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High Efficiency Non-Dopant Blue Organic Light-Emitting Diodes Based on Anthracene-Based Fluorophores with Molecular Design of Charge Transport and Red-Shifted Emission Proof

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A new series of 9,10-diphenylanthracene (DPA)-based blue fluorophores have been synthesized and characterized for OLED applications. These fluorophores have bulky substituent on C-2 position, such as triphenylsilane of TPSDPA and mesitylene of TMPDPA. C-2 substituent also includes electron transport diphenylphosphine oxide of PPODPA and dimesitylene borane of BMTDPA, or hole transport of N-phenylnaphthalen-1-amine of NPADPA. For TMPDPA blue fluorophores, 9,10-diphenyl substituents of the anthracene core are further attached with hole-transporting 9H-carbazole (CBZDPA) and electron-transporting 2-phenyl-1,3,4-oxadiazole (OXDDPA). Absorption and emission spectroscopic properties of all DPA-derived fluorophores, either in solution or in condensed phase, were fully characterized and HOMO/LUMO energy levels of these fluorophores were determined. The frontier molecular orbitals of these DPA derivatives were analysed by theoretical methods in gauging the possible intramolecular charge transfer (ICT) characteristic. Whereas the blue emission is best preserved in TMPDPA, of which non-conjugated and bulky mesitylene group suppresses emission from red shifting, ICT is attributed to the deteriorate emission of NPADPA and BMTDPA. In solid state, PPODPA suffered from red-shifted and weakening emission due to the adverse crystallization, which is promoted by the dipolar nature of diphenylphosphine oxide substituent. Non-dopant OLEDs were fabricated with DPA, TPSDPA, TMPDPA, PPODPA, CBZDPA and OXDDPA, respectively. Compared with that of DPA OLED, except for PPODPA, electroluminescence efficiency of these DPA derivatives was found significantly improved. Particularly, CBZDPA and OXDDPA OLEDs exhibited the best external quantum efficiency of 4.5 and 4.0 % with true blue colour, CIEx,y (0.17, 0.17) and CIEx,y (0.16, 0.18), respectively. Improved electroluminescence efficiency can be attributed to the molecular charge transport design of CBZDPA and OXDDPA.

Introduction

Organic light-emitting diodes (OLEDs) remain a subject of intense investigation because of their potential applications in high-quality flat-panel displays and solid state lighting, with some consumer devices such as cell phones and digital cameras incorporating OLED screens already available in the market. OLEDs for full colours displays are showing great promise, and are required for red, green and blue-emitting materials. However, highly efficient true-blue (a Commission Internationale de l’Eclairage, CIEx,y coordinate of y < 0.20) phosphorescent emitters are still relatively rare. More critically, there is still rare true-blue phosphorescent emitter with high photoluminescent quantum efficiency that is stable enough for practical applications. Therefore, blue electrofluorescence materials have been revived and become highly demanded by the energy-saving solid-state lighting (SSL) utilizing hybrid white OLED. Anthracene has been intensively used as an attractive building block and starting material for blue fluorescence OLEDs, since its derivatives usually have high fluorescence quantum yield and wide energy band-gap in solution. However, the planarity of anthracene molecular structure is prone to aggregate in solid state, which causes fluorescence quenching and emission wavelength red-shifting. For examples, two perpendicular phenyl substituents at C-9 and C-10 positions of 9,10-diphenylanthracene (DPA) cannot completely overcome the fluorescence quenching and red-shifting problems through steric hindrance approach. The bulky substituent at C-2 position of DPA can further prevent the molecule from aggregation and hence improve the performance of OLED further. However, red-shifted emission is still observed in many cases of 2-substituted DPA derivatives.

In this paper, in order to reduce the emission red-shifting in solution as well as in solid state, we have synthesized and systematically examined a series of chemical functionality with
sterical hindrance at C-2 position of DPA. We have mesitylene, triphenylsilane, diphenylphosphine oxide, dimesitylboration, and N-phenynaphthalen-1-amine of TMPDPA, TPSDPA, PPODPA, BMTDPA, and NPADPA, respectively (Figure 1).

Moreover, by introducing charge transporting moieties, either 9H-carbazole or 2-phenyl-1,3,4-oxadiazole, on the phenyl substituent at C-9 and C-10 positions of TMPDPA, the performance of OLEDs based on either CBZDPA or OXDDPA was found significantly improved in terms of electroluminescence (EL) efficiency with little compromise of blue colour purity (Fig. 1).

