

Optoelectronic properties of New Synthesized phthalocyanine

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Abstract: One novel Zn-phthalocyanine bearing different substituent was synthesized. The resulting compounds were characterized by NMR and FTIR. The corresponding polymer was synthesized via cyclic voltametry. The optical properties of these π -conjugated systems were investigated by UV-Visible absorption and photoluminescence (PL) spectroscopy. The electrochemical behavior was reported. The optical and electrochemical gaps were estimated. Those complexes, having low gap energy, have been identified as holding much promise for the development of photovoltaic device.

Keywords: Phthalocyanine, Polymer Poly (Zn-Pc), Electrochemical Conductivity, UV Conductivity

1. Introduction

Metallo - Phthalocyanine (PCs) is a metal organic compound with four pyrole units linked to form symmetrical 18 π - electron aromatic macrocycle, allowing the incorporation of more than 70 metals or non-metal ions into their inner core.

Due to its high thermal and chemical stability, these conjugated compounds have attracted much research interest in the fabrication of electronic molecular devices such as opto-electronic devices [1], gas sensors [2,3], static induction transistors [4], and photoreceptor devices in laser beam printers and photocopiers [5]. Phthalocyanine thin films exist in many polymorphic forms depending on their growth conditions.

A major disadvantage of PCs is their low solubility in organic solvents even in dimethylsulfoxide (DMSO) and it has been overcome by introducing electron-donating substituents[6], electron-withdrawing substituents or polar ionizable substituents. A suitable functionalization of the PCs has a strong influence on the π -electron conjugation of the macromolecule since it makes salvation easier, decreasing thus the gap energy (the difference between HOMO and LUMO orbital).

Recent advances in synthetic methods and chromatographic separation techniques have made possible a wide range of new Pc derivatives with different substituent. Consequently, a variety of functionalized Pc

derivatives have now become available, and their spectroscopic and electrochemical properties have been studied extensively in order to develop these for technological applications [7].

Firstly, we report the synthesis and characterisation of new Zn (II) phthalocyanine (ZnPC) tetrasubstituted by (2-phormyl-4-methoxy) groups and the corresponding polymer (poly(Zn-Pc)). UV – Visible spectroscopy, Fourier Transform Infrared Spectrophotometry (FT-IR) and fluorescence spectrophotometry. are used to confirm the formation of phthalocyanine tetrasubstituted. Secondly, the electrochemical properties of synthesized phthalocyanine were reported. Finally, single-layer devices fabricated using vacuum deposition based on an indium-tin-oxide/Zn-phthalocyanine/aluminum, and characterized by photoluminescence and electric measurement.

2. Experimental

2.1. Materials and Measurement

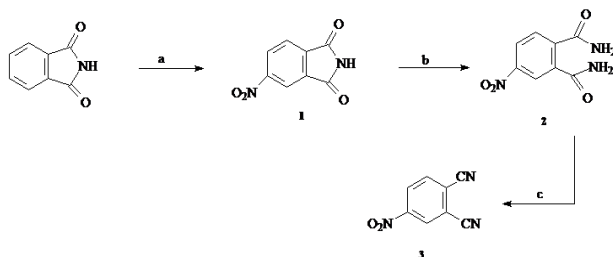
N,N'-dimethylformamide (DMF), Dimethylsulfoxide (DMSO), diethylether, chloroform were freshly used, alcohols and initiator products were used as received from Aldrich. 4-nitrophthalonitrile was synthesized from phthalic anhydride using procedure with four steps, Potassium carbonate (K_2CO_3) was dried before use.

¹H-NMR spectral data were obtained on a AV 300 spectrometer. FTIR spectra were acquired on a Perkin-

Elmer BX FT-IR system spectrometer by dispersing sample in KBr pellets. UV-Vis absorption spectra were recorded on a Cary 2300 spectrophotometer. Photoluminescence (PL) spectra were obtained on a Spectra-Physics stabilite 2017 spectrometer model 3900S.

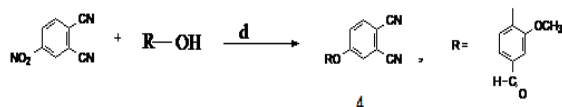
2.2. Synthesis

The synthesis of the macrocycle zinc (II) phthalocyanines ZnPC begins with the nitration in position 4 of phthalimide followed by reaction of the amine hydroxide, to form the 4-nitrophthalimide 2. The dehydration of 2 by the thionyl chloride in N, N-dimethylformamide leads to 4-nitrophthalonitrile 3 (scheme 1).



