Carbazole based ionic small molecule emitter for non-doped light-emitting electrochemical cells

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ABSTRACT

Great efforts have been made to develop blue emitting organic small molecules for light-emitting electrochemical cells. Herein, blue emitting CPC (CarPhenCar) was synthesized and its emissive properties were studied. CPC exhibits blue fluorescence in toluene solution as well as in solid thin-films. CPC exhibits good thermal and electrochemical stabilities. Application of CPC molecule in solution processed light-emitting electrochemical cells resulted blue emission centered at 485 nm with brightness of 454 cd/m^2, current efficiencies of 1.33 cd/A and external quantum efficiencies of 1.76%. These results adequately demonstrate the practicability of tuning the emission color of phenothiazine derivative into blue region.

1. Introduction

In the past three decades, organic semiconducting materials have attracted intense scientific attentions due their vast applications in flat-panel displays and solid-state lightings [1]. The introduction of organic electroluminescent materials into the lightings have recently break-through more attention on solution processing organic light-emitting diodes (OLEDs). However, the solution processing require severe control of the fabrication process to control the thickness of the layer in nanometer-scale. Moreover OLEDs have other disadvantages like complicated and time-consuming multi-layer process. To simplify the barriers of OLED fabrication techniques, an efficient and promising alternative called light-emitting electrochemical cells (LECs) have been proposed by Pei and coworkers in 1995 [2]. LECs structure consists of single light-emitting layers with mobile ions enable to operate LECs in distinct fashion compared with OLEDs. The movement of mobile ions towards respective electrodes under an applied current will create electrochemical doping near the electrodes [3,4]. This accumulation leads to decrease the energy barrier so that the charge injection can take place easily in the organic emitters. The light-emitting materials for LECs are typically polymer compounds and ionic transition metal complexes (iTMCs) have been well utilized to date for constructing devices. Both the emitters have been widely studied their performances in LEC devices for their application in lightings [5–12]. Especially, cationic iridium based metal complexes are the far most materials used

for LECs compared to other metal complexes [13–19]. However, both materials have some defects that the purification of polymers and the cost of metals for the synthesis complexes leads to complicate the device cost. High performing metal complexes reported so far are longer wavelength emitting devices so that the tuning color of iTMCs implies to the reduction of stability and efficiency of the LEC devices [18–20]. Therefore, the drawbacks of well explored materials leads to the development of organic materials as active components in light-emitting devices enable their potential use in electronics and lighting applications. Small molecules have the advantages of high brightness, color purity and color tunability through the synthetic modification. The implementation of organic small molecules by Hill et al. as light-emitting materials in the fabrication of LECs made the great breakthrough of avoiding rare metal complexes in LEC devices [21]. Since the material was perylene based neutral small molecule which uses the additional ions in the active layer. An ionic species are essential for electrochemical doping in LEC devices, so Chen et al. reported LEC devices based on an ionic terfluorene active emitter to simplify the device architecture [22]. A wide range of organic small molecules have been developed for LECs from the last decade. Among them, an ionic organic small molecules have been attracted tremendously due to their intrinsic ionic nature and tunable emission color in recent years [23–39]. The variety of light emission were occurred by utilizing different ionic small molecules in LEC devices. Small molecules represent the significant development of solution processed, low-cost light-emitting LEC devices.
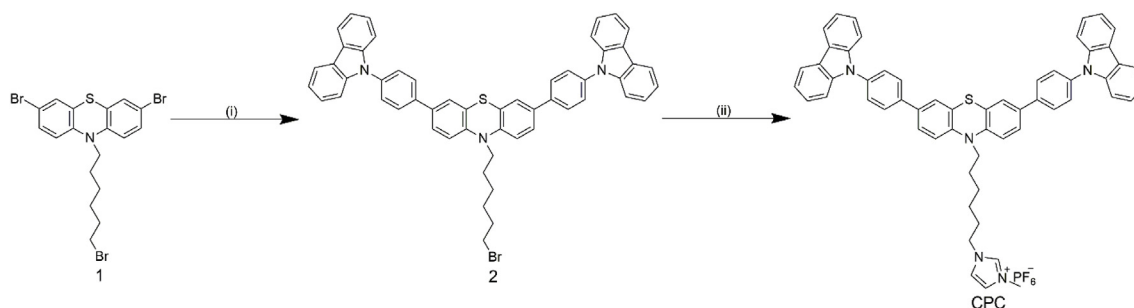
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Scheme 1. i) Pd(PPh₃)₄, TBAB, K₂CO₃, THF/H₂O. ii) 1-methylimidazole, Toluene.

