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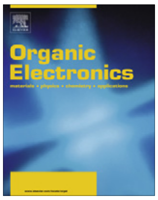

Efficient nondoped blue organic light-emitting diodes based on phenanthroimidazole-substituted anthracene derivatives

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ABSTRACT

A series of new blue materials based on highly fluorescent di(aryl)anthracene and electron-transporting phenanthroimidazole functional cores: 2-(4-(anthracen-9-yl)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (**ACPI**), 2-(4-(10-(naphthalen-1-yl)anthracen-9-yl)phenyl)-1-p-henyl-1H-phenanthro[9,10-d]imidazole (**1-NaCPI**), 2-(4-(10-(naphthalen-2-yl)anthracen-9-yl)phenyl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (**2-NaCPI**) were designed and synthesized. These materials exhibit good film-forming and thermal properties as well as strong blue emission in the solid state. To explore the electroluminescence properties of these materials, three layer, two layer and single layer organic light-emitting devices were fabricated. With respect to the three layer device **4** using **ACPI** as the emitting layer, its maximum current efficiency reaches 4.36 cd A^{-1} with Commission Internationale del'Eclairage (CIE) coordinates of (0.156, 0.155). In the single layer device **10** based on **ACPI**, maximum current efficiency reaches 1.59 cd A^{-1} with Commission Internationale del'Eclairage (CIE) coordinates of (0.169, 0.177). Interestingly, both device **4** and **10** has low turn on voltage and negligible efficiency roll off at high current densities.

1. Introduction

Since the pioneering work by Tang and Van Slyke [1], significant progresses in materials and device engineering have led to the potential application of full-color OLEDs and solid-state lighting [2]. For full-color 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, blue phosphorescent devices are still the bottleneck for the high CIE coordinates (y-coordinate value >0.30) and short device lifetime [3]. Therefore, to achieve marketable OLEDs, the hunt for blue fluorescent materials and devices are still a subject of current interest [4].

Based on anthracene, an well-known building block and starting material in OLEDs, new diverse of blue material and corresponding devices have been reported previously [5]. For example, Park group [6] have synthesized carbazole-based anthracene derivatives 3,6-di(anthracen-9-yl)-9-phenyl-9H-carbazole (P-DAC) and attained device efficiency of 3.14 cd A^{-1}, color coordinates (0.16, 0.14), and threshold voltage 3.8 V. Li's team [7] have shown fluorene based naphthylanthracene derivatives with a maximum luminance efficiency of 4.04 cd A^{-1}, CIE coordinates of (0.15, 0.13) and a turn on voltage of 4.1 V. Recently, phenanthroimidazole derivatives have attracted great attention as electroluminescent materials because of their high thermal stability and efficient electron transporting ability. Huang's group [8] reported bis(phenanthroimidazolyl)biphenyl

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derivatives as excellent non-doped blue emitting materials with optimized device efficiency of 7.3 lm W^{-1}, CIE coordinates of (0.15, 0.14). By using phenanthroimidazole as a building block for luminescent materials, Ma's group [9] also reported pure blue devices with luminance efficiency of 6.87 cd A^{-1}, CIE coordinates of (0.15, 0.21) and a turn on voltage of 2.8 V. Although these relatively successful blue materials were reported, many of them, the efficiency roll off at high current densities, so it is still a great need to design and synthesize stable blue materials which exhibit little efficiency roll off at high current densities [4a,5a,5b,5e,8]. One of the basic designs for blue materials is to increase their electron affinities to realize balanced charge injection and transport [8,9]. It should be noted that, in spite of increasing electron transporting properties, the incorporation of electron-withdrawing moiety in those saturated blue-emitted materials always results in lower HOMO levels, which mismatch with side layer and generate larger hole-injection barriers at the hole-transporter/emitter junctions. Hence, in designing pure blue light emitting materials for OLEDs, a compromise is needed between electron transporting ability and adjusting the HOMO/LUMO levels.

In previous work [10,11], we have introduced electron-rich benzothiophene or flourene moieties into anthracene, to adjust the emitter's HOMO/LUMO level and carrier transporting ability. Here, we designed and synthesized three asymmetric phenanthroimidazole-substituted anthracene derivatives. The introduction of phenanthroimidazole moieties effectively increases the electron injection and transport ability and finely adjusts the ionization potentials (Ip) of the compounds, and further reduces the hole injection barrier at the interface of the hole-transporting layer (HTL) and the emissive layer and balanced recombination [12]. As expected, these materials show perfect thermal stability and excellent EL performance with low onset voltages, which indicate that these new materials are a promising class of blue emitters for practical applications in panel display.

