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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-place. OLEDs for full colour displays are showing great promise, and require red, green, and blue-emitting materials. However, highly efficient true-blue (Commission Internationale de l'Éclairage coordinate (CIE_{x,y}) of y < 0.20) phosphorescent

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High efficiency non-dopant blue organic lightemitting 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 organic light-emitting diode (OLED) applications. These fluorophores have a bulky substituent, such as triphenylsilane in TPSDPA and mesitylene in TMPDPA, on the C-2 position. The C-2 substituent also includes electron transporting diphenylphosphine oxide in PPODPA and dimesitylene borane in BMTDPA, or hole transporting N-phenylnaphthalen-1-amine in NPADPA. For TMPDPA blue fluorophores, 9,10-diphenyl substituents of the anthracene core are further attached to holetransporting 9H-carbazole in CBZDPA and electron-transporting 2-phenyl-1,3,4-oxadiazole in OXDDPA. Absorption and emission spectroscopic properties of all DPA-derived fluorophores, either in solution or in the condensed phase, were fully characterized and the HOMO/LUMO energy levels of these fluorophores were determined. The frontier molecular orbitals of the DPA derivatives were analysed by theoretical methods to determine the possible intramolecular charge transfer (ICT) characteristics. Whereas the blue emission is best preserved in TMPDPA, in which the non-conjugated bulky mesitylene group suppresses red-shifted emissions, the ICT is attributed to the deterioration in the emissions of NPADPA and BMTDPA. In the solid state, PPODPA suffered from red-shifted and weakened emissions because of adverse crystallization, which is promoted by the dipolar nature of the diphenylphosphine oxide substituent. Non-dopant OLEDs were fabricated with DPA, TPSDPA, TMPDPA, PPODPA, CBZDPA, and OXDDPA. Except for PPODPA, the electroluminescence efficiency of these DPA derivatives was significantly improved compared with that of the DPA OLEDs. In particular, CBZDPA and OXDDPA OLEDs exhibited the best external quantum efficiency of 4.5% and 4.0% with a true blue colour, with $CIE_{x,y}$ coordinates of (0.17, 0.17) and (0.16, 0.18), respectively. The improved electroluminescence efficiency can be attributed to the molecular charge transport design of CBZDPA and OXDDPA.

> emitters are still relatively rare. More critically, true-blue phosphorescent emitters with high photoluminescent quantum efficiency that are stable enough for practical applications are rarer still.¹⁻⁵

> Therefore, use of blue electrofluorescent materials has been revived and they are in high demand for energy-saving solidstate lighting that uses hybrid white OLEDs.⁶⁻⁹ Anthracene has been widely regarded as an attractive building block and starting material for blue fluorescence OLEDs,^{10–60} because its derivatives usually have a high fluorescence quantum yield and wide energy band-gap in solution. However, the planarity of anthracene means it is prone to aggregation in the solid state, which causes fluorescence quenching and emission wavelength red-shifting. For example, two perpendicular phenyl substituents at the C-9 and C-10 positions of 9,10-diphenylanthracene (**DPA**) cannot completely overcome the fluorescence quenching and red-shifting problems through the steric hindrance

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Fig. 1 Left: chemical structure of DPA derivatives. Right: solution (dichloromethane) and solid state fluorescence image of, from left to right, DPA, TMPDPA, TPSDPA, PPODPA, BMTDPA, NPADPA, CBZDPA, and OXDDPA.

approach.¹⁰ The bulky substituent at the C-2 position of **DPA** can further prevent the molecule from aggregating, and thus improve the performance of OLEDs further.^{13,14} However, red-shifted emissions are still observed in many 2-substituted **DPA** derivatives.

In this research, in order to reduce the emission red-shifting in solution as well as in the solid state, we have synthesized and systematically examined a series of chemical functionalities with steric hindrance at the C-2 position of **DPA**. We used mesitylene (TMP), triphenylsilane (TPS), diphenylphosphine oxide (PPO), dimesitylborane (BMT), and *N*-phenylnaphthalen-1-amine (NPA) groups in **TMPDPA**, **TPSDPA**, **PPODPA**, **BMTDPA**, and **NPADPA**, respectively (Fig. 1).

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

Results and discussion

Synthesis

As shown in Scheme 1, 2-bromo-9,10-diphenylanthracene (1) was lithiated with *n*-butyllithium at -78 °C, followed by reaction

with different electrophiles to give TPSDPA (2a), PPODPA (2b), and BMTDPA (2c). In contrast, NPADPA (2d) was obtained from 1 via Pd-catalyzed amination with N-phenylnaphthalen-1amine. CBZDPA (6a), TMPDPA (6b), and OXDDPA (6c) were synthesized through a three-step procedure. Firstly, 2-bromoanthracene (3) was coupled to 2,4,6-trimethylboronic acid via a Suzuki-Miyaura coupling reaction to give 2-(1,3,5-trimethylphenyl)anthracene (4). Secondly, compound 4 was brominated at the C-9 and C-10 positions using N-bromosuccinamide (NBS). Thirdly, the resulting 9,10-dibromo-2-(1,3,5-trimethylphenyl) anthracene (5) was converted to CBZDPA, TMPDPA, or OXDDPA via the Suzuki-Miyaura coupling reaction with a presynthesized boronic ester or boronic acid. The compounds were readily purified by column chromatography. Further purification of materials by gradient sublimation was necessary prior to device fabrication. All these DPA derivatives were fully characterized by ¹H-NMR and ¹³C-NMR and mass spectrometry and the data obtained 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 are shown in Fig. 2 and Table 1. **TMPDPA**, **TPSDPA**, **PPODPA**, **BMTDPA** and



