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Phenanthroimidazole derivatives for single component blue light-emitting electrochemical cells

Mihye Son and Youngson Choe

School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea

ABSTRACT

Light emitting electrochemical cells (LECs) are considered to be the future generation of lighting sources for full color displays and solid-state lightings. The recent report on LEC devices with small organic molecules presents a plausible way for this potential lighting technology. Novel blue emitting phenanthroimidazole derivatives were synthesized and characterized by thermal, photophysical, electrochemical and electroluminescence properties. Solution processed LEC devices were fabricated using both the emitters as a light-emitting layer. The fabricated single-component LEC devices exhibited blue-electroluminescence centered at 485 nm and 480 nm with CIE$_{x,y}$ of (0.18, 0.26) and (0.17, 0.16) for compound 1 and 2, respectively.

KEYWORDS
Blue electroluminescence; ionic small molecules; LECs; phenanthroimidazole

Introduction

An increasing level of global energy demands solid-state organic fluorescent materials have received great attention in recent years owing to their promising applications in optoelectronic devices. The pioneering work of Tang et al. [1] on multi-layered organic light-emitting diodes (OLEDs) has reached quite promising performances. The multi-stack OLEDs are constructed by the thermal evaporation of active species under high vacuum. However, the manufacturing cost of OLEDs still remains a challenge. Light-emitting electrochemical cells (LECs) are another type of electroluminescent devices which converts electric current to light within an active layer. LECs are the most anticipating alternative for the OLED devices. LEC has several attractive features such as simple device architecture and fabricated from solution under ambient condition for low-cost electroluminescent devices as compared to OLEDs [2–5]. Air stable material were used as a electrodes, since the carrier injection is less sensitive makes LECs more cost-efficient. In LECs single emitters either neutral conjugated polymer (CP) [6, 7] or an ionic transition metal complex (iTMC) [8–12] enables both ionic and electronic conduction which performs carrier injection upon applied bias [2, 13]. The unique potential makes LECs more impressive as compared to OLEDs. Number of solution processed high performance LECs were reported for blue-green, yellow and red light-emission based on ionic iridium (III) complexes [14–23]. Laboriousness in synthesis and purification of polymers hinders device performances [24].

CONTACT Prof. Youngson Choe choe@pusan.ac.kr School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea.

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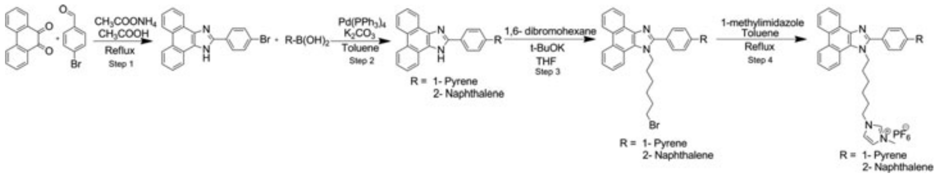
The synthesis laboriousness of polymers and low abundance, high cost of iridium, impede the large scale low-cost application of LEC devices. Recently considerable attention has been focused on organic small molecules for developing high performance full-color flat panel displays and solid-state lighting technologies. The development of organic small molecules and the endowment of their structural properties are essential to construct lighting devices. Organic small molecule based LEC were reported by Hill et al. in which the device structure were similar to polymer LECs [25]. The number of small molecule LECs were reported by using neutral organic small molecules [3, 26]. To simplify the device, Chen et al. shows that LEC devices based on an ionic terfluorene derivative are active emitters [27]. The invention of ionic small molecules increase great attention to develop charged organic small molecules for low cost efficient lighting devices. Recently solution processed LECs based organic small molecules mostly charged as an efficient material serves both, charge transport and emitter in the fabricated LECs with efficient emission [28–36]. Organic materials with multifunctional groups are promising candidates for developing high performance electroluminescent devices. In this work, we utilized phenanthroimidazole/pyrene and phenanthroimidazole/naphthalene hybrid design strategy to obtain the new blue emitters and its, photophysical and electroluminescence characteristics were investigated. Synthesized emitter shows high thermal stability and deep blue emission in solution. The electroluminescent characteristics were evaluated in single-layered LEC devices by employing the charged organic emitters. The electroluminescence characteristics of the material were investigated by employing the active material as emitter in a suitable device structure which was similar to iTMC-LECs due the intrinsic ionic nature of the emitter. Non-doped LECs based on the novel fluorophores show blue light emissions centered at 485 and 450 nm with CIE$_{x,y}$ of (0.18, 0.26) and (0.17, 0.16) for compound 1 and 2, respectively. The LEC devices show maximum brightness of 277 and 160 cd/m^2 for compound 1 and 2, respectively. The results recommend that the phenanthroimidazole based derivatives are promising building block to construct the energy saving full color displays.

