Manipulation in Properties of Materials Built Of Symmetric Heterocycle Structures

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INTRODUCTION

The construction of conducting material with increasing complexity exhibiting a precise architecture, size, shape and functionality is a challenging domain of rapidly growing interest. It founds its incentives in the increasing needs for molecular devices which accompany the developmnet of nanotechnologies [1]. A major support for the advancement in the design of functional molecular nanoobjects is our improving ability to control their macromolecular structure in great detail often by using proper polymerization techniques or other deposition methods (*Langmuir - Blodgett*).

Particularly, investigations on structurraly ordered thin films built of symmetric bis(ethylenedioxythiophene)-, bis(thiophene)- and bis(pyrrole)derivatives of carbazole or fluorene are important, since such a films are used for fabrication the valuable surface layers for microsensors or optoelectronic devices[2].

The widely adopted approaches to prepare structurally ordered thin films are the self-assembled monolayer, controlled electropolymerization, *Langmuir Blodgett* techniques.

The LB technique (Fig. 1) is very special method which allow to manipulate with film properties, that fabricates *Langmuir* layers at the air/water interface and subsequently transfers those films onto a solid substrate, also allows to control the structure of the film at the molecular level.
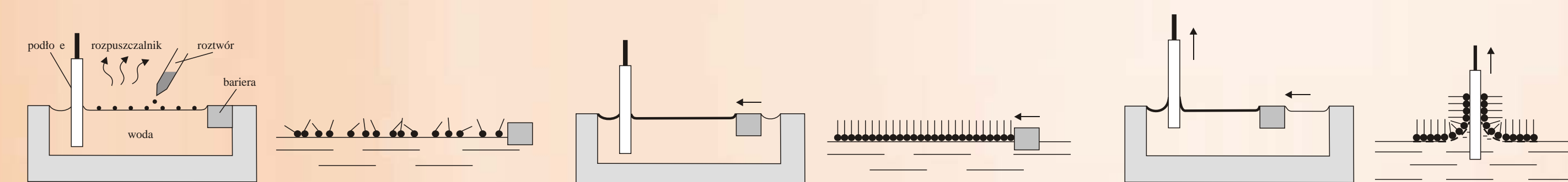

Fig. 1 The scheme of LB film deposition

The type of deposition, however, does not guarantee the structure of multiple LB films, and a distinction should be made between the type of deposition and the resulting overall structure. The most common structure, also denoted as the basic unit, is the centrosymmetric, head to head, tail to tail configuration. Moreover, there would be a great deal of applications for Y type deposition if they could render symmetric LB films[3].

EXPERIMENTAL SECTION

Synthesis of Monomers

Bis(thiophene) derivatives of N-alkylcarbazole were synthesized by *Stille* type coupling reaction[4]. Whereas 9,9-dialkyl- or 9-alkyl-2,7-bis(pyrrolyl)fluorene by modified *Engel* and *Steglich* procedure[5].

