Bipolar deep-blue phenanthroimidazole derivatives: Structure, photophysical and electroluminescent properties

Zhong-Yi Wang[a,1], Bin Liu[a,1], Jue-Wen Zhao[b], Gui-Lin Ruan[a], Si-Lu Tao[b,**], Qing-Xiao Tong[a,*]

[a] Department of Chemistry, Shantou University, No.243 University Road, Shantou, Guangdong, 515063, PR China
[b] School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu, 610054, PR China

ABSTRACT

Two efficient fluorescence molecules, named 1-(4-trifluoromethylphenyl)-2-(4′-(1,4,5-triphenyl-1H-imidazole-2-yl)-[1,1′-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazole (**PPI-PIM-1**) and 1-(4-trifluoromethylphenyl)-2-(4′-(2,4,5-triphenyl-1H-imidazole-1-yl)-[1,1′-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazole (**PPI-PIM-2**) were designed and synthesized, in which the electron-withdrawing trifluoromethyl group was introduced firstly to N1-position benzene of phenanthroimidazole to improve the electron transporting ability and tune the charge transfer (CT) component. In addition, compared to biphenanthroimidazole derivatives, here, we break one rigid plane of phenanthroimidazole to inhibit aggregation-induced-quenching (ACQ) and change the position from C1 to N1 to restrict the conjugation length simultaneously. The devices based on **PPI-PIM-1** and **PPI-PIM-2** exhibited stable deep-blue emission with CIE coordinates of (0.15, 0.08) and (0.15, 0.07) and achieved maximum external quantum efficiencies of 4.3% and 4.5% respectively. More importantly, the corresponding exciton utilization efficiencies are as high as 27.0% and 30.3%.

1. Introduction

The development of blue emitters is crucial in OLED applications as full-color displays and energy-saving lighting [1]. In full-color display, blue emission is essential not only as one of the primary colors, it can also reduce power consumptions efficiently and extend the color gamut [2]. In lighting, blue emitters play a key role in managing the color temperature and color rendering index to enable multi-purpose white lighting. Furthermore, blue emitters can also excite lower energy luminophors via energy transfer to realize white emission [3]. Nevertheless, the development of blue OLEDs lags that of green and red counterparts due to the intrinsically wider energy gaps of blue emitters resulting in contradictory optical and electrical properties [4]. The development of organic materials with high efficiency and stable blue emission is still a great challenge.

Recently, phenanthro[9,10-d]imidazole (PI) derivatives have attracted much attention due to their facile synthesis, appropriate π-conjugated length for blue emitting, high photoluminescence (PL) efficiency, potential bipolar properties, and high thermal stability [4]. To enhance fluorescent yield, the so-called "two-in-one" strategy in which two identical chromophores are jointed with a suitable bridge were

adopted [5]. However, the linkage of two moieties will inevitably increase the conjugation length and often lead to redshift and broadening of the emission spectra. For example, BPPI was reported as a highly efficient blue emitter block and showed excellent thermal properties, high fluorescence quantum yields and bipolar property by Ma et al. [6,7]. However, the CIE coordinates of (0.15, 0.21) are far inferior to the blue standard of National Television System Committee (NTSC) (0.14, 0.08), because of large molecular conjugation. Moreover, The BPPI-based device showed obvious efficiency roll-off, high turn-on voltage and low exciton utilization efficiency (EUE) (18.0%) due to unbalanced carrier transportability that the hole transporting property is far superior to electron transporting property [8,9]. By using molecular twisting and bulky side group substitution, we successfully developed two deep-blue emitters, BiPI-1 and BiPI-2. These two twisted linear molecules retain the excellent photophysical and electrical properties of planar analogue and remarkably suppressed redshifts in solid state emission [10].
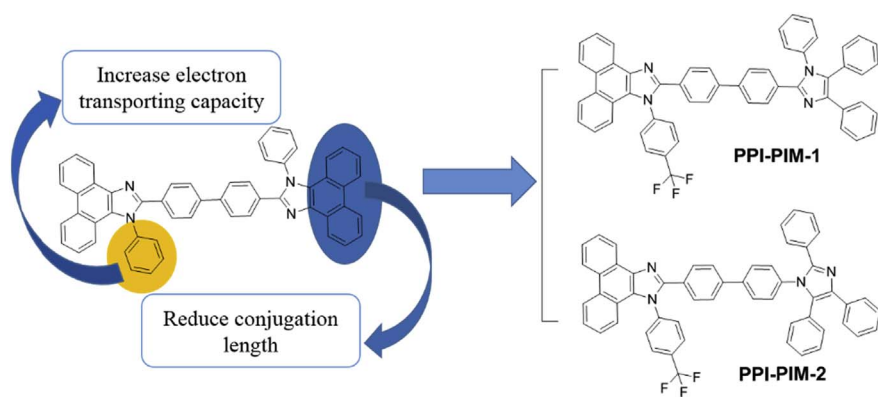
We ever reported a series of biphenanthroimidazole derivatives by using three phenyl rings as linkage to increase molecular distortion degree. Tert-buty group was also introduced at the N1-position of phenanthroimidazole to improve molecular solubility and color purity

---

Scheme 1. Molecular structure and design strategy of **PPI-PIM-1** and **PPI-PIM-2**.