Experimental section

General information

^{1}H NMR spectra were measured with Varian unity Inova-300 MHz spectrometer at room temperature. Purification and spin coating process were carried out under an ambient condition. Differential scanning calorimetry (DSC) was performed using a TA instruments Q200 KBSI operated at a heating rate of 10°C min^{-1}. The glass transition temperature (Tg) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken using a Netzsch TG 209 instrument. The thermal stability of the samples under nitrogen atmosphere was determined by measuring their weight losses while at a heating rate of 20°C min^{-1}. The UV-visible absorption and photoluminescence spectra of the compound were recorded on a UV-VIS spectrometer, Lamda-20, PerkinElmer and Hitachi F-7000 FL spectrophotometer, respectively. The optical band gap (Eg) energy level was obtained from the absorption onset potential. Cyclic voltammetry (CV) measurements were performed on cyclic voltammetry (CV) model of potentiostat/galvanostat (Iviumstat) voltammetric analyzer with platinum as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode at a scanning rate 100 mV s^{-1}. Tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$, 0.10 M) was used as the supporting electrolyte and acetonitrile as the solvent, respectively. The experiments were calibrated with the standard ferrocenium/ferrocene



Scheme 1. Synthetic routes of Compound 1 and 2.

(Fc^+/Fc) system. The HOMO energy level of the molecule calculated from the onset of oxidation potentials using the formula $E_{HOMO} = -4.4$ -E_{onset} (ox) [37] and the LUMO was obtained by the summing the E_g to the calculated HOMO energy level.

Synthesis

All reagents and solvents used for synthesis were purchased from commercial suppliers and used as received without further purification. The synthetic routes of the compounds were outlined in Scheme 1.

Step 1

Refluxing of phenanthrene-9, 10-dione (4.8 mmol) and 4-bromo benzaldehyde (4.8 mmol) with ammonium acetate (58.7 mmol) in glacial acetic acid for 12 h under argon atmosphere. The reaction mass was cooled to room temperature, solid was filtered, washed with water and ether then dried to give pale green solid. Yield 60%. ^{1}H NMR (300 MHz, d_6-DMSO, δ): 13.55 (1H, s), 8.80 (2H, d), 8.58 (2H, d), 8.20 (2H, d) and 7.70 (6H, m).

Step 2

Step 1 product (1.0 mmol), 1-pyreneboronic acid and 2-naphthaleneboronic acid (1.2 mmol), $Pd(PPh_3)_4$ (0.02 mmol), TBAB (0.10 mmol) and K_2CO_3 (5.00 mmol) were added to 2:1 (V/V) mixture of toluene/ethanol/water under argon atmosphere. The reaction mixture was stirred at 80°C for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane and dried over Na_2SO_4. After the solvent had been removed, the residue was purified via chromatography by n-hexane/ethyl acetate (7/3; v/v) to give product (Yield 67%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): For pyrene derivative. 13.55 (1H, s), 8.90 (2H, d), 8.65–8.55 (4H, m), 8.45–8.10 (9H, m), 7.90 (2H, m), 7.80 (2H, m) and 7.68 (2H, m). For naphthalene derivative. 13.55 (1H, s), 8.90 (2H, d), 8.60–8.20 (5H, m), 8.20–7.80 (6H, m), and 7.80–7.40 (6H, m).

