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Blue Light Emitting Materials for Organic Light Emitting Diodes: Experimental and Simulation Study

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***Abstract*—Novel blue light-emitting materials were designed by the substitution at the 4-position of 1,8-naphthalimide with electron-donating phenoxy group. The effect of molecular structure on the photophysical, electronic structure properties of the derivatives was explored by UV-visible absorption spectroscopy, photoluminescence spectroscopy, cyclic voltammetry and quantum chemical calculations. Both UV-visible absorption and emission spectra of derivatives indicate that the emission is in blue region. Electrochemical studies of the molecules revealed that they have low-lying energy levels of the lowest unoccupied molecular orbital (LUMO) and energy levels of the highest occupied molecular orbital (HOMO) indicating that the derivatives possess good electron-transporting or hole-blocking properties. To further reveal the electronic structure and the optical properties, the structural and electronic properties of the synthesized derivatives were calculated. These results indicate that molecules may offer potential as dopants as well as non-doping light-emitting materials with good electron injection capabilities for fabrication of blue organic light-emitting diodes.**

***Index Terms*-Organic light-emitting diodes, naphthalimide, blue light emitting, optical properties, electrochemical properties, molecular simulation.**

I. INTRODUCTION

Owing to there huge potential in full-color flat panel displays and solid-state lighting applications, organic light emitting devices (OLEDs) have gained considerable attention and matured considerably. The distinguished characteristics for displays include high efficiency, wide viewing angle, fast response time, low power on consumption and potentially low cost. The interest in new organic materials has grown tremendously since Pope et al. first reported organic electroluminescence from a single crystal of anthracene [1-4] and thousands of π-conjugated molecules have been developed as charge transport and/or light emitting materials as a consequence of their wide variety of semiconducting and conducting properties. The key point of OLED development for full-color display is to find out stable materials with high emission efficiency for pure colors of red, green and blue [4-6]. While a large number of exceptional red and green emitters have been developed that satisfy the requirements for OLEDs, efficient and stable organic blue emitters are still rare because blue emitters display much poorer performance compared to red and green emitters [6]. This is due to poor carrier injection efficiency into the emitters. Moreover it is hard to find an appropriate deep blue emitter as they have higher barrier for electron injection (low electron affinities) because of their wide band gap. As a result, it is important to improve the luminescent efficiency, stability for lifetime, thermal stability and narrow emission wavelength for purity of color of blue OLEDs [7].

Some materials for blue light emission have been developed with a wide energy gap and high luminescent efficiency. Among these blue-emitting materials, naphthalimide derivatives have been intensively studied as n-type (electron-transport) organic semiconductors over the past few years [8,9]. Naphthalimide derivatives have attracted much attention as an attractive building block and starting material in OLEDs owing to their excellent photoluminescence (PL) and bright pure blue electroluminescence (EL) emission, thermal and chemical stabilities. By introducing different electron-donating substituents, their PL emission color can be readily tuned from yellowish green to pure blue. Furthermore, it has been reported that naphthalimides generally have high electron affinity due to the existence of electron-deficient center and should display good electron transporting or hole-blocking capabilities that are appropriate for balanced carrier injection in OLEDs [8].

In addition to desirable macroscopic device characteristics, such as luminescence efficiencies and low drive voltages for OLEDs, an insight into the optical and electronic properties is also required to elucidate structure–function relationships. Surprisingly, investigations on synthesis, photophysical and electrochemical properties of small molecules, which may serve as structurally well-defined model systems for the corresponding naphthalimide derivatives, are limited. In order to guide the synthesis of novel materials with high band gaps, quantum-chemical methods have been increasingly applied to predict the band gap of conjugated systems [9,10].

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In this study, two novel blue-light emitting materials were designed by introducing bromo-phenoxy as substituent group at the 4-position of 1,8-naphthalimide derivatives for OLED applications. Photophysical and electrochemical properties of the derivatives were studied. As a result, the derivatives were proposed as good blue light emitting materials. Quantum chemical calculations were also performed to gain insight into the electronic properties and the geometries of these compounds.

II. EXPERIMENTAL DETAILS

A. Materials

Two naphthalimides were designed and synthesized using 6-bromo-2-(2-hydroxyethyl) - 1H - benzo [de] isoquinoline-1,3 (2H) - dione [8] as starting material**.** The crude product was purified to obtain 6 - (4 - bromophenoxy) – 2 - (2 - hydroxyethyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione [1a]. Acetylation of derivative 1a gave 2-[6-(4-bromophenoxy)-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl]ethyl acetate **[**1b**].**

The detail of the synthesis of the derivatives will be reported elsewhere. The molecular structures of the compounds are shown in Fig. 1. All the reagent and solvents were purchased from Aldrich and were used without further purification. The solvents are of analytical grade and freshly distilled before use. And the solvents [N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO)] were dried with CaH_2 and freshly distilled using standard procedures. Spectroscopic grade $CHCl_3$ was used for all absorption and emission experiments.

