



Synthesis and characterization of thiophene and fluorene based donor–acceptor conjugated polymer containing 1,3,4-oxadiazole units for light-emitting diodes

M.G. Murali^a, P. Naveen^a, D. Udayakumar^{a,*}, Vandana Yadav^b, Ritu Srivastava^b

^a Department of Chemistry, National Institute of Technology Karnataka, Surathkal, PO Srinivasnagar 575 025, India

^b Organic Light-emitting Diode Lab, Polymeric and Soft Material Division, National Physical Laboratory, New Delhi 110012, India

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ABSTRACT

A new donor–acceptor (D–A) conjugated polymer (**PDTOF**) containing 3,4-didodecyloxythiophene, fluorene and 1,3,4-oxadiazole units is synthesized by using Wittig reaction methodology. The synthesized polymer is characterized by ¹H NMR, FTIR, GPC, and elemental analysis. The optical energy band gap of the polymer is found to be 2.42 eV as calculated from the onset absorption edge. The electrochemical studies of **PDTOF** reveal that, the HOMO and LUMO energy levels of the polymer are –5.45 eV and –3.58 eV, respectively. The polymer is thermally stable up to 320 °C. Polymer light-emitting diode devices are fabricated with a configuration of ITO/PEDOT: PSS/PDTOF/Al using **PDTOF** as the emissive layer. The electroluminescence (EL) spectrum of the device showed green emission with CIE coordinate values (0.34, 0.47). By current density–voltage characteristics, threshold voltage of the PLED device is found to be 6.5 V.

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In the last two decades, the design and synthesis of electroluminescent conjugated polymers as the active materials in the field of polymer light-emitting diodes (PLEDs) have received much attention because these materials are potential candidates in flat panel display and lighting applications.^{1,2} Extensive research has also been performed to develop highly efficient light-emitting polymers with tunable emission, long lifetimes, and color purity.³ However the focus on the area of conjugated polymers has drawn great interest mainly because of easy processing, low operating voltages, faster response times, and facile color tuning over the full visible range, which makes them suitable for large-area flat panel displays.⁴ Due to this reason, the design and synthesis of new conjugated polymers of varied optoelectronic properties play a vital role in the area of display technology.⁵ In this regard, a wide range of conjugated polymers such as poly(*p*-phenylenevinylene) (PPV),⁶ poly(thiophene) (PT),⁷ poly(pyrrole),^{8–10} poly(*p*-phenylene) (PPP),¹¹ poly(fluorene) (PF),¹² and their derivatives have been extensively investigated as emissive materials in LEDs. It is known that to obtain highly efficient light emitting devices, the balance in the injection and transportation of both holes and electrons into the polymer emissive layer is necessary. Several approaches have been used in order to achieve high electroluminescence efficiency in PLEDs.^{13–15} Among them, donor–acceptor (DA) type polymers, introduced by Havinga et al.¹⁶ in the macromolecular systems via alternating electron rich and electron deficient substituents along

a polymer backbone are the well known approach to obtain efficient devices.¹⁷ In this system, the electron or hole affinity can be enhanced simultaneously or controlled independently.^{18,19} In the categories of conjugated polymers, polythiophene, and polyfluorene and their derivatives occupy a significant position. In particular, polythiophenes are more attractive candidates for PLEDs because of their good thermal stability both in the neutral and doped states and their wide electronic and optical tenability.^{20–22} Also polyfluorene derivatives are attractive active materials for light-emitting diodes because of their thermal and chemical stability and their exceptionally high solution and solid-state fluorescence quantum yields.^{12,23} Moreover, the facile substitution at the 9-position of the fluorene monomer allows the control of polymer properties such as solubility, processability, and morphology. Since 3,4-dialkoxythiophene and fluorene derivatives are both electron rich and hole transporting, it is necessary to introduce electron withdrawing units to the main chains or side chains to attain large electron affinities. The strong electron withdrawing 1,3,4-oxadiazole unit is the widely used electron injection and hole blocking material because of its high electron affinity, good thermal, and chemical stability.^{24,25}

Herein we report the synthesis, characterization, and electroluminescent properties of a new donor–acceptor (D–A) type conjugated polymer **PDTOF**. The polymer structure consists of 3,4-didodecyloxythiophene and fluorene moieties as electron donor units and 1,3,4-oxadiazole moiety as the electron acceptor unit along with vinylene linkages. The thermal, optical, and electrochemical properties of the polymer are studied. Polymer light-emitting diodes are fabricated using **PDTOF** as emissive material

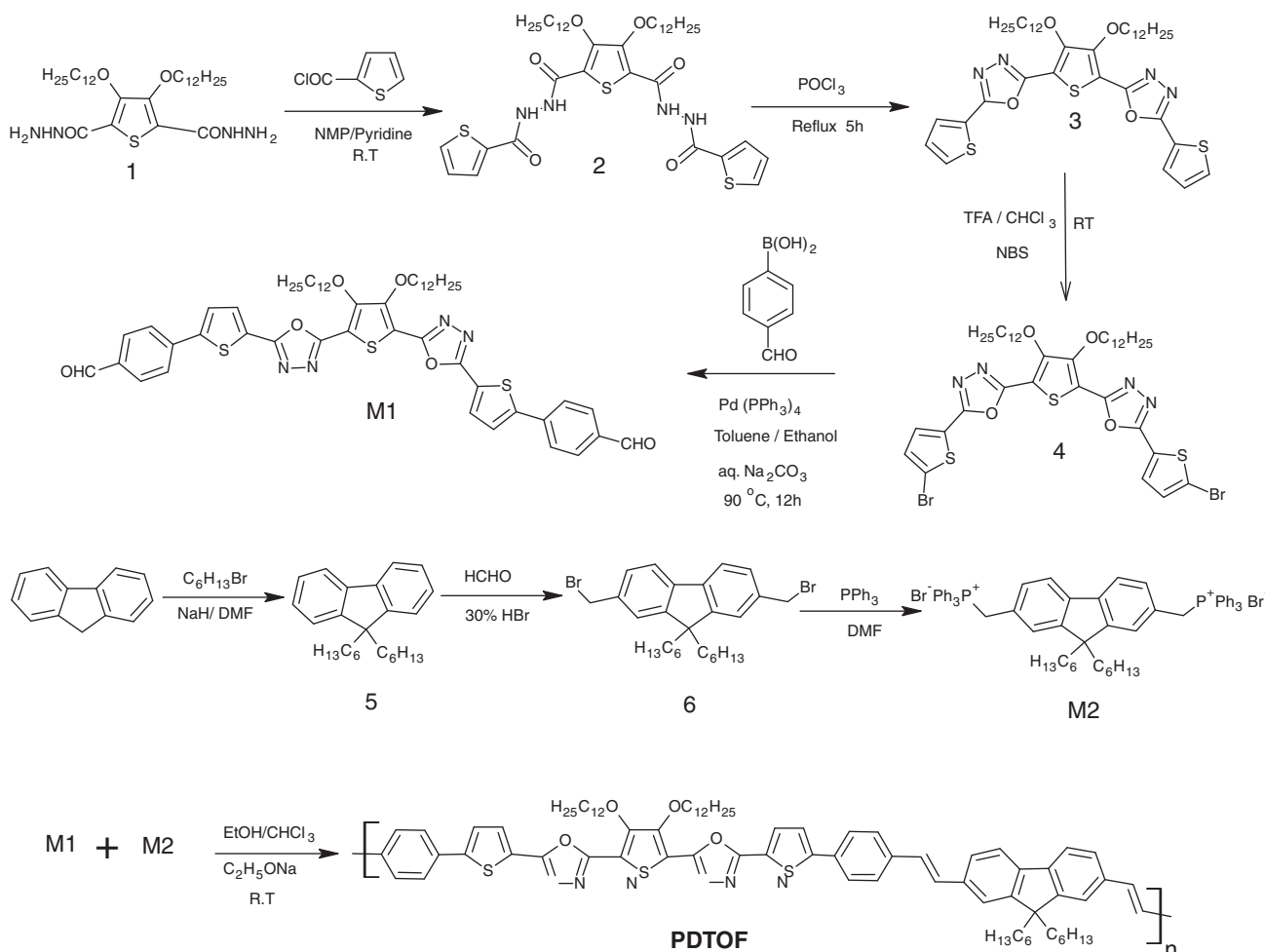
* Corresponding author. Fax: +91 824 2474033.

