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Simple and rapid synthesis of conducting metallopolymers, their electrochemical characterizations and application in electrochromics

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Dedicated to Professor Evamarie Hey-Hawkins on the Occasion of her 60th Birthday.

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ABSTRACT

Conducting metallopolymers have attracted a great deal of attention due to their multifunctional properties based on presence of metal centers as well as the interactions metal and p-conjugated polymer backbone. Due to their multifunctional properties, conducting metallopolymers have a great potential to use in various technological applications. In this work, starting with Lawesson's reagent and hydroxyl functionalized thiophene, a simple and rapid synthesis method for design conductive metallopolymer is proposed. Structural and electrochemical characterization of trans–bis[O-(thiopheneth-3-yl)(4-methoxyphenyl)dithiophosphonato]nickel(II) (TBTNi) were achieved. Spectroelectrochemical and electrochromic properties of the copolymer of TBTNi with thiophene were investigated.

1. Introduction

Polymeric materials can be finely tuned to obtain desired chemical and physical properties by embedding metal elements into polymeric scaffolds. The optical, mechanical and electronic properties of resulting metallopolymer are a combination of both the properties of the metal and carbon-based polymer [1–3]. Metal center plays an important role in determining the function of these metal containing polymers. Different types of metal centers from transition- and main group metals to lanthanides can be used to adjust polymer properties [3,4]. Since the synthesis of the first metallopolymer in 1990s, successful synthesis of hundreds of metal containing polymers with novel optical, electrical and mechanic properties have triggered potential applications in various areas [5–8].

Recently, conductive polymers containing metal centers, conducting metallopolymers, have attracted a great deal of attention due to theirs multifunctional properties based on the interactions metal and p-conjugated polymer backbone. Due to their multifunctional properties, metallopolymers have a great potential to use in various technological applications such as sensing, catalysis, solid-state memory, energy storage, and light-emitting diodes [9–12].

Electrochromism is one of the further applications of the conducting metallopolymers. Up to now, a limited number of studies on electrochromic properties of metallopolymers obtained by electropolymerization have been performed. When take a quick glance to the relevant literature, the important studies on this subject can be listed as follows.

Electropolymerization and near-infrared electrochromic properties of ruthenium(II) complexes of vinyl or thiophene groups functionalized N-N bidentate ligands have been studied by Nie and coworkers [13], [14]. Another interesting work is investigation of electrochromic properties of heterocyclic carbene-based metallopolymers, including silver, iridium, gold or copper metal cores with thiophene groups [15–17] Having good electrochromic properties such as optical contrast and stability etc., conducting metallopolymers have a potential for use in electrochromic device applications. For example, N-(pyridin-2-ylmethylidene)-2,5-bis(thiophen-2-yl)aniline ligand complex with Fe(II) was prepared to build a electrochromic device with a color change from

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