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Highly Efficient Non-doped Deep-blue Organic Light-Emitting Diodes by Employing a Highly Rigid Skeleton

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Abstract

Two novel deep-blue emitters based on a highly rigid unit, IDC-PA and IDC-Py, were prepared by respectively introducing the 7,7-dimethyl-5-phenyl-5,7-dihydro indeno [2,1-b] carbazole (IDC) unit with anthracene and pyrene derivatives. The emitters exhibit high quantum efficiency, excellent thermal stability, narrow full width at half maximum and deep-blue emission. Moreover, the IDC-PA and IDC-Py-based devices demonstrated maximum EQEs of 4.41% and 6.08% and maintain 4.35% and 5.35% as applied in non-doped devices even at the brightness of 5000 cd m⁻² with CIE coordinates of (0.15, 0.10) and (0.15, 0.08), respectively.

Keywords

Fluorescent OLED; Non-doped; High Rigidity; Deep-blue.

1. Introduction

Organic light-emitting diodes (OLEDs) have drawn considerable attention due to the potential application in future illuminations and information displays, such as residential lamps, automobile tail lights, TVs and computer monitors.^{1,2} Therefore, many material systems have been explored over the past decades for the goal of highly efficient OLED emitters with fluorescence,³⁻⁷ phosphorescence,⁸⁻¹² or thermally activated delayed fluorescence (TADF).¹³⁻¹⁶ The fluorescent emitters were firstly investigated covering the whole visible region, but the maximum internal quantum efficiency is limited to 25% because they can only harvest singlet excitons. This fact promotes researchers to develop phosphorescent or TADF emitters which can harness all the electron-generated excitons in theory. The phosphorescent dyes, however, are limited by the high cost of noble metal elements and it is difficult to achieve deep-blue emission, i.e. giving a Commission International de l'Eclairge "y" coordinate (CIEy) < 0.15.¹⁷ This problem can be partly ascribed to the host-guest doping system for the application of phosphorescent and TADF emitters. Given a deep-blue emitter, a wider band-gap host is necessary to prevent any energy back transfer. However, the consequence is that the carrier injection from neighboring transport layer to the emitting layer could be very tough. On the other hand, the TADF materials with deep-blue emission for OLEDs are still lacking,¹⁸ and they also faced the challenge in reducing the efficiency roll-off at high operation luminance. According to the standard of National Television System Committee (NTSC), the CIEy of blue emission should be further limited to 0.08. In this regard, the fluorescent emitters regenerated new interest because they could be used without host and the molecular design aiming for deep-blue emitters with low efficiency roll-off could be achievable.¹⁹⁻²⁵

Anthracene and pyrene are two important candidate blocks for fluorescent blue emitters because of their high quantum efficiency, good carrier mobility, and chemical stability.²⁶⁻³³ However, the anthracene and pyrene derivatives also suffer from aggregation induced red-shift due to intermolecular packing in the film state, which is ascribed to their plate-like structure. In this work, we report the synthesis and characterization of two new fluorescent dyes, named IDC-PA and IDC-Py, to introduce highly rigid skeleton unit, 7,7-dimethyl-5-phenyl-5,7-dihydroindeno[2,1-*b*]carbazole (IDC), which can effectively alleviate the aggregation effect. They also exhibit good thermal stability and show strong blue emission in both solution and film. Both of dyes can act as the emitters in non-doped OLEDs without any hole-injection layers, giving the maximum external quantum efficiency (EQE) of 4.41% for IDC-PA and 6.08% for IDC-Py, respectively. Consequently, they present deep-blue electroluminescence, for which the CIEys are 0.10 and 0.08, subsequently.