In this study we present synthesis and characterization of an ionic organic small molecule for solution processed LEC applications.

2. Experimental section

All the chemical reagents were used as received from the commercial suppliers. All the reactions carried out under an inert gas atmosphere. Compound 1 was prepared by following the previously reported procedure. ^{1}H NMR spectra were recorded on Varian Unity Inova 500 MHz FT-NMR spectrometer in CDCl₃ and DMSO-d_6 using tetramethylsilane (TMS) as internal standard. High resolution mass spectra were measured on a FAB high resolution MS/MS system. Ultraviolet (UV)-visible (vis) absorption spectra of both the compounds in dilute solutions were recorded on 8453 UV-vis Agilent spectrophotometer. Photoluminescence spectra of solution and thin-film were measured with F-7000 FL spectrophotometer. The fluorescence quantum yields were determined using 9, 10-diphenylanthracene as standard. Thermal stabilities of the materials were examined by thermogravimetric analysis (TGA) Netzsch TG 209 instruments and differential scanning calorimetry (DSC) TA Instruments Q200. Cyclic voltammetry (CV) experiments were carried out in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 100 mV/s by using platinum as working electrode, platinum wire as counter electrode and Ag/AgCl as the reference electrode on CV model of potentiostat/galvanostat (Iviumstat) voltammetric analyzer.

3. Synthesis of 2

A mixture of 1 (0.50 g, 0.96 mmol), boronic ester (0.70 g, 2.40 mmol), Pd(PPh₃)₄ (0.05 g, 0.04 mmol), potassium carbonate (0.66 g, 4.80 mmol) in tetrahydrofuron/water mixture was stirred at 65 °C for overnight under Ar. Subsequently, the reaction mixture was cooled to room temperature, water and dichloromethane was adder for extraction. The extracted organic layer was dried over sodium sulphate and concentrated in vacuum. The resulting crude was purified by column chromatography on silica gel eluting with n-hexane/ethyl acetate (7/3; v/v) to give the product. The desired product was recrystallized from dichloromethane/hexane as a yellow solid in 72% yield. ^{1}H NMR (CDCl₃, δ): 8.18 (m, 4H), 7.78 (m, 4H), 7.60 (m, 4H), 7.50 (m, 12H), 7.30 (m, 4H), 6.95 (m, 2H), 3.95 (t, 2H), 3.40 (t, 2H), 1.90 (m, 4H), 1.65 (m, 2H), 1.45 (m, 2H).

4. Synthesis of CPC

Compound 2 (0.50 g, 0.59 mmol) was refluxed with excess 1-methylimidazole in 5 mL toluene for overnight under argon atmosphere. Then the mass was concentrated and the solid was obtained by adding saturated KPF₆ solution and stirred for 2 h and filtered washed with excess water and dried. The final compound was purified from dicholoromethane/hexane recrystallization as yellow solid in 83% yield. ^{1}H NMR (CDCl₃, δ): 8.40 (s, 1H), 8.15 (m, 4H), 7.80–7.60 (m, 5H), 7.60–7.50 (m, 4H), 7.45–7.35 (m, 11H), 7.32–7.25 (m, 6H), 7.10 (m, 2H), 4.10 (t, 2H), 4.00 (t, 2H), 3.80 (s, 3H), 1.80 (m, 4H), 1.50 (m, 2H), 1.30 (m, 2H).

5. Device fabrication and measurements

LEC devices were grown on ITO coated glass substrates by solution process spin of materials by spin coating techniques. Before prior to coating materials on ITO substrates, the substrates were cleaned ultrasonically in mixture solvents and dried under vacuum. Then the hole transporting PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)) were coated and dried at 120 °C for 30 min in a vacuum oven. The materials (2%) were dissolved in acetonitrile and filtered for process. Active layer was spin coated on PEDOT:PSS layer and dried in vacuum oven at 80 °C for 1 h. And, finally aluminium cathode was thermally evaporated under high vacuum through a shadow mask on the top of the active layer. Current-brightness-voltage characteristics were measured through constant voltage scanning to evaluate the LEC device properties. Electroluminescence and CIE (Commission International de I'Eclairage) color coordinates were measured by using Avantes luminance spectrum. Keithley 2400 source meter coupled with an OPC optical spectrum analyzer were used to characterize the device performances. All the device measurements were carried out in an ambient atmosphere.

