Synthesis and photophysical characterization of an ionic fluorene derivative for blue light-emitting electrochemical cells

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ABSTRACT

A highly fluorescent an ionic fluorene derivative 1 was synthesized and its photophysical, electrochemical and electroluminescence characteristics were investigated. Deep blue emissions were observed for compound 1 in solid as well as in dilute solutions. The synthesized compound shows high fluorescence quantum yield around 77% indicates that compound 1 can perform its role as efficient ionic emitter in LEC devices. Light-emitting electrochemical cell (LEC) devices were fabricated incorporating compound 1 without (device I) and with (device II) ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM·PF$_6$). Devices I and II exhibited blue electroluminescence maximum centered at 455 and 454 nm with CIE coordinates of (0.15, 0.21) and (0.16, 0.22), respectively. Maximum luminance and current efficiency of 1105 cd m^{-2} and 0.14 cd A^{-1} respectively, has achieved for device I while that of device II resulted in 1247 cd m^{-2} and 0.14 cd A^{-1} respectively.

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1. Introduction

Solution processed light-emitting electrochemical cells (LECs) are anticipated to be the forthcoming generation of flat-panel displays and solid state lighting sources. LEC have great attention due to their high compatibility with low cost and handy fabrication approaches. LECs are conveniently processed from solution and the use of air stable electrodes such as Al, Ag and Au allows non-rigorous encapsulation of the device that operates at low voltages. LECs does not rely on the charge-injection layers due to the presence of mobile ions in the active layer, which makes LECs more impressive compared to the conventional organic light-emitting diodes (OLEDs). Working mechanism of LEC devices involves the transfer of mobile ions present in the active layer which induce electrochemical doping near to the respective electrodes facilitating the injection of holes and electrons and results high power efficiencies in the form of light under the application of an external voltage. In contrast to more stable and highly efficient, sophisticated OLEDs are composed of neutral small molecules processed from thermal evaporation, which makes them more expensive compared to LECs.

In 1995, Pei et al. were reported the first solid state LEC device [1] which consists of a tricomponent blend of a light-emitting polymer, an ion conducting polymer and an inorganic salt. And a year later, Rubner et al. was introduced an alternative using ionic transition metal complexes (iTMCs) as the active material [2]. For the first time, LEC device using iridium-iTMC (Ir-iTMC) were reported in 2004 and produced an intense yellow luminescence with an efficiency of 5% [3]. The Ir-iTMC based LEC devices received great attention in recent years over polymer LECs due to the high photophysical stability, color tunability and phosphorescent nature of the former. An intrinsic ionic character of iTMC has extensive attraction compared to polymer material since iTMC-LEC avoids the use of additional inorganic salts and an ion conducting polymer (polyethylene oxide) as used in polymer LECs. Till to date, Ir-iTMCs have been greatly explored for their performance in LECs and achieved high stabilities, efficiencies and good color purity [4–6].

An extensive number of LEC devices were reported having yellow, orange and red light-emission with remarkable stability and efficient luminescence using cationic iridium complexes [7–18]. However the blue LECs based on iridium complexes are hard-to make because the wide optical energy gaps for blue emitters involve high-energy excitons and exhibited emissions in the bluish-green region [19,20]. Moreover, LECs based on such blue emitting cationic iridium complexes resulted in low efficiency and luminance lifetime [21–24]. Moreover, the high cost and low

