OLEDs

# Efficient Nondoped Blue Fluorescent Organic Light-Emitting Diodes (OLEDs) with a High External Quantum Efficiency of 9.4% @ 1000 cd m<sup>-2</sup> Based on Phenanthroimidazole–Anthracene Derivative

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Organic light-emitting diodes (OLEDs) can promise flexible, light weight, energy conservation, and many other advantages for next-generation display and lighting applications. However, achieving efficient blue electroluminescence still remains a challenge. Though both phosphorescent and thermally activated delayed fluorescence materials can realize high-efficiency via effective triplet utilization, they need to be doped into appropriate host materials and often suffer from certain degree of efficiency roll-off. Therefore, developing efficient blue-emitting materials suitable for nondoped device with little efficiency roll-off is of great significance in terms of practical applications. Herein, a phenanthroimidazole-anthracene blue-emitting material is reported that can attain high efficiency at high luminescence in nondoped OLEDs. The maximum external quantum efficiency (EQE) of nondoped device is 9.44% which is acquired at the luminescence of 1000 cd  $m^{-2}$ . The EQE is still as high as 8.09% even the luminescence reaches 10 000 cd m<sup>-2</sup>. The maximum luminescence is ≈57 000 cd m<sup>-2</sup>. The electroluminescence (EL) spectrum shows an emission peak of 470 nm and the Commission International de L'Eclairage (CIE) coordinates is (0.14, 0.19) at the voltage of 7 V. To the best of the knowledge, this is among the best results of nondoped blue EL devices.

# **1. Introduction**

New-generation organic light-emitting diodes (OLEDs) materials with aspect of low cost like pure organic aromatic fluorescent compounds while remaining high efficiency as iridium (Ir) phosphorescent materials are being developed.<sup>[1]</sup> Especially, efficient blue fluorescent materials are highly desired because they not only can provide one of the RGB (red, green, and

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blue) primary colors but also act as host for red and green dopants in full color display and white lightings.<sup>[2]</sup> In many cases, the high efficiency is acquired by doping strategy which demands appropriate host material and fine-tuning doping concentration.<sup>[3]</sup> This will complicate device fabrication and increase commercial cost. In addition, reducing efficiency roll-off is another crucial issue toward practical application because high luminescence is required for display and lightings. Hence, it is of great significance to develop blueemitting materials capable of achieving high efficiency at high luminescence for nondoped OLEDs. Though phosphorescent materials, generally Ir- or Pt- based complexes, can harvest all triplet excitons, they should be dispersed into host materials with high triplet energy to reduce the quenching effect of the long-lived triplet excitons at high luminescence and avoid back energy transfer from dopant to host.<sup>[4]</sup> Furthermore, the scarcity of

these noble metal elements is not economical for commercial production. Thermally activated delayed fluorescence (TADF) materials can also utilize triplet excitons and obtain nearly 100% internal quantum efficiency.<sup>[5]</sup> However, the slow reverse intersystem crossing process from  $T_1$  (the lowest triplet excited state) to S1 (the lowest singlet excited state) renders accumulation of triplet excitons at high luminescence. As a result, like phosphorescent materials, most TADF materials are also needed to be doped into proper host with high triplet energy and suffer from a certain degree of efficiency roll-off.<sup>[6]</sup> Triplet-triplet annihilation (TTA) can also effectively harness triplet excitons in the form of generating one singlet exciton by fusing two triplets.<sup>[7]</sup> In principle, TTA materials are applicable for efficient nondoped OLEDs with reduced efficiency roll-off. However, many TTA molecules still remain to be doped into appropriate host materials to attain high efficiency.<sup>[8]</sup> Therefore, developing efficient blue-emitting fluorescent materials suitable for nondoped device which can achieve high efficiency at high luminescence is a pressing issue toward practical applications, such as display and lightings.



In this work, we report a highly efficient blue-emitting

material PIAnCN which is constructed by connecting phenanthroimidazole (PI) with cyano substituted anthracene.

PI has high photoluminescence quantum yield (PLQY) because of its rigid planar  $\pi$  conjugation.<sup>[9]</sup> In addition, the

amine N atom in the imidazole ring together with the con-

jugation plane of whole molecule endows PI weak electron

donating ability and proper highest occupied molecular

orbital (HOMO) energy level to reduce hole injection barrier

in device.<sup>[10]</sup> Moreover, PI emits in the near ultraviolet region

because of its limited conjugation.<sup>[9]</sup> All these features make

PI a promising building block for blue-emitting molecules.

On the other hand, anthracene is also a highly emissive blue-

emitting moiety which is often adopted as functional group

to construct TTA materials.<sup>[7,11]</sup> By combining phenanthro-

imidazole with anthracene, it is anticipated that the obtained

molecule can possess efficient blue emitting as well as effec-

tive triplet fusion to utilize the nonemissive triplet excitons. Cyano group is incorporated into the molecular structure. The electron withdrawing property of cyano can lower the lowest

unoccupied molecular orbital (LUMO) energy level and reduce electron injection barrier in device. Furthermore, the

presence of cyano group can enhance intermolecular interac-

tions.<sup>[12]</sup> For example, the existence of cyano group can pro-

mote tight intermolecular packing through enhanced supra-

molecular interactions in cyano substituent distyrylbenzene

(CN-DSB) derivatives.<sup>[12a]</sup> Considering TTA occurs between

two individual molecules, we assume that the introduction of

cyano group may facilitate TTA process and improve device

efficiency. We fabricated the doped device of PIAnCN which

shows deep blue emission with an electroluminescence (EL)

peak of 444 nm and CIE coordinates of (0.15, 0.07). Though

the maximum external quantum efficiency (EQE) of doped

device can achieve 6.77%, the efficiency roll-off is serious.

On the contrary, the nondoped device exhibits little efficiency roll-off. The maximum EQE is 9.44% (13.16 cd  $A^{-1}$ ) which is achieved at high luminescence of 1000 cd  $m^{-2}$ . The EQE

can still remain as high as 8.09% (11.29 cd  $A^{-1}$ ) even when the luminescence is increased to 10 000 cd  $m^{-2}$ . The EL peak

locates at 470 nm with a CIE coordinates of (0.14, 0.19). The

maximum luminescence is  $\approx 57\ 000\ \text{cd}\ \text{m}^{-2}$ . We assume that

TTA is the main reason for the high performance of non-

doped device. To the best of our knowledge, this is among the

best results of nondoped blue-emitting fluorescent OLEDs.<sup>[13]</sup>

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# 2. Results and Discussion

### 2.1. Synthesis and Characterization

The synthetic route of PIAnCN is shown in **Scheme 1**. The PPIBr is attained by one-pot reaction in high yield according to our previous report.<sup>[9]</sup> Then PPIBr is treated with *n*-BuLi and isopropoxyboronic acid pinacol ester at low temperature to obtain 1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (PPIB). BrAnCN is synthesized via Suzuki coupling reaction using 9,10-dibro-moanthracene and 4-cyanophenylboronic acid as reactants. Finally, PPIB is coupled with BrAnCN via Suzuki reaction to afford the target compound PIAnCN. The purity and chemical structure of PIAnCN are well characterized by NMR, mass spectrum (MS), and elemental analysis. The synthetic details are provided in the Supporting Information.

#### 2.2. Thermal Properties

Thermal properties are examined by thermal gravimetric analysis and differential scanning calorimetry (DSC). As displayed in Figure S1a (Supporting Information), and **Table 1** the decomposition temperature (*Td*, corresponding to 5% weight loss) is 483 °C, indicating that PIAnCN can endure high temperature and would not go through decomposition during device fabrication and operation. The DSC of the as-synthesized amorphous sample is shown in Figure S1b (Supporting Information). Upon heating procedure, no obvious exo- or endothermic signal can be seen until 344 °C which can be ascribed to the melting point (*T*<sub>m</sub>). No glass transition (*T*<sub>g</sub>) temperature can be observed demonstrating that PIAnCN can keep amorphous morphology in a wide range of temperature which is beneficial for OLEDs application.

#### 2.3. Photophysical Properties

To investigate the lowest singlet ( $S_1$ ) excited state of PIAnCN, photoluminescence (PL) is measured in various solvents with different polarities. As displayed in **Figure 1**, the solvatochromic effect is negligible as the PL does not change much upon increasing solvent polarity. The emission peak shifts from 434 nm in nonpolar slovent *n*-hexane to 446 nm in high



Scheme 1. Synthesis route of PIAnCN: a) CH<sub>3</sub>COONH<sub>4</sub>, acetic acid, 120 °C, N<sub>2</sub> protection, overnight; b) n-BuLi, –78 °C, stirring for 3 h under N<sub>2</sub> atmosphere, then isopropoxyboronic acid pinacol ester is added afterward. The mixture is stirred overnight at room temperature under N<sub>2</sub> protection; c) Suzuki coupling: Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> (2 M aq), toluene, 90 °C, 24 h under N<sub>2</sub> protection.

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Table 1. Photophysical properties of PIAnCN.

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Compound	T <sub>d</sub> /T <sub>m</sub> <sup>a)</sup> [°C]	λ <sub>max, abs</sub> b) [nm]	E <sup>c)</sup> [eV]	λ <sub>max, PL</sub> <sup>d)</sup> [nm]	PLQY <sup>h)</sup> (%)	HOMO/LUMO <sup>m)</sup> [eV]	ES <sub>1</sub> /ET <sub>1</sub> <sup>n)</sup> [eV]
PIAnCN	483/344	394/374/360/315/260	2.97	$464^{e)}/444^{f)}/442^{g)}$	$50^{ij}/80^{jj}/82^{kj}/62^{lj}$	-5.55/-2.78	2.86/1.74

<sup>a)</sup> $T_d$ : decomposition temperature;  $T_m$ : melting point; <sup>b)</sup> $\lambda_{max, abs}$ : absorption maximum in dilute THF (10<sup>-5</sup>); <sup>c)</sup> $E_g$ : Optical gap calculated from the absorption onset in dilute THF (10<sup>-5</sup>), <sup>d)</sup> $\lambda_{max, PL}$ : emission peak of nondoped film; <sup>f)</sup>Emission peak of doped film (15% in polymethyl methacrylate (PMMA); <sup>g)</sup>Emission peak in dilute THF (10<sup>-5</sup>); <sup>h)</sup>PLQY: photoluminescence quantum yield measured by integrating sphere; <sup>i)</sup>PLQY of nondoped film; <sup>i)</sup>PLQY of doped film (15% in PMMA); <sup>k)</sup>PLQY of doped film (15% in CzSi); <sup>i)</sup>PLQY in dilute THF (10<sup>-5</sup>); <sup>m)</sup>HOMO/LUMO energy levels estimated from cyclic voltammetry measurement; <sup>n)</sup> $E_{51}/E_{T1}$ : energy levels of  $S_1$  and  $T_1$  states.  $E_{51}$  is calculated from emission maximum in *n*-hexane and  $E_{T1}$  is calculated from the first vibronic peak of its phosphorescence at 77 K in THF.