Scheme 1 Reagents and conditions: (i) (a) *n*BuLi, ether, $-78 \degree$ C, 45 min, (b) chlorotriphenylsilane, $-78 \degree$ C \rightarrow RT, 12 h, (ii) (a) *n*-BuLi, ether, $-78 \degree$ C, 45 min, (b) chlorodiphenylphosphine, $-78 \degree$ C \rightarrow RT, 12 h, (c) H₂O₂, 12 h, (iii) (a) *n*-BuLi, THF, $-78 \degree$ C, 45 min, (b) dimesitylboron fluoride, $-78 \degree$ C \rightarrow RT, 12 h, (iv) *N*-phenylnaphthalen-1-amine, NaOtBu, P(t-Bu)₃, Pd(OAC)₂, xylene, 120 °C, 16 h, (v) 2,4,6-trimethylphenylboronic acid, catalyst: Pd(PPh₃)₄, 2 M K₂CO_{3(aq)}, ethanol, toluene, 80 °C, 12 h, (vi) NBS, CHCl₃, 50 °C, 2 h, (vii) phenylboronic acid or pinacolborane derivative of 9-phenyl-9*H*-carbazole or 2,5-diphenyl-1,3,4-oxadiazole, catalyst: Pd(PPh₃)₄, 2 M K₂CO_{3(aq)}, ethanol, toluene, 80 °C, 12 h.



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

Table 1 Optical and thermal properties of DPA-based derivatives

DPA derivatives	Solution			Solid						
	$\lambda_{\max}^{ab}, \lambda_{on set}^{ab}{}^{ab},$ (nm)	$\lambda_{\max}^{\text{fl}}{}^{b}, \lambda_{\max}^{\text{fl}}{}^{c}, \lambda_{\max}^{\text{fl}}{}^{d}$ (nm)	$\Phi_{\mathrm{f}}^{\;c}\left(\% ight)$	$\lambda_{\max}^{\mathrm{fl}},$ (nm)	$\Phi_{ m f}$ (%)	$T_{\mathrm{g}}\left(^{\circ}\mathrm{C}\right)$	$T_{\rm g} (^{\circ} {\rm C}) = T_{\rm c} (^{\circ} {\rm C})$	$T_{\rm m}$ (°C)	$T_{\rm d}$ (°C)	LUMO/HOMO ^f (eV)
DPA	375, 410	432, 433, 433	90	442	~ 60	е	165	253	315	2.87/5.81
TMPDPA	378, 413	438, 438, 439	90	444	${\sim}40$	109	е	227	332	3.04/5.94
TPSDPA	380, 421	443, 446, 444	86	456	${\sim}70$	97	189	277	361	2.96/5.93
PPODPA	384, 420	448, 452, 450	83	487	~ 30	104	202	289	398	3.04/5.90
BMTDPA	413, 460	473, 480, 490	61	499	${\sim}50$	104	е	220	378	3.23/5.87
NPADPA	429, 473	490, 502, 507	33	513	${\sim}20$	97	е	е	335	3.20/5.46
CBZDPA	379, 417	442, 442, 445	94	459	${\sim}60$	188	е	е	416	3.07/5.94
OXDDPA	379, 413	443, 443, 446	88	461	${\sim}70$	162	е	е	449	2.86/5.74
	, = -	-, -,								

^{*a*} In THF. ^{*b*} In toluene. ^{*c*} In dichloromethane. ^{*d*} In DMF. ^{*e*} Not observed. ^{*f*} Highest occupied molecular orbit (HOMO) energy was determined using an AC-2 photoelectron spectrometer (Riken Keiki); lowest unoccupied molecular orbital (LUMO) energy was determined as the lowest photoexcitation state energy from the onset absorption energy of the thin film absorption spectra.

NPADPA, which were 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. Furthermore, **CBZDPA** and **OXDDPA** have even higher decomposition temperatures of 416 and 449 °C, respectively. Based on the high T_d , all these **DPA** derivatives are capable of enduring the vacuum thermal deposition process in OLED fabrication. Among these **DPA** derivatives, including the parent **DPA**, a distinct exothermic signal for the crystallization temperature (T_c) was only identified for **DPA**, **TPSDPA**, and **PPODPA**. Of these three compounds, only **PPODPA** possesses bipolar characteristics because of the electron deficient diphenylphosphine oxide moiety. The crystallization features of the bipolar material are particularly undesirable for light emission in OLED applications.

The glass transition (T_g) values of **CBZDPA** and **OXDDPA** were 188 and 162 °C, respectively, which were much higher than those for the other derivatives (T_g around 97–109 °C). In addition to **NPADPA**, **CBZDPA** and **OXDDPA** were the only two **DPA** derivatives where both the melting (T_m) and crystallization (T_c) temperatures were not detected (less than 350–400 °C). 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 possibly the efficiency of the devices. From the thermal property studies, the structural features of **CBZDPA** and **OXDDPA** were identified as the most effective for use in OLEDs.