9,9-dihexadecyl-2,7-bis(pyrrolyl)fluorene - DHFP

N-nonyl-3,6-bis(2-thiophene)carbazole TPC
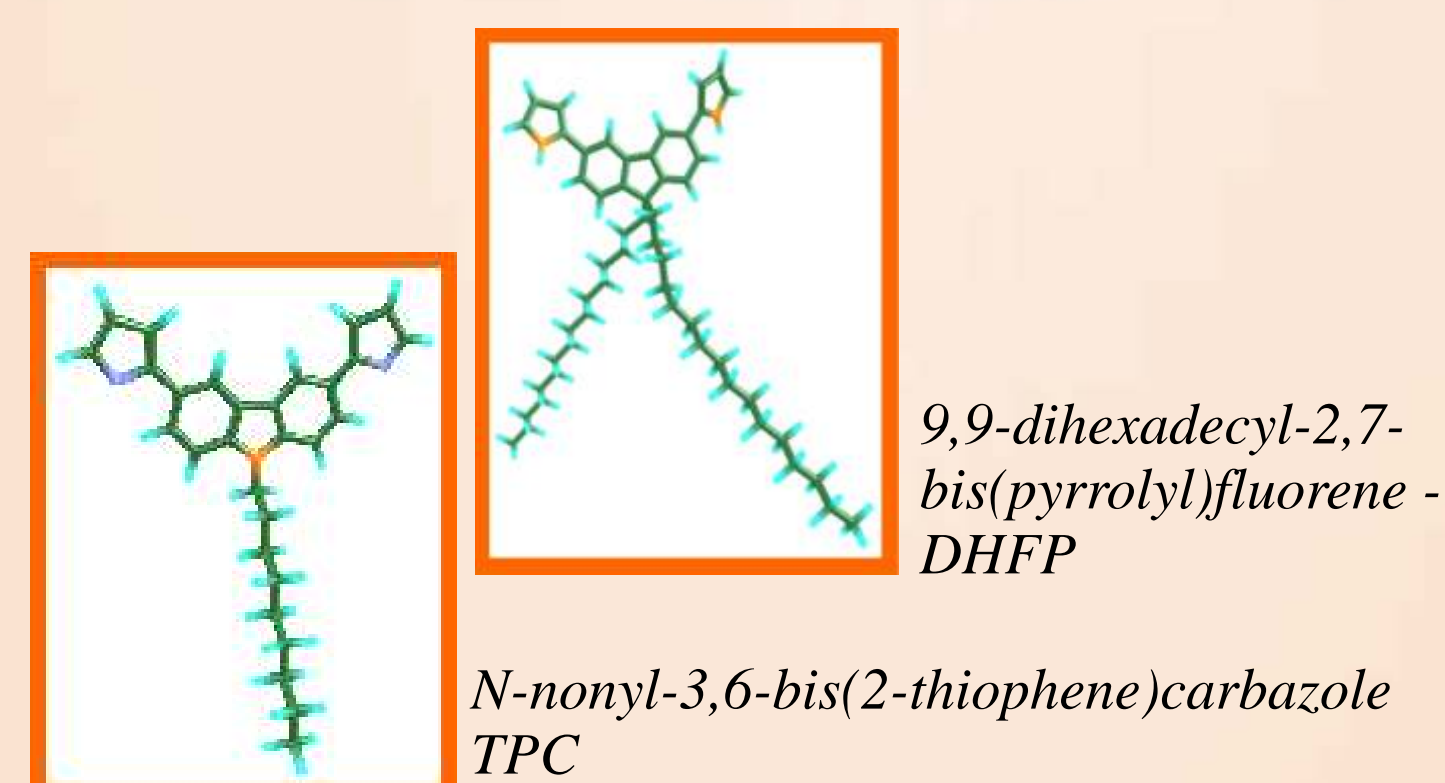
Langmuir and Langmuir Blodgett Films Preparation

To obtain *Langmuir* films, the synthesized compounds were dissolved in chloroform (HPLC grade). Concentrations of solutions were maintained to ca. 1 mg/ml.

The films of desired composition were formed by dropwise spreading of proper symmetric derivatives solutions, with or without docosanoic acid - DA, poly(octadecylthiophene) pODT and 22 tricosenoic acid used as film facilitators on high purity water at 295 K. Befrore deposition of LB films, substrates were washed in the standard way, using consecutive sonication in non ionic detergent (1% solution of DECON 90), rinsing with deionized water, etching in the ethanolic solution of NaOH, to make them hydrophilic and finally copious water and drying uder the stream of dry argon. The composition of 3:1, 1:1 and 1:3 binary systems were maintained by resulting molar composition of the deposition mixture. The π-A isotherms were measured and the LB films were deposited by means of commercial LB trough (KSV, System 5000), using Pt hydrophilic Wilhelmy plate. The compression rates in our experiments ranged between 25 and 100 mm/min, depending on rigidity of the films. LB films of 1, 3, 5 monomolecular layers were prepared by means of vertical emerging and dipping of the substrate at the surface pressure of around 15 mN/m.