polar solvent acetonitrile with a 12 nm variation, indicating the localized excited property of  $S_1$  state. To clarify the origin of the PL of PIAnCN, we further measured the PL of 1,2-diphenylphenanthroimidazole (PPI) and 4-(10-phenylanthracen-9-yl)benzonitrile (AnCN) in different solvents, respectively. The synthesis of PPI and AnCN is displayed in Scheme S1 (Supporting Information). The results show that the PL of PIAnCN is similar with that of AnCN while totally different from that of PPI as can be seen in Figures S3 and S4 (Supporting Information). Therefore, the  $S_1$  state of PIAnCN may mostly localize on the AnCN part. The absorption of PIAnCN in different solvents is nearly the same. The well-resolved 360, 374, and 394 nm absorption bands are characteristics of the  $\pi$ - $\pi$ \* transition of anthracene moiety.<sup>[14]</sup> Compared with the absorption of AnCN (Figure S4a, Supporting Information), the newly emerged absorption band of PIAnCN centered at 315 nm (Figure 1) can be assigned to the  $\pi$ - $\pi$ \* transition of PPI moiety. The absorption at 260 nm arises from the  $\pi$ - $\pi$ \* transition of the phenyl ring anchored at the N atom in the imidazole ring.<sup>[15]</sup> The molar absorption coefficient ( $\varepsilon_{max}$ ) at the longest absorption maximum (394 nm) is determined to be about  $2.25\times 10^4~L~mol^{-1}~cm^{-1}$  according to Figure S6 and Equation S1 (Supporting Information). Then the radiative decay constant  $(k_r)$  of  $S_1$  state is estimated to be  $2.25 \times 10^8$  s<sup>-1</sup> according to Equation S2 (supporting information). As displayed in Figure 2, the PIAnCN in tetrahydrofuran (THF) shows a monoexponential decay with a lifetime  $(\tau_{\rm s})$  of 2.31 ns. No delayed component can be observed, indicating the emission exclusively originates from prompt decay of S<sub>1</sub> state. The PLQY of PIAnCN in THF is measured to be 62%, in combination with  $\tau_s$ , the radiative decay constant  $k_r$ 



Figure 1. Absorption spectrum of PIAnCN in THF ( $10^{-5}$  M) and emission spectra of PIAnCN in different solvents ( $10^{-5}$  M).

can thus be calculated to be 2.68  $\times$  10<sup>8</sup> s<sup>-1</sup> according to Equation S3 listed in Supporting Information. This value is in good agreement with the  $k_{\rm r}$  derived from  $\varepsilon_{\rm max}$ , demonstrating the validity of our experimental data.

As shown in Figure S7 (Supporting Information), we are not successful in obtaining the phosphorescence of PIAnCN directly by normal phosphorescence measurement mode of PL spectrometer in glassy THF at 77 K probably due to the inefficiency of intersystem crossing (ISC) of  $S_1 \rightarrow T_1$  as well as the strong vibrational coupling between  $T_1$  and  $S_0$  as a result of the narrow band gap of  $T_1$ - $S_0$  (energy gap law).<sup>[16]</sup> The key to acquire phosphorescence of PIAnCN is forming large amounts of  $T_1$  excitons of PIAnCN. PtOEP is an archetype of phosphorescent material featuring fast and efficient ISC from  $S_1 \rightarrow T_1$ .<sup>[17]</sup> Therefore, the phosphorescence of PIAnCN is recorded at 77 K in glassy THF using PtOEP as sensitizer. The  $S_1$  and  $T_1$  energy of PtOEP is obtained according to literature.<sup>[18]</sup> As displayed in Figure 3, excited by 550 nm ps laser source, PtOEP is pumped to excited state, followed by fast triplet energy transfer to the  $T_1$ state of PIAnCN. Delayed by 10 ms, strong phosphorescence of PIAnCN can be detected (Figure 3 and Figure S7, Supporting Information). The first vibrational peak of phosphorescence is 713 nm, corresponding to a  $T_1$  energy of 1.74 eV. The phosphorescence originates from the anthracene moiety and is in good accordance with literature.<sup>[19]</sup> Based on the PL peak of PIAnCN in *n*-hexane (434 nm), the  $S_1$  energy is estimated to be 2.86 eV. Obviously, TADF cannot occur considering the large  $S_1-T_1$  energy gap. However, TTA is energy favorable because



Figure 2. PL decay of PIAnCN in THF (10<sup>-5</sup> M) at ambient condition.