Absorption and emission spectroscopic characterization

The absorption and emission spectra of **DPA** derivatives were studied in various solvents [toluene, dichloromethane, dimethylformamide (DMF), and tetrahydrofuran (THF)] as well as in solid thin films, which were prepared by spin-coating a dichloromethane solution on to quartz plates. As shown in Fig. 3, the parent compound, **DPA**, exhibits broadening and redshifting of the absorption and emission spectra in the solid state, when compared with **DPA** in solution. In its solid state the $\Phi_{\rm f}$ of **DPA** is ~60%, which is reasonably good but it is a significant decrease from the value of ~90% obtained for **DPA** in solution. This is very common for planar polycyclic aromatic hydrocarbons such as **DPA**. The spectroscopic features (including vibronic structures) observed for **DPA** are attributed to the π - π * electronic transition and its corresponding energy is sensitive to the molecular interactions (π - π molecular stacking) in the condensed phase.

Among the C-2 modified **DPA** derivatives, the broadening and red-shifting of spectroscopic features is significantly suppressed, especially in **TMPDPA**. Based on the present results, the sterically hindered mesityl group at the C-2 position is a very effective structural feature for preserving the deep blue fluorescence color of **DPA** derivatives in the solid state. The C-2 modified **DPA** derivatives, **TPSDPA**, **PPODPA**, **BMTDPA**, and **NPADPA**, are designed along these lines. However, the absorption and emission spectra are significantly red-shifted, which is detrimental to the purity of the blue color, particularly for **PPODPA**, **BMTDPA**, and **NPADPA**. Based on these spectroscopic observations, it was deduced that the broadening and redshifting spectroscopic features of these **DPA** derivatives are caused by various factors.



Fig. 3 The absorption and photoluminescence (PL) spectra of DPA and DPA derivatives in solution and in the condensed phase.

It was not expected that the triphenylsilyl group would not be as effective as the mesityl group in preventing the spectra of **DPA** from broadening or red-shifting in the solid state. However, it was noticed that both the solution λ^{ab}_{max} and λ^{fl}_{max} of TPSDPA are substantially longer than those of **TMPDPA**, which has a λ_{\max}^{ab} and λ_{max}^{fl} only slightly longer than those of DPA (Table 1). The more red-shifted spectra observed for TPSDPA than for TMPDPA can be ascribed to the σ -conjugation of the silvl group. In the solid state, the molecular packing of TPSDPA probably intensifies the σ conjugation and further red-shifts the emission spectra. However, the molecular packing slightly reduces its solid state $\Phi_{\rm f}$. It remains as high as \sim 70%, slightly less than the 86% obtained for **TPSDPA** in solution. In terms of Φ_f , **TPSDPA** is different from TMPDPA, where the fluorescence is significantly quenched in the solid state with a solid state $\Phi_{\rm f}$ of only ~40%, which is much smaller than the 90% obtained in solution. Based on this, it is thought that the pronounced red-shifting in the thin film or powder emission spectra of PPODPA may also be explained by molecular packing, because its solution λ_{max}^{fl} is at a relatively short wavelength (448-452 nm vs. 487 nm in the solid state). In addition, the molecular packing of PPODPA may be the factor that reduces its solid state $\Phi_{\rm f}$ to 30%, which is significantly lower than the solution $\Phi_{\rm f}$ of 83% (Table 1). Potentially, excimer formation may arise from the molecular packing of PPODPA. These solid state properties make PPODPA an unsuitable blue light-emitting material for OLEDs.

On the other hand, the relatively long wavelength for the solution λ_{max}^{fl} observed for both BMTDPA and NPADPA can be attributed to the electronic effect of the N-phenylnaphthalen-1amine π -donor and the dimesitylborane π -acceptor, respectively. In other words, the intramolecular charge transfer (ICT), which is lower in energy when compared with that of the π - π * transition, contributes to the electronic transition process. The less well resolved vibronic bands observed in the absorption spectra (Fig. 3) of BMTDPA and NPADPA are consistent with our conclusion. In addition, BMTDPA and NPADPA are the two DPA derivatives that show the most distinct fluorescence solvatochromism trend (Table 1), which is also consistent with the ICT that we propose above. Otherwise, the low $\Phi_{\rm f}$ and solventdependent PL wavelength may be attributed to photoinduced electron transfer, which has been observed for arylaminesubstituted electron deficient fluorophores.⁶¹⁻⁶³ In fact, NPADPA has the lowest $\Phi_{\rm f}$ of 33% and 20%, in solution and solid state, respectively, among the DPA derivatives in the present study.

