



Synthesis and Computational Bandgap Engineering of New 3,4-Alkylenedioxyppyrrrole (ADOP) Derivatives and Investigation of Their Electrochromic Properties

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This research highlights the degree of conformity between our electrochemical and theoretical studies conducted on the newly designed electropolymerizable monomers (BuDOP, BenDOP and BenzoDOP) possessing 3,4-alkylenedioxyppyrrrole (ADOP) backbone (BuDOP). We tried to select logical enhancing of the structures in a stepwise in order to discuss the effects of benzene (BenDOP) and benzodioxane (BenzoDOP) like aromatic subunits to the electrochromic properties of the target monomers. Following to the completion of the synthetic steps, appropriate structural analyses of monomers were performed (FT-IR, GC-MS, ¹H-NMR, ¹³C-NMR). Subsequently, their corresponding polymers were prepared by electrochemical oxidation and characterized. Afterwards, our consecutive efforts have been contributed to theoretical studies in order to obtain information about their structural properties. To this aim, geometry optimizations were carried out using hybrid density functional theory (DFT/B3LYP/LANL2DZ) and HOMO, LUMO energy levels, HOMO-LUMO energy gaps (ΔE), electron affinity (EA) as well as ionization potential (IP) values were calculated. Theoretical data were then used for identifying the structure-electronic properties relationship and we aimed to determine the electrochromic properties of the studied monomers. Our results from the B3LYP/LANL2DZ calculations indicated that P(BenDOP) has the lowest HOMO-LUMO gap and we predicted that theoretical data were in good agreement with the experimental studies. © 2016 The Electrochemical Society. [DOI: 10.1149/2.0131610jes] All rights reserved.

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The past forty years have seen increasingly rapid advances in the field of conducting polymers (CPs) and these advanced materials still continue to attract ever-increasing attention.¹⁻³ In a general point of view, CPs are accepted as pivotal components which open new frontiers in polymeric materials and electronics. Furthermore; optical, mechanical and electrical properties of CPs could be modified under the guidance of rational chemical modification processes in order to bring them desired attributions.^{4,5} So they have found a wide range of technological applications in various fields of chemical and biosensors,^{6,7} field-effect transistors,^{8,9} electrochromic display devices,^{10,11} supercapacitors,¹² actuators¹³⁻¹⁵ and separation membranes¹⁶⁻¹⁸ as a feasible alternative to metallic or inorganic semiconductor counterparts. These conjugated polymers combine the electrical properties of metals with characteristics of organic polymers that can be tailor-made as per requirements of the applications through modifications of the polymer structure and varying the functional groups in the organic moiety. Thus, the synthesis and characterization of CPs has become a subject of great interest both academic and industrial researchers in diverse domain of science and technology.¹⁹⁻²¹

These conducting organic polymers have been the focus of numerous theoretical and experimental studies since their discovery in 1977.^{22,23} One of the goals of the field of CPs is the molecular designing of polymers with tailor-made conduction properties. The main reason is that there is an incomplete understanding of the relationship between the chemical structure of a polymer and its electronic properties.

On the other hand, over the last two decades, the quantum theory of polymers and design of efficient organic CPs have witnessed a growing interest related to their appealing properties.^{24,25} Quantum chemistry is expected to play a major role in the development of novel materials with specific and especially predicted electronic and optical properties (structure, bonding, reactivity, etc.).^{26,27} In this context, because of their structural simplicity, linear polyenes and polyacetylene have so far been the focus of most of experimental and theoretical studies.^{28,29} The detailed understanding of the phenomena occurring on the conjugated chains upon photoexcitation requires the description of the electronic structure of the lowest singlet excited states. This has helped in forgoing a fundamental understanding of the electronic and optical characteristics of the conjugated materials and in guid-

ing the experimental efforts toward novel compounds with enhanced characteristics.^{30,31}

3,4-ethylenedioxythiophene (EDOT), 3,4-alkylenedioxyppyrrrole (ADOP) and their improved derivatives are certainly the most attractive organic conducting polymers due to both their good conductivity and stability properties.³²⁻³⁵ These compounds are also known as competitors to other existing low band-gap polymers. A large amount of research has been dedicated to the preparation and investigation of properties of EDOT including donor-acceptor-donor type oligomers³⁶⁻³⁹ but less has been done about clarifying electronic effects of aromatic ring systems directly substituted on ADOP. On that account, the main purpose of this research is centered around the question of how to explain the effects of benzene and benzodioxane subunits to the electrochromic properties of the conducting polymers of ADOP derivatives. For this reason, as a first step, we have synthesized three inventive 3,4-alkylenedioxyppyrrrole derivatives; BuDOP, BenDOP and BenzoDOP (Fig. 1). The characterization of the synthesized compounds was carried out by FT-IR, GC-MS, ¹H-NMR, ¹³C-NMR techniques and elemental analysis. Electrochemical polymerizations of the monomers were performed potentiostatically by using acetonitrile (ACN) as solvent and lithium perchlorate (LiClO₄) as supporting electrolyte. The polymerizations of the new monomers were performed successfully and effects of the benzene and benzodioxane subunits to the electrical and electrochromic properties of polymers were explained with both experimental and theoretical studies.

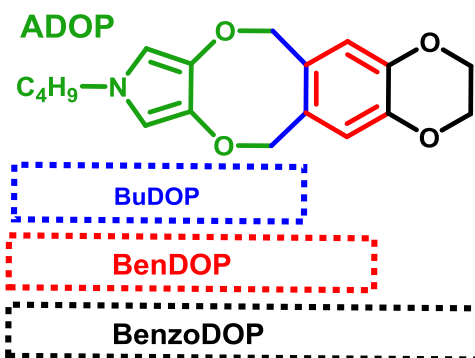


Figure 1. Structure and nomenclature of BuDOP, BenDOP and BenzoDOP monomers.

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