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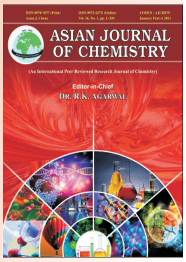

Synthesis and Properties of Imidazole-π-phenothiazine Derivatives as Light-Emitting and Ambipolar Materials†

JING SHAO[1,2], XIN ZHAO[1,2,*], XING HE[1,2], ZHENGYIN ZHANG[1,2] and RONGJIA ZHAI[1,2]

[1]College of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215011, Jiangsu, P.R. China
[2]Jiangsu Key Laboratory of Environmental Functional Materials, Suzhou 215009, Jiangsu Province, P.R. China

*Corresponding author: E-mail: zhaoxinsz@126.com

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Novel phenothiazine derivatives were designed and synthesized for application as electroluminescent materials. They were characterized by means of ^{1}H, ^{13}C NMR and FTIR. The optical, electrochemical and thermal properties were also investigated. The relationship between the chemical structure and the properties of these materials was evaluated. Due to the introduction of thiophene ring, these compounds exhibited efficient emission from blue to green and red shifs in absorption and photoluminescence spectra. With respect to thermal properties and the oxidation potentials, it can be turned by varying the conjugation length of compounds and the length of alkyl chains. Mostly, all four compounds had suited HOMO and LUMO energy levels which can be used not only hole-transporting but also electron-tansporting materials in organic light-emitting devices.

Keywords: Phenanthroimidazole, Phenothiazine, Light-emitting materials, Bipolar, Organic light-emitting diode.

INTRODUCTION

Since the pioneering work on organic light-emitting devices (OLEDs) was developed by the Kodak group, extensive research has been carried out to bring OLEDs into commercial applications in flat-panel displays and solid-state lightings[1,2]. Although the photoelectronic properties of OLEDs have been investigated thoroughly and great advances have been made in developing novel organic light-emitting materials, with high stability, powerful brightness and high current efficiency remain great interests[3,4].

Charge transport and balancing are key factors for obtaining high device efficiency. Recently some deep-blue emitters were realized by simultaneously incorporating donor and acceptor groups into one molecule and proved to be a promising method for obtaining a high performance deep-blue emitter[5-9]. Phenanthroimidazole is a class of molecules with π-conjugated system and planar structure and the imidazole group is an electron-deficient ring used as an acceptor unit. And more, phenanthroimidazole derivatives have been proved to be high efficient for electron injection or hole blocking[10] as well as blue emission[11]. Phenothiazine (PTZ) is a non-planar heterocyclic compound which has electron rich sulfur and nitrogen atoms with a butterfly conformation at the ground state[12]. The additional electron rich sulfur atom renders phenothiazine a stronger donor than other amines. In addition, its "butterfly" non-planar structure impedes π-stacking aggregation and intermolecular excimer formation, resulting in diverse optoelectronic applications[13,14]. Thermally and electrochemically stable phenothiazine is a strong electron donor, even better than triphenylamine, tetrahydroquinoline, carbazole and iminodibenzyles[15,16]. Not only phenothiazine is low cost but commercially available. It can be easily tailored by connecting soluble groups such as alkyl chains to the N atom to improve solubility. Thus, it is important for developing cost-effective and high properties organic light-emitting materials leading to the commercial application.

In this work, we use the donor-π-acceptor approach to design four new molecules by using phenanthroimidazole as the acceptor for its good electron-transporting mobility and phenothiazine (PTZ) as the donor for its good hole transport mobility and connecting them with different linkers, such as thiophene. The introduction of thiophene would allow a long π-conjugated system to be achieved, while integration of the alkyl chains could increase the solubility of materials. The physical and photophysical properties of these compounds

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were investigated with the aim of understanding the structure-property relationships and developing novel molecular π-conjugated bipolar materials for OLEDs.