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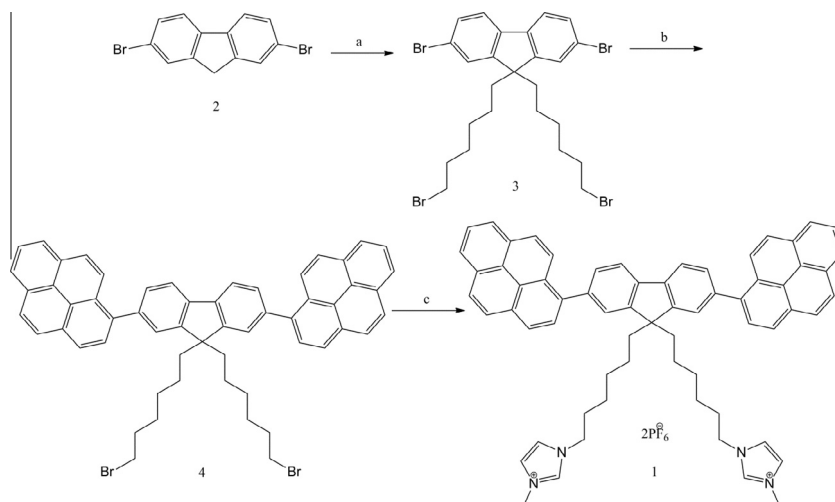
Scheme 1. (a) 1,6-Dibromohexane, TBAB, KOH/H₂O, 75 °C, 15 min; (b) pyrene-1-boronic acid, Pd(PPh₃)₄, K₂CO₃, Toluene/H₂O; (c) 1-methylimidazole, toluene.
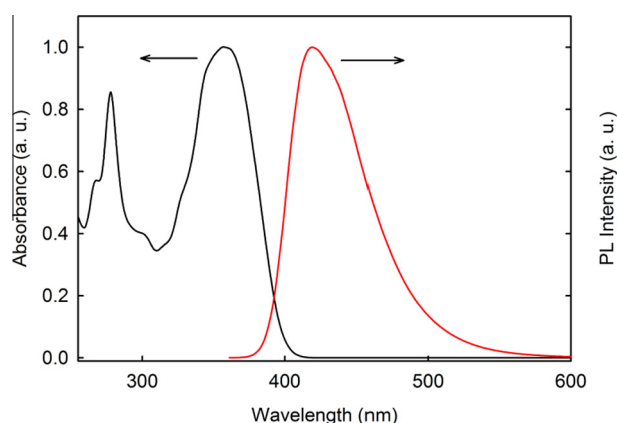

Fig. 1. Normalized absorption and PL spectra of compound 1 in acetonitrile solution (10^{-5} M).

abundance of iridium suppress the large scale production of LEC devices in the future, and hence the development of efficient blue organic emitters for LEC application is highly desirable. In recent years, organic semiconducting materials have attracted much attention due to their excellent performance in optoelectronic devices. By the use of organic semiconductors, efficiency and stability of electroluminescent devices have considerably improved compared to the conventional inorganic materials over a short period of time [25]. In 2013, Tang et al. reported a LEC device using organic non-ionic small molecules (SMs) blended with polyethylene oxide and an inorganic salt as the emitting layer, which exhibited green electroluminescence with peak quantum efficiency of 2.25 cd A^{-1} [26]. Where an ionic organic emitter leads to simpler

thin film architecture were reported for blue LECs with a maximum external quantum efficiency of 1.14% and 1.06% [27,28] respectively, while the cyanine dyes in a host–guest configuration used as active material in LEC device exhibits the luminescence near infra-red region with 0.44% external quantum efficiency [29]. Currently, the low molecular weight compounds, such as an ionic hole-transporter mixed with a neutral polar electron-transporter and a neutral blue-phosphorescent iridium (III) emitter gives an efficient blue LEC with an efficacy of 5 cd A^{-1} [30].

Fluorene including polyfluorenes and its derivatives are used as blue emitters in optoelectronic devices because of their enormous properties, such as large energy gaps, tunable emission color, high luminescence and possible functionalization of the fluorene ring [31–36]. The low molecular weight fluorene analogs have advantages in synthesis, purification and highly pure emission color in comparison with the polyfluorenes [37–39]. In this work, we synthesized an organic ionic small molecule based on a fluorene derivative for their application in electroluminescent devices.

Here, we present a solution processed new blue light-emitting devices exclusively based on an ionic fluorene derivative compound 1 as a light-emitting material without any additional inorganic salt and conducting polymers. LEC devices were fabricated from acetonitrile solution utilizing compound 1 (device I) and the compound 1 containing 10 wt% ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM·PF₆). The fabricated electroluminescent devices exhibits blue electroluminescence for device I and II with Commission Internationale de l'Eclairage (CIE) coordinates of (0.15, 0.21) and (0.16, 0.22), respectively. The maximum luminance of 1105 cd m^{-2} were resulted for device I whereas that of 1247 cd m^{-2} for device II respectively. Our results show that the organic ionic small molecule yields electroluminescence like the ionic phosphorescent molecules without additional components.

Table 1
Photophysical properties of compound 1.

