

# Electrically conducting transparent films of biphenyl / 3-octylthiophene copolymers synthesized by cyclic voltammetry

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Electrically conducting transparent films of biphenyl and 3-octylthiophene copolymers and also films of the homopolymers polyphenylene, and poly(3-octylthiophene), for comparison reasons, were synthesized by electropolymerization. The films were studied by FTIR, UV-Vis, SEM-EDAX and their electrical conductivity was determined. Based on the change of scan rate, the electropolymerization mechanism was determined as a diffusion – controlled process for scan rates up to 100 mVs<sup>-1</sup>, and as controlled by charge transfer for scan rates between 150 up to 200 mV s<sup>-1</sup>. The copolymers had higher conductivity (appr. 10<sup>-2</sup> S/cm) than that of the corresponding polyphenylene and one order of magnitude lower than that of poly(3-octylthiophene).

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**Keywords:** Conducting copolymers, 3-octylthiophene, Biphenyl, Electropolymerization mechanism

## 1. Introduction

Electrically conducting polymers based on  $\pi$ -conjugated structures are very interesting materials with potential applications for electrochromic displays and smart windows, light emitting diodes (LEDs), sensors, solar cells etc [1,2]. Some of their advantages are their low density, mechanical flexibility and easy processability. Conducting polymers can be synthesized by chemical polymerization or by electropolymerization, whereas the latter offers many advantages, such as direct formation of the doped polymer film on the electrode surface, absence of catalyst, easy control of the film thickness and the possibility of performing in situ characterization of the deposited film by electrochemical and other techniques [2].

Poly(paraphenylene) has high mechanical strength, excellent chemical resistance, considerable thermal stability in air even at high temperatures and high conductivity [3,4]. On the other hand, Poly(3-octylthiophene) (P3OT), is soluble in some organic solvents, exhibits high electrical conductivity, environmental stability and furthermore produce stable interfaces with electrodes commonly used in electronics (such as indium tin oxide, ITO) and their films are transparent and exhibit a large absorption coefficient in the visible range of the electromagnetic spectrum [5]. These characteristics make polythiophene and its derivatives interesting materials for solar cell applications.

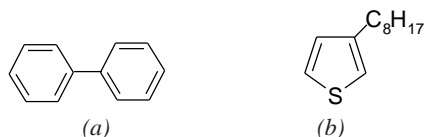
Apart from the conducting of homopolymers, copolymers based on different types of monomers have gained great scientific interest, because new electrically

active materials could be produced combining characteristic properties of both homopolymers [6]. 3-octylthiophene is a quite expensive reagent so that its copolymers with lower cost monomers have also practical importance. In the literature the copolymerization of thiophene with 3-methyl thiophene [7] or 3-hexyl thiophene [8] have been reported, as well as the copolymerization between various 3-alkyl substituted thiophene derivatives [9,10]. Copolymers of biphenyl with 3-octylthiophene, synthesized by potentiodynamic cycling or by galvanostatic polymerization have been reported for producing soluble copolymers [6,11], however they have not been yet thoroughly investigated.

The aim of this work is to copolymerize biphenyl with 3-octylthiophene by electropolymerization using Cyclic Voltammetry and to produce soluble and electrically conducting films. Their structure, morphology and electrical conductivity were examined in comparison to that of the corresponding homopolymers. Furthermore, the electropolymerization mechanism of the copolymer was also studied.

## 2. Experimental

Biphenyl (Biph) and 3-octylthiophene (3OcT) were used as received, from Fluka and Aldrich companies respectively. Tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) was received from Merck, and was dried at 110 °C up to constant weight. Acetonitrile (ACN), (water content ~ 0.05 %) was stored over molecular sieves (4 Å, 8–12 mesh) for about one month. The chemical structure of the monomers is shown in Scheme 1.



Scheme 1. Chemical structure of: (a) biphenyl and (b) 3-octylthiophene.

