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## Novel bipolar D- $\pi$ -A type phenanthroimidazole/carbazole hybrid material for high efficiency nondoped deep-blue organic light-emitting diodes with NTSC CIE<sub>y</sub> and low efficiency roll-off

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## **ABSTRACT:**

Tremendous efforts have been devoted to developing efficient deep-blue organic light-emitting diodes (OLEDs), but deep-blue OLEDs with high external quantum efficiency (EQE) and CIE<sub>y</sub> < 0.10 (Commission Internationale de L'éclairage (CIE)), especially matching the National Television System Committee (NTSC) standard blue CIE (x, y) coordinates of (0.14, 0.08), are still limited. Herein, we report the synthesis, photophysical properties, thermostability and electrochemical characterization of two phenanthroimidazole/carbazole-based compounds (CBPMCN and CPBPMCN). Single X-ray crystal data of CPBPMCN indicates that it adopts a severely twisted structure, resulting in a low degree of intermolecular  $\pi$ - $\pi$  stacking, which is appropriate to be employed as a nondoped deep-blue emitter. Nondoped devices based on CPBPMCN exhibited deep-blue electroluminescence (EL) with CIE coordinates of (0.15, 0.08), which is extremely close to the NTSC standard blue. Meanwhile, the devices showed impressively high EQE<sub>max</sub> up to 5.80% with relatively small efficiency roll-off.

## **1. INTRODUCTION**

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Since the invention of a bilayer structure for electroluminescent devices by Tang and VanSlyke in 1980s,<sup>1</sup> organic light-emitting diodes (OLEDs) have experienced rapid advances in the past few decades and nowadays even been hailed as new generation of flat-panel display and solid-state lighting technologies, owing to their unique features,<sup>2-4</sup> such as low driving voltage, rapid response, high brightness, flexibility, full-color display, etc. Nevertheless, some issues related to performance and reliability remain urgently to be resolved, of which efficient and stable blue especially deep-blue devices may be of the most crucial significance. A deep-blue emitter would not only cut down power consumptions efficiently and increase the color gamut of full-color OLEDs but also be utilized to generate other visible emissions and white lightings via energy transfer to a suitable emissive dopant with lower energy.<sup>5-8</sup> However, in contrast to the fact that many red and green emitters have been developed to satisfy the practical requirements for OLEDs, the development of high efficiency deep-blue emitters that reach the level of NTSC standard blue with CIE coordinates of (0.14, 0.08) and high EL efficiency lags behind, which remains a challenge to realize the practical full-color displays and thus attracted considerable research attention.

Although transition metal complexes, such as iridium (Ir) complexes, have already reached a very high EQE over 20% as blue phosphorescent emitters,<sup>9-11</sup> they suffer from severe efficiency roll-off at high current density, along with poor stability and degradation during device operation.<sup>12</sup> Furthermore, it is difficult to design a deep-blue phosphorescent molecule, as a nonradiative process along metal d-orbitals becomes competitive when elevating the metal to ligand charge-transfer (MLCT) orbital to generate high energy blue emission.<sup>13</sup> Actually, lots of efforts have been paid on deep-blue fluorescent materials with pure aromatic structures which can be listed as the derivatives of anthracene, imidazole, fluorene, pyrene, triarylamine,<sup>14-18</sup> etc. Unfortunately, it is embarrassing to simultaneously take into account NTSC 2/24

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standard deep-blue emission and high EL efficiency of the devices based on these emitters. Recently, Adachi and other researchers reported a series of extremely efficient blue fluorescent materials with thermally activated delayed fluorescence (TADF) characteristic,<sup>19-24</sup> which have a theoretically 100% internal guantum efficiency (IQE) through a reverse intersystem crossing (RISC) process converting triplet to singlet states by thermal activation. However, most of them demonstrated a sky blue or bluish-green emission on account of strong intramolecular charge transfer (ICT) interaction between electronic donor (D) and acceptor (A),<sup>25, 26</sup> and need to be doped in appropriate host materials to weaken efficiency roll-off phenomenon arising from concentration quenching of triplet states, which is against the easy fabrication of device in comparison with the nondoped OLEDs. In addition, Ma's group and others recently established a series of nondelayed fluorescent materials, whose excited states are featured as hybridized local and charge-transfer (HLCT) state.<sup>27-29</sup> Based on HLCT mechanism, they have reported several nondoped deep-blue OLEDs with notable efficiency,<sup>17, 30-32</sup> but there are still urgent demands for further research dedicated to corresponding materials. Overall, although a wide variety of blue fluorescent materials have been researched, only a few can simultaneously realize satisfactory deep-blue emission as well as a high value of EQE. Therefore, a more intensive study should be devoted to developing favorable deep-blue fluorescent emitters for practical commercial application of OLEDs.