**Figure 3.** Phosphorescence measurement diagram of PIAnCN by using PtOEP as sensitizer ( $10^{-4} \text{ M}$  PIAnCN +  $10^{-4} \text{ M}$  PtOEP in THF, 77 K). The  $T_1$  energy of PIAnCN is calculated from the first vibrational peak of its phosphorescence spectrum. The  $T_1$  and  $S_1$  energy of PtOEP is obtained from literature.<sup>[13]</sup>

 $2T_1 > S_1$ . Therefore, we assume that TTA may exert positive effect in boosting device efficiency.

## 2.4. Theoretical Calculations

To further examine the excited states properties of PIAnCN, natural transition orbitals (NTOs) are performed using TD-M062x/6-31G(d, p) method based on the optimized  $S_1$  geometry.<sup>[20]</sup> As shown in **Figure 4**, the NTOs of  $S_1$  state mainly localize on the AnCN part, which is in accordance with the result of solvatochromism measurement discussed above. The calculated  $S_1$  state energy is 2.81 eV which agrees with the emission energy of PIAnCN in *n*-hexane (434 nm, 2.86 eV). According to literatures, the  $T_1$  energies of anthracene derivatives are as low as ≈1.8 eV arising from the long conjugation axis of anthracene.<sup>[21]</sup> As revealed by the NTOs diagram in



**Figure 4.** NTOs of PIAnCN on  $S_1$  geometry,  $S_0$ : singlet ground state;  $S_1$ : the lowest singlet excited state;  $T_1$ : the lowest triplet excited state;  $T_2$ : the second triplet excited state. The percentage indicates the possibility of the transition.

Figure 4 and Figure S8 (Supporting Information), the  $T_1$  of PIAnCN mainly distributes on the AnCN moiety and the corresponding energy is calculated to be 1.58 eV, and is close to the value in the literature as well as our experimental value 1.74 eV. The good agreement between calculated values and experimental data demonstrates that the theoretical method we adopted is valid for the calculation of lowest excited states, i.e., the  $S_1$  and  $T_1$  states. The calculated  $T_2$  state mainly locates on PI moiety and the corresponding energy is 2.80 eV. The calculated results of more high lying excited states are summarized in Figure S8 (Supporting Information).

## 2.4. Electrochemical Properties

The HOMO/LUMO energy levels are derived from cyclic voltammetry measurement (Figure S9, Supporting Information). The oxidation and reduction onset against ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) redox couple are 0.75 and -2.02 V, respectively. Thus, the HOMO and LUMO energy levels are calculated to be -5.55 and -2.78 eV according to Equations S4 and S5 (Supporting Information). This HOMO/LUMO energy alignment is beneficial for balanced charge injection and can avoid charge accumulation at the interface between emission layer and adjacent charge transporting layers of OLEDs device. These advantages are in favor of improving device performance.<sup>[22]</sup>

#### 2.5. Electroluminescence Properties

To examine the potential application of PIAnCN as solid state emitter, we fabricated the nondoped OLEDs with the device structure of indium tin oxide (ITO)/HATCN (6 nm)/TAPC (25 nm)/TCTA (15 nm)/PIAnCN (20 nm)/TPBI (40 nm)/LiF (0.5 nm)/Al (120 nm), where ITO (indium tin oxide) is the anode, hexaazatriphenylenehexacabonitrile (HATCN) is the hole injecting layer, TAPC (di-(4-(N,N-ditolyl-amino)-phenyl) cyclohexan) is the hole transporting layer (HTL), TCTA (tris(4carbazoyl-9-ylphenyl)amine) is the buffer layer, PIAnCN is the





Figure 5. Current efficiency (circle) and external quantum efficiency (triangle) of nondoped and doped devices.

