Extremely deep-blue fluorescent emitters with CIEy ≤ 0.04 for non-doped organic light-emitting diodes based on an indenophenanthenrene core

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A R T I C L E   I N F O
Article history:
Received 31 March 2017
Received in revised form 24 April 2017
Accepted 5 May 2017
Available online 6 May 2017

Keywords:
Deep-blue emitter
Non-doped system
Fluorescent organic light-emitting diodes
Indenophenanthenrene
Charge balance

A B S T R A C T
The fluorescent molecules 7,7-dimethyl-NN-diphenyl-7H-indeno[1,2-a] phenanthren-9-amine (DIP) and 4-(7,7-dimethyl-7H-indeno[1,2-alphenanthren-9-vyl]-NN-diphenylaniline (TIP), with indenophenanthenrene cores and attached arylamine structures, were synthesized for use as extremely deep blue fluorescent emitting materials. A non-doped device using DIP as an emitting material exhibited a maximum external quantum efficiency of 3.27% and had Commission Internationale de l’Eclairage (CIE) color coordinates of (0.158, 0.040).

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1. Introduction

Full-color displays and white lighting require three primary color emissions (red, green, and blue (RGB)) of relatively equal stability, efficiency, and color purity [1]. In particular, extremely deep-blue-emitting materials play an important role in the development of efficient organic light-emitting diodes (OLEDs) because the deep blue emission is more energy efficient than a normal blue color when strong microcavity structures are chosen to enhance color purity [2].

Current deep-blue emitters are based on chromophores consisting of flat aromatic compounds such as anthracene, fluorene, and pyrene, which show high electroluminescence efficiencies. The 9-alkylated fluorene moiety is expected to be a good electroluminescent backbone for blue-emitting materials because of its excellent fluorescence properties and excellent morphological, thermal, and electrochemical stabilities [3,4]. However, in most planar aromatic compounds utilized for emitting materials, excimers or exciplexes are usually formed by intramolecular or intermolecular interactions between the emitters, resulting in bathochromic shifts of the Commission Internationale de l’Eclairage (CIE) chromaticity coordinates and low quantum efficiencies; this occurs because the emitters tend to be closely packed and aggregated in the emitting layer [5–7]. To overcome these problems, bulky side groups or spiro moieties were introduced to reduce packing between the molecules and limit the emission quenching, and this should enhance the purity and stability of the blue emissions, along with the photoluminescence (PL) quantum efficiency [4,8,9]. However, the introduction of bulky side groups or spiro moieties in flat blue emitters sometimes results in an unexpected bathochromic shift of the emitters in the solid state [10,11]. Therefore, an alternative way of developing deep blue emitters is required.

Deep-blue fluorescence OLEDs based on spirocyclic aromatic hydrocarbon derivatives and purine derivatives exhibit CIE coordinates of (0.16, 0.08) with a maximum current efficiency of 1.1 cd/A and CIE coordinates of (0.15, 0.06) with an external quantum efficiency (EQE) of 3.1%, respectively [12,13]. In addition, deep-blue emitters based on twisted asymmetric anthracene derivatives with triphenyltriazine- or triphenylamine-substituted xylene units have been reported to exhibit EQEs of 4.62 and 6.6% with CIE coordinates of (0.154, 0.049) and (0.145, 0.068), respectively [3,14]. Nevertheless, there have been few reports concerning color-pure, deep-blue fluorescent materials with CIE y-values around 0.04 and EQEs greater than 3% in non-doped devices [15].
In this study, we designed and synthesized two extremely deep-blue emitting materials based on an indenophenanthrene core for non-doped blue OLEDs with excellent color purity: 7,7-dimethyl-N,N-diaryl-7H-indeno[1,2-a]phenanthrene-9-amine (DIP) and 4-(7,7-dimethyl-7H-indeno[1,2-a]phenanthrene-9-yl)-N,N-diaryl-9H-anthracene. Because phenanthrene is less conjugated than anthracene, we designed an indenophenanthrene core by hybridizing a phenanthrene moiety with fluorene to induce a deep blue emission.

2. Materials and general methods

2.1. Materials

All solvents and materials were used as received from commercial suppliers without further purification. Synthetic routes to DIP and TIP are outlined in Fig. 2. The two final products (DIP and TIP) were purified by temperature gradient vacuum sublimation.