Results and discussion

Synthesis

As shown in Scheme 1, 2-bromo-9,10-diphenylanthracene (1) was lithiated with n-butyl lithium at -78 °C, followed by the reaction of different electrophile to afford TPSDPA (2a), PPODPA (2b), and BMTDPA (2c). Differently, NPADPA (2d) was obtained from 1 via Pd-catalyzed amination with N-phenyl-1-naphthalen-1-amine. CBZDPA (6a), TMPDPA (6b), and OXDDPA (6c) were synthesized through a three-step procedure. First, 2-bromoanthracene (3) was coupled to 2,4,6-trimethylboronic acid via Suzuki-Miyaura coupling reaction to afford 2-(1,3,5-trimethylphenyl)anthracene (4). Second, compound 4 was brominated at C-9 and C-10 positions by NBS. Third, the resulting 9,10-dibromo-2-(1,3,5-trimethylphenyl)anthracene (5) was converted to desired CBZDPA, TMPDPA, and OXDDPA via Suzuki-Miyaura coupling reaction with presynthesized boronic ester or boronic acid. The compounds were readily purified by column chromatography. Further purification of materials by gradient sublimation is necessary prior to device fabrication. All of these DPA derivatives were fully characterized by 1H and 13C NMR and mass spectrometry and they were consistent with the proposed chemical structures.

Thermal Properties

The thermal properties of these DPA derivatives were characterized by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All key data were shown in Fig. 2 and Table 1. TMPDPA, TPSDPA, PPODPA, BMTDPA and NPADPA, C-2 modified DPA derivatives, exhibited high decomposition temperatures (T_d, corresponding to 5% weight loss) of 332, 361, 398, 378, and 335 °C, respectively. Moreover, CBZDPA and OXDDPA have a even higher decomposition temperatures, 416 and 449 °C, respectively. Based on the high T_d, all these DPA derivatives are capable of enduring vacuum thermal deposition process in OLED fabrication. Among these DPA derivatives including parent DPA, distinct exothermic signal of crystallization temperature (T_c) was identified only for DPA, TPSDPA, and PPODPA. Only PPODPA of these three compounds possesses bipolar characteristic due to the electron deficient diphenylphosphine oxide. The crystallization feature of the bipolar material is particularly unflavoured for light emitting in OLED application.

![Diagram of DPA derivatives and their synthesis](https://example.com/diagram.png)
The \( T_g \) values of CBZDPA and OXDDPA were 188 and 162 °C, which were much higher than other derivatives (\( T_g \) around 97–109 °C). In addition to NPADPA, CBZDPA and OXDDPA are the only two DPA derivatives without being detected (less than 350–400 °C) for both melting (\( T_m \)) and crystalization (\( T_c \)) temperatures. The superior thermal properties of CBZDPA and OXDDPA could increase the phase stability of the amorphous thin film, which is beneficial to the operation lifetime and maybe the efficiency of devices. From thermal property studies, the structural feature of CBZDPA and OXDDPA can be identified as most effective considering the application for OLEDs.

Absorption and Emission Spectroscopic Characterization

The absorption and emission spectra of DPA derivatives were studied in various solvents (toluene, dichloromethane, DMF, and THF) as well as in the solid thin film, which was prepared by spin-coating dichloromethane solution on quartz plates. As shown in Fig. 3, parent compound DPA exhibits broadening and red-shifting spectra of absorption and emission in solid state, when compared with those in solution. Its solid state \( \Phi_f \) is ~60%, which is reasonable good but significantly decreases from ~90% in solution. This is very common for planar polycyclic aromatic hydrocarbons (PAHs) such as DPA. Spectroscopic feature (including those vibronic structures) observed for DPA is attributed to the \( \pi\pi^* \) electronic transition, of which corresponding energy is sensitive to the molecular interaction (\( \pi\pi \) molecular stacking) in condense phase.

Fig. 2 DSC thermograms of DPA, TMPDPA, TPSDPA, PPODPA, BMTDPA, NPADPA, CBZDPA and OXDDPA.

Among C-2 modified DPA derivatives, such broadening and red-shifting spectroscopic feature is significantly especially in the case of TMPDPA. Based on the present study, sterically hindered mesityl group on C-2 position is a very effective structural factor for preserving the deep blue fluorescence color of DPA derivatives in solid state. C-2 modified DPA derivatives, TPSDPA, PPODPA, BMTDPA, and NPADPA, are designed along the line. However, significantly red-shifted spectra of both absorption and emission take place and it is detrimental to the blue color purity, particularly for PPODPA, BMTDPA, and NPADPA, the most serious three. Based on our spectroscopic observation, we deduce that the broadening and red-shifting spectroscopic features of these DPA derivatives are caused by various reasons.