B. Measurements

The chemical structures of synthesized molecules were confirmed by ^{1}H NMR, ^{13}C NMR, infrared and mass spectra. ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded (DMSO-d6) on a Bruker spectrometer with working frequency of 400 MHz using tetramethylsilane (TMS) as the internal standard. Mass spectrometric measurements were carried out using LC-MS- Agilent 1100 series and API 2000 LC/MS/MS system. The IR spectra (in KBr pellets) were recorded on a Thermo Nicolet avatar 330-FT-IR spectrophotometer. Completion of the reaction was checked by thin layer chromatography (TLC) on silica gel coated aluminium sheets (silica gel 60 F254). Melting points were determined by open capillary method. UV-Vis absorption spectra were obtained on a UV-visible Spectrophotometer (Version Optics Inc. SD 2000). Steady state fluorescence spectra were recorded using a JASCO FP6200 spectrofluoremeter. The fluorescence quantum yields (Φ) were estimated by integrating the fluorescence bands and by using 9,10-diphenylanthracene (DPA) as the standard [11]. Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell system using a Pt working electrode, a Pt wire as counter electrode and an Ag/AgNO3 reference electrode on a computer controlled AUTOLAB PGSTAT 30 electrochemical analyzer at room temperature. Computations were performed using Materials visualizer, VAMP, Materials Studio.

Fig. 1. Molecular structures of 1a (left) and 1b (right)

III. RESULTS AND DISCUSSIONS

The synthesized derivatives showed excellent solubility in common organic solvents such as chloroform, chlorobenzene, tetrahydrofuran and dichloromethane. The derivatives have melting points > 192^0C.

A. Photophysical properties

An understanding of the photophysical properties of organic materials is fundamental to the understanding of the functioning in many applications. The photophysical properties of the derivatives under study are basically related to the polarization of the 1,8-naphthalimide molecules on irradiation and may be influenced by the environmental effect of the media.

Basic Ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) characteristics of the newly designed derivatives such as the absorption (λ_A) and fluorescence (λ_F) maxima, optical band gaps (E_g^{opt}), extinction coefficient (log ε), Stokes shift (ν_A - ν_F), oscillator strength (*f*), fluorescent quantum (Φ_F) yields and energy (E_F) yields were measured in dilute chloroform ($CHCl_3$) solution (10^{-5} mol L^{-1}) as well as in the form of solid thin films and shown in Fig. 2. The photophysical data are summarized in Table 1 and Table 2.

Both the derivatives display very similar UV-vis absorption characteristics. The absorption is clearly localized on the naphthalimide moiety. The maximum absorption peaks, which can be assigned to the π-π* electronic transitions are situated in the broad wavelength range of UV region at 356-363 nm in dilute $CHCl_3$ solutions and thin solid films. The solid-state absorption bands are significantly red shifted from the dilute solution ones. The ~10 nm red shifts in absorption maximum suggest that there is a slight increase in conjugation length in the solid state. Optical band gaps (E_g^{opt}) determined from the absorption edge of the solid-state spectra of these blue materials are given in Table 2. Derivatives showed absorption maxima (max) at 363 nm and 360 nm respectively for 1a and 1b with corresponding optical band gaps for the derivatives are 2.84 eV and 2.89 eV. In the visible region, the molar extinction coefficients (ε) of the compounds are high indicating that the long wavelength band of the absorption spectra (in the visible region) is a charge transfer (CT) band, due to (π, π *) character of the $S_0 \rightarrow S_1$ transition.

The PL emission was observed in the visible region with well-pronounced maxima (λ_F) at 419-461nm. The display of blue fluorescence may be attributed to the charge transfer

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interaction between the electron-donating substituent at the 4-position and the electron accepting carbonyl groups of the 1,8-naphthalimide moieties. The emission peaks of the derivatives in thin solid films (λ_F = 461 and 458 nm) with broadened full width at half maximum (FWHM) of > 59 nm were red shifted by ~ 40 nm compared to that in dilute chloroform solution (λ_F = 423 and 419 nm respectively) with much narrower FWHM of 42 and 41 nm due to the intense intermolecular aggregation and stacking in solid film states of 1a and 1b. The narrow FWHM of the derivatives make them excellent candidate for use as an efficient blue-light-emitting material in OLEDs.