2.2. Synthetic procedure

2.2.1. 1-(Z)-2-(2-Bromophenyl)-1-ethenyl)-2-iodobenzene (2)

To a cooled (0 °C) suspension of (2-bromobenzyl)triphenylphosphonium bromide (1) (33.000 g, 64.425 mmol) in tetrahydrofuran (THF, 350 mL), potassium tert-butoxide (8.434 g, 75.163 mmol) in THF (50 mL) was added. After 30 min, 2-iodobenzaldehyde (12.457 g, 53.688 mmol) in THF (100 mL) was added over 1 h. The reaction was left to warm to room temperature (RT) and was stirred for 24 h. Then, water (100 mL) was added. The aqueous phase was separated and extracted with diethyl ether (3 × 300 mL). The combined organic extracts were dried (MgSO4), concentrated in vacuo, the resulting mixture was extracted with dichloromethane (50 mL). The combined organic extracts were washed successively with water and brine and dried using anhydrous sodium sulfate. The resulting mixture was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried using anhydrous sodium sulfate, which was filtered through celite and potassium fluoride.

2.2.2. 1-Bromophenanthrene (3)

A solution of stilbene (2:9:1 mixture of (Z)- and (E)-isomers, 15.1 g, 39.217 mmol), tributyltin hydride (13.697 g, 47.060 mmol), and azobisisobutyronitrile (AIBN) (1.288 g, 7.843 mmol) in toluene (200 mL) was heated at 90 °C for 16 h in nitrogen atmosphere and then cooled to RT. Additional tributyltin hydride (2.283 g, 7.843 mmol) and AIBN (0.258 g, 1.569 mmol) were added, and the reaction was heated for a further 8 h at 90 °C. After cooling to RT and concentration in vacuo, the resulting mixture was extracted with excess dichloromethane. The organic layer was washed successively with water and brine and dried using anhydrous sodium sulfate, which was filtered through celite and potassium fluoride. The product mixture was purified by column chromatography (10% KF/SiO2, hexane) to afford 1-bromophenanthrene (8.4 g, 32.668 mmol, 83.3%) as a white solid.

2.2.3. Phenanthren-1-ylboronic acid (4)

1-Bromophenanthrene (3) (3.0 g, 11.667 mmol) was dissolved in dry THF (100 mL) under an atmosphere of nitrogen. This solution was cooled to −78 °C, followed by the dropwise addition of n-butyllithium (2.5 M in hexane, 11.667 mL, 29.168 mmol). This mixture was stirred for 1 h and then treated with trimethylborate (6.539 mL, 58.336 mmol). After stirring at RT for 15 h, the reaction mixture was added to an aqueous solution of HCl (1 N) and stirred for 2 h. The aqueous phase was separated and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried using sodium sulfate, concentrated in vacuo, and purified by column chromatography (SiO2, dichloromethane:methanol = 9:1) to afford phenanthren-1-ylboronic acid (1.8 g, 8.105 mmol, 69.5%) as a white solid.

2.2.4. Methyl 5-bromo-2-(phenanthren-1-yl)benzoate (5)

A mixture of methyl 5-bromo-2-iodobenzoate (3.849 g, 11.259 mmol), phenanthren-1-ylboronic acid (4) (3 g, 13.510 mmol), 2 M aqueous potassium carbonate (30 mL), and tetrakis(triphenylphosphine)palladium (0.651 g, 0.563 mmol) in THF (100 mL) and methanol (30 mL) was heated at reflux in a nitrogen atmosphere for 24 h. After the reaction mixture had been concentrated in vacuo, the resulting mixture was extracted with dichloromethane. The organic layer was washed with water and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture that was purified by column chromatography (SiO2, dichloromethane:hexane = 1:4) to afford methyl 5-bromo-2-(phenanthren-1-yl)benzoate (3.5 g, 8.945 mmol, 79%) as a white solid.