2. Experimental

2.1. Chemicals and Characterization

All reagents used in the synthesis procedure were purchased from Shanghai Titan Scientific Co., Ltd without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system. Tris (4-(9*H*-carbazol-9-yl) phenyl)amine (TCTA), *N,N'-bis*-(1-naphthalenyl)-*N,N'-bis*-phenyl-(1,1'-biphenyl)-4,4' diamine (NPB), *1,3,5-tris*(1-phenyl-1*H*-benzimidazole-2-yl)benzene (TPBi), 8-Hydroxyquinolinolato-lithium (Liq) and aluminum (Al) were purchased from Lumtec Company. ¹H NMR spectra were recorded using Bruker 400 MHz and 600 MHz NMR instrument, while ¹³C

NMR spectra were recorded on an Agilent DD2-600 MHz NMR instrument. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 K min⁻¹ under nitrogen. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 K min⁻¹ under nitrogen. Elemental Analysis (EA) was determined by ELEMENTAL Vario III elemental analyzer. The film surface morphologies were evaluated by atomic force microscopy (AFM, Multimode V, Veeco). Ultraviolet photoelectron spectroscopy (UPS) measurement was carried out in a Kratos AXIS UltraDLD ultrahigh vacuum (UHV) surface analysis system. The electroluminescence (EL) and current density-voltage (J-V) characteristics of the devices were measured using a constant current source meter unit (Keithley 2400s Source Meter) equipped with a photometer (Photo Research PR 655 spectrophotometer).

2.2. Synthetic Process

2.2.1 Methyl 2-(9-phenyl-9*H*-carbazol-3-yl) benzoate (1)

(9-phenyl-9*H*-carbazol-3-yl) boronic acid (10.0 g, 34.8 mmol), methyl 2-iodobenzoate (10.0 g, 38.3 mmol), K_2CO_3 (2M in water, 20 mL) and Pd(PPh₃)₄ (0.4 g, 0.35 mmol) were dissolved in toluene (120 mL), the mixture was stirred at 100 °C under nitrogen for 48 h. After cooling to room temperature, the organic phase was separated and concentrated. The residue was purified by silica gel column chromatography using an eluent mixture of dichloromethane and petroleum ether in the volume ratio of 1:2 to give a white solid with

10.1 g (yield: 83.6%). ¹H NMR (600 MHz, DMSO-d6) δ 8.29 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 1.2 Hz, 1H), 7.77 (dd, J = 7.8, 1.2 Hz, 1H), 7.71 (t, J = 7.8 Hz, 2H), 7.67 – 7.64 (m, 3H), 7.57 (dd, J = 7.8, 2.4 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.42 (d, J = 1.2 Hz, 1H), 7.40 (s, 1H), 7.32 (ddd, J = 14.4, 8.4, 1.2 Hz, 2H), 3.59 (s, 3H). ¹³C NMR (CDCl₃, 400 MHz) (δ , ppm): 169.66, 142.94, 141.27, 140.20, 137.66, 133.21, 131.25, 131.17, 129.90, 129.71, 127.50, 127.08, 126.73, 126.70, 126.08, 123.43, 123.36, 120.36, 120.04, 119.94, 109.90, 109.35, 52.03. Anal. calcd for C₂₆H₁₉NO₂(%): C, 82.74; H, 5.07; N, 3.71. Found: C, 82.41; H, 5.25; N, 3.52. MS (EI) m/z: 377.21 [M⁺].

2.2.2 2-(2-(9-phenyl-9*H*-carbazol-3-yl) phenyl) propan-2-ol (2)

2-(9-phenyl-9*H*-carbazol-3-yl)benzoate (4.0 g, 10.6 mmol) was dissolved in anhydrous tetrahydrofuran, CH₃MgCl (2M in THF, 21 mL, 42.4 mmol) was added dropwise at room temperature, the mixture was heated up to 65 °C and kept at same temperature for 10 hours under nitrogen atmosphere. After cooling to room temperature, the reaction was quenched with NH₄Cl solution. The organic layer was dried by anhydrous sodium sulfate, and concentrated. The residue was purified by silica gel column chromatography using an eluent mixture of ethyl acetate and petroleum ether in the volume ratio of 1:4, a white amorphous powder was obtained with 2.9 g (yield:72.5%). ¹H NMR (600 MHz, DMSO-d6) δ 8.26 (d, *J* = 7.8 Hz, 1H), 8.11 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.66 (m, 4H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.36 (s, 2H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 6.0 Hz, 1H), 4.86 (s, 1H), 1.24 (s, 6H). ¹³C NMR (CDCl₃, 400 MHz) (δ , ppm): 146.64, 141.35, 140.47, 139.93, 137.58, 135.12, 132.96, 127.66, 127.57, 127.33, 127.10, 126.25,

