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Alkyl chain engineering in the hybrid bithiophene-3,4-ethylenedioxythiophene: Synthesis, electronic properties, and electropolymerization

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ABSTRACT

Most recently, bithiophene unit has became a good choice as monomer unit for alternating π-conjugated copolymers for optoelectronic materials, because it gives good charge mobility to the corresponding polymers and serves as an appropriate donor unit in donor–acceptor polymers with narrow energy band gap. Herein, in order to get a comprehensively understanding of the structure–property relationship of the bithiophene based comonomers and copolymers, five hybrid oligomers which employed alkyl (C_nH_{2n+1},n = 0, 1, 6, 8, 12) functionalized bithiophene unit as the core and 3,4-ethylenedioxythiophene unit as the terminals were synthesized. Structure–property relationships of these oligomers and the corresponding polymers were analyzed by optical, electrochemical techniques, theoretical calculations, and spectroelectrochemistry. It was found that as the pendant alkyl length increased from the H to the hexyl, the electronic spectra of these oligomers were blue-shifted while the fluorescence quantum yield reduced and the oxidation peaks were positively shifted. When the number of carbon atoms in the linear alkyl chain was higher than six, these values of them became almost stable. Density functional theory calculations confirmed these trends by comparing with the dihedral angles of each oligomer because of the steric effect caused by alkyl substitution. And the steric hindrance of the alkyl substitution still remains in the polymer films although the effects are very slight. These results clearly indicated that by the simple alky chain engineering, the optoelectronic and electrochemical properties of the oligo-/polythiophenes would be tuned due to the steric hindrance of the alkyl substituent. The hybrid polymers with band gap range from 1.75 to 1.83 eV and electrochromic nature with color changing from violet and purplish in the reduced form to transparent sky blue/green upon oxidation. Combining with good stability and favorable electrochemical activity, these materials hold promise for electrochromic devices and display applications.

1. Introduction

Oligothiophenes (OT) and polythiophenes (PT), one of the most widely investigated class of functional π-conjugated systems, have attracted more and more attentions for their applications in low-cost, large-area, and flexible electronic and photonic devices such as thin-film organic field effect transistors (OFETs) [1], organic electroluminescent diodes (OLEDs) [2], and organic photovoltaic devices (OPVs) [3]. At the same time, the development of these various fields creates a continuous demand for the molecular design and synthesis of new monomers and careful modifications on the back bone to control the energy band gap (HOMO (the highest occupied molecular orbital)–LUMO (the lowest unoccupied molecular orbital)), and thus with the goal to control and tune their crucial optical and electrical properties such as ionization potential, electron affinity, absorption and emission properties [4]. This situation, in turn, generates a need for new synthetic routes, new methods of functionalization and new building blocks [5].

Up to now, the polymers based on thiophene units, such as thieno[3,2-*b*]thiophene [6], bithiophene (BT) [6–8], thiophene [7], benzo[1,2-*b*:4,5-*b*′]dithiophene [9], *etc*., have been developed and fabricated optoelectronic devices. Among them, the simple BT unit has gained the researchers' increasing attention for the facile construction of the structure and the outstanding performances of devices based on its copolymers. Some polymers based on BT unit are among the best organic semiconductors [10–15]. There are

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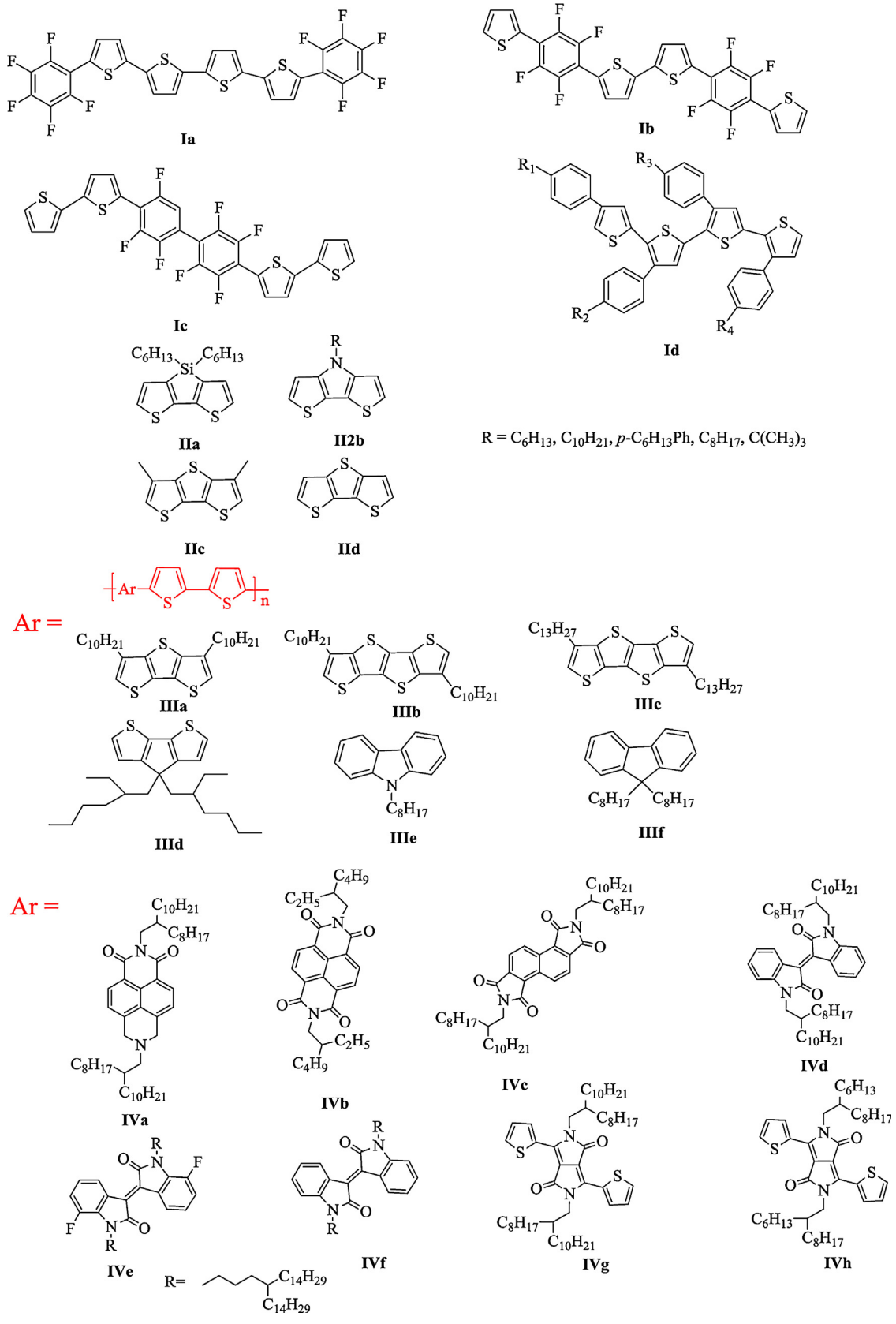
several virtues for BT unit (Scheme 1): (1) it is a key intermediate of a variety of oligothiophene derivatives, which are widely applied as advanced organic materials (Ia–Id) [16,17]; (2) the bromination of the aromatic core is easy to implement, enabling the modification of aromatic core for diverse semiconducting materials (IIa–IId) [18–20]; (3) the BT unit is a good choice as monomer unit for alternating π-conjugated copolymers for optoelectronic materials because it would give good charge mobility to the corresponding



Scheme 1. Some representative structures of bithiophene-based conjugated systems for optoelectronic applications.