Supporting Information

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

Elif Büşra Çelebi, [a, b] Nebahat Demirhan, [b] Ferda Hacıvelioğlu [a]*

a. Gebze Technical University, Department of Chemistry, 41400, Gebze/Kocaeli/Türkiye.
b. Yildiz Technical University, Department of Chemistry, Davutpaşa, İstanbul/Türkiye.
*Corresponding author; ferda@gtu.edu.tr

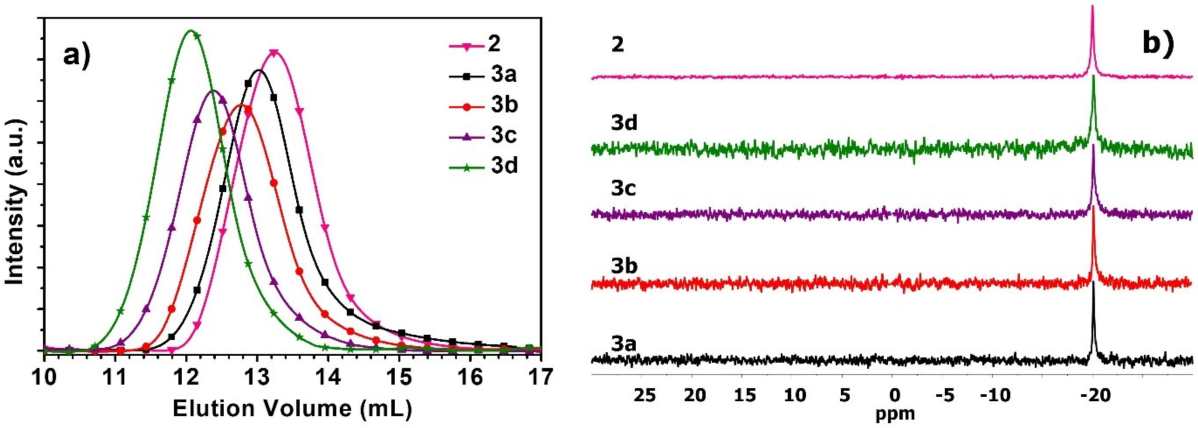

Figure S1. a) GPC elugram and b) ^{31}P NMR of **2** and **3a**-**d** copolymers in D_2O solution.

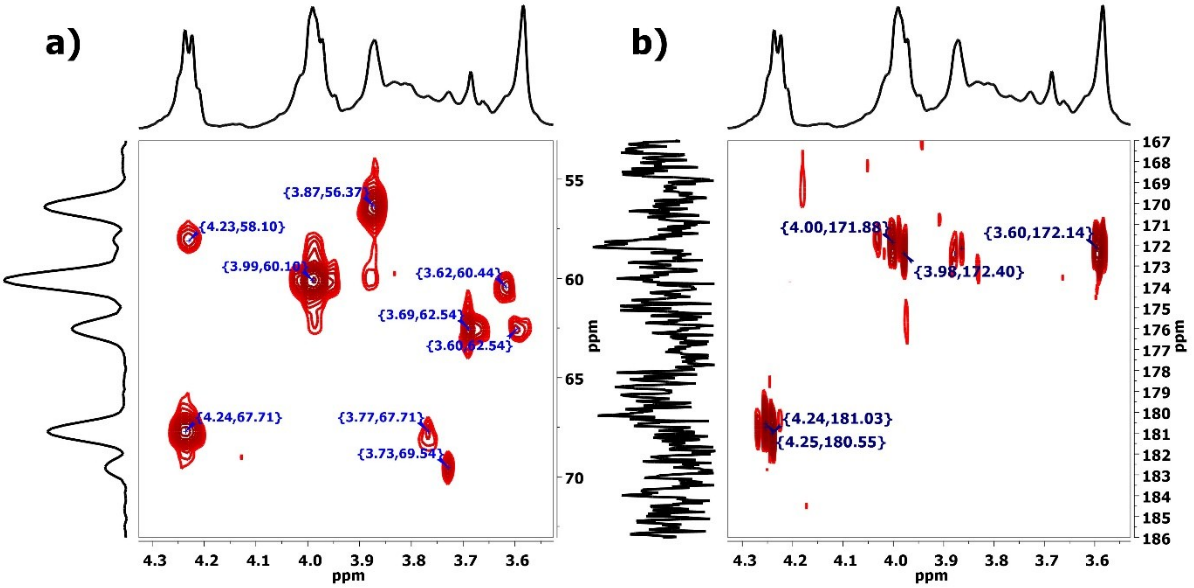

Figure S2. ^{1}H-^{13}C a) HSQC spectra, and b) HMBC spectra of **3d** in D_2O solution.