We did not expect that triphenylsilyl group is not as effective as mesityl group in preventing spectra of DPA from broadening or red-shifting in solid state. However, we notice that both solution \( \lambda_{\text{max}}^{ab} \) and \( \lambda_{\text{max}}^{n} \) of TPSDPA are substantially longer than those of TMPDPA, of which \( \lambda_{\text{max}}^{ab} \) and \( \lambda_{\text{max}}^{n} \) are only slightly longer than those of DPA (Table 1). The more red-shifted
spectra observed for TPSDPA than TMPDPA can be ascribed to the σ-conjugation of silyl group. In solid state, molecular packing of TPSDPA probably intensifies such σ-conjugation and further red-shifts the emission spectra. However, such molecular packing slightly impacts its solid state Φ<sub>f</sub>. It remains as high as ~70%, moderately less than 86% in solution. In terms of Φ<sub>f</sub>, TPSDPA is rather different from TMPDPA, of which fluorescence is significantly quenched in solid state showing solid state Φ<sub>f</sub> only ~40%, much smaller than 90% in solution. Within the context, we think the especially pronounced red-shifting thin film or powder emission spectra of PPODPA may be also explained by molecular packing, since its solution λ<sub>max</sub><sup>fl</sup> is relatively short in wavelength (448~452 nm vs. 487 nm in solid state). In addition, the molecular packing of PPODPA may be the adverse factor that more or less jeopardizes its solid state Φ<sub>f</sub> ~ 30%, which is significantly lower than solution Φ<sub>f</sub> ~ 83% (Table 1). Potentially, there is excimer formation from the molecular packing of PPODPA. Such solid state properties make PPODPA an unfavorable blue light-emitting material in OLEDs.

On the other hand, relatively long wavelength of solution λ<sub>max</sub><sup>fl</sup> observed for both BMTDPA and NPADPA should be attributed to the electronic effect of the π-donor of N-phenylphthalaline-1-amine and the π-acceptor of dimesitylboration, respectively.

In other words, intramolecular charge transfer (ICT), which is lower in energy compared with that of ππ*<sup>ab</sup>, contributes to the electronic transition process. Less well resolved vibronic bands observed in the absorption spectra (Fig. 3) of BMTDPA and NPADPA is consistent with our inference. In addition, BMTDPA and NPADPA are two DPA derivatives showing the most distinct trend of fluorescence solvatochromism (Table 1), which is also consistent with the ICT feature that we propose above. Otherwise, low Φ<sub>f</sub> and solvent dependent PL wavelength may be attributed to photoinduced electron transfer (PET), which has been observed for arylamine-substituted electron deficient fluorophores. In fact, NPADPA has the lowest Φ<sub>f</sub> of 33 and 20%, in solution and solid state, respectively, among DPA derivatives in present study.

Since TMPDPA has the least broadening and red-shifting spectra among DPA derivatives, we choose it for further functionalization with charge transport, i.e., hole transport of CBZDPA and electron transport of OXDDPA. Based on their well resolved vibronic band of the absorption spectra and relatively high solid state Φ<sub>f</sub> 60 and 70%, respectively (Fig. 3 and Table 1), we can reasonably infer that there is little ICT involved in the spectroscopy electronic transition of both CBZDPA and OXDDPA. Solution absorption λ<sub>max</sub><sup>ab</sup> and emission λ<sub>max</sub><sup>fl</sup> of both CBZDPA and OXDDPA are nearly as
short as those of TMPDPA (Fig. 3 and Table 1), indicating there is limited π-conjugation between the charge transport substituent and anthracene core. Finally, based on $\Phi_f$ data both in solution and in solid state, all of DPA derivatives reported herein exhibit $\Phi_f$ values common and typical aggregation caused quenching (ACQ) emission instead of aggregation-induced emission (AIE) or aggregation induced enhanced emission (AIEE).\textsuperscript{64-66}

