Synthesis and Photophysical Investigation of Phenothiazine Derivative

Kanagaraj Shanmugasundaram\textsuperscript{1,a}, Hyeonji Lee\textsuperscript{1,b}, Yeonah Jo\textsuperscript{1,c}, Jongseong Kim\textsuperscript{1,d}, Hangyu Park\textsuperscript{1,e}, Jumi Park\textsuperscript{1,f} and Youngson Choe\textsuperscript{1,*}

\textsuperscript{1}School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea.

\textsuperscript{a}k.shanraj@gmail.com, \textsuperscript{b}guswl4507@naver.com, \textsuperscript{c}whdusdk1@gmail.com, \textsuperscript{d}qnrhwhtjl@naver.com, \textsuperscript{e}atonnz@naver.com, \textsuperscript{f}qkrwnal55@naver.com

*Corresponding author

Keywords: Organic Small Molecule, Fluorescence, Phenothiazine.

Abstract. Organic small molecules have emerged as an attractive materials due to their potential application in optoelectronic devices. Phenothiazine based small molecule was synthesized and photophysically characterized. Compound shows high thermal stability and blue color emission both in solution as well as in solid states. The favorable photophysical properties of the compound shows their potentials in optoelectronic devices.

Introduction

Organic fluorescent materials have received great attention due to their potential application in optoelectronic devices. The rapid development progress of organic electronics will reduce the global warming caused efficiently from the general lightings. The last two decades, organic light-emitting diodes (OLEDs) were studied effectively and high performing OLEDs were demonstrated which now entered into display market. [1] However, efficient OLEDs were multi-layer devices from the sequential evaporation of the active materials under high vacuum which leads to high device cost. Single-layered electroluminescent devices, called light-emitting electrochemical cells (LECs), were introduced by Pei et al. in 1995 has simple device architecture utilizing air stable electrodes. [2] The charge transport in LEC devices were arises due to the presence of mobile ions in the active layer, thus makes LECs are superior alternative to OLEDs. Light-emitting materials in LECs are either ionic-transition metal complexes (iTMCs) [3-5] or polymers. [6-8] Organic small molecules have attracted much attention and found their way as an active material into LECs with polyethylene oxide and an inorganic salt. [9-11] However, the use of tri-component blend for charge transport process in LECs leads to phase separation in thin films. [2] To avoid the need for tri-component blend, emitters with charge transporting abilities are emerging materials for LECs. Recently, charged small molecules were successfully utilized as light-emitting material and serves dual role in LECs. [12-21] In this study, we report synthesis and photophysical characterization of sulfone form of charged naphthalene-phenothiazine derivative. The oxidized form of molecule resulted high thermal stabilities and blue emission in both solution as well as in thin-films. As a result of high thermal stability and favorable photophysical properties compound suggest that it would be beneficial for LEC device application.

Experimental Section

Reagents and solvents used for synthesis were purchased from commercial suppliers and were used as received. \textsuperscript{1}H spectra were measured on Varian unity Inova-300 MHz spectrometer with tetramethylsilane (TMS) as the internal standard. Lambda-20, PerkinElmer spectrophotometer and Hitachi F-7000 FL spectrophotometer were used to measure UV and PL. The electrochemical measurements were performed on cyclic voltammetry (CV) model of potentiotstat/galvanostat (Iviumstat) voltammetric analyzer with platinum working electrode and platinum wire counter electrode at a scanning rate 100 mV s\textsuperscript{-1} against Ag/AgCl as reference electrode. The HOMO energy
level of the molecule was calculated from the estimated onset potential of oxidation using the formula $E_{HOMO} = -4.40 - E_{onset (ox)}$ and the LUMO were obtained by summing the $E_g$ to the calculated HOMO energy level.

**Synthesis**

The synthetic routes of the intermediates and target compound were illustrated in Scheme 1. The intermediate (1) was synthesized according to our previous report. [21]

**Synthesis of 2**

To a stirred solution of compound 1 (1g, 3.84 mmol) in 60 mL dichloromethane (CH$_2$Cl$_2$) was added excess m-chloroperoxybenzoic acid (m-CPBA) at 0 °C. The resulting reaction mixture was stirred for 4h under inert atmosphere. After completion of reaction, the mass was diluted with 2M K$_2$CO$_3$ solution. The mixture was extracted with DCM and dried over Na$_2$SO$_4$, and evaporated to dryness. The crude product was purified by column chromatography on silica gel eluted with hexane/ethyl acetate to offer off-white solid of 2. Yield: 68%. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 8.21-8.16 (s, 2H), 7.74-7.64 (d, 2H), 7.28-7.16 (d, 2H), 4.20 (t, 2H), 3.40 (t, 2H), 1.95-1.82 (m, 4H), 1.61-1.40 (m, 4H).