TABLE I. UV-VIS ABSORPTION AND PL CHARACTERISTICS OF THE NAPHTHALIMIDES IN CHLOROFORM SOLUTION

Cpd	**λ_A (nm)**	**log ε (l mol^{-1} cm^{-1})**	**λ_F (nm)**	**FWHM (nm)**	**Φ_F**	**E_F**
1a	355	4.119	423	42	0.45	0.38
1b	351	4.105	419	41	0.39	0.33

TABLE II. UV-VIS ABSORPTION, PL CHARACTERISTICS AND OPTICAL BAND-GAP OF THE NAPHTHALIMIDES IN THIN FILM FORM

Cpd.	**λ_A (nm)**	**λ_F (nm)**	**FWHM (nm)**	**ν_A - ν_F (cm^{-1})**	***f***	**E_g^{opt} (eV)**
1a	363	461	59	4528	0.29	2.84
1b	360	458	62	4623	0.37	2.89

The Stokes shift (ν_A - ν_F) indicates the differences in the properties and structure of the fluorescent materials between the ground state, S_0 and the first excited state, S_1. The Stokes shifts (cm^{-1}) were calculated by (1)

$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \qquad (1)$$

The oscillator strength (*f*) is an important parameter that reveals the effective number of electrons taking part in the transition from the ground state to the excited state, and it is proportional to the area under the absorption spectrum. The oscillator strength values were calculated using (2) where $\Delta\nu_{1/2}$ is the width of the absorption band (in cm^{-1}) at 1/2 (ε_{max}).

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2}\, \varepsilon_{\max} \qquad (2)$$

The Stokes shift (4528-4623 cm^{-1}) and oscillator strength (0.29-0.37) values for derivatives 1a and 1b summarized in Table 2 were in accordance with the data for other investigations on blue-emitting 1,8-naphthalimide derivatives [12, 13]. These values do not indicate remarkable changes in the geometry of the first singlet-excited state due to the excitation.

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F), which is estimated on the basis of the absorption and fluorescence spectra using 9,10-diphenylanthracene in cyclohexane (Φ_{ref} = 0.90) [11] as a standard according to (3) where A_{ref}, S_{ref}, n_{ref} and A_{sample}, S_{sample}, n_{sample} represent the absorbance at the exited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively. As seen from the data in Table 1, the derivatives have fluorescence quantum yields of 0.45 for 1a and 0.39 for 1b.

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n^2{}_{sample}}{n^2{}_{ref}}\right) \qquad (3)$$

The energy yield of fluorescence E_F (Table 1), calculated by (4), could also be used instead of FF.

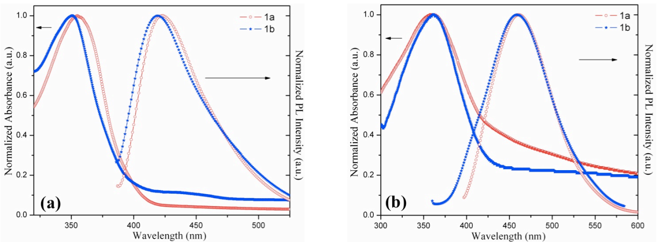

Fig. 2. Absorption and PL spectra of derivatives in $CHCl_3$ solution (a) and thin film state (b)

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \qquad (4)$$

Since the overlap between absorption and fluorescence spectra is small and the concentration of derivative is low, the reabsorption and aggregation effects are negligible.

B. *Electrochemical properties*

To gain information on the charge injection capabilities, the electrochemical behavior of the synthesized molecules was investigated by cyclic voltammetry in 1 mmol L^{-1} acetonitrile solutions on Pt containing 0.1 mol L^{-1} of Bu_4NPF_6 as supporting electrolyte and ferrocene/ferrocenium as calibrant, referenced with $Ag/AgNO_3$ electrode [6]. Both derivatives have free hydroxyl groups, which form hydrogen bonds with the solvent and exhibit quasi-reversible reduction waves upon the cathodic sweeps, with onset reduction potentials of -1.49 V and -1.48 V vs $Ag/AgNO_3$, while the oxidation processes exhibit irreversible waves when sweep anodically, the onset potentials of oxidation for the derivatives 1a and 1b are located at 1.41 V and 1.51 V vs $Ag/AgNO_3$. HOMO and LUMO levels were estimated from the onset potentials by comparison to ferrocence (4.8 eV versus vacuum). Electron affinities (LUMO) estimated from the onset of the reduction wave (Electron Affinity = E^{red}_{onset} +4.8) are 3.31 eV in 1a and 3.32 eV in 1b (below vacuum). This reveals that the derivatives have low-lying LUMO energy levels and promising electron-transport properties (n-type) or hole-blocking blue electroluminescent materials for OLEDs. The estimated ionization potentials (HOMO) of the derivatives estimated from the onset of the oxidation wave (Ionization Potential = E^{ox}_{onset} + 4.8) are 6.21 eV and 6.31 eV. The HOMO-LUMO energy gaps of the derivatives are 2.93 eV in 1a and 2.99 eV in 1b. The electrochemical data are summarized in table 3.