Table 1. Optical and thermal properties of DPA-based derivatives

<table>
<thead>
<tr>
<th>DPA Derivatives</th>
<th>Solution</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{em}}$ (nm)</td>
<td>$\Phi_f$ (%)</td>
</tr>
<tr>
<td>DPA</td>
<td>375, 410</td>
<td>432, 433, 433</td>
</tr>
<tr>
<td>TMPDPA</td>
<td>378, 413</td>
<td>438, 438, 439</td>
</tr>
<tr>
<td>TPSDPA</td>
<td>380, 421</td>
<td>443, 446, 444</td>
</tr>
<tr>
<td>PPODPA</td>
<td>384, 420</td>
<td>448, 452, 450</td>
</tr>
<tr>
<td>BMTPDA</td>
<td>413, 460</td>
<td>473, 480, 490</td>
</tr>
<tr>
<td>NPADPA</td>
<td>429, 473</td>
<td>490, 502, 507</td>
</tr>
<tr>
<td>CBZDPA</td>
<td>379, 417</td>
<td>442, 442, 445</td>
</tr>
<tr>
<td>OXDDPA</td>
<td>379, 413</td>
<td>443, 443, 446</td>
</tr>
</tbody>
</table>

[a] In THF. [b] in toluene. [c] in dichloromethane. [d] in DMF. [e] not observed. [f] HOMO energy was determined using an AC-2 photoelectron spectrometer (Riken-Keiki AC-2); LUMO energy was determined as the lowest photoexcitation state energy from the onset absorption energy of thin film absorption spectra.

Theoretical Estimation of Frontier Molecular Orbitals

The molecular structures of DPA, TPSDPA, BMTPDA, PPODPA, BMTPDA, NPADPA, CBZDPA, and OXDDPA were optimized by applying density functional theory (DFT) with the hybrid B3LYP functional and 6-31G* basis set. With the optimized structure, calculations on the electronic ground states of these DPA derivatives were processed using DFT with the hybrid B3LYP functional and 6-31G* basis set.\textsuperscript{67} The singlet excited states of these DPA derivatives were studied with time-dependent density functional theory (TD-DFT) by using the hybrid B3LYP functional.\textsuperscript{68} All calculations were performed with a developmental version of Q-Chem.\textsuperscript{69} We display a comparison of the corresponding HOMO and LUMO of these DPA derivatives in $S_0$ state, where materials are in gas phase approximate to the solution state instead of condense phase. Because electronic excitation from the HOMO to the LUMO produces the first singlet excited state $S_1$ (a Franck-Condon excited state), the orbital features presented in Fig. 4 provide important clues towards understanding the nature of optical accessible first excited state.

From the contour plots of DPA, TMPDPA, TPSDPA, and PPODPA, both HOMO and LUMO mainly consist of the π-conjugation of anthracene core. Similar HOMO/LUMO contour plots were found for OXDDPA with little π-conjugation extended into substituents on C-9 and C-10 positions. Differently, the HOMO and/or the LUMO of BMTPDA and NPADPA were found significantly extended beyond anthracene core into N-phenylanthalene-1-amine and dimesitylboration, respectively. Such theoretical findings are quite consistent with ICT feature proposed from the spectroscopic characterization in previous section.

Considering the large twist angle (dihedral angle ~80°) between the phenyl ring and anthracene core, it is to our surprise that π-conjugation based on HOMO contour plots of CBZDPA actually expands extensively into one of the phenylxidiazole substituents on C-9 and C-10 positions, whereas π-conjugation of LUMO is pretty much confined on the anthracene core. The implication from such theoretical results of CBZDPA is somewhat contradictory to spectroscopy experimental results, i.e., well resolved solution absorption vibronic bands, no clear trend of fluorescence solvatochromism, and reasonable solution $\Phi_f$.\textsuperscript{70}
Characterization of OLEDs and Charge Transport

All OLEDs were fabricated by sequential thermal vacuum deposition of thin film layer of organic material and LiF-Al as the final cathode electrode on ITO (indium-tin-oxide)-coated glass substrate. Excluding the spectroscopy unsatisfied BMTDPA and NPADPA, six devices were fabricated for six blue DPA derivatives, with the device configuration of ITO/NPB(30 nm)/TCTA(10 nm)/DPA(30 nm)/TPBI(30 nm)/LiF(1)/Al, where 4,4’-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl (NPB) is a common hole-transporting layer, 2,2’,2”-(1,3,5-benzenetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBI) is a common electron-transporting layer, and LiF/Al were used as the electron injecting layer and cathode. In each device, between NPB and DPA light-emitting layers, there is a thin layer of tris(4-carbazoyl-9-ylphenyl)amine (TCTA), which serves multi-function including hole-transporting layer, exciton blocking layer, and smoothing the alignment of HOMO energy level inside the device. Such interlayer can decrease turn-on voltage and enhance the charge recombination of the device. The device performances are summarized in Fig. 5 and the corresponding data are listed in Table 2.