Step 3

Step 2 compounds (1 mmol) were alkylated with excess 1,6-dibromohexane in the presence of t-BuOK in THF under argon at 60°C for 16 h. After cooling to room temperature, the mixture was extracted with dichloromethane and dried over Na_2SO_4. The residue was purified via chromatography by n-hexane/ethyl acetate (7/3; v/v) to give product (Yield 71%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): For pyrene derivative. 9.05–9.00 (1H, d), 8.80 (1H, d), 8.65 (1H, d), 8.50–8.45 (2H, m), 8.38–8.32 (2H, m), 8.30–8.25 (4H, m), 8.20–8.10 (2H, m), 8.05 (2H, m), 7.90 (2H, m), 7.85–7.65 (3H, m), 4.85 (2H, t), 3.45 (2H, t), 1.90 (2H, m), 1.70 (2H, m) and

1.30–1.10 (4H, m). For naphthalene derivative. 9.05–8.80 (2H, m), 8.60 (1H, d), 8.40 (2H, m), 8.20–7.90 (8H, m), 7.80–7.50 (6H, m), 4.80 (2H, t), 3.45 (2H, t), 1.85 (4H, m), and 1.30–1.00 (4H, m).

Step 4 (Compound 1 and 2)

Step 3 compounds (1 mmol) were refluxed with excess 1-methylimidazole for 16 h under an inert atmosphere. Reaction mass was concentrated, then dissolved in 3 mL methanol and followed by anion exchange with a saturated aqueous NH_4PF_6 solution. Then the mass was filtered, washed with excess water, ether and dried. (Yield 74%). ^{1}H NMR (300 MHz, d_6-DMSO, δ): For compound 1. 9.10–8.95 (2H, m), 8.90 (1H, d), 8.65 (1H, m), 8.50–8.45 (2H, m), 8.40–8.35 (2H, m), 8.30–8.25 (4H, m), 8.18–8.12 (2H, m), 8.10–8.02 (2H, m), 7.93–7.90 (2H, m), 7.86–7.52 (6H, m), 4.85 (2H, t), 4.05 (2H, t), 3.75 (3H, s), 1.90 (2H, m), 1.70 (2H, m) and 1.30–1.10 (4H, m). For compound 2. 9.10–8.80 (3H, m), 8.60 (1H, m), 8.40 (2H, m), 8.20–7.90 (8H, m), 7.80–7.50 (8H, m), 4.80 (2H, t), 4.00 (2H, t), 3.75 (3H, s), 1.82 (2H, m), 1.60 (2H, m) and 1.20–1.00 (4H, m).

Device fabrication and characterization

Indium tin oxide (ITO) coated glass substrates were thoroughly cleaned in ultrasonic bath of acetone, ethanol and isopropyl alcohol, dried in oven at 120°C. After drying, PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)) layer was spin-coated onto the ITO anode as a buffer layer and then dried in a vacuum over 120°C for an hour. Then the active layer was spin-coated on top of PEDOT/PSS layer, 2 wt% solution in acetonitrile solution followed by annealing at 80°C for 1 h in vacuum. Sequentially aluminum cathode contacts were deposited by thermal evaporation at high vacuum through a shadow mask on top of the active layer. EL luminescence spectra and CIE color coordinates were measured using an Avantes luminance spectrum. And the current density and luminance *versus* voltage characteristics were measured by using Keithley 2400 source meter under ambient atmosphere.

Results and discussion

Thermal properties

Thermal properties of both the compounds were evaluated by thermal gravimetric analysis and differential scanning calorimetry under an inert atmosphere. Figure 1 shows the high thermal decomposition temperatures (T_d) (corresponding to 5% weight loss) of 416 and 375°C for both the compounds.

In addition, as shown in Figure 2 both the materials shows glass transition temperatures (T_g) of 131 and 99°C obtained via differential scanning calorimetry (DSC). High thermal stability of the materials indicates their high morphological stability in the deposited thin films which would benefit for the LEC applications. Good thermal stability of the materials is highly prerequisite for their application in organic electroluminescence devices.

Photophysical properties

Optical properties of Compound 1 and 2 were analyzed using ultraviolet-visible (UV-vis) and photoluminescence (PL) spectrometers. Figure 3 exhibits the absorption and emission spectra of both compounds in dilute acetonitrile solutions at room temperature.

