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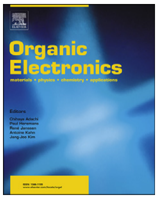

Removing shortcomings of linear molecules to develop high efficiencies deep-blue organic electroluminescent materials

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ABSTRACT

By using molecular twisting and bulky side group substitution, we successfully develop 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 supress redshifts in solid state emission. Especially, **BiPI-1** showed deep-blue emission in both solution and solid phase, and high carrier mobilities with $\mu_h > 10^{-3}$ cm^2 V^{-1} s^{-1} and $\mu_e > 10^{-5}$ cm^2 V^{-1} s^{-1}. Standard blue electroluminescence (color purity: (0.15, 0.08)) and high device efficiency (CE: 4.62 cd A^{-1}, EQE: 6.18%) were observed in a non-doped OLED of **BiPI-1**.

1. Introduction

Development of deep-blue emitters for OLEDs (organic light-emitting diodes) has always been a hot topic of research [1,2]. Because efficient deep-blue emitters are indispensable for high performance white OLEDs and critical for improving color gamut as well as reducing power consumption of full-color displays [3,4]. However, compared to the other two primary colors, green and red, progress on the development of blue emitter is lagging behind [5,6].

Ideal deep-blue materials should possess outstanding photophysical and electrical properties, including deep-blue emission, high photoluminescent quantum yield (ϕ_{PL}) and good carriers injection/transport ability [6,7]. It is reported that ϕ_{PL} increase with the molecular conjugation length in similar molecular systems [8–10]. For example, biphenyl shows a ϕ_{PL} of only 2% in solution, while when it linearly extended to *p*-quinquephenyl the corresponding figure is 91% [10]. Similar phenomena are observed in solid state. Fluorophore TPE presented a ϕ_{PL} of only 14.63%, but high ϕ_{PL} of 50% can be achieved in conjugation-extended DPBPPE [11]. Further extending molecule to be BTPE also leads to higher ϕ_{PL} [12]. The excellent electroluminescent materials building block PPI exhibits a ϕ_{PL} of 40% in thin film of itself. But the ϕ_{PL} of its "two-in-one" analogue BPPI is more than double, up to 85% [13]. In terms of electrical properties, linear extension of π system is conducive to synergistically raising the highest occupied molecular orbital (HOMO) and lowering the lowest unoccupied molecular orbital (LUMO). Thus linear system is able to facilitate the injection/transport of hole and electron [14]. In addition to the above-mentioned attractive merits, linear molecules tend to present high proportion of horizontal dipole in thin-film, which is beneficial to improve their devices efficiencies with enhancing outcoupling efficiencies [15,16]. However, molecular emission will be red-shifted with the extension of molecular conjugation. Another drawback in solid state is that linear molecular structure increase the probability of intermolecular π-π stacking [16,17], which often results in spectral bathochromic shifts and even considerably quenched fluorescence.

With the aim of tackling the disadvantages of linear molecule, herein, we used molecular twisting and substitution of bulky

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groups in a linear molecular system of biphenantro[9, 10-*d*]imidazole, designed and synthesized two linear molecule, named 2,2'-(2-methyl-[1,1'-biphenyl]-4,4'-diyl)bis(1-phenyl-1*H*-phenantro[9, 10-*d*]imidazole) and 2,2'-(2-methyl-[1,1'-biphenyl]-4,4'-diyl)bis(1-(4-(*tert*-butyl)phe-nyl)-1*H*-phenanthro [9,10-*d*]imidazole) (**BiPI-1** and **BiPI-2**, Fig. 1), as deep-blue emitters for OLED applications. A methyl group was added to the *biphenyl* bridge which links the two phenantroimidazole (PI) fluorophores, aiming at adding an appropriate torsional angle between the two PI planes without breaking the linear π conjugated system. High conjugation extent maintains the high ϕ_{PL} of the materials and the twisted structure should help in avoiding π-π stacking in solid state. A bulky *tert*-butyl group (**BiPI-2**) is added to each of the fluorophore unit to further suppress intermolecular interaction. With the two materials as emitters, non-doped OLEDs achieved standard deep-blue emissions with the same Commission internationale de l'éclairage (CIE) coordinates of (0.15, 0.08) and high electroluminescent efficiencies of maximum current efficiencies (CE) of 4.62 and 3.38 cd A^{-1}, power efficiencies (PE) of 4.55 and 3.44 l m W^{-1} and external quantum efficiencies (EQE) of 6.18% and 4.52% for **BiPI-1**- and **BiPI-2**-based device respectively. In the following sections, we would like to report the synthesis methods, thermal stabilities, photophysical and electrical properties in detail.

