BOOK OF ABSTRACTS

8TH INTERNATIONAL CONFERENCE ON ADVANCED POLYMERS VIA MACROMOLECULAR ENGINEERING

APME 2009

October 4th to 7th, 2009
Dresden, Germany

Leibniz-Institut für Polymerforschung Dresden e. V.

TECHNISCHE UNIVERSITÄT DRESDEN

Organic-inorganic conducting polymer hybrid with green color in neutral state

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The application of electrical stimuli can result in drastic changes in the chemical, electrical, optical and mechanical properties of conducting polymers. Thanks to these properties, these materials are used for making smart devices. Because of changing optical properties via electrochemical means, CPs can be used in smart windows and polymeric data storage devices. For synthesis desired polymers that used in these technological applications, design of monomer is so crucial [1,2].

A new monomer; O-2-(thiophen-3-yl)ethyl ferrocenyldithiophosphonate (ThFc) was synthesized and characterized. P(ThFc) films were synthesized electrochemically through the direct oxidation of ThFc in pure boron trifluoride diethyl etherate (BFEE). Under these conditions, BFEE serves not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte is needed. P(ThFc) has C-atoms in the main chain and contains inorganic elements in side groups connected to the organic network. The idea of this concept is to obtain a synergistic effect between inorganic and organic phases.

P(ThFc) revealed color changes between green and blue in the neutral and oxidized states respectively. Having green color in neutral state is another interesting property of the polymer. Although many red and blue colored polymers in their neutral form have been reported, only a *few reports* are found in the *literature* of green colored conducting polymer because of the difficulty to obtain the absorptions required in the visible region to reflect the color green [3].

The optical properties, the absorption spectra and the kinetics of the polymer were examined. Spectroelectrochemical analysis showed that P(ThFc) has an electronic band gap (due to p-p* transition) of 2,23 eV at 418 nm.

References:

1- O. Turkaslan, M. Ak, C. Tanyeli, I. M. Akhmedov and L. Toppare, "J. Polym. Sci., Part:A Polym. Chem., 45(19), 2007, 4496-4503.

2- M. Ak, B. Gacal, B. Kiskan, Y. Yagci, L. Toppare Polymer, 49(9), 2008, 2202-2210.

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ORGANIC INORGANIC POLYMER HYBRID WITH GREEN COLOR IN NEUTRAL STATE

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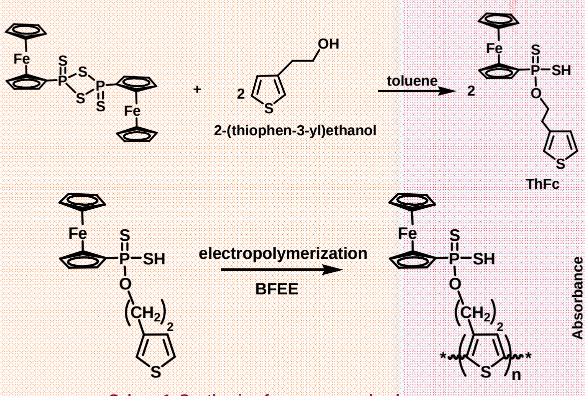
Introduction

The discoveries in the last two decades of the 20th century brought conjugated polymers to full commercialization with applications in electrochromic rearview mirrors, smart windows, thin-film transistors, displays, sensors, OLEDs and electrochromic devices [1].

Electrochromism is the reversible change in optical property which can occur when the electrochromic material is electrochemically oxidized or reduced. Conducting polymers have gained a considerable attention since they offer superior properties due to their relative ease in molecular engineering to achieve desired colors for electrochromic devices with respect to inorganic materials [2]. For synthesis desired polymers that used in these technological applications, design of monomer is so crucial.