2.2.5. 2-(5-Bromo-2-(phenanthren-1-yl)phenyl)propan-2-ol (6)

To a solution of methyl 5-bromo-2-(phenanthren-1-yl)benzoate (5) (dissolved in dry THF (120 mL) under a nitrogen atmosphere, a solution of methylmagnesium bromide solution in diethyl ether (1.4 M, 14.85 mL, 21.162 mmol) was slowly added. The mixture was heated at reflux for 4 h. After the reaction mixture had been concentrated in vacuo, the resulting mixture was extracted with dichloromethane. The organic layer was washed with water and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture that was purified by column chromatography (SiO2, ethyl acetate:hexane = 1:20) to afford the 2-(5-bromo-2-(phenanthren-1-yl)phenyl)propan-2-ol (2.7 g, 6.900 mmol, 75%) as a white solid. 1H NMR (300 MHz, CDCl3): δ (ppm) 8.77 (d, J = 5.1 Hz, 2H), 8.03 (d, J = 1.8 Hz, 1H), 7.89 (d, J = 4.5 Hz, 1H), 7.88–7.62 (m, 4H), 7.52–7.47 (m, 2H), 7.33 (d, J = 9.3 Hz, 2H), 7.03 (d, J = 8.1 Hz, 1H), 1.39 (s, 3H), 1.22 (s, 3H). 13C NMR (75 MHz, CDCl3): δ (ppm) 149.5, 140.4, 136.7, 134.2, 131.7, 131.0, 130.3, 130.2, 128.5, 127.2, 126.8, 126.7, 125.7, 123.9, 122.9, 122.4, 121.5, 52.1. HR-Mass (El+): calcd for C21H18BrO2 392.0255, found 392.0257.

2.2.6. 9-Bromo-7,7-dimethyl-7H-indeno[1,2-a]phenanthrene (7)

Concentrated sulfuric acid (4.5 mL) was added to a stirred...
solution of 2-(5-bromo-2-phenanthren-1-yl)phenylpropan-2-ol (6) (2.7 g, 6.918 mmol) in acetic acid (139 mL) at 100 °C. After stirring for 3 h at 100 °C, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture that was purified by column chromatography (SiO2, hexane) to afford 9-bromo-7,7-dimethyl-7H-indeno[1,2-a]phenanthrene (1.8 g, 4.830 mmol, 70%) as a white solid. 1H NMR (400 MHz, CDCl3): δ (ppm) 8.76 (t, J = 5.4 Hz, 2H), 8.63 (d, J = 9.3 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.97–7.91 (m, 2H), 7.71–7.59 (m, 4H), 1.59 (s, 6H). 13C NMR (75 MHz, CDCl3): δ (ppm) 150.7, 152.7, 130.2, 128.6, 127.9, 126.9, 126.7, 126.5, 126.2, 124.7, 123.0, 122.3, 120.9, 120.7, 46.5, 26.9. HR-Mass (EI−): calcd for C37H29N 372.0514, found 372.0514.

2.2.7. 7,7-Dimethyl-N,N-diphenyl-7H-indeno[1,2-a]phenanthren-9-amine (DIP)

To a mixture of 9-bromo-7,7-dimethyl-7H-indeno[1,2-a]phenanthrene (7) (2.65 g, 7.099 mmol), diphenylamine (1.561 g, 9.229 mmol), and palladium acetate (0.111 g, 0.497 mmol) in dry toluene (80 mL) under an N2 atmosphere, a solution of tri-tert-butylyphosphine (0.28 g, 1.420 mmol) and potassium tert-butoxide (3.187 g, 28.389 mmol) in toluene (20 mL) was added. The mixture was heated to reflux under nitrogen. After 12 h, the reaction mixture was concentrated in vacuo, and the resulting mixture was extracted with dichloromethane. The organic layer was washed successively with water and brine and dried using anhydrous sodium sulfate. The filtrate was concentrated in vacuo to give a crude mixture, which was purified by column chromatography (SiO2, hexane) to afford 7,7-dimethyl-N,N-diphenyl-7H-indeno[1,2-a]phenanthren-9-amine (2.15 g, 4.658 mmol, 66%) as a bright yellow solid. 1H NMR (400 MHz, CDCl3): δ (ppm) 7.72 (m, 4H), 7.18 (m, 6H), 7.12 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.26–7.18 (m, 6H), 7.12–7.05 (m, 4H), 6.98 (t, J = 7.2 Hz, 2H), 1.54 (s, 6H). 13C NMR (75 MHz, CDCl3): δ (ppm) 157.0, 152.7, 130.2, 128.6, 127.9, 126.9, 126.7, 126.5, 126.2, 124.7, 123.0, 122.9, 122.3, 120.7, 47.5. HR-Mass (EI−): calcd for C41H31N 537.2457, found 537.2457.