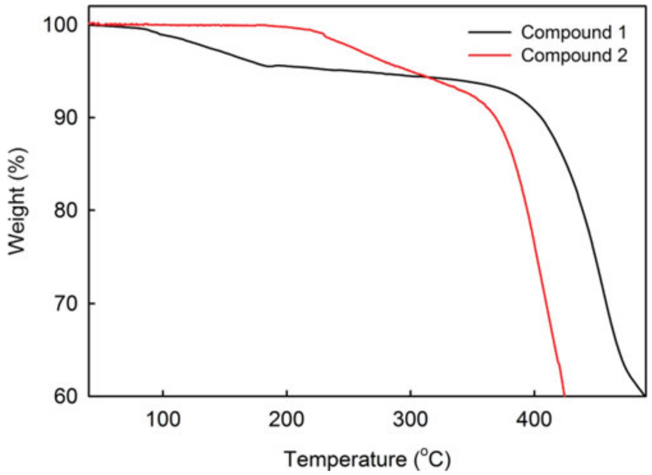


Figure 1. TGA curves of Compound 1 and 2.

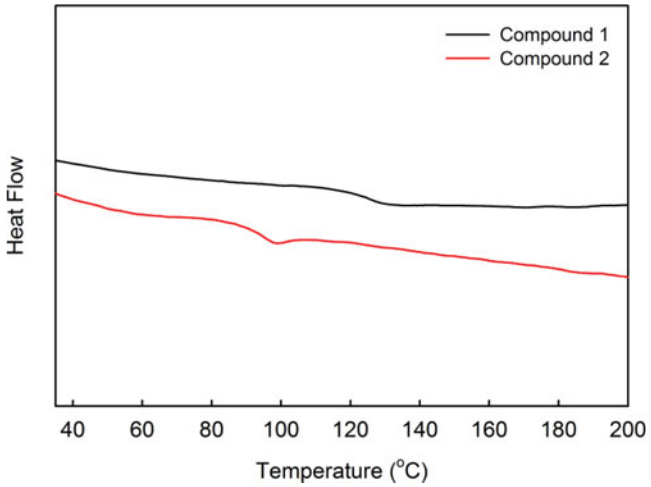


Figure 2. DSC curves of Compound 1 and 2.

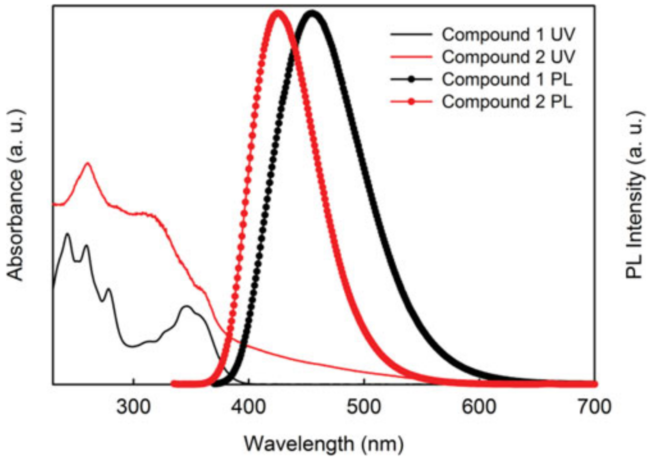


Figure 3. Normalized absorption and PL spectra of Compounds 1 and 2 in ACN (10^{-5} M).

Table 1. Photophysical, electrochemical and thermal Properties of 1 and 2.

Compound	$\lambda_{UV,max}$ [a] (nm)	$\lambda_{PL,max}$ [b] (nm)	E_{HOMO} [d] (eV)	E_{LUMO} [d] (eV)	E_g [e] (eV)	T_d [f] (°C)
1	345	455	−5.58	−2.37	3.21	416
2	314	425	−5.63	−2.37	3.26	375

[a] Absorption in ACN (10^{-5} M).
[b] Photoluminescence in ACN (10^{-5} M).
[c] HOMO calculated from onset of oxidation potential.
[d] LUMO calculated by summing the HOMO and the energy gaps (E_g).
[e] Optical band gap calculated from onset of absorption spectrum.
[f] Thermal decomposition (T_d) temperature.