Absorption		Emission λ_{max} (nm)			PLQY[b]	Electrochemical data		
λ_{max} (nm)[a]	Molar absorptivity $\varepsilon \times 10^4$ M^{-1} cm^{-1}	Solution[a]	Solid	Film		HOMO[c] (eV)	LUMO[d] (eV)	E_g[e] (eV)
266, 278, 356	5.12, 7.57, 7.98	420	453	454	0.77	−5.64	−2.54	3.10

[a] Measured in acetonitrile solution (10^{-5} M) at room temperature.
[b] Photoluminescence quantum yields of the compound 1 in acetonitrile solution were measured using 9,10-diphenylanthracene ($\Phi \sim 0.9$) as the standard [45].
[c] HOMO energy level were calculated from oxidation onset potential.
[d] LUMO energy level were obtained by adding the optical band gap (E_g) to the calculated HOMO energy.
[e] The optical band gap (E_g) calculated from the onset of absorption spectrum.
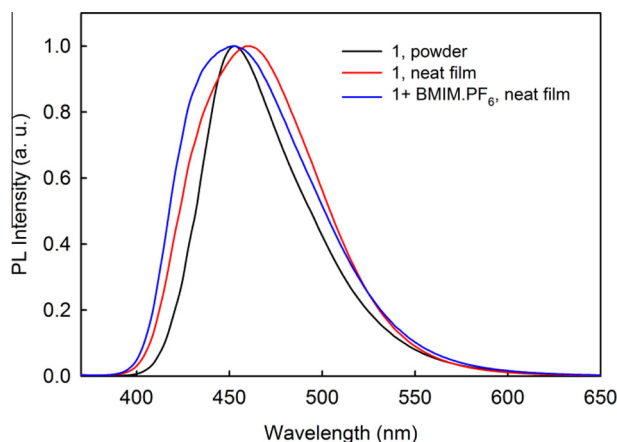
Fig. 2. Normalized PL spectra of solid (powder) and thin films of compound 1.

2. Results and discussion

2.1. Synthesis

Scheme 1 outlines the synthetic route of compound 1. Suzuki coupling of 2,7-dibromo-9,9-bis(6-bromohexyl)fluorene (3) [40–42] with pyrene-1-boronicacid gave the coupled product (4). The final product 1 was synthesized by treating (4) with 1-methylimidazole, followed by an ion exchange reaction with potassium hexafluorophosphate in 72% yield of compound 1.

2.2. Photophysical properties

The UV–visible absorption and emission spectra were measured in dilute acetonitrile solution at room temperature as shown in Fig. 1. The absorption spectrum of compound 1 in acetonitrile solution exhibits broad and highly intense absorption band at 356 nm which is a characteristic of π–π^* transition of pyrene substituted fluorene conjugated system [43]. Photophysical characteristics were summarized in Table 1. Photoluminescence (PL) spectrum of compound 1 in solution shows an intense fluorescence with an emission centered at 420 nm which corresponds to the light emission in blue region and exhibits a high quantum yield of 77% in solution. The optical energy gap (E_g) was calculated from the onset potential of the absorption spectrum of compound 1 to be 3.10 eV. Thin film and solid (powder of compound1) PL spectra were also measured as shown in Fig. 2. Thin films were prepared
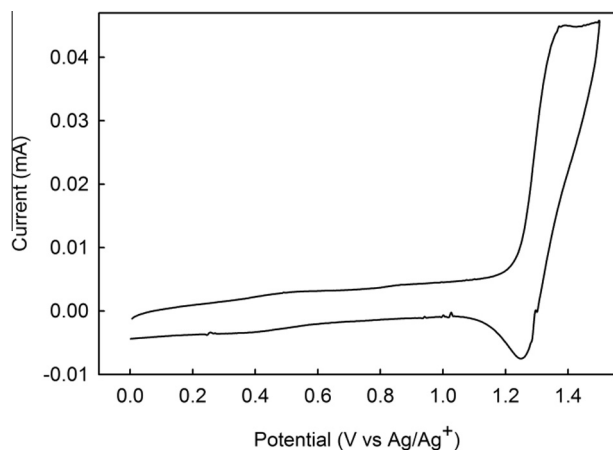
from acetonitrile solution of compound 1 with and without ionic liquid BMIM·PF$_6$ on glass substrates by spin coating.

