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Synthesis, photophysical and electroluminescent properties of phenanthroimidazole derivatives with terminal carbazole or pyrene

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ABSTRACT

New phenanthroimidazole derivatives **PSC**, **PDC**, **PCC** and **PPP** bearing terminal carbazole or pyrene unit have been synthesized. They exhibited excellent solubility in common organic solvents. It was found that the obtained phenanthroimidazole derivatives could emit strong fluorescence in cyclohexane, and the fluorescence quantum yields of the phenanthroimidazole derivatives were in the range of 0.49–0.83 using quinine sulfate (0.1 N in H_2SO_4) as a standard. We fabricated the organic light-emitting diode with the configuration of ITO/NPB (45 nm)/phenanthroimidazole derivatives (15 nm)/TPBI (40 nm)/LiF/Al, and a saturated blue emission with $CIE_{x,y}$ of (0.16, 0.17) was achieved from the device based on **PSC**. In addition, the devices based on other phenanthroimidazole derivatives could emit bluish green or green light. The turn-on voltage, current efficiency and maximum luminance of the devices based on **PSC**, **PDC**, **PCC** and **PPP** were 3.4 V, 3.4 V, 3.8 V, 3.4 V and 0.92 cd/A, 1.83 cd/A, 1.28 cd/A, 0.32 cd/A, as well as 1190 cd/m^2, 1930 cd/m^2, 1270 cd/m^2, 1149 cd/m^2, respectively, meaning the phenanthroimidazole derivatives might become candidates as emitting materials employed in OLEDs.

1. Introduction

Organic conjugated molecules have attracted much attention due to their unique optoelectronic properties because they have potential applications in many fields [1], such as organic thin film transistors (OTFTs) [2], organic light-emitting diodes (OLEDs) [3], and photovoltaic cells [4]. Till now, lots of conjugated systems, including porphyrins, thiophene, fluorene, and so on, have been prepared and employed in optoelectronic devices. Among the conjugated units, phenanthroimidazole is a typical near-ultraviolet emitter [5] as well as electron injection or hole blocking material [6]. Therefore, some deep-blue emitters based on phenanthroimidazole derivatives exhibiting high performance in OLEDs were synthesized [7]. For example, Wang and co-workers have prepared 4,4′-bis(1-phenylphenanthro[9,10-d]imidazol-2-yl)biphenyl, which was used as electron transport layer and fluorescence host material in OLED, and the maximum luminance and turn-on voltage for the corresponding device reached 40 000 cd/m^2 and 2.8 V [5]. Lee et al. have synthesized triphenylamino terminal phenanthroimidazole (TPA-TPI), and found the device based on TPA-TPI showed maximum current, power, and external quantum efficiencies were of 2.63 cd/A, 2.53 lm/W and 3.08%, respectively [7a]. On the other hand, as a candidate in OLEDs, pyrene has attracted significant attention because of its pure blue fluorescence and long fluorescence lifetime. Meanwhile, carbazole has high hole-transporting ability arising from the lone pair electrons in nitrogen atom and its derivatives are also usually used as promising blue light-emitting materials [8]. Although blue-emitting materials based on phenanthroimidazole derivatives have been synthesized [5,7], the requirement in practical application could not be fulfilled. In addition, to the best of our knowledge, the reports on the relationship between the performance of phenanthroimidazole derivatives in devices and their molecular structures are rare. Herein, we designed four phenanthroimidazole derivatives with terminal carbazole units linked by different bridges (such as, phenylene for **PSC**, phenylvinyl for **PDC** and phenylvinyl carbazolylvinyl for **PCC**) or pyrene unit linked by phenylvinyl (**PPP**) (Scheme 1) in order to obtain new blue-emitting materials. It was found that the obtained phenanthroimidazole derivatives were high emissive in cyclohexane. Meanwhile, we fabricated the organic light-emitting diode with the configuration of ITO/NPB (45 nm)/phenanthroimidazole derivatives (15 nm)/TPBI (40 nm)/LiF/Al, in which **PSC**, **PDC**, **PCC** and **PPP** were used as emitting materials. A saturated blue emission with $CIE_{x,y}$ of (0.16, 0.17) was achieved from the device based on **PSC**. In addition, the devices based on other phenanthroimidazole derivatives could emit bluish green or green light. The turn-on voltage, current efficiency and maximum luminance of