125.98, 125.78, 123.12, 122.86, 121.09, 120.39, 120.08, 109.94, 109.09, 74.24, 32.70. Anal. calcd for C₂₇H₂₃NO (%): C, 85.91; H, 6.14; N, 3.71. Found: C, 85.85; H, 6.25; N, 3.62. MS (EI) m/z: 377.53 [M⁺].

2.2.3 7,7-dimethyl-5-phenyl-5,7-dihydroindeno[2,1-*b*]carbazole (3)

2-(2-(9-phenyl-9*H*-carbazol-3-yl)phenyl)propan-2-ol (3.8 g, 10.0 mmol) was dissolved in dichloromethane (50 mL) and cooled to 0 °C, a mixture of polyphosphoric acid (3.0 g) in methanesulfonic acid (2 mL) was also added and left for 1 hour at 0 °C, ethanol (100 mL) was added, and heated up to 80 °C and kept it for 2 h. Dichloromethane was evaporated and a colorless precipitate was filtered off, washed twice with methanol which gives a white solid with 2.7 g (yield: 75.0%). ¹H NMR (400 MHz, CDCl₃) δ 8.55 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.66 – 7.51 (m, 6H), 7.45 – 7.31 (m, 6H), 1.93 (s, 6H). ¹³C NMR (CDCl₃, 400 MHz) (δ ppm): 154.04, 147.99, 145.95, 141.75, 141.71, 139.74, 137.59, 131.98, 129.94, 127.86, 126.87, 125.95, 125.55, 124.49, 122.16, 121.73, 119.88, 119.22, 118.81, 118.03, 109.96, 108.90, 47.97, 24.08. Anal. calcd for C₂₇H₂₁N (%): C, 90.21; H, 5.89; N, 3.90. Found: C, 90.35; H, 5.68; N, 3.97. MS (EI) m/z: 359.29 [M⁺].

2.2.4 2-bromo-7,7-dimethyl-5-phenyl-5,7-dihydroindeno[2,1-b]carbazole (4)

7,7-dimethyl-5-phenyl-5,7-dihydroindeno[2,1-*b*]carbazole (7.5 g, 20.9 mmol) was dissolved in *N*,*N*-dimethylformamide, while *N*-bromosuccinimide (3.7 g, 20.9 mmol) was added over the course of 30 min at room temperature in the dark, The mixture was stirred for 8 h and poured into the Na₂CO₃ solution (3M, 1 L). The product was extracted with

dichloromethane, and the organic phase was separated and concentrated. The residue was recrystallized to give the product as a white solid with 8.3 g (yield: 92%). ¹H NMR (600 MHz, CDCl₃) δ 8.60 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 4H), 7.50 (d, *J* = 9.6 Hz, 1H), 7.40 – 7.29 (m, 4H), 1.89 (s, 6H). ¹³C NMR (CDCl₃, 400 MHz) (δ , ppm): 153.92, 148.13, 141.99, 140.40, 139.46, 137.14, 132.38, 130.07, 128.26, 128.20, 127.75, 127.18, 126.96, 126.86, 126.18, 123.48, 122.21, 118.90, 118.75, 112.57, 111.35, 109.14, 48.00, 24.17. Anal. calcd for C₂₇H₂₀BrN (%): C, 73.98; H, 4.60; N, 3.20. Found: C, 73.85; H, 4.68; N, 3.02. MS (EI) m/z: 437.31 [M⁺].

