



Phenothiazine derivatives as an easily accessible emitter for green light-emitting electrochemical cells

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ABSTRACT

A new phenothiazine derivatives of an ionic small molecules were synthesized and its photo- and electrochemical properties were evaluated. The compounds NPzN and PPzP exhibits good thermal stabilities and shows positive solvatochromism upon increasing the polarity of the solvents. The single-component electrochromism devices were fabricated from solution by incorporating both the emitters. Light-emitting electrochemical cell devices exhibited green color electroluminescence for both the compounds with the CIE coordinates of (0.28, 0.43) and (0.32, 0.41). These results indicate that phenothiazine derivatives have a promising prospect in the application of solution processed green LECs.

1. Introduction

The use of organic molecules as light-emitter have received great interests in recent years. Organic materials offer promising structural modification to found their application in optoelectronic devices. The significant growth of organic light-emitting diodes (OLEDs) [1] have been reached commercialization through mobile phones, displays and televisions. The layers in the OLED devices were fabricated by high vacuum thermal evaporation technique. This technique leads to increase the device cost for bulk preparation of efficient OLED devices. The fabrication limitation of OLEDs stimulates the researcher to find the alternatives over OLEDs. Light-emitting electrochemical cells (LECs) [2–10] referred to as solid-state lighting devices having simpler device architecture than OLEDs. LECs are simple device structure and fabricated from solution under ambient condition for low-cost electroluminescent devices as compared to OLEDs. The first ever LEC was reported by Pei and coworkers in 1995 using the fluorescent polymer as the electroluminescent material mixed with an ionic transporting polymer and an inorganic salt were sandwiched between two metal electrodes. The electroluminescent materials in LECs are organic emitters either neutral conjugated polymer (CP) [11–17] or an ionic transition metal complex (iTMC) [18–22] enables both ionic and electronic conduction. In general, iTMC based LECs are derived from second- and third-row transition metal ions, due to their strong metal-ligand interaction and luminescent efficiencies [23–27]. Nowadays organic small molecules have been focused for developing high

performance full-color flat panel displays and solid-state lighting technologies. Therefore, the synthesis of organic small molecules and establishment of their structural properties are essential for commercialization of cheaper products. The first organic small molecule based solid-state light emitting electrochemical cell was reported by Hill et al. [28]. The device architecture was similar to polymer based LEC devices. Thereafter, to simplify the thin film architecture, Chen et al. reported LEC devices based on an ionic terfluorene derivative as an active emitter [29]. An intrinsic ionic nature emerged great attention in LECs to develop charged organic small molecules for the ease of LEC fabrication. A solution processed LECs based organic small molecules have been effectively reported in recent years. Non-ionic [30–39] and ionic [40–50] small molecules are most commonly using active materials in LECs. The dual role of an ionic small molecules has attracted intensively to synthesize the fluorescent materials for LECs. In this study, we report an ionic phenothiazine based small molecules NPzN and PPzP comprising of naphthalene and phenanthrene cores. Both the compounds show green electroluminescence centered at 499 and 505 nm for compound NPzN and PPzP respectively, for the constructed LEC devices.

2. Experimental section

2.1. General information

¹H NMR spectra was measured with Varian unity Inova-300 MHz spectrometer at room temperature. Purification and spin coating

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process were processed under an ambient condition. Differential scanning calorimetry (DSC) was performed using a TA instruments Q200 KBSI operated at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken using a Netzsch TG 209 instrument. The thermal stability of the samples was determined by measuring their weight loss at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$. The UV–visible absorption and photoluminescence spectra of the compound were recorded on a UV–VIS spectrometer, Lambda-20, PerkinElmer and Hitachi F-7000 FL spectrophotometer, respectively. Photoluminescence quantum yield (PLQY) was measured in toluene solution using 9, 10-diphenylanthracene as a standard. The optical band gap (E_g) was obtained from the absorption onset potential. Cyclic voltammetry (CV) measurements were performed on cyclic voltammetry (CV) model of potentiostat/galvanostat (Iviumstat) voltammetry 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 hexafluoro phosphate (TBAPF₆, 0.10 M) was used as the supporting electrolyte and acetonitrile as the solvent, respectively. The experiments were calibrated with the standard ferrocenium/ferrocene (Fc⁺/Fc) system. The HOMO energy level of the molecule calculated from the onset of oxidation potentials using the formula $E_{\text{HOMO}} = -4.40 - E_{\text{onset}}(\text{ox})$ and the LUMO was obtained by adding the E_g to the calculated HOMO energy level. All the reported quantum chemical calculations have been performed with Gaussian 09 program and for a computational simplicity, we have modeled the compounds NPzN and PPzP by removing the methyl group (on imidazole) and PF₆⁻ counter ion. First, the ground state structures of two compounds were optimized using the density functional theory (DFT). We used B3LYP [51–53] exchange-correlation functional in combination with 6-31G(d) basis set for optimization and frequency analysis. The optimized geometries were then subjected to the vibrational frequency analysis to confirm that the obtained configuration is indeed a minimum on the potential energy surface. The time dependent DFT (TDDFT) simulations were also performed on the optimized geometries to calculate the excitation energies. The TDDFT simulations were performed at the same [6-31G(d)] level of theory as used for the geometry optimization using CAM-B3LYP [54] functional which includes the long-range corrections. We model the experimental toluene solution using the polarizable continuum model (PCM) [55,56] in TDDFT simulations for correct description.

