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Studies on polythiophenes containing fused polyaromatic rings as side chains

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ABSTRACT

The influence of fused polyaromatic and polyphenylene side chains on polythiophene absorption and photoluminescence was studied in detail. The above polymers were used as emissive layer in Light emitting diodes (LEDs) and the influence of structure and packing on current density, color and intensity of emission was studied in detail. The current density of the LEDs with poly 3-[4-(10-Phenyl-anthracen-9-yl)-phenyl]-thiophene (poly DPAT) and light emission intensity are high and there is a band narrowing of peaks at high voltages along with very high intensity of electroluminescence. The above properties are due to the presence of diphenyl anthracenyl group which produces molecular overcrowding and high spatial distribution off the π-Conjugated backbone.

1. Introduction

Since the discovery in 1990, that conducting polymers can be used as emissive layer in light emitting diodes, (LEDs) extensive work has been done in this new field [1–3]. π-Conjugated semiconducting polymers are molecular analogs of inorganic semiconductors, which are having the ability to form junctions with well-defined electronic properties. These materials are the prominent materials used for the fabrication of various organic electronic devices [4,5] such as light emitting diodes [6,7] and photovoltaic devices [8,9]. Among various conjugated polymers, polythiophenes have received considerable attention due to their excellent electrical characteristics [10–12]. Moreover polythiophene family were well known for their environmental stability, melt and solution processability and versatile synthesis that allows us to have a significant control over optical and electronic properties [13]. The dual goals of extending the length of π-Conjugation and improving the charge transport properties were achieved by employing thiophene derivatives.

The drawback with the organic materials for optoelectronics is that the number of electrons in the junction of a diode is less than the number of holes. Due to this the efficiency of the device is less. The present materials technology with conjugated systems for display devices uses multi layer technology. Multi layer LEDs use functionalized low molecular weight materials for enhancing the number of electrons and blocking the number of holes, so that more number of recombination of holes and electrons can take place at the emissive layer. Even though, the multi layer polymer LEDs has comparable efficiency to that of conventionally used inorganic semiconductors, the thickness of the device is increased. Because of this, the applied voltage is also high in many cases. Moreover the low molecular weight materials, which are used for Electron Transport (to enhance the number of electrons) and Hole Blocking (to filter/reduce the number of holes in the junction of the semiconductor layer and increase the probability of electron–hole recombination within the emissive layer) (ETHB) application, tend to crystallize over time, leading to the failure of the devices. It will be beneficial, if a thin film forming material combines the functions of both electron transporting and hole blocking apart from acting as emissive layer. The material, which can emit all the three

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base colors with high efficiency from single layer LED, is also useful for producing white light.

A great number of different polymers have been synthesized and extensive efforts have been made to obtain high performance devices from these polymeric materials, as they combine the Processability and outstanding mechanical properties of polymer with light emission [14–18]. The EL properties of the functionalized polythiophenes are also studied [19–21], although the quantum efficiency is low due to quenching/intersystem crossing, which can be improved by suitably functionalizing thiophene. In this process, thiophenes functionalized with bulky substituent require a detailed knowledge of both the electronic and steric factors. In the present study, properties of polythiophenes substituted with poly phenylene and fused aromatic rings were studied in order to understand the influence of side chain contribution of π-electrons towards the enhancement of optical properties and electroluminescence. In the present study, optical properties of the polymers of 3,4-Diphenyl-thiophene (DPT), 3-Biphenyl-4-yl-thiophene (BPT), 3-[1,1′,4′,1″]Terphenyl-4-yl-thiophene (TPT), 3-(10-Phenyl-anthracen-9-yl)-thiophene (PAT), 3-[4-(10-Phenyl-anthracen-9-yl)-phenyl]-thiophene (DPAT) (Fig. 1) were studied.