2.2.5 7,7-dimethyl-5-phenyl-2-(10-phenylanthracen-9-yl)-5,7-dihydroindeno [2,1b]carbazole (IDC-PA) and 7,7-dimethyl-5-phenyl-2-(pyren-1-yl)-5,7dihydroindeno[2,1-b]carbazole (IDC-Py)

2-bromo-7,7-dimethyl-5-phenyl-5,7-dihydroindeno[2,1-*b*]carbazole (0.9 g, 2.0 mmol), 1.5 equivalent of arylboronic acid, 2M K₂CO₃ (10 mL), and Pd(PPh₃)₄ (0.023 g, 0.02 mmol) were added to 1,4-dioxane (80 mL), and stirred at 100 °C for 12 h under nitrogen atmosphere. The organic layer was concentrated and purified by silica gel column chromatography using an eluent mixture of dichloromethane and petroleum ether in the volume ratio of 1:3, which give a white powder with 0.96 g (yields: 77%) and 0.84 g (yields: 73%), respectively. IDC-PA: mp: 334 °C (760 mmHg). IR (KBr): *v* 3062, 2955, 1595, 1505, 1452, 1388, 1298, 1230, 763, 752 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 8.65 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.69 (m, 8H), 7.62 (dd, *J* = 15.6, 7.8 Hz, 4H), 7.59 – 7.55 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.31 (m, 6H), 7.26 (d, J = 7.2 Hz, 1H), 1.77 (s, 6H). ¹³C NMR (CDCl₃, 400 MHz) (δ , ppm): 154.10, 148.23, 142.22, 141.12, 139.69, 138.65, 137.64, 132.93, 132.25, 131.60, 131.11, 130.37, 130.07, 128.89, 128.35, 128.19, 128.04, 127.89, 127.49, 127.43, 127.30, 126.90, 126.64, 126.03, 126.02, 125.58, 125.03, 124.75, 124.73, 122.20, 118.86, 118.32, 109.91, 109.12, 48.07, 24.16. Anal. calcd for C₄₇H₃₃N (%): C, 92.27; H, 5.44; N, 2.29. Found: C, 92.31; H, 5.17; N, 2.52. MS (EI) m/z: 611.46 [M⁺].

IDC-Py: mp: 288 °C (760 mmHg). IR (KBr): v 3045, 2966, 1600, 1500, 1457, 1382, 1288, 1230, 810, 752 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 8.78 (s, 1H), 8.39 (d, J = 9.0 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 7.2 Hz, 1H), 8.20 – 8.09 (m, 5H), 7.85 (d, J = 8.4 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.70 – 7.65 (m, 4H), 7.56 (dd, J = 10.2, 6.0 Hz, 2H), 7.43 (dd, J = 9.6, 4.2 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 1.87 (s, 6H). ¹³C NMR (CDCl₃, 400 MHz) (δ , ppm): 154.10, 148.20, 142.13, 141.20, 139.67, 139.19, 137.96, 137.67, 136.95, 132.20, 131.39, 131.35, 130.55, 130.35, 130.05, 130.01, 129.21, 128.41, 128.01, 127.91, 127.44, 127.36, 127.31, 127.27, 127.24, 126.98, 126.92, 126.86, 125.97, 125.00, 124.97, 124.87, 122.16, 121.83, 119.18, 118.83, 118.31, 109.87, 109.10, 48.05, 24.06. Anal. calcd for C₄₃H₂₉N (%): C, 92.27; H, 5.22; N, 2.50. Found: C, 92.39; H, 5.27; N, 2.34. MS (EI) m/z: 559.39.

3. Results and discussions

The synthetic routes to IDC-PA and IDC-Py are illustrated in scheme 1. Methyl 2-(9-phenyl-9*H*-carbazol-3-yl) benzoate is prepared by Suzuki Miyaura coupling reaction with more than 80% yield. The precursor of tertiary alcohol is afforded by the nucleophilic addition process. The chemical equilibrium of isomers can achieve directional

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development by strictly controlling the temperature and the acid ratio in the process of dehydration. After the high yield electrophilic substitution reaction and the Suzuki Miyaura coupling reaction, IDC-PA and IDC-Py are prepared.

Fig. 1 shows the optimized structure of IDC-PA and IDC-Py. Density functional theory (DFT) calculations are carried out with Gaussian 09 using a B3LYP method with a basis set of 6-31G(d). The dihedral angles between IDC and phenylanthracene/pyrene are 81.08° and 53.08° for IDC-PA and IDC-Py, respectively. The large steric hindrance structures provide the possibility to restrain the aggregation effect.

