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BOOK OF ABSTRACTS



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SENSOR APPLICATION OF QUINOXALINE BASED CONDUCTING POLYMER



Pamukkale Travertines

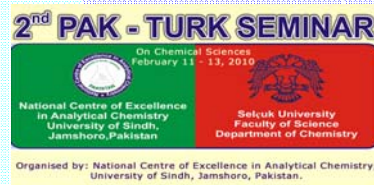
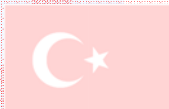
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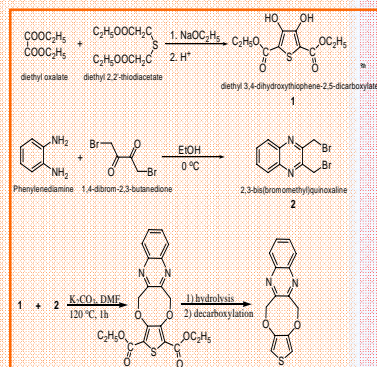
Introduction

Creative new design and development strategies led to interesting new materials and enhanced performance in certain devices. The ability of molecular designers in understanding how to gain control over the structure in polythiophenes makes the synthesis of polythiophenes a critical subject in the development of new advanced materials[1].

The study of redox-active receptor molecules, in which a change in the electrochemical behaviour of a signaling redox unit is used to monitor the complexation of neutral or ionic guest species, is an increasingly important area of supramolecular chemistry. This type of molecular and ion recognition sensor is based on a host-guest arrangement involving the receptor molecule and the analyte. The application of this mechanism to thin solid films is particularly relevant for the construction of sensor devices. In this context, the use of conjugated polymers is an important area of research and considerable efforts have been directed towards the use of versatile polythiophene derivatives[2].

Experimental Part

We synthesized and characterized a new thiophene monomer: 5,12-dihydrothieno [30,40:2,3][1,4]dioxocino[6,7-b]quinoxaline (Q) (Scheme 1)



Scheme1. Synthesis of monomer and polymer

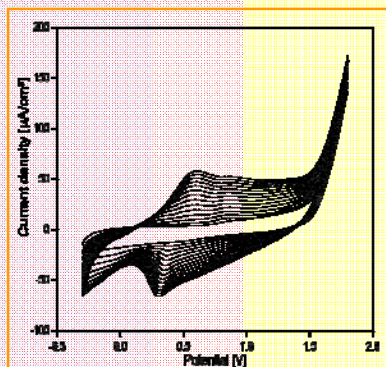


Fig.1. Cyclic Voltammetry of P(Q)

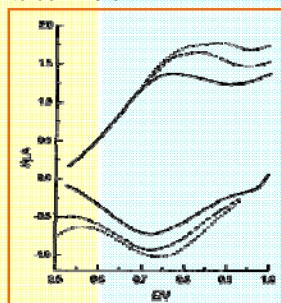


Fig.4. CV response of Poly(Q)

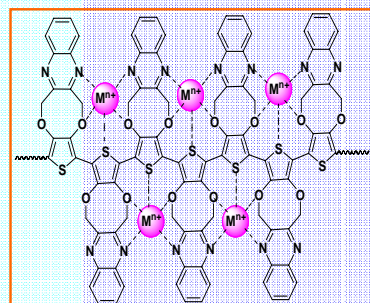


Fig.5. Predicted complexation structure of P(Q)

Electrochemical polymerization of Q via cyclic voltammetry was performed in a single compartment cell equipped with Pt working and counter electrodes and a Ag/Ag⁺ reference electrode in the presence of 50 mg Q, 0.1 M TBAFB in acetonitrile (AN) (1:4) with the 250mV scan rate and applied potentials between -0.3:1.8V. The surface morphology of electrochemically synthesized P(Q) was investigated by Scanning Electron Microscope(Fig.2). Spectroelectrochemical analysis of the P(Q) film was studied in order to elucidate electronic transitions upon doping of the polymer (Fig.3).

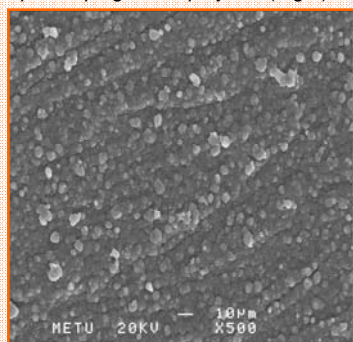


Fig.2. Surface Morphology of P(Q)

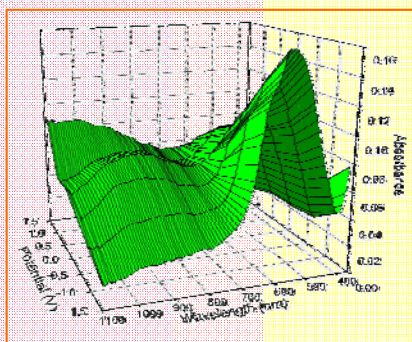


Fig.3. Spectroelectrochemistry of P(Q)

Result and Discussion

In this work, we report the synthesis and characterization of:5,12-dihydrothieno [3',4':2,3][1,4]dioxocino[6,7-b]quinoxaline (Q1) and the interaction and electrochemical recognition of silver and mercury cations with electropolymerised P(Q1) films.

