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Comparative Investigation of Peripheral and Nonperipheral Zinc Phthalocyanine-Based Polycarbazoles in Terms of Optical, Electrical, and Sensing Properties

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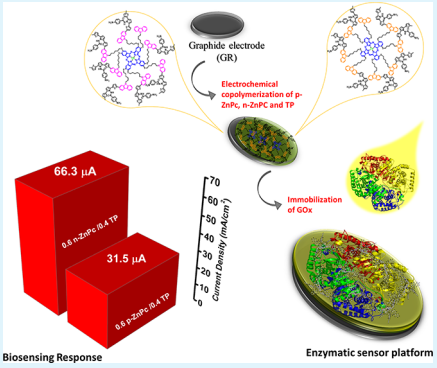
ABSTRACT: In this study, nonperipherally alkyl-linked carbazole conjugated novel zinc(II) phthalocyanine was synthesized by cyclotetramerization reaction of 6-(9*H*-carbazol-9-yl)hexane-1-thiol and 3,6-bis(tosyloxy) phthalonitrile in a one-step reaction. Optical, electrical, and sensing properties of this super structured polycarbazole obtained by electropolymerization are compared with peripherally alkyl-linked polycarbazole-based zinc(II) phthalocyanine. It has been found that the attachment of alkyl-linked carbazoles to the phthalocyanine molecule in either peripheral or nonperipheral positions has a great effect on the optical and electrical properties and sensing ability of the resulting polycarbazole derivatives. P(n-ZnPc) has the highest electrochromic contrast (70.5%) among the derivatives of zinc(II) phthalocyanines in the literature. In addition to these, the sensor platform has been successfully established, and analytical optimizations have been carried out. When the sensors prepared with zinc(II) phthalocyanine are examined, it was specified that the n-ZnPc-*co*-TP/GOx was ranked first in the literature with high sensor response and stability. As a result, by changing of the peripheral and nonperipheral position of phthalocyanines, their physical properties can be tuned to meet the requirements of desired technological application.



KEYWORDS: *polycarbazoles, substitute phthalocyanine, electrochromic, sensors, optical properties*

1. INTRODUCTION

Carbazole is one of the indole-based heterocyclic organic compounds containing two six-membered rings on either side of pyrrole.[1−3] Substituted carbazole derivatives have been widely investigated in different areas due to their extraordinary properties such as the preparation of organic light-emitting devices (OLEDs); pharmacological activities especially anti-tumor, antifungal, and antiviral activities; nonlinear optic materials; dyes for solar cells; dyestuffs; and plastics.[4−9]

Polycarbazole derivatives, one of the most important and well-known conductive polymers, are frequently used in a variety of applications such as light-emitting diodes,[10] electrochromic devices,[11−14] field effect transistors,[15] and sensors.[16] However, it is one of the most important research topics to obtain polycarbazole films with desired optical, electrical, and mechanical properties for practical applications due to their poor processing capabilities. For this purpose, researchers are intensively researching the synthesis of highly cross-linked polycarbazole derivatives formed from super-structured monomers to further improve their optical and electrical properties as well as other physicochemical properties. These superstructural polycarbazole derivatives that obtained electropolymerization of two or more carbazole-derivative-containing electroactive monomers have been found to be superior in optical and mechanical properties.[17−19]

Peripheral or nonperipherally functionalized phthalocyanines have been investigated in a variety of areas because of their numerous properties such as chemical and thermal stability that possess unique physical and chemical properties.[20−22] These kinds of compounds possess intense blue-green color due to the electronic delocalization of their 18-π electrons. These properties caused them to be initially utilized in various fields such as photosensitizers in photodynamic therapy,[23−26] chemical and biosensors,[27−30] catalysts,[31] liquid crystals,[32,33] and sensitizers in photodynamic therapy.[34−37]

Recently, we have focused our research on the synthesis, characterization, electropolymerization, and electro-optic and biosensor application of peripherally octa-substituted carbazole zinc phthalocyanine.[20] In this study, first the zinc(II) phthalocyanines containing octa-substituted with hexyl-linked carbazole in the nonperipheral positions and carbazole-substituted disulfur compounds were synthesized and characterized. It is well-known that some properties of phthalocyanines such as NIR shifting of the Q-band, decrease in aggregation, high triplet quantum yield, physicochemical properties, and solubility depend on the position or types of

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