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Graphical Abstract

Violet/deep-blue fluorescent organic lightemitting diode based on high-efficiency novel carbazole derivative with large torsion angle

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A novel and highly efficient violet/deep-blue fluorescent carbazole-based compound (1) is designed and synthesized. The compound shows intensive violet/deep-blue fluorescence, high photoluminescence efficiency (0.72 in CH₂Cl₂, 0.65 in film) and narrow full width at half maximum (48 nm). The large torsion angles between carbazole and naphthalene guarantee the weak intermolecular interactions and suppress the π - π interactions in solid state, resulting the highly efficient violet/deep-blue fluorescence. The maximum emission peak, luminance and external quantum efficiency for violet/deep-blue electroluminescence are 410 nm, 1326 cd/m² and ~2%, respectively.





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Violet/deep-blue fluorescent organic light-emitting diode based on highefficiency novel carbazole derivative with large torsion angle

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ABSTRACT

A novel and highly efficient violet/deep-blue fluorescent carbazole and naphthalene-based compound (1) is designed and synthesized. The compound shows intensive violet/deep-blue fluorescence, high photoluminescence efficiency (0.72 in CH₂Cl₂, 0.65 in film) and narrow full width at half maximum (48 nm). The large torsion angles between carbazole and naphthalene guarantee the weak intermolecular interactions and suppress the π - π interactions in solid state, resulting in the highly efficient violet/deep-blue fluorescence. The maximum emission peak, luminance and external quantum efficiency for violet/deep-blue electroluminescence are 410 nm, 1326 cd/m² and ~2%, respectively.

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The blue emission is the essential chromaticity component for both display and solid-state lighting.^[1,2] Deep-blue emitters greatly affect the efficiency and lifetime of organic light-emitting diodes (OLEDs) due to their inherent defect, thus limiting industrialization of organic electroluminescence (EL).[3,4] The current materials system for blue emitters are the pure organic fluorescent materials, noble metal-based phosphors and thermally activated delayed fluorescent (TADF) materials.^[5] Although the phosphors and TADF materials could realize high peak efficiency, the high cost and efficiency roll-off are still the main challenge suffering from the triplet-triplet annihilation of excitons under the high current density. In addition, it is quite difficult to achieve pure blue emission (deep-blue emission) for phosphors and TADF materials, and they often show broad emission spectrum, reducing the color purity. Thus, from the above point of view, the pure organic emitters with flexible structural design ability have plenty room to develop pure blue emitters. Very recently, we developed novel blue fluorescent emitters structured by linking triphenylamine, naphthalene and anthracene derivatives for OLEDs with external quantum efficiency (EQE) exceeding 5%, however, the 1931 Commission Internationale de L'Eclairage (CIE) coordinates of this device is still not in the region of deep-blue.^[2a] This encourages us to enrich this family of blue emitters by more rational molecular design for further realizing the deep-blue electroluminescence.

In this letter, one novel highly efficient violet/deep-blue fluorescent emitter (1) was developed by linking carbazole and naphthalene with large torsion angles. The large torsion angles between carbazole and naphthalene moiety could not only give rise to the weak intermolecular interactions and suppress the π - π interactions in solid state, guaranteeing the highly efficient violet/deep-blue fluorescence. The fluorescent emitter developed shows bright violet/deep-blue fluorescence with quite high photoluminescence efficiency (Φ_{PL}) and narrow full width at half maximum (FWHM) suitable for high-performance deep-blue electroluminescence. The maximum emission peak, brightness and external quantum efficiency for violet/deep-blue electroluminescence are 410 nm, 1326 cd/m² and ~ 2%, respectively.

The highly efficient violet/deep-blue fluorescent carbazole and naphthalene-based compound was synthesized in several steps with high yields. As shown in **Scheme 1**, the target compound was prepared in high yield of 92% by coupling reaction of naphthalen-1-ylboronic acid with 3,6-dibromo-9-butyl-9H-carbazole under the under catalysis of Pd(PPh₃)₄ in toluene at 85 °C. And 3,6-dibromo-9-butyl-9*H*-carbazole was obtained through deprotonation, alkylation and bromination in one-pot process.



Scheme 1. Synthetic route, chemical structure and the ORTEP diagram of 1. The compound was purified as colorless crystals and fully

elemental analyses and single crystal X-ray diffraction (Supporting Information). The four-carbon chain butyl group was introduced into the carbazole for increasing the solubility in common organic solvent. The NMR spectra were recorded in chloroform-d. Although the much large torsion angles between carbazole and naphthalene moiety, in the proton NMR, eight well-resolved signals of aromatic protons were observed, corresponding to the two equivalent part of the whole molecule, originated from the C_2 symmetry owing to the rapid rotation of naphthalene unit in the solution state at room temperature. Similar situation was observed in carbon NMR, there are sixteen resonances in the aromatic region of ¹³C NMR spectrum corresponding to the sixteen different aromatic carbons on the two equivalent part of the whole molecule. Resonance signal in 4.47 ppm should be assigned to the proton attached to the carbon bonded to the nitrogen atom of carbazole. Quite different from the solution state, the large torsion angles between carbazole and naphthalene moiety of compound 1 were clearly observed in the single crystals, as shown in Figure 1, torsion angles are up to 59.09 and 58.42°, respectively. Such large torsion angles indeed induce much weaker intermolecular interactions and suppress the π - π interactions in solid state, resulting in the highly efficient violet/deep-blue fluorescence. In the crystals, only weak CH- π interactions between adjacent molecules could be observed (Figure 1). Notably, this large torsion angle design strategy effectively reduce the intermolecular π - π interactions, which commonly cause the red shift of emission spectrum and the aggregation induced quenching of fluