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Non-doped active layer, benzo[*k*]fluoranthene-based linear acenes, for deep blue- to green-emissive organic light-emitting diodes



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ABSTRACT

This work studies a series of fluorescent materials, benzo[k]fluoranthene-based linear acenes, and uses these materials directly as the non-doped active layer to fabricate deep blue- to green-emissive organic light emitting diodes (OLEDs). Experimental results indicate that benzo[k]fluoranthene-based linear acenes with different substituents in pristine films have a wide range and strong intensity of the luminescence spectra. The substituents of benzo[k]fluoranthene derivatives modulate the lifetime of the excited state and PL spectra of excitonic, excimer or both emissions in the solid state. Controls of emission spectra are exploited in fabricating high-performance non-doped deep blue to green OLEDs with electroluminescence in the deep blue region (420–460 nm), green region (480–580 nm) or both (430–580 nm).

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1. Introduction

Deep blue emitting materials for organic light-emitting diodes (OLEDs) have been of interest for many years [1]. They exhibit the emissions of shorter wavelengths in fabricating white-emissive OLEDs of high color rendering index (CRI) [2–7] for display [8] and lighting [9] applications. In phosphorescence OLED, deep blue phosphorescent materials with favorable performance are rare. The most widely used blue phosphorescent material, (iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C^{2'}]picolinate (FIrpic)), only emits in the "bluish region" [10], with Commission Inter-

nationale de l'Eclairage (CIE) chromaticity coordinates (x, y) of (0.16, 0.29) [11]. Alternatively, many fluorescent materials exhibit deep blue emission and own a good potential of producing deep blue light. However, while we apply the blue-emissive materials as the dopant in the light-emitting layer, the precise control of the doping concentration over a large area in the manufacturing process is difficult. The development of the non-doped fluorescent materials directly used as the active layer is of great importance to simplify the fabrications.

In solution, several planar aromatic molecules are highly fluorescent and have high quantum yields. These include anthracene [12–15], fluorene [16,17], pyrene [18,19], fluoranthene [20–23], etc. [24], but they are only weakly fluorescent in the solid state. In these materials, strong intermolecular interactions between emissive molecules cause a red-shift of the emission spectra by aggregation



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[25] or the quenching of their emissive properties [20,26]. Tailoring the molecular structures to impart the steric hindrance would markedly improve the solid-state photophysical properties of the planar conjugated molecules as reported elsewhere [16,19]. Our previous studies had successfully demonstrated that benzo[k]fluoranthene-based linear acenes own the deep blue PL and can be used as dopants with the host material to fabricate efficient deep blue-emissive OLEDs [27]. A decent non-doped emitting material (pristine film) must exhibit sufficiently strong fluorescence in its solid state for lighting applications. In molecular engineering, steric hindrance is utilized to solve the aforementioned problems [18]. The pendant aryl groups increase the distance between emitters and prevent crystallization. In non-doped blue OLEDs, such as applying derivatives of anthracene [12], fluorene [17], pyrene [18,19], fluoranthene [20], etc. [24] as light-emitting layers, this method has been used to yield excitonic blue light luminescence with high color purity [28–30]. Accordingly, the control of the luminescence properties in the nondoped OLEDs requires the systematic investigations of the effects of different substituents on emissive materials in pristine films must be carried out.

This study systematically investigates the PL properties of pristine benzo[*k*]fluoranthene-based linear acenes [31,32] films and applies them in non-doped deep blue to green OLEDs. The steric hindrance effect is exploited to maintain the strong excitonic PL emission properties of pristine films that comprise compounds (in Scheme 1) 7.12-diphenvlbenzolklfluoranthene (DPBF) and 7.14diphenylnaphtho[2,3-*k*]fluoranthene (DPNF). The methyl and methoxyl substituents in 9,10-dimethyl-7,12-diphenvlbenzo[k]fluoranthene (DPBF-ME) and 9.10-dimethoxy-7.12-diphenylbenzolklfluoranthene (DPBF-OME). respectively, modulate these PL emissive properties. The results indicate a clear shift of the PL spectra of the amorphous DPBF-ME and DPBF-OME pristine films mainly owing to the long lifetime of the excited state. The electroluminescence (EL) spectra of non-doped OLEDs are consistent with the results from of previous PL. EL emission colors with CIE chromaticity coordinates (x, y) of (0.17, 0.16) in DPBF-based OLED, (0.25, 0.48) in DPBF-ME-based OLED and (0.22, 0.27) in DPBF-OME-based OLED are reported in this study. The excellent electrical properties of these devices are as follows; a low turn-on voltage of approximately 3 V, and a maximal luminous efficiency (LE), maximum brightness and corresponding external quantum efficiency (EQE) of 5.1 cd A^{-1} , 19282 cd m^{-2} and 1.8%, respectively.

2. Results and discussion

Scheme 1 presents the chemical structures in detail. The abbreviations for all benzo[*k*]fluoranthene-based linear acenes prepared in this study are; benzo[*k*]fluoranthene (BF), 9,10-dimethylbenzo[*k*]fluoranthene (BF-ME), 7,12-diphenylbenzo[*k*]fluoranthene (DPBF), 9,10-dimethyl-



Scheme 1. The molecular structures of benzo[k]fluoranthene based linear acenes, BF, BF-ME, DPBF, DPBF-OME and DPNF.

7,12-diphenylbenzo[*k*]fluoranthene (DPBF-ME), 9,10dimethoxy-7,12-diphenylbenzo[*k*]fluoranthene (DPBF-OME) and 7,14-diphenylnaphtho[2,3-*k*]fluoranthene (DPNF). Benzo[*k*]fluoranthene (BF) (>99%) was purchased from Aldrich and used as received.

2.1. Synthesis of benzo[k]fluoranthene-based linear acenes

The simple synthetic route of benzo[k]fluoranthenebased linear acenes, BF-ME, DPBF, DPBF-ME, DPBF-OME, and DPNF is in Scheme 1. The benzo[k]fluoranthene-based linear acenes were synthesized by single-step Pd-catalyzed [(2+2)+2] cycloadditions of a diyne, such as 1,8-diethynylnaphthalene (1), 1,8-bis(trimethylsilylethynyl)naphthalene (2), and an aryl iodide, such as iodobenzene (A), 1,2-diiodo-4,5-dimethylbenzene (B), 1,2diiodo-4,5-dimethoxybenzene (C) or 2,3-diiodonaphthalene (D). The [(2+2)+2] cycloaddition involves diyne and an aryl iodide, which provide a four-carbon building block and a two-carbon building block, respectively. In the synthesis of BF-ME, the cycloaddition between (1) and (B) formed a mixture of mono- and bis(trimethylsilvl)-substituted cycloadducts in low yield. These two compounds were converted into 9,10-dimethylbenzo[k]fluoranthene (BF-ME) by treatment with acetic acid. The reactions were performed in *p*-xylene at 110 or 130 °C. More details of the synthesis can find in the literature [32].

2.2. Photoluminescence characteristics of benzo[k]fluoranthene-based linear acenes

Fig. 1 presents the PL properties (dash lines) (dilute in dichloromethane (CH₂Cl₂), 10^{-5} M) of benzo[k]fluoranthene-based linear acenes in solution. All of the benzo[k]fluoranthene derivatives in solution exhibit strong blue excitonic (monomeric) emission signals at short visible wavelengths. The shortest and strongest PL spectral signals from BF (Fig. 1a), BF-ME (Fig. 1b), DPBF (Fig. 1d), DPBF-ME (Fig. 1e) and DPBF-OME (Fig. 1f) are 412 nm, 419 nm, 425 nm, 431 nm and 436 nm, respectively (Table 1), which are associated with a 0-0 transition. This observation indicates that the electron-donating groups (such as methyl, methoxyl and phenyl ring) attached to benzo[k]fluoranthene-based linear acenes may affect the conjugated system by the inductive effect to shift PL spectra. Additionally, applying a naphtho[2,3-k]fluoranthene core markedly extends the conjugated system. In Fig. 1c, DPNF, with the longest conjugation has the PL emission wavelength of 458 nm, which is 33 nm longer than that of DPBF. Although benzolklfluoranthene-based linear acenes have excellent PL properties in solution, PL characteristics in the solid state are even more important for lighting and display applications.

The solid lines in Fig. 1 correspond to the pristine film of benzo[*k*]fluoranthene derivatives with a thickness of 15 nm on glass substrates. In the pristine film, the short distance between the molecules results in the formation



Fig. 1. Photoluminescence (PL) spectra of benzo[*k*]fluoranthene based linear acenes, (a) BF, (b) BF-ME, (c) DPNF, (d) DPBF-ME, and (f) DPBF-OME. Dash lines are materials in dichloromethane (CH_2CI_2 , 10^{-5} M) and solid line are pristine films 15 nm on glass, respectively.

Compound	HOMO ^a (eV)	LUMO (eV)	Band gap^b (eV)	$PL_{sol}^{c}(nm)$	PL _{film} ^c (nm)	EL ^c (nm)
BF	_	-	2.95	412, 435	414, 434, 462	_
BF-ME	-	-	2.90	419, 440	441, 474, 504	-
DPBF	5.70	2.84	2.86	425, 445	428, 446	427, 451
DPBF-ME	5.74	2.91	2.83	431, 452	472, 501	477, 507
DPBF-OME	5.64	2.81	2.82	436, 453	441, 457	440, 464
DPNF	5.48	2.83	2.65	458, 485	466, 488	466, 494

Photophysical properties of benzo[k]fluoranthene based linear acenes.

Table 1

^a HOMO level measured from cyclic voltammetry, detail calculation is in Ref. [27].

^b Band-gaps were obtained from onset point of absorption edge.

^c The terms PL_{sol} and PL_{film} indicate the major PL signals in solution and film state, respectively. EL indicates the major emission signals from devices.

of intermolecular interactions [25,33-36]. PL spectra reveal excitonic emission and the aggregation (or crystallization)-induced emission [34], such as from dimer or trimer, as well as excimer emission in the long-wavelength region. The unmodified planar materials, BF and BF-ME, have a relatively rough surface in the pristine film due to the crystallization. As a result, the weak PL peaks of the BF film at 487 nm and 520 nm are associated with dimer emission [31]. As displayed in Fig. 1d and e, the PL spectra of DPBF and DPBF-ME films reveal two distinct emissive features - the strong deep blue excitonic emission of DPBF films, and the green emission of DPBF-ME films. These two significantly different features suggest that the methyl group of benzo[*k*]fluoranthene derivatives play a critical role to modulate the intermolecular interaction. The molecular packing-induced dimer emission is vanished in the DPBF film as shown in Fig. 1d, implying that the phenyl substituents changing order packing into amorphous film.

In Fig. 1c and e, the PL emission of pristine DPBF-ME film is compared with that of the long-conjugated material, DPNF. The PL spectral shape of pristine DPNF film is close to that of DPNF in solution, which emits mostly excitonic signals. The major PL peaks of the DPBF-ME film are at 472 nm and 501 nm, and those of the DPNF film are at 466 nm and 488 nm. The PL spectrum of the DPBF-ME film is even more red-shift than that of the longer conjugated material, DPNF, in the green wavelength region. These results indicate that the PL of benzo[k]fluoranthene-based linear acenes with (or without) methyl groups in a pristine film has a very wide range of emission signals. The benzo[k]fluoranthene-based linear acene with another substituent, methoxyl group, DPBF-OME, is also studied. Fig. 1d-f clearly shows the variation among the PL spectra of DPBF, DPBF-ME and DPBF-OME films. The DPBF film exhibits strong excitonic emission. DPBF-ME exhibits green emission by strong intermolecular interactions and DPBF-OME exhibits the both of these emissions. These results suggest that the PL spectra of pristine benzo[k]fluoranthene-based linear acenes films can be tuned by varying the substituents.

2.3. Extra emissive states by molecular packing and amorphous films by steric hindrance

Fig. 2a and b shows the excitation spectra of benzo[k]fluoranthene derivatives, BF and DPBF, in 10^{-5} M CH₂Cl₂ (dashed line) and in pristine films with a thickness of 15 nm (solid line), obtained using incident light with



Fig. 2. Excitation spectra of benzo[*k*]fluoranthene based linear acenes. (a) BF and (b) DPBF in CH_2Cl_2 , 10^{-5} M and pristine films on glass, 15 nm. (c) Pristine BF-ME, DPBF-ME and DPBF-OME films, 15 nm. Incident light wavelength is between 380 and 500 nm and detected position is 520 nm.

wavelengths of 380–500 nm and a detected wavelength of 520 nm. The spectrum offset of BF and DPBF solution are 419 nm (2.95 eV) and 433 nm (2.86 eV), respectively, which are the same as their optical band gaps (Table 1). BF and DPBF present the strong monomer emission properties. It is noted that pristine BF films have many extra states. Molecular packing can have many effects, such as molecular aggregation and the formation of a polycrystalline structure whose photo-physical properties are influenced by extra states. The energy levels of the extra states are lower than their optical gaps, and the results herein indicate that these extra states can contribute to PL emission at long wavelengths. A comparison with Fig. 2c demonstrates that the ratio of the intensities of the extra states in the BF-ME film is smaller than that of those in the BF film, but the green PL emission signals are much stronger than those of the BF (Fig. 1a and b). It is suggested that the methyl groups are critical to change the strength of the intermolecular interaction. The extra states are attributed to the face-to-face contact of planar molecules, strong molecular aggregation or the polycrystalline structure.

An amorphous emissive layer outperforms a polycrystalline emissive layer in OLEDs, because of the absence of grain boundaries and the larger distance between emissive molecules [37,38]. Fig. 2b and c shows the excitation spectra of pristine DPBF, DPBF-ME, and DPBF-OME films. The phenyl rings are pushed out of the plane of the benzo[k]fluoranthene emissive core by steric hindrance, increasing the distance between the emissive molecules and thereby reducing face-to-face contact. The absence of signals from the extra states of pristine DPBF, DPBF-ME, and DPBF-OME films implies the decrease of face-to-face contact. Fig. 3 presents the X-ray diffraction (XRD) patterns of 15 nm-thick pristine BF and DPBF films on glass substrates. The figure clearly indicates that a film of planar BF molecules yields the signals of a crystal structure, and that pristine DPBF film is much more amorphous (DPBF-ME, DPBF-OME and DPNF are also amorphous, data not shown here). The structural analysis of benzo[k]fluoranthene-based linear acenes can be found in our previous publication [32]. The steric hindrance increases the distance between emission cores and makes the emissive layer close to amorphous. More importantly, the shifts in the PL spectra of pristine DPBF, DPBF-ME, DPBF-OME films are attributable to the different functional groups (methyl and methoxyl), which increase the excimer emission in the spectra. The correlations about the substituents with the change of the emission spectra should be examined.

2.4. Excited state lifetime control the PL spectra

Excimer usually has long lifetimes, which are associated with a high probability of energy transfer with emission in the long-wavelength region. The lifetime of an excimer is always a few times, or one to two orders of magnitude larger than, the lifetime of an exciton [39]. Fig. 4a shows time-resolved photoluminescence (TRPL) measurements



Fig. 3. X-ray diffraction (XRD) patterns of 15 nm pristine BF and DPBF films on glass.

of 15 nm-thick pristine DPBF, DPBF-ME and DPBF-OME films made at 500 nm. Table 2 presents a more detailed analysis of the TRPL results. The decay rates of TRPL intensity as a function of time at 500 nm increase in the order of DPBF-ME > DPBF-OME > DPBF, in which the excited states have mean lifetimes of 20.88 ns. 6.44 ns and 2.93 ns. respectively. The DPBF-ME film has the excited state with the longest lifetime, which is over seven times of magnitude than that of DPBF film. The deep blue PL of the pristine DPBF film is assumed to be arising mainly from excitonic emission. The excited state of DPBF-ME film exhibits a relatively longer lifetime for the TRPL measurement as shown in Fig. 4. Accordingly, we would estimate that the greenish PL spectrum of DPBF-ME film is mainly generated from the excimer emission. The additional fine structures in PL spectrum as observed in Fig. 1b and e probably are correlated with the emission from 0-3 to 0-4 transition, which is the preferred transition for BF-ME and DPBF-ME in solid state. The lifetime of the excited



Fig. 4. Time-resolved photoluminescence (TRPL) measurement results. (a) TRPL curves of DPBF, DPBF-ME and DPBF-OME films at 500 nm. (b) Collection the average initial intensity of TRPL signals (>1 ns) of DPBF, DPBF-ME, DPBF-OME and DPNF films. (c) Average excited state lifetime of DPBF, DPBF-ME, DPBF-OME and DPNF films.

Results of time-re	solved photol	uminescence fo	or 15 nm pr	istine benzo[k	Jfluoranthene de	rivatives film	n at 440 nm an	d 500 nm.	Excitation at 3	75 nm.ª
Compound	440 nm (o	ompound 1d at 460 nm)				500 nm (compound 1d at 520 nm)				
	A_1^a	τ_1^{a} (ns)	<i>A</i> ₂	τ_2 (ns)	$\tau_{Iav}^{b}(ns)$	<i>A</i> ₁	τ_1 (ns)	A ₂	τ_2 (ns)	$\tau_{Iav}^{b}(ns)$
DPBF	14790	1.37	788	5.41	2.072	3192	1.45	360	6.07	2.93
DPBF-ME	12620	0.28	434	15.28	10.04	2698	0.79	702	21.08	20.88
DPBF-OME	15310	1.38	293	7.38	1.94	3523	1.76	607	10.85	6.44
DPNF	9640	0.48	714	2.10	1.34	2764	0.51	187	4.8	2.73

^a The results are fitted to a sum of two exponentials, the parameters, A and τ , are the amplitude and lifetime of the fitted curves. All the measurements are in the ambient temperatures.

Calculating the value of average lifetime by intensity weight.

Table 2

state for DPBF-OME film is between that of DPBF and that of DPBF-ME. The deep blue excitonic emission and green excimer emission are both observed in the PL spectra (Fig. 1f) of the DPBF-OME film. In other words, the lifetime of the excited state of the DPNF film is 2.18 ns (at 520 nm), which is as short as that of the DPBF film. Fig. 1c clearly shows the excitonic emission signals. These results indicate that excimer emission is responsible for the shift in the PL spectra of amorphous benzo[k]fluoranthene derivatives films.

The instantaneous intensity of TRPL is dominated by emission states, including the band gap of the emitting molecule (excitonic emission) and the new emission states (dimer and trimer emission) that are produced by molecular packing. The initial emission intensities of TRPL at different wavelengths reveal whether the emission occurs immediately or a long time after an intermolecular interaction. Fig. 4b present the maximum initial TRPL intensities of DPBF, DPBF-ME, DPBF-OME and DPNF films at various wavelengths. The initial intensities of all of studied samples decay beyond 440 nm (DPNF at 460 nm) and their shapes are similar to those of PL curves of the materials in solution, as illustrated in Fig. 1, suggesting that all of the initially excited states are excitons. This finding suggests that pristine DPBF. DPBF-ME. DPBF-OME and DPNF films do not form a new emission state, consistent with the results of the excitation spectra that are shown in Fig. 2.

Fig. 4c shows the average lifetimes of the excited states for benzo[k]fluoranthene derivative films. The average lifetimes of the excited states in DPBF and DPNF films are almost independent of wavelength. However, the lifetime of DPBF-ME films is correlated and increased with the wavelength. For DPBF-OME film, the lifetime shows a slight change with wavelength under 470 nm and an increase with wavelength above 470 nm. This observation agrees well with the previous PL results as presented in Fig. 1, explaining why DPBF-OME exhibits both excitonic and excimer emissions whereas DPBF-ME only exhibits strong green excimer emission. Accordingly, non-doped OLEDs of broad emission spectra can be fabricated by directly applying pristine benzo[k]fluoranthene derivatives of different substituents as the light-emissive layers.

2.5. Benzo[k]fluoranthene-based linear acenes with different substituents in deep blue to green non-doped OLEDs

Fig. 5 presents EL results of DPBF (in Fig. 5a), DPBF-ME (in Fig. 5b), DPBF-OME (in Fig. 5c) and DPNF-based (in

Fig. 5d) devices. A comparison of the EL emission profiles with the PL emission profiles in Fig. 1c-f indicates that the EL spectra are close to their solid-state PL spectra (summary in Table 1). Strong emission of the DPBF-based device is observed at 427, 451 and 481 nm in deep blue



Fig. 5. The electroluminescence (EL) spectrums of benzo[k]fluoranthene derivatives-based OLEDs. (a) DPBF-based, (b) DPBF-ME-based, (c) DPBF-OME-based, and (d) DPNF-based OLED. The inset in (a) is corresponding CIE coordination.



Fig. 6. The electrical properties of benzo[k]fluoranthene derivativesbased devices. (a) Current density–luminescence–voltage (*J*–*L*–*V*) properties and inset in (a) is device structure. (b) Luminous efficiency (LE) curves.

region, and the device clearly exhibits strong excitonic emission. The DPBF-OME device has emission intensities of 440 and 464 nm. The EL spectrum extends to 600 nm because it includes both excitonic and excimer emissions. The EL spectrum of the DPBF-ME-based device exhibits strong excimer emission that is quite close to the green region, and the strongest emissive signal is at 507 nm, with two shoulders at 477 nm and 542 nm. The inset in Fig. 5a displays the corresponding CIE chromaticity coordinates (x, y) of these devices. The CIE coordinates of the DPBFbased device are (0.17, 0.16) in the deep blue region; those of the DPBF-ME-based device are (0.25, 0.48) in the green region, and those of the DPBF-OME-based device are in the middle, (0.22, 0.27). Those of the DPNF-based device are at (0.19, 0.32) in the bluish region because the emitting material has longer conjugation than the other materials.

Table 3

The electroluminescence properties of benzo[k]fluoranthene derivatives based OLEDs.

The functional groups of benzo[k]fluoranthene-based linear acenes can be varied to tune EL spectra from the deep blue to green regions.

Fig. 6a plots the current density-luminescence-voltage (I-L-V) curves of DPBF, DPBF-ME, DPBF-OME and DPNFbased devices. The devices structure are indium-tin-oxide glass/N.N'-bis-(1-naphthyl)-N.N'-diphenyl-(ITO)-coated 1,1'-biphenyl-4,4'-diamine (NPB)(50 nm)/benzo[k]fluoranthene-based linear acenes (15 nm)/4,7-diphenyl-1,10-(Bphen)(30 nm)/lithium phenanthroline fluoride (LiF)(1 nm)/aluminum (Al)(100 nm), as shown in the inset of Fig. 6a. Fig. 6b plots their luminous efficiency (LE) versus current density curves. The electrical properties of pristine benzo[k]fluoranthene-based linear acene films as the lightemissive layers in OLEDs reveal a low operating voltage and excellent light output properties. The light turn-on voltage (V_{op}) of the DPNF-based device was 2.9 V, and that of DPBF, DPBF-ME and DPBF-OME-based devices was 3.2 V, 3.2 V and 3.3 V, respectively. These values are close to the photon energy gaps, suggesting that the dissipation of energy associated with carrier injection or transportation is low. The LE curves show a relatively stable light output. even when the current density approaches 300 mA cm⁻², and EL spectrum do not change in operating conditions. The DPBF-ME-based device had the highest LE and external quantum efficiency (EQE) of 5.0 cd A⁻¹ at 100 cd m⁻² and 1.8%, respectively, yielding a maximum luminance of 19,282 cd m^{-2} at 7.3 V. The LE and EQE of the other devices were between 1.1 and 2.2 cd A^{-1} and approximately 1%, respectively. The maximum brightness of all devices exceeded 4000 cd m⁻². Table 3 summarizes all of the *J*-*L*-*V* properties. The performance of these devices remains high at 100 and 1000 cd m⁻² (LE_{100} and LE_{1000}) as list in Table 3, showing the decent operational stability. The results indicate that benzo[k]fluoranthene-based linear acenes-based OLEDs exhibit the promising electrical performance for applications of tunable EL spectra from the deep blue to green regions.

3. Conclusions

In conclusion, this study presents PL and EL properties of various pristine benzo[k]fluoranthene-based linear acenes films and uses them in non-doped deep blue to green OLEDs. The results demonstrate that steric hindrance causes the benzo[k]fluoranthene derivatives to exhibit

Device	V _{on} ^a (V)	$L_{\rm max}^{a}$ (cd m ⁻²)	$\frac{\text{LE}_{100,1000}^{\text{a}}}{(\text{cd }\text{A}^{-1})}$	LE_{max}^{a} (cd A ⁻¹)	$\frac{PE_{max}^{a}}{(1 \text{ m W}^{-1})}$	EQE ^b (%)	CIE (<i>x</i> , <i>y</i>)	Emission type (exciton, excimer)
DPBF	3.2	4167	1.1, 1.0	1.1	1.0	1.0	(0.17, 0.16)	Exciton
DPBF-ME	3.2	19282	2.9, 4.8	5.1	3.2	1.8	(0.25, 0.48)	Excimer + 0-3, 0-4 transition
DPBF- OME	3.3	5752	2.2, 2.1	2.2	1.8	1.0	(0.22, 0.27)	Exciton + excimer
DPNF	2.9	7143	2.0, 1.9	2.0	2.0	1.1	(0.19, 0.32)	Exciton

^a The light turn-on voltage at 1 cd m⁻² is defined as V_{on} . The maximum brightness is defined as L_{max} . Luminous efficiency (LE) at 100, 1000 cd m⁻² and maximum value are defined as LE₁₀₀, LE ₁₀₀₀, and LE_{max}, respectively. Maximum power efficiency (PE) is defined as PE_{max}.

^b The external quantum efficiency (EQE) calculation is in Ref. [40].

strong PL in a pristine film. More importantly, PL emission properties of the pristine film can be modulated from the deep blue region to the green region by varying the substituents around the emissive core. It is also characterized that the lifetime of the excited state are correlated with the emission spectrum. All devices of interest herein exhibit the stable electrical properties even biased at the high current density regimes. Controlling the intermolecular interaction by choosing the different functional groups has implications for the design of new organic materials and applications in organic electronics devices.

4. Experiment sections

4.1. Fabrication of OLEDs

The device configuration, as shown in the inset of Fig. 6a, comprises indium-tin-oxide (ITO)-coated glass substrate as anode, N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'biphenyl-4,4'-diamine (NPB) as hole transport layer (50 nm), benzo[k]fluoranthene-based linear acenes as emitting layer (15 nm), 4,7-diphenyl-1,10-phenanthroline (Bphen) as electron transport layer (30 nm), the cathode is lithium fluoride (LiF \sim 1 nm) and aluminum (100 nm) bi-layer. ITO-glass substrates are cleaned by solutions under ultrasonic cleaner and then used UV-ozone treatment for 25 min. All of the materials are deposited by vacuum thermal evaporation on ITO-coated glass substrates under the vacuum level arriving 10^{-6} torr. The shadow mask is changed for cathode design. In this step, the sample is stored in high-purity nitrogen glove box environment and breaking the vacuum and transfer process both are not exposure to the atmosphere. The active pixel area of the device is 0.06 cm^2 .

4.2. The current-brightness-voltage measurement of OLEDs

The current density-brightness-voltage (J-L-V) measurements are using a Keithley 2400 source-meter and a Keithley 2000 digital multimeter, with a silicon photodiode, measuring the brightness current, and calibrated using a PR-650 luminosity meter (Photo Research, USA). The device electrical measurement was also obtained inside the glove box. The EL spectrum was detected using a PR-650 luminosity meter.

4.3. Excitation spectra and Photoluminescence (PL) measurements

The excitation spectra and PL measurement of solution state (dichloromethane (CH_2Cl_2)) was measured using quartz cell and the concentration is 10^{-5} M. The sample of solid state excitation spectra and PL measurement was fabricated on glass substrates, 15 nm. Glass substrates were cleaned by solutions under ultrasonic cleaner. The testing materials were deposited under the vacuum level arrive 10^{-6} torr. The excitation spectra and PL measurement were using LS-55 fluorescence spectrometer. The excitation wavelength of PL measurement is 350 nm and incident area is constant. The incident light wavelength of excitation spectra is between 380 and 500 nm and de-

tected position is 520 nm. All the measurements were under atmosphere.

4.4. X-ray diffraction (XRD) measurement

The XRD patterns of the benzo[k]fluoranthene-based linear acenes thin film, 15 nm on glass substrates, were obtained at the Beamline 17A of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The diffraction pattern was recorded with a Mar345 imaging plate, the pixel size of was 100 µm. The distance between detector and sample is approximately 212 mm and exposure duration time is 15–20 min. The one-dimensional diffraction profile was converted with program FIT2D and caketype integration. The diffraction angles were calibrated according to Bragg positions of Ag-Benhenate and Si powder (NBS640b) standards. The wavelength of the X-ray beam was calibrated to be 0.13320 nm.

4.5. Time-resolved photoluminescence (TRPL) measurement

For TRPL measurements, a picosecond diode laser (Pico-Quant) generates optical pulses of 100 ps width with a 40 MHz repetition rate. The excitation energy is 3.32 eV (wavelength is 375 nm) for pumping the testing samples, 15 nm on glass substrates. Light emitted from the sample is detected by a photomultiplier (PMT) and a monochromator. The signal from the PMT was recorded by means of time-correlated single-photon-counting (TCSPC) technology (Model TimeHarp 200, Pico-Quant). The resolution is 50 ps.

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References

- [1] S. Tang, W. Li, F. Shen, D. Liu, B. Yang, Y. Ma, J. Mater. Chem. 22 (2012) 4401.
- [2] G. Zhou, W.Y. Wong, S. Suo, J. Photochem. Photobiol. C-Photochem. Rev. 11 (2010) 133.
- [3] S. Chen, G. Tan, W.Y. Wong, H.S. Kwok, Adv. Funct. Mater. 21 (2011) 3785.
- [4] K.T. Kamtekar, A.P. Monkman, M.R. Bryce, Adv. Mater. 22 (2010) 572.
- [5] J.H. Jou, Y.C. Chou, S.M. Shen, M.H. Wu, P.S. Wu, C.R. Lin, R.Z. Wu, S.H. Chen, M.K. Wei, C.W. Wang, J. Mater. Chem. 21 (2011) 18523.
- [6] S.J. Su, E. Gonmori, H. Sasabe, J. Kido, Adv. Mater. 20 (2008) 4189.
- [7] Q. Wang, J. Ding, D. Ma, Y. Cheng, L. Wang, F. Wang, Adv. Mater. 21 (2009) 2397.
- [8] Y. Xiong, W. Xu, C. Li, B. Liang, L. Zhao, J. Peng, Y. Cao, J. Wang, Org. Electron. 9 (2008) 533.
- [9] B.W. D'Andrade, S.R. Forrest, Adv. Mater. 16 (2004) 18.
- [10] R.J. Holmes, S.R. Forrest, Y.J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thompson, Appl. Phys. Lett. 82 (2003) 15.
- [11] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 79 (2001) 2082.
- [12] C.J. Zheng, W.M. Zhao, Z.Q. Wang, D. Huang, J. Ye, X.M. Ou, X.H. Zhang, C.S. Lee, S.T. Lee, J. Mater. Chem. 20 (2010) 1560.
- [13] S.H. Lin, F.I. Wu, H.Y. Tsai, P.Y. Chou, H.H. Chou, C.H. Cheng, R.S. Liu, J. Mater. Chem. 21 (2011) 8122.
- [14] Z.Y. Xia, Z.Y. Zhang, J.H. Su, Q. Zhang, K.M. Fung, M.K. Lam, K.F. Li, W.Y. Wong, K.W. Cheah, H. Tian, C.H. Chen, J. Mater. Chem. 20 (2010) 3768.

- [15] S. Tao, Y. Zhou, C.S. Lee, S.T. Lee, D. Huang, X. Zhang, J. Phys. Chem. C 112 (2008) 14603.
- [16] K.T. Wong, Y.Y. Chien, R.T. Chen, C.F. Wang, Y.T. Lin, H.H. Chiang, P.Y. Hsieh, C.C. Wu, C.H. Chou, Y.O. Su, G.H. Lee, S.M. Peng, J. Am. Chem. Soc. 124 (2002) 11576.
- [17] S. Tao, Z. Peng, X. Zhang, P. Wang, C.S. Lee, S.T. Lee, Adv. Funct. Mater. 15 (2005) 1716.
- [18] J.N. Moorthy, P. Natarajan, P. Venkatakrishnan, D.F. Huang, T.J. Chow, Org. Lett. 9 (2007) 5215.
- [19] K.M. Omer, S.Y. Ku, K.T. Wong, A.J. Bard, Angew. Chem. Int. Ed. 48 (2009) 9300.
- [20] R.C. Chiechi, R.J. Tseng, F. Marchioni, Y. Yang, F. Wudl, Adv. Mater. 18 (2006) 325.
- [21] Q.X. Tong, S.L. Lai, M.Y. Chan, Y.C. Zhou, H.L. Kwong, C.S. Lee, S.T. Lee, Chem. Mater. 20 (2008) 6310.
- [22] Q.X. Tong, S.L. Lai, M.Y. Chan, Y.C. Zhou, H.L. Kwong, C.S. Lee, S.T. Lee, T.W. Lee, T. Noh, O. Kwon, J. Phys. Chem. C 113 (2009) 6227.
- [23] Q.X. Tong, M.Y. Chan, S.L. Lai, T.W. Ng, P.F. Wang, C.S. Lee, S.T. Lee, Dyes Pigm. 86 (2010) 233.
- [24] S.L. Lin, L.H. Chan, R.H. Lee, M.Y. Yen, W.J. Kuo, C.T. Chen, R.J. Jeng, Adv. Mater. 20 (2008) 3947.
- [25] W.Z. Yuan, Y Gong, S. Chen, X.Y. Shen, J.W.Y. Lam, P. Lu, Y. Lu, Z. Wang, R. Hu, N. Xie, H.S. Kwok, Y. Zhang, J.Z. Sun, B.Z. Tang, Chem. Mater. 24 (2012) 1518.
- [26] Y. Zhou, J.W. Kim, R. Nandhakumar, M.J. Kim, E. Cho, Y.S. Kim, Y.H. Jang, C. Lee, S. Han, K.M. Kim, J.J. Kim, J. Yoon, Chem. Commun. 46 (2010) 6512.

- [27] Y.H. Lee, T.C. Wu, C.W. Liaw, T.C. Wen, T.F. Guo, Y.T. Wu, J. Mater. Chem. 22 (2012) 11032.
- [28] L.J. Zhu, J. Wang, T.G. Reng, C.Y. Li, D.C. Guo, C.C. Guo, J. Phys. Org. Chem. 23 (2010) 190.
- [29] G. Zhou, C.L. Ho, W.Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T.B. Marder, A. Beeby, Adv. Funct. Mater. 18 (2008) 499.
- [30] Y.S. Yao, Q.X. Zhou, X.S. Wang, Y. Wang, B.W. Zhang, J. Mater. Chem. 16 (2006) 3512.
- [31] E.F. Fabrizio, A. Payne, N.E. Westlund, A.J. Bard, P.P. Magnus, J. Phys. Chem. A 106 (2002) 1961.
- [32] Y.H. Kung, Y.S. Cheng, C.C. Tai, W.S. Liu, C.C. Shin, C.C. Ma, Y.C. Tsai, T.C. Wu, M.Y. Kuo, Y.T. Wu, Chem. - Eur. J. 16 (2010) 5909.
- [33] R.M. Adhikari, R. Mondal, B.K. Shah, D.C. Neckers, J. Org. Chem. 72 (2007) 4727.
- [34] Y. Liu, S. Chen, J.W.Y. Lam, F. Mahtab, H.S. Kwok, B.Z. Tang, J. Mater. Chem. 22 (2012) 5184.
- [35] S. Varghese, S. Das, J. Phys. Chem. Lett. 2 (2011) 863.
- [36] N.S.S. Kumar, S. Varghese, C.H. Suresh, N.P. Rath, S. Das, J. Phys. Chem. C 113 (2009) 11927.
- [37] C.A. Landis, S.R. Parkin, J.E. Anthony, Jpn. J. Appl. Phys. 44 (2005) 3921.
- [38] J.C. Ostrowski, R.A. Hudack Jr., M.R. Robinson, S. Wang, G.C. Bazan, Chem. - Eur. J. 7 (2001) 4500.
- [39] J. Kalinowski, G. Giro, M. Cocchi, V. Fattori, P.D. Marco, Appl. Phys. Lett. 76 (2000) 2352.
- [40] S. Okamoto, K. Tanaka, Y. Izumi, H. Adachi, T. Yamaji, T. Suzuki, Jpn. J. Appl. Phys. 40 (2001) 783.