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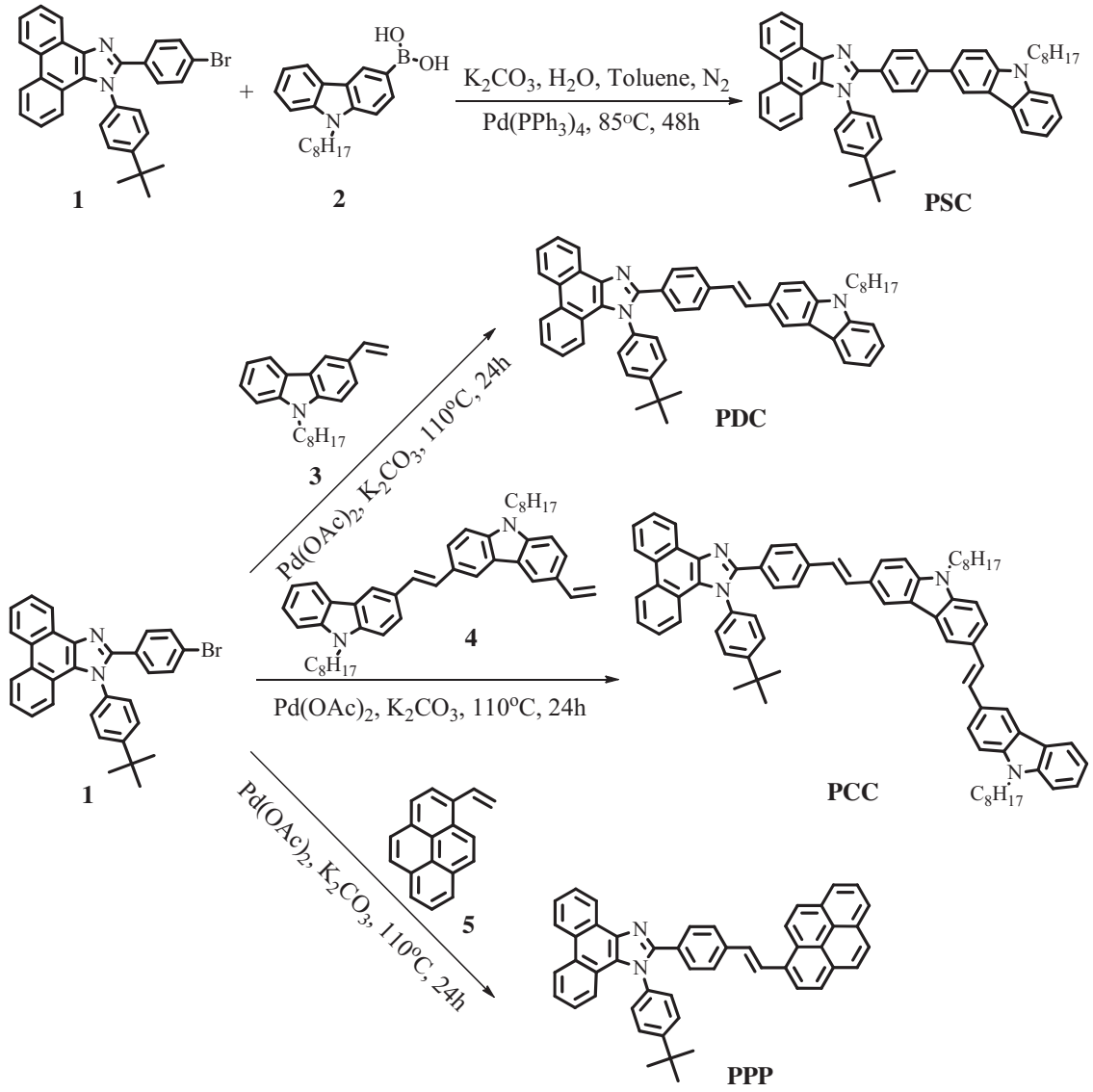

Scheme 1. The synthetic routes for the phenanthroimidazole derivatives.

the devices based on **PSC**, **PDC**, **PCC** and **PPP** were 3.4 V, 3.4 V, 3.8 V, 3.4 V and 0.92 cd/A, 1.83 cd/A, 1.28 cd/A, 0.32 cd/A, as well as 1190 cd/m^2, 1930 cd/m^2, 1270 cd/m^2, 1149 cd/m^2, respectively. It suggested that the phenanthroimidazole derivatives might become candidates as emitting materials employed in OLEDs.

2. Results and discussion

In order to improve the solubility of the phenanthroimidazole derivatives, tert-butylphenyl was introduced into the target molecules. The synthetic routes for the phenanthroimidazole derivatives with terminal carbazole or pyrene unit (**PSC**, **PDC**, **PCC** and **PPP**) are summarized in Scheme 1. 1-(4-tert-butylphenyl)-2-(4-bromophenyl)-1H-phenanthro[9,10-d]imidazole (**1**) [7a], 9-octyl-9H-carbazol-3-yl-3-boronicacid (**2**) [9], 9-octyl-3-vinyl-9H-carbazole (**3**) [10], 9-octyl-3-((E)-2-(9-octyl-9H-carbazol-6-yl)vinyl)-6-vinyl-9H-carbazole (**4**) [10] and 1-vinylpyrene (**5**) [11] were synthesized according to the procedures reported in the literatures. Compound **PSC** was prepared from compounds **1** and **2** via Suzuki cross-coupling reaction catalyzed by $Pd(PPh_3)_4$ in a yield of 46%. Compounds **3–5** were easily transformed into **PDC**, **PCC**, **PPP** through Heck reaction with compound **2** in yields of 70%, 65% and 65%, respectively. The final products were purified by column chromatography and characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, and MALDI/TOF mass spectrometry. It was found that the vinyl groups adopted the *trans*-conformation in the synthesized compounds on account of the absence of the signal at ~6.56 ppm in ^{1}H NMR spectra, which was assigned to the proton in the *cis*-form. In addition, in the FT-IR spectra the appearance of the vibration absorption at ca. 960 cm^{-1} and the absence of the absorption at ca. 830 cm^{-1} due to *cis*-double bond further indicated CH=CH were in *trans*-forms.

2.1. UV–vis absorption and fluorescence emission spectra

The UV–vis absorption spectra of **PSC**, **PDC**, **PCC** and **PPP** in dilute solution (cyclohexane, 4×10^{-6} M) and in the films were given in Fig. 1. The corresponding photophysical data were listed in Table 1. As shown in Fig. 1a, all the compounds exhibited similar absorption bands at ca. 250 nm, which can be assigned to the π–π^* translation of the K band of benzene ring [12]. As to compounds **PSC**, **PDC**, **PCC** with terminal carbazole, the bands at ca. 300 nm were ascribed to the π–π^* translation of the carbazole moieties. The maximal absorption bands of **PSC** appeared at 338 nm,