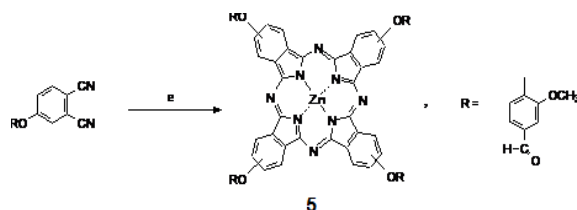
Scheme 1. Reaction conditions: (a) HNO_3 , H_2SO_4 , 0°C , 5 h; (b) NH_2OH 25%; (c) DMF, SOCl_2 , $0-2^\circ\text{C}$, 5h

Dinitriles 4 were prepared by a nucleophilic substitution reaction of 4-nitrophthalonitrile with the corresponding alcohol in the presence of K_2CO_3 (scheme 2).



Scheme 2. Reaction conditions: (d) K_2CO_3 , DMSO, room temperature, 48 h

The cyclo-tetramerisation of dinitriles compound with zinc (II) acetate in the presence of urea and ammonium molybdate was performed in nitrobenzene (scheme 3).



Scheme 3. Reaction conditions: (e) ZnOAc_2 , nitrobenzene, urea and ammonium molybdate

2.2.1. Synthesis of 4-Nitrophthalimide 1

4-nitrophthalimide 1 was prepared by nitration of phthalimide using nitric acid and sulfuric acid in presence of an ice bath as described before by Hajri.A [8].

$\text{RMN}^1\text{H}(\text{DMSO}-d_6)$: δ : 8.003 (d, $J = 5.7 \text{ Hz}$, 1H); 8.342 (s, 1H); 8.540 (d, $J = 6.9 \text{ Hz}$, 1H); 11.761 (s, 1H). $\text{RMN}^{13}\text{C}(\text{DMSO}-d_6)$: δ : 118.16; 124.92; 129.87; 134.42; 137.66; 151.71; 167.61; 167.91.

2.2.2. Synthesis of 4-Nitrophthalimide 2

4-Nitrophthalimide was stirred in 32% ammonia solution (70mL) for 24 hours to obtain 4-nitrophthalimide 2. The resulting deep yellow product was filtered and washed with cold water until the excess of ammonia could not be detected. The title compound was dried at 110°C , a 95% yield. $\text{RMN}^1\text{H}(\text{DMSO}-d_6)$: δ : 7.636 (s, 2H); 7.704 (d, $J = 8.1 \text{ Hz}$, 1H); 8.020 (s, 1H); 8.079 (s, 1H); 8.297 (dd, $J = 2.4 \text{ Hz}$, $J = 8.7 \text{ Hz}$, 1H); 8.338 (d, $J = 2.1 \text{ Hz}$, 1H). $\text{RMN}^{13}\text{C}(\text{DMSO}-d_6)$: δ : 122.35; 124.38; 129.11; 137.19; 142.65; 147.02; 167.67; 168.67.

2.2.3. Synthesis of 4-Nitrophthalonitrile 3

The 4-nitrophthalimide 2 was converted to 4-nitrophthalonitrile via dehydration of the amide by using thionyl chloride and DMF as solvent.

$\text{RMN}^1\text{H}(\text{DMSO}-d_6)$: δ : 8.439 (d, $J = 8.7 \text{ Hz}$, 1H); 8.685 (dd, $J = 2.1 \text{ Hz}$, $J = 8.4 \text{ Hz}$, 1H); 9.033 (d, $J = 2.1 \text{ Hz}$, 1H). $\text{RMN}^{13}\text{C}(\text{DMSO}-d_6)$: δ : 114.55; 114.86; 116.59; 120.22; 128.52; 128.81; 135.27; 149.69.

FTIR: 3091 (C-H aromatic), 2242 (CN), 1534 (asymmetric N=O band), 1349 (symmetric N=O band), 853 (C-N).

