Dyes and Pigments 101 (2014) 93–102

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis, characterization, physical properties, and blue electroluminescent device applications of phenanthroimidazole derivatives containing anthracene or pyrene moiety

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A R T I C L E I N F O

Article history:
Received 3 July 2013
Received in revised form
30 August 2013
Accepted 30 August 2013
Available online 13 September 2013

Keywords:
Blue host material
Phenanthro[9,10-d]imidazole
Anthracene
Pyrene
Organic light-emitting device
High Tg

A B S T R A C T

By introducing a highly fluorescent anthracene, 9-(naphthalen-2-yl)anthracene or pyrene unit at the N1-phenyl of 1,2-diphenyl-1H-phenanthro[9,10-d]imidazole, three novel blue-emissive materials (**ANPI**, **2-NaNPI** and **PNPI)** were synthesized and characterized, of which HOMO and LUMO orbitals are specifically segregative. Their high luminescence efficiency and excellent stability render them promising materials in electroluminescent device. The undoped three layers device using **PNPI** exhibits a maximum current efficiency of 4.99 cd A^{-1} with Commission Internationale d'Eclairage ($CIE_{x,y}$) color coordinates of ($x = 0.15$, $y = 0.17$). Meanwhile, the property differences between N1-substituted and C2-substituted of diphenyl-1H-phenanthro[9,10-d]imidazole derivatives were studied. The results indicate that the change of conjugated position and moiety for those blue hosts can affect the electrical field polarization of device. Specifically, all the blue host materials containing anthracene moiety show an impressive luminous current efficiency around 12 cd A^{-1} when doped with sky blue fluorescent material BUBD-1.

1. Introduction

Organic light emitting diodes (OLED) have been expected to find applications as next generation display devices [1,2]. For realizing active matrix full-color OLED displays, it is essential to have the three primary colors, red, green and blue. Red and green phosphorescent electroluminescent devices with high efficiencies, long lifetimes, and proper CIE coordinates have been well developed. However, efficient blue phosphorescent electroluminescent devices remain a challenge due to their high CIE coordinates (y-coordinate value >0.30) and short device lifetime [3–5]. In this context, highly efficient blue fluorescent materials have been considered as a promising alternative to promote the commercialization of OLEDs. Significant efforts have been made to design versatile blue fluorescent materials aiming at further improving device efficiency, chromaticity and lifetime. Intrigued by the good PL properties of anthracene in solution, much effort has been devoted to develop anthracene derivatives as deep-blue emitters with reduced close packings and consequent high fluorescent quantum yields in films [6,4a]. Besides anthracene, fluorene derivatives have also been widely investigated as blue emitters due to their high fluorescent quantum yields and good thermal stabilities [7]. In addition to small molecules, oligofluorene have been of much interest for use in OLEDs because of the associated high quantum yield, good optical stability, and film forming ability along with the easy tuning of the structures [8].

Phenanthroimidazole derivatives have also attracted great attentions as blue electroluminescent materials because of their high thermal stability and efficient electron transporting ability. For example, 4,4′-Bis(1-phenyl-1H-phenanthro[9,10-d]phenanthroimidazolyl-2-yl)biphenyl (PPIP) was reported recently as an excellent non-doped blue emitting material, corresponding to a high external quantum efficiency of 6.31% and power efficiency of 7.30 lm W^{-1} [9]. Very recently, pure blue device was fabricated with

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http://dx.doi.org/10.1016/j.dyepig.2013.08.027

