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Processable Amide Substituted 2,5-Bis(2-thienyl)pyrrole Based Conducting Polymer and Its Fluorescent and Electrochemical Properties

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While majority of conductive polymers are insoluble and infusible, theirs solution processable derivatives are more desirable for preparing large size flat panel display and solid state applications because they are compatible with low cost, large area roll-to-roll manufacturing process. For this purpose, a solution-processable fluorescent conjugated polymer (PDOB), consisting of electron rich N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(dodecyloxy) benzamide (DOB) and its copolymer with 3,4-ethylenedioxythiophene P(DOB-co-EDOT) were synthesized by electrochemical polymerization technique. Electrochemical and optical properties of P(DOB) and P(DOB-co-EDOT) were investigated cyclic voltammetry, UV-vis absorption and fluorescence emission measurements, respectively. The optical bandgap values of P(DOB) and P(DOB-co-EDOT) determined by spectroelectrochemical data were 1.92 eV and 1.62 eV, respectively. P(DOB) and P(DOB-co-EDOT) were exhibited favorable redox activity and electrochromic performance. Further kinetic studies demonstrated that the P(DOB) and P(DOB-co-EDOT) have high optical contrast ratios (60–25%), favorable coloration efficiencies (139.1 $cm^2.C^{-1}$ and 80.6 $cm^2.C^{-1}$), fast response time (1.5 s; 1.0 s), high stability. When compared to soluble poly (2,5-dithienyl pyrrole) derivatives in literature, P(DOB) have lowest oxidation potential and bandgap and have highest optical contrast. As a result, these materials provide more plentiful electrochromic colors which useful for display application and hold promise for other solution-processable applications.

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Electroactive polymers have received a great deal of attention in the last decade due to their excellent optical, electrical and electronic properties.[1–6] Due to these excellent properties, conjugated polymers have potential applications in the fields of sensors, electrochromic device, smart windows and camouflage materials.[7–11] However, in the literature despite the many conducting polymers available, the biggest disadvantage of these polymers is solubility and processability. Thiophene and pyrrole are widely used as a base material for synthesizing conducting polymers, but their polymers have a solubility problem. Hence application of this type of conducting polymer is very limited due to the solubility and processability. In order to alleviate the problem, attachment of flexible pendent groups onto the conjugated backbone is necessary and in the new sites one can incorporate chemically.[12–14] The addition of side chains not only allows an easier processing of some electroactive polymers but can also modulate the electronic properties of the conjugated main chain.[15–17] For instance, it has been reported that the introduction of strong electron-donating alkoxy side chains decreases the oxidation potential of the resulting polymers, giving a better stability and solubility for the conducting state.[18–25] Alkoxy groups were introduced on the conducting polymer, in order to not only provide donor character to the polymer but also improve the polymer processability.

Besides all these, Poly(2,5-dithienylpyrrole) derivatives (PSNS) are one of the most encouraging conducting polymers due to their low oxidation potential, and easy electrochemical polymerization. A number of 2,5-bis(2-thienyl)-1*H*-(pyrrole) (SNS) derivatives have been synthesized with substituted alkoxy derivatives,[6] phenyl derivatives,[26] aryl derivatives,[27] amide derivatives.[28,29] These polymers are reported to have satisfactory electrochromic capacity. A novel electrochromic materials will be brought to literature combining the capabilities of Poly(2,5-dithienylpyrrole) and alkoxy group for getting better electrochromic properties and soluble polymer.

A number of P(2,5-bis(2-thienyl)-1*H*-(pyrrole)) derivatives have been synthesized with different substituted groups and theirs electrochromic properties have been investigated.[6,27,28] Among them, amide substituted derivatives have superior properties such as the film quality and electrochromic properties.[28,29] Theoretical analysis has shown that presence of amide bond on thienyl pyrrole group is forced to structural planarity. Rotational order around interannular single bonds contributes to the delocalization of p-electrons along the conjugated backbone and hence to decrease bandgap. Having more planar structure, amide substitute SNS compound has lower bandgap and has better optical properties compared with other SNS derivatives.[30]

Another approach to enhance electrochromic properties of SNS derivatives is copolymerization. Copolymerization is an easy, facile method to combine the electrochromic properties of the comonomers. Copolymers based on poly(3,4-ethylenedioxythiophene) (PEDOT) have a bandgap lower than polythiophene and alkyl-substituted polythiophenes due to the presence of two electron donating oxygen atoms adjacent to the thiophene unit. Doped PEDOT is almost transparent in the visible region and the neutral polymer is dark blue.[31]

In this study, to achieve soluble, fluorescent, electrochromic polythienylpyrroles, we synthesized a novel monomer in which amid substituted 2,5-dithienylpyrrole moiety was incorporated alkoxy spacer group. In this way, electrochromic properties and processability of the polymer have been improved.

The monomer (N-(2,5-di(thiophen-2-yl) -1H- pyrrol-1-yl)-4-(dodecyloxy) benzamide, (DOB) was subjected to electrochemical polymerization. Electrochromic properties of P(DOB) were investigated via spectroelectrochemistry, kinetic and colorimetry measurements. Also electrochromic properties of the copolymer with EDOT were investigated in comparison with the homopolymer. The novel electrochromic material will be brought to literature combining the capabilities of amide substituted poly(2,5-dithienylpyrrole) and alkoxy group for getting better electrochromic properties and soluble polymer.

Experimental

Equipment.—Ivium Compactstat potentiostat/galvanostat was used for electrochemical synthesis and cyclic voltammetry experiments. An Agilent 8453 UV-vis spectrophotometer was used to conduct the spectroelectrochemical studies of the conducting polymers. All fluorescence experiments were carried out using a Carry Eclipse spectrophotometer.

Synthesis of DOB.—Firstly, for the synthesis of N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)-4-(dodecyloxy)benzamide, 4-(dodecyloxy) benzohydrazide was sythesized as in literature.[32] For

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