2. Experimental section

2.1. General methods

All reagents and solvents were purchased from commercial sources and used as received without further purification unless otherwise stated. ^{1}H NMR was 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) spectra were measured on a Perkin-Elmer Lambda 950 UV/vis Spectrometer and a PerkinElmer 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 TGAQ50 and a TA Instrument DSC2910, 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. The HOMO energy levels of the materials which evaporated on ITO substrates were detected via ultraviolet photoelectron spectroscopy (UPS) in a VG ESCALAB 220i-XL surface analysis system. 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. Molecular orbitals were obtained at the same level of theory. Crystallographic data collections of **BiPI-1** and **BiPI-2** were performed on an Oxford Diffraction Gemini E (Cu X-ray source, Kα, λ = 1.54178 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.

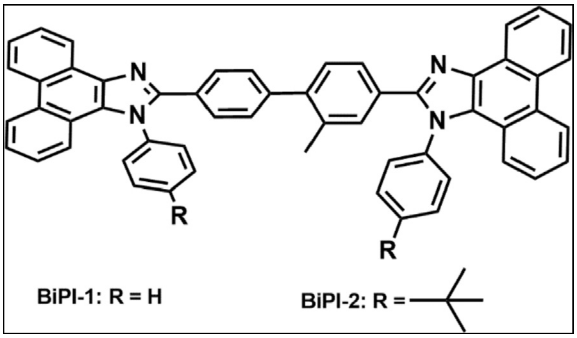

Fig. 1. Structures of new deep-blue emitters.

2.2. Device fabrication and measurement

Devices were fabricated on pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω square^{-1}. After a 15 min UV-ozone treatment, the ITO substrates were immediately transferred into a deposition chamber with a base pressure of 5×10^{-6} torr for organic and metal deposition. EQE was calculated according to the formula below:

$$\mathbf{EQE} = \frac{\boldsymbol{\pi \cdot L \cdot e}}{683 \cdot \boldsymbol{I \cdot h \cdot c}} \cdot \frac{\int_{380}^{780} \boldsymbol{I}(\boldsymbol{\lambda}) \cdot \boldsymbol{\lambda d\lambda}}{\int_{380}^{780} \boldsymbol{I}(\boldsymbol{\lambda}) \cdot \boldsymbol{K}(\boldsymbol{\lambda}) \boldsymbol{d\lambda}}$$

where L (cd m^{-2}) is the total luminance of device, I (A) is the current flowing into the EL device, λ (nm) is EL wavelength, I(λ) is the relative EL intensity at each wavelength and obtained by measuring the EL spectrum, K(λ) is the CIE chromaticity standard photopic efficiency function, e is the charge of an electron, h is the Planck's constant, c is the speed of light.

Current density-Voltage (*J-V*) characteristics and EL luminescence properties of the devices were recorded with a Keithley 2400 SourceMeter and a Spectrascan PR650 photometer respectively.

2.3. Synthesis methods

2.3.1. 2-Methyl-[1,1'-biphenyl]-4,4'-dicarbaldehyde (m-BCHO)

This intermediate was synthesized according to lectures [18,19]. The 4-bromobenzaldehyde (0.93 g, 5 mmol), (4-formyl-2-methylphenyl)boronic acid (0.84 g, 5.1 mmol), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol), and K_2CO_3 aqueous (2 M, 7 mL) in toluene (15 mL) and ethanol (3 mL) was heated to reflux in an argon atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na_2SO_4 and concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether: CH_2Cl_2, 1:2) to obtain the pure product as white powder. (yield: 91.4%, 1.03 g). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.08 (s, 1H), 10.03 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.81 (s, 1H), 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 1.58 (s, 3H).

2.3.2. 2,2'-(2-methyl-[1,1'-biphenyl]-4,4'-diyl)bis(1-phenyl-1H-phenanthro[9,10-d]imidazole) (**BiPI-1**)

The m-BCHO (0.45 g, 2 mmol), 9,10-phenanthrenequinone(0.94 g, 4 mmol), aniline (0.0.38 g, 4 mmol), and ammonium acetate (2.31 g, 30.0 mmol) were added into glacial acetic acid (20 mL) and the mixture refluxed for 24 h under an argon atmosphere. After cooling to room temperature, an orange-yellow mixture was obtained and poured into methanol under stirring. The raw product was separated by filtration and washed with methanol, and then dried under vacuum. The product was purified by column chromatography (petroleum ether: CH_2Cl_2, 1:4) on silica gel to give a white powder, with a 54% yield (0.81 g) ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.69 (dd, *J* = 21.2, 8.2 Hz, 4H), 7.72–7.43 (m, 21H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.21 (t, *J* = 8.3 Hz, 4H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.16