



Blue organic light emitting materials: Synthesis and characterization of novel 1,8-naphthalimide derivatives



Hidayath Ulla ^{a,*}, B. Garudachari ^b, M.N. Satyanarayan ^a, G. Umesh ^a, A.M. Isloor ^b

^a Department of Physics, National Institute of Technology Karnataka, Mangalore 575 025, India

^b Department of Chemistry, National Institute of Technology Karnataka, Mangalore 575 025, India

ARTICLE INFO

Article history:

Received 25 July 2013

Received in revised form 29 October 2013

Accepted 13 November 2013

Available online 8 December 2013

Keywords:

OLED

Blue

Naphthalimide

Electron-transporting

Hole-blocking

CIE

ABSTRACT

A series of naphthalimide derivatives were designed and synthesized by substituting electron-donating phenoxy groups at the 4th position of 1,8-naphthalimide. Photophysical, thermal, electrochemical properties of the synthesized derivatives were studied. The photophysical studies revealed that by varying the substituents at the 4th position of the 1,8-naphthalimide backbone, the photoluminescence spectra can be readily tuned in the range 410–423 nm (solution) and 457–468 nm (thin film). The derivatives have high Stokes' shifts and the Commission Internationale de l'Eclairage (CIE) coordinates are positioned in the deep blue region of the chromaticity diagram. Thermal analysis showed that the melting points are in the range 135–270 °C with good thermal stability of 260–275 °C. Electrochemical studies show the derivatives to have low-lying energy levels revealing that they possess good electron-transporting and hole-blocking properties. The ionization potentials and electron affinity are in the region of 6.30–6.36 eV and 3.31–3.43 eV, respectively, with energy band-gaps in the range 2.93–3.0 eV. The studies reveal that these energy values are relatively higher than the commonly used electron transporting materials. Hence these derivatives are potential candidates not only as electron transporting but also as hole blocking blue emitters for organic light-emitting diode applications.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Since the breakthrough work by Tang and Van Slyke in 1987 [1], organic light-emitting diodes (OLEDs) and organic π -conjugated materials have grabbed researchers' interest as OLEDs promise high efficiency, high brightness, simple flat structure and potential color tunability, as well as low cost application. To use organic materials for device applications, three basic color components, i.e. red, blue and green, are essential for achieving white light emission [2–5]. A large number of efficient red and green emitters have been reported in recent years [6–10]. But the functioning of blue emitters still remain much inferior relative to red and green [11–13]. The fundamental barrier to obtain efficient blue emitter is their large optical band-gap, which is necessary to attain relatively high-energy emission. Materials with large optical band gap possess limited delocalization and consequently hamper the electron injection characteristics and the conductivity. This has centralized the material research on the establishment of stable and highly efficient blue emitters and the study of their electroluminescent properties [13,14]. For using organic materials in device applications, the primary hurdle is still dearth of their stability, lifetime

and efficiency issues. The efficiency of an OLED can be improved by balancing the transport of charge carriers, which can be done by implementing a hole-transport layer and an electron-transport layer in the OLED architecture [13–16]. Excellent organic blue emitters with hole-transporting properties are reported; but studies on electron-deficient blue emitters possessing electron-transporting properties are inadequate [17–21].

Some wide energy-gap blue derivatives with high luminescent efficiency based on fluoranthene, pyrazolo-quinoline, pyrene, oxadiazole and naphthalimide [22–27] have been developed. Out of these, naphthalimide derivatives [20,27–30] are the most frequently studied candidates as they are promising materials for efficient blue emissions. 1,8-naphthalimides are a special class of fluorescent materials which are environmentally sensitive and are of great interest owing to their strong fluorescence, excellent photoluminescence (PL) quantum efficiency, good photo-stability and film-forming properties as well as desirable chemical and thermal stabilities [20,21,27–31]. It has been reported that the presence of an electron-deficient center generally makes naphthalimide derivatives acquire high electron affinity and hence validates the possibility of its use as electron-transporting or hole-blocking material in OLEDs [32–34]. One possibility to achieve this is by the substitution of electron donating groups at the 4th position of 1,8-naphthalimide [27]. By substituting electron-donating C-substituted groups, N-substituted groups or O-substituted

* Corresponding author. Tel.: +91 8242474000(3295); fax: +91 8242474033.