The photophysical properties of compound 1 and 2 are summarized in Table 1. In the absorption spectra, compound 1 and 2 in acetonitrile solution shows absorption bands around 345 and 314 nm attributable to the $\pi-\pi^*$ transition of the molecular backbone. From the solution onset absorptions, energy gap (E_g) was estimated to be 3.21 and 3.26 eV for compound 1 and 2 respectively, which was calculated from the threshold of the absorption spectra in solutions. The compounds were excited at its maximum absorption, and exhibited emission peak around 455 and 425 nm in acetonitrile solution for both the compounds. The synthesized materials show deep blue emission in solution photoluminescence spectrum. Blue color materials are highly desirable for full-color displays and flat-panel solid-state lighting applications.

Electrochemical properties

Electrochemical properties of the compound 1 and 2 were investigated by cyclic voltammetry to measure the highest occupied molecular orbital (HOMO) levels of the compound. The oxidation potentials were measured in acetonitrile solution and tetra-butylammonium hexafluorophosphate was used as supporting electrolyte are shown in Figure 4. The HOMO levels were estimated from the onset of oxidation potentials was found to be −5.58 and −5.63 eV for compounds 1 and 2, respectively.

Their lowest unoccupied molecular orbital (LUMO) energy levels were calculated by summing the HOMO and the energy gaps (E_g) determined from their absorption edges of

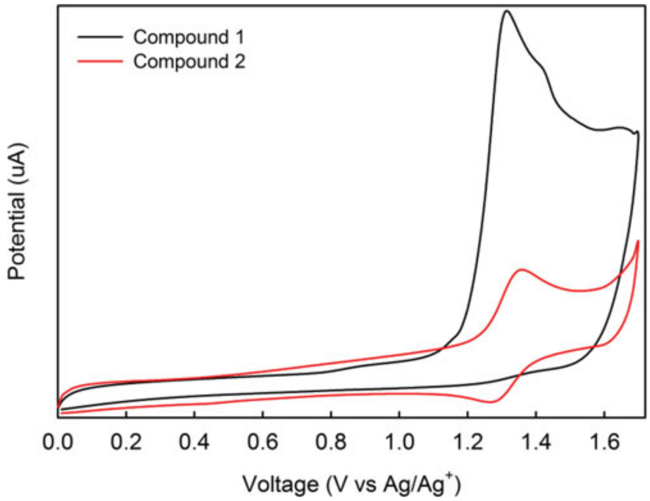


Figure 4. Cyclic voltammogram of compounds 1 and 2.

UV-visible spectra. The estimated LUMO levels were found to be −2.37 eV for both the compounds.

Electroluminescent properties

To evaluate the electroluminescent properties of the compounds 1 and 2, non-doped single-layered LEC devices with a configuration of ITO/PEDOT:PSS/Compounds 1 and 2/Al were fabricated by spin coating from the acetonitrile solution of active materials under ambient conditions. The fabricated LEC devices were subjected into Keithley 2400 source meter to determine LEC device performances. Figure 5 shows the blue electroluminescence (EL) spectra of single-components LECs utilizing compounds 1 and 2, respectively. EL spectra were measured by using single voltage scan (current 10 mA) with sweep rate of 0.5 V/s. The EL spectra were observed at 485 and 450 nm with the CIE coordinates of (0.17, 0.26) and (0.17, 0.16) for compound 1 and 2, respectively. Compared to compound 1, compound 2 shows blue shifted electroluminescence with CIE coordinates of (0.17, 0.16).

As shown in Figure 5, the EL spectra of compounds were red-shifted compared to their PL spectra due the intramolecular interactions in the solid state [38]. However, both materials show blue color electroluminescence with CIE coordinates close to pure blue color coordinates in single-component LEC devices.

Figure 6 shows the time-independent brightness (L–V) and current density (J–V) plots of the single-layer devices based on compound 1. Compound 1 shows the low turn-on voltage of 5 V (at B > 1 cd/m^2). The devices were investigated by voltage scanning with sweep rate of 0.5 V/s. compound 1 exhibited maximum brightness of 277 cd/m^2 and maximum current density of 131 mA/cm^2.

Compound 2 shows the maximum brightness of 160 cd/m^2 and maximum current density of 84 mA/cm^2 with sweep rate of 0.5 V/s were presented in Figure 7. Compound 2 shows the low turn-on voltage of 5 V (at B > 1 cd/m^2). All the compounds shows maximum brightness at 8.5 V and the turn-on voltage at 5 V which is good compared to previously reported LECs based on phenanthroimidazole derivatives [33]. The attainment of such a maximum brightness at 8.5 V in a single-layer LEC device shows the simplicity of the charge transport in the active layer due to the D-A character of the compounds 1 and 2.