2.2.8. 4-(7,7-Dimethyl-7H-indeno[1,2-a]phenanthren-9-yl)-N,N-diphenylaniline (TIP)

A mixture of 9-bromo-7,7-dimethyl-7H-indeno[1,2-a]phenanthrene (7) (1.5 g, 4.018 mmol), 4-(diphenylamino)phenylboronic acid (2.2 mmol), 4-(diphenylamino)-phenylboronic acid potassium tert-butoxide (3.187 g, 28.389 mmol) in toluene (20 mL) was added. The mixture was heated to reflush under nitrogen. After 12 h, the reaction mixture was concentrated in vacuo to give a crude mixture, which was purified by column chromatography (SiO2, hexane) to afford 4-(7,7-dimethyl-7H-indeno[1,2-a]phenanthren-9-yl)-N,N-diphenylaniline (TIP) (1.4 g, 2.2 mmol, 64.8%) as a yellow solid. 1H NMR (300 MHz, CDCl3): δ (ppm) 8.66 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 9.2 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 9.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.26–7.18 (m, 6H), 7.12–7.05 (m, 4H), 6.98 (t, J = 7.2 Hz, 2H), 1.43 (s, 6H). 13C NMR (100 MHz, CDCl3): δ (ppm) 150.7, 152.7, 130.2, 128.6, 127.9, 126.9, 126.7, 126.5, 126.2, 124.7, 123.0, 122.9, 122.7, 122.3, 121.0, 120.8, 46.5, 27.1. HR-Mass (EI−): calcd for C43H33N 537.2457, found 537.2457.

2.3. General methods

1H and 13C NMR spectra were recorded using an Agilent 400 MHz Varian spectrometer in CDCl3. 1H NMR chemical shifts in CDCl3 were referenced to CHCl3 (7.27 ppm). 13C NMR chemical shifts in CDCl3 were reported relative to CHCl3 (77.23 ppm). UV–visible spectra were recorded on a Beckman DU650 spectrophotometer. Fluorescence spectra were recorded on a Jasco FP–6500 spectrophotometer. Mass spectra were obtained using matrix-assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF-MS) from Bruker. High-resolution masses were measured by either fast atom bombardment (FAB) or electron ionization (EI) using a JEOL HP 5890. Analytical thin-layer chromatography was performed using Kieselgel 60F-254 plates from Merck. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh). Decomposition temperatures (Td) and glass transition temperatures (Tg) were obtained by thermogravimetric analysis (TGA, Q-5000-IR) and differential scanning calorimetry (DSC, DSC-Q-1000), respectively. The TGA and DSC analyses were performed at a heating rate of 10 °C/min under a nitrogen atmosphere. The Tg was determined from the third heating scan. The electrochemical properties of DIP and TIP were studied using cyclic voltammometry (CV) in CH2Cl2 solutions (1.00 mM) with 0.1 M tetra-n-butylammonium hexafluorophosphate ([BAF6]2) as the supporting electrolyte. A glassy carbon electrode was employed as the working electrode and referenced to a Ag reference electrode. All potential values were calibrated against the ferrocene/ferrocinium (Fc/Fc+) redox couple. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

2.4. Theoretical calculations

The optimized geometries and frontier molecular orbital energy levels for DIP and TIP were obtained using density functional theory (DFT) calculations with Gaussian 09. The geometries were optimized using the Becke 3-parameter Lee−Yang−Parr (B3LYP) functional with the 6-311G-level atomic basis set.

2.5. Device fabrication & characterization

N,N′-Di[1-naphthyl]-N,N′-diphenyl-(1′,1′-biphenyl)-4,4′-diamine (NPB), 4,4′,4′′-tris[N-carbazolyl]triphenylamine (TCTA), and 1,3,5-tris[N-phenylbenzimidazol-2-yl]benzene (TPBI) were purchased from commercial sources and used without purification. The fabrication of OLEDs was conducted by the high-vacuum (2 × 10−6 Torr) thermal evaporation of the organic materials onto indium tin oxide (ITO)-coated glass (sheet resistance: 15 Ω/square; Applied Film Corp.). Glass substrates with patterned ITO electrodes were washed with isopropl alcohol and then cleaned by O2 plasma treatment. The OLED devices were fabricated with a configuration of ITO/NPB/TCTA/DIP or TIP/TPBI/LiF/Al. NPB and TCTA (hole transporting layers), TPBI (electron transporting layer), LiF (electron injection layer), and Al electrodes were deposited sequentially on the substrate. The emission properties were determined using a PR-650 SpectraScan SpectraColorimeter as a source meter. The current–voltage characteristics were measured using a programmable electrometer equipped with current and voltage sources (Keithley 2400).