The copolymer films based on Biph and 3OcT and the corresponding homopolymers were electrochemically synthesized by Cyclic Voltammetry. The electropolymerization medium consists of: biphenyl and 3-octylthiophene at a concentration ratio of  $[3OcT] / [Biph] = 0.05 \text{ M} / 0.05 \text{ M}$  as monomers, tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>, 0.1 M) as supporting electrolyte and acetonitrile (ACN) as solvent. The corresponding homopolymers polyphenylene (PP) and poly(3-octylthiophene) (P3OT) were also synthesized for comparison reasons at a concentration of  $[Biph]$  or  $[3OcT] = 0.1 \text{ M}$ . The electropolymerization was carried out in an one – compartment electrochemical cell with ITO or Pt-plated Pt electrode as anode, Pt-plated Pt electrode as cathode and a calomel electrode (SCE) as reference, placed into a Luggin capillary. The electropolymerization solution was deoxygenated by bubbling nitrogen for 10 min before the beginning of the electropolymerization. The thickness of the synthesized films was estimated from the amount of charge during the electropolymerization based on the curve of current ( $i$ ) versus time ( $t$ ). After polymerization, the synthesized films were immersed in acetonitrile to remove TBABF<sub>4</sub> residues and the soluble oligomers and then were vacuum dried at 30°C up to constant weight.

The solubility of the synthesized films was tested in various common solvents (chloroform, tetrahydrofuran etc.). The FTIR spectra of the polymers were recorded using a PerkinElmer Spectrum GX spectrometer using KBr discs. The morphology of the films was examined using a FEI Quanta 200 Scanning Electron Microscope with simultaneous Energy Dispersive X-Ray Analysis (EDAX). The electrical conductivity of the films (deposited on the Pt-plated Pt electrode) was determined at room temperature by the two-probe technique. The electropolymerization mechanism, for different scan rates (between 25 and 200 mV / sec), was examined based on the curves analysis of peak current ( $i_p$ ) versus square root of scan rate ( $v^{1/2}$ ).

### 3. Results and discussion

#### 3.1. Synthesis of polymer films

Table 1 presents the synthesis parameters, the film thickness and conductivity of synthesized polymeric films deposited on ITO or on Pt-plated Pt electrode. The homopolymer and copolymer films were synthesized in the potential range, from 0 to +2 V, for different number of scans (see Table 1). According to literature [3], the synthesis of a polyphenylene film with a thickness of 1  $\mu\text{m}$

requires 142.8  $\text{mC}/\text{cm}^2$  ( $Q_{PP}$ ), whereas that of poly(3-octylthiophene) requires 170  $\text{mC}/\text{cm}^2$  ( $Q_{P3OT}$ ) [5]. Given that there are no relative information concerning the copolymers of biphenyl and 3-octylthiophene, it was assumed that the charge required for the synthesis of a 1  $\mu\text{m}$  thick copolymer film ( $Q_{PP-P3OT}$ ) corresponds to the harmonic mean of  $Q_{PP}$  and  $Q_{P3OT}$ :

$$Q_{PP-P3OT} = (2 * Q_{PP} * Q_{P3OT}) / (Q_{PP} + Q_{P3OT}) \quad (1)$$

Thus,  $Q_{PP-P3OT} = 155.2 \text{ mC}/\text{cm}^2$ . The harmonic mean is always the least of the three means (arithmetic, geometric and harmonic). Since the harmonic mean of a list of numbers tends strongly toward the least elements of the list, it tends (compared to the arithmetic mean) to mitigate the impact of large outliers and aggravate the impact of small ones.

The conductivities of the copolymer films are in the order of magnitude of  $10^{-2} \text{ S}/\text{cm}$ , whereas that of P3OT is approximately one order of magnitude higher and that of PP one order of magnitude lower.

Fig. 1 shows the cyclic voltammograms during synthesis of the copolymer (PP-P3OT) deposited on Pt-plated Pt electrode, in the potential range from 0 up to +2 V for different sweeps.

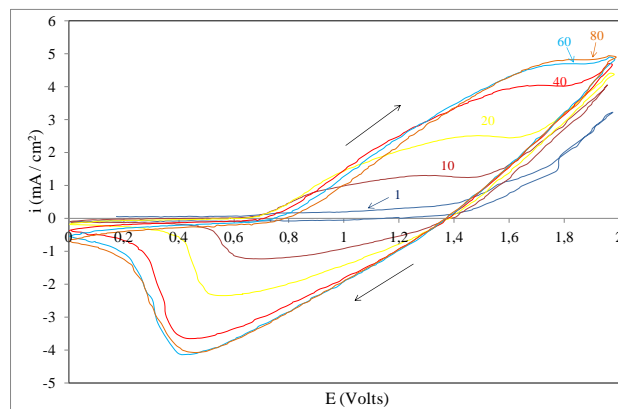


Fig. 1. Cyclic voltammograms of copolymer film (PP-P3OT) using Pt as working electrode, in the scan range 0 up to +2 V vs SCE (scan rate  $100 \text{ mVs}^{-1}$ ) from 1<sup>st</sup> up to 80<sup>th</sup> sweep.