2. Experimental section

2.1. Materials and methods

All reagents and solvents were used as purchased from Aldrich and were used without further purification. ^{1}H-NMR spectra were recorded using a Bruker-AF301 at 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) analysis was performed under a nitrogen atmosphere at a heating rate of 10 °C/min using a PE Instruments DSC 2920. Thermogravimetric analysis (TGA) was undertaken using a PerkinElmer Instruments (Pyris1 TGA) under nitrogen atmosphere at a heating rate of 10 °C/min. AFM was measured using Veeco (DIMENSION 3100). To measure the PL quantum yields (Φf), degassed solutions of the compounds in CH2Cl2 were prepared. The concentration was adjusted so that the absorbance of the solution would be between 0.05 and 0.1. The excitation was performed at 330 nm and 9,10-diphenylanthracene (DPA) in cyclohexane ($\Phi = 0.9$ in cyclohexane) was used as a standard [13]. Cyclic voltammetry measurements were carried out in a conventional three electrode cell using a Pt button working electrode of 2 mm in diameter, a platinum wire counter electrode, and a Ag/AgNO3 (0.1 M) reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Oxidations CV of all compounds were performed in dichloromethane containing 0.1 M tetrabutylammoniumhexafluorophosphate (Bu4NPF6) as the supporting electrolyte. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram and calibrated to the ferrocene/ferrocenium (Fc|Fc+) redox couple. DFT calculations have been performed to characterize the 3D geometries and the frontier molecular orbital energy levels of ACPI, 1-NaCPI and 2-NaCPI at the B3LYP/6-31G* level by using the ADF2009.01 program.

2.2. Preparation of compounds

2.2.1. Synthesis of compound 1

A 250 ml round-bottomed flask was charged with 9,10-phenanthrenequinone (2.08 g, 10 mmol), aniline (0.93 g, 10 mmol), 4-bromobenzaldehyde (1.85 g, 10 mmol) and ammonium acetate (9.24 g, 120 mmol) under nitrogen atmosphere. Subsequently, 120 mL acetic acid was added to the solution and the reaction mixture was stirred under reflux for 36 h under an argon atmosphere. After cooled to room temperature, the mixture was poured into water. The separated solid was filtered off, washed with methanol and dried to give a white solid without futher purification. Yield 3.68 g (82%). ^{1}H-NMR: (DMSO-d6, 400 MHz): δ (ppm) 8.94 – 8.91 (d, J = 8.4 Hz, 1H), 8.89 – 8.86 (d, J = 8.4 Hz, 1H), 8.71 – 8.68 (dd, J = 1.2, 8.0 Hz, 1H), 7.80 – 7.67 (m, 7H), 7.58 – 7.54 (m, 3H), 7.51 – 7.49 (dd, J = 2.0, 6.8 Hz, 2H), 7.51 – 7.49 (t, J = 7.2 Hz, 1H), 7.09 – 7.07 (d, J = 8.0 Hz, 1H). MS (APCI) (m/z): [M+H$^+$] calcd for $C_{27}H_{18}BrN_2$, 450.3; found, 450.4.

2.2.2. Synthesis of compound ACPI

A 100 ml two-neck round-bottomed flask was added compound 1 (0.90 g, 2 mmol), anthracen-9-ylboronic acid (0.49 g, 2.2 mmol), toluene (30 ml), ethanol (15 ml), 2 M K2CO3 (30 ml, 60 mmol) aqueous solution and tetrakis-(triphenylphosphine) palladium (0) (0.12 g, 0.1 mmol) in turn, then the reaction mixture was refluxed under nitrogen for 24 h in the absence of light. After the reaction was completed, cooled to room temperature. The solution was extracted with dichloromethane, dried by MgSO4. The organic layer was concentrated under a reduced pressure and purified by column chromatography and dried under vacuum to yield a white solid. Yield: 90%. ^{1}H-NMR: (DMSO-d6, 400 MHz): δ (ppm) 8.95 – 8.93 (d, J = 8.0 Hz, 1H), 8.90 – 8.88 (d, J = 8.0 Hz, 1H), 8.79 – 8.76 (d, J = 8.0 Hz, 1H), 8.66 (s, 1H), 8.15 – 8.12 (d, J = 8.0 Hz,