In accordance with their solid state PL, TMPDPA exhibits deepest blue EL, of which wavelength (444 nm) is nearly as short as that of DPA (442 nm) and the EL band width (66 nm) is nearly as narrow as that of DPA (56 nm). Therefore, 1931 CIE_x,y of two OLEDs are comparable deep blue (0.15, 0.05) and (0.17, 0.10) for DPA and TMPDPA, respectively. EL spectra of TPSDPA, CBZDPA, and OXDDPA are a little red-shifted and broadening, although 1931 CIE_x,y chromaticity of these devices remains satisfactory blue colour (all y-values are less than 0.20, Table 2). However, EL spectrum of PPODPA is significantly worsening and its 1931 CIE_x,y (0.22, 0.37) indicates that it is not a blue OLED having unsatisfactory colour purity.
For EL efficiency concerns, both TMPDPA and TPSDPA OLEDs greatly outperform DPA OLED with just little compromise of blue color purity. In fact, current density or brightness of TMPDPA and TPSDPA OLEDs is far more superior compared with that of DPA OLED (Figure 5). More specifically, TPSDPA OLED is better than TMPDPA OLED in EL efficiency, which can be mostly attributed to the higher $\Phi_f$ of TPSDPA than TMPDPA in solid state. Nevertheless, TMPDPA OLED is slightly better than TPSDPA OLED in blue color purity (1931 CIE $x, y$ in Table 2). For PPPODA, OLED performance is much inferior in all aspects, current density, brightness, blue colour purity, and EL efficiency (Figure 5). The unsatisfactory performance of PPPODA OLED is mainly due to its poor $\Phi_f$ and red-shifted emission in solid state, which can be attributed to its bipolar structure feature that promotes the material crystallization in solid state. PPPODA is the one of two DPA derivatives studied herein showing T($c$) in thermal property measurement (see Fig. 2). Following our previous analysis of spectroscopic data of PPPODA, excimer formation is highly possible in the non-dopant device and it explains the low solid state $\Phi_f$ (and hence low brightness), low current density (because of charge trapping nature of excimer), and long EL wavelength and hence poor 1931 CIE $x, y$ for blue colour.

From the structural design, CBZDPA and OXDDPA are considered as two derivatives of TMPDPA having charge transporting moiety on the phenyl rings at C-9 and C-10 positions of anthracene core. EL efficiency of CBZDPA and OXDDPA OLEDs has been drastically improved in comparison with that of TMPDPA OLEDs (Fig. 5, Table 2). OLEDs exhibit EL efficiency of 4.5 and 4.0% at electroluminescence of 100 cd/m$^2$, respectively; 3.3 and 3.6% at electroluminescence of 1000 cd/m$^2$, respectively. TMPDPA OLED exhibits EL efficiency only 2.8 and 1.1% at electroluminescence of 100 and 1000 cd/m$^2$, respectively. At the first glance, much higher solid state $\Phi_f$ of CBZDPA and OXDDPA than that of TMPDPA provides a logical explanation for the acquired EL efficiency of these OLEDs. Furthermore, we think that the charge transport molecular structures of CBZDPA and OXDDPA also contribute to the enhancement of EL efficiency.

In order to understand the hole and electron transporting nature of TMPDPA, CBZDPA, and OXDDPA, we also fabricated two kinds of single-charge carrier-dominated devices for exploring the nature of material charge carrier in terms of the current density of such devices. The hole dominated device has a configuration of ITO/NPB(40 nm)/TCTA(10 nm)/TPBI(50 nm)/NPB(20 nm)/Al(100 nm). The electron dominated device has a configuration of ITO/BCP(10 nm)/DPA derivative(50 nm)/TPBI(20 nm)/LiF(1 nm)/Al(100 nm). As shown in the inset of Fig. 6, we used high lying LUMO NPB to limit the electron carrier in hole dominated device and low lying HOMO BCP and TPBI to limit the hole carrier in electron dominated device. One should note that the current density of a single-charge carrier-dominated device is determined by several factors, hole injection barrier between the electrode and organic layers, the difference of the HOMO energy levels between adjacent organic layers, and the charge mobility of each organic layers. In the case studied herein, the HOMO energy levels of TMPDPA and CBZDPA are very similar, which implies the current density of hole dominated device depending on the charge mobility of the blue emitter solely. The HOMO energy level of OXDDPA is about 0.20 to 0.23 eV higher than the other two, which implies the hole carrier should be easier to pass through the device. Considering all factors, the current density of such
device indicates that the hole mobility of three DPA derivatives is descending in CBADPA > TMPDPA > OXDDPA order. The situation of the current density of electron dominated device is quite similar but in a reverse order. The LUMO energy levels of TMPDPA, CBZDPA, and OXDDPA are all lower than the LUMO energy level of TPBI (2.7 eV), which implies there is no apparent electron injection barrier at the interface of two layers. The magnitude of current density clearly is decreasing in order OXDDPA > TMPDPA > CBZDPA, which is accordant with the anticipated order of material electron mobility based on the structure feature of electron deficiency.