The intensity of the current increases from the first sweep up to the 80<sup>th</sup>. The copolymer film exhibits a broad oxidation peak (ranging from +1.2 up to +1.8 V) and a broad reduction peak (ranging from +0.3 up to +0.7 V). The oxidation peak is shifted to higher potential with increasing sweeps, whereas the reduction peak is shifted to lower potential. The oxidation peak is attributed to the doping of the film with BF<sub>4</sub><sup>-</sup>, whereas the reduction peak is attributed to the undoping process. During the electropolymerization of the copolymer, the solution becomes conducting due to the electrolyte (TBABF<sub>4</sub>). Simultaneously, the latter dopes the produced copolymer by offering its counter ion (BF<sub>4</sub><sup>-</sup>). Therefore by oxidation, radical - cation of the monomers are formed leading to the start and the growth of the macromolecule; simultaneously,

by oxidation, takes place the doping of the macromolecule forming radical cation (polaron) in some monomer units. The color of the copolymer film changes during a scan

from orange (oxidized form) to blue (reduced form). The final color of both (PP-P3OT)-Pt40 and (PP-P3OT)-Pt80 was dark.

Table 1. Synthesis parameters, film thickness and conductivity of synthesized films

Cyclic Voltammetry parameters				Film formation onto		Synthesized films	
Code	Scan Range *	No. of sweeps (cycles)	Total oxidation charge ( $C/cm^2$ )	Pt-plated Pt electrode	ITO electrode	Film thickness ( $\mu m$ )	Conductivity (S/cm)
PP-Pt40	0 $\rightarrow$ +2 V $\rightarrow$ 0	40	0.26	x	-	1.80	$9.10 \cdot 10^{-4}$
P3OT-Pt40	0 $\rightarrow$ +2 V $\rightarrow$ 0	40	0.97	x	-	5.68	$1.90 \cdot 10^{-1}$
P3OT-ITO7	0 $\rightarrow$ +2 V $\rightarrow$ 0	7	0.08	-	x	0.48	-
(PP-P3OT)-Pt40	0 $\rightarrow$ +2 V $\rightarrow$ 0	40	0.47	x	-	3.05	$1.00 \cdot 10^{-2}$
(PP-P3OT)-Pt80	0 $\rightarrow$ +2 V $\rightarrow$ 0	80	1.62	x	-	10.42	$6.78 \cdot 10^{-2}$
(PP-P3OT)-ITO7	0 $\rightarrow$ +2 V $\rightarrow$ 0	7	0.09	-	x	0.55	-

\*In all cases, the scan rate was 100 mV/s

Fig. 2 shows the cyclic voltammograms during synthesis of the copolymer (PP-P3OT) deposited on ITO electrode, in the potential range from 0 up to +2 V from 1<sup>st</sup> up to 7<sup>th</sup> sweep, and the deposited film is transparent.

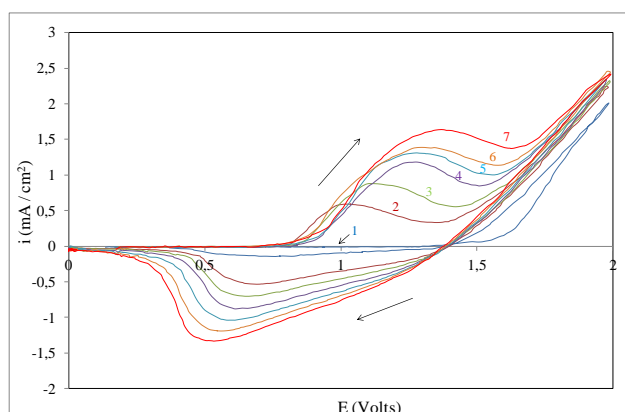


Fig. 2. Cyclic voltammograms of copolymer film (PP-P3OT) using ITO as working electrode, in the scan range 0 up to +2 V vs SCE (scan rate  $100 \text{ mVs}^{-1}$ ) from 1<sup>st</sup> up to 7<sup>th</sup> sweep.