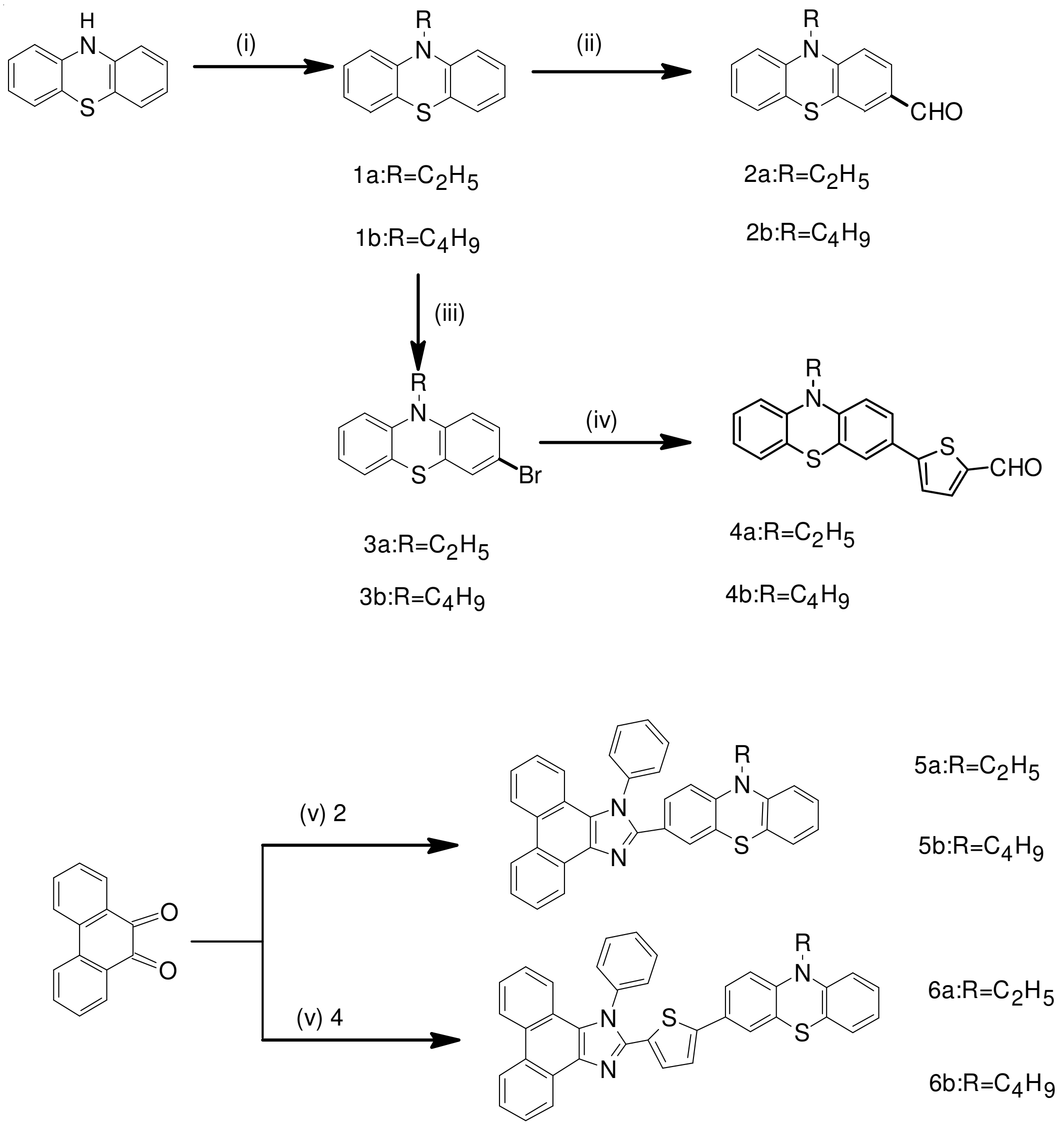
EXPERIMENTAL

All reagents were commercially used without further purification. Petroleum ether for column chromatography was redistilled.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400 MHz spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent. Infrared (IR) spectra were measured on a Perkine-Elmer FTIR spectroscopy spectrum RXI spectrometer as potassium bromide (KBr) disc. Ultraviolet visible (UV-VIS) spectra were recorded as a diluted solution in spectroscopic grade dichloromethane on a Perkine-Elmer UV Lambda 25 spectrometer. Photoluminescence spectra and the fluorescence quantum yields (Φ_F) were recorded with a Perkin-Elmer LS 50B Luminescence Spectrometer as a dilute solution in spectroscopic grade dichloromethane. Differential scanning calorimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a METTLER DSC823 thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, with heating rate of 10 °C/min under nitrogen atmosphere. Cyclic voltammetry (CV) measurements were carried out on an Autolab Potentiostat PGSTAT 12 with a three-electrode system (platinum counter electrode, glassy carbon working electrode and SCE electrode) at scan rate of 50 mV/s in dichloromethane under argon atmosphere. The concentrations of an analytical material and supporting electrolyte TBAP were 10^{-3} and 0.1 M, respectively.