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3. Results and discussion

3.1. Theoretical calculation

Optimized geometries and frontier molecular orbital energy levels for DIP and TIP were obtained from DFT calculations at the B3LYP/6-311G level using Gaussian 09. As shown in Fig. 1, the indenophenanthrene moiety is slightly distorted from the perfect planarity because of the syn-pentane-like interactions between the hydrogen at the C5 position and the hydrogen at the C14 position of DIP and the C13 position of TIP. The calculated results show that the dihedral angle connecting the C5-C4-C9-C14 of DIP is twisted about 1.7°, and the dihedral angle connecting the C5-C4-C8-C14 of TIP is 2.4°, respectively. In TIP, the dihedral angle between additional phenyl ring and indenophenanthrene moiety is 37.1°. The introduction of the twisted structure of the diphenylamine and triphenylamine moieties inhibited the aggregation of DIP and TIP in the non-doped film. The highest occupied molecule orbitals (HOMOs) of DIP and TIP are localized on the diphenylamine and triphenylamine moieties along with the fluorene moiety of indenophenanthrene, while the lowest unoccupied molecular orbitals (LUMOs) of DIP and TIP are dispersed over the indenophenanthrene core [18]. The DFT-calculated HOMO and LUMO energies are similar, at 5.23 and 1.60 eV for DIP and 5.21 and 1.58 eV for TIP, respectively [19].

3.2. Synthesis

The synthetic routes to DIP and TIP are illustrated in Fig. 2. The synthesis of 9-bromo-7,7-dimethyl-7H-indeno[1,2-a]phenanthrene (7) was started from 1-bromophenanthrene (3) [20]. Methyl 5-bromo-2-(phenanthren-1-yl)benzoate (5) was obtained using a Suzuki cross-coupling reaction between phenanthren-1-ylboronic acid (4) and methyl 5-bromo-2-iodobenzoate. Next, Grignard methylation followed by Friedel-Craft cyclization under acidic conditions afforded compound 7. DIP and TIP consist of two main components: either diphenylamine or triphenylamine as the hole-transporting moiety and indenophenanthrene as the emissive moiety; these two components were connected by the Buchwald

Fig. 1. Optimized structures and calculated highest occupied molecular orbital and lowest occupied molecular orbital density maps obtained from DFT calculations of DIP and TIP, performed at the B3LYP/6-311G level of theory.
cross-coupling and the Suzuki cross-coupling reactions, respectively [21]. DIP and TIP were characterized by 1H NMR, 13C NMR, and low- and high-resolution mass spectrometry. These two blue emitting materials were purified further by train sublimation under reduced pressure (<10⁻⁴ Torr).

3.3. Thermal properties

The thermal properties of DIP and TIP were investigated using DSC and TGA (Fig. 3). DIP and TIP exhibit high thermal stability with a decomposition temperature (T_d, corresponding to 5% weight loss) of 326.9 and 354.4 °C, respectively, and a T_g of 90.3 and 112.8 °C, respectively. TIP is more thermally stable than DIP because of the additional phenyl linker moiety [22].

3.4. Photophysical properties

Fig. 4 shows the normalized UV–vis absorbance and PL spectra of DIP and TIP (Table 1). All absorption bands between 330 and 400 nm for DIP and TIP originate from the intramolecular charge-transfer transitions from the arylamine to indenophenanthrene moiety. The absorption band shape of the brominated indenophenanthrene (7), an intermediate synthetic compound, is similar compared to those of DIP and TIP (Fig. S1). In toluene, the PL λ_max peaks of DIP and TIP were observed around 420 nm. Compared to the solution state, the emission maxima of DIP and TIP in the solid state show a slight bathochromic shift of about 10 nm, indicating that the aggregation effect is rarely observed in the solid states of DIP and TIP. Despite the extra phenyl unit introduced in TIP, the PL

![Fig. 2. Synthetic routes to DIP and TIP.](image)

![Fig. 3. DSC and TGA graphs of DIP and TIP.](image)