Since **TMPDPA** has the least broadening and red-shifting of the **DPA** derivatives in its spectra, it was chosen for further functionalization for charge transport, *i.e.*, for hole transport in **CBZDPA** and electron transport in **OXDDPA**. Based on the wellresolved vibronic bands in the absorption spectra and the relatively high solid state Φ_f of 60% and 70%, respectively, (Fig. 3 and Table 1), it can be reasonably deduced that there is little ICT involved in the spectroscopic electronic transitions of both **CBZDPA** and **OXDDPA**. The solution absorption, λ_{max}^{ab} , and emission, λ_{max}^{fl} , 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 the anthracene core. Finally, based on the Φ_f data, both in solution and in the solid state, all the **DPA** derivatives reported here exhibit common typical aggregation causedquenching emission instead of aggregation-induced emission or aggregation-induced enhanced emission.⁶⁴⁻⁶⁶

Theoretical estimation of frontier molecular orbitals

The molecular structures of DPA, TPSDPA, TMDDPA, PPODPA, BMTDPA, 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, the electronic ground states of these DPA derivatives were calculated using DFT with the hybrid B3LYP functional and 6-31G* basis set.⁶⁷ The singlet excited states of these DPA derivatives were studied with time-dependent density functional theory by using the hybrid B3LPY functional.68 All calculations were performed with a developmental version of Q-Chem software.⁶⁹ We display a comparison of the corresponding HOMO and LUMO of these DPA derivatives in the S₀ state, where materials are in the gas phase to approximate the solution state instead of in the condensed phase. Because electronic excitation from the HOMO to the LUMO produces the first singlet excited state S1 (a Franck-Condon excited state), the orbital features presented in Fig. 4 provide important clues towards understanding the nature of the optically accessible first excited state.

From the contour plots of **DPA**, **TMPDPA**, **TPSDPA**, and **PPODPA**, both the HOMO and LUMO consist mainly of the π -conjugation of the anthracene core. Similar HOMO/LUMO contour plots were found for **OXDDPA** with little π -conjugation extended into substituents on the C-9 and C-10 positions. In contrast, the HOMO and/or the LUMO of **BMTDPA** and **NPADPA** were significantly extended beyond the anthracene core into *N*-phenylnaphthalen-1-amine and dimesitylborane, respectively. These theoretical findings are consistent with the ICT proposed from the spectroscopic characterization described in the previous section.

Considering the large twist angle (dihedral angle ~80°) between the phenyl ring and anthracene core, it is surprising that the π -conjugation shown by the HOMO contour plots of **CBZDPA** actually expands extensively into one of the phenyl-oxadiazole substituents on the C-9 and C-10 positions, whereas the π -conjugation of the LUMO is pretty much confined to the anthracene core. The implication from the theoretical results for **CBZDPA** is somewhat contradictory to the experimental spectroscopy results, *i.e.*, well-resolved vibronic absorption bands in solution, no clear trend in fluorescence solvatochromism, and a reasonable solution $\Phi_{\rm f}$.

Characterization of OLEDs and charge transport

All OLEDs were fabricated by the sequential thermal vacuum deposition of a thin film layer of the organic material and LiF–Al as the final cathode electrode on indium tin oxide (ITO)-coated glass substrate. Excluding **BMTDPA** and **NPADPA**, which were spectroscopically unsatisfactory, six devices were fabricated from six blue **DPA** derivatives, with the device configuration of ITO/NPB (30 nm)/TCTA (10 nm)/DPAs (30 nm)/TPBI (30 nm)/LiF



Fig. 4 Calculated spatial distributions of the HOMO and LUMO of DPA and DPA derivatives.

(1 nm)/Al, where 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-1-amino]biphenyl (NPB) is a common hole-transporting layer, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1*H*-benzimidazole) (TPBI) is a common electron-transporting layer, and LiF–Al were used as the electron injecting layer and cathode. In each device, between the NPB and **DPA** light-emitting layers, there is a thin layer of tris(4-carbazoyl-9-ylphenyl)amine (TCTA), which serves multiple functions, including as a hole-transporting layer, exciton blocking layer, and in smoothing the alignment of the HOMO energy levels inside the device. Such interlayers can decrease the 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 its solid state PL, **TMPDPA** exhibits the deepest blue EL, with a wavelength (444 nm) nearly as short as that of **DPA** (442 nm) and an EL band width (66 nm) nearly as narrow as that of **DPA** (56 nm). Therefore, the 1931 $\text{CIE}_{x,y}$ of the **DPA** and **TMPDPA** OLEDs are a comparable deep blue; (0.15, 0.05) and (0.17, 0.10), respectively. The EL spectra of **TPSDPA**, **CBZDPA**, and **OXDDPA** are slightly red-shifted and broadened, although the 1931 $\text{CIE}_{x,y}$ chromaticity of these devices remains a

satisfactory blue colour (all *y*-values are less than 0.20, Table 2). However, the EL spectrum of **PPODPA** is significantly worse and its 1931 $\text{CIE}_{x,y}$ (0.22, 0.37) indicates that it is not a blue OLED because of its unsatisfactory colour purity.

For EL efficiency, both TMPDPA and TPSDPA OLEDs greatly outperform the DPA OLED with just a small compromise in the purity of the blue color. In fact, the current density and brightness of TMPDPA and TPSDPA OLEDs are far superior to that of the DPA OLED (Fig. 5). More specifically, the EL efficiency of the TPSDPA OLED is better than the TMPDPA OLED, which can be mostly attributed to the higher $\Phi_{\rm f}$ of **TPSDPA** than TMPDPA in the solid state. Nevertheless, the purity of the blue color (1931 $\text{CIE}_{x,y}$ in Table 2) of the TMPDPA OLED is slightly better than that of the TPSDPA OLED. For PPODPA, the OLED performance is inferior in all aspects, including current density, brightness, blue colour purity, and EL efficiency (Fig. 5). The unsatisfactory performance of the PPODPA OLED is mainly because of its poor $\Phi_{\rm f}$ and red-shifted emission in the solid state, which can be attributed to its bipolar structure that promotes its crystallization in the solid state. PPODPA is the one of two DPA derivatives here that shows a T_c in the thermal