RESULTS AND DISCUSSION

Synthesis: The molecular structures and synthetic route of the target compounds are outlined in **Scheme-I**. As illustrated in **Scheme-I**, we synthesize two series of four anthracenes bearing phenanthroimidazole, thiophene and phenothiazine. In the first series, we began the synthesis 1a with alkylation of phenothiazine at N-10 position with ethyl chain followed by Vilsmeier Reaction with $POCl_3$ and DMF to give **2a** in a fair



Scheme-I: Synthetic route to **5a**, **5b**, **6a** and **6b**. Reagents and conditions: (i) NaOH, DMSO, rt; (ii) DMF, $POCl_3$, reflux; (iii) NBS, DMF, rt; (iv) $Pd(PPh_3)_4$, 1 M Na_2CO_3, 1,2-dioxane, reflux; (v) phenanthraquinone, ammonium acetate, glacial acetic acid, 140 ºC yield of 78 %. Target **5a** was formed by Debus-Radziszewski imidazole synthesis reaction with **2a**, 9,10-phenanthrenequinone and ammonium acetate in 43 % yield as dark yellow solids. In order to enhance the solubility of organic light-emitting materials, we insert the butyl chain at N-10 position of phenothiazine to get **5b**, which is similar to **5a** in all synthetic steps. To study the employment of the thiophene ring in organic light-emitting materials, we synthesize another series of two compounds containg a thiophene. A two-step synthesis was carried out by regioselective bromination at C-3 position of **1a** with NBS in DMF followed by palladium-catalyzed Suzuki cross-coupling of the obtained 3a with Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ and 5-formyl-2-thiophen boronic acid in 1,2-dioxane at 100 ºC. Anthracene **4a** was obtained as a light yellow solid in an overall yield of 35 %. Using a simlar approach for **5a** by replacing **2a** with **4a**, a yellow solid **6a** was finally obtained in a good yield of 41 %. In the same way, **6b** was gained as a deep yellow solid in 47 % yield. All newly synthesized compounds were fully characterized by standard spectroscopic methods. They had good solubility in most organic solvents at room temperature, resulting from the presence of ethyl and butyl groups at the N-10 position of phenothiazine.

Photophysical properties: The photophysical properties of compounds **5a-6b** were examined by UV-visible spectroscopy and fluorescence spectroscopy in dilute CH$_2$Cl$_2$ solution at room temperature. All the data are summarized in Table-1 including compounds absorption maxima (λ_{abs}), photoluminescence emission maxima (λ_{em}), fluorescence quantum yields (Φ_F) and the Stokes shifts.

Fig. 1 presents UV-visible absorption and photoluminescence spectra of the four compounds in dilute CH$_2$Cl$_2$ solutions. For the absorption spectra, it can be seen that all compounds show similar absorption bands at a wavelength of 260 nm, which can be attributed to the π-π* transition of their common thiophene ring and benzene ring. The longer wavelength absorption bands vary in the range of 332-401 nm, which might be originated from the π-π* transition from the substituent on the 2-imidazole position to the phenanthroimidazole acceptor. On the other hand, it is worth noting that the difference in spectra of **5a** and **6a** is due to the introduction of the thiophene ring between phenanthroimidazole and phenothiazine, which enhances the extent of intramolecular charge transfer in **6a** and thus leads to a red shift (35 nm) of the absorption spectra. Whereas the UV-visible spectra of **5a** and **5b**, **6a** and **6b** were duplicate, it indicated that the effect of alkyl chain is slight.

