White electroluminescence generated by a blend of bis(di-*p*-tolylamino)dihydroindenoindene and DCJTB

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Abstract Structural analysis and photophysical study of bis(di-*p*-tolylamino)dihydroindenoindene were conducted. On the basis of its bi-functional property, a simple WOLED was fabricated in the host–guest configuration. White light fluorescence obtained from a single device was generated by two components emitting simultaneously, via an energy-transfer process.

Keywords OLED \cdot WOLED \cdot White OLED \cdot Electroluminescence \cdot White light fluorescence

Introduction

Since pioneering work by Pope et al. [1], methods for generating electroluminescence (EL) from organic compounds have been sought. In 1987, Tang and VanSlyke [2] reported the first promising multi-layer, high-efficiency, organic lightemitting diodes (OLED); soon after, Burroughes et al. [3] successfully developed polymer organic light-emitting diodes (PLED). These have since been used in flatpanel displays [4–7] and for lighting [8–10]. This innovative technology has a variety of merits, including rapid response, high contrast, high resolution, low operating voltage, high efficiency, color tunability, and stability. Recently, the potential of white OLEDs as substitutes for candlelight and daylight lamps in our everyday lives has been demonstrated. Methods of producing white emission can be classified into two major groups: wavelength conversion and color mixing. There

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are several color mixing techniques; the most general integrates multi-color emitters in a single device, for example, blue and yellow and/or orange; green, red, and blue; and blue and red and/or orange emitting materials. To enhance EL efficiency, however, the corresponding device architecture is complicated [11-13]. We therefore planned to resolve this problem by using multi-functional materials for a single-component white OLED.

Bis(diarylamino)dihydroindenoindene derivatives have been proved to be good hole-transporting and emitting materials in OLEDs. They emit sky-blue to greenish blue fluorescence with high efficiency and maximum emission peaks (Em. λ_{max}) in the range 432–492 nm [14]. Because of their bi-functional property they have potential for use in white OLEDs. Among all candidates, 2,7-bis(*N*,*N*,-di-(*p*tolyl)amino)-5,5,10,10-tetraphenyl-5,10-dihydroindeno[2,1-*a*]indene (**3**) has an appropriate oxidation potential for hole injection. Its synthesis is illustrated in Scheme 1.

Experimental

Materials

Compounds 1–3 were synthesized in accordance with literature methods [14]. All reagents were purchased from Acros Organics, Sigma-Aldrich, TCI, or Alfa-Aesar, and used directly without further purification. Solvents used for experiments were reagent grade unless stated otherwise. Diethyl ether and toluene were dried over Na with benzophenone-ketyl intermediate as indicator.

5,5,10,10-Tetraphenyl-5,10-dihydroindeno[2,1-*a*]indene (1)

A solution of (Z)-2,2'-dibromostilbene (6,761 mg, 20 mmol) in diethyl ether (100 mL) was placed in a 250-mL, three-necked, round-bottomed flask. The flask was cooled to 0 °C, and *n*-BuLi (1.6 M in hexanes, 27.5 mL, 44 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min, then a solution of benzophenone (8,018 mg, 44 mmol) in diethyl ether (20 mL) was added. The resulting mixture was gradually warmed to ambient temperature and then quenched with saturated NaHCO_{3(aq)} (50 mL). After filtration, the precipitate was washed with distilled water (100 mL) and hexanes (100 mL) then dried under reduce pressure. The crude residue dissolved in acetic acid (50 mL), and placed in a 100-mL, two-necked, round-bottomed flask. HCl (12 M, 36 µL, 1 mmol) was then added and the reaction mixture was heated under reflux for 2 h. After cooling to ambient temperature, saturated NaHCO_{3(aq)} (50 mL) was added again and the mixture was stirred vigorously for 20 min. The precipitate was isolated by filtration and the yellow solid was washed with distilled water (100 mL), methanol (100 mL), and hexanes (100 mL) in turn, then dried under reduce pressure to give 1, which was re-crystallized from CH₂Cl₂ to afford 2,441 mg pure 1 (24 %): T_m 376 °C (DSC); M.W.: 508.65; ¹H NMR (600 MHz, CDCl₃) δ 7.42 (dd, J = 6.8, 1.8, 2H), 7.30–7.23 (m, 20H), 7.18–7.11 (m, 6H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 157.7,