6. Results and discussion

The synthesis of CPC used in this study was outlined Scheme 1. The brominated phenothiazine was used for Suzuki coupling with carbazole derivative and the product was subsequently reacted with excess 1-methylimidazole to obtain final compound.

7. Photophysical properties

The electronic absorption and photoluminescence spectra of CPC in dilute toluene solution was depicted in Fig. 1 and all the spectral data were summarized in Table 1.

In the absorption spectra, compound shows absorption features at 361, 338, 323 and 312 nm are seen for compound CPC. These peaks were attributed from π−π* transition of the molecule and the optical energy gap of the molecule was calculated from the onset of absorption spectrum, estimated to be 3.18 eV. To investigate the luminescent properties of compound CPC, photoluminescence spectra were recorded in solution as well as in thin films, both neat and doped with ionic liquid (BMIM.PF₆). The PL emission profile of compound CPC was characterized by maximum emission at around 478 nm in toluene solution indicates that the compound exhibited blue fluorescence in solution. The PL quantum yield (PLQY) in solution was calculated to be 24% in solution. The PL spectra of neat film and doped film were shown in Fig. S1. The emission profiles were found to be similar for both the films. Thin film photoluminescence spectra of both the films were centered at 484 nm which is slightly red shifted compared to the
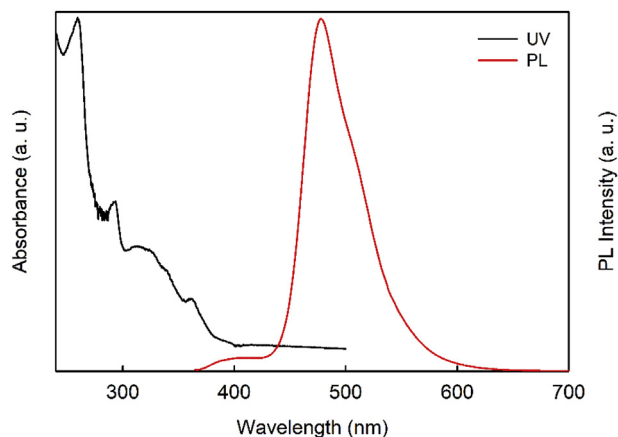
Fig. 1. Normalized absorption and PL spectra of CPC in toluene solution $(10^{-5}\,M)$.

Fig. 2. Cyclic voltammogram of CPC.

solution emission spectrum. The emission spectra of compound in different solvent polarity were measured to examine the solvatochromic behavior of the compound. The spectra were presented in Fig. S2. Upon increasing the polarity of the solvent, less pronounced positive solvatochromism with red shifted emission were observed due to the intramolecular charge transfer of the molecules. These results shows that the CPC has very low dependence on solvent polarities compared with previously reported molecules [30,33] and the all above prominent characteristics of CPC making to perform in LEC devices.

8. Electrochemical properties

The electrochemical characteristics were studied by cyclic voltammetry (CV) as shown in Fig. 2.

The system was characterized by reversible oxidation feature to calculate the highest occupied molecular orbital (HOMO) of the compound. Oxidation was occurs from the electron rich carbazole and phenothiazine units. The HOMO of the molecule was calculated from the onset of oxidation curve found to be −5.07 eV. The electrochemical band gap was obtained from the edge of UV-visible absorption spectroscopy in toluene solution to be 3.18 eV. The lowest unoccupied molecular orbital (LUMO) was calculated by summing the energy gap and the HOMO of the molecule was found to be −1.88 eV.

9. Thermal properties

Thermal stability of synthesized compound was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an inert condition. As seen Fig. 3, the thermal decomposition temperature of the material was measured to be 374 °C which defined as the 5% weight loss of compound at this temperature.

