Supporting Information

Novel water-soluble and self-doped conducting hybrid copolymer; poly(4-oxybenzenesulfonic acid)phosphazene-g-poly(3,4-ethylenedioxythiophene) †

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Figure S1. a) GPC elugram and b) 31P NMR of 2 and 3a-d copolymers in D2O solution.

Figure S2. 1H-13C a) HSQC spectra, and b) HMBC spectra of 3d in D2O solution.
Figure S3. XRPD of 2, 3a-d and sPEDOT powdered samples.

Figure S4. SEM images of 3a-d drop cast films.
Experimental
Materials and methods

Hexachlorocyclotriphosphazene (trimer) was obtained from Aldrich (98%) and purified by vacuum sublimation before the ring opening polymerization. 3,4-(ethyleneoxy)thiophene (EDOT) and 4-(thiophen-3-yl)phenol was obtained from Aldrich (97%) and used without further purification. Ammonium peroxydisulfate (APS) was obtained from Alfa Aesar (98%). The deuterated solvent, D2O for NMR spectroscopy and the following chemicals were obtained from Merck: NaH (60% suspension in mineral oil), H2SO4 (98%), tetrahydrofuran (THF). Deionized (DI) water (18 MΩ) was obtained from Millipore water purification system. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

AC conductivity properties of the PSAP-g-PEDOT polymers (3a-d) and sPEDOT were measured using a Hioki IM3536 LCR meter. 13 mm diameter pressed pellets of the samples were sandwiched between gold plated blocking electrodes on Novocontrol BDS 1200 sample holder and the conductivities were measured in the frequency range of 4 Hz to 200 kHz under 500 mL/min.\(^{-1}\) spectro grade argon flow between 30-100 °C at 10 °C intervals. Absolute value of AC impedance (IZ), phase angle (θ), loss factor (D, tanδ) and dielectric constant (ε') values obtained from the measurements and frequency dependent AC conductivity (σ\(\omega\)) is calculated using the equation 1;

\[
σ'(\omega) = σ_0(\omega) = \omega ε_0 ε' \tan \delta
\]

where \(σ'(\omega)\) is the real part of conductivity, \(\omega=2\pi f\) is the angular frequency, \(ε_0\) is the vacuum permittivity (\(ε_0=\,8.852\times10^{-12} F/cm\)) and \(ε'\) is the imaginary part of complex dielectric permittivity which is calculated via multiplication of dielectric constant (\(ε'\)) with loss factor (\(ε''=ε'\tan δ\)).

The DC conductivity properties of pressed pellets of the samples were also measured in the DC mode of the same instrument from the same setup and calculated from the equation 2;

\[
σ_{dc} = \frac{l}{R_{dc} \times A}
\]

, where \(σ_{dc}\) is the DC conductivity, \(l\) is the thickness of the sample (cm), \(R_{dc}\) is the resistance (Ω) of the sample and \(A\) is the area of the pellet (1.3273 cm\(^2\)).

Equipment

Elemental analyses were carried out using a LECO CHNS-932 instrument. The stock solutions (~5% w/w) of 3a-d were centrifuged at 12000 rpm for 2 h in a Gyrozen/1580 model centrifuge and no sediments detected on the wall of the tubes. Gel permeation chromatography was performed on an Agilent 1100 series GPC system equipped with Chemstation software with the aid of “GPC Add On” software to calculate the average molecular weights (Mw and Mn) against polystyrene sulfonic acid standards. \(^1\)H, \(^{13}\)C and \(^{31}\)P NMR spectra were recorded in D2O solution on a Varian 500 MHz spectrometer. 2D (HSQC and HMBC) NMR measurements were recorded in D2O solutions on a Bruker 500 MHz spectrometer. Thermal properties of the compounds were investigated on Mettler Toledo TGA/SDTA 851 thermogravimetric analysis (TGA) equipped with Mettler Toledo Star\(^+\) software at a heating rate of 10 °C min\(^{-1}\) under argon flow (50 mL min\(^{-1}\)) between 25–700 °C. UV-Vis spectra of the polymers 3a-d were recorded on an Ocean Optics MAYA 2000\(^{\text{pro}}\) in the range of 250 to 1110 nm in 200 ppm water solutions whereas the saturated DMSO solution of sPEDOT filtered through a 0.45 μm filter and measured in the same range. The XRPD analysis of the finely powdered samples was carried out using Bruker D8 Advance X-ray diffractometer and recorded in the 2θ range of 5°- 90° using Cu Kα radiation (λ = 1.5059 Å). The SEM images of polymers were taken in a Philips XL 30 SFEG operated at 15 kV. The XPS measurements were performed using a Phoibus 150 Specs charged particle analyzer, which uses conventional Al Kα radiation (hυ = 1486.6 eV) at 300 W (15kV and 20 mA) under a 10\(^{-10}\) mbar of constant vacuum. The ESR spectra of finely powdered samples (~15 mg) were placed in a quartz tube and recorded on a Jeol JES FA 300 X-band (9.15 GHz) spectrometer.

Synthesis

Polydiichlorophosphazene (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazene in a sealed evacuated tube at 250 °C according to the literature procedure.\(^{51}\) Ethyl 4-hydroxybenzenesulfonate was synthesized according to the literature procedure.\(^{52}\) sPEDOT was synthesized according to literature procedure where the isopropanol is used as dispersant for EDOT.\(^{53}\)
**Synthesis of poly[4-(thiophene-3-yl) phenoxy][4-oxy benzenesulfonic acid]phosphazene (2)**

Synthesis of 2 was achieved by sequential substitution of the PDCP with 4-(thiophen-3-yl)phenol and ethyl 4-hydroxybenzenesulfonate and then simultaneously hydrolysis to corresponding sulfonic acid under basic conditions. The reagent amounts and reaction conditions are given in Table S1. The polymer 2 was then transferred into a Teflon petri dish and dried in a vacuum oven at 50 °C for 3 days. The polymer 2 was obtained as a white solid (2.57 g, 80%).

Table S1. Used reagent amounts for preparation of 3a-d copolymers against the constant amount (0.1 g) of 2 and some of the experimental results.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>EDOT (mg)</th>
<th>APS (mg)</th>
<th>Ratio (eq./eq.) Adj.</th>
<th>Yield (%)</th>
<th>Mw(kDa.)/PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>18.2</td>
<td>29.2</td>
<td>1:0.5</td>
<td>68.7</td>
<td>554.20/4.94</td>
</tr>
<tr>
<td>3b</td>
<td>36.4</td>
<td>58.4</td>
<td>1:1</td>
<td>74.2</td>
<td>559.35/5.89</td>
</tr>
<tr>
<td>3c</td>
<td>54.6</td>
<td>87.6</td>
<td>1:1.5</td>
<td>74.8</td>
<td>567.15/4.83</td>
</tr>
<tr>
<td>3d</td>
<td>72.8</td>
<td>116.8</td>
<td>1:2</td>
<td>73.7</td>
<td>587.61/4.77</td>
</tr>
</tbody>
</table>

* Calculated from elemental analysis results.

**Notes and references**