The (PP-P3OT) film deposited on ITO electrode exhibits a broad oxidation peak (ranging from +1.0 up to +1.36 V) which is attributed to the doping of the film with the  $\text{BF}_4^-$  and a broad reduction peak (ranging from +0.5 up to +0.7 V) which is attributed to the undoping process. The oxidation peak is shifted to higher potential with increasing sweeps, whereas the reduction peak is shifted to lower potential. The color of the film changes from orange (oxidized form) to blue (reduced form).

### 3.2 Electropolymerization mechanism

Fig. 3 represents the cyclic voltammograms for the copolymer film (PP-P3OT)-Pt, using Pt as working electrode concerning one sweep with different scan rates.

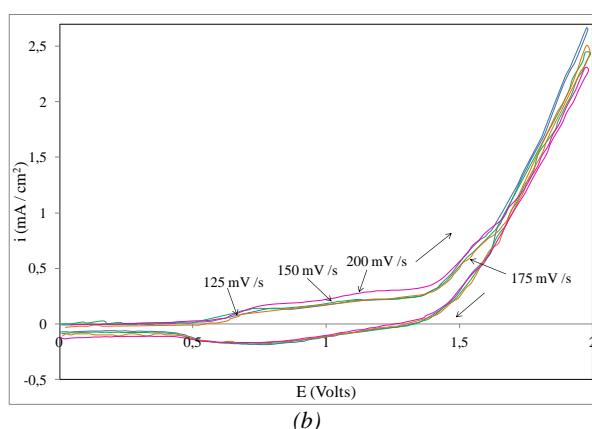
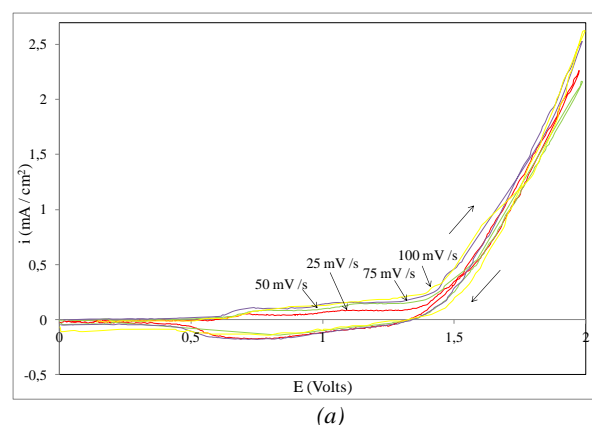


Fig.3. Cyclic voltammograms of the 1<sup>st</sup> cycle, of copolymer films (PP-P3OT) using Pt as working electrode, in the scan range 0 up to +2 V vs SCE (a) scan rate from 25 up to  $100 \text{ mVs}^{-1}$  (b) scan rate from 125 up to  $200 \text{ mVs}^{-1}$ .

The dependence of the peak currents on the square root of scan rates of (PP-P3OT) is presented in Figure 4. The peak currents are linearly proportional to the square root of scan rates, for scan rates: 25, 50, 75,  $100 \text{ mVs}^{-1}$ , which suggests that the system has reversible behavior and the oxidation and reduction of the copolymer is a diffusion

– controlled process. For the scan rate  $125 \text{ mVs}^{-1}$  a deviation of the slope is observed. For scan rates 150, 175 and  $200 \text{ mV s}^{-1}$  the system has irreversible behavior and the oxidation and reduction of the copolymer is controlled by charge transfer [2,12].

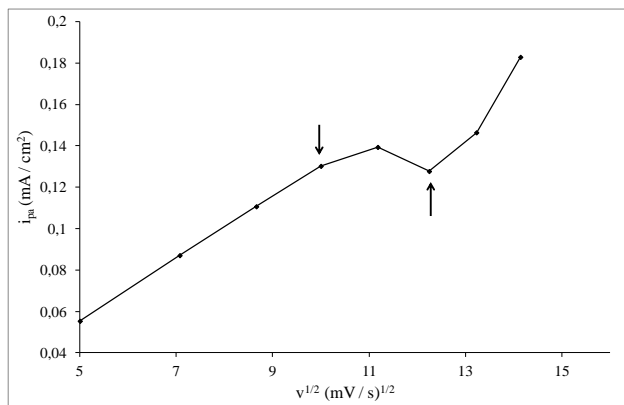


Fig. 4. Dependence of the peak currents on the square root of scan rates of copolymer films (PP-P3OT)-Pt concerning one sweep.