2.2.4. Synthesis of Dinitriles 4

(2-phormyl-4-methoxy)phenoxyphthalonitrile 4. To a mixture of 4-nitrophthalonitrile 3 (0.5g, $2.88 \cdot 10^{-3}$ mol) and Vaniline (0.438g, $2.88 \cdot 10^{-3}$ mol), in DMSO was added anhydrous K_2CO_3 ($4.03 \cdot 10^{-3}$ mol, 0.571g). The mixture was stirred for a further 48 h. Then, the reaction mass was poured into water (25 mL) and the precipate formed was filtered off, washed with water, and crystallized from EtOH-water to give the product as a yellow crystalline powder. Yield: 60% $^1\text{H-NMR}$ (300 MHz, CDCl_3 , ppm): 7.2(d, $J = 8.7 \text{ Hz}$, 1H), 7.6 (t, $J = 7.7 \text{ Hz}$, $J = 2.5 \text{ Hz}$, 1H), 7.76-8 (m, 5H), 8.5(t, $J = 8.5 \text{ Hz}$, $J = 2.7 \text{ Hz}$, 1H), 8.8(d, $J = 8.75 \text{ Hz}$, 1H). $\text{RMN}^{13}\text{C}(\text{DMSO}-d_6)$: δ : 108; 118; 119; 122.51; 128; 136; 137; 148; 150; 163.

2.2.5. Synthesis of Phthalocyanines Derivatives 5

Phthalocyanine PC5. A mixture of (2-phormyl-4-methoxy)phenoxyphthalonitrile 4 (0.2mol), ZnAC_2 (0.010mol), molybdate sel(0.02g) and urea(20g) was refluxed in nitrobenzene for 7 hours at 170°C . Then methanol and water were added to induce precipitation. The solid was filtered and washed sequentially with water and methanol. The solid was dried under vaccum to give 45% of pure product as a green powder. The structure of the phthalocyanine was confirmed by UV-vis absorption, NMR and FTIR.

2.3. Fabrication and Characterization of Device

The organic photovoltaic cell monolayers are generally described as Schottky type Single-layer devices were elaborated as sandwich structure between an aluminum (Al) cathode and an indium tin oxide (ITO) anode as seen in figure 1.



Figure 1. The structure of the device fabricated

The clean of the ITO glass is a step of great importance enabling the adhesion of the organic materials deposited thereafter. The slides are cleaned by successive rinsing, with desionised water, warm acetone and warm ethanol for 10 min each time in an ultrasonic bath.

The phthalocyanines compounds solutions ($3 \cdot 10^{-2}$ M in DMF) were evaporated onto ITO glass to obtain a film about 40 nm thick. The glass slide was $15\text{mm} \times 10\text{mm} \times 1.1\text{mm}$ with a 120-160 nm thick layer of ITO. A thin aluminum layer (150 nm) was deposited by thermal evaporation at $3 \cdot 10^{-6}$ Torr. Devices were fabricated and characterized in air at room temperature.

3. Results and Discussion

In general, zinc phthalocyanine (ZnPC) is known to show poor solubility in organic solvents, and strong tendency to aggregate due to its planar conjugated structure, for these reason we introduce substituents in their structures.

The phtalonitriles derivatives were synthesized following the method employed before in our laboratory [9]. Complex 6 was prepared by the template reaction of the phtalonitrile derivative (precursor) with zinc acetate and urea in nitrobenzene.

The PC5 complex was found to be more soluble (completely), then non substituted zn-phthalocyanine [10], in dimethylformaamide and dimethylsulfoxide. The new compound obtained in this study was been characterized as far as possible by spectroscopic techniques (IR and $^1\text{H-NMR}$).

The formation of phtalocyanine compound was confirmed by the disappearance of the characteristic nitrile ($\text{C}\equiv\text{N}$) stretch at 2226 cm^{-1} present in compound 4 (Figure2).

The IR spectrum of PC5 are very similar to those seen in literature. Aromatic C-H peaks were observed around 3032 cm^{-1} and aromatic C-O-C stretching was observed at 1225 cm^{-1} . The stretching frequency of methoxy group was observed at 2760 cm^{-1} . And the adehyde group seen was observed at 1690 cm^{-1} .

In the $^1\text{H-NMR}$ spectrum of PC5 taken in DMSO- d_6 , the methoxy protons appeared as multiplets at 3.8 ppm, the aromatic protons as multiplets from 7.74 to 6.93 ppm and the formyl protons a singlet at 11.1 ppm.

The Q band of the PC5 complex in DMF was typical of nonaggregated species, as it can be observed on Fig 3, at concentrations lower than 5×10^{-5} M. It's shown that PC5 exhibit the typical optical features of phtalocyanines: a

broad absorption band at around 348 nm, assigned to the Soret band of the phthalocyanine moiety and a strong one at 681 nm assigned to Q-absorption band.