Experimental

Synthesis of Monomer and Polymer



Schene1. Synthesis of monomer and polymer

A new monomer; O-2-(thiophen-3-yl)ethyl ferrocenyl dithiophosphonate (ThFc) was synthesized and characterized. P(ThFc) films were synthesized electrochemically through the direct oxidation of ThFc in pure boron trifluoride diethyl etherate (BFEE) (Scheme1). Under these conditions, BFEE serves not only as the solvent but also as the supporting electrolyte, and no other supporting electrolyte is needed. P(ThFc) has C-atoms in the main chain and contains inorganic elements in side groups connected to the organic network. The idea of this concept is to obtain a synergistic effect between inorganic and organic phases.

Spectroelectrochemistry

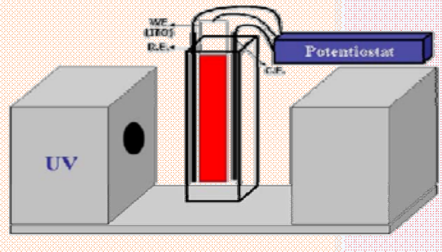


Fig.1. Experimental setup of the spectroelectrochemical investigations

The best way of examining the changes in optical properties of conducting polymers upon voltage change is via spectroelectrochemistry (Fig.1). It also gives information about the electronic structure of the polymer such as band gap (Eg) and the intergap states that appear upon doping. P(ThFc) film was potentiostatically synthesized at 1.8 V on ITO electrode and then spectroelectrochemistry investigated in monomer free BFEE

Results and Discussion

P(ThFc) revealed color changes between green and blue in the neutral and oxidized states respectively (Fig.x) whereas polythiophene reveals red and blue color (Fig.y).

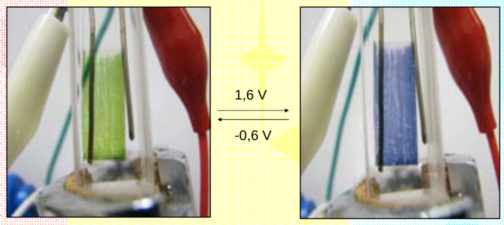


Fig.2. Redox color of the P(ThFc) in BFEE

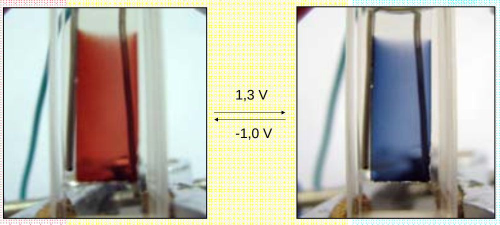


Fig.3. Redox color of the P(Th) in BFEE

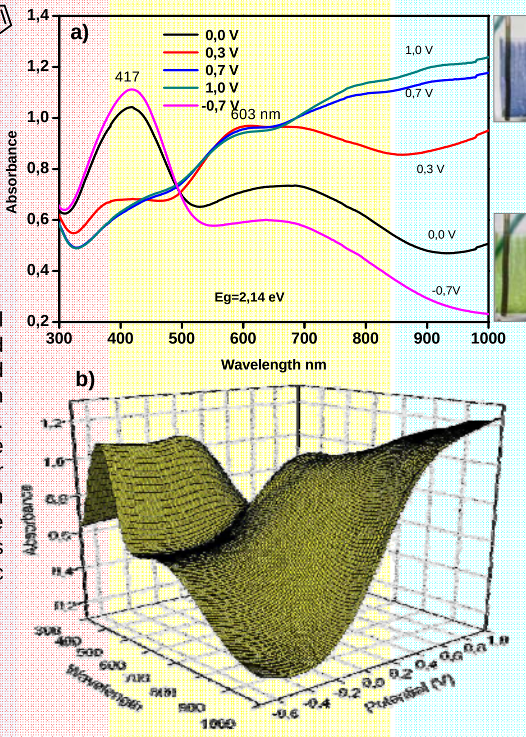


Fig.4. Optoelectrochemical spectra of P(ThFc) film in BFEE at applied potentials between -0.7 and +1.0 V a) (2D) b) (3D)