The high stability indicates the application potential of the material in lighting devices. The glass transition temperature of the molecule was determined from the DSC curve depicted in Fig. S3 was detected at 134 °C. No crystallization peak was observed when heating up to 200 °C
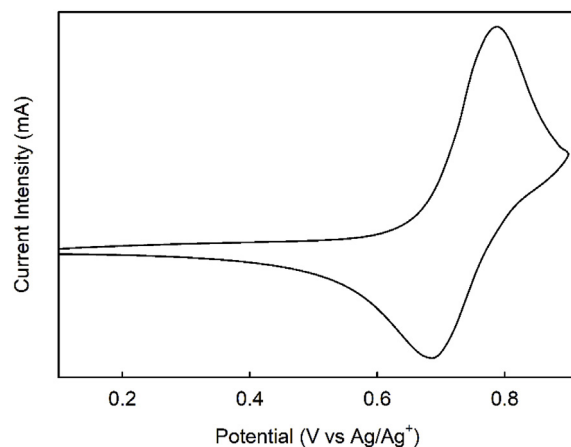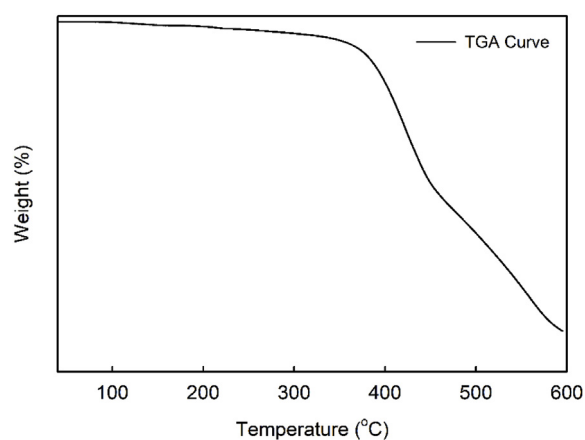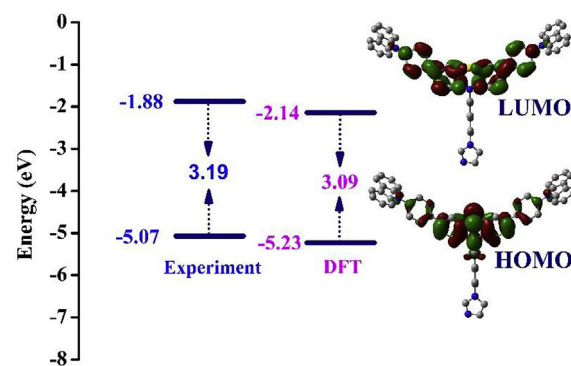

Fig. 3. TGA curve of CPC.

Fig. 4. The electron density contours calculated for the frontier molecular orbitals of the compound CPC.

Table 1
Photophysical and thermal properties of CPC.

Compound	$\lambda_{UV,max}^{a}$ (nm)	$\lambda_{PL,max}^{a}$ (nm)	$\lambda_{UV,max}^{b}$ (nm)	$\lambda_{PL,max}^{b}$ (nm)	Φ_f^{c}	E_g^{d} (eV)	T_d^{e} (°C)
CPC	**361**	**478**	**345**	**484**	**0.24/0.02**	**3.18**	**374**

[a] Measured in toluene $(10^{-5}\,M)$ solution.
[b] Measured in film state.
[c] Photoluminescence quantum yield measured in toluene and film state.
[d] Optical band gap as determined from onset of absorption edge.
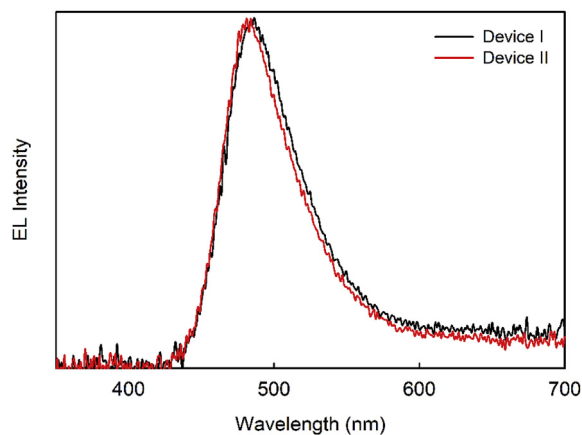[e] Thermal decomposition (T_d) temperature.