On the other hand, for the purpose of massive commercial production and application of OLEDs, apart from high electro-optical conversion efficiency, low-cost preparation technology is also a crucial factor. Conventionally, doping of fluorescent materials into a host is an effective way to suppress the bathochromic effect of emission wavelength and a decrease in the photoluminescent quantum yield (PLQY) attributing to the enhanced intermolecular aggregation in condensed phase.<sup>33</sup> Unfortunately, this dopant-host system greatly increases the complication of manufacturing process and production cost of devices. Moreover, it's desirable to find bipolar hosts with sufficiently wide energy gap to transfer energy to the dopant. In

this regard, a nondoped system has an advantage of a simple device architecture that employs only a single emitting material without additional host materials, thus reducing the energy of excitons, which is helpful to the improvement of power efficiency and device stability. In spite of the aforementioned problems in neat films state, many attempts have been taken to avoid their negative influence on the performance of devices, including EL efficiency and emission region, such as the introduction of bulky sterically hindered groups or/and highly twisted structure into the designed deep-blue fluorescent molecule.<sup>34</sup>

In this paper, we report the synthesis, photophysical properties, thermostability and electrochemical characterization of two deep-blue materials, 4-(2-(4-(9H-carbazol-9-yl)phenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (CBPMCN) and <math>4-(2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-1H-phenanthro [9,10-d]imidazol-1-yl)benzonitrile (CPBPMCN) (Scheme 1). Furthermore, nondoped deep-blue OLEDs incorporating CPBPMCN as the emitter were fabricated and exhibited high EQE<sub>max</sub> of 5.80% with CIE coordinates of (0.15, 0.08) near the NTSC standard deep-blue.

## 2. RESULTS AND DISCUSSION

## 2.1. Molecular design

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To achieve efficient deep-blue emission, deliberate considerations need to be taken into the molecular design strategy of the emitter materials, where a delicate balance of charge carrier injection and mobility plays a crucial role. It has been proven to be a useful strategy to lower charge injection barrier and broaden carrier recombination zone in the emissive layer that a bipolar donor-acceptor (D-A) structure molecule is constructed through incorporating electron-accepting and electron-donating groups into the designed molecular entity.<sup>17, 35</sup> But a strong ICT interaction between D and A tends to result in red-shift of emission, so it is really necessary to carefully choose donor and acceptor segments to regulate energy levels so that the wanted deep-blue emission could be accomplished. Carbazole unit is selected as the constructive block

of target molecules originating from the following considerations: 1) moderate electron-donating property; 2) good thermal stability; 3) good hole transporting capacity; and 4) conformational rigidity.<sup>36</sup> Phenanthroimidazole is often utilized to participate in the design of blue fluorescent molecule as a highly efficient deep blue/violet chromophore. With variational bonding substituents of the imidazole ring, phenanthroimidazole demonstrates electronic dual nature (D or A).<sup>27, 37</sup> Here, phenanthroimidazole is selected as the weak electron donor ascribing to introducing of a strong electron-withdrawing group (-CN) into side benzene of the imidazole ring. Besides, one more phenyl ring is inserted into CPBPMCN to increase the molecular conjugation length, so as to modulate its emission wavelength and PLQY.<sup>38</sup>

## 2.2. Synthesis and Identification

The synthetic routes and chemical structures of CBPMCN and CPBPMCN are depicted in **Scheme 1**. Firstly, an intermediate compound BrBPMCN was synthesized via a one pot synthesis of 4-bromobenzaldehyde, phenanthrenequinone, and 4-aminobenzonitrile with high yield up to 84%. Then, CBPMCN was synthesized through Ullmann coupling reaction of BrBPMCN with carbazole, while CPBPMCN was synthesized through Palladium-catalyzed cross-coupling reaction of BrBPMCN with *p*-carbazolyl phenylboronic acid with very high yield up to 96%. All the two compounds were purified by silica gel chromatography and subsequently thermal gradient sublimation. The identification of the two compounds was established on the basis of <sup>1</sup>H-NMR spectroscopy, mass spectrometry and elemental analysis. The details of synthesis and identification are presented in the Experimental Part.



Scheme 1. Synthesis routes of CBPMCN and CPBPMCN.

