. Dark blue solid. Mn = 1200 gmol⁻¹, Mw = 4750 gmol⁻¹, PDI = 2.5; \( T_d = 392{\degree}C; T_g = 59{\degree}C \). \(^1\)H NMR (400 MHz, CDCl₃, TMS/ppm): δ 8.66-7.36 (m), 4.29-3.67 (m) 1.97-0.62 (m).

**Figure S1.** \(^1\)H-NMR spectrum in CDCl₃ of POR.
Synthesis of Poly(3-Hexylthiophene), P3HT

Poly(3-hexylthiophene), P3HT. Poly(3-hexylthiophene) was synthesized according to a previously reported procedure.\textsuperscript{1,2} The excess of iron (III) ion in the polymers was completely removed by washing with 2% aq. HCl solution until negative essay with NH\textsubscript{4}SCN. The resulting polymer was further purified by removing the shorter fractions soluble in methanol and acetone. $\rightarrow$ Yield 50%. Dark red solid. M\textsubscript{n}= 25800 gmol\textsuperscript{-1}, M\textsubscript{w}= 48000 gmol\textsuperscript{-1}, PDI = 1.87. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, TMS/ppm): $\delta$ 7.02 (s), 7.00 (s), 6.98 (s), 6.95 (s), 2.82-2.73 (m), 2.58-2.48 (m), 1.72-1.50 (m), 1.44-1.20 (m), 0.91-0.81 (m).

Figure S2. \textsuperscript{1}H-NMR spectrum in CDCl\textsubscript{3} of P3HT.
II. Scheme of NPs formation and DLS characterization

P3HT or POR nanoparticles were prepared by dissolving the polymer in THF and adding the solution dropwise to surfactant-free distilled water or ethanol, respectively, under vigorous stirring.

![Scheme of nanoparticles formation by nanoprecipitation method](image)

**Scheme S3** – Scheme of nanoparticles formation by nanoprecipitation method\textsuperscript{3-5}.

**Table S1.** Dimensions of P3HT-NPs and POR-NPs obtained by DLS

<table>
<thead>
<tr>
<th></th>
<th>Size</th>
<th></th>
<th>Size</th>
<th></th>
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<tbody>
<tr>
<td><strong>P3HT-NPs</strong></td>
<td>100±18</td>
<td><strong>POR-NPs</strong></td>
<td>130±3 (0.5 mg)</td>
<td></td>
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<tr>
<td></td>
<td>116±20</td>
<td></td>
<td>177±3 (1 mg)</td>
<td></td>
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<tr>
<td></td>
<td>150±19</td>
<td></td>
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<td></td>
<td>200±22</td>
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<td></td>
<td>380±18</td>
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<td>214±3 (2 mg)</td>
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<td></td>
<td>400±20</td>
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</table>
III. X-ray diffraction of a thin film of P3HT cast from chloroform and a film of 100 nm Nps

![Figure S3](image)

**Figure S3.** Specular XRD scans of a thin film of P3HT spray-coated from chloroform (red line) and of a film of 100 nm nanoparticles (black line).

Figure S3 shows the specular XRD scans of the continuous P3HT film and the film based on P3HT NPs with 100 nm size. They were obtained using a laboratory X-ray source which is characterized by a photon flux lower than the synchrotron radiation used for GIXRD measurements. This explains the absence of reflections in the film based by P3HT NPs.
IV. Cyclic Voltammetry of P3HT and different sized P3HT NPs

Figure S4. – Cyclic voltammograms of P3HT and different sized P3HT NPs spray-coated on PET-ITO substrates. The cyclic voltammograms were performed using Ag/AgCl as reference electrode, a platinum wire as counter-electrode, working electrode the PET-ITO substrate with the material deposited on top and an electrolytic solution of LiClO$_4$ (0.1M) in acetonitrile.
V. Optical and redox properties and ECDs data of POR Polymer

**Table S2** – Optical and redox properties of POR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{Abs max}}$ (nm)</th>
<th>$\lambda_{\text{em max}}$ (nm)</th>
<th>Stokes Shift (eV)</th>
<th>$E_g$ (eV)</th>
<th>$E_{\text{onset ox}}$ (V)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>PolyORAM2-3,4 (a)</td>
<td>654</td>
<td>805</td>
<td>0.36</td>
<td>1.47</td>
<td>0.13</td>
<td>-4.52</td>
<td>-3.05</td>
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<tr>
<td>130 nm NPs (b)</td>
<td>697</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) Deposition from CHCl$_3$ solutions.
(b) Deposition of NPs from ethanol dispersions.
(c) vs. Ag/AgCl, thin-films measured in acetonitrile solutions.

**Table S3** – Optical and redox properties of POR in the ECDs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{Abs max}}$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta$$\text{Abs}_{\text{max}}$</th>
<th>$Q_{\text{ox}}$ (mC.cm$^{-2}$)</th>
<th>$Q_{\text{red}}$ (mC.cm$^{-2}$)</th>
<th>CE (cm$^2$ C$^{-1}$)</th>
<th>$\tau_{\text{ox}}$ (s)</th>
<th>$\tau_{\text{red}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PolyORAM2-3,4 (a)</td>
<td>715</td>
<td>1.32</td>
<td>0.099</td>
<td>1.48</td>
<td>-0.91</td>
<td>100</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>130 nm NPs (b)</td>
<td>703</td>
<td>1.38</td>
<td>0.040</td>
<td>0.37</td>
<td>-0.23</td>
<td>159</td>
<td>1.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

(a) Deposition from CHCl$_3$ solutions.
(b) Deposition of NPs from ethanol dispersions.

**Figure S5.** (A) Switching cycles of POR after ECD assembly from thin-films cast from chloroform solutions and cast from ethanol dispersions of 130 nm nanoparticles. (B) Spectroelectrochemistry of the same samples between -1.5V and 1.5V.
VI. Switching of ECD’s (P3HT-NPs 100nm vs P3HT)

Figure S6 – Caption of Video S1 representing the switch of assembled ECD’s

References


