



Blue emitting halogen–phenoxy substituted 1,8-naphthalimides for potential organic light emitting diode applications



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ABSTRACT

In this paper, we report the synthesis and characterization of six 1,8-naphthalimides [**4a–4c** and **5a–5c**] obtained by the substitution of electron donating halogen–phenoxy groups at the C-4 position. The derivatives were characterized using ¹H NMR, ¹³C NMR, mass spectra, FT-IR, single crystal XRD; photo-physical, thermal, surface morphological and electrochemical properties were also investigated. The derivatives exhibit deep blue photoluminescence in the range 414–423 nm (in CHCl₃) and 457–466 nm (in thin film state) on UV excitation with high Stokes' shifts and good chromaticity. The TGA and DSC analysis showed that the derivatives possess good thermal stability (271–284 °C) and melting points (138–201 °C). The HOMO and LUMO energy levels estimated by cyclic voltammetry are in the range 6.21–6.34 eV and 3.31–3.41 eV respectively corresponding to energy band gaps of 2.98–3.15 eV. These energy values are relatively higher than the commonly used electron transporting materials. The optical and electronic properties of the derivatives were tuned by the introduction of different electron donating halogen–phenoxy groups through C-4 position of the naphthalimide moiety. The emissive and electron-transporting properties of the naphthalimide derivative **4a** were studied by fabricating a bi-layer and tri-layer devices. Further a phosphorescent device with **4a** as electron transport layer (ETL) exhibited superior performance than the device without any ETL and was comparable with the device using standard Alq₃ as ETL. These results indicate that the synthesized naphthalimide derivatives could play an important role in the development of OLEDs.

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1. Introduction

Organic π -conjugated materials have been attracting great attention since the breakthrough work of Tang and Van Slyke [1] owing to their attractive characteristics and potential applications. For device applications, three primary colors, i.e., red, blue and green are imperative [2–5]. Efficient red and green emitters have been widely reported [6–10] but blue emitters still lag behind in terms of efficiency, lifetime and stability [11–13]. Moreover, due to their large energy band-gaps, blue emitters possess limited delocalization which hampers the electron injection and hence efficiency. This has challenged the material research community to develop stable and efficient electron injecting blue emitters [12,14]. By balancing the transport of charge carriers, the OLED efficiency could be improved [12,14–16]. Efficient p-type blue emitting materials have been developed; but studies on n-type

blue materials are inadequate [17–21]. The lack of stability and efficiency of n-type blue emitting materials are the key issues hindering the growth of commercialization of OLEDs.

Some blue derivatives with high luminescent efficiency based on fluoranthene, pyrazolo-quinoline, pyrene, oxadiazole and naphthalimide [22–28] have been developed. 1,8-Naphthalimides continue to show considerable interest in organic electronics, especially in organic light-emitting diodes (OLEDs), as they are promising materials for efficient blue emissions [17,24,28–31]. The presence of electron-deficient center makes these derivatives possess high electron affinity [32–36]. These derivatives exhibit strong fluorescence; have excellent photoluminescence (PL) quantum efficiency, good photo-stability and film-forming properties with desirable chemical and thermal stabilities as well [17,21,24,28–31]. The PL emission color of these derivatives can be readily tuned from yellowish green to pure blue by the introduction of different electron-donating substituents [24,33–35,37]. These derivatives possess wide energy band-gaps and low reduction potentials [38–42] and hence be used as n-type emitting materials in OLEDs.