## 2.3. Molecular Structure and Crystal Packing

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The molecular structure and intermolecular packing mode of CPBPMCN was further confirmed by single-crystal X-ray analysis. The single crystal of CPBPMCN was prepared by a vacuum thermal sublimation method (Crystal data of CPBPMCN has been submitted to the Cambridge Crystallographic Data Centre and the CCDC deposition number is: 1572995). The important crystallographic data are listed in **Table S1**, while the molecular structure and crystal packing diagrams are shown in Figure 1. In the crystal, CPBPMCN adopts a highly twisted conformation with dihedral angles (torsion angles) of 89.5° between carbazole plane and the adjacent benzene ring, 78.3° between phenanthroimidazole plane and side benzene ring, 48.8° between phenanthroimidazole plane and the adjacent benzene ring, and 43.1° between bridging biphenyl group, respectively. To study the possible intermolecular interactions of CPBPMCN, Figure 1b gives its packing details. The benzene ring linked with -CN group, can be observed to be nearly perpendicular to the adjacent carbazole plane, indicating that the weak intermolecular edge-to-face  $\pi$ - $\pi$  stacking interactions exist with a CH/ $\pi$  distance of 2.56 Å. The intermolecular offset face-to-face  $\pi$ - $\pi$  stacking can also be found between the carbazole and the phenanthroimidazole planes, but due to the slightly long distance (3.64 Å) and

dihedral angle (12.4°), the interaction is considerably weak. Moreover, two neighboring parallel phenanthroimidazole planes have a certain degree of overlap, but the distance between them reaches up to 4.32 Å so that the  $\pi$ - $\pi$  stacking interaction can be ignored, where it is generally accepted that high-efficient intermolecular interaction often occurs within effective distance smaller than 3.7 Å. In conclusion, from the analysis on single X-ray crystal data of CPBPMCN, we can know that this compound adopts a severely twisted molecular configuration, leading to a low degree of aggregation in the solid state, which may be beneficial for it to serve as a nondoped emitter in OLEDs.



Figure 1. The molecular structure a) and packing diagram b) of CPBPMCN from single X-ray crystal data.

## 2.4. Photophysical Properties

The normalized ultraviolet (UV) absorption and PL spectra of CBPMCN and CPBPMCN were studied in dilute solution and neat film, as shown in **Figure 2**. They have similar absorption bands ranging from 250 to 380 nm. The absorption peak at around 290 nm may originate from the carbazole-centered  $\pi$ - $\pi$ \* transition,<sup>39</sup> while the absorption band at around 340 nm could be assigned to  $\pi$ - $\pi$ \* transition of the 7/24

phenatheroimmidazole chromophore.<sup>40</sup> As expected, two compounds show strong blue emission with maximum emission bands at 450 and 429 nm in dichloromethane solution (10<sup>-5</sup> M), and at 449 and 443 nm in the neat film for CBPMCN and CPBPMCN, respectively. Compared with CBPMCN, the PL peak of CPBPMCN exhibits 21 nm blue-shift in dilute solution which is actually unexpected opposite to the common sense that increasing conjugation length generally leads to a red-shift of emission. This unusual phenomenon could be explained by the special luminescence mechanism of the compound, *i.e.* HCTL (see Electroluminescence Studies Section).<sup>30</sup> In details, upon the insertion of an additional phenyl ring, the LE (locally emissive) component in CPBPMCN is enhanced and which leads to the red shift of PL spectrum, meanwhile the CT (charge-transfer) component is suppressed seriously and which results in the blue shift of PL spectrum. As for the result, the latter factor is more dominant than the former one, leading to a blue-shifted PL spectrum for CPBPMCN. In addition, the PLQY of CBPMCN and CPBPMCN were measured on C9920-02 absolute quantum yield measurement system. Key photophysical data of the two compounds are summarized in **Table 1**. CPBPMCN has higher PLQY of 72% than that of CBPMCN (14%) in the solid film state probably resulting from the extended  $\pi$  conjugated system.<sup>38</sup> Therefore, CPBPMCN is more efficient and potential as a deep-blue emitter in OLEDs.

Compound	$\lambda_{abs}^{a}$	$\lambda_{PL}{}^{b}$	$\lambda_{PL}^{c}$	PLQY <sup>d</sup>	$T_d/T_g$	Ege	HOMO/LUMO
	[ <b>nm</b> ]	[nm]	[nm]	[%]	[°C]	[eV]	[eV]
CBPMCN	260, 293,	450	449	14/9	446/147	3.25	-5.86/-2.61 <sup>g</sup>
	342						-5.59/-2.30 <sup>f</sup>
CPBPMCN	261, 294,	429	443	72/20	487/169	3.20	-5.72/-2.52 <sup>g</sup>
	343						-5.60/-2.28 <sup>f</sup>

1 CDDDMCN

Table	I.	The properties	01	CBPMCN	and	CPBPMCN.