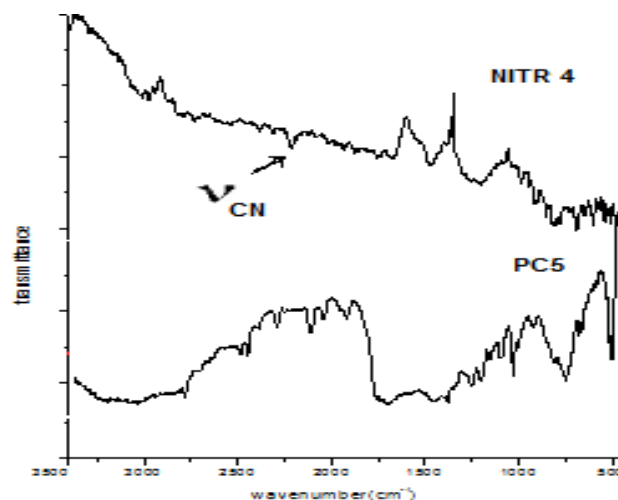


Figure 2. IR-spectroscopy spectra of PC5

3.1. Optical Properties

The UV-Visible absorption and photoluminescence spectra of PC5 were recorded at room temperature, in diluted DMF solutions and in thin solid film while those of Poly(PC5) in electrodeposited film.

3.1.1. UV-Vis Absorption Spectroscopy

Absorption spectrum seems to be the most important characteristic of phtalocyanines complexes and related compounds. The ground state electronic spectra are especially useful to identify the structure of these macrocycles.

ITO conductive glass electrodes were used to obtain the UV-visible absorption spectra of the electropolymerized films.

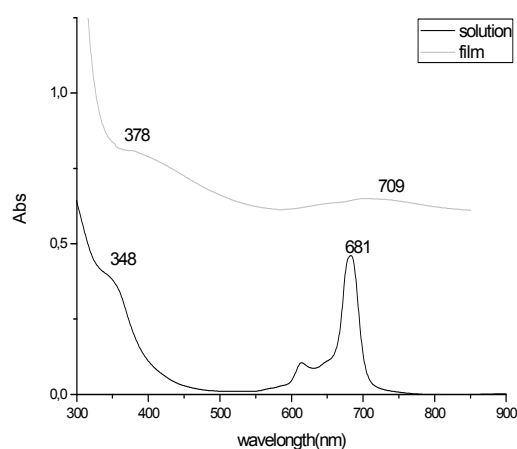


Figure 3. UV-vis absorption spectra of PC5 [thin film and dilute solution in DMF ($5 \cdot 10^{-5}$ M)]

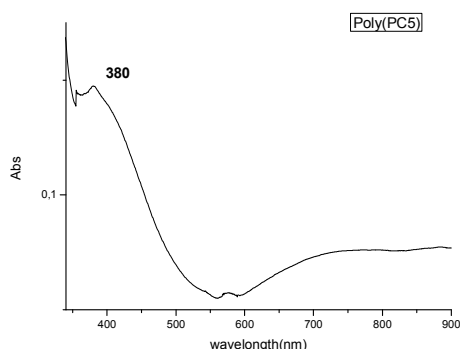


Figure 4. UV-vis absorption spectra of Poly(PC5)

In dilute solution, the spectrum shows two absorption maxima at 348, and 681nm which are the characteristic band of phtalocyanine (Figure 3). Nevertheless, the spectrum was slightly redshifted (11 nm) in comparison with that of nonsubstituted phtalocyanine [10,11]. This behavior can be in fact attributed to the electronic effect of methoxy and formyl groups.

The optical band gaps were estimated from the absorption onset of the polymer films and according to the formula $E = hc/\lambda$. The calculated value was 1.75 for PC5 and lower then 1.37 for Poly(PC5) as shown in table 1.

Table 1. $\lambda_{max}(nm)$, and $\lambda_{onset}(nm)$ optical band gap (ev) of PC5(film), PC5(solution) and Poly(PC5)

Compounds	λ_{max}/nm		λ_{onset}/nm	Optical band gap $E_{gap\ op}(ev)$
	B band	Q band		
PC5(solution)	348	681	706	1.75
PC5(Film)	378	709	834	1.48
Poly(PC5)	380	Higher then 822	Higher then 900	Lower then 1.37

Going from solution to film the PC5 absorption spectrum preserves the same allure while shifting toward the lowest energies. This bathochromic effect was assigned to the p-stacking of the phtalocyanine moieties and aggregate formation in the solid state. An optical band gap of 1.48 eV was estimated from the absorption onset of the film sample. Comparing monomer and polymer film (Figure 4) we note that the second one was red shifted which can be explained by the conjugation growth.