For compound 1, thin film emission spectrum shows an intense fluorescence emission centered at 454 nm which is red shifted up to 34 nm as compared to their solution spectrum due to molecular polarization effects in organic small molecules [44], whereas thin film with 10% BMIM·PF$_6$ also exhibits the same. The addition of ionic liquid BMIM·PF$_6$ did not shows any significant changes in the photoluminescence properties of compound 1. The PL spectra of compound 1 in its solid (powder form) were shifted up to 30 nm centered at 453 nm as compared to their solution PL spectrum which may be due to the π–π stacking interaction in solid state.

2.3. Cyclic voltammetry

The electrochemical properties were measured by cyclic voltammetry experiment to determine the HOMO (highest occupied molecular orbital) energy level of compound 1. The voltammogram experiments were carried out in acetonitrile solution containing 0.1 M of Bu$_4$PF$_6$ as a supporting electrolyte. The energy level of compound 1 were estimated by using the ferrocene/ferrocenium ion (Fc/Fc$^+$) as the reference redox system. Compound 1 was dissolved in the electrolyte solution with the concentration of 10^{-3} M solution. Fig. 3 shows the electrochemical property of compound 1.

The onset oxidation potential of compound 1 was 1.24 V and the corresponding highest occupied molecular orbital (HOMO) energy level was calculated by using the formula $E_{HOMO} = -4.4 - E_{onset\ (ox)}$ to be −5.64 eV [46]. The lowest unoccupied molecular orbital (LUMO) energy was −2.54 eV by adding the optical band gap (E_g) to the calculated HOMO energy level.

2.4. Density functional theory (DFT) calculations

Density functional theory (DFT) calculations were carried out for compound 1 using Gaussian 09 program package [47]. The
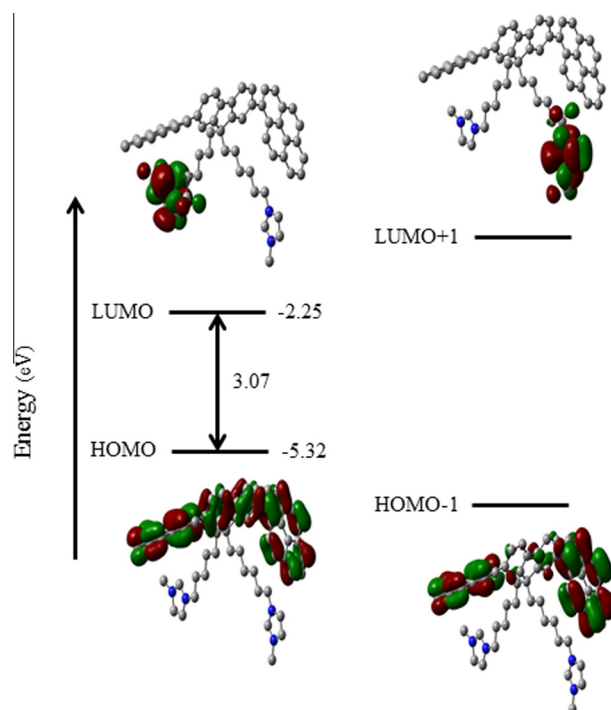

Fig. 3. Cyclic voltammogram of compound 1.

Fig. 4. Energy and electron density contours calculated for the HOMO − 1 to the LUMO + 1 of compound 1 in ground state.

ground state geometry (S_0) of the compound 1 was fully optimized with Becke's [48,49] three-parameter functional and the correlation functional of Lee–Yang–Parr [50] (B3LYP) using a standard 6-31G(d,p) basis set on all atoms. Vibrational frequency calculations were performed at the same level of theory to confirm that the configuration was a minimum on the potential energy surface. On the basis of the optimized structure of compound 1, the population analysis simulations were carried out to obtain the electron isodensity contours (Fig. 4) of selected frontier molecular orbitals. Using the DFT calculations, the structure and electronic properties of compound 1 were obtained. The two pyrene rings present on the fluorene (at 2,7 positions) are oriented in the opposite direction with a dihedral angle of *ca.* −50°. Two hexyl groups are present on the sp³ carbon of fluorene, i.e. at the 9th position and each of the hexyl group has one N-methyl imidazole ring. The spatial orientation of two pyrene rings and two hexyl chains in compound 1 gave a pseudo tetrahedral geometry.