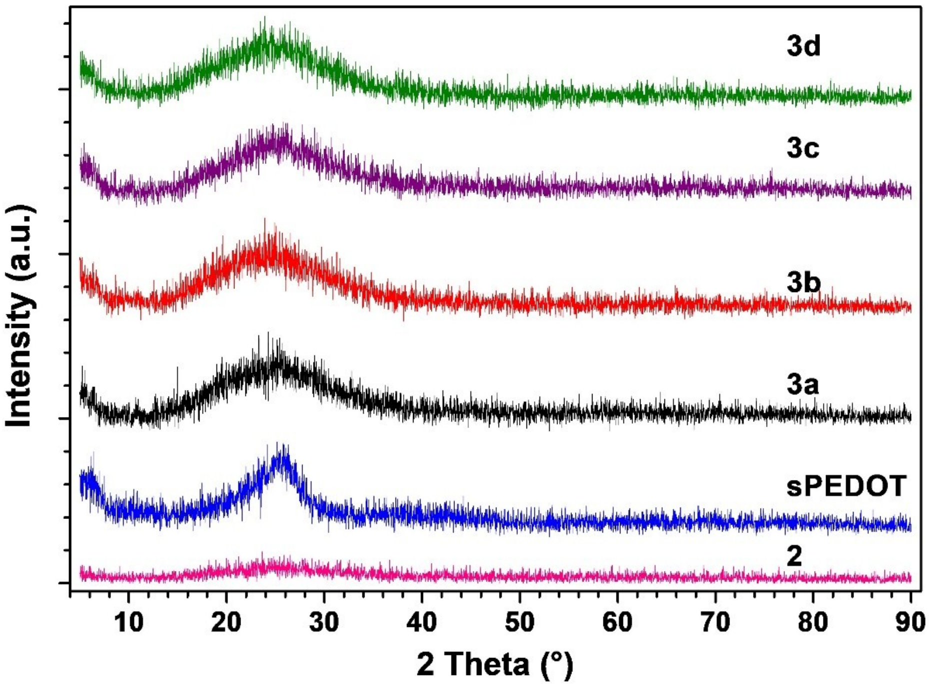

Figure S3. XRPD of **2**, **3a**-**d** and **sPEDOT** powdered samples.