Conclusions

In summary, we have synthesized and characterized a series of DPA derivatives, TPSPDA, TMDDPA, PPODPA, BMTPDA, NPADPA, CBZDPA, and OXDDPA. Some of these new fluorophores are capable of emitting EL nearly as blue as the EL from DPA. All these DPA derivatives are designed with bulky or sterically hindered substituent on C-2 position to prevent the solid state emission from red-shifting and broadening. In addition to one failure PPODPA that tends to adversely crystallize to form excimer in condense phase, the emission of BMTPDA and NPADPA was found seriously quenched and red-shifted due to the electronic reason, i.e., ICT. The non-doped OLEDs fabricated with charge transport bearing CBZDPA or OXDDPA exhibited the highest external quantum efficiency of 4.5 and 4.0 %, respectively, among all, including DPA OLED, which showed only 1.5% with the same device structure. The charge transporting nature of CBZDPA and OXDDPA has been verified by the current density of hole dominated and electron dominated devices. We have successfully demonstrated that mesityl group on C-2 position are potent in preserving the deep blue fluorescence of DPA in solid state. The EL efficiency of DPA OLED have been greatly improved by incorporating charge transporting moiety on the phenyl rings at C-9 and C-10 positions of anthracene core.

Experimental

General Information

UV-visible electronic absorption spectra were recorded on a Hewlett-Packard 8453 Diode Array Spectrophotometer. Fluorescence spectra were obtained on Hitachi F-5400 fluorescence spectrophotometer with the excitation at 380 nm. The solution fluorescence quantum yields of interesting compounds were determined relative to that of DPA in dichloromethane at 298 K (Φf = 0.9). The solid-state fluorescence quantum yields (Φf) of the blue emitters were determined by the integrating-sphere method. The ionization potentials (or HOMO energy levels) of DPA derivatives were determined by low energy photo-electron spectrometer (Riken-Keiki AC-2). LUMO energy levels were estimated by subtracting the energy (ΔE) from HOMO energy levels. ΔE was determined by the on-set absorption energy from the absorption spectra of the thin film materials. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere on a Perkin-Elmer DSC-7 differential scanning calorimeter, using a scan rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer DSC-7 thermogravimetric analyzer to determine the decomposition temperatures (Tg) of the compounds under nitrogen atmosphere, using a scan rate of 10 °C/min. 1H and 13C NMR spectra were recorded on Bruker AV-400 or Bruker AV3-400, using deuterated chloroform as the internal standard. High resolution mass spectrometric measurements were obtained on JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) from Mass Spectroscopic Laboratory in-house service of the Institute of Chemistry.

Fabrication and Characterization of Light-Emitting Diodes.

OLED devices were fabricated by thermal vacuum deposition. The substrate was an indium-tin-oxide (ITO) coated glass (Shin An SNP, Taiwan) with a sheet resistance of ≤30 Ω/sq. The pretreatment of ITO includes a routine chemical cleaning using detergent, deionized water, acetone and isopropyl alcohol in sequence, followed by oxygen plasma cleaning. The thermal evaporation of organic materials was carried out using CRYOTEC-10 at a chamber pressure of 10⁻⁶ Torr. The thickness...
of each layer was determined by quartz thickness monitor (STM-100/MF and STM-2XM). The cathode of LiF/Al was prepared first thermally deposited a LiF thin film (10 Å) followed by the deposition of Al metal (1000 Å) as the top layer. The thickness of each layer material was determined similarly as before. The devices were all encapsulated with glass slides, which were attached to the device by UV-cured epoxy glue. The effective size of the emitting diode was 4.00 mm², which is significantly smaller than the active area of the photodiode detector, a condition known as “under-filling”, satisfying the measurement protocol. This is one of the most conventional ways in measuring the EL efficiency of OLEDs, although sometimes experimental errors may arise due to the non-Lambertian condition known as the measurements for devices were made at room temperature under ambient condition. The EL was measured using the fluorescence spectrophotometer (Hitachi F5400) by blocking the incident light.

