

Dipolar 1,3,6,8-tetrasubstituted pyrene-based blue emitters containing electro-transporting benzimidazole moieties: Syntheses, structures, optical properties, electrochemistry and electroluminescence

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ABSTRACT

A series of dipolar 1,3,6,8-tetrasubstituted pyrene-based compounds (**py1**, **py2**, **mpy1** and **mpy2**) were designed and synthesized with two 4-*tert*-butylphenyl segments at 1,8-positions and two electron-transporting benzimidazole moieties at 3,6-sites of the pyrene core. These compounds were structurally characterized and their photoelectric properties were investigated by spectroscopy, electrochemical and theoretical studies. Moreover, the structure of compound **py1** was determined by single-crystal X-ray diffraction analysis, indicating that the compound has a non-coplanar structure and there is no π - π stacking between the molecules. The benzimidazole moieties attached on the pyrene ring via *para*- and *meta*-linking modes and by changing the molecular linkage from *para*- to *meta*-mode can effectively tune the emission to pure blue region. The four compounds exhibit high absolute fluorescence quantum yields in dichloromethane (99.89–100%) and in film states (54.56–86.78%). In addition, the *meta*-linked compounds **mpy1** and **mpy2** exhibit higher absolute fluorescence quantum efficiencies in solution and film states than the *para*-linked compounds **py1** and **py2**, which demonstrates that the *meta*-linked architecture can more effectively twist the molecule and suppress the intermolecular interactions. All these compounds exhibit high thermal stability and can form morphologically stable amorphous thin films with glass transition temperature in the range of 182–215 °C. Two types of non-doped blue OLED devices were fabricated using compounds **py2** and **mpy2** as representatives to investigate their light-emitting and electron-transporting properties and the devices exhibit promising device performance. The devices using *meta*-linked compound **mpy2** as emitting and electron-transporting layers shows pure blue color purity (0.16, 0.10) with high current and power efficiencies (2.70 cd A⁻¹, 1.97 lm W⁻¹).

1. Introduction

Organic light-emitting diodes (OLEDs) have drawn great scientific and commercial attentions over the last two decades due to their potential applications in flat-displays and solid-state lighting [1–3]. The exploration for stable and highly efficient red, green, and blue emitters is extremely important for the fabrication of full-color OLEDs [4–6]. Recently, highly efficient red and green emitters have been achieved by phosphorescent transition metal complexes [7–14]. However, the blue emitting materials of both fluorescent and phosphorescent systems generally exhibit a remarkably inferior electroluminescence performance with regard to efficiencies, lifespan, color quality, and charge-carrier injection/transport [4,14–19]. Hence, it is very important to explore new blue emitters using various synthetic methodologies and potential starting precursors. Among the numerous building blocks,

polyaromatic pyrene has been paid everlasting attentions for designing small organic electroluminescent materials due to its native blue fluorescence with high quantum yield, long fluorescence lifetime, excellent thermal stability and high charge carrier mobility [20–25]. However, the high tendency toward π - π stacking of the pyrene moieties generally leads to strong intermolecular interactions of the pyrene-containing emitters in the solid state, which usually results into a substantial red shift of their fluorescence emission and a decrease of the fluorescence quantum yield [20,26]. A simple efficient way to suppress the excimer formation is to introduce bulky peripheral attachments into the suitable positions of pyrene ring, which allows the control of the molecular architecture and thus the supramolecular structure. Indeed, various excellent pyrene-based materials have been synthesized and employed as hole-transporting or host emitting materials for high performance OLEDs [20,27–31]. However, highly efficient pyrene-based

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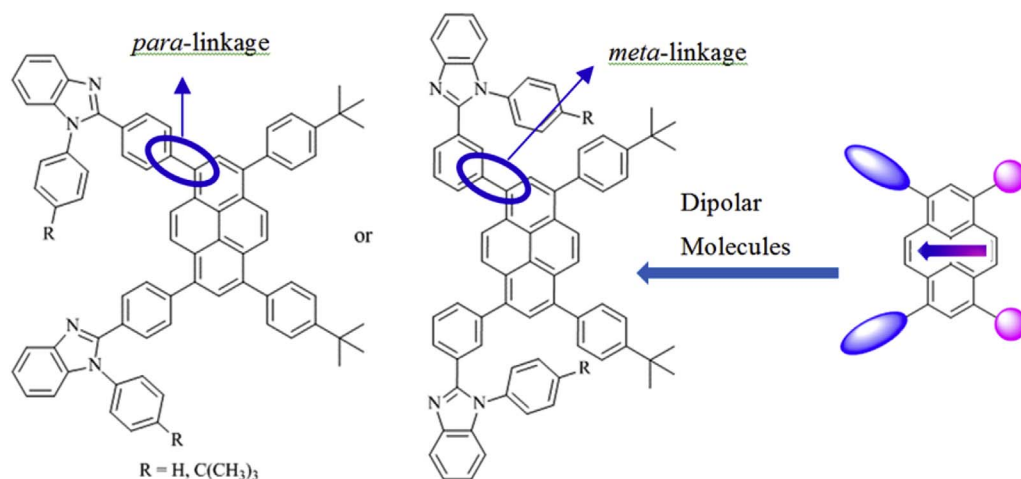
blue emitters for OLEDs are less explored. Besides improving the solid luminous efficiency of the emitters, another approach to achieve high performance device is to balance charge carrier recombination because the hole transport in OLED is usually much higher than the electron mobility under the same electric field [32–36]. Thus, the concept of incorporating electron-withdrawing moieties into various cores to enhance the electron-transporting abilities and achieve more balanced injection/transporting abilities has been applied to develop new emitters [37–39]. Benzimidazoles are known to be excellent electron conductors due to their electron deficient nature [40]. In recent years, many benzimidazole-based derivatives are designed and synthesized as excellent electron transporting/hole blocking materials used in OLEDs [40–44]. Moreover, the introduction of benzimidazole group can enhance the thermal stability, which is also an essential property for OLED materials [5,45]. Therefore, the incorporation of benzimidazole unit into different building blocks is an effective strategy to obtain excellent emitting materials for high performance OLEDs.