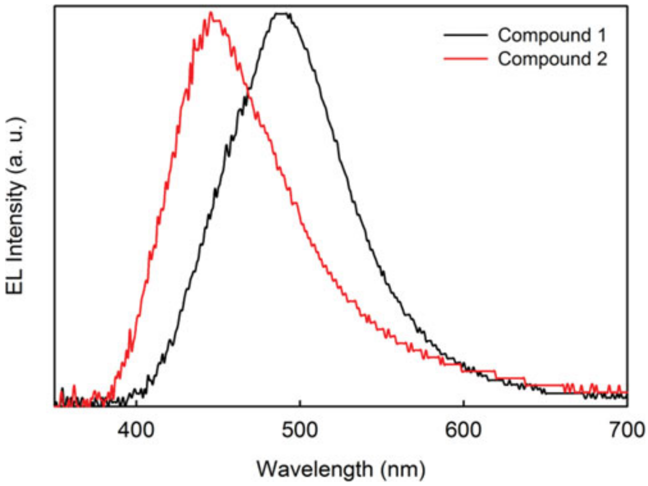


Figure 5. Electroluminescence spectra of compounds 1 and 2.

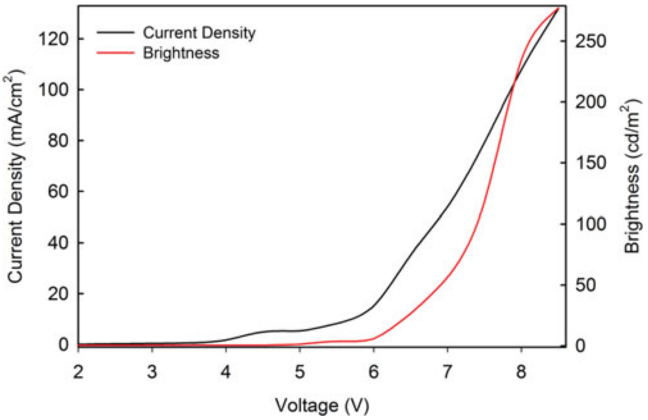


Figure 6. Current density-voltage-luminescence (J-V-L) characteristics of compound 1.

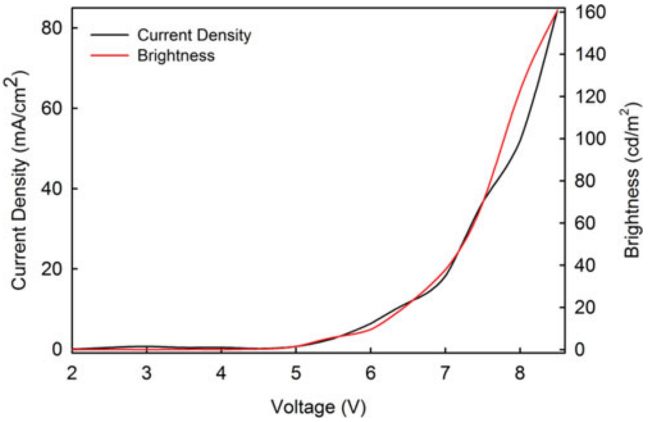


Figure 7. Current density-voltage-luminescence (J-V-L) characteristics of compound 1.

Conclusions

We have described the synthesis of new blue light-emitting compounds 1 and 2, containing phenanthroimidaole as a central core with pyrene and naphthalene fluorophores. The synthesized compounds were intrinsically ionic to mediate the charge transport in single-layered electroluminescence devices. The compounds were characterized by thermal, photophysical, electrochemical and electroluminescence investigations. The compounds 1 and 2 were exhibited blue color emission in acetonitrile solution. The non-doped single-layered LEC devices shows blue electroluminescence centered at 485 and 450 nm with the CIE coordinates of (0.17, 0.26) and (0.17, 0.16) for compound 1 and 2, respectively. The LEC device shows low turn-on voltage of 5.0 V and maximum brightness of 277 and 160 cd/m^2 for compounds 1 and 2.

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