The Kohn–Sham orbitals (with isosurface value of 0.02 e Å^{-3}) of compound 1 are displayed in Fig. 4. In the highest occupied molecular orbital (HOMO), the electron density is evenly distributed over fluorene and two pyrene rings. In HOMO − 1 however, the electron density is mainly localized on two pyrene rings. For the lowest unoccupied molecular orbital (LUMO), the electron density is completely shifted to one of the imidazole ring. In LUMO + 1, the electron density is shifted to another imidazole ring. The computed HOMO, LUMO and HOMO–LUMO gap (HLG) values are −5.32, −2.25 and 3.07 eV, respectively and for HOMO − 1 and LUMO + 1 are −5.50 and −2.08 eV, respectively.

2.5. Electroluminescent properties of LEC devices

The favorable photophysical properties reveals that compound 1 can be applicable for LEC applications. The constructed device structure have the configuration of glass substrate/ITO/poly(3,4-e

thylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, 40 nm)/emissive layer (ca. 75 nm)/Al (100 nm). Table 2 summarizes the detailed electroluminescent properties of the compound 1. Device I consist of neat film of compound 1 whereas device II is a thin film of compound 1 containing 10 wt% BMIM·PF$_6$ spin coated from acetonitrile solution. Ionic liquid BMIM·PF$_6$ was added to improve the ionic conductivity of the LEC device. Electroluminescence (EL) spectra of LEC devices I and II are displayed in Fig. 5.

LEC based on compound 1 exhibits the broad and structure less electroluminescence centered at 455 and 454 nm for devices I and II, respectively. The device containing ionic liquid (device II) did not show any characteristic change as compared to the device I EL spectrum. The EL spectra of devices I and II were shifted to longer wavelength due to formation of intermolecular excimers [44]. LEC based on both devices emitted blue light with CIE coordinates of (0.15, 0.21) and (0.16, 0.22) for device I and II respectively. The EL spectra of devices I and II were shifted to longer wavelength due to formation of intermolecular excimers [44]. LEC based on both devices emitted blue light with CIE coordinates of (0.15, 0.21) and (0.16, 0.22) for device I and II respectively.

The time-independent luminance versus voltage curves of devices I and II operated with a sweep rate of 0.5 V/s are shown in Fig. 6.

Both LEC device characteristics were summarized in Table 2. Fig. 7 displays the current density versus voltage curves of devices I and II operated with a sweep rate of 0.5 V/s. The luminance and

Table 2
LEC device characteristics of compound 1.

Device	Maximum luminance (cd m^{-2})	Maximum current density (mA cm^{-2})	Maximum current efficiency (cd A^{-1})	EL λ_{max} (nm)[a]	CIE coordinates[b]
I	1105	773	0.14	455	(0.15, 0.21)
II	1247	881	0.14	454	(0.16, 0.22)

[a] EL peak wavelength.
[b] CIE coordinates of EL spectra.

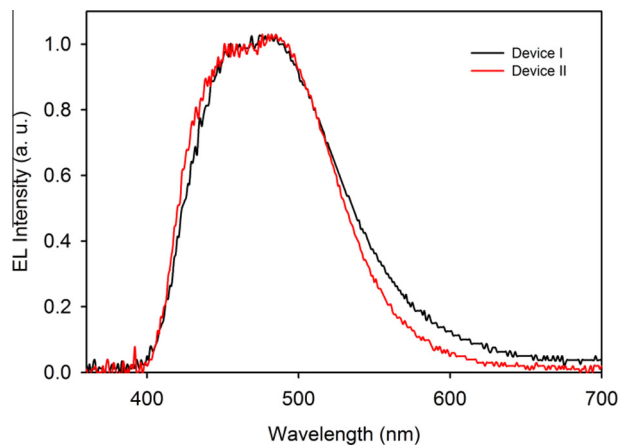**Fig. 6.** Luminance versus voltage curves of device I and II.