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In our previous work [28,30,31], a series of 1,8-naphthalimides containing electron-donating substituents at the C-4 position were investigated. These materials showed blue emission with excellent electron-transporting and hole-blocking properties. Our experiments revealed that different substituents at C-4 position of the naphthalimide moiety may have a clear influence on the electronic, thermal and optical properties. Results of these investigations with other previous reports [24,33–35,37,43] have encouraged our effort toward the design of analogues derivatives with halogen-phenoxy substituents. It is known that n-type materials can be obtained by attaching strong electron-withdrawing groups such as F, CN, alkanoyl and perfluorobenzene, [43,44]. Studies on halogenation of a carbon based system reveal the lowering of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. A decreased LUMO allows electron injection by lowering the charge injection barrier which will facilitate the electron injection. Additionally, a lower LUMO makes the electrons in the LUMO less susceptible to ambient oxidation and hence allow us to use more stable cathodes during the OLED fabrication [43,44]. In the present investigation, we describe the synthesis and characterization of six novel derivatives [4a–4c and 5a–5c] by nucleophilic substitutions of electron donating halogen-phenoxy groups at the C-4 position of 1,8-naphthalimide. The photo-physical, thermal, morphological and electrochemical properties of the naphthalimide derivatives were investigated. Unoptimized bi-layer and tri-layer devices using naphthalimide derivative **4a** was fabricated. In addition, with **4a** as electron transporter, a multi-layer phosphorescent device was fabricated and the device performance is compared with the devices without any electron transporter and with standard electron transporter, Alq₃. The work resulted in the continuation of our effort for preparing novel n-type molecules that are potential candidates for OLED applications [28,30,31].

2. Experimental section

2.1. Materials and methods

All the chemicals were received from commercial sources (Sigma–Aldrich), and were used directly as received without further purification unless otherwise mentioned. The organic solvents for spectral analysis were of spectroscopic grade; they were dried with calcium hydride, followed by fresh distillation using standard procedures. All reactions were carried out under nitrogen (N₂) atmosphere. ¹H NMR and ¹³C NMR spectra were recorded (chemical shifts given as δ in ppm) on a Bruker spectrometer in DMSO-d₆ as solvent using tetramethylsilane (TMS) as internal standard with working frequency of 400 MHz at room temperature. Mass spectra were obtained using a LC-MS-Agilent 1100 series and API 2000 LC/MS/MS system. Fourier transform infrared (FT-IR) spectra were recorded in KBr pellets using a Thermo Nicolet AVATAR 330-FT-IR spectrophotometer with a resolution of 2 cm⁻¹. The progress and completion of the reaction was monitored using thin layer chromatography (TLC) on silica gel coated aluminum sheets (silica gel 60 F254). The photo-physical properties were studied using UV-visible spectrophotometer (Ocean Optics Inc. SD 2000) and JASCO FP6200 spectrofluorometer. The measurements were carried out in CHCl₃ (10⁻⁵ M) and thin solid films. The fluorescence quantum yield of the derivatives was determined on the basis of absorption and PL spectra in chloroform (CHCl₃) by a comparative method using 9,10-diphenylanthracene (Φ_{ref} = 0.90 in cyclohexane) as a standard [45,46]. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTG) were carried out up to 600 °C on EXSTAR 6000, TG/DTA 6300 thermal analyzer. Melting points were estimated using open capillary method and differential scanning

calorimetry (DSC). DSC measurements were performed using a SHIMADZU DSC-60. A constant heating rate of 10 °C min⁻¹ was used to melt and decompose the derivatives under nitrogen atmosphere at a flow rate of 30 mL min⁻¹ for both DSC and TGA. Surface morphology was studied using JOEL JSM-6380LA analytical scanning microscope. Cyclic voltammetry (CV) measurements were carried out in a conventional three-electrode cell system using AUTOLAB PGSTAT-30 electrochemical analyzer (scanning rate of 10 mV s⁻¹) at room temperature; tetrabutyl ammonium hexafluoro phosphate solution (0.1 M acetonitrile) as supporting electrolyte [24]. All solutions in the cell were purged with ultra-high-pure N₂ for 10–15 min before each experiment, and a blanket of nitrogen was used during the experiment. Ag/AgNO₃ in 0.1 M acetonitrile was used as reference electrode, platinum play the role of working electrode as well as counter electrode. Each measurement was calibrated with ferrocene/ferrocenium (Fc/Fc⁺) redox system as internal standard [24]. Single crystal X-ray diffraction (XRD) data was generated using the BRUKER APEX II Duo CCD single Crystal X-ray Diffractometer equipped with a micro-focus Mo K α radiation (λ = 0.71073 Å) at room temperature. The ORTEP diagram and packing diagram were created using Mercury 3.1.