C. *Theoretical calculations*

To gain insight into the electronic properties and the geometries of the derivatives, quantum chemical calculations

TABLE III. ELECTROCHEMICAL PROPERTIES OF THE NAPHTHALIMIDE DERIVATIVES

Cpd	**E^{ox}_{onset} vs E_{fc} (V)**	**HOMO (eV)**	**E^{red}_{onset} vs E_{fc} (V)**	**LUMO (eV)**	**E_g^{EC} (eV)[a]**
1a	1.41	-6.21	-1.49	-3.31	2.93
1b	1.51	-6.31	-1.48	-3.32	2.99

[a] $E_g^{ec} = (E^{ox}_{onset} - E^{red}_{onset})$

were performed. The calculation of lowest excitation energies was performed at the fully optimized geometries of the ground states. The optimized structures of the compounds reveal that the substituted moieties attached to molecule are nearly non-planar with the naphthalimide backbone. The optimized structures and molecular orbitals of the derivatives are shown in Fig. 3. The HOMO-LUMO energy differences are presented in Table 3. These predicted E_g^{cal} values are much higher than those estimated from the experimental onset of UV-vis absorption (E_g^{opt}) and the cyclic voltammograms (E_g^{EC}). There are factors, which may be responsible for the errors because the orbital energy difference between HOMO and LUMO is still an approximate estimation to the transition energy since the transition energy also contains significant contributions from some two- electron integrals.

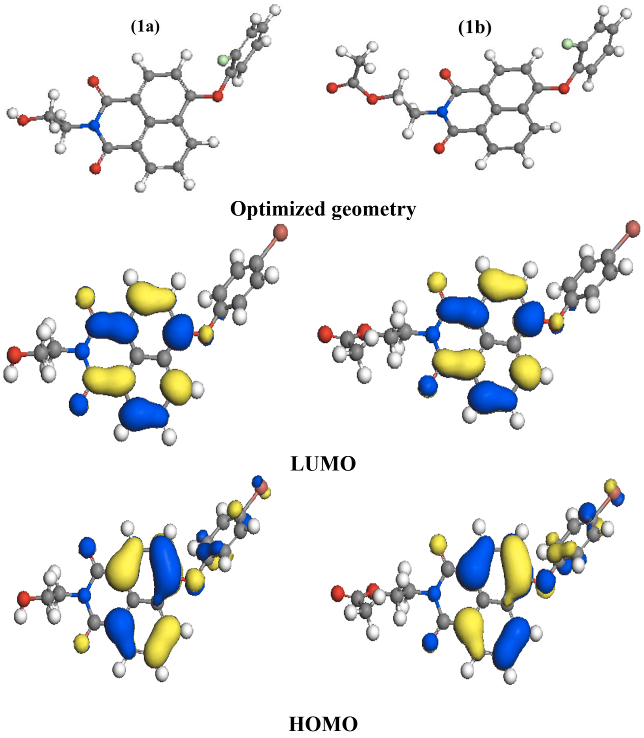

Fig. 3. Optimized geometry and HOMO-LUMO of the naphthalimide derivatives

TABLE IV. ENERGY VALUE THEORETICALLY CALCULATED FOR MOLECULES IN CHLOROFORM SOLUTION

Cpd	**Heat of formation (Kcal/mol)**	**HOMO (eV)**	**LUMO (eV)**	**E_g^{cal} (eV)**	**λ^{Abs}_{max} (nm)**	**E_g^{opt} (eV)**	**λ_{onset} (nm)**
1a	-60.96	-6.63	-3.34	3.29	387	3.02	411
1b	-92.95	-6.74	-3.4	3.34	388	3.03	409

The electronic absorption of the two derivatives was calculated using chloroform as the solvent and the results are listed in Table 3.The heat of formation of the derivatives 1a and 1b are -69.09 and -103.13 Kcal/mol respectively suggesting that the formation of the derivatives is endothermic.

D. *Conclusions*

Two naphthalimide derivatives have been investigated by UV-vis absorption spectrometry, photoluminescence emission spectrometry and cyclic voltammetry respectively in order to explore the optical and electrochemical properties of π -conjugated naphthalimides. The broad featureless UV-vis absorption spectra with red shifts from the dilute solution ones indicated there was a slight increase in conjugation length in the solid state. The PL emission spectra have large Stokes shifts in the solid state. The investigation on electrochemical properties showed that the derivatives have low-lying LUMO energy levels and promising electron-transport properties (n-type) for OLEDs. Quantum chemical calculations revealed that the derivatives have non-planar structures. The results indicate that the molecules offer potential as non-doping light-emitting materials with good electron transporting or hole-blocking properties for fabrication of blue organic light-emitting diodes.

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