Fig. 5. Electroluminescence (EL) spectra of device I and device II.
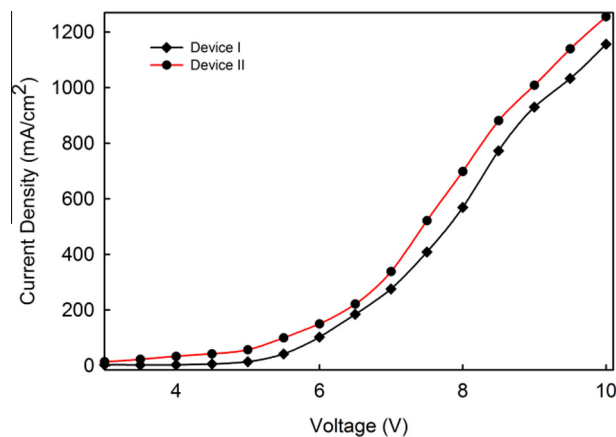
Fig. 7. Current density versus voltage curves of device I and II.

current density of both devices increased slowly with the increase of voltage, which reveals the characteristics of LEC devices. The luminance and current density of both the devices increases rapidly and reaches a luminance of 1105 cd m^{-2} and current density of 773 mA cm^{-2} for device I, whereas device II results a high luminance of 1247 cd m^{-2} and current density of 881 mA cm^{-2}. Current efficiency of device I and II are 0.14 cd A^{-1} and 0.14 cd A^{-1}, respectively. Device incorporating BMIM·PF$_6$ shows shorter response time to reach the maximum luminance than the device without ionic liquid because of the increased rate of accumulation of mobile ions near the electrodes, results the formation of doped regions [20]. In comparison to the reference 27, we reported the synthesis of active compound without using any ligand for synthesis of compound 1 (Scheme 1). And the theoretical validation of the properties using DFT studies were also done to gain insight into the photophysical and electrochemical properties of compound 1, which went in hand with the experimental results.

3. Conclusions

The strong fluorescence in solution and solid state ionic fluorene derivative were designed and synthesized. The fluorescence quantum yield of compound 1 in solution reaches 77%. Utilizing the intrinsic ionic nature of compound 1, efficient solution processed blue LECs are fabricated. Compound 1 has been used as the single active component in LEC devices employing air-stable electrodes. The fabricated LEC devices resulted blue color electroluminescence centered at 455 and 454 nm for device I and II with CIE coordinates of (0.15, 0.21) and (0.16, 0.22) respectively. Moreover, a high luminance of 1105 cd m^{-2} and 1247 cd m^{-2} were achieved for devices I and II, respectively. This is a big success because the reports demonstrate that the ionic fluorescent molecules can yield like the phosphorescent molecules and efficient electroluminescence without additional components.

4. Experimental section

4.1. Materials and methods

All the reactants and solvents were purchased from commercial suppliers used without any further purification. ^{1}H NMR spectra of compounds were recorded at room temperature using a Varian unity Inova 500 MHz spectrometer. Handling, purification and spin coating process were carried out under ambient condition. UV–visible absorption and photoluminescence emission spectra were measured at room temperature using UV–VIS spectrometer, Lamda-20, PerkinElmer and Hitachi F-7000 FL spectrophotometer in 10^{-5} M acetonitrile solution. Photoluminescence quantum yields (PLQYs) of compound 1 were measured in acetonitrile solution using 9, 10-diphenylanthracene as a standard. The optical band gap (E_g) energy level was obtained from the absorption onset potential of compound 1. Thin film PL spectra were measured by spin-coating the compound 1 from acetonitrile solution on glass substrate. Electrochemical properties of compound 1 were measured in acetonitrile solution (10^{-3} M) using cyclic voltammetry (CV) model of potentiostat/galvanostat (Iviumstat) voltammetric analyzer with a scan rate 100 mV s^{-1}. An electrochemical cell consists of platinum as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode. 0.1 M acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$) was used as a supporting electrolyte. All the potentials were recorded against ferrocenium/ferrocene Fc$^+$/Fc) was used as an internal standard. The HOMO energy level of the molecule calculated from onset oxidation potentials using the formula $E_{HOMO} = -4.4 - E_{onset\ (ox)}$ and the LUMO was calculated by the

adding the E_g to the calculated HOMO energy level. Density Functional theory (DFT) calculations were performed by using Gaussian 09 program package.