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Fig. 5 Electroluminescence characteristics of DPA and DPA derivatives

Table 2 Characteristics of OLEDs^a

DPA derivatives	Turn-on voltage ^b (V)	Max. luminance, voltage (V)	Max. efficiency ^c (%, cd A^{-1} , lm W^{-1})	λ_{\max} EL, fwhm ^d (nm)	1931 CIE chromaticity $(x, y)^d$	Efficiency at 100 and 1000 cd m^{-2} (%, cd A^{-1} , lm W^{-1})
DPA	3.5	1134. 15	1.5, 0.7, 0.4	440, 56	(0.15, 0.05)	1.6, 0.8, 0.4; 0.3, 0.7, 0.2
TMPDPA	4.0	1477, 15	3.0, 2.5, 1.9	444, 66	(0.17, 0.10)	2.8, 2.4, 1.5; 1.1, 0.8, 0.3
TPSDPA	3.5	4501, 15	3.8, 4.4, 3.8	458, 76	(0.16, 0.15)	3.7, 4.2, 2.8; 2.9, 3.2, 1.4
PPODPA	4.0	7891, 15	0.7, 2.5, 1.1	496, 96	(0.22, 0.37)	0.6, 1.7, 0.9; 1.1, 2.5, 0.9
CBZDPA	3.5	3377, 15	4.5, 5.7, 3.9	454, 72	(0.17, 0.17)	4.5, 5.6, 3.7; 3.3, 4.0, 1.8
OXDDPA	3.5	6985, 15	4.0, 5.2, 5.1	460, 78	(0.16, 0.18)	4.0, 5.2, 3.6; 3.6, 4.7, 2.3

^{*a*} ITO/NPB (30 nm)/TCTA (10 nm)/9,10-**DPA** based derivatives (30 nm)/TPBI (30 nm)/LiF (1 nm)/Al. ^{*b*} With electroluminance at 1 cd m⁻². ^{*c*} At a current density of 1 mA cm⁻². ^{*d*} fwhm denotes full-width-at-half-maximum and the EL spectra were recorded at 8.0 V and the same EL spectra for 1931 CIE chromaticity.

property measurements (see Fig. 2). Following our previous analysis of the spectroscopic data of **PPODPA**, excimer formation is highly probable in the non-doped device. This explains the low solid state Φ_f and thus, the low brightness, the low current density because of the charge trapping nature of the excimer, and the long EL wavelength and thus the poor 1931 $\text{CIE}_{x,y}$ for blue purity.

From their structures, **CBZDPA** and **OXDDPA** are considered as derivatives of **TMPDPA** with charge transporting moieties on their phenyl rings at the C-9 and C-10 positions of the anthracene core. The EL efficiency of the **CBZDPA** and **OXDDPA** OLEDs is drastically improved in comparison with that of the **TMPDPA** OLEDs (Fig. 5 and Table 2). OLEDs exhibit an EL efficiency of 4.5% and 4.0% at an EL of 100 cd m⁻², respectively; and 3.3% and 3.6% at an EL of 1000 cd m⁻², respectively. The **TMPDPA** OLED exhibits an EL efficiency of only 2.8% and 1.1% at an EL of 100 and 1000 cd m⁻², respectively. At first glance, the much higher solid state $\Phi_{\rm f}$ of CBZDPA and OXDDPA than that of TMPDPA provides a logical explanation for the improved EL efficiency of these OLEDs. Furthermore, we think that the charge transport molecular structures of CBZDPA and OXDDPA also contribute to the enhancement of the EL efficiency.

In order to understand the hole and electron transporting properties of **TMPDPA**, **CBZDPA**, and **OXDDPA**, we also fabricated two kinds of single-charge carrier-dominated devices⁷⁰ for exploring the nature of the material charge carrier in terms of the current density of these devices. The hole-dominated device has a configuration of ITO/NPB (40 nm)/TCTA (10 nm)/**DPA** derivative (50 nm)/NPB (20 nm)/Al (100 nm). The electron-dominated device has a configuration of ITO/BCP (10 nm)/**DPA**



Fig. 6 Current density-voltage (I-V) characteristics of the hole-dominated device (left) and the electron-dominated device (right).

derivative (50 nm)/TPBI (20 nm)/LiF (1 nm)/Al (100 nm). As shown in the inset of Fig. 6, we used a high-lying LUMO NPB to limit the electron carrier in the hole-dominated device and a low-lying HOMO BCP and TPBI to limit the hole carrier in the electron-dominated device. One should note that the current density of a single-charge carrier-dominated device is determined by several factors: the hole injection barrier between the electrode and organic layers, the difference in the HOMO energy levels between adjacent organic layers, and the charge mobility of each organic layer. In this case, the HOMO energy levels of TMPDPA and CBZDPA are very similar, which implies that the current density of the hole-dominated device depends solely on the hole-mobility of the blue emitter. The HOMO energy level of OXDDPA is about 0.20 to 0.23 eV higher than the other two, which implies that it should be easier for the hole carrier to pass through the device. Considering all the factors, the current density of the device indicates that the hole mobility of the three DPA derivatives is in the order CBZDPA > TMPDPA > OXDDPA. The current density of the electron-dominated device is similar but in 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 that there is no apparent electron injection barrier at the interface of the two layers. The magnitude of the current density clearly decreases in the order OXDDPA > TMPDPA > CBZDPA, which is in accordance with the anticipated order of the electron mobility of the material based on the electron deficient structural features.