**Scheme.** i) m-CPBA, DCM. ii) Pd(PPh$_3$)$_4$, TBAB, K$_2$CO$_3$, THF/H$_2$O. iii) 1-methylimidazole, Toluene.

**Synthesis of 3**

Compound 3 was synthesized according to previous report [21] as yellow solid. Yield: 62%. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 8.52-8.45 (m, 2H), 8.10-7.88 (m, 4H), 7.80-7.60 (m, 6H), 7.30-7.50 (m, 2H), 7.30-7.10 (m, 4H), 4.40 (t, 2H), 3.95 (s, 6H) 3.45 (t, 2H), 2.20-1.80 (m, 4H), 1.50-1.20 (m, 4H).

**Synthesis of Final Compound**

Final compound was synthesized and purified by following previous study. [21] Yield: 73%. $^1$H NMR (300 MHz, d$_6$-DMSO, $\delta$): 9.05 (s, 1H), 8.40-8.10 (m, 6H), 8.00-7.80 (m, 8H), 7.78-7.60 (m, 2H), 7.40-7.10 (m, 4H), 4.50 (t, 2H), 4.15 (t, 2H), 3.80 (s, 3H), 2.00-1.75 (m, 4H), 1.50-1.20 (m, 4H).

**Results and Discussion**

**Thermal Properties**

Thermal properties of the compound was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen flow at a scanning rate of 10 °C min$^{-1}$ were shown in Figure 1. The decomposition temperature ($T_d$, corresponding to 5% weight loss) of compound was high as 383 °C and high glass transition temperature ($T_g$) of 115 °C. The high glass transition temperature of the compound indicates stable glasses in its film state. The results of TGA and DSC studies were revealed that the compound possess higher thermal stability due to rigid molecular conformation of compound. The good thermal stability and high glass transition were prerequisite to form morphologically stable film for their application in optoelectronics.
Photophysical Properties

Photophysical properties of the compound were evaluated by measuring UV-visible absorption and photoluminescence spectrum in toluene solution and was shown in Fig. 2 (left). Compound shows maximum absorption at 340 nm were assigned to $\pi-\pi^*$ transition of the molecular backbone.

![Figure 2. UV-Visible Absorption and PL Spectrum of Compound in Toluene Solution (Left) and UV-Visible Absorption and PL Spectrum of Compound in Thin-Film (Right).](image)

The optical energy gap was measured from the onset of the absorption spectrum was estimated to be 3.24 eV. The emission maximum of compound in toluene solution was located at 395 nm. The fluorescent quantum yield of compound was found to be 0.21. The absorption and photoluminescence spectrum in thin films were displayed in Figure 2 (right). Its shows red-shifted emission spectrum up to 13 nm compared to its solution emission spectrum clearly indicate the presence of intermolecular interactions.

Electrochemical Properties

CV (Fig. 3) measurement was performed to evaluate the oxidation potential of the the material in acetonitrile solution was shown in Fig. 3. HOMO energy level of molecule was calculated from the onset of oxidation potential was found to be -5.56 eV. The LUMO energy level was calculated by summing the optical energy gap and HOMO energy level of the compound. The calculated LUMO energy level was found to be -2.32 eV. Compared with the previous molecule [21] reduced HOMO and LUMO energy levels were obtained for sulfone derivative which attributed from the strong electron affinity of sulfone unit. This results were revealed that change in the oxidation state of sulfur lowers the energy level of the molecule.
Electroluminescence Properties

To investigate the EL properties, electroluminescent devices were fabricated with the configuration of ITO/PEDOT:PSS/Active layer/Al. The light-emitting layer was processed from acetonitrile solution and the EL spectrum (Figure 4) of the devices were exhibited an emission band maximum at 498 nm with the observed CIE coordinates of (0.21, 0.31).

In comparison with their thin-film photoluminescence spectrum the observed EL were red-shifted up to 35 nm due to the intermolecular interaction between the molecules in the excited state. Devices showed a maximum brightness of 129 cd/m² and maximum current density of 101 mA/cm² at a voltage of 9.0 V.

Conclusions

The synthesized compound was exhibits deep blue emission in solution and as well as in thin-films. LEC devices were fabricated and devices shows red-shifted electroluminescence compared to its film emission due to molecular interaction in the solid-states. We believe that our results can provide the development of new emitters based on phenothiazine derivatives for future lighting applications.
Acknowledgements

This research work has been supported by Basic Science Research program through National Research Foundation of Korea (NRF) financial support by Ministry of Education, Science and Technology (NRF-2016R1D1A1B02013505) and Brain Korea 21 Plus project.

References