UV-Vis absorption and photoluminescence (PL) spectra of IDC-PA and IDC-Py in the dilute dichloromethane solution are shown in **Fig. 2**. Three absorption peaks at 358, 375, and 397 nm, are attributed to the vibrational structure of the anthracene unit of IDC-PA. The absorption peak around 350 nm of IDC-Py is due to π - π * transition derived from the conjugated substituted pyrene backbone. The optical energy gaps are 2.93 and 3.07 eV for IDC-PA and IDC-Py, respectively, which are determined from the UV-Vis absorption edges. The emission maximum (λ_{em}) of IDC-PA and IDC-Py are 450 and 439 nm in dilute CH₂Cl₂ solution, and the counterparts are 453 nm and 443 nm in films. The negligible red-shit indicates there are almost no intermolecular interactions in the films. As expected, the aggregation effect is suppressed by the twisted chemical structures. The morphologies of IDC-PA and IDC-Py film are also measured by AFM, the surface roughness values (in Root Mean Square, RMS) of the vacuum evaporated films are 0.63 and 0.97 nm for IDC-PA and IDC-Py, respectively (see Fig. S13). The PL quantum yields in dichloromethane solution are estimated to be 0.84 and 0.78 by using 9,10-diphenylanthrancene as the reference.³⁴

The thermal properties of the two 3-monosubstituted compounds were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (see **Fig. 3**). Both the compounds were found to be highly stable under a nitrogen atmosphere, and with thermal decomposition temperature (T_d , 5% weight-loss) at 424 and 389 °C, for IDC-PA and IDC-Py, respectively, showing the stable nature of the material to compete for the temperature of vacuum vapor deposition. During the second DSC traces of heating (10 K min⁻¹), the glass transition temperatures were observed at 186 and 157 °C for IDC-PA and IDC-Py.

Ultraviolet photoelectron spectroscopy (UPS) with a helium lamp emitting at 21.2 eV is used to ascertain the HOMO energy levels. As shown in **Fig. 4**, from the ionization potential (HOMO-edge position) and the secondary cut-off regions of the UPS spectra, the HOMO energy levels of IDC-PA and IDC-Py are -5.69 and -5.57 eV, respectively. The bandgaps are determined to be -2.93 and -3.07 eV, thus the LUMO levels of IDC-PA and IDC-Py are determined to be -2.76 and -2.50 eV, respectively. All the pertinent data of IDC-PA and IDC-Py are summarized in Table 1.

To investigate the electroluminescence (EL) properties, non-doped devices were fabricated with a structure of ITO/NPB (70 nm)/TCTA (10 nm)/Emitter (20 nm)/TPBi (40 nm)/Liq (1 nm)/Al (100 nm). **Fig. 5** shows the energy level diagram of devices, NBP and TPBi are respectively used as the hole-transporting layer and the electron-transporting layer, and TCTA is adopted as a buffer for confining excitons within the emitting layer. **Fig. 6a** gives current density (*J*)-voltage (*V*)-luminance characteristics (*L*) of blue OLEDs, the turn-on voltages (the driving voltage with the brightness of 1 cd/m²) of the devices are 3.50 and 3.51 V for IDC-PA and IDC-Py-based devices, respectively. A