emitting layer (EML), TPBI (1,3,5-tris-(N-phenylbenzimidazol-2-yl)benzene) is the electron transporting layer, LiF is the electron injecting layer and Al is the cathode. The turn-on voltage is only 3.0 V indicating effective charge injection and recombination in the EML. The EL spectra can coincide with the nondoped PL spectrum and are very stable at various driving voltages, demonstrating the EL is from the EML. The EL shows an emission peak of ≈470 nm and CIE coordinates of (0.14, 0.19) at 7 V. The maximum power efficiency is 10.44  $\text{lm W}^{-1}$ (Figure S11, Supporting Information). As displayed in Figure 5, the maximum EQE is 9.44% which is obtained at high luminescence of 1000 cd m<sup>-2</sup>. The efficiency roll-off is quite small. Even at a luminescence of 10 000 cd  $m^{-2}$ , the EQE can still remain 8.09%. To the best of our knowledge, this is among the best results of nondoped fluorescent blue OLEDs.<sup>[13]</sup> A comparison between our result and other nondoped blue-emitting OLEDs is presented in Table S1 (Supporting Information). The high efficiency at high luminescence makes PIAnCN a promising candidate for practical application.

We also optimized the doped devices by tuning the thickness of hole transporting layers, changing the host materials, and varying doping concentration. Detailed description of device optimization is illustrated in Supporting Information. The best result is obtained from the device of ITO/HATCN (6 nm)/TAPC (25 nm)/TCTA (15 nm)/CzSi: PIAnCN 15% (20 nm)/TPBI (40 nm)/LiF (0.5 nm)/Al (120 nm) where CzSi

(9-(4-tert-Butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole) is the host material. The doped device shows deep blue emission with EL peak of 444 nm and CIE coordinates of (0.15, 0.07) at 7 V as shown in Figure S13e (Supporting Information) and **Table 2** or Table S2 (Supporting Information). The turn-on voltage is increased to 3.6 V in comparison with that of nondoped device. The EL spectra are very stable at various voltages. The maximum power efficiency is 5.34 lm W<sup>-1</sup> (Figure S12b and Table S2,



Supporting Information). The maximum luminescence is  $\approx 16$  000 cd A<sup>-1</sup>. The doped device suffers from serious efficiency roll-off: the maximum EQE is 6.77% which is obtained at initial luminescence (0.77 cd m<sup>-2</sup>); the EQE decreased to 5.97% at 100 cd  $\mathrm{m}^{-2}$  and 4.77% at 1000 cd  $\mathrm{m}^{-2}$  and 3.21% at 10 000 cd m<sup>-2</sup>. By tuning the thickness of hole transporting layers and selecting proper host materials, high efficiency as well as deep blue emission can be obtained for the doped device. We assume that cavity effect may be accountable for this.<sup>[23]</sup> Besides, compared with the PL of 4,4'-Bis(Ncarbazolyl)-1,1'-biphenyl (CBP), the PL of CzSi exhibits larger overlap with the absorption of PIAnCN (Figure S14, Supporting Information), demonstrating more efficient Förster energy transfer from CzSi to PIAnCN which can also lead to the high efficiency. We notice that the nondoped and doped devices display opposite trend in terms of EQE curves (Figure 5). The EQE of doped device suffers from continuous efficiency roll-off upon the device is turned on, while the EQE of nondoped device goes through uphill process before  $\approx$ 1000 cd m<sup>-2</sup> then slight roll-off afterward. This implies that the singlet excitons are severely quenched with increasing current density for doped device. However, for nondoped device, TTA process becomes more effective at higher current density which can explain the roll-up trend of EQE curve before  $\approx 1000$  cd m<sup>-2</sup>. With higher current density, triplet quenching processes such as single-triplet quenching or tripletcharge quenching may be dominant over TTA process, leading to efficiency roll-off. But the TTA process can convert triplet excitons into singlet ones to compensate the efficiency loss at high current density, resulting in reduced efficiency roll-off at high current density for nondoped device.