4.2. Synthesis of 2,7-dibromo-9,9-bis-(6-bromohexyl)fluorene (3)

2,7-Dibromofluorene (2) (1.62 g, 5 mmol) was added to a mixture of aq. potassium hydroxide (100 mL, 50 wt%), tetrabutylammonium bromide (0.32 g, 1 mmol) and 1,6-dibromohexane (12.20 g, 50 mmol) at 75 °C, maintained for 15 min, after that mixture was cooled to room temperature, extracted with dichloromethane. The combined organic layers were washed with water, aq. HCl and brine solution, dried over sodium sulfate and evaporated. The crude was purified by silica-gel column chromatography using hexane and ethyl acetate as the eluent, recrystallized from ethanol and dichloromethane as a white crystal (1.4 g, 43%).

4.3. Synthesis of 1,1′-(9,9-bis(6-bromohexyl)-9H-fluorene-2,7-diyl)dipyrene (4)

Suzuki cross-coupling between 2,7-dibromo-9,9-bis-(6-bromo hexyl)fluorene (3) (0.35 g, 0.53 mmol) and pyrene-1-boronic acid (0.29 g, 1.16 mmol) in the presence of Pd(PPh$_3$)$_4$ (46 mg, 0.04 mmol) and K$_2$CO$_3$ (0.69 g, 5.00 mmol) in toluene/water (2:1, v/v) was degassed for 45 min and then refluxed for 16 h under argon atmosphere. The reaction mass was cooled to room temperature, extracted with dichloromethane and organic layer washed with water, aq. sodium bicarbonate and brine solution, dried over sodium sulfate and solvent was evaporated. The residue was purified by silica-gel column chromatography using hexane and ethyl acetate as the eluent in 62% yield. ^{1}H NMR (300 MHz, CDCl$_3$, ppm) δ 8.28–8.22 (m, 8H), 8.14 (m, 7H), 8.07–8.01 (m, 5H), 7.67 (d, 4H), 3.33 (t, 4H), 2.11 (m, 4H), 1.75 (m, 4H), 1.32–1.20 (m, 8H), 0.96 (m, 4H).

4.4. Synthesis of (1)

A solution of (4) (0.27 g, 0.30 mmol) and 1-methylimidazole (55 mg, 0.66 mmol in 5 mL toluene was heated to reflux for 24 h and cooled to room temperature. Then the reaction mass was concentrated, then dissolved in 3 mL methanol and aqueous solution of KPF6 (0.27 g, 1.50 mmol) was added, stirred for 30 min. Off-white powder was collected by filtration to yield (1) in 72%. ^{1}H NMR (300 MHz, DMSO-d$_6$, ppm) δ 9.03 (s, 2H), 8.42 (d, 2H), 8.34–8.32 (m, 4H), 8.27 (d, 4H), 8.15 (m, 10H), 7.78 (d, 2H), 7.66 (m, 4H), 7.60 (d, 2H), 4.05 (t, 4H), 3.73 (s, 6H), 2.15 (m, 4H), 1.63 (m, 4H), 1.13 (m, 8H), 0.82 (m, 4H).

4.5. Fabrication and characterization of LEC devices

Electroluminescence devices were fabricated on ITO coated glass substrate using buffer layer poly(3,4-ethylenedioxythiophene):poly styrenesulfonate (PEDOT:PSS) and compound 1 in acetonitrile solution as an emissive layer. Initially the ITO coated glass substrate were cleaned in an ultrasonic bath containing mixed solvents such as acetone, ethanol and isopropanol for 1 h and UV-ozone treated for 30 min. A 80 nm layer of PEDOT:PSS was spin-coated onto ITO substrate at 2000 rpm for 20 s in air and baked at 120 °C for 30 min. For LEC devices emissive layer of compound 1 was spin-coated onto the ITO/PEDOT:PSS layer from acetonitrile solution and annealed at 80 °C for 1 h. Devices I and II were spin-coated from acetonitrile solution of compound 1 and device II containing 10 wt% BMIM·PF$_6$. All the process was performed under air and moisture environment. Finally, the devices were subjected into thermal evaporation of aluminium onto the emissive layer in a closed vacuum chamber under high pressure.

Electroluminescence characteristics of the LEC devices were measured using a Keithley 2400 source meter and calibrated with a silicon photodiode. The EL spectrum and CIE coordinates were measured by using an Avantes luminance spectrometer.

Acknowledgements

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