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Novel heterocyclic based blue and green emissive materials for opto-electronics

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ABSTRACT

Two different novel heterocyclic compounds namely 2,5-bis(1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)thiophene (Material **I**) and 2,5-bis(3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)thiophene (Material **II**) were designed, synthesized and characterized by spectral methods. The synthesized materials were confirmed by standard techniques such as FT-IR, ^{1}H NMR and elemental analysis. Physical properties include thermal, surface morphology of the materials were explained from TGA, DSC and SEM analysis. Optical properties such as absorption, emission, solvent effect have been investigated by UV–Visible and fluorescence spectrophotometers. The blue and green emission of the materials was confirmed by using UV light as well as fluorescence spectrophotometers. Bandgap energies of these materials were obtained by both experimental and theoretical calculation from of cyclic voltammetry, UV–Visible spectrophotometer and DFT calculation. *I–V* characteristic analysis used to determine the threshold voltage (V_{on}) of the two materials. The obtained results of the materials have promising to be applicable for opto-electronic applications.

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1. Introduction

Organic fluorescent materials are much intensive to the urgent opto-electronics research domain, attributed to informative electron transfer and essential energy of the respective materials towards electronics applications [1–3]. In general optical materials takes an important role in various field such as OLED, solar cell, fluorescent lamp, lightening agent, light modulator and some opto-electronics fields. They have been widely used as whitening, brightening reagents for synthetic fibers and fluorescence probes in biological research, clinical diagnosis [4–6]. The efficiency of the materials is derived from specific structural construction of materials, various fashioned molecule could important to the particular applications. It is necessary to introduce new advanced materials to overcome the earlier materials in use. Pyrazoline core molecules are taking an imperative role in OLED device fabrication and optical fields, ascribed to its extensive emission behavior [7–9]. This molecule could exhibits blue, green and red emission with respect to substituent group present in the targeted molecule. Green and blue emissive materials are much needed to increase the efficiency of OLED devices [10–13]. 1,3,5-Triaryl-2-pyrazoline derivatives have attracted much interest ascribed to their favorable photo-physical properties including high hole-transport efficiency and excellent emission behavior [14,15]. Properties of organic light-emitting devices (OLED's) have been intensively studied for their potential application in flat-panel displays [16–19]. Although the development of emissive OLED's has progressed impressively, the development of high color-purity red OLED's is still in much demand [20–22]. Accordingly, the present attempt deals with synthesis and characterization of two novel pyrazoline based materials and provide a comparative study of phenyl and naphthyl substituent effect on pyrazoline compound. They act as good emissive material, based on the extended ring conjugation [23,24]. Physical properties such as thermal stability, surface morphological analyses were subjected to TGA-DSC and SEM analysis. Optical properties include absorption and emission behaviors were examined by UV–Visible, fluorescence spectrophotometers. Bandgap energies of the materials were determined from theoretical and experimental calculations. Turn-on voltage (V_{on}) of the materials was obtained from *I–V* characteristic analysis.

2. Experimental

2.1. Materials and method

All the chemicals such as 2,5-thiophenedialdehyde, acetophenone, 1-acetonaphthone, sodium hydroxide, ethanol and

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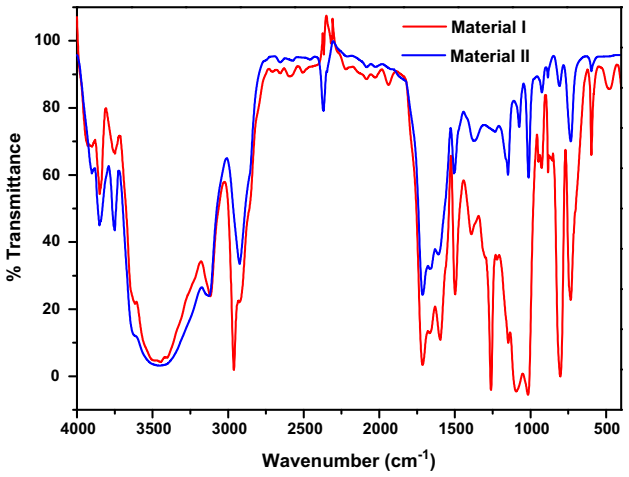

Fig. 1. FT-IR spectra of pyrazoline materials **I** and **II**.

phenylhydrazine hydrochloride were purchased from Sigma Aldrich (USA). A typical Claisen-Schmidt condensation reaction was followed to synthesize intermediate chalcone compound from respective aldehyde and ketone [25,26]. The well-known condensation reaction between chalcone and phenylhydrazine hydrochloride was used to synthesize the target pyrazoline compounds [27,28].