3.1.2. Photoluminescence Measurements

The luminescence properties of the materials were studied by analyzing the photoluminescence spectra of the material in the visible region with wavelength excitation of 488nm. The sample for PL spectra was loaded on a solution and film sample. Figure 5 and Figure 6 shows the photoluminescence spectra of PC5 (solution and film) and Poly(PC5)(electrodeposited film) respectively.

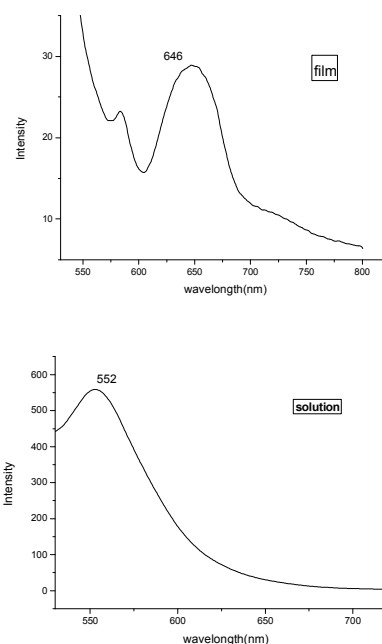


Figure 5. PL spectra of PC5 in thin films and dilute solutions in DMF ($5.10^{-5}M$)

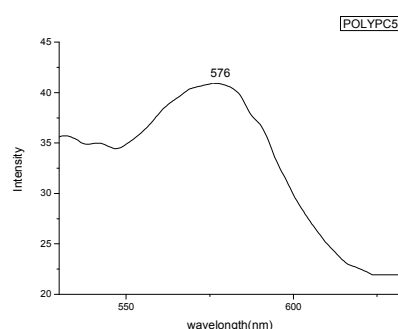


Figure 6. PL spectra of polyZnPC

The p-p stacking of conjugated moieties also influenced the film emission, and broad, redshifted PL spectra were obtained as a result to excimer formation in comparison with the solution spectra [12]. An important red emission (646nm) was observed for PC5 (film), and a green emission was obtained (563 nm) for PC5 (solution). In the case of the Poly(PC5), a yellow emission was detected (576nm) which is certainly explained by the growth of the conjugation.

3. 2.Electrochemistry

3.2.1. Electrochemical Measurement

This technique provides information on the position of the energy levels (the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)). The electrochemical experiments were performed, by cyclic voltametry, at room temperature in a conventional three electrode cell. The glass ITO was utilized as working electrode, platinumium wire as auxiliaire

electrode and ECS as reference electrode and scanned in $\text{LiClO}_4/\text{dimethylformamid}$.

All processes are ring based since the central Zn metal is electroinactive [13,14]. Complex PC5 exhibits one irreversible oxidation pic at 0.437 V and a reversible reduction pic at -1.55 V. The voltammograms obtained are shown in figure 7.

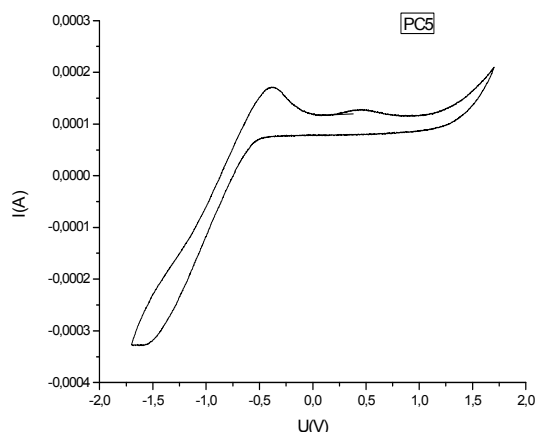


Figure 7. Cyclic voltammograms of PC5 in 0.1M $\text{LiClO}_4/\text{DMF}$ (scan rate: 100mVs^{-1} Working electrode=ITO, Auxiliaire electrode= platinum wire and reference electrode = ECS)

The HOMO energy level (E_{HOMO}), LUMO energy level (E_{LUMO}), and the electrochemical gap ($E_{\text{g-el}}$) were calculated according to an empirical method [15]. The calculated E_{HOMO} , E_{LUMO} and $E_{\text{gap el}}$ values are summarized in Table 2.