2.2. Synthesis

2.2.1. General procedure for the syntheses of 2-(2-hydroxyethyl)-6-(phenoxy)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4a–4c**)

4-Bromophenol (0.28 g, 0.0016 mol) and anhydrous potassium carbonate (0.22 g, 0.0016 mol) were added to a solution of intermediate **3** (0.5 g, 0.0015 mol) in anhydrous dimethylformamide (10 ml). The mixture was stirred for 2 h at 100 °C under N₂ atmosphere. The reactant mixture was cooled to room temperature and then poured into cooled water (50 ml). The resulting yellow precipitate was collected, treated with charcoal (ethyl acetate 50 ml at 40 °C, 1 h) and purified by column chromatography (eluent:petroleum ether:ethyl acetate 8:2) to afford pale yellow solid.

2.2.2. 6-(4-Bromophenoxy)-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4a**)

IR (KBr_{v,max} cm⁻¹): 1241 (—O— str); 1649, 1693 (C=O str); 2959, 3022 (C—H str); 3460 (O—H str); ¹H NMR (400 MHz, DMSO-d₆): δ ppm 3.60 (q, 2H, CH₂, J = 12.60 Hz, J = 6.36 Hz), 4.17 (s, 2H, CH₂), 4.80 (t, 1H, OH, J = 5.96 Hz), 7.06 (t, 1H, ArH, J = 5.84 Hz), 7.27 (d, 2H, ArH, J = 8.68 Hz), 7.71 (d, 2H, ArH, J = 8.68 Hz), 7.88–7.93 (m, 3H, ArH), 8.41 (t, 1H, ArH, J = 8.00 Hz), 8.55 (t, 1H, ArH, J = 7.08 Hz), 8.64 (t, 1H, ArH, J = 7.52 Hz); ¹³C NMR: 42.11, 58.15, 112.12, 117.28, 117.98, 122.67, 123.01, 123.71, 127.68, 128.51, 129.52, 131.90, 132.99, 133.95, 154.51, 158.76, 163.34, 164.01. m/z: 413 (M+1).

2.2.3. 6-(2-Chlorophenoxy)-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4b**)

IR (KBr_{v,max} cm⁻¹): 1231 (—O— str); 1650, 1693 (C=O str); 2927, 3072(C—H str); 3479(O—H str); ¹H NMR (400 MHz, DMSO-d₆): δ ppm 3.60 (q, 2H, CH₂, J = 12.04 Hz, J = 6.12 Hz), 4.14 (t, 2H, CH₂, J = 6.20 Hz), 4.79 (t, 1H, OH, J = 5.80 Hz), 6.82 (d, 1H, ArH, J = 8.20 Hz), 7.42–7.57 (m, 3H, ArH), 7.72 (d, 1H, ArH, J = 7.88 Hz), 7.91–7.97 (m, 1H, ArH), 8.37 (d, 1H, ArH, J = 8.16 Hz), 8.55 (d, 1H, ArH, J = 7.08 Hz), 8.70 (d, 1H, ArH, J = 8.28 Hz); ¹³C NMR: 42.23, 58.27, 110.26, 117.17, 122.81, 123.08, 123.98, 126.19, 127.70, 128.11, 128.39, 129.22, 129.91, 131.66, 131.90, 132.99, 150.00, 158.36, 163.32, 163.94. m/z: 367 (M+1).

2.2.4. 6-(4-Fluorophenoxy)-2-(2-hydroxyethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (**4c**)

IR (KBr_{v,max} cm⁻¹): 1187 (—O— str); 1649, 1693 (C=O str); 2954, 3071 (C—H str); 3506 (O—H str); ¹H NMR (400 MHz, DMSO-d₆):

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