2.2. Synthesis

The active compounds NPzN and PPzP were designed and synthesized through multi-step reactions as depicted in Scheme 1. The intermediate compound 1 was synthesized according to previous report [48].

2.3. Synthesis of 2

Compound 1 (0.50 g, 0.96 mmol), 2-naphthalene boronic acid (0.41 g, 2.40 mmol), Pd(PPh₃)₄ (0.04 g, 0.04 mmol), TBAB (0.03 g, 0.10 mmol) and K₂CO₃ (0.66 g, 5.00 mmol) were added to 2:1 (V/V) mixture of tetrahydrofuran/water under argon atmosphere. The reaction mixture was refluxed at $70\text{ }^{\circ}\text{C}$ for 24 h. Upon completion of the reaction, the mass was cooled to room temperature, the mixture was extracted with dichloromethane and dried over sodium sulfate. The extracted mass was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with *n*-hexane/ethyl acetate (9/1; v/v) to afford compound 2 as solid. Yield: 76%. ¹H NMR (300 MHz, CDCl₃, δ): 7.94–7.82 (m, 4H), 7.78–7.66 (m, 4H), 7.60–7.36 (m, 10H), 7.16–7.06 (m, 2H), 3.80 (t, 2H), 3.45 (t, 2H), 2.10–1.90 (m, 4H), 1.75–1.50 (m, 4H).

2.4. Synthesis of 3

Using above synthetic procedure compound 3 was obtained as a solid by replacing 9-phenanthrene boronic acid instead of 2-naphthalene boronic acid. Yield: 79%. ¹H NMR (300 MHz, CDCl₃, δ): 7.93–7.78 (m, 6H), 7.70–7.58 (m, 10H), 7.45–7.35 (m, 4H), 7.25–7.20 (m, 4H), 3.83 (t, 2H), 3.40 (t, 2H), 2.15–1.96 (m, 4H), 1.79–1.52 (m, 4H).

2.5. Synthesis of NPzN

To the solution of compound 2 (0.25 g, 0.41 mmol) in 5 mL toluene was added excess 1-methylimidazole (2 mL) and the resulting reaction mixture was refluxed for overnight under argon atmosphere. After completion of reaction, the reaction mass was concentrated and the final product NPzN was obtained by adding saturated NH₄PF₆ solution and stirred for 2 h. Then the resulting solid was filtered and washed several times with water and hexane. The product was dried in vacuum at $45\text{ }^{\circ}\text{C}$ for 16 h. Yield: 72%. ¹H NMR (300 MHz, d₆-DMSO, δ): 9.12–9.05 (s, 1H), 8.14–8.06 (m, 2H), 7.90–7.80 (m, 4H), 7.80–7.68 (m, 4H), 7.66–7.52 (m, 6H), 7.34–7.28 (m, 2H), 7.20–7.08 (m, 4H), 4.20 (t, 2H), 4.10 (t, 2H), 3.80 (s, 3H), 1.95–1.75 (m, 4H), 1.60–1.30 (m, 4H).

2.6. Synthesis of PPzP

Using a similar synthetic procedure of NPzN, compound PPzP was obtained by changing compound 3 instead of compound 2. Yield: 83%. ¹H NMR (300 MHz, d₆-DMSO, δ): 9.12–9.05 (s, 1H), 8.00–8.82 (m, 4H), 8.10–7.95 (m, 6H), 7.70–7.60 (m, 10H), 7.45–7.35 (m, 4H), 7.25–7.20 (m, 2H), 4.23 (t, 2H), 4.12 (t, 2H), 3.81 (s, 3H), 1.98–1.70 (m, 4H), 1.68–1.26 (m, 4H).

2.7. LEC device fabrication and characterization

Indium tin oxide (ITO) coated glass substrates were cleaned in ultrasonic bath of acetone, ethanol and isopropyl alcohol, dried in oven at $120\text{ }^{\circ}\text{C}$. 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 $120\text{ }^{\circ}\text{C}$ 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 $80\text{ }^{\circ}\text{C}$ 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. Constant voltage scan was subjected to evaluate our device properties. Electroluminescence spectra and CIE color coordinates were measured using an Avantes luminance spectrum. The current density and luminance *versus* voltage characteristics were measured by using Keithley 2400 source meter coupled with an OPC 2100 optical spectrum analyzer.

3. Results and discussion

3.1. Thermal and photophysical properties

Thermal decomposition temperatures (T_d) and glass transition temperatures (T_g) of compounds were evaluated by using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments. Both the compounds show high T_g of 102 and $118\text{ }^{\circ}\text{C}$ for compounds NPzN and PPzP respectively. The thermal decomposition temperatures (T_d) (corresponding to 5% weight loss) of 383 and $303\text{ }^{\circ}\text{C}$ for NPzN and PPzP were shown in Figs. S1 and S3. Photophysical characteristics of compounds were measured in dilute toluene solutions by using Ultraviolet-Visible (UV–vis) and photoluminescence (PL) spectrometers (Figs. 1 and 2).

NPzN shows maximum absorbance at 300 nm could be assigned to the π - π^* transition of the molecular backbone. The compound was

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