relatively low opening voltage can be obtained without a hole-injection layer, which may attribute to the two materials possessing a good carrier injection and transportation. Fig. S14 exhibits the EL emission spectra of the blue OLEDs at different voltages. It can be seen that the EL spectra and the PL spectra are almost the same, which suggests that the EL can be attributed to the emission from the singlet excited state. In addition, the full width at half maximum (FWHM) of the EL spectra is 58 and 56 nm for IDC-PA and IDC-Py-based device, respectively. The emission peaks are 452 and 440 nm, the corresponding color coordinates are (0.15, 0.10) and (0.15, 0.08). The stability of the spectra is also very impressive because the electroluminescent peaks of the device do not show any drift even at a higher voltage. In our non-doped devices, the long wavelength emission is not observed, which is due to the non-planar molecular structure with a greater steric hindrance of the materials. Fig. 6b shows the current and external quantum efficiencies of IDC-PA and IDC-Py-based blue devices at different voltages. The maximum current and external quantum efficiencies for the IDC-PA-based device are 4.80 cd A⁻¹ and 4.41%, whereas those for the IDC-Py-based device are 4.13 cd A⁻¹ and 6.08%, respectively. Interestingly, the IDC-Py-based device has a lower current efficiency, but a higher external quantum efficiency, just owing to the minor difference of CIE_v values. It is noteworthy that the external quantum efficiency roll-off from 1000 cd m^{-2} to 5000 cd m^{-2} of the IDC-PA-based device is extremely low, with the value of 0.7%. The detailed device performance parameters are summarized in Table 2. To further understand the origin of the high EQEs, we study the excited state energy levels of the emitters by timedependent density functional theory (TD-DFT), the calculated results are summarized in Table S1. The triplet energy (T₁) levels of IDC-PA and IDC-Py are 1.77 and 2.08 eV, respectively, which can be ascribed to the transition in the anthracene and pyrene units. In a triplet-triplet annihilation (TTA) process, twice the T₁ should be higher than its singlet energy (S₁), and the energy should near with any of highly excited S_n (n > 1) to ensure the exothermic energy transfer to S₁. In **Fig. S15**, twice T₁ energy levels of IDC-PA and IDC-Py are close to corresponding S₃ and S₉, respectively, which may achieve the efficient energy transfer to S₁ by Förster energy transfer. Historically, anthracence and pyrene chromophores are widely reported in TTA-based devices.³⁵⁻³⁸ Therefore, the highy efficient OLEDs may be ascribed to the efficient up-conversion of triplet excitons through TTA.

4. Conclusion

In summary, we have designed and synthesized two novel deep-blue emitters with highly rigid structures and also successfully suppressed the negative aggregation effect. Both of these compounds exhibit good thermal stability and excellent quantum yield, which provide a potential to develop them as the emitter of OLEDs. The simple non-doped devices based on these emitters exhibit high efficiencies of up to 4.80 and 4.13 cd A⁻¹, and maximum EQEs of 4.41% and 6.08% with CIE coordinates of (0.15, 0.10) and (0.15, 0.08) for IDC-PA and IDC-Py-based devices. In particular, the devices also maintain almost negligible efficiency roll-off, even at the very high brightness of 5000 cd m⁻². These results provide a strategy of molecular design to achieve deep-blue emission in the non-doped device.

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Table 1. The photophysical and thermal properties of IDC-PA and IDC-Py.

	$\lambda_{abs}^{a)}$	$\lambda_{\rm em} \left(\Phi_{\rm F} \right)^{\rm a)}$	T _d	$T_{\rm g}$	HOMO ^{b)}	LUMO ^{c)}	E_{g}^{d}
	(nm)	(nm)	(°C)	(°C)	(eV)	(eV)	(eV)
IDC-PA	289, 375, 397	450 (0.84)	424	186	-5.69	-2.76	2.93
IDC-Py	278, 310, 350	439 (0.78)	389	157	-5.57	-2.50	3.07

^{a)} Measured in dichloromethane solution; ^{b)} measured by UPS; ^{c)} calculated using HOMO and E_g ; ^{d)} the onsets of the UV–Vis absorption edges.

Table 2. Electroluminescence characteristics of the devices.

Device	$V^{a}(V)$	$\eta_{\rm c}^{\rm b)}({\rm cd}{\rm A}^{-1})$	$\eta_{\rm ext}^{\rm b)}(\%)$	<i>CIE</i> (x,y)
IDC-PA	3.50	4.80, 4.75, 4.62	4.41, 4.38, 4.35	(0.15, 0.10)
IDC-Py	3.51	4.13, 4.11, 3.64	6.08, 6.05, 5.35	(0.15, 0.08)

^{a)} Turn-on voltage. ^{b)} Current efficiency (η_c) and external quantum efficiency (η_{ext}) in the order of maximum, at 1000 cd m⁻² and at 5000 cd m⁻².