Galvanostatic Electropolymerization

Polymer electrochemistry was carried out on a standard model galvanostat employing a platinum disk working electrode or *ITO* (area = 1.55 cm²) disk working electrode, and a platinum plate counter electrode. Spectroelectrochemistry experiments were carried out on a Cary 100 Bio Varian UV-vis spectrophotometer. Polymer films were deposited onto *ITO* coated glass plates (9.8 x 50.0 x 0.5 mm, 20 Ω/square, Delta Technologies). Insoluble polymers were cast onto *ITO* or platinum plates (10 x 70 x 0.2 mm) from dry acetonitrile.

Electroconducting Experiments

An investigations of the electrical conductivity of *Langmuir-Blodgett* films consisting one monolayer of 9-hexadecyl- or 9,9-dihexadecyl-bis(pyrrole-2-yl)fluorene (respectively: MHFP[7] and DHFP[8]) a potential precursors of the new conducting polymers, exposed to different concentrations of gases or vapors (nitrogen dioxide, ammonia, acetonitrile and ethyl alcohol) were carried out. The films were deposited onto a set of eight interdigital, buried Au electrodes (200 μm. wide and spaced) photo-lithographically fixed on SiO₂ thermally coated silicon substrates, which configuration of electrodes provides flat, ready to LB deposition surface of the sensors. Monomelecular films built of DHFP or MHFP were prepared by means of vertical dipping of the substrate and stored in vacuum desiccator prior to use.