Scheme 1 Synthetic strategy for preparation of 1–3. Reagents and conditions: *a* n-BuLi and benzophenone, ether, 0 °C, 2 h. *b* cat. HCl, acetic acid, reflux, 4 h. *c* CuBr₂–Al₂O₃, CCl₄, reflux, 18 h. *d* Pd₂(dba)₃, P(*t*-Bu)₃, NaO(*t*-Bu), and di-*p*-tolylamine, toluene, reflux, 4 h

155.7, 143.0, 138.6, 128.7, 128.6, 127.4, 127.3, 126.2, 125.3, 121.1, 63.4; EIMS (negative) calcd for $C_{40}H_{28}$ [M⁻]: 508.2, found: 508.3; TLC R_f 0.75 (CH₂Cl₂-hexanes, 1:3).

2,7-Dibromo-5,5,10,10-tetraphenyl-5,10-dihydroindeno[2,1-a]indene (2)

A suspension of **1** (1,017 mg, 2 mmol), CuBr₂ (3,350 mg, 15 mmol), and Al₂O₃ (10,050 mg) in CCl₄ (20 mL) was placed in a 250-mL, three-necked, roundbottomed flask. The reaction mixture was heated to reflux for 16 h. After cooling to ambient temperature, excess CuBr₂ and Al₂O₃ were removed by filtration through Celite. The filtrate was evaporated under reduce pressure and the residue was recrystallized from toluene to afford 1,093 mg pure **2** (82 %): $T_{\rm m}$ 393 °C (DSC); M.W.: 666.44; ¹H NMR (600 MHz, CD₂Cl₂) δ 7.54 (d, J = 1.7, 2H), 7.31–7.24 (m, 22H), 7.03 (d, J = 8.2, 2H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 159.6, 155.2, 141.8, 137.3, 130.7, 129.0, 128.7, 128.5, 127.7, 122.3, 120.4, 63.6; TLC $R_{\rm f}$ 0.70 (CH₂Cl₂– hexanes, 1:3).

2,7-Bis(*N*,*N*,-di-(*p*-tolyl)-amino)-5,5,10,10-octaphenyl-5,10-dihydroindeno[2,1-*a*]indene (**3**)

A solution, in toluene (20 mL), of **2** (666 mg, 1 mmol), $Pd_2(dba)_3$ (18 mg, 0.02 mmol), NaO(*t*-Bu) (288 mg, 3 mmol), P(*t*-Bu)₃ (0.03 M in toluene, 2 mL, 0.06 mmol), and di-*p*-tolylamine (434 mg, 2.2 mmol) was placed in a 25-mL, two-necked, round-bottomed flask. The reaction mixture was heated under reflux for 4 h then cooled to ambient temperature, filtered, and the precipitate was washed with toluene (100 mL). The crude residue was sublimed at 393 °C under 5×10^{-6} Torr

to afford 557 mg pure **3** (62 %): $T_{\rm m}$ 433 °C (DSC); M.W.: 899.17; ¹H NMR (600 MHz, CD₂Cl₂) δ 7.23 (s, 20H), 7.15 (d, J = 2.0, 2H), 6.98 (d, J = 8.3, 8H), 6.91 (d, J = 8.3, 2H), 6.86 (d, J = 8.3, 8H), 6.65 (dd, J = 8.3, 2.0, 2H), 2.25 (s, 12H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 158.6, 153.8, 146.5, 145.6, 143.6, 132.9, 130.0, 128.8, 128.6, 127.1, 124.7, 121.4, 120.7, 120.4, 63.3, 20.8; TLC $R_{\rm f}$ 0.75 (CH₂Cl₂-hexanes, 1:3); ESI–MS (positive) calcd for C₆₈H₅₄N₂ [M⁺]: 898.4, found: 898.4.