We measured the transient EL decay of both nondoped and doped devices at different driving voltages. As displayed in Figure S15 (Supporting Information), upon a fast electrical excitation pulse, the transient EL decay of doped device shows both a prompt EL decay at the timescale of submicroseconds and a delayed EL response at the timescale of several tens of microseconds. The prompt decay component can be assigned to the fast fluorescence of PIAnCN. The delayed EL decay shows little difference at different driving voltages which may be assigned to the recombination of trapped charges since we cannot give a short-time period reverse bias to eliminate these trapped charges under our experimental condition. Likewise, as shown in Figure 6, the transient EL decay of nondoped device also consists of two components, a rapid EL decay which originates from the prompt fluorescence and a delayed EL response on the order of several tens of microseconds. For the nondoped

Table 2. EL performance of PIAnCN-based devices.

			EQE <sup>d)</sup> [%]			
Device	V <sub>on</sub> <sup>a)</sup> [V]	L <sub>max</sub> <sup>b)</sup> [cd m <sup>-2</sup> ]	CE <sub>max</sub> c) [cd A <sup>-1</sup> ]	Max/1000/10 000	EL [λ <sub>max</sub> ] <sup>e)</sup>	CIE <sup>f)</sup> [nm] [x, y]
Nondoped	3.0	57787	13.16	9.44/9.44/8.09	470	0.14, 0.19
Doped	3.6	16107	5.95	6.77/4.77/3.21	444	0.15, 0.07

<sup>a)</sup>V<sub>on</sub>: turn-on voltage at the luminescence of 1 cd m<sup>-2</sup>; <sup>b)</sup>L<sub>max</sub>: maximum luminescence; <sup>c)</sup>CE<sub>max</sub>: maximum current efficiency; <sup>d)</sup>EQE<sub>max</sub>/1000/10 000: EQE of maximum/at 1000 cd m<sup>-2</sup>/10 000 cd m<sup>-2</sup>; <sup>e)</sup>EL  $\lambda_{max}$ : emission peak of EL spectrum at 7 V; <sup>f)</sup>CIE coordinates at 7 V.







Figure 6. a) Transient EL decay of nondoped device at different voltages; b) comparison of transient EL decay between nondoped and doped devices at the same current density; and c) amplified EL decay of the delayed component of PIAnCN nondoped device.

device, the ratio of delayed component gradually decreases from 5 to 10 V. We assume the delayed response is not simply caused by the recombination of trapped charges since higher driving voltage would result in more trapped charges and therefore an increased ratio of the delayed portion. The experimental result in Figure 6a is exactly the other way around. On the other hand, by comparing the transient EL decay profile of both doped and nondoped devices at the same current density (Figure 6b), the ratio of delayed component of nondoped device is obviously larger than that of doped device. This may also indicate that the delayed component of nondoped device is not solely from the recombination of trapped charges. Considering the large  $S_1$ - $T_1$  energy gap, TADF is not the reason for the delayed component. To further exclude the TADF mechanism, we also measured the transient EL decay of a TADF 10,10'-(sulfonylbis(4,1-phenylene))bis(9,9-dimethylemitter 9,10-dihydroacridine) (DMAC-DPS).<sup>[5a]</sup> As shown in Figure S16 (Supporting Information), the DMAC-DPS shows much more prominent delayed component and much slower EL decay than PIAnCN at the same current density. This demonstrates that the delayed component of PIAnCN decays much faster than that of the TADF emitter DMAC-DPS. Therefore, we can conclude that TADF does not account for the delayed component of PIAnCN nondoped device. We assume that the delayed EL results from TTA process. At the driving voltage of 5 V, the TTA is very effective, resulting in a large proportion of delayed component which can contribute to the enhanced device efficiency. By increasing driving voltages, the triplet excitons may be quenched by charges or go through other quenching processes which would lead to the decrease of delayed component and correspondingly a decrease of the EQE. The transient EL response is inconsistent with the driving voltage-dependent EQE curves as shown in Figure S10d (Supporting Information). The EQE achieves its maximum at  $\approx 5$  V then slowly decreases at higher voltages. To supply more straightforward evidence of TTA, we measured the EL decay at 20 V under a short time period pulse. The 20 V bias is to guarantee enough triplet excitons, while the short time period pulse is to avoid the device being burned at such high voltages. We amplified the delayed component and take the logarithm of EL intensity as *Y* and logarithm of time as *X* as shown in Figure 6c. According to Monkman and co-workers,<sup>[24]</sup> if TTA is predominant in the device, the delayed EL intensity should be proportional to  $t^{-2}$  (t is the time). Therefore, by taking the logarithm of EL intensity as Y and logarithm of time as X, the slope of obtained curve should be -2 for TTA mechanism. Our result is consistent with it as shown in Figure 6c which strongly supports TTA process to be valid in PIAnCN nondoped device.