All electrical measumerents were done in room temperature with constant voltage, different for different gases, using the *Keithley 614* aparatus. The current-voltage characteristics were found to be linear over the whole measuring range i.e 0.1 to 4.0 V in ambient atmosphere and for all gases of interest. The nominal concentrations of toxic gases ranged between 0.92 mg/m³ (0.2 ppm) for NO₂ and 150 mg/m³ (886 ppm) for NH₃.

RESULTS AND DISCUSSION

Aggregation Properties of bis(thiophene) N-alkylcarbazoles

From the measured π-A isotherms of all synthesized derivatives of N-alkylcarbazole it was clear that the derivatives with an even number of C atoms in alkyl chains do not form stable Langmuir films. Therefore N-nonyl-3,6-bis(2-thiophene)carbazole (TPC) the derivative with odd number of C atoms in the alkyl chains was chosen for further experiments. Although pure TPC forms good Langmuir films (Fig. 2) their LB films are not very stable because the transfer occurs under a relatively low surface pressure.
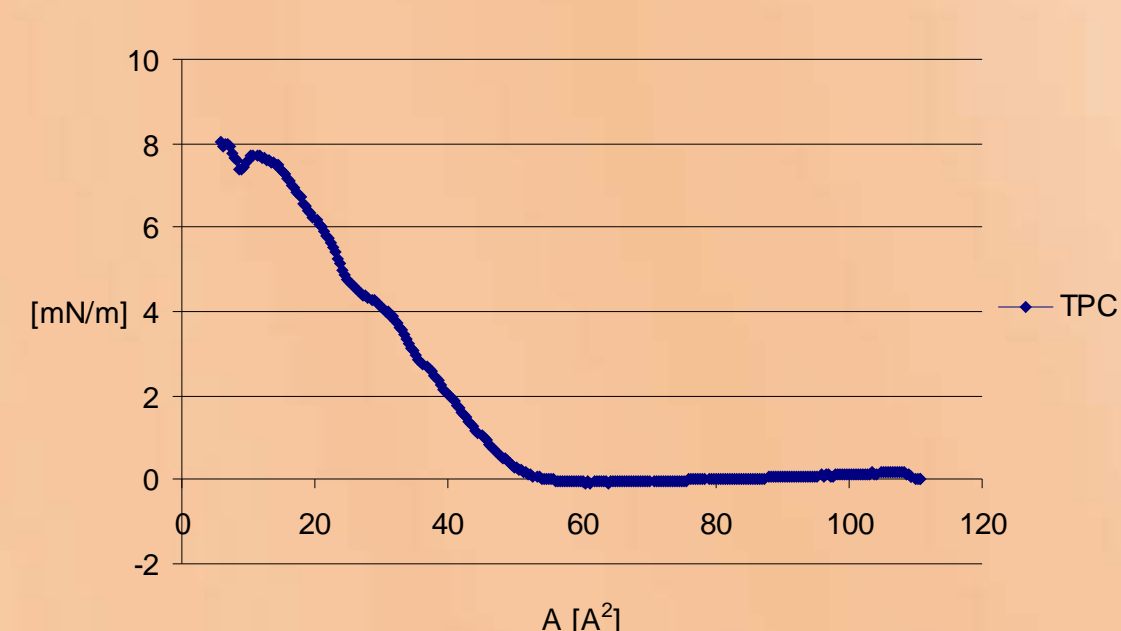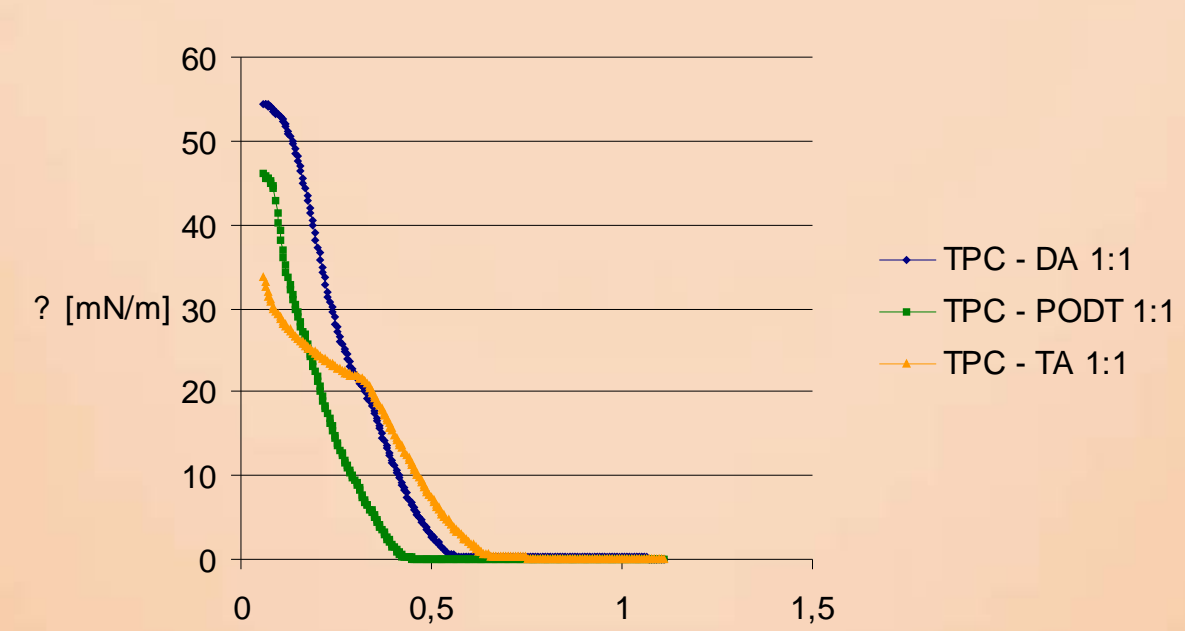