### 3.3 Structural characterization and morphology of the copolymers

FTIR spectra of the copolymers (PP-P3OT)-Pt40 and (PP-P3OT)-Pt80 and homopolymers PP-Pt40 and P3OT-Pt40, for comparison reasons, are obtained and the results are presented in Table 2. According to literature [3,6,13-16], the interpretation of various absorption bands under the aspect of the polymers' chemical bonds were taken into consideration. The FTIR spectra of the synthesized copolymer films contain the characteristic bands of the homopolymers. However these characteristic bands appear in the same regions and thus they overlap.

The UV-vis spectra of copolymers (PP-P3OT)-Pt40 and (PP-P3OT)-Pt80 dissolved in chloroform are presented in Figure 5. According to literature [17], it is known that para-phenylene homologue oligomers have their main absorption band at 251 nm (biphenyl), 280 nm (terphenyl), 298 nm (quaterphenyl), 310 nm (quinquephenyl), 318 nm (sexiphenyl), and 323 nm

(septaphenyl). Poly(para-phenylene) has its main absorption band at 340 nm and it also exhibits a "shoulder" in the region of 420 with 440 nm. On the other hand, the absorption maxima for electrochemically synthesized poly(3-octylthiophene) have been reported between 438 and 517 nm depending on the electropolymerization conditions used [5,11,18]. For oligothiophenes, the absorption maximum shifts from 360 nm for the smallest oligomer to 440 nm for the larger oligomers. Copolymer (PP-P3OT)-Pt40 exhibits a band at 280 nm, which can be attributed to the structural units of biphenyl. On the other hand, the band at 414 nm, which extends up to  $\sim 530 \text{ nm}$  should be attributed to P3OT. The copolymer (PP-P3OT)-Pt80 exhibits one absorption band at 278 nm and the main band at 408 nm is shifted to lower wavelength compare to that of 40 sweeps.

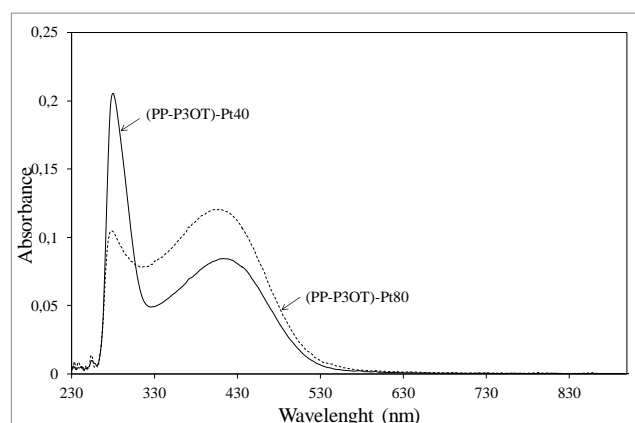


Fig. 5. UV-Vis spectra of copolymers (PP-P3OT)-Pt40 and (PP-P3OT)-Pt80.

The SEM micrographs of homopolymers and copolymers are presented in Figure 6. According to Fig. 6(a), PP-Pt40 has distinct parts with uniform distribution. The P3OT-Pt40 (Fig. 6b) has a cauliflower-like and porous morphology with aggregates of sizes from 3 up to 6  $\mu\text{m}$ . The films of copolymers have a sponge like morphology with characteristics of both homopolymers. The morphology of (PP-P3OT)-Pt40 (Fig. 6c) appears more compact than that of (PP-P3OT)-Pt80 (Fig. 6d).