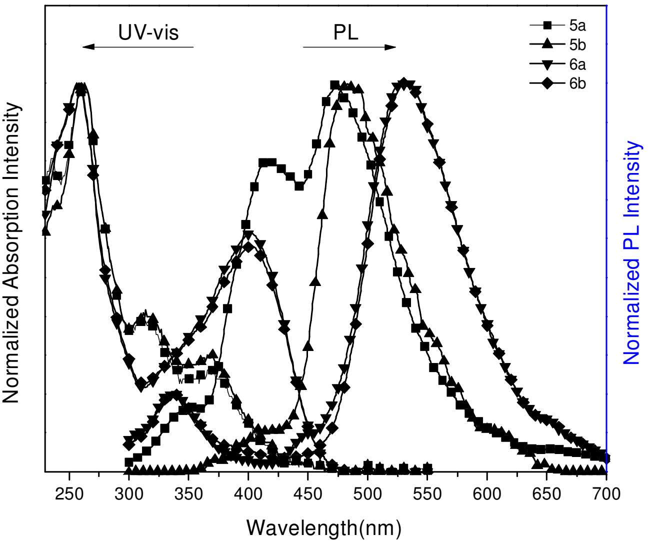


Fig. 1. UV-visible absorption and photoluminescence spectra of **5a**, **5b**, **6a** and **6b** measured in dilute CH$_2$Cl$_2$ solution

For the photoluminescence spectra, compounds **5a**, **5b**, **6a** and **6b** in solution CH$_2$Cl$_2$ ranging from blue to bright green colours with the peaks at 475, 483, 533 and 529 nm, respectively. The solution photoluminescence spectrum of **6a**, **6b** red-shifted with respect to that of **5a**, **5b**, whereas the photoluminescence spectra of **6a** and **6b** were duplicate. These results were in agreement to what was observed from the theoretical and UV-visible experiments.

The fluorescence quantum yields (Φ_F) were measured in CH$_2$Cl$_2$ using Rhodamine B (Φ = 0.69) as standard. The Φ value of 0.36 is observed for **5a**, which is higher than that of **5b**. This might be due to the increase of alkyl chain at N-10 position of phenothiazine resulted in the photoluminescence emission quenching of **5b**. For **6a** and **6b**, this change was also suitable. These materials showed a Stokes shift (109-132 nm) suggesting energy loss during the relaxation process and efficient fluorescence.

Electrochemical properties: Electrochemical behaviours of all four compounds were investigated by cyclic voltammetry (CV) in CH$_2$Cl$_2$ containg 0.1 M TBAP as a supporting electrolyte. Electrochemical band gaps were calculated from onset potentials of the anodic and cathodic waves. The HOMO energy levels of all compounds were calculated from the onset potential of oxidation (E_{onset}) with the formula expressed to E_{HOMO}= - [4.74 + E_{onset}(ox)], (-4.74 eV for SCE with respect to

TABLE-1
PHYSICAL AND PHOTOPHYSICAL DATA OF **5a**, **5b**, **6a** AND **6b**

Compound	λ_{abs}[a] (nm)	λ_{em}[a] (nm)	Stokes shift[b] (nm)	Φ_F[c]	T_g/T_d[d] (ºC)	E_g[e] (eV)	E_{HOMO}[f] (eV)	E_{LUMO}[f] (eV)	E_{onset}[g] (V)
5a	260, 317, 366	475	109	0.36	79/251	2.94	-5.61	-2.67	0.87
5b	262, 311, 365	483	118	0.19	134/298	2.85	-5.68	-2.83	0.94
6a	255, 401	533	132	0.34	–/374	2.71	-5.67	-2.96	0.93
6b	257, 401	529	128	0.17	–/250	2.71	-5.57	-2.86	0.83

[a]Measured in a dilute CH$_2$Cl$_2$ solution. [b]Stokes shift calculated from the difference between λ_{max} of the absorption and emission spectra. [c]Determined in CH$_2$Cl$_2$ solutions (A < 0.1) at room temperature using Rhodamine B solution in ethanol (Φ_F = 0.69) as a standard. [d]Obtained from DSC on the second heating cycle and TGA measurements under N$_2$ at a heating rate of 10 ºC/min. [e]Estimated from the onset of the absorption spectra (E_g = 1240/λ_{onset}). [f]Calculated using the empirical equation: E_{HOMO} = -(4.74 + E_{onset}) and E_{LUMO} = HOMO + Eg. [g]Measured using a three-electrode systemfitted with a glassy carbon working electrode, a platinum rod counter electrode and SCE reference electrode in degassed CH$_2$Cl$_2$ containing 0.1 M TBAP as a supporting electrolyte at a scan rate of 50 mV/s.

the zero vacuum level). Moreover, we calculated the LUMO energy levels from the HOMO energy levels and their respective band gap energy obtained from the tail-end of their UV-VIS absorptions. Fig. 2 presents the CV traces of **5a**, **5b**, **6a** and **6b**, whereas Table-1 lists their band gap energies and LUMO and HOMO energy levels. The results suggest that compounds **5a**, **5b**, **6a** and **6b** may be capable of hole- and electro-transporting.