Fig. 2 π-A Isotherm of TPC

Fig. 3 π-A Isotherms of TPC-DA, TPC-PODT, TPC-TA complexes

Comparison of π-A isotherms of Fig. 3 shows that when using binary films, it is possible to obtain much higher surface pressures and therefore closer packing, and PODT facilitates this process the most effectively. This is caused by synergy between the structures of TPC and PODT.

During compression, in this case, is observed a "sweavel transition"occurrence, molecules of binary system can slip each under the other forming a "spoon like" stacking (Fig. 4) and in close packed phase both calculated and measured, from π-A isotherm, the area per molecule amounts to ca. 0.4 nm². Tricosenoic and docosanoic acids, the model amphiphiles can also be effectively used for creation of binary systems of interest.

Fig. 4 Model scheme of "spoon like" stacking of TPC molecules in binary system
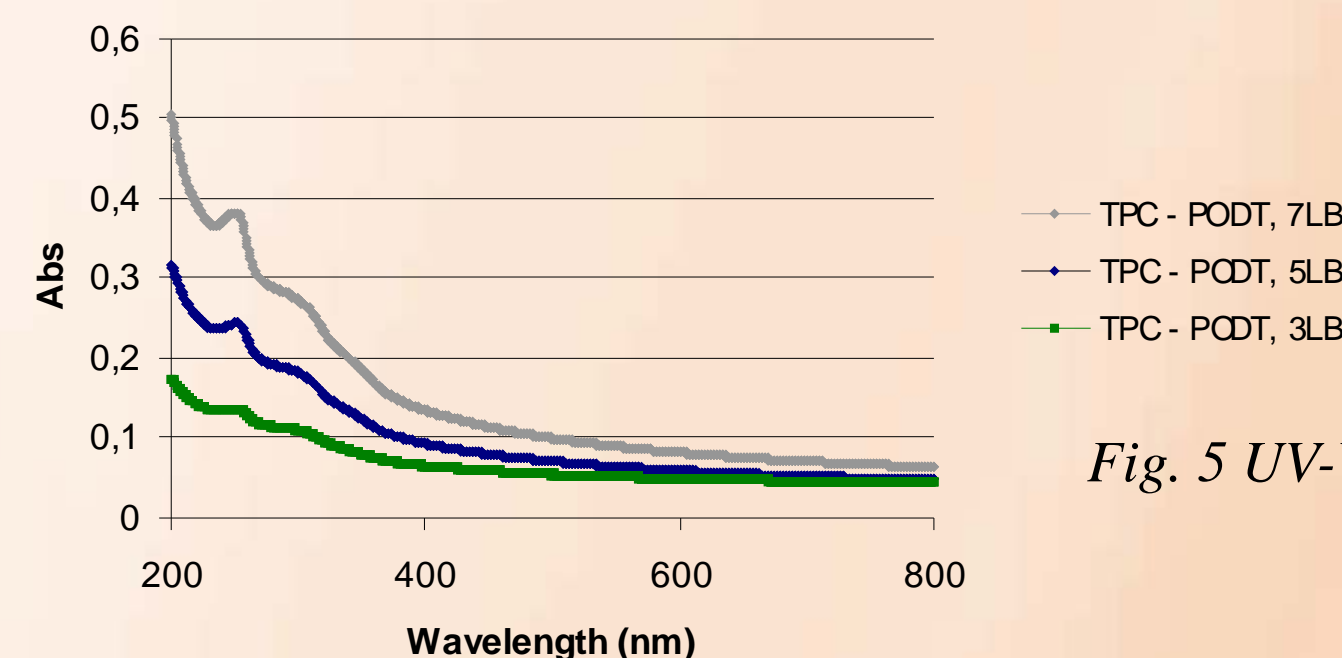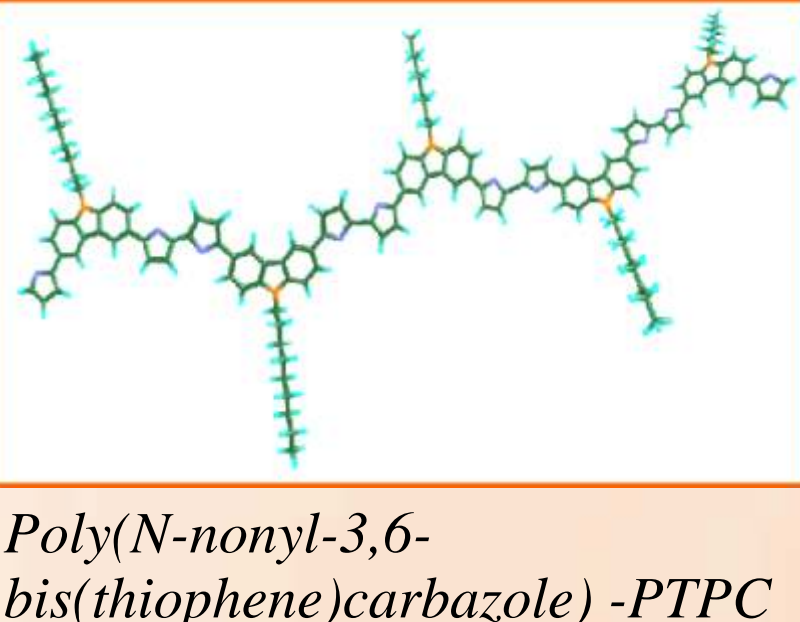
Deposited LB films are complete and of high quality, as confirmed by additivity of UV-vis spectra (Fig. 5).

Fig. 5 UV-Vis spectra of binary complex's (TPC-PODT) LB films

Electrochemical Characterization of PTPC

To enable a comparison of the conductivity of LB films in different binary systems, electrochemically deposited PTPC - poly(N-nonyl-3,6-bis(thiophene)carbazole) films were generated. The preferred method of polymer synthesis for optimum film formation was the application of potential near 1.4 V in an electrolyte solution of (Bu)₄N(BF₄) 0.2 M/acetonitrile. The deposition of PTPC was found to proceed rapidly and the synthesis of thick PTPC films was not complicated and we were able to obtain homogenous and stable electroconductive polymer (δ = 6.25x 10⁻⁸ S/cm).