Anthracene derivatives are useful building blocks with oxidation stability and a planar extended π-conjugation system [22]. Incorporation of the anthracene unit into polymer backbone has been attempted in order to decrease the electronic gap of the polymer [23–25]. This is due to the fact that incorporation of the anthracene unit into the polymer main chain will minimize the energy difference between the aromatic and quinoid structure. Photophysics of polymers containing pendent anthracene groups are also studied [26–29]. The reason of selection of anthracene being that the fluorescence quantum yields is close to unity [30,31]. In the case of di phenyl anthracene, because of the extensive steric hindrance, it does not exhibit singlet excimer formation, photo-dimerisation or concentration quenching.

2. Experimental

2.1. General method of preparation of 3-(aryl) thiophenes

Grignard compound of 3-bromothiophene was prepared by reacting it with magnesium using 1,2-dibromo ethane as entrainer in dry diethyl ether medium and it was coupled with aromatic halide in the presence of Nickel catalyst. The resulting materials were purified by column chromatography (Scheme 1). In the case of TPT and DPAT, synthesis of mono bromo precursors (4″-Bromo-[1,1′,4′,1″] terphenyl and 9-(4-bromophenyl)-10-phenyl-anthracene) was not possible by the conventional methods. Therefore a new procedure was used for the selective mono bromination using thallium acetate as catalyst (For detailed experimental procedure and NMR data for all monomers refer Support information 1). The preparation of 3,4-diphenyl thiophene monomer is presented in Scheme 1.

The polymers were prepared by using iron (III) chloride as oxidizing agent. The excess iron chloride was removed by soxhleting and subsequently purified by stirring with hydrazine hydrate (for detailed polymerization procedure, NMR data and molecular weight of polymers refer Support information 2).

To support the experimental results, theoretical prediction of properties of the polymers were performed using the Gaussian 03 (revision E 0.1) suite of programs [32]. The geometries of the molecules were optimized and the energy calculations were carried out by Density-Functional Theory (DFT) B3LYP/3-21G* basis set. The oligomeric approach is followed to extrapolate the values obtained for the monomer, dimer, trimer and tetramer, which are plotted against the reciprocal of the number of repeating unit to obtain the band gap of the polymers. The absorption edges of the polymers were calculated by using ZINDO.

The polymer thin films for absorption and fluorescence spectroscopic studies (over quartz) were prepared by spin coating (at 2000 rpm using Ducom photo resist spinner for 60 s) of the chloroform solution of the polymers (concentration −1 mg/mL). The thickness of the polymer thin films were measured using interference method using UV–visible absorption spectroscopy using quartz plates of 6.25 cm^2. The fringes were obtained by removing a small area (~1 cm^2) of thin film using chloroform from the(6.25 cm^2) coated quartz plate and sandwiching the same plate with other optically clean uncoated quartz plate (6.25 cm^2). The plates were appropriately placed as a sandwich in the UV–Visible spectrophotometer and the fringes were recorded. The number of fringes between any two fixed points of the resultant spectra is inversely proportional to the thickness of the space between quartz plates (polymer film thickness). The thickness of the polymer thin films was ~100 nm for reasonable comparison.

The UV–Visible spectra of the compounds were recorded using CARY 50 Bio UV visible spectrophotometer while CARY eclipse spectro fluorometer containing solid sample holder was used to record the fluorescence. For the thin film studies, spin coated thin films, as mentioned above were used. For the solution studies, the concentrations of the polymers were 1.6×10^{-3} g dm^{-3} for absorption spectroscopy. Since the obtained spectrum is broad, the peaks were identified from second derivative curves of the original spectra. The absorption and emission spectral data of polymer solutions are given in Support information 3 (Tables ST4 and ST5).

2.2. Fabrication of polymer LEDs

Light emitting diodes were fabricated by spin coating the emissive polymer layer over the Indium tin oxide (ITO) coated (100 nm thickness) glass plates. Aluminum was coated over the electroemissive (electroluminescent) polymer layer by vacuum coating using Edwards coating unit, at 10^{-5} torr vacuum. Aluminum serves as cathode and ITO acts as anode in the diode.

The total emission intensity of the LEDs was tested as a function of voltage using Nucleonix Luminometer containing photo multiplier tube housing with drawer assembly type PT 168. The wavelength of electro emission (electroluminescence) was studied using Cary Eclipse fluorescence Spectrophotometer in bio/chemiluminescence mode (by switching off the source).