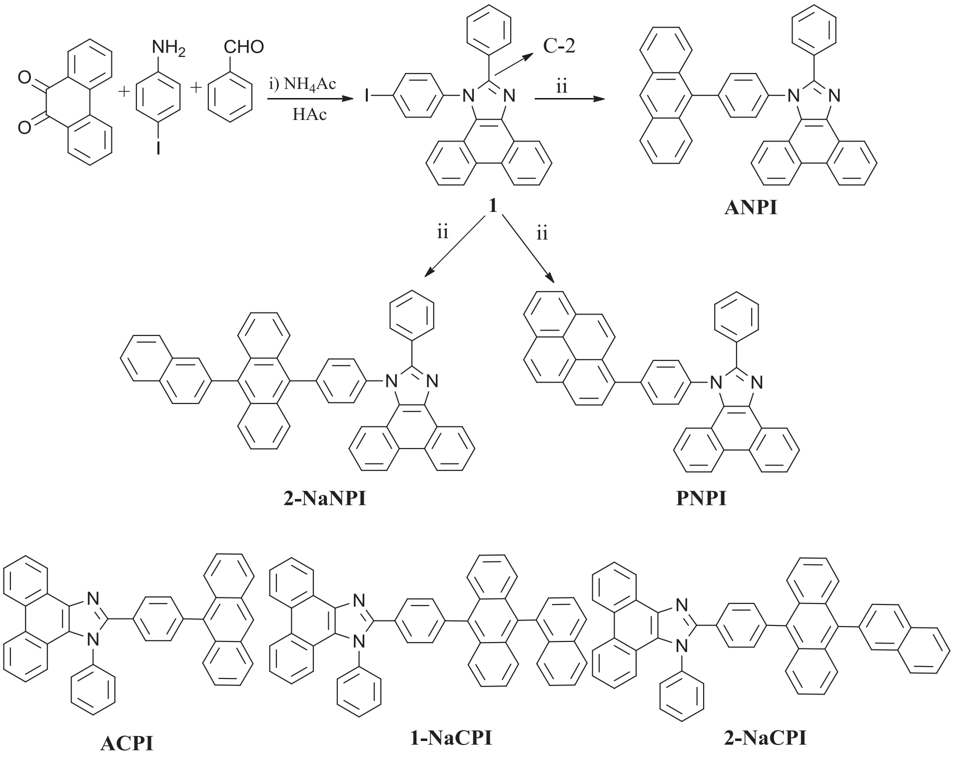
an attractive luminance efficiency of 6.87 cd A^{-1}, CIE coordinates of (0.15, 0.21) and a turn on voltage of 2.8 V, in which PPIP was used as a bifunctional luminescent material [10]. In addition, a series of phenanthroimidazole derivatives bridged by thiophene or benzene ring have also been synthesized and applied as emitting or function layers in organic light-emitting devices [11]. Among them, the best device performance using deep-blue emitting phenanthroimidazole derivative with a structure of donor-linker-acceptor was obtained by Tong and Ma's group [12]. Specifically, an impressive device performance with an external quantum efficiency (EQE) of 7.8% and a current efficiency of 10.4 cd A^{-1} has been reported based on excellent blue dopant PPIE containing n-type imidazole moiety [13]. However, device performances of blue materials often suffer from the retarded charge injection and transportation in the emission layer [14]. The preparation of blue materials by a facial synthetic process with multiple functions, such as high emissive efficiency, balanced charge injection and transport properties and good morphological and thermal stability still remains one of the most active and challenging areas in this field. In our previous work, we designed and synthesized some asymmetric phenanthroimidazole C2-phenyl position substituted anthracene derivatives [15]. The introduction of anthracene moieties can effectively increase the electron injection and transport ability and finely adjust the ionization potentials (Ip) of the compounds, resulting in reduced hole injection barrier and balanced recombination ability. In the subsequent research, some hybrid bipolar phosphorescent hosts for green and orange OLEDs have also been synthesized by conjugating carbazole moiety to the rigid skeleton **1**, 2-diphenyl-1H-phenanthro[9,10-d]imidazole (Scheme 1), and we found that the host with carbazole unit conjugated to N-1 position exhibited better performance than that of C-2 position substituted in electroluminescent devices [16]. Note that the structural engineering of the phenanthroimidazole by changing the conjugated position and moiety can affect the EL device performance of the materials obtained. Is there any principle for designing versatile materials and fabricating highly efficient devices based on phenanthroimidazole?

In this contribution, by introducing a highly fluorescent anthracene, 9-(naphthalen-2-yl)anthracene or pyrene unit at the N1-phenyl of 1,2-diphenyl-1H-phenanthro[9,10-d]imidazole, three new blue-emissive materials (**ANPI**, **2-NaNPI** and **PNPI)** were synthesized and characterized by thermal, photophysical and electrochemical studies. The undoped three layers device **PNPI** exhibits a maximum current efficiency of 4.99 cd A^{-1} with Commission Internationale d'Eclairage ($CIE_{x,y}$) color coordinates of ($x = 0.15$, $y = 0.17$). Meanwhile, the property differences between N1-substituted and C2-substituted of diphenyl-1H-phenanthro[9,10-d]imidazole derivatives were studied carefully. It was found that all the blue host material containing anthracene moiety showed an impressive luminous current efficiency around 12 cd A^{-1} when doped with sky blue fluorescent material BUBD-1.

2. Experimental section

2.1. Material and methods

All reagents and solvents were purchased from Aldrich and used without further purification. ^{1}H NMR spectra were recorded using a Bruker-AF301 400 MHz. Mass spectra were carried out on an Agilent (1100 LC/MSD Trap) using APCI ionization. Elemental analyses of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Fluorescence spectra were obtained on Edinburgh instruments (FLSP920 spectrometers) and UV–Vis spectra were measured using a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). The differential scanning calorimetry (DSC) analyses were performed on PE Instruments DSC 2920 under a nitrogen atmosphere at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were undertaken on PerkinElmer



Scheme 1. Synthetic routes of **ANPI**, **2-NaNPI** and **PNPI** and structure of ACPI, 1-NaCPI,2-NaCPI Reagents and conditions: i) NH_4Ac, HAc, reflux; ii) toluene, K_2CO_3, ethanol, aryl boric acid, $Pd(PPh_3)_4$, reflux.