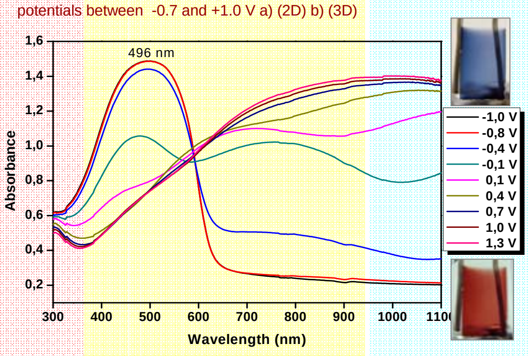
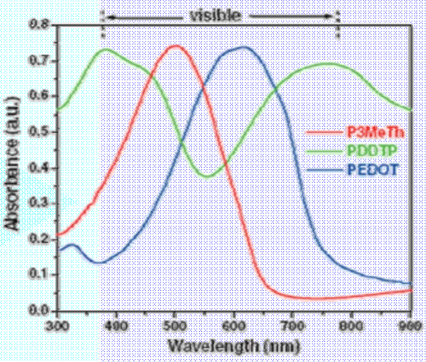


Fig.5. Optoelectrochemical spectra of P(Th) filmin BFEE at applied potentials between -1.0 and +1.3 V



The ability to have three complementary colors, red, green, and blue (RGB) constitutes an important step forward to the use of conducting polymers in polymeric electrochromic devices. Although many red and blue colored polymers in their neutral form have been reported, a few green colored conducting polymer has been reported to date cause of the difficulty to obtain the absorptions required in the visible region to reflect the color green.

P(ThFc) revealed color changes between green and blue in the neutral and oxidized states respectively (Fig 2-3). Having green color in neutral state is another interesting property of the polymer. Although many red and blue colored polymers in their neutral form have been reported, only a *few reports* are found in the *literature* of green colored conducting polymer [3] because of the difficulty to obtain the absorptions required in the visible region to reflect the color green (Fig.6-8) .

The optical properties, the absorption spectra of the polymer were examined. Spectroelectrochemical analysis showed that P(ThFc) has an electronic band gap (due to p-p* transition) of 2,14 eV at 417 nm.(Fig.4-5)

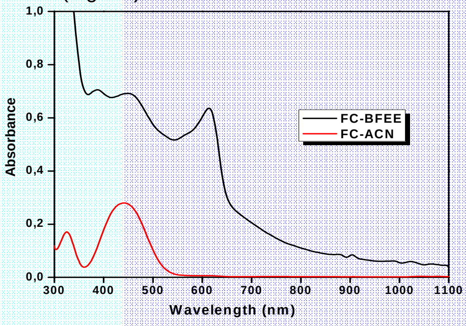


Fig.7. UV spectra of FC in ACN and BFEE

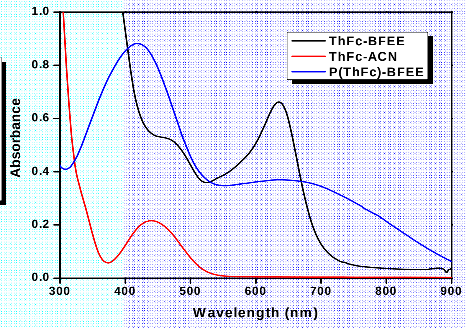


Fig.8. UV spectra of ThFc and P(ThFc) in ACN and BFEE

Conclusions

A new monomer; (ThFc) was synthesized and inorganic-organic conducting polymer hybrid P(ThFc) were electrochemically synthesized in BFEE without using electrolyte. Because of polythiphene based main chain absorption and ferrocene and BFEE interaction absortion, P(ThFc) film is green colored in neutral state. Spectroelectrochemical analyses revealed that the polymer has an electronic band gap of 2.39 eV

References

[1] M. Ak, L. Toppare Mat. Chem. Phys 114 (2009) 789–794
[2] O. Turkaslan, M. Ak, C. Tanyeli, I. M. Akhmedov and L. Toppare, J. Polym. Sci, Polym. Chem., 45(19), 2007, 4496-4503
[3] G. Sonmez, C. K. F. Shen, Y. Rubin, F. Wudl, Angew. Chem. Int. Ed. 2004, 43, 1497