The charge transporting properties of light-emitting materials is one of the paramount factors in enhancing the EL efficiency and reducing the efficiency roll-off of non-doped OLEDs such as those used in the present study. Whereas the hole transporting nature of CBZDPA enhances the EL efficiency in the low to medium current density range, the electron transporting nature of OXDDPA enhances the EL efficiency in the high current density range. This difference in current densitydependent EL efficiency enhancement makes CBZDPA the most efficient EL in the low current density range although OXDDPA becomes the most efficient EL in the high current density range (Fig. 5). The efficiency roll-off is more pronounced in the CBZDPA OLED than in the OXDDPA OLED, which is consistent with our conclusions. In addition, from the experimental results for the PPODPA EL efficiency (Fig. 5 and Table 2), there is no efficiency roll-off, rather a "roll-up" at current densities as high as 100 mA cm⁻². Like **OXDDPA**, diphenylphosphine oxidebearing **PPODPA** is bipolar and has potential for electron transport.

Conclusions

In summary, we have synthesized and characterized a series of DPA derivatives, TPSDPA, TMDDPA, PPODPA, BMTDPA, 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 a bulky or sterically hindered substituent at the C-2 position to prevent the solid state emission from red-shifting and broadening. In addition to one failure, PPODPA, which tends to crystallize and form excimers in the condensed phase, the emission of BMTDPA and NPADPA were strongly quenched and red-shifted because of the ICT. The non-doped OLEDs fabricated with charge transport moiety-bearing CBZDPA or OXDDPA exhibited the highest external quantum efficiencies of 4.5% and 4.0%, respectively, of all the OLEDs, including the DPA OLED, which was only 1.5% with the same device structure. The charge transporting properties of CBZDPA and OXDDPA were verified by the current density of hole-dominated and electron-dominated devices. We have successfully demonstrated that the mesityl group on the C-2 position is excellent in preserving the deep blue fluorescence of DPA in the solid state. The EL efficiency of DPA OLEDs have been greatly improved by incorporating charge transporting moieties on the phenyl rings at the C-9 and C-10 positions of the 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 a Hitachi F-5400 fluorescence spectrophotometer with excitation at 380 nm. The solution fluorescence quantum yields of the compounds of interest were determined relative to that of **DPA** in dichloromethane at 298 K ($\Phi_{\rm f} = 0.9$).⁴⁴ The solid-state fluorescence quantum yields ($\Phi_{\rm f}$) of the blue emitters were determined by the integrating sphere method.^{71,72} The ionization potentials (or HOMO energy levels) of **DPA** derivatives were determined by a low-energy Riken Keiki AC-2 photo-electron spectrometer. LUMO energy levels were estimated by subtracting the energy (ΔE) from the HOMO energy levels. ΔE was determined by the onset absorption energy from the absorption spectra of the thin film materials. 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⁻¹. TGA was carried out on a Perkin-Elmer DSC-7 thermogravimetric analyzer to determine the decomposition temperatures (T_d) of the compounds under a nitrogen atmosphere, using a scan rate of 10 °C min⁻¹. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AV-400 or Bruker AV-III 400 MHz instrument, using deuterated chloroform (CDCl₃) as the internal standard. Electroionization-high-resolution mass spectrometric (EI-HRMS) measurements were obtained from the Mass Spectroscopic Laboratory in-house service of the Institute of Chemistry, using a Jeol JMS-700 double focusing mass spectrometer.

Fabrication and characterization of light-emitting diodes

OLED devices were fabricated by thermal vacuum deposition. The substrate was ITO coated glass (Shinan SNP, Taiwan) with a sheet resistance of $\leq 30 \ \Omega \ sq^{-1}$. The pretreatment of ITO included 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 a CRYOTEC-10 at a chamber pressure of 10⁻⁶ Torr. The thickness of each layer was determined by a quartz thickness monitor (Sycon STM-100/MF and Sycon STM-2XM). The LiF-Al cathode was prepared first by thermal deposition of a LiF thin film (10 Å) followed by the deposition of Al (1000 Å) as the top layer. The thickness of each layer of material was determined as described previously. 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 was significantly smaller than the active area of the photodiode detector, a condition known as "under-filling", which satisfied the measurement protocol.73 This is one of the most conventional ways of measuring the EL efficiency of OLEDs, although sometimes experimental errors may arise because of the non-Lambertian emission of OLEDs.74 Current-voltage-luminance (I-V-L) measurements were made simultaneously using a Keithley 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photodiode. The measurements of the devices were made at room temperature under ambient conditions. The EL was measured using the Hitachi F-5400 fluorescence spectrophotometer by blocking the incident light.

Synthesis of materials

Unless specified, all reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. All commercially available chemical reagents were used directly without further purification. Compounds such as 2-bromo-9,10-diphenylan-thracene (1),⁷⁵ 2-bromoanthracene (3),⁷⁶ 2,4,6-trimethylphenylboronic acid,⁷⁷ 9-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-

phenyl]-9*H*-carbazole,⁷⁸ and 2-phenyl-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole⁴¹ were prepared according to methods in the literature. For the materials used in device fabrication, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was commercially available. NPB⁷⁹ TPBI⁸⁰ and TCTA⁸¹ were prepared *via* published methods and were subjected to gradient sublimation prior to use.