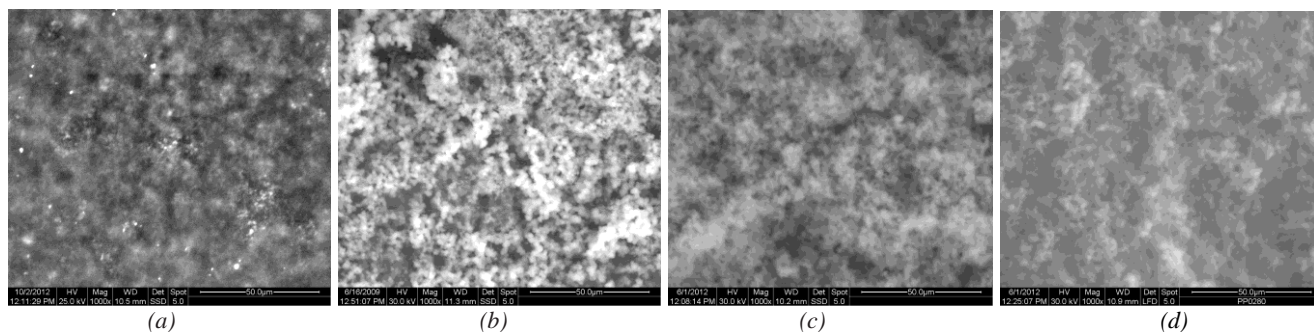


Fig. 6. SEM micrographs ( $\times 1000$ ) of (a) homopolymer PP-Pt40, (b) homopolymer P3OT-Pt40, and (c), (d) copolymer (PP-P3OT)-Pt40, (PP-P3OT)-Pt80, respectively (for the codes see Table 1).

For the copolymers, the ratio of the structural unit derived from biphenyl per that derived from 3-octylthiophene was calculated based on EDAX analysis according to literature [3]. For copolymer (PP-P3OT)-Pt40, the ratio of structural units Biph/3OcT was 1/2.3 and

for (PP-P3OT)-Pt80 was 1/1.1, i.e., the copolymers contain more structural units of 3OcT than Biph in their macromolecules. The number of structural units of 3OcT decreases with increasing number of sweeps.

Table 2. Description of FTIR bands of homopolymers and copolymers

Characteristic bonds	Wavenumber according to literature (cm <sup>-1</sup> )	Homopolymers		Copolymers	
		Polyphenylenes	Poly(3-octylthiophene)		
		PP-Pt40	P3OT-Pt40	(PP-P3OT)-Pt40	(PP-P3OT)-Pt80
>CH <sub>2</sub> : aliphatic (cyclic and linear) Parts	2980-2950	2962	2924	2922	2957, 2922
	2890-2850	2856	2852	2851	2855
C=O: bending vibrations	1740-1710	1736	-	1713	-
C=C: stretching vibrations of aromatic ring	1600	1680-1550	-	-	-
	1570	-	-	-	-
	1530	-	-	-	-
	1499-1490	-	-	-	1489
C-C bending vibrations of aromatic ring	1460	-	1464	1458	1458
	1480	1487	-	-	-
C-H "in plane" bending vibrations	1400	1399	1377	-	1377
	1150-1110	1144	-	-	1113
C-H "out of plane" bending vibrations	1094-1000	1093, 1041	1086	1084, 1036	1083, 1056, 1036
					6
C-H: "out of plane" bending vibrations, characteristic of separated H in aromatic ring	876	880	-	-	-
C-H: "out of plane" band from thiophene ring	821	-	821	828	827
C-H: "out of plane" bending vibrations of two neighboring H in aromatic ring	806	801	-	-	-
C-H: bending vibrations of four or five neighboring H in aromatic ring	765	760	-	-	-
o-substitution in benzene ring	740	742	-	-	-
CH <sub>2</sub> : aliphatic (cyclic and linear) parts	722	n	723	721	-
C-H: deformation vibrations "out of plane" in aromatic ring	695	670	-	-	-

n: negligible

#### 4. Conclusions

Electrically conducting copolymer films were synthesized by electropolymerization of biphenyl with 3-octylthiophene, having different structure and properties than the corresponding homopolymers. The oxidation and reduction of the copolymer is a diffusion – controlled process for scan rates up to 100 mVs<sup>-1</sup>, and is controlled by charge transfer for scan rates from 150 up to 200 mV s<sup>-1</sup>. The copolymers have sufficient conductivity (appr. 10<sup>-2</sup> S/cm) and solubility, attractive characteristics for many

applications such as LEDs, photovoltaic cells, batteries and sensors.

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