Synthesis of Materials

Unless specified condition, all reaction were performed under nitrogen atmosphere using standard Schlenk techniques. All commercially available chemical reagents were used directly without further purification. Compounds like 2-bromo-9,10-diphenylanthracene (1), 2-bromoanthracene (3), 2,4,6-trimethylphenylboronic acid, 9-(4-(4-(4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)9H-carbazole, and 2-phenyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)1,3,4-oxadiazole were prepared according to literatures. For the materials used in device fabrication, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) was commercially available. NPB (4,4′-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl) was prepared by using column chromatography (silica gel, 10% CH₂Cl₂/EtOAc) to afford PPPODA (0.4 g, 30%) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃) : δ (ppm) : 7.86-7.28 (d, J = 0.8 Hz, 1H), 7.58-7.68 (m, 3H), 7.60-7.33 (m, 22H), 7.29-7.26 (m, 2H). ¹³C NMR (100 MHz CDCl₃) : δ (ppm) : 139.08, 138.39, 137.73, 137.29, 134.50, 134.29, 132.73, 132.06, 131.96, 131.75, 131.32, 131.21, 130.98, 130.36, 130.25, 129.35, 128.53, 128.42, 128.35, 128.30, 127.75, 127.58, 127.46, 127.30, 127.03, 126.12, 125.57, 124.97, 124.87. EI-IRMS: calculated 530.1800, m/z = 530.1801 (M⁺).

9.10-Diphenyl-(2-diphenylphosphinyl)anthracene (PPODA, 2b)

To a dry THF solution (60 mL) of 2-bromo-9,10-diphenylanthracene (1.0 g, 2.45 mmol) was added n-ButLi (1.96 mL, 4.90 mmol, 2.5M in hexane) slowly in -78 °C. The mixture was stirred for 45 minutes under nitrogen atmosphere. Chlorotriphenylphosphine (1.6 mL, 7.1 mmol) was added dropwise at -78 °C and the mixture was stirred at room temperature for 6 hours. After reaction quenched by water, the mixture was extracted with dichloromethane. The separated organic layer was evaporated till dryness under reduced pressure. The residue solid was re-dissolved in CH₂Cl₂ (10 mL) and was treated with H₂O₂ (10 mL, 30 wt% in H₂O) and stirred for another 24 hours. The separated organic layer was dried with magnesium sulphate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, 10% CH₂Cl₂/acetone) to afford BMTDPA (0.4 g, 30%) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃) : δ (ppm) : 7.83 (s, 1H), 7.78-7.75 (d, J = 8.4 Hz, 1H), 7.71-7.69 (d, J = 8Hz, 1H), 7.59-7.47 (m, 6H) ; 7.42-7.29 (m, 8H), 6.73 (s, 4H), 2.28 (s, 6H), 1.97 (s, 12H). ¹³C NMR (75 MHz CDCl₃) : δ (ppm) : 141.69, 140.48, 140.03, 139.75, 138.87, 138.20, 136.47, 133.90, 132.73, 132.65, 129.65, 129.54, 128.32, 127.92, 127.41, 127.27, 126.91, 125.67, 125.48, 124.86, 123.63, 122.72, 23.42, 21.12. EI-IRMS: calculated 578.3145, m/z = 578.3141 (M⁺).

9.10-Diphenyl-(2-dimethyloctyl)anthracene (BMTDPA, 2c)

To a dry THF solution (30 mL) of 2-bromo-9,10-diphenylanthracene (0.4 g, 0.98 mmol) was added n-ButLi (1.1 mL, 2.84 mmol, 2.5M in hexane) slowly in -78 °C. The mixture was stirred for 45 minutes under nitrogen atmosphere. Dimesitylboron fluoride (0.86 g, 3.23 mmol) in THF (5 mL) was added dropwise at -78 °C and the mixture was stirred at room temperature for 12 hours. After reaction quenched by water, the mixture was extracted with dichloromethane. The organic layer was dried with magnesium sulphate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, hexane) to afford BMTDPA (0.12 g, 21%) as a yellow-green solid. ¹H NMR (400 MHz, CDCl₃) : δ (ppm) : 7.83 (s, 1H), 7.78-7.75 (d, J = 8.4 Hz, 1H), 7.71-7.69 (d, J = 8Hz, 1H), 7.59-7.47 (m, 6H) ; 7.42-7.29 (m, 8H), 6.73 (s, 4H), 2.28 (s, 6H), 1.97 (s, 12H). ¹³C NMR (75 MHz CDCl₃) : δ (ppm) : 141.69, 140.48, 140.03, 139.75, 138.87, 138.20, 136.47, 133.90, 132.73, 132.65, 129.65, 129.54, 128.32, 127.92, 127.41, 127.27, 126.91, 125.67, 125.48, 124.86, 123.63, 122.72, 23.42, 21.12. EI-IRMS: calculated 578.3145, m/z = 578.3141 (M⁺).