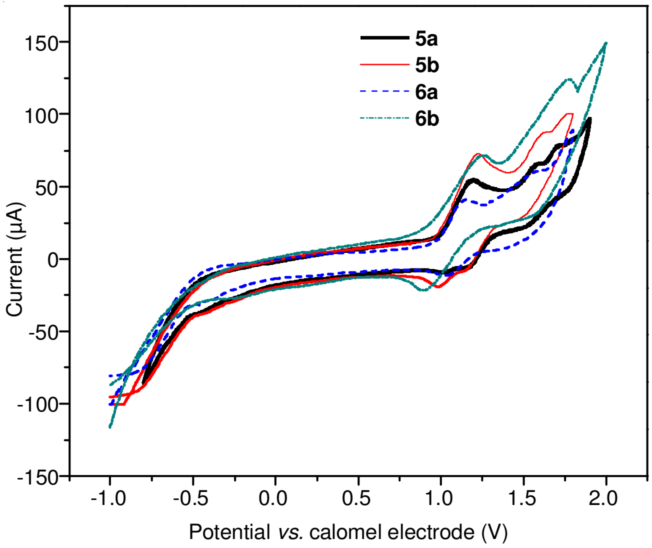


Fig. 2. CV curves of **5a**, **5b**, **6a** and **6b** measured in CH_2Cl_2 at a scan rate of 50 mV/s

The HOMO energy levels of these four materials ranged from -5.68 to -5.61 eV matching well with the work functions of indium tin oxide electrodes. The HOMO energy levels are similar with that of NPB31 (-5.46 eV), which is one of the most widely used hole-transport materials in OLEDs. Thus, they would be beneficial for hole injection and transportation. The LUMO energy levels of **5a**, **5b**, **6a** and **6b** were -2.67, -2.83, -2.96 and -2.86 eV, respectively. The difference between the LUMO energy levels of our four compounds and TPBI (-2.70 eV) or Alq (-3.0 eV) was smaller. Consequently, superior EL performance could be also realized if TPBI were to be used as ETL in OLEDs based on our four materials. The band gap energies of **5a**, **5b**, **6a** and **6b** were 2.94, 2.85, 2.71 and 2.71 eV, respectively. We suspect that **6a** and **6b** had a lower band gap energy than **5a** and **5b** because its thiophen group featured a greater conjugation length. Moreover, we expected good colour purities for the blue emissions from OLEDs fabricated from with such large band gap energies.

Thermal properties: The thermal properties of the four compounds were investigated by the thermogravimetic analysis (TGA) and differential scanning calorimetry (DSC) and the results are summarized in Table-1.

With the introduction of the rigid phenanthroimidazole and phenothiazine moiety, all compounds exhibit good thermal stability. These results suggest that all compounds were thermally stable with 5 % weight loss temperature were over 250 ºC. During the first heating DSC scan of sample **5a**, only endothermic melting peaks (T_m) at 135 ºC were detected, while under a second heating cycle, only endothermic baseline shift owing to glass transition (T_g) at 79 ºC was detected with no crystallization and melting peaks at higher temperature being observed. For compound **5b**, T_g was found at 134 ºC, which investigated that **5a** and **5b** all have good film-forming ability. However, it is worth noting that, for **6a** and **6b**, no obvious T_g could be detected.

Conclusion

Two series of four novel compounds containing phenanthroimidazole and phenothiazine have been synthesized. Their optical, electrochemical, thermal properties were studied. All of them were thermally stable with degradation temperature well above 250 ºC, in addition, **5a** and **5b** also had good film-forming ability due to the fact that their T_g were 79 and 134 ºC, respectively. As believed, these compounds showed efficient emission from blue to green. Moreover, the compounds exhibit suited HOMO ranges (-5.68 to -5.57 eV) and LUMO ranges (-2.96 to -2.67 eV), which have promising potential for application in OLEDs as hole- and electron-transporting bipolar materials.

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