9,10-Diphenyl-(2-triphenylsilanyl)anthracene (TPSDPA, 2a)

To a dry diethyl ether solution (60 mL) of 2-bromo-9,10-diphenylanthracene (0.96 g, 2.35 mmol) was added n-BuLi (1.66 mL, 4.16 mmol, 2.5 M in hexane) slowly at -78 °C. The mixture was stirred for 45 min under a nitrogen atmosphere. Chlorotriphenylsilane (1.0 g, 3.39 mmol) in diethyl ether (10 mL) was added dropwise at -78 °C and the mixture was stirred at room temperature for 12 h. After the reaction was guenched with water, the mixture was extracted with dichloromethane. The organic layer was dried with magnesium sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, 10% CH₂Cl₂hexane) to give TPSDPA (0.7 g, 44%) as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.93 (s, 1H), 7.71-7.65 (m, 3H), 7.59-7.45 (m, 13H), 7.38–7.24 (m, 17H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 138.96, 138.42, 137.84, 136.82, 136.26, 134.08, 131.34, 131.08, 130.98, 130.52, 130.28, 130.03, 129.92, 129.44, 129.24, 128.37, 128.15, 127.79, 126.92, 125.69, 125.27, 124.93. EI-HRMS: calculated 588.2273, $m/z = 588.2270 (M^+)$.

9,10-Diphenyl-(2-diphenylphosphinyl)anthracene (PPODPA, 2b)

To a dry THF solution (60 mL) of 2-bromo-9,10-diphenylanthracene (1.0 g, 2.45 mmol) was added n-BuLi (1.96 mL, 4.90 mmol, 2.5 M in hexane) slowly at -78 °C. The mixture was stirred for 45 min under a 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 h. After the reaction was quenched with water, the mixture was extracted with dichloromethane. The separated organic layer was evaporated to dryness under reduced pressure. The solid residue was re-dissolved in CH2Cl2 (10 mL) and was treated with H₂O₂ (10 mL, 30 wt% in H₂O) and stirred for another 24 h. The separated organic layer was dried with magnesium sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, 10% CH₂Cl₂-EtOAc) to give PPODPA (0.4 g, 30%) as a light yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.86–7.28 (d, J = 0.8Hz, 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, 134.39, 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-HRMS: calculated 530.1800, m/z =530.1801 (M⁺).

9,10-Diphenyl-(2-dimesitylboranyl)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-BuLi (1.1 mL, 2.84 mmol, 2.5 M in hexane) slowly at -78 °C. The mixture was stirred for 45 min under a 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 h. After the reaction was quenched by water, the mixture was extracted with dichloromethane. The organic layer was dried with magnesium sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, hexane) to give **BMTDPA** (0.12 g, 21%) as a yellow-green solid. ¹H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.83 (s, 1H), 7.78–7.75 (d, J = 8.4 Hz, 1H), 7.71–7.69 (d, *J* = 8 Hz, 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, 131.28, 130.58, 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-HRMS: calculated 578.3145, m/z =578.3141 (M⁺).

9,10-Diphenyl-(2-phenylnaphthalen-1-amino)anthracene (NPADPA, 2d)

To a mixture of N-phenylnaphthalen-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, 2.35 mmol), 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 the mixture was stirred at 120 °C for 16 h. 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 sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, 10% CH₂Cl₂hexane) to give NPADPA (0.91 g, 84%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.88–7.84 (t, J = 8 Hz, 2H), 7.72–7.70 (d, J = 8 Hz, 1H), 7.65-7.61 (m, 2H), 7.57-7.54 (t, J = 4 Hz, 2H),7.51–7.45 (m, 4H), 7.43–7.41 (d, J = 8 Hz, 1H), 7.37–7.33 (t, J = 8 Hz, 1H), 7.29-7.14 (m, 10H), 7.09-7.07 (d, J = 8 Hz, 4H), 6.95-6.91 (t, J = 8 Hz, 1H), 6.86–6.85 (d, J = 12 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 147.65, 144.56, 143.14, 139.09, 138.53, 136.78, 135.23, 131.24, 131.04, 130.80, 130.15, 128.96, 128.29, 127.87, 127.78, 127.35, 127.00, 126.84, 126.65, 126.40, 126.23, 126.07, 125.95, 124.99, 124.17, 124.00, 122.54, 122.46, 122.32, 114.46. EI-HRMS: calculated 547.2300, m/z = 547.2292 (M⁺).