[11]. Compared to BPPI, although the BBTPI-based device exhibited excellent device performance with significantly improved color purity, its CIE coordinates (0.15, 0.10) still did not meet NTSC standard. Additionally, the BBTPI-based single carrier devices showed higher carrier mobility with 7.32×10^{-3} cm^2 V^{-1} S^{-1} for hole mobility and 1.49×10^{-5} cm^2 V^{-1} S^{-1} for electron mobility. Amazingly, the hole mobility of BBTPI is higher than that of commonly used hole transporting material N,N′-di-1-naphthyl-N,N′-diphenylbenzidine (NPB) and the electron mobility is also comparable to typical electron-transport material 1,3,5-tri(phenyl-2-benzimidazolyl)-benzene (TPBI) [12,13].

To further improve color purity and balance carrier transporting properties simultaneously, in this paper, we designed two new molecules, named **PPI-PIM-1** and **PPI-PIM-2** (Scheme 1). We introduced trifluoromethyl group to the N1 position of phenanthroimidazole and broke one rigid plane of phenanthroimidazole to restrict conjugation length. At the same time, we changed the connect positions from C2 to N1 to comparatively study the relationship between molecular structures and photophysical properties. It is well known fluorine atom possesses strong electron withdrawing ability, which can not only control charge transfer (CT), but also impact the intramolecular and intermolecular interactions. In addition, the trifluoromethyl group can lower the lowest unoccupied molecular orbital (LUMO) energy level of the molecule, making electron injection easier [14–16]. Moreover, the C-H···F interaction of fluorinated organic molecules can increase charge mobility of materials [17–19]. Lastly, compared to biphenanthroimidazole derivatives, breaking one rigid plane of phenanthroimidazole can effectively restrain solid aggregation effect and molecular conjugation degree. As expected, the non-doped devices based on **PPI-PIM-1** and **PPI-PIM-2** exhibited stable deep-blue emission with maximum external efficiencies of 4.3% and 4.5%, exciton utilization efficiencies of 27.0% and 30.3%, and standard CIE coordinates of (0.15, 0.08) and (0.15, 0.07) respectively.

2. Experimental section

2.1. General methods

All the reagents and solvents for the synthesis were purchased from commercial sources and used directly without further purification. All the reactions were performed in argon atmosphere. ^{1}H NMR and ^{13}C NMR were recorded with a Varian Gemin-400 spectrometer. Mass spectra were recorded on a PE SCIEX API-MS spectrometer. Elemental analysis (C, H, N) was performed using a Vario EL III CHNS elemental analyzer. UV–vis absorption and photoluminescence (PL) spectrometer were measured on a Perkin-Elmer Lambda 950 UV/vis Spectrometer and a Perkin-Elmer LS50 fluorescence spectrometer, respectively. Absolute ϕ_{PL} was measured with a Labsphere™ integrating sphere using a monochromatized Xe lamp (Newport™) as exciting source. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) were performed on a TA Instrument TGA-50 and a TA

Instrument DSC-50, respectively. The heating rate of TGA and DSC are 10 °C min^{-1} and DSC is carried out with two cycle scanning from 50 to 400 °C. Cyclic voltammetry (CV) was scanned with a CHI600 voltammetric analyzer featuring a three-electrode system (glassy carbon electrode as working electrode, platinum wire as auxiliary electrode, Ag/AgCl as reference electrode). Ferrocene was used as internal standard with an absolute highest occupied molecular orbital level of −4.80 eV. Degassed 0.1 mol/L tetrabutylammoniumhexafluorophosphate CH_2Cl_2 solution was employed as a supporting electrolyte. The HOMO levels were calculated by measuring oxidation potentials. The LUMO energy levels were estimated by subtracting from the HOMO energy levels with optical band gaps. For the theoretical calculation, geometrical properties was optimized at B3LYP/6-31 g(d, p) level using the Gaussian 09 program. Crystallographic data collections of **PPI-PIM-1** and **PPI-PIM-2** were performed on an Oxford Diffraction Gemini E(Cu X-ray source, Kα, λ = 1.54184 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature. The structures were solved by direct methods (SHELXTL-97), all non-hydrogen atoms were refined with anisotropic thermal parameters.

2.2. Device fabrication and measurement

Devices were fabricated on pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω/sq. Before use, the substrates were swabbed with Decon-90solution, and treated by15 min ultrasonic baths in acetone and deionized water respectively, and then rinsed with isopropanol. The solvent on the surface was removed with by dry N_2 flow, and then the clean substrates were stored in an oven at 120 °C. After a 20 min UV-ozone treatment, the substrates were transferred into a deposition chamber with vacuum better than 10^{-6} Torr. Current density-voltage characteristics and electroluminescence radiation were recorded with a Keithley 2400 power source and a Spectrascan PR650 photometer, respectively. Device measurement was performed under ambient conditions.

2.3. Synthesis methods

2.3.1. 4′-(1,4,5-triphenyl-1H-imidazol-2-yl)-[1,1′-biphenyl]-4-carbaldehyde (3)

The starting materials 1 and 2 were prepared as reported previously [20,21]. The starting material 1 (1.8 g, 9 mmol), (4-formylphenyl) boronic acid (1.6 g, 10.5 mmol), Pd(PPh3)4 (0.28 g, 0.45 mmol), K2CO3 aqueous (2 M, 10 ml) in toluene (30 ml) and ethanol (30 ml) were heated to 90 °C and refluxed for 24 h in argon atmosphere. The solution was cooled to room temperature and extracted with dichloromethane, the extracts were concentrated by rotary evaporation. The residue was further purified by column chromatography (petroleum ether:CH_2Cl_2, 2:1) to get pure white powder (1.60 g, 78%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ10.04 (s, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.2 Hz,