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<sup>a</sup> The maximum absorption wavelength, measured in  $CH_2Cl_2$  (1×10<sup>-5</sup> mol L<sup>-1</sup>) at room temperature; <sup>b</sup> The maximum fluorescent emission peak, measured in  $CH_2Cl_2$  (1×10<sup>-5</sup> mol L<sup>-1</sup>) at room temperature; <sup>c</sup> The PL spectra measured in neat film; <sup>d</sup> Photoluminescence quantum yield measured in neat film and  $CH_2Cl_2$  solution; <sup>e</sup> Optical gap calculated from the absorption onset in  $CH_2Cl_2$ ; <sup>g</sup> Experimental value, calculated from cyclic voltammetry data and optical gap; <sup>f</sup> Theoretical value, based on DFT calculations.



Figure 2. UV absorption and PL spectra of CBPMCN and CPBPMCN in  $CH_2Cl_2$  (10<sup>-5</sup> M) and neat film.

## 2.5. Thermal Properties

The thermal stability of the luminescent materials is significant for achieving high-performance and long-lifetime optoelectronic devices. Thermal properties of the two compounds were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. As depicted in **Figure 3a**, they have high decomposition temperatures (T<sub>d</sub>, corresponding to 5% weight loss) of 446 °C and 487 °C for CBPMCN and CPBPMCN respectively, which is capable of vapor deposition method in OLED fabrication. High glass transition temperature (T<sub>g</sub>) is also indispensable for increasing morphological stability of the luminescent materials to increase the device lifetime. As depicted in **Figure 3b**, they have rather high T<sub>g</sub> of 147 °C and 169 °C for CBPMCN and CPBPMCN, respectively. Moreover, the insertion of an additional phenyl ring makes CPBPMCN having better thermal and morphological stability than CBPMCN. Therefore, CPBPMCN may serve as a more excellent emitter in stable deep-blue OLEDs.



**Figure 3.** a) Thermal gravimetric analysis (TGA) and b) differential scanning calorimetry (DSC) of CBPMCN and CPBPMCN.

#### 2.6. Frontier Molecular Orbital Studies

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Cyclic voltammetry was employed to investigate the electrochemical properties of the two compounds and hence to estimate their HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) energy levels. The oxidation process was conducted in degassed CH<sub>2</sub>Cl<sub>2</sub> solution with ferrocene (F<sub>c</sub>) as an internal standard. They all exhibit irreversible oxidation waves like most carbazole derivatives, as shown in Figure 4a. The HOMO energy levels were estimated from the oxidation potentials to be 5.86 and 5.72 eV for CBPMCN and CPBPMCN, respectively, using the empirical formula reported in the literature.<sup>41</sup> The LUMO energy levels were deduced from HOMO energy levels and optical band gaps  $E_g$  estimated by the onset of UV absorption, which are 2.61 and 2.52 eV for CBPMCN and CPBPMCN, respectively. The frontier orbital energy levels of the two compounds are appropriate for hole and electron injection from common ТСТА charge-transporting materials respectively, such as TPBi (tris(4-carbazoyl-9-ylphenyl)amine) (HOMO = 5.7 eV) and (1,3,5-tris(1-phenyl-1Hbenzimidazol-2-yl)benzene) (LUMO = 2.7 eV).



**Figure 4.** a) Cyclic voltammetry curves and b) DFT calculated HOMO (bottom) and LUMO (upper) of CBPMCN and CPBPMCN.

Density functional theory (DFT) calculations were also employed to investigate the two compounds for a deeper insight into their electronic properties. B3LYP/6-311G\*\* was chosen to optimize their geometry structures and calculate their frontier orbital energy levels. The electron density distributions of the frontier molecular orbitals are displayed in **Figure 4b**. For both compounds, their LUMO and HOMO spatial distributions are similar. The LUMO is mainly centralized on benzonitrile due to the strong electron withdrawing properties of -CN group, while the HOMO is located at the carbazole-(bi)phenyl -phenanthroimidazole backbone [C(P)BPM]. It can be seen that both two compounds show clear separation of HOMO and LUMO energy levels were calculated to be -5.59 eV and -2.30 eV for CBPMCN and -5.60 eV and -2.28 eV for CPBPMCN, respectively. These results indicate that two D-A molecules are constructed successfully with potentially bipolar charge transporting properties.

## 2.7. Electroluminescence Studies

Based on aforementioned studies, CPBPMCN is found superior to its analog CBPMCN, reflected in better thermal stability, higher glass transition temperature, deeper blue emission and higher PLQY in the neat film. Hence, to verify the potential of CPBPMCN as deep-blue emitter, nondoped devices were fabricated with a simple structure (**Figure 5a**) of ITO/MoO<sub>3</sub> (2 nm)/TCTA: MoO<sub>3</sub> (20 wt.%, 40 nm)/TCTA (10 nm)/CPBPMCN (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm). ITO (indium tin

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oxide) was used as anode. A 2-nm-thick layer of MoO<sub>3</sub> was used to modify the work function of ITO to enhance hole injection. A 40-nm layer of TCTA was doped by 20 wt.% MoO<sub>3</sub> (p-type doping) to enhance hole injection,<sup>42, 43</sup> followed by another 10-nm pristine TCTA as the hole transporting layer (HTL). TPBi was used as electron transporting layer as well as the hole blocking layer because of its low-lying HOMO level. LiF was used as electron injecting layer, and Al was used as cathode. The energy level diagrams and molecular structures of these materials are exhibited in **Figure 5b** and **5c**.



**Figure 5.** a) The schematic device structure of fabricated nondoped OLEDs; b) the energy level diagrams and c) molecular structures of the compounds used in OLEDs.

The performance of the nondoped devices is summarized in **Figure 6**. As **Figure 6a** depicted, the nondoped device exhibited deep-blue EL with a peak wavelength of 440 nm at a luminance of 1000 cd m<sup>-2</sup>, which is almost the same as the corresponding PL spectra in the neat film state, indicating that the EL is indeed from pure CPBPMCN emitter without excimer or exciplex emission. The device demonstrated excellent performance with an EQE<sub>max</sub> of 4.71%, maximum luminance ( $L_{max}$ ) of 10800 cd m<sup>-2</sup> and particularly, high-quality deep-blue emission with CIE coordinates of (0.15, 0.08). The EQE can still remain 4.56%, even at a brightness of 1000 cd m<sup>-2</sup>.

12/24

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efficiency at very high brightness. Furthermore, in order to improve the device efficiency, we optimized the hole transporting layer: changing from TCTA:  $MoO_3$  (20 wt.%, 40 nm)/TCTA (10 nm) to TCTA: MoO<sub>3</sub> (20 wt.%, 20 nm)/TCTA (40 nm), while keeping the other layers unchanged. The optimized device showed the same CIE coordinates of (0.15, 0.08) with a higher EQE<sub>max</sub> (5.80%), accompanied by slightly higher maximum power efficiency ( $PE_{max}$ ) and current efficiency ( $CE_{max}$ ). The performance data of these devices are listed in **Table 2**. To the best of our knowledge, the performance is impressive among the reported nondoped deep-blue OLEDs with similar color purity. Notably, the value of  $EQE_{max}$  (5.80%) has indeed exceeded the upper limit (5%) of fluorescent materials.<sup>44, 45</sup> To verify whether a TADF or HLCT process can occur, we measured the fluorescence and phosphorescence of CPBPMCN in 2-methyl tetrahydrofuran (2-MeTHF) at 77 K, as shown Figure S1. The energy gap of singlet (S1) and triplet (T1) is as large as 0.74 eV, which is much larger than a sufficiently small T-S energy splitting (< 0.2 eV) necessary to effectively realize the RISC process in TADF mechanism.<sup>25</sup> We further studied the HLCT characteristic of the compound using its PL spectra in solvents of different polarities (Figure S2). As the solvent polarity increased from hexane to acetonitrile, the emission demonstrated obvious solvatochromic shift of 30 nm, indicating that the emissive state of CPBPMCN is of typical CT feature.<sup>27, 46</sup> Especially, in low-polarity solvent such as hexane, CPBPMCN exactly showed a LE-like character because of the vibrational fine structure in PL spectrum. To better understand the solvatochromic effect, the Stokes shift  $(v_a - v_f)$  versus the orientation polarizability  $f(\varepsilon, n)$  was fitted according to the Lippert-Mataga model (Section 3, Supporting Information).<sup>47</sup> As shown in Figure S2, the compound displays two independent linear relationships, suggesting the existence of two different excited states, whose excited-state dipole moments  $\mu_e$ were calculated to be 7.3 D in low-polarity solvents and 19.9 D in high-polarity solvents. The small  $\mu_e$  can be attributed to the LE-based HLCT state, whereas the large  $\mu_e$  can be treated as CT-dominated HLCT state . Further lifetime measurement indicated that this intercrossed excited state in the moderately polar solvents should be

a classical HLCT state. As shown in **Figure S1**, its transient PL decays reveal a mono-exponential lifetime of 2.41 ns, indicating that the LE and CT components are integrated into the HLCT state.<sup>17</sup> Moreover, the variation of PLQY with increased solvent polarity displayed the influence of combination of the LE component and the CT component with different proportions on PL efficiency (**Figure S2**), which is also consistent with the previous works.<sup>31, 48</sup>