Fig. 1. Optimized structures of IDC-PA and IDC-Py obtained at B3LYP/6-31G* level.



Fig. 2. Absorption and photoluminescence spectra of IDC-PA and IDC-Py in solution, inset: photoluminescence spectra of IDC-PA and IDC-Py in films.



Fig. 3. TGA curves of IDC-PA and IDC-Py measured at a heating rate of 10 K min⁻¹. Inset: DSC traces measured at a heating rate of 10 K min⁻¹.







Fig. 6. a. Current density-voltage-luminance characteristics; b. the current efficiency and EQE versus voltage.

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Supporting Information for:

Highly Efficient Non-doped Deep-blue Organic Light-Emitting Diodes

by Employing a Highly Rigid Skeleton

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Fig. S3. ¹H NMR spectrum of 2-(2-(9-phenyl-9*H*-carbazol-3-yl) phenyl) propan-2-ol (2).



Fig. S4. ¹³C NMR spectrum of 2-(2-(9-phenyl-9*H*-carbazol-3-yl) phenyl) propan-2-ol (2).





Fig. S8. ¹³C NMR spectrum of 2-bromo-7,7-dimethyl-5-phenyl-5,7-dihydroindeno[2,1-*b*]carbazole (4).



Fig. S10. ¹³C NMR spectrum of IDC-PA.



Fig. S12. ¹³C NMR spectrum of IDC-Py.



Fig. S13. The morphology images of IDC-PA and IDC-Py film measured by AFM.



Fig. S15. Energy level of the excited state of the compounds obtained by TD-DFT calculation.

Table S1. Calculated energy levels	, oscillator strengths (f) of IDC-PA and IDC-Py
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IDC-PA					IDO	C-Py	
excited	$E_{\rm g}$	$E_{\rm g}$	f	excited	$E_{\rm g}$	E_{g}	f
state	(eV)	(nm)	J	state	(eV)	(nm)	J
\mathbf{S}_1	3.20	387.39	0.1768	S_1	3.29	377.24	0.3585
S_2	3.29	376.82	0.0796	S_2	3.64	340.84	0.2420
S_3	3.71	334.28	0.0005	S_3	3.73	332.35	0.0286
S_4	3.75	330.79	0.0067	S_4	3.76	329.60	0.0179
S_5	3.84	322.92	0.0668	S_5	3.93	315.11	0.1324
S_6	3.95	313.96	0.0015	S_6	3.98	311.57	0.0313
S_7	4.03	307.90	0.2113	S_7	4.02	308.50	0.1215
S_8	4.14	299.18	0.0289	S_8	4.14	299.37	0.0026
S ₉	4.20	295.06	0.0076	S ₉	4.17	297.23	0.2257
S_{10}	4.21	294.23	0.0492	S_{10}	4.31	287.37	0.0517
T ₁	1.77	700.60	0.0000	T ₁	2.08	595.89	0.0000
T ₂	2.98	416.54	0.0000	T ₂	2.96	418.41	0.0000
T ₃	3.20	387.03	0.0000	T ₃	3.17	390.51	0.0000
T_4	3.24	382.24	0.0000	T_4	3.31	374.26	0.0000
T ₅	3.33	372.51	0.0000	T ₅	3.42	362.96	0.0000
T ₆	3.45	359.34	0.0000	T ₆	3.48	356.27	0.0000

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T ₇	3.56	348.62	0.0000	T_7	3.57	347.10	0.0000
T ₈	3.59	345.76	0.0000	T ₈	3.60	344.25	0.0000
T ₉	3.70	335.04	0.0000	T ₉	3.67	337.92	0.0000
T ₁₀	3.74	331.69	0.0000	T ₁₀	3.73	332.82	0.0000

Highlights

- Two new blue emitters with rigid backbone are synthesized.
- The IDC-PA and IDC-Py-based devices demonstrated maximum EQEs of 4.41% and 6.08%
- CIE coordinates are (0.15, 0.10) and (0.15, 0.08), respectively, belonging to the deep-blue region.