E-mail address: hidayath2010nitk@gmail.com (H. Ulla).

groups at the 4th position of 1,8-naphthalimides, fluorescent quantum yields can be increased and the emission color can be conveniently tuned from yellowish green to pure blue [27,33–36].

Recently, a series of 1,8-naphthalimides reported by our group [28,30] show the lowest energy absorption bands and they show blue fluorescence in solution and thin film form. The results suggest that these compounds have a potential application as electron-transporting electroluminescent materials, which provided motivation to perform further detailed investigation of these naphthalimides. In this communication, the synthesis and detailed characterization of these molecules along with other novel blue emitting naphthalimides obtained by the substitution of electron donating phenoxy groups at the 4th position of 1,8-naphthalimide derivatives is presented. The luminescence, thermal and electrochemical properties were studied.

2. Experimental section

2.1. Materials and methods

All the starting materials, reagents were purchased from Aldrich and were used without any further treatment and purifications. The organic solvents were of spectroscopic grade; they were dried with CaH₂ and freshly distilled using the standard procedures.

The chemical structures of the synthesized materials were confirmed by ¹H NMR, ¹³C NMR, infra-red and mass spectra. ¹H NMR spectra and ¹³C NMR spectra were recorded using DMSO-d₆ on a Bruker spectrometer with tetramethylsilane (TMS) as internal reference at a working frequency of 400 MHz. Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded on a Thermo Nicolet avatar 330-FT-IR spectrophotometer with a resolution of 2 cm⁻¹. Mass spectrometric measurements were recorded on a LC-MS- Agilent 1100 series and API 2000 LC/MS/MS system. Thin layer chromatography (TLC) on silica gel coated aluminum sheets (silica gel 60 F254) was used to confirm the completion of the reaction. The photophysical properties for 10⁻⁵ M solutions in a 1 cm path length quartz cuvette as well as thermally deposited thin solid films were collected. UV-Vis absorption was recorded on a UV-visible Spectrophotometer, Ocean Optics Inc. SD 2000 with 0.6 nm resolution at room temperature. The corrected excitation and photoluminescence spectra were carried out on a JASCO FP6200 spectrofluorometer. The fluorescence quantum yields (Φ) were calculated compared to 9,10-diphenylanthracene ($\Phi_{ref} = 0.90$, in cyclohexane) by integrating the fluorescence bands [37]. Melting points of the derivatives were determined by open capillary method and Differential Scanning Calorimetry (DSC). DSC was carried out using a SHIMADZU DSC-60 under nitrogen atmosphere. Thermo Gravimetric Analysis (TGA) was performed using EXSTAR 6000, TG/DTA 6300 under nitrogen atmosphere. The electrochemical studies of the synthesized molecules were performed on a computer controlled AUTO-LAB PGSTAT 30 electrochemical analyzer with a constant scanning rate of 10 mV s⁻¹. The measurements were done at room temperature in acetonitrile (10⁻³ M) solutions of the samples with tetrabutyl ammonium hexafluoro phosphate solution (0.1 M in acetonitrile) as supporting electrolyte. Cyclic Voltammetry (CV) measurements were carried out in a three-electrode conventional cell system using a platinum (Pt) working electrode, a Pt wire as counter electrode and an Ag/AgNO₃ as the reference electrode (0.1 M in CH₃CN) in nitrogen atmosphere, and each measurement was calibrated with ferrocene/ferrocenium redox system as internal standard [27]. All the solutions in the cell were purged with ultrahigh-pure nitrogen for 10–15 min before each experiment, and a blanket of nitrogen was used during the experiment.

2.2. Synthesis

The detailed synthetic routes adopted for the synthesis of the new derivatives 5a–c and 6a–c is depicted in Schemes 1 and 2. Intermediate 4 was synthesized according to the procedure reported [21]. The derivatives 5a–c and 6a–c were obtained by the nucleophilic substitutions at the 4-position of 4-bromo-1,8-naphthalimide by phenol derivatives, with a slight modification of the reported procedure [27].