Poly(N-nonyl-3,6-bis(thiophene)carbazole) -PTPC

Figure 6 shows the conductivity dependence as a current-voltage plot, which is linear over the range of film thickness.
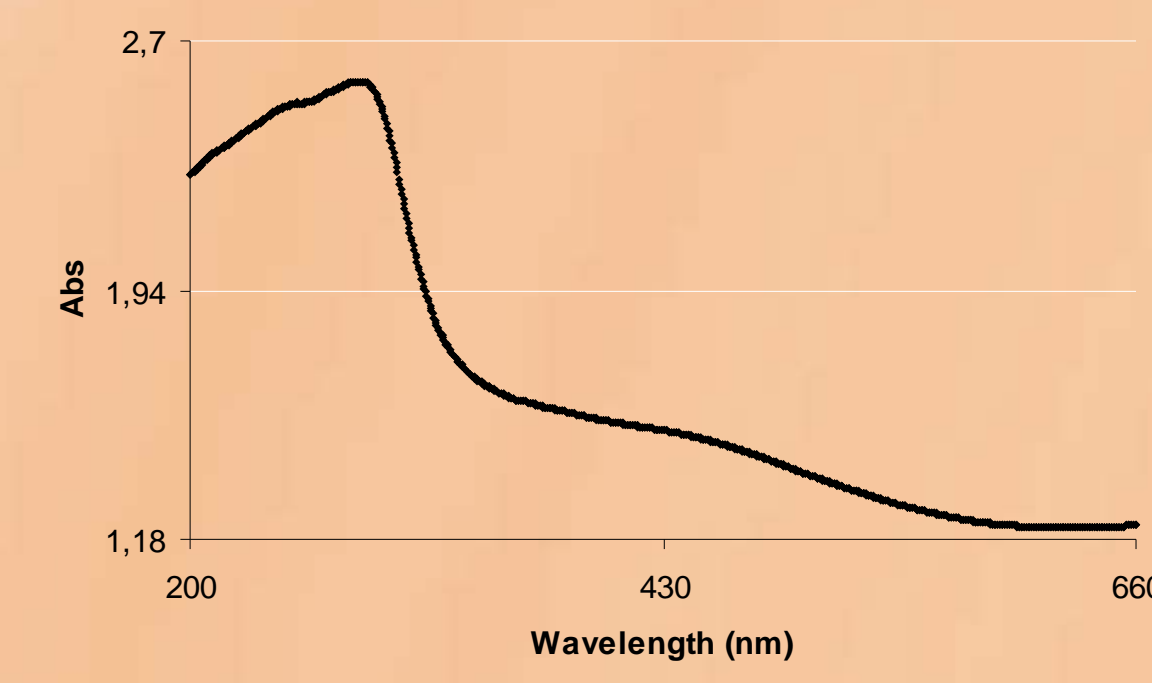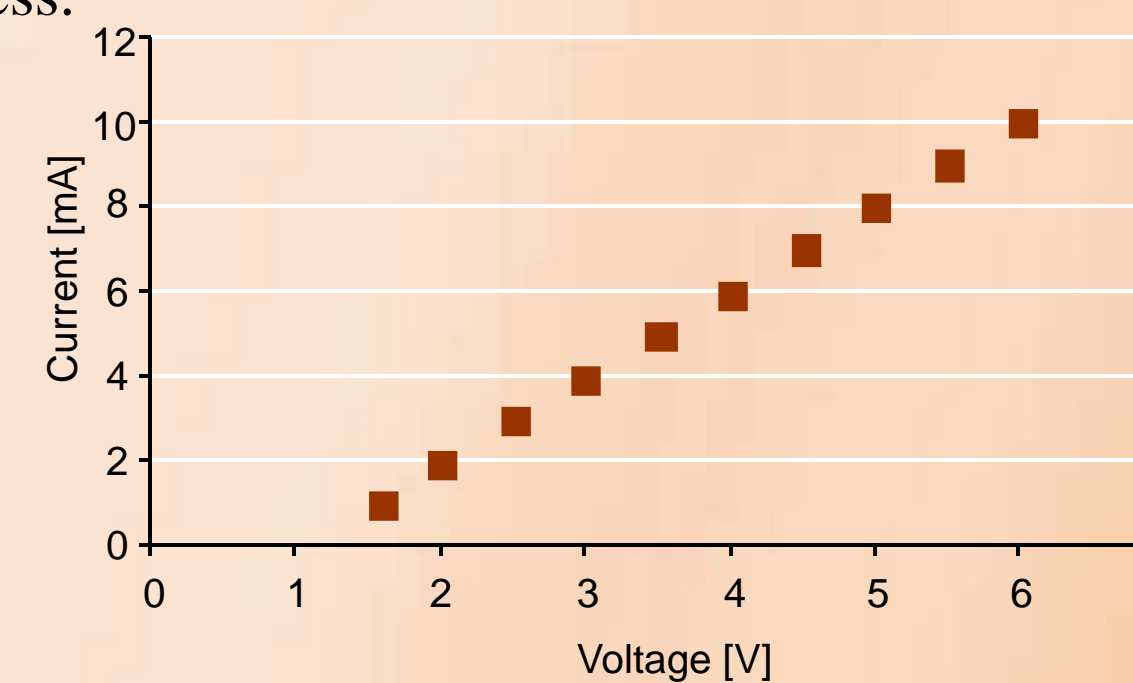

Fig. 6 The current voltage characteristic of PTPC electropolymer *Fig. 7 The UV-vis spectrum of electropolymer PTPC film*

The absorbance spectrum of the thin PTPC layer (Fig. 7) suggests a ground state electronic structure..

Electrical Effects of monomolecular LB films obtained of 9,9-dihexadecyl- (DHFP) and 9-hexadecyl-2,7-bis(pyrrolyl)fluorene (MHFP)

The major results of LB films electrical conductivity investigations was found in case of 9-hexadecyl- or 9,9-dihexadecyl-bis(pyrrolyl)fluorene LB monolayers, which exposed to different concentrations of toxic gases and vapors (ethyl alcohol, ammonia and nitrogen dioxide) changed an electrical conductivity[6,7].