The typical voltammogram for electropolymerization is represented in Fig.1 Cyclic voltammogram of DDQ indicated an oxidation peak at 0.60 V and a reduction peak at 0.30 V. When the range between 0.30 V and +1.8 V was scanned, electroactivity increased with increasing scan number. This process promotes an electrochromic change of the film into a plum-gray color, while a gray cloud is formed around the electrode.

P(DDQ) coated ITO glass electrodes was investigated by UV-vis spectroscopy in the same but monomer free electrolytic system via switching between 1.4 and +1.4 V with incremental increases in applied potential. Upon applied voltage, decrease in the intensity of the $\pi-\pi^*$ transition (556 nm) and formation of charge carrier bands were observed. There was a gradual decrease in the peak intensity at around 556 nm upon increase in the applied potential, which was accompanied by the increase in the intensity of peaks at around 950 nm due to the formation of polaron bands at interval potentials. The onset energy for the $\pi-\pi^*$ transition (electronic band gap) was found to be 1.73 eV.

The interaction of several transition metal cations was investigated and, most notably, Ag⁺ exhibited definitive indications of recognition behaviour. Addition of the Ag⁺ cation led to a change of CV response of polymer film, such that the both oxidation (E_p) and reduction (E_p) peak potentials shifted positively (Fig.4). A change in the CV shape was also observed. The response to Ag⁺ starts at the concentration level of 10⁻⁴ M and saturates at about 10⁻² M with a maximum shift up to ca. 150 mV.

Conclusions

The novel quinoxaline based thiophene monomer (Q) has been synthesized and electropolymerised. P(Q) exhibits an interaction and electrochemical recognition of silver cations. The Ag⁺ ion coordinates with Poly(Q) as a metal complexation agent, in two ways (Fig.5): (i) an apical conformation involving the two oxygene and (ii) a lateral - complex with a contribution from the quinoxaline nitrogens. Also sulphur atom in thiophene can involve the complexation. The polymer films exhibit a transformation in voltammetric response corresponding to a positive shift in redox potential in the presence of silver cation, the maximum shift being 150 mV in acetonitrile.

References

1. M. Ak, M. S. Ak, M. Gullu, L. Toppare, Smart Mater. Struct. 16 (2007) 2621-2626
2. L.M. Goldenberg, P.J. Skabara, J.Mater.Chem.,10 (2000), 2458-2465

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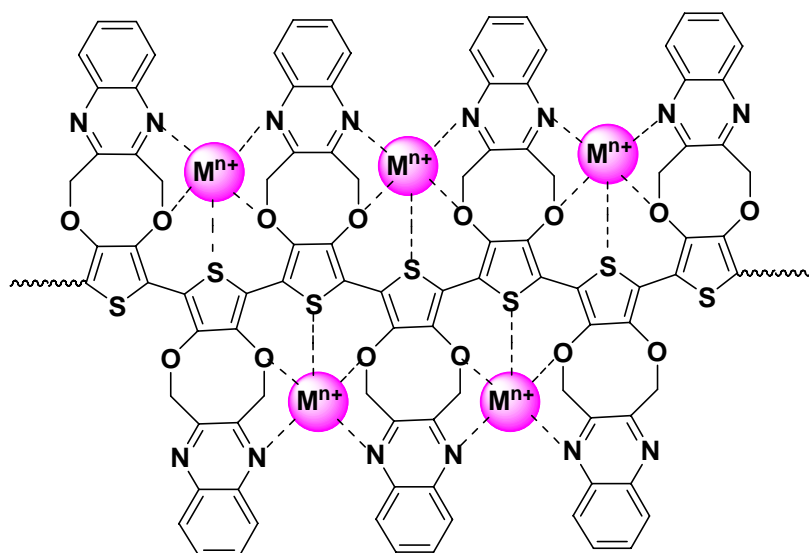


Fig.1. Proposed structure of complexation between P(Q1) and metal ions

References:

1. M. Ak, M. S. Ak, M. Gullu, L. Toppare, Smart Mater. Struct. 16 (2007) 2621–2626
2. L.M. Goldenberg, P.J. Skabara, D.M. Roberts, R. Berridge, E. Orti, P.M. Viruela, R. Pou-Amerigo, J. Mater. Chem., 10 (2000), 2458-2465