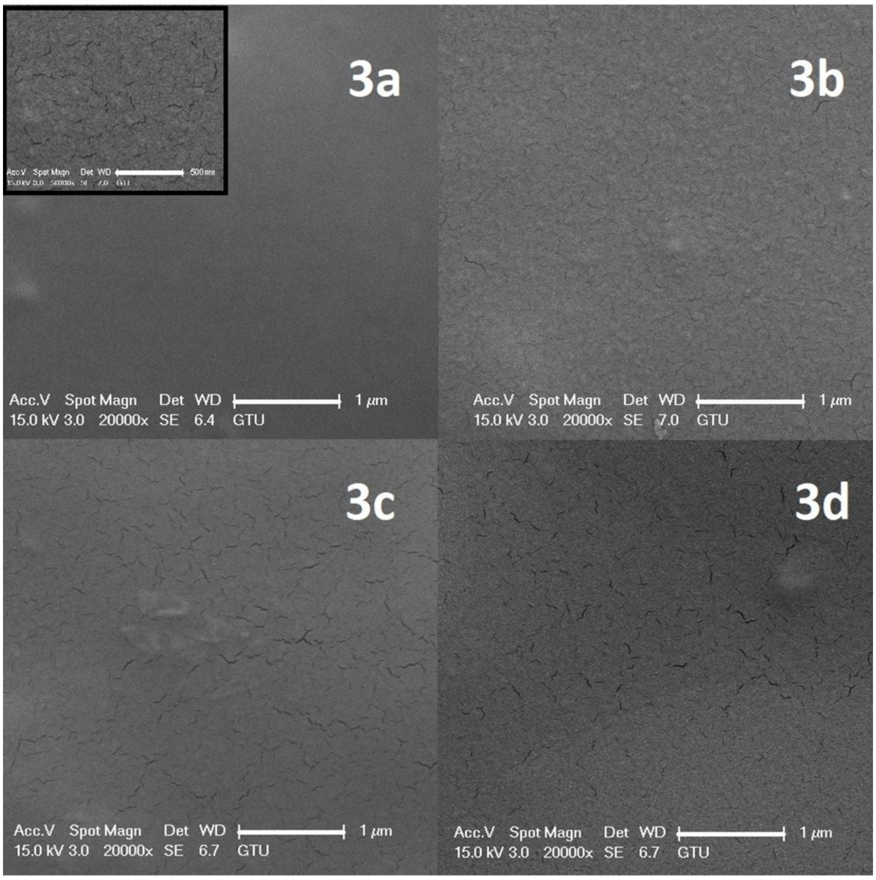

Figure S4. SEM images of **3a**-**d** drop cast films.

Experimental

Materials and methods

Hexachlorocyclotriphosphazene (trimer) was obtained from Aldrich (98%) and purified by vacuum sublimation before the ring opening polymerization. 3,4-(ethylenedioxy)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, D_2O for NMR spectroscopy and the following chemicals were obtained from Merck: NaH (60% suspension in mineral oil), H_2SO_4 (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 $\mathrm{mLmin.^{-1}}$ spectro grade argon flow between 30-100 °C at 10 °C intervals. Absolute value of AC impedance (|Z|), phase angle (θ), loss factor (D, *tanδ*) and dielectric constant (ε') values obtained from the measurements and frequency dependent AC conductivity ($\sigma_{ac}(\omega)$) is calculated using the equation 1;

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \omega\, \varepsilon''\, \varepsilon_0 \tan\delta \qquad (1)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14}$ F/cm) and ε" is the imaginary part of complex dielectric permittivity which is calculated via multiplication of dielectric constant (ε') with loss factor ($\varepsilon'' = \varepsilon' \tan\delta$).

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;

$$\sigma_{dc} = l/(R_{dc} * A) \qquad (2)$$

, 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. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in D_2O solution on a Varian 500 MHz spectrometer. 2D (HSQC and HMBC) NMR measurements were recorded in D_2O 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^e 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^{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 Phoibos 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

Polydichlorophosphazene (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazene in a sealed evacuated tube at 250 °C according to the literature procedure.[S1] Ethyl 4-hydroxybenzenesulfonate was synthesized according to the literature procedure.[S2] sPEDOT was synthesized according to literature procedure where the isopropanol is used as dispersant for EDOT.[S3]

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 sodium salt of 4-(thiophen-3-yl)phenol (29.8 mg, 0.16 mmol, 0.02 eq.) was prepared by reacting with NaH (6.6 mg, 0.16 mmol) in 10 mL of dry THF in a 50 mL round bottomed flask under argon atmosphere. This solution was then added to 100 mL THF solution of PDCP (0.95 g, 8.2 mmol, 1 eq.) in a round bottomed 250 mL flask under dry argon in a glove box. The reaction mixture was let to stir for 6 hours at room temperature and then sodium salt of ethyl 4-hydroxybenzenesulfonate which was separately prepared by reacting the ethyl 4-hyrdoxybenzenesulfonate (3.78 g, 18.7 mmol, 2.3 eq) with NaH (0.75 g, 18.7 mmol, 2.3 eq) in 50 mL of dry THF, was added and stirred for overnight. The reaction flask was then removed from the glove box and refluxed for 48 h to achieve complete substitution of the PDCP. The reaction mixture cooled to room temperature, 22 mL 2M NaOH methanol solution is then added and again refluxed for overnight to achieve hydrolysis of sulfonate ester which is precipitated bottom of the reaction flask. Then all the volatiles were removed in a rotary evaporator and 88 mL 10% water solution of H_2SO_4 was added for conversion of sodium sulfonate salt of the polymer to the free acid form. The obtained solution was transferred into a dialysis membrane (cut off, 2 kDa.) and dialysed against deionised water for two days. The solution of 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%). Found: C 42.92, H 2.88, N 3.53, S 16.41% $[C_{28}H_{22}N_2O_{13}P_2S_4]_n$ requires C 42.86, H 2.83, N 3.57, S 16.44%. $\{^1H\}^{31}P$ NMR (D_2O) $\delta = -20.0$ ppm [br s, $\underline{P}(OPhR)_2$, R= $-SO_3H$, $-C_4H_3S$)]. ^1H NMR (D_2O) $\delta = 6.56$ and 7.37 ppm [two br s, aromatic phenyl protons]. ^{13}C NMR (D_2O) $\delta = 120.5$ and 127.2 ppm (di substituted benzene), 139.3 and 152.2 ppm (di substituted benzene ipso carbons). GPC: $M_w = 5.51 \times 10^5$, PDI = 5.7.