Our previous investigation of CN-DSB derivatives discloses that the --CN group plays an important role in keeping tight



intermolecular packing through enhanced supramolecular interactions.<sup>[12a]</sup> We infer that the introduction of -CN group may also enhance intermolecular interactions in PIAnCN neat film and accordingly facilitates TTA process since TTA occurs between two individual molecules. To clarify the functionality of -CN group, we synthesized the molecule without -CN group PPIAn. The molecular structure and synthetic details are presented in Scheme S1 (Supporting Information). We also fabricated the nondoped device of PPIAn and measured the transient EL decay. The device structure is ITO/HATCN (6 nm)/TAPC (25 nm)/TCTA (15 nm)/ PIAnCN (20 nm)/TPBI (40 nm)/LiF (0.5 nm)/Al (120 nm). As displayed in Figure S17c and Table S3 (Supporting Information), the maximum EQE is 4.20% which is inferior to that of PIAnCN nondoped device, implying that the -CN group can improve device efficiency to a great extent. As can be seen in Figure S18 (Supporting Information), the transient EL decay of PIAnCN nondoped device shows larger delayed component than that of PPIAn nondoped device, indicating that the -CN containing molecule PIAnCN possesses stronger TTA effect than PPIAn without -CN group. This evidences that the existence of -CN group can indeed promote TTA process. In addition, balanced charge recombination is crucial for TTA devices since the triplet excitons are subject to quenching by redundant charges which will lead to severe efficiency roll-off.<sup>[8c,22]</sup> The electron withdrawing ability of -CN group can lower electron injection barrier and is beneficial for balanced charge recombination. As shown in Figures S19 and S9 (Supporting Information), the PIAnCN and PPIAn display similar HOMO energy but different LUMO energy. The LUMO energy of PIAnCN is ≈0.18 eV lower than that of PPIAn. Hence, the charge recombination may be more balanced in the case of PIAnCN nondoped device, leading to higher device efficiency.

# 3. Conclusion

In conclusion, an efficient blue-emitting molecule PIAnCN, which consists of PI and cyano substituted anthracene (AnCN), is designed and synthesized. The doped device shows a maximum EQE of 6.77% and deep blue electroluminescence with CIE coordinates of (0.15, 0.07). More importantly, the nondoped OLEDs exhibit a maximum EQE of 9.44% which is acquired at high luminescence of 1000 cd m<sup>-2</sup>. The efficiency roll-off is negligible. Even when the luminescence increases to 10 000 cd m<sup>-2</sup>, the EQE is still as high as 8.09%. This result is among the best of nondoped blue fluorescent OLEDs. We assume that TTA is the reason for such high device efficiency. We believe that our result is valuable for further practical applications, such as display and lightings, which required to be operated at high luminescence.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Keywords**

blue electroluminescence, high quantum yield, low efficiency roll-off, nondoped devices, organic light-emitting diodes (OLEDs)

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