2-(1,3,5-Trimethylphenyl)anthracene (4)

To a deoxygenated mixture of 2-bromoanthracene (0.18 g, 0.70 mmol), 2,4,6-trimethylphenylboronic acid (0.2 g, 0.77 mmol), $K_2CO_{3(aq)}$ (1.2 mL, 2.31 mmol, 2 M in H_2O), and ethanol (1 mL) in toluene (5 mL) was added tetrakis(triphenylphosphine) palladium (0.04 g, 0.04 mmol) and the mixture was stirred at

80 °C for 12 h. After the reaction was cooled to room temperature, toluene was removed under reduced pressure and the residue was extracted with dichloromethane and H₂O. The organic layer was dried with magnesium sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, hexane) to give 2-(1,3,5-trimethylphenyl)anthracene (0.15 g, 55%) as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.63–8.56 (m, 3H), 8.37 (s, 1H), 7.63–7.60 (m, 2H), 7.45–7.42 (dd, *J* = 1.2 Hz, 1H), 7.00 (s, 2H), 2.36 (s, 3H), 2.06 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ (ppm): 138.81, 138.09, 136.71, 136.11, 131.89, 131.69, 130.65, 128.16, 128.05, 127.91, 127.72, 126.03, 125.77, 125.38, 125.23, 21.02, 20.74. Fast atom bombardment-MS: calculated 296.16, *m*/*z* = 296.2 (M⁺).

9,10-Dibromo-2-(1,3,5-trimethylphenyl)anthracene (5)

To a chloroform solution (2 mL) was added 2-(1,3,5-trimethylphenyl) anthracene (0.2 g, 0.67 mmol) and N-bromosuccinimide (0.33 g, 1.87 mmol) and the resulting mixture was stirred at 50 °C for 2 h under a nitrogen atmosphere. After the reaction was cooled to room temperature, the mixture was poured into 2 N NaOH_(aq) and extracted with dichloromethane. The organic layer was dried with magnesium sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The residue was purified by using column chromatography (silica gel, hexane) to give 9,10dibromo-2-(1,3,5-trimethylphenyl) anthracene (0.2 g, 65%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.63–8.56 (m, 3H), 8.37 (s, 1H), 7.63–7.60 (m, 2H), 7.45–7.42 (dd, J = 1.2 Hz, 1H), 7.00 (s, 2H), 2.36 (s, 3H), 2.06 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ (ppm): 140.36, 137.94, 137.17, 135.95, 131.26, 130.98, 130.10, 129.98, 129.75, 128.44, 128.30, 128.24, 128.19, 128.05, 127.45, 127.30, 123.4, 123.33, 21.00, 20.78. Matrix-assisted laser desorption/ionization (MALDI)-MS: calculated 451.98, $m/z = 451.9 (M^+).$

9,10-Bis(4-carbazole)phenylene-2-(1,3,5-trimethylphenyl) anthracene (CBZDPA, 6a)

This compound was prepared by a similar method to that of 9,10-diphenyl-2-(1,3,5-trimethylphenyl) anthracene, except that 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9Hcarbazole (0.37 g, 0.99 mmol), two drops of Aliquat 336 and triphenylphosphine (0.034 g, 0.13 mmol) were added to the reaction and the reaction continued for 24 h. A mixed solvent of 15% EtOAc-hexane was used as the eluent for column chromatography. CBZDPA was obtained as a white solid (0.15 g, 60%). 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, 127.66, 127.43, 127.00, 126.88, 126.82, 126.73, 126.05, 125.98, 125.55, 125.39, 123.58, 120.42, 120.33, 120.14, 120.10, 110.10, 109.95, 20.99, 20.96. EI-HRMS: calculated 778.3348, m/z = 778.3329 (M⁺).

9,10-Diphenyl-2-(1,3,5-trimethylphenyl)anthracene (TMPDPA, 6b)

To a deoxygenated mixture of 9,10-dibromo-2-(1,3,5-trimethylphenyl)anthracene (0.2 g, 0.44 mmol), phenylboronic acid (0.13 g, 1.1 mmol), K₂CO_{3(aq)} (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 the resulting mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the toluene solvent was removed under reduced pressure and the residue was extracted with dichloromethane and water. The organic layer was dried with magnesium sulfate. After removal of the drying agent, the organic solution was evaporated to dryness under reduced pressure. The resulting solid was purified by using column chromatography (silica gel, 10% dichloromethane-hexane) to give TMPDPA (0.1 g, 50%) as a white solid. ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 7.74-7.59 (m, 6H), 7.56-7.44 (m, 10H), 7.32-7.30 (m, 2H), 7.15–7.12 (dd, J = 4 Hz, 1H), 6.90 (s, 2H), 2.29 (s, 3H), 1.99 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm): 139.14, 137.35, 137.00, 136.65, 136.14, 133.57, 133.07, 132.17, 131.38, 131.26, 130.16, 129.97, 129.86, 128.86, 128.41, 128.14, 127.57, 127.46, 126.91, 126.09, 125.00, 124.88, 123.38. EI-HRMS: calculated 448.2191, $m/z = 448.2197 (M^+)$.

9,10-Bis[3-(3-phenyl-2,4,5-oxadiazole)phenylene]-2-(1,3,5-trimethylohenyl)anthracene (OXDDPA, 6c)

This compound was prepared by a similar method to that of TMPDPA, except that 2-phenyl-5-(3-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole (1.91 g, 5.5 mmol) was used in the reaction. In addition, a mixed solvent of 20% EtOAc-hexane was used as the 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, 1H), 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), 6.89–6.86 (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, 135.85, 134.59, 134.53, 131.70, 130.01, 129.87, 129.76, 129.53, 129.43, 129.01, 128.81, 128.21, 126.91, 126.63, 126.46, 126.28, 125.64, 125.52, 124.46, 123.85, 20.82. EI-HRMS: calculated 736.2838, m/z = 736.2845 (M⁺).

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