Table 2. Specific E_{HOMO} (V), E_{LUMO} (V) and electrochemical band gap (eV) of PC5

	E_{HOMO}	E_{LUMO}	Electrochemical gap $E_{\text{gap el}}(\text{eV})$
PC5	-4.33	-2.35	1.98

3.2.2. Electropolymerization of PC5 on ITO Electrodes

The deposition of the phtalocyanine complex onto indium tin oxide electrodes by electrochemical polymerizations of the phtalocyanine complex was accomplished by cycling the potential applied to the working electrode from 2 V to -2 V.

After 100 scan (Figure 8) we note an increase in currents of the voltammogram envelop which indicates that a deposit was formed on the electrode. Thus, different phtalocyanine film thickness can be obtained by controlling the number of the electropolymerizing scans.

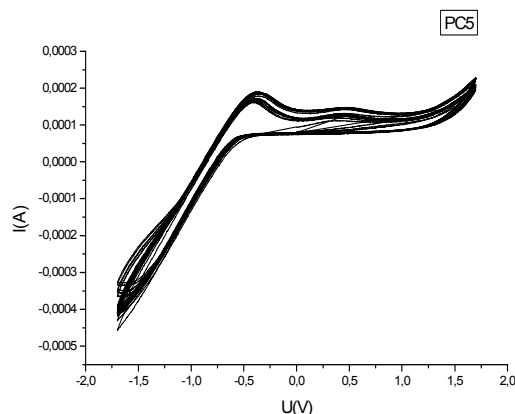


Figure 8. Cyclic voltammograms of PC5 in 0.1M $\text{LiClO}_4/\text{DMF}$ (scan rate: 100mVs^{-1} Working electrode=ITO, Auxiliaire electrode= platinum wire and reference electrode = ECS)

3.3. Current - Voltage Measurements

The measurement of current-density (J) – voltage (V) characteristics is an important technique for characterizing diode. Two single-layer devices with an ITO/PC/Al configuration were fabricated to investigate the current-voltage (I-V) characteristics of the phtalocyanine based materials.

As shown in Figure. 8, the two I-V curves are very close and indicate typical diode behavior with relatively low turn-on voltages of 1.33 and 1.39V for Poly(PC5) and PC5 respectively. Nevertheless, no electroluminescence could be recorded for these simple devices. The reason is probably unbalanced charge injection which increases the probability of radiation less exciton quenching at the electrode/phtalocyanine material interface [16]. Therefore, we consider that the devices turn-on voltages indicate the threshold of a hole-governed unipolar injection. In fact, work is in progress to built electroluminescent photovoltaic devices.

4. Conclusion

A Zn-phtalocyanine semi-conducting materials (PC5) was synthesized and characterized by UV and IR spectroscopy. Electrochemically, we have synthesized a new polymeric compound with yellow emission. The optical study revealed that in thin film, the emission was red-shifted when compared with solution and that the optical gap changed from 1.75 to 1.48 eV. The I-V characteristics of devices with an (ITO/PC5/Al) and (ITO/Poly(PC5)/Al) configurations demonstrate typical diode behavior with relatively low turn-on voltages. All these features make these compounds promising active materials for phtalocyanine-based OLEDs.

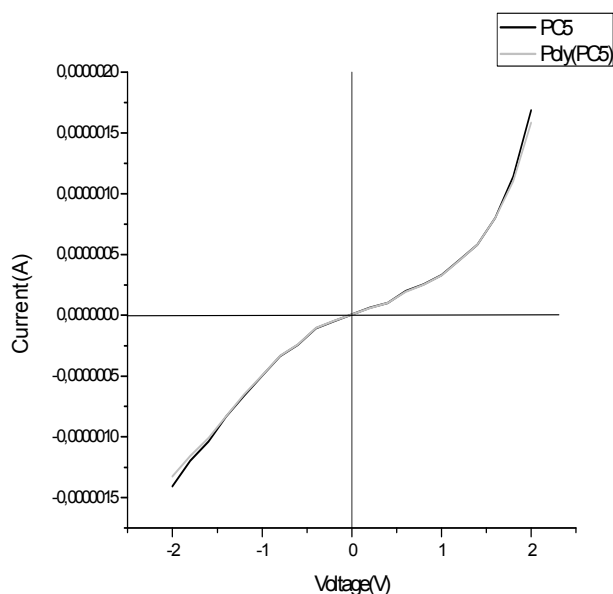


Figure 9. Current-voltage curves for [ITO/PC5(/Al)] and [ITO/Poly(PC5)/Al] devices

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