With an aim toward developing efficient electron-transporting blue emitters, we investigated four new benzimidazole-appended pyrene derivatives wherein pyrene acts as an emitter and benzimidazole units as electron transporters. The four blue emitters are dipolar 1,3,6,8-tetrasubstituted pyrenes with two *tert*-butylphenyl groups and two benzimidazole derivatives at the 1,8- and 3,6-positions of the pyrene core, respectively (Scheme 1). The intermolecular interactions between the planar pyrene rings can be prevented by the peripheral *tert*-butylphenyl segments and benzimidazole moieties and the incorporation of electron-withdrawing benzimidazole units can improve the electron-injection and electron transporting capability of the materials. Furthermore, by changing the molecular linkage between benzimidazole groups and pyrene core from *para*-to *meta*-mode can effectively tune the electrical structures and emission region of the materials. All these compounds exhibit excellent thermal stability, high absolute fluorescence quantum yields, and appropriate HOMO/LUMO energy levels making them promising bifunctional blue emitters. Herein, we report the design, synthesis and photoelectrical properties of the new series of dipolar pyrene-based blue emitters with two different functional attachments (**py1**, **py2**, **mpy1** and **mpy2**). In addition, two types of non-doped OLED devices with two representative compounds **py2** and **mpy2** were fabricated to systematically investigate their emitting and electron-transporting properties.

2. Results and discussion

2.1. Synthesis

The synthetic routes of the intermediates and target compounds are shown in Scheme 2. We prepared 3,6-dibromo-1,8-bis(4-*tert*-



Scheme 1. The syntheses strategy for the dipolar 1, 3,6,8-tetrasubstituted pyrene-based blue emitters containing electron-transporting *N*-phenylbenzimidazole moieties.

butylphenyl)pyrene (**py-2Br**) using a stepwise synthetic method according to our previously report [46]. Firstly, the key intermediates **1a**, **2a**, **m1a** and **m2a** were synthesized using amine and aldehyde derivative through a cyclization reaction in high yields. Then, the resulting bromides were transformed to their boronic ester analogs using bis (pinacolato)diboron reagent. Finally, the target compounds **py1**, **py2**, **mpy1** and **mpy2** were achieved by the boronic ester of benzimidazole derivatives reacting with the dibromide **py-2Br** through suzuki coupling reaction in good yields. The chemical structures were fully characterized and confirmed via nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS) and elemental analysis (EA). Moreover, the compound **py1** was further confirmed by single crystal X-ray diffraction technique.

2.2. Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of the compounds **py1**, **py2**, **mpy1** and **mpy2** in dichloromethane are shown in Fig. 1. The detailed photophysical data are presented in Table 1. The four compounds with the longest wavelength absorptions at ca. 387–395 nm can be attributed to pyrene localized π - π^* transitions. As a comparison, the absorption spectra of the *meta*-linked compounds **mpy1** and **mpy2** are blue-shifted compared with those of *para*-linked compounds **py1** and **py2**, suggesting that the *meta*-linkage strategy can decrease the π -electron conjugation of molecule. Additionally, the optical band-gaps of **py1**, **py2**, **mpy1** and **mpy2** in dichloromethane solution are estimated from the onset of absorption to be 2.83 eV, 2.90 eV, 2.94 eV and 2.94 eV, respectively. From the PL spectra of the four compounds in dichloromethane solution, compounds **py1**, **py2**, **mpy1** and **mpy2** exhibit deep-blue emission with peaks at 449 nm, 449 nm, 427 nm and 427 nm, respectively. The *para*-linked compounds **py1** and **py2** exhibit obvious red-shift (~22 nm) emission bands relative to compounds **mpy1** and **mpy2**, which is induced by their extended π -conjugation. It is also indicated that electron delocalization in compounds **mpy1** and **mpy2** is effectively confined via the *meta*-linkage strategy. The emission spectra of compounds **py2** and **py1** are identical, as are the compounds **mpy2** and **mpy1**, suggesting that introducing *tert*-butyl group into the side-capping benzene ring attached to the benzimidazole unit cannot influence the PL spectra of the compounds in solution. In addition, compounds **py1**, **py2**, **mpy1** and **mpy2** show small stokes shifts (2091–3174 cm⁻¹ in dichloromethane), indicating less energy loss during the relaxation process and thereby ensuring efficient fluorescence. The PL spectra of these compounds in the film states are shown in Fig. 2. The emission spectra of *para*-linked compounds **py1** and **py2** in film states locate at sky-blue region and the *meta*-linked compounds **mpy1** and **mpy2** exhibit pure blue emission. The PL spectra of the four compounds in thin films exhibit relatively

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