Device	HTL <sup>a</sup>	V <sub>on</sub> [V]	L <sub>max</sub> <sup>b</sup> [cd m <sup>-2</sup> ]	PE <sub>max</sub> <sup>c</sup> [lm W <sup>-1</sup> ]	CE <sub>max</sub> <sup>d</sup> [cd A <sup>-1</sup> ]	EQE <sub>max</sub>	EQE <sup>e</sup> [%]	CIE [x, y]
1	40P+10 nm	3.4	10800	2.21	3.11	4.71	4.56	0.15, 0.08
2	20P+40 nm	3.8	9755	2.86	3.82	5.80	4.39	0.15, 0.08

 Table 2. EL performance of nondoped devices using CPBPMCN as deep-blue emitter.

<sup>a</sup> "40P+10 nm" means "TCTA:MoO<sub>3</sub> (20 wt.%, 40 nm)/TCTA (10 nm)", while "20P+40 nm" means "TCTA:MoO<sub>3</sub> (20 wt.%, 20 nm)/TCTA (40 nm)"; <sup>b</sup> Maximum luminance; <sup>c</sup> Maximum power efficiency; <sup>d</sup> Maximum current efficiency; <sup>e</sup> Value at 1000 cd m<sup>-2</sup>.

## 2.8. Single-Carrier Devices

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The excellent performance of the nondoped devices may benefit from high PLQY and bipolar carrier transporting capacity of CPBPMCN. Hence, to evaluate the bipolar charge transporting properties of CPBPMCN, we fabricated single-carrier devices with structures of ITO/MoO<sub>3</sub> (10 nm)/CPBPMCN (50 nm)/MoO<sub>3</sub> (10 nm)/Al (100 nm) for hole-only device and ITO/TPBi (10 nm)/ CPBPMCN (50 nm)/TPBi (10 nm)/LiF (1 nm)/Al (100 nm) for electron-only device. As shown in Figure 6d, the two single-carrier devices showed significant currents at low applied voltages, illustrating that CPBPMCN is capable of transporting both holes and electrons. Moreover, we used the the space-charge-limited current (SCLC) method to estimate the values of carrier mobilities.<sup>34</sup> The current density-voltage curves were fitted using the Mott-Gurney equation:  $J = 9\varepsilon\varepsilon_0 \mu V^2/8L^3$ , where  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon$  is the relative permittivity,  $\mu$  is the carrier mobility and L is the thickness of active layer (see Figure S3). Then the hole mobility  $\mu_h = 5.03 \times 10^{-4} \ cm^2 \ V^{-1} \ s^{-1}$  and electron mobility  $\mu_e = 1.97 \times 10^{-6} \ cm^2 \ V^{-1} \ s^{-1}$  at zero-electric field were derived, comparable to general carrier transporting which is materials (NPB)

N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl) benzidine<sup>49</sup> for hole and  $Alq_3^{50}$  for electron, respectively. Furthermore, based on the these single-carrier devices data, we can better understand why **device 2** has higher EQE<sub>max</sub> than the **device 1** but the efficiency roll-off of the **device 2** is larger than that of the **device 1**. Though CPBPMCN is capable of transporting both holes and electrons, it's better for hole transporting than electron transporting at relatively high voltage, implying unbalance of charge carrier mobility. So it is important to optimize device structure to balance hole and electron in the whole device. For the **device 2**, it may show a much better charge balance, and contributing to a better EQEmax at low operating voltage. However, the hole and electron may become more unbalanced in **device 2** at high applied voltage, which results in larger efficiency roll-off. (see **Figure 6c**).



**Figure 6.** a) EL spectra at 1000 cd m<sup>-2</sup>, b) Current density-voltage-luminance (*J-V-L*) characteristics and c) Power efficiency-luminance-external quantum efficiency (PE-*L*-EQE) of the nondoped devices; and d) Current density-voltage curves of the hole-only and electron-only devices. ["40P+10 nm" means "TCTA: MoO<sub>3</sub> (20 wt.%, 40 nm)/TCTA (10 nm)", while "20P+40 nm" means "TCTA: MoO<sub>3</sub> (20 wt.%, 20 nm)/TCTA (40 nm)".]