E-mail address: udayaravi80@gmail.com (D. Udayakumar).

with a configuration of ITO/PEDOT: PSS/PDFOB/Al. The EL properties of **PDTOF** reveal that the polymer is a green light-emitting material for efficient light-emitting diodes.

The synthetic route for preparing the monomers and the polymer (**PDTOF**) are outlined in Scheme 1.²⁶ The detailed synthetic procedures of the intermediate compounds and their spectral data are given in the Supplementary data. The final conjugated polymer (**PDTOF**) containing 3,4-didodecyloxythiophene, fluorene, and 1,3,4-oxadiazole units is synthesized by using Wittig reaction method. The chemical structures of all the intermediates and the polymer were confirmed by NMR spectroscopy, FTIR spectroscopy, and elemental analysis. The compound 3,4-didodecyloxythiophene-2,5-carbonyldihydrazide (**1**) was prepared according to the previously reported method.²⁷ To prepare 3,4-bis(dodecyloxy)-*N*'2,*N*'5-di(thiophene-2-carbonyl)thiophene-2,5-dicarbohydrazide (**2**), the dihydrazide (**1**) was condensed with thiophene-2-carbonyl chloride in *N*-methylpyrrolidinone (NMP) in the presence of pyridine at room temperature. Conversion of dihydrazide to dicarbohydrazide was confirmed by ¹H NMR and FTIR studies. The ¹H NMR spectrum of **2** showed two >NH protons as singlet at δ 10 and 9.39. The three doublet peaks in the range of 7.69–7.68, 7.54–7.52, and 7.10–7.08 ppm are assigned to thiophene ring protons at positions 2, 4 and 3 respectively. The triplet peak at 4.29 ppm is due to the –OCH₂– protons of the alkoxy chains of the thiophene ring and the multiple peaks in the range 1.96–0.87 ppm are due to the –(CH₂)₁₀–CH₃ protons of the alkoxy chains. The FTIR spectrum of **2** showed sharp peaks at 3380 and

1677 cm⁻¹ due to >NH and >C=O groups, respectively. Cyclization of compound (**2**) to bisoxadiazole (**3**) was achieved by using POCl₃ and the completion of the reaction was confirmed by using ¹H NMR and FTIR spectral studies. In the ¹H NMR spectrum, the disappearance of two singlet peaks due to >NH protons confirms the cyclization. Further, the FTIR spectrum of (**3**) showed no absorption peaks corresponding to >NH and >C=O groups while a new peak appeared at 1568 cm⁻¹ due to –C=N– stretching, indicating the formation of the oxadiazole ring. The synthesis of monomer **M1** from compound (**3**) requires two additional steps (Scheme 1). The first step consists of bromination of compound (**3**). The reaction of Br₂ in chloroform with (**3**) did not give the required brominated product (**4**). We have tried the method of *N*-bromosuccinimide (NBS) using different solvents like DMF, CCl₄, and benzene which were also unsuccessful. The failure of these methods could be due to the deactivation of thiophene rings in **3** toward bromination by the presence of electron deficient 1,3,4-oxadiazole units attached to the thiophene rings. However bromination reaction was successful when compound **3** is treated with NBS in trifluoroacetic acid/chloroform (3:1) solvent mixture, yielding the dibromo compound **4** in reasonable yield. The structure of compound **4** was confirmed by ¹H NMR spectrum, which showed the disappearance of double doublet peak of thiophene ring proton at position 2 and conversion of all double doublets into doublet peaks. The monomer **M1** was obtained by coupling between dibromo compound **4** and 4-formylphenylboronic acid through Suzuki coupling reaction. ¹H NMR spectrum of **M1** showed two (–CHO) protons as singlet at δ



Scheme 1. Synthetic route of monomers and the polymer.

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