Steady-state photophysical study

Absorption spectra were measured on a Thermo Scientific Evolution 60S spectrophotometer; spectrophotometric CH_2Cl_2 and toluene were used as solvents. On excitation, emission spectra were measured on a Jasco FP-6500 fluorescence spectrometer under the same solutions.

Device fabrication and measurements

Before use, all materials were subjected to gradient sublimation twice. The cathode was indium tin oxide (ITO)-coated glass with a shear resistance of ~ 30 Ω /sq. Prepatterned ITO substrate was cleaned sequentially by sonication in detergent solution, doubly distilled water, and EtOH for 5 min, in turn, before blow-drying with a stream of nitrogen. Advanced surface cleaning was accomplished by oxygen plasma treatment for 3 min. PEDOT:PSS and the emitting layer [DCJTB (4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran; 2 wt%):**2**] were then spin-coated at 3,000 rpm on to the substrate before loading into a vacuum chamber. Layer by layer deposition was conducted thermally under a pressure of 5 × 10⁻⁶ Torr. EL efficiency was determined and spectra were recorded by use of a Keithley 2400 source meter and a Photo Research PR-655 SpectraScan spectroradiometer, respectively. All the measurements were made under atmospheric conditions. Device configuration is described as follows: ITO/PEDOT:PSS (30 nm)/emitting layer (40 nm)/LiF (1 nm)/Al (150 nm).

Results and discussion

The structural features of **1** were determined by X-ray crystallographic analysis. As depicted in Fig. 1, the central aromatic dihydro-indeno-indene framework is planar. Therefore, the charges generated in individual di-*p*-tolylamine segments of **3** may communicate more easily. Moreover, the pendent phenyl groups are tilted at $73.7 \pm 8.5^{\circ}$, resulting in a rigid structure that facilitates thermal stability and prevents unexpected intermolecular π - π stacking.

It has been reported that compound **3** emits sky-blue fluorescence with Em. λ_{max} at 459 nm and full-width at half-maximum (fwhm) of 47 nm [14]. Stacking this emission profile with the absorption bands of DCJTB [15] suggests the energy can be successfully transferred (Fig. 2). Accordingly, the emission behavior of mixtures



Fig. 1 ORTEP diagram for the X-ray crystal structure of 3 (ellipsoids are shown at 30 % probability level)



Fig. 2 Stacked plots of the absorption and emission spectra of 3 and DCJTB

of **3** and DCJTB in toluene solutions were examined (Fig. 3). On UV excitation at 410 nm, energy transfer does not occur until the molar ratio of DCJTB is >0.7; broad emission with Em. λ_{max} at 459 and 565 nm can then be observed (Fig. 3 inset). It is composed of dual emission from both molecules, which supports our concept.

On the basis of this preliminary study, we further fabricated a trilayer device to gain more insight into the EL for blending **3** and DCJTB. PEDOT:PSS [16]



Fig. 3 Stacked plots of the emission spectra of mixtures of 3 and DCJTB



Fig. 4 The EL spectrum of 3

and TPBI [17] were used as hole-injection and electron-transporting materials, respectively, along with electrodes.¹ As shown in Fig. 4, while light emission with $\text{CIE}_{x,y}$ at (0.33, 0.40) was obtained, as expected. This phenomenon can be explained by the energy-level diagram (Fig. 5). Because the HOMO and LUMO energies of **3** are higher than those of DCJTB by 0.7 ± 0.29 eV, the excitons generated in the host cannot completely transfer their energies to the guest. Therefore, a broad fluorescence spectrum is observed when **3** and DCJTB emit simultaneously.

¹ Details of the device are given in the "Experimental" section.



Fig. 5 Illustration of relative energy levels

Conclusions

In summary, we have fabricated a single-component white OLED on the basis of the bi-functional property of compound **3**. When DCJTB is used as guest material, white EL is generated, because of incomplete energy transfer. The configuration of the device will be optimized in due course.

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