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Zinc(II) phthalocyanine fused in peripheral positions octa-substituted with alkyl linked carbazole: Synthesis, electropolymerization and its electro-optic and biosensor applications

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ABSTRACT

Zinc(II) phthalocyanine fused in peripheral positions octa-substituted with alkyl linked carbazole has been prepared by cyclomerization reaction of 4,5-bis(6-carbazole-9-yl-hexylsulfanil)phthalonitrile in the presence of anhydro Zn(II) acetate and a strong organic base (DBU). Synthesis steps were optimized and higher efficiency synthesis was achieved. The purpose of combining of carbazole moieties with phthalocyanine on the peripheral position is to enhance some properties such as photo and electrochemical properties because of strong electron-donating properties of carbazole group. This molecule has been electrochemically polymerized and the electrical and optical properties of the resulting conductive polymer have been investigated. Amperometric detection was carried out following oxygen consumption at −0.7 V vs. the Ag reference electrode in phosphate buffer (50 mM, pH 6.0). The novel biosensor showed a linear amperometric response for glucose within a concentration range of 0.05 mM to 1.5 mM (LOD: 0.024 mM). This result shows that modification of the proposed biosensor by copolymerization have provided to give perfect response to different glucose concentrations. Because of its superior spectral and electrochemical properties and contained zinc metal which can act as a mediator during biochemical reactions, this material has been used as a glucose biosensor platform to detection for real samples.

1. Introduction

Phthalocyanines (Pc) as tetrapyrrolic macrocycle have been the important research topics over 75 years. This great interest is because of their exceptional chemical and thermal stability, unique unexpected photophysical, photochemical and electrochemical properties (Bekaroglu, 1996; Dumoulin et al., 2010). These extra-ordinary properties give opportunities for their applications in different areas such as chemical sensors (Valli, 2005; Sizun et al., 2011), nonlinear optics (de la Torre et al., 2004; Germa et al., 1997; Mensing et al., 2013), electrochromic materials (Gümrükçü et al., 2011), liquid crystals (Swarts et al., 2001; Nolte et al., 2006; Özmen et al., 2012) second generation photosensitizers in photodynamic theraphy (Ali and van Lier, 1999), optical limiting devices (Calvete et al., 2004) and solar cell (Hagfeldt et al., 2010; Ragoussi et al., 2013). A disadvantage of phthalocyanines is their limited solubility in common organic solvents. The solubility of phthalocyanines in solvents is improved by making suitable substitutions on periheral or non-peripheral positions of aromatic rings (Brewis et al., 2000; Ogunbayo and Nyokong, 2009). Metal free or metallo phthalo-cyanines containing alkyl thio groups on peripheral or non-peripheral positions have been less studied (Ogunbayo and Nyokong, 2009; Gurek and Bekaroglu, 1994; Karimi and Khodadadi, 2012; Bıyıklıoğlu et al., 2010). In addition to that thioalkyl linked carbazole derivatized phthalocyanines have not been investigated.

Electroactive conducting polymers (ECPs) are a part of a new generation of smart materials that allow the direct delivery of electrical, optical, electrochemical and electromechanical stimulation. Additionally, these properties can be altered and controlled through stimulation (e.g. electricity, light, pH) even after synthesis. These and a number of other unique characteristics of ECPs that make them well-suited for integration with many technological applications such as OLED, fuel cell, biosensor, gas sensor, smart windows, displays etc (Soganci et al., 2016, 2014; Tekbaşoğlu et al., 2017; Akbulut et al., 2015; Guler et al., 2016; Ureta-Zañartu and Gutiérrez, 2016; Acar et al., 2014). Carbazole and its derivatives are one of the most studied conductive polymers. They have a strong interest due to their valuable properties by chemists, biologists and medicinal chemists (Knölker and Reddy, 2002; Zhang et al., 2010). Also, carbazole derivatives draw much attention because of their importance to understand the relation-

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