Fig. 5. Electroluminescence spectra of devices I&II.

clears that the molecules are amorphous in nature. Emissive small molecules with thermal and morphological stabilities are highly beneficial for the construction electroluminescent devices.

10. Theoretical calculations

To understand further insight into structural, electronic and optical properties of CPC were studied by using density functional theory (DFT) and time-dependent DFT (TD-DFT) on B3LYP/6-311G(d,p) level [40–44]. Fig. S4 illustrates the optimized ground state geometry of CPC and the corresponding dihedral angles on both side of phenothiazine ring are found to be similar. The butterfly structure were confirmed from the bond angles at S and N atom of 99.0° and 121.8°.

The calculated HOMO and LUMO energy levels of the compound were shown in Fig. 4. The HOMO electron density clouds were mainly falls on phenothiazine ring and the LUMO clouds were extended to the phenyl ring attached to the phenothiazine. The obtained HOMO and LUMO energy levels were found to be −5.23 and −2.14 eV. The LUMO energy is calculated by adding the TDDFT transition energy ($E_{S_0 \to S_1}$) to the Kohn-Sham eigenvalue of HOMO. The TDDFT energy values are in good agreement with the corresponding experimental values. In order to understand the electronic absorption in a solvent, TDDFT calculations were performed in toluene solvent. The calculated electronic absorption spectrum of the compound is shown in Fig. S5. The results obtained from TDDFT calculations of the first five singlet excitations are shown in Table S1. The calculated electronic absorption band observed at 402 nm which arises mainly from HOMO to LUMO excitation.

11. Device performance

The efficient solid state emission as well as high thermal stability of CPC prompts to investigate the effectiveness of material in LECs. The single component non-doped LEC devices were fabricated by using CPC from acetonitrile solution with the simple device configuration of ITO/PEDOT:PSS/CPC/Al. The electroluminescence spectrum of devices I

was peaked at 484 nm showing CPC emits blue light with Commission International de L'Eclairage (CIE) coordinates of (0.16, 0.33) are shown in Fig. 5.

The LEC device II containing ionic liquid BMIM.PF$_6$ shows blue light emission with CIE coordinates of (0.17, 0.33). Compared with the thin-film emission, no characteristic shift were observed for the electroluminescence of both the devices were resembles the emission of the thin-films. The light emission of the devices were turned to blue region compared with previously studied phenothiazine derivatives indicates that the carbazole moieties have high color tuning tendency of the phenothiazine derivatives compared with pyrene moieties [30,32]. The devices were turned on at low voltages and the brightness were reaches maximum values of 430 and 454 cd/m^2 for device I and device II, respectively. Devices were exhibits maximum current efficiencies of 1.29 cd/A and external quantum efficiency of 1.05% for device I, whereas maximum current efficiencies of 1.33 cd/A and maximum external quantum efficiency of 1.76% were achieved for device II. The current density-voltage-luminance curves were depicted in Figs. S6 and S7. The data were summarized in Table 2.

Relatively high luminance and efficiencies of device II were caused by addition of ionic liquid facilitates good charge injection and balanced charge transport properties of the devices. Overall these results reveal that the CPC is favored to tune the emission color of the devices with good performances.

12. Conclusions

This work demonstrates that the introduction of carbazole groups to phenothiazine core tune the emission color of the compound. The properties of the CPC were investigated experimentally and theoretically. The compound have high thermal stability and blue emission in solution as well as thin-films. Non-doped LEC devices were fabricated with CPC as an active material demonstrate good electroluminescent characteristics. The devices exhibit blue color emission with the CIE coordinates of (0.16, 0.33). The LEC devices incorporating BMIM.PF$_6$ shows slightly better performance than the pristine devices. This reports provides the development blue-emitting materials with improving the luminescence efficiencies of LEC devices.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2019.01.025.

Table 2
Electroluminescence performance of devices.

Devices	EL,$_{max}$[a] (nm)	CIE[b] (x,y)	Luminance (cd/m^2)[c]	Current efficiency (cd/A)[d]	EQE (%)[e]
I	484	(0.16, 0.33)	430	1.29	1.05
II	484	(0.17, 0.33)	454	1.33	1.76

[a] Maximum luminescence.
[b] Commission International de I'Eclairage coordinates.
[c] Maximum luminescence.
[d] Maximum current.
[e] Maximum external quantum efficiency.

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