The FT-IR spectra of materials **I** and **II** were recorded using a Bruker IFS 66 V Fourier transform IR spectrometer and the spectra is depicted in Fig. 1. High resolution ^{1}H NMR spectra were recorded on a 500 Hz AVANCE III spectrometer in $CDCl_3$ with TMS as an internal standard and rendered in Fig. 2. Thermogravimetric analysis (TGA) was performed on a Mettler TA 3000 thermal analyzer under a nitrogen atmosphere at a heating rate of 5 °C min^{-1} with a sample weight of 2–4 mg. The absorption spectra were recorded on Shimadzu (2450) UV–Vis spectrophotometer using DMSO as a solvent. Emission spectra were obtained from Perkin-Elmer II fluorescence spectrophotometer. Fluorescence lifetime of pyrazoline **I** and **II** were measured by time correlated single photon counting (TCSPC) analysis. The fluorescence decay curves are measured by exciting the molecules at 375 nm, 200 ps light using Nano LED. The fluorescence quantum yields of these compounds were measured using quinine sulfate ($\Phi = 0.55$) as a standard. Cyclic voltammetry measurements were performed on a CHI 600D electrochemical analyzer at room temperature with three electrode cell in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scanning rate of 100 mV s^{-1}. Wherein, Glassy Carbon (GC) electrode acts as working electrode and a platinum foil used as a counter electrode and an Ag/AgCl electrode as reference electrode. Reference electrode was calibrated after each measurement with ferrocene (Fc). *I–V* devices were made-up with an arrangement of ITO/TPD/TPBI:pyrazoline material/TPBI/Mg:Ag. ITO (glass iridium tin oxide) as anode and pure TPD (N,N-diphenyl-N,N-bis(3-methylphenyl)-[1-1-biphenyl]-4-4-diamine) (60 nm) was used as hole-transporting layer HTL. TPBI doped with various pyrazoline derivatives were used as emission layer (EML) (2 wt.%, 30 nm) while the pure TPBI used as an electron-transporting layer and Mg:Ag deposited as a cathode.

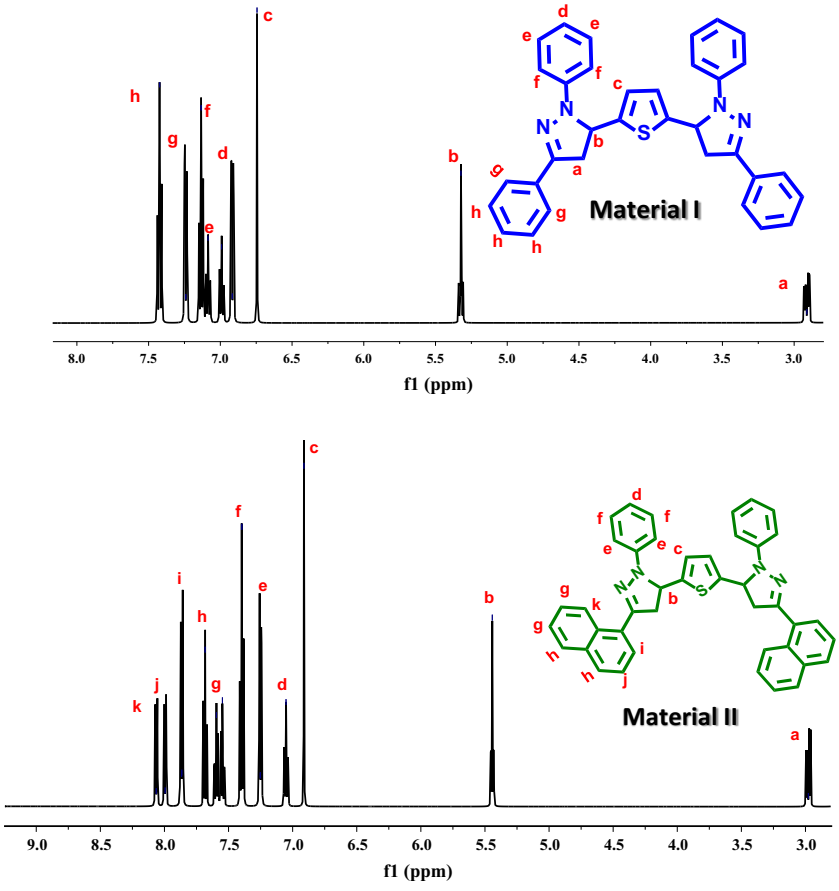

Fig. 2. ^{1}H NMR spectra of pyrazoline materials **I** and **II**.

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