9.10-Diphenyl-(2-phenylnaphthalen-1-amine)anthracene (NPADPA, 2d)

A mixture of N-phenyl-naphthalen-1-amine (0.64 g, 2.94 mmol), 2-bromo-9,10-diphenylanthracene (0.8 g, 1.96 mmol), sodium tert-butoxide (0.22 g, 2.35mmol), and palladium acetate (0.01 g, 0.05 mmol) in xylene (7 mL) was added tri-tert-butylphosphine (0.05 mL, 0.2 mmol) and stirred at 120 °C for 16 hours. After the...
reaction was cooled to room temperature, the xylene was removed under reduced pressure. The residue was extracted with dichloromethane and H2O. The organic layer was dried with magnesium sulphate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, 10% CH2Cl2/hexane) to afford 9,10-diphenyl-2-(1,3,5-trimethylphenyl)anthracene (0.2 g, 0.44 mmol), phenylboronic acid (0.13 g, 1.1 mmol), K2CO3 (1.2 mL, 2.31 mmol, 2 M in H2O), and ethanol (0.5 mL) in toluene (2.2 mL) was added tetrakis(triphenylphosphine)palladium (0.04 g, 0.04 mmol) and stirred at 80 °C for 12 hours. After cooling to room temperature, the toluene was removed under reduced pressure and the residue was extracted with dichloromethane and H2O. The organic layer was dried with magnesium sulphate. After removal of drying agent, the organic solution was evaporated till dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, hexane) to afford 2-(1,3,5-trimethylphenyl)anthracene (0.15 g, 55%) as a white solid. 1H NMR (400 MHz, CDCl3): δ (ppm): 8.21-8.17 (m, 4H), 7.94-7.85 (m, 4H), 7.74-7.66 (m, 7H), 7.53-7.46 (m, 6H), 7.38-7.29 (m, 5H), 6.97 (s, 1H), 2.32 (s, 3H), 2.09 (s, 6H). 13C NMR (100 MHz, CDCl3): δ (ppm): 140.91, 140.77, 138.77, 138.16, 138.02, 137.88, 137.22, 136.91, 136.36, 136.16, 132.86, 132.74, 130.45, 130.04, 129.00, 128.33, 128.18, 128.16, 127.43, 127.00, 126.88, 126.82, 126.73, 126.05, 125.98, 125.55, 125.39, 125.58, 120.42, 130.23, 120.14, 120.10, 110.10, 109.95, 20.99, 20.96. EI-HRMS: calcld 778.3348, m/z = 778.3329 (M+).

9.10-Dibromo-2-(1,3,5-trimethylphenyl)anthracene (6a)

This compound was prepared similarly to that of 9,10-diphenyl-2-(1,3,5-trimethylphenyl)anthracene, except that 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole (1.91 g, 5.5 mmol) used in the reaction. In addition, a mixed solvent of 20% EtOAc/hexane was used as eluent for column chromatography. OXDDPA was obtained as a white solid (1.2 g, 74%). 1H NMR (400 MHz, CDCl3): δ (ppm): 8.41-8.38 (m, 1H), 8.31-8.30 (s, J = 4 Hz, 2H), 8.25 (s, 1H), 8.12-8.08 (t, J = 8 Hz, 4H), 7.84-7.80 (dt, J = 8 Hz, 7H), 7.76-7.66 (m, 6H), 7.52-7.47 (m, 7H), 7.39-7.36 (m, 2H), 7.23-7.19 (d, J = 4 Hz, 1H), 6.69-6.65 (d, J = 12 Hz, 2H), 2.25 (s, 3H), 2.00 (s, 6H). 13C NMR (100 MHz, CDCl3): δ (ppm): 164.70, 164.47, 140.13, 140.01, 138.46, 138.09, 136.85, 135.97, 135.83, 132.86, 132.74, 131.38, 131.26, 131.23, 130.65, 130.53, 130.16, 129.57, 129.56, 129.00, 128.86, 128.81, 128.41, 128.14, 127.57, 127.46, 126.91, 126.90, 125.97, 125.38, 125.23, 21.02, 20.74. FAB-MS: calcd 448.2191, m/z = 448.2197 (M+).
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References

Charge transport bearing 9,10-diphenylanthracene derivatives for true blue and efficiency enhancing electroluminance.