![Fig. 4. UV–vis absorption and PL spectra of DIP (black squares) and TIP (red circles). (Dashed lines and open symbols: UV–vis absorption in toluene (10 μM); solid lines and open symbols: PL spectra in toluene (10 μM); and solid lines and filled symbols: PL spectra in the film state.)](image)
emission spectra in solution and solid states of DIP and TIP are very
similar [19]. These results demonstrate that the additional phenyl
ring of TIP does not contribute to the extension of the conjugation
length because of the distorted dihedral angle (37.1° C14
C) between the
additional phenyl ring and the indenophenanthrene moiety.
The fluorescence quantum yields (Φfl) of DIP and TIP were
measured to be 0.77 and 0.90, respectively, using 9,10-di(naphth-2-
yl)anthracene (ADN, Φfl = 0.57) as a reference at room temperature
(Table 1) [23]. And the fluorescence quantum yields (Φfl) of solid
DIP and DIP are 0.44 and 0.52, respectively (Table 1).

The absorption onsets of the UV–vis spectra of DIP and TIP
were both found to be 400 nm, which corresponds to an optical
bandgap of 3.1 eV. From the optical bandgap and the HOMO en-
ergy levels of 5.3 and 5.4 eV for DIP and TIP, respectively, esti-

3.5. Electroluminescence properties

OLED devices were fabricated using DIP or TIP as a non-doped
deep-blue fluorescent emitter in the emitting layer (EML). The
device configuration was ITO/NPB (40 nm)/TCTA (20 nm)/EML (DIP
or TIP, 30 nm)/TPBI (15 nm)/LiF (1 nm)/Al (100 nm). Fig. 5(a) shows
the current density–voltage characteristics of the OLED devices
containing DIP and TIP used as the EML, and the performances of
the OLEDs are summarized in Table 2 and Fig. S3. Both of the de-

Table 1
Thermal and photophysical properties of DIP and TIP.

<table>
<thead>
<tr>
<th></th>
<th>Td/Tg (°C)</th>
<th>λabs a (nm)</th>
<th>λPL a (nm)</th>
<th>λPL b (nm)</th>
<th>Φfl</th>
<th>Eg c (eV)</th>
<th>HOMO d/LUMO e (eV)</th>
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</thead>
<tbody>
<tr>
<td>DIP</td>
<td>326.9/90.3</td>
<td>364, 382</td>
<td>415</td>
<td>426</td>
<td>0.77, 0.44b</td>
<td>3.1</td>
<td>5.3, 2.2</td>
</tr>
<tr>
<td>TIP</td>
<td>354.4/112.8</td>
<td>358, 370</td>
<td>413, 429</td>
<td>428</td>
<td>0.90, 0.52b</td>
<td>3.1</td>
<td>5.4, 2.3</td>
</tr>
</tbody>
</table>

a 10 μM in toluene.
b Neat film.
c Onset absorption wavelength in toluene.
d CV oxidation potential in dichloromethane (Fc/Fc+ as reference: 4.7 eV).
e Deduced from HOMO and Eg.

Fig. 5. Device performance of the deep-blue OLEDs containing DIP and TIP. (a) The current density-voltage characteristics (inset: energy level diagram of the devices), (b) lumin-

ance–voltage characteristics, (c) quantum efficiency–current density characteristics, and (d) electroluminescence spectra (inset: device structure and thickness of each layer).
Table 2
The performance of the non-doped deep blue devices containing DIP and TIP as the emitting layers.

<table>
<thead>
<tr>
<th>EML</th>
<th>$V_{on}$ (V)</th>
<th>$\text{EQE}_{\text{max}}$ (%)</th>
<th>$\text{EQE}_{\text{b}}$ (%)</th>
<th>$\text{LE}_{\text{max}}$ (cd A$^{-1}$)</th>
<th>$\text{PE}_{\text{max}}^d$ (lm W$^{-1}$)</th>
<th>$\text{EL}_{\text{max}}$ (nm)</th>
<th>CIE$^c$ (x, y)</th>
<th>FWHM$^b$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIP</td>
<td>3.2</td>
<td>3.27</td>
<td>3.25</td>
<td>1.11</td>
<td>0.89</td>
<td>424</td>
<td>(0.158, 0.040)</td>
<td>44</td>
</tr>
<tr>
<td>TIP</td>
<td>3.2</td>
<td>1.77</td>
<td>1.70</td>
<td>1.00</td>
<td>0.83</td>
<td>428</td>
<td>(0.158, 0.069)</td>
<td>52</td>
</tr>
</tbody>
</table>

$^a$ Turn-on voltage at 1 cd/m$^2$.
$^b$ At 10 mA/cm$^2$.
$^c$ Luminance efficiency (LE).
$^d$ Power efficiency (PE).