The current flowing through asdeposited films in most cases ranged between 10⁻¹⁰ A and 1.2·10⁻⁷ A at room temperatures.

Upon exposition of NO₂ the conductivity of a pristine film of monosubstituted derivative increased substantially. The first admission of nitrogen dioxide gas causes a growth of conductivity on NO₂ concentration exhibiting rather strong tendency to saturation at higher gas concentration (first step, Fig. 8). After the complete series of measurements, measuring box was opened to the air and recovery of conductivity was observed for ca. 20 minutes.The second and all consecutive admissions of gases resulted in a similar dependence of conductivity of NO₂ concentrations, but with a higher sensitivity of the sensor. The subsequent exposition to air resulted in decreasing the conductivity almost to the initial value. The effect was found to be reversible in all cases.

Similar experimets were performed also for ammonia and ethanol however, the electrical conductivity of the film decreased with increasing of the NH₃ and EtOH concentrations (Fig. 9).
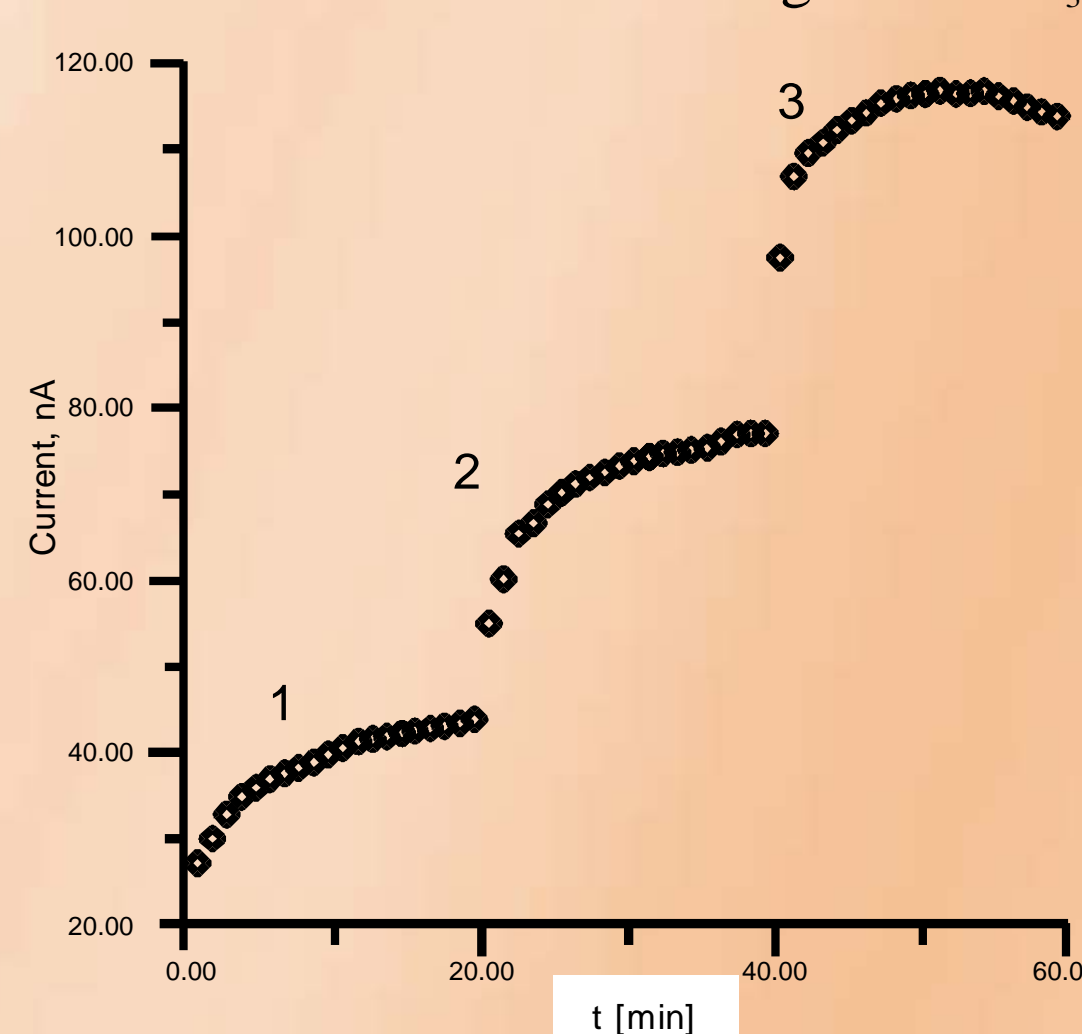