2.2.1. Synthesis of 5-bromoacenaphthene (2)

To a suspension of acenaphthene **1** (20.0 g, 0.12 mol) in dimethylformamide (50 ml), a solution of N-bromosuccinimide (23.08 g, 0.12 mol) in dimethylformamide (50 ml) was added at room temperature. The solution was stirred for 2 h and then mixed with 200 ml of cold water; filtered to give 31.0 g of crude product. The crude product on recrystallization with ethanol yielded 5-bromoacenaphthene (27.0 g), yield: 89.4%. mp: 55–56 °C [21,27].

2.2.2. Synthesis of 4-bromo-1,8-naphthalic anhydride (3)

20.0 g (0.085 mol) of 5-bromoacenaphthene **2** was taken in 500 ml round-bottomed flask. 200 ml of acetic acid and potassium dichromate (76.7 g, 0.257 mol) were added to the flask. The reaction mixture was refluxed for 3 hrs at 120 °C. The solvent was extracted in vacuum, and the resulting chromium salt was separated from the residue using boiling water and the white crude product was recrystallized using glacial acetic acid to yield white needle precipitates (20.5 g), yield: 86.4%. mp: 268–269 °C [21,27].

2.2.3. Synthesis of 6-bromo-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (4)

To a solution of 4-bromo-1,8-naphthalic anhydride **3** (10.0 g, 0.036 mol) in ethanol (100 ml), ethanalamine (2.64 g, 0.043 mol) was added slowly. The reaction mixture was then refluxed for 4 h and the resultant solution was allowed to cool. The product was filtered, washed and dried under vacuum. (8.2 g), yield: 71.3%. mp: 200–201 °C [21,27].

2.2.4. General procedure for the syntheses of 2-(2-hydroxyethyl)-6-(phenoxy)-1H-benzo[de]isoquinoline-1,3(2H)-dione (5a–c)

To a solution of 0.5 g intermediate **4** (0.0015 mol) dissolved in 10 ml of anhydrous DMF, 2-methylphenol (0.17 g, 0.0016 mol) and anhydrous potassium carbonate (0.22 g, 0.0016 mol) were added. The mixture was stirred for 2 h at 100 °C under nitrogen atmosphere. After the reactant was cooled down, 50 ml of cold water was added, and the yellow precipitate was collected. The solids were dissolved in 50 ml of ethyl acetate and purified by column chromatograph (eluent:petroleum ether:ethyl acetate 8:2) to afford a pale yellow solid.

2.2.4.1. 2-(2-Hydroxyethyl)-6-(2-methylphenoxy)-1H-benzo[de]isoquinoline-1,3(2H)-dione (5a). IR (KBr_{vmax} cm⁻¹): 1240 (—O— str); 1647, 1691 (C=O str); 2957, 3051 (C—H str); 3396 (O—H str); ¹H NMR (400 MHz, DMSO-d₆): δ ppm 2.16 (s, 3H, CH₃), 3.60 (q, 2H, CH₂, J = 12.68 Hz, J = 6.40 Hz), 4.16 (t, 2H, CH₂, J = 6.48 Hz), 4.76 (t, 1H, OH, J = 5.96 Hz), 6.78 (d, 1H, ArH, J = 8.28 Hz), 7.22–7.47 (m, 4H, ArH), 7.94 (t, 1H, ArH, J = 8.00 Hz), 8.39 (d, 1H, ArH, J = 8.24 Hz), 8.58 (d, 1H, ArH, J = 7.28 Hz), 8.77 (d, 1H, ArH, J = 8.32 Hz); ¹³C NMR: 15.89, 42.16, 58.40, 109.85, 116.44, 121.77, 122.84, 123.23, 126.54, 127.51, 128.52, 128.56, 129.54, 130.39, 131.87, 132.52, 133.29, 152.57, 159.17, 163.42, 164.10. m/z: 348 (M + 1).

2.2.4.2. 4-[[2-(2-Hydroxyethyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6yl]oxy] benzaldehyde (5b). IR (KBr_{vmax} cm⁻¹): 1242 (—O— str); 1578 1647, 1687 (C=O str); 2927 (C—H str); 3507

Download English Version:

<https://daneshyari.com/en/article/1494456>

Download Persian Version:

<https://daneshyari.com/article/1494456>

[Daneshyari.com](https://daneshyari.com)