Indicate that the electroluminescent (EL) performance of the DIP-based device is more efficient than that of the TIP-based device. The quantum efficiency—current density of two devices is plotted in Fig. 5(c). The DIP-based device shows a better maximum EQE of 3.27% compared to that (1.77%) of the TIP-based device. Fig. 5(d) shows the normalized EL spectra of the DIP and TIP-based devices with maximum peak wavelengths at 424 and 428 nm, respectively, which originates from the singlet exciton of each emitter without any other emission from the adjacent layers. The CIE coordinates of the DIP and TIP-based devices are (0.158, 0.040) and (0.158, 0.069), respectively. The much smaller y-coordinate value of the DIP-based device results from its narrower EL spectrum (the full width at half maximum (FWHM) of 44 nm) compared to the TIP-based device (the FWHM of 52 nm) [25].

For the investigation of the carrier balance of the DIP and TIP-based devices, hole-only and electron-only devices were also fabricated. The configuration of the hole-only devices was ITO/NPB (40 nm)/TCTA (20 nm)/DIP or TIP (30 nm)/Al (100 nm), and the electron-only devices had an ITO/TPBI (5 nm)/DIP or TIP (30 nm)/TPBI (15 nm)/LiF (1 nm)/Al (100 nm) structure. NPB (LUMO: 2.3 eV) on the cathode side of the hole-only devices and TPBI (HOMO: 6.3 eV) on the anode side of the electron-only devices were utilized to block electron injection from Al (4.3 eV, corresponding to a large energy barrier of 2.0 eV) and hole injection from ITO (4.8 eV, corresponding to a large energy barrier of 1.5 eV), respectively. Fig. 6 shows the current density–voltage curves of hole-only and electron-only devices of DIP and TIP, respectively. Both the hole and electron carrier densities of the TIP-based device are higher than carrier density of the DIP-based device at the same voltage. However, in the case of the TIP-based device, the hole density is lower in comparison with electron density at the same voltage, whereas, in the case of the DIP-based device, the hole and electron densities are well matched at the same voltage. This phenomenon can be explained by the differences in the HOMO and LUMO energy levels between DIP and TIP. Because of the higher HOMO energy level of 5.3 eV of DIP and 5.4 eV of TIP than that (5.7 eV) of TCTA, neither have a hole injection barrier from the hole transport layer (HTL) to the EML. In contrast, the LUMO energy levels of DIP and TIP are 2.1 and 2.2 eV, respectively, indicating that electron injection from the electron transport layer (ETL) to the EML of TIP is easier than that of TIP. Despite the small difference in the energy levels of both deep-blue emitters, there is a discrepancy in the current densities at the same voltage (Fig. 5(a)).

Thus, the DIP-based device is more efficient than the TIP-based device because of the relatively better hole and electron charge balance. Although more excitons were generated from the TIP-based device than the DIP-based device, the excess electron injection caused exciton-polaron quenching, arising from the hole and electron imbalance. Therefore, the DIP-based device exhibited higher efficiency than the TIP-based device [19,26]. These results agree with the energy level diagrams of devices using DIP and TIP as EMLs (Fig. 5(a) inset).

4. Conclusion

Novel luminescent molecules with indenophenanthrene cores attached to either triphenylamine or diphenylamine moieties were designed and synthesized for use as extremely deep blue fluorescent emitting materials. Because the DIP-based OLED device has a well-matched hole and electron density at the same voltage, the DIP-based device exhibited a higher efficiency than the TIP-based device. A non-doped device using DIP as the emitting material exhibited a maximum EQE of 3.27% with CIE color coordinates of (0.158, 0.040). The introduction of the indenophenanthrene moiety reported in this study suggests a new strategy for the molecular design of highly efficient non-doped deep blue OLED materials.

Acknowledgements

This work was supported by the NRF grant (2015R1A2A1A15055347) funded by the MSIP. We thank the Samsung Display Co., Ltd. for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.05.014.

References


