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Review

Dithieno[3,2-*b*:2′,3′-*d*]pyrrole-based materials: Synthesis and application to organic electronics

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ABSTRACT

The application of dithieno[3,2-*b*:2′,3′-*d*]pyrroles (DTPs) in conjugated organic polymers has resulted in a variety of materials with reduced and low band gaps that exhibit high carrier mobilities, as well as enhanced solution and solid-state fluorescence. While DTP-based materials date back to the early 1990s, significant advances in the preparation and scope of these materials have been reported over the past decade. In this current report, we provide the first full review of DTP-based materials, highlighting in particular the recent advances made in the synthesis of both monomeric DTPs and their resulting materials, as well as the current progress of their application to various devices, including FETs, OPVs, OLEDs, and electrochromics.

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1. Introduction

The field of conjugated polymers began in the 1950s as synthetic models of high conductivity carbon blacks [1]. While the majority of the initial materials studied were essentially insulators, reports of conducting organic polymers began in the 1960s, with worldwide interest in such materials by the late 1970s as a result of the now well-known reports by MacDiarmid, Heeger, and Shirakawa of metallic-looking polyacetylene films [1–4]. Since this initial work, conjugated polymers have continued to attract significant academic and technological interest due to their combination of the electronic and optical properties of inorganic semiconductors with the attractive properties typically associated with organic plastics, including mechanical flexibility and low costs for production [5–9]. This unique combination of properties has resulted in rapid growth of the field of organic electronics with strong emphasis being focused on technological applications such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), electrochromics, and sensory devices [5–15].

One of the primary characteristics of this class of materials is the energetic difference between the filled valence band and the empty conduction band, commonly referred to as the band gap (E_g) [16–20]. As the band gap corresponds to the HOMO–LUMO gap of the bulk solid-state material, it determines material properties such as the lowest energy absorbance or the energy of any potential emission. In addition, a smaller separation between the valance and conduction bands can result in enhanced thermal population of the conduction band, thus increasing the number of intrinsic charge carriers. Lastly, the lower potential of oxidation often associated with lower band gaps can contribute to stabilization of the doped or oxidized state of the material [16]. Thus it is of no surprise that significant effort has been applied to developing methods for controlling the E_g of conjugated materials, with the goal of producing technologically useful polymers that provide low or reduced band gaps [16–20].

Throughout the conjugated polymer literature, there are a number of adjectives used to modify the term band gap when describing various ranges of E_g values. The most common of these is *low band gap*, a term which is unfortunately used somewhat carelessly in the literature to refer to a wide range of E_g values. In 1998, Pomerantz proposed a working definition for low band gap conjugated materials as those with an E_g value below 1.5 eV [17,18,20]. This energetic cutoff has logic as none of the commonly studied parent conjugated polymers are considered low band gap materials, and the lowest E_g value of this family is that of polyacetylene at 1.5 eV [17,19]. Of course, polythiophene has become one of the most commonly studied conjugated polymers, particularly as absorbing materials in organic solar cells. The unfunctionalized parent polythiophene has an E_g of ~2.0 eV [16–20] and thus it is common for some to refer to thiophene-based systems with an E_g value below 2.0 eV as low band gap materials. In fact, some authors have even gone so far as to redefine the definition of low band gap as $E_g < 2.0$ eV [21]. However, as this use includes nearly all thiophene-based materials, this tends to make the description somewhat meaningless and leads to confusion in the literature. As a solution, we have continued to support Pomerantz's original definition for low band gap materials, while encouraging the use of the description *reduced band gap* for those materials between 1.5 and 2.0 eV [20]. It is these terms and definitions that will be used in this current review.

A successful strategy for tuning polymer properties such as the E_g value has been the annulation of aromatic rings to the monomeric repeat units. One such approach has been to insert a bridging unit between the adjacent thiophene rings of 2,2′-bithiophene in attempts to improve the material properties. One of the most common examples of this is the fused species 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT, **1**) initially reported by Zotti and coworkers (Fig. 1) [22,23]. The added structural rigidity eliminates rotation around the interannular bond helping to planarize the material, thus allowing more efficient electron delocalization and a reduction in band gap. In addition, introduction of side chains at the bridging unit allows the functionalized molecule to remain symmetrical, thus reducing possible problems with regioirregularity in the resulting polymer [19,24]. In addition to carbon-bridged systems, heteroatom-bridged systems have also become quite popular with one of the earliest systems investigated being dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT, **2**), reported by Taliani and coworkers in the mid-1980s [25,26]. While DTT was limited in terms of possible sites for functionalization, its nitrogen analog dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP, **3**)

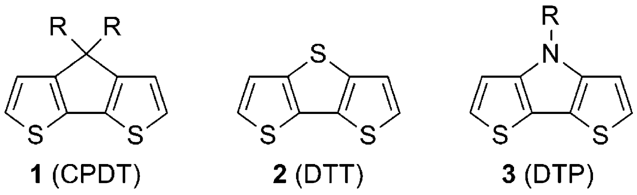

Fig. 1. Fused-ring bithiophenes.