Fig. 9 Temporal response of 1 LB layer thick the DHFP sensor to increasing concentration of NH₃. In each step concentration was elevated by 15 ppm. U=0.5 V

Fig.8 Temporal response of 1 LB layer thick the MHFP sensor to increasing concentration of NO₂. In each step concentration was elevated by 1.18 ppm. U=0.5 V
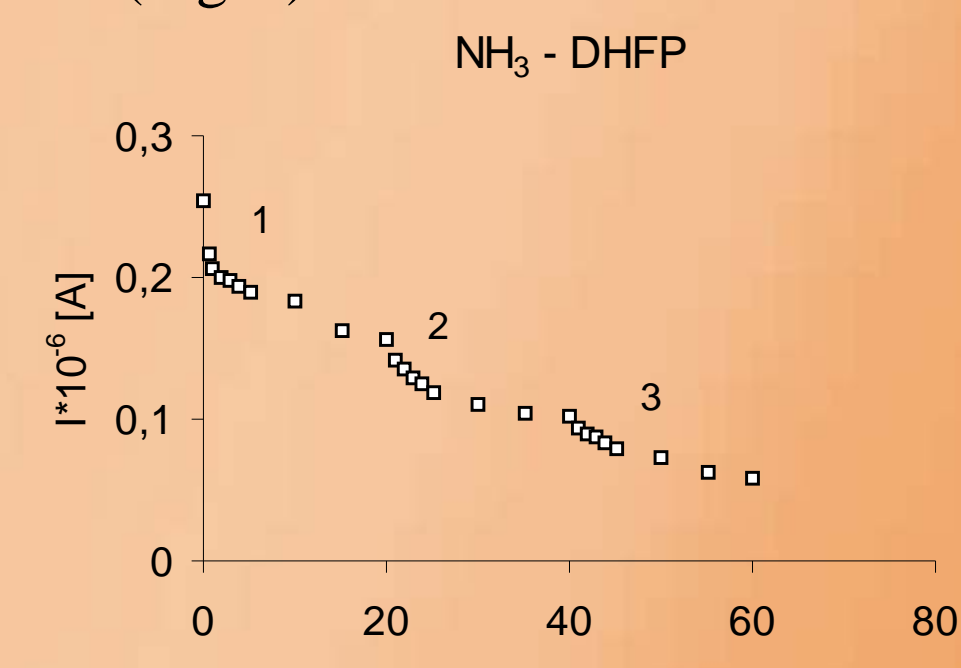
The electon acceptor character of pyrrole ring in the MHFP and DHFP structures causes an increase in electrical conductivity in the presence of oxidative gases, and a decrease of conductivity in presence of reductive ones, both circumstances were observed (Fig.9).

Relatively short response times and fair sensitivity at room temperatures make these materials a very promising candidates for gas sensing elements.

Molecular modeling results

The electronic density distribution is based on natural bond analysis[8] and on the Mulliken population scheme utilizing the DFT/B3LYP function. All the calculations were performed using the Gaussian-03W software.[9]
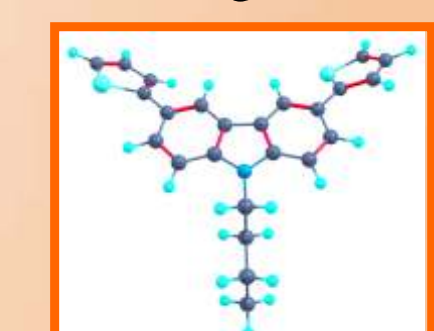

In the minimum energy the dihedral angle between ring thiophene is 33-35°, there is possibility of rotation of thiophene ring, the barrier euquals is only 12 kJ/mol. The calculated band gaps and vertical ionization potentials show, that this kind of molecules have possibility of electro conducting and electropolymerization.

Fig. 10 The optimized structure of TPC

CONCLUSIONS

A series of N-alkylcarbazole derivatives have been synthesized using the *Stille* coupling reaction. Carbazole derivatives mixed with substances facilitating film building gave stable and good quality *Langmuir* and *Langmuir-Blodgett* films of desired composition. We examined the electroconductivity of LB films built with TPC monomer in a binary system. The electrical properties of a thin polymer film of PTPC, obtained by electrochemical polymerization, were determined.

It is shown that the monomolecular layers built of bis(pyrrolyl)fluorene derivatives can be successfully deposited as *LangmuirBlodgett* films, which may be used as gas sensors responding to nitrogen dioxide, ethanol and ammonia. The changes of electrical conductivities observed in experiments show beyond any doubt that the films are sensitive to work reliably in the usual concentration range.

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