## **3. CONCLUSION**

In conclusion, we successfully synthesized two blue fluorescent D-A molecules composed of carbazole, phenanthroimidazole and cyano group, named as CBPMCN and CPBPMCN respectively. A systematic study was conducted on the two compounds, including photophysical properties, thermostability and electrochemical properties. Compared with CBPMCN, deeper blue emission, higher PLQY and better thermostability, makes CPBPMCN more attractive as a potential nondoped deep-blue emitter. The nondoped device of CPBPMCN showed deep-blue EL with CIE coordinates of (0.15, 0.08) exactly close to the NTSC standard blue, and an EQE<sub>max</sub> of 4.71% with rather small efficiency roll-off (only drop by 3.2% at 1000 cd m<sup>-2</sup>). Furthermore, the optimization of the hole transporting layer enables the nondoped device to obtain a higher EQE<sub>max</sub> up to 5.80%. We believe these experimental results will provide some beneficial enlightenment for further molecular design to realize efficient nondoped deep-blue electroluminescence.

## 4. EXPERIMENTAL SECTION

## **General information**

All the reagents and solvents used for the synthesis were purchased from commercial resources and used as received. <sup>1</sup>H-NMR spectra were recorded on a Bruker-400MHz NMR spectrometer using CDCl<sub>3</sub> or DMSO- $d_6$  as solvent. The chemical shift for each signal was reported in ppm units with tetramethylsilane (TMS) as an internal reference, where  $\delta$  (TMS) = 0. Mass spectra were obtained from a Bruker Apex IV FTMS. Elemental analyses were performed on a VARIO EL analyzer (GmbH, Hanau, Germany).

## 4-(2-(4-bromophenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (BrBPMCN)

A mixture of 10 mmol (1.84 g) 4-bromobenzaldehyde, 10 mmol (2.08 g) phenanthrenequinone, 40 mmol (4.72 g) 4-aminobenzonitrile, and 50 mmol (3.70 g) ammonium acetate with 30 mL acetic acid were added into a 250 mL flask and 16/24

refluxed at 120 °C for 2 h under nitrogen atmosphere. After cooling down, the solid product was filtrated and washed with 60 mL 1:1 water/acetic acid and 100 mL water successively, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and dried with Na<sub>2</sub>SO<sub>4</sub> overnight, purified by silica gel chromatography to afford white product (3.98 g, yield 84%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.86-8.77 (m, 2H), 8.71 (d, 1H, *J* = 8.3Hz), 7.94-7.89 (m, 2H), 7.78-7.73 (m, 1H), 7.71-7.62 (m, 3H), 7.56 (ddd, 1H), 7.49-7.44 (m, 2H), 7.37-7.28 (m, 3H), 7.09 (dd, 1H, *J* = 8.3 Hz). MS: 474.1 [MH<sup>+</sup>].

## 4-(2-(4-(9H-carbazol-9-yl)phenyl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitr ile (CBPMCN)

A mixture of 3 mmol (1.42 g) BrBPMCN, 3.3 mmol (0.55 g) carbazole, 3.15 mmol (0.60 g) cuprous iodide, and 18 mmol (2.49 g) potassium carbonate with 10 mL DMAc were added into a 50 mL flask and stirred at 160 °C for 24 h under nitrogen atmosphere. After cooling down, the reaction mixture was poured into 100 mL water and filtrated. The solid product was dried in vacuum and then purified by silica gel chromatography to afford CBPMCN (0.42 g, yield 25%). The compound was further purified by thermal gradient sublimation (300 °C-240 °C-90 °C) at low pressure (10<sup>-4</sup> Pa). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.95 (dd, 2H, *J* = 22.9 Hz), 8.77-8.71 (m, 1H), 8.26 (d, 4H, *J* = 8.5 Hz), 8.11 (d, 2H, *J* = 8.5 Hz), 7.87-7.79 (m, 3H), 7.76-7.58 (m, 4H), 7.50-7.39 (m, 5H), 7.35-7.28 (m, 2H), 7.10 (d, 1H, *J* = 8.2 Hz). MS: 561.2 [MH<sup>+</sup>]. EA: C:85.77%, H:4.18%, N:9.93% (theoretical value: C, 85.69%; H, 4.31%; N, 9.99%).

## 4-(2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzonitrile (CPBPMCN)

A mixture of 3 mmol (1.42 g) BrBPMCN, 3.15 mmol (0.95 g) (4-(9H-carbazol-9-yl)phenyl)boronic acid, 0.078 mmol (0.09 g) tetrakis-(triphenylphosphine)-palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>), and 30 mmol (4.15 g) potassium carbonate with 15 mL deionized water, 20 mL ethyl alcohol and 30 mL toluene were added into a 100 mL flask and refluxed at 90 °C for 24 h under nitrogen atmosphere. The organic phase was washed with 40 mL water and extracted with CH<sub>2</sub>Cl<sub>2</sub>, then

was dried with Na<sub>2</sub>SO<sub>4</sub> overnight and purified by silica gel chromatography to afford white product (1.84 g, yield 96%). The compound was further purified by thermal gradient sublimation (320 °C-260 °C-110 °C) at low pressure (10<sup>-4</sup> Pa). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.93-8.70 (m, 3H), 8.16 (d, 2H, *J* = 7.7 Hz), 7.95 (d, 2H, *J* = 8.5 Hz), 7.83 (d, 3H, *J* = 8.5 Hz), 7.75-7.54 (m, 10H), 7.44 (d, 4H, *J* = 12.1 Hz), 7.31 (s, 3H), 7.18-7.12 (m, 1H). MS: 637.2 [MH<sup>+</sup>]. EA: C: 86.76%, H: 4.38%, N: 8.82% (theoretical value: C, 86.77%; H, 4.43%; N, 8.80%).

#### **Photophysical measurement**

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UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Fluorescence spectra were recorded on an Edinburgh Analytical Instruments FLS920 spectrophotometer. PLQYs were measured on C9920-02 absolute quantum yield measurement system from Hamamatsu Company.

## **Thermal Properties Measurements**

Thermogravimetric analysis was undertaken with a Q600SDT instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 15 °C min<sup>-1</sup> from 25 to 500 °C. Differential scanning calorimetry was performed on a Q100DSC instrument unit at a heating rate of 15 °C min<sup>-1</sup> from 20 to 300 °C under nitrogen. The glass transition temperature was determined from the second heating scan.

## Cyclic voltammetry measurements

Cyclic voltammetry was carried out in nitrogen-purged  $CH_2Cl_2$  solution at room temperature with a CHI600C voltammetric analyzer, tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M) as the supporting electrolyte and ferrocene as an internal standard. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl wire pseudo-reference electrode. The scan rate is = 100 mV/s.

## **Theoretical Calculations**

For calculation of HOMO and LUMO energy levels, density functional theory (DFT) calculations were performed for optimized molecular structures at the

B3LYP/6-311G\*\* levels, respectively, using a Gaussian suite of programs (Gaussian 09, Revision A.01).

## **OLED** fabrication and measurements

The ITO-coated glass, hole injection material MoO<sub>3</sub>, hole transporting material TCTA, electron transporting material TPBi, electron injection material LiF and cathode Al were commercially available. ITO anode has a sheet resistance of 14  $\Omega$  square<sup>-1</sup> and 80-nm thickness. Before loading into a deposition chamber, the ITO substrate was cleaned with detergent, deionized water, acetone and ethanol. The organic and metal layers were deposited in different vacuum chambers with a base pressure lower than  $8 \times 10^{-5}$  Pa. The devices were capsulated in a glove box under a nitrogen atmosphere. All electrical testing and optical measurements were performed under ambient conditions. The EL spectra, current density-voltage-luminance (J-V-L) and EQE characteristics were measured by computer controlled Keithley 2400 source meter and absolute EQE measurement system (C9920-12, Hamamatsu Photonics) with the photonic multichannel analyzer (PMA-12, Hamamatsu Photonics).

## **ASSOCIATED CONTENT**

#### **Supporting Information**

The Supporting Information is available, including the summary of the crystal data of CPBPMCN (**Table S1**), low-temperature phosphorescence and decay lifetime measurement of CPBPMCN (**Figure S1**), the solvatochromic Lippert-Mataga model (**Figure S2**, **Table S2**), the SCLC model of single-carrier devices of CPBPMCN (**Figure S3**) and the <sup>1</sup>H-NMR spectra of CBPMCN and CPBPMCN (**Figure S4** and **Figure S5**).

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## **Table of Contents**

Nondoped OLEDs utilizing a new emitter exhibited EL with NTSC  $CIE_y$  and high  $EQE_{max}$  (5.80%) with low efficiency roll-off.