General procedure for preparation of poly(4-oxybenzenesulfonic acid)phosphazene-g-PEDOT (3a-d) copolymers

Syntheses of PSAP-*g*-PEDOT copolymers (**3a-d**) were similar except the used stoichiometric ratio of EDOT to **2**. The specific reagent amounts and reaction conditions are given in Table S1 and general experimental procedure for synthesis of polymer **3a** is described. A known amount of polymer **2** (0.1 g, 0.26 mmol, 1 eq.) was dissolved in 10 mL of DI water in a round bottomed 50 mL flask and desired stoichiometric amount of EDOT (18.2 mg, 0.13 mmol, 0.5 eq. for **3a**) was added by vigorous stirring. The reaction mixture stirred for half an hour and the oxidant APS (29.2 mg, 0.13 mmol, 0.5 eq.) was added slowly. The reaction turned light blue in 2 hours and allowed to stir for 2 days. The resulting dark blue reaction mixture was then completely transferred into dialysis membrane (cut off, 2 kDa.) and dialysed against water for 3 days for removal of unreacted monomer, inorganic salts and then concentrated by rotary evaporation to obtain ~5% *w/w* water solutions. 1 mL of the product was transferred into a Teflon petri dish and dried in a vacuum oven at 30 °C for 24 h. $\{^1H\}^{31}P$ NMR (D_2O) $\delta \approx -20.1$ ppm [br s, $\underline{P}(OPhR)_2$, R= $-SO_3H$, $-C_4H_3S$)]. ^1H NMR (D_2O) $\delta = 6.5$ and 7.6 [two br s, aromatic phenyl protons], $\delta = 4.3$ to 3.5 ppm [multiple broad resonances, $-OC\underline{H}_2C\underline{H}_2O-$, PEDOT]. ^{13}C NMR (D_2O) δ = ~182-170 ppm (multiple resonances), 152.2, 139.0, 127.2, 120.5 ppm [di substituted benzene], $\delta = 67.7$, 60.2, 58.0 and 56.4 ppm [br m, aliphatic C atoms, PEDOT].

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.

Polymer	EDOT (mg)	APS (mg)	Ratio (eq./eq.)		Yield (%)	Mw(kDa.)/PDI
			Adj.	Calc.*		
3a	18.2	29.2	1:0.5	1:0.27	68.7	554.20/4.94
3b	36.4	58.4	1:1	1:0.49	74.2	559.35/5.89
3c	54.6	87.6	1:1.5	1:0.71	74.8	567.15/4.83
3d	72.8	116.8	1:2	1:1.45	73.7	587.61/4.77

* Calculated from elemental analysis results.

Notes and references

(S1) H. R. Allcock, R. L. Kugel, K. J. Valan, *Inorg. Chem.*, 1966, **5**, 1709.
(S2) E. B. Çelebi, F. Hacıvelioğlu, *Polym. Chem.*, 2017, **8**, 3022.
(S3) W. W. Chiu, J.Travaš-Sejdić, R. P. Cooney, G. A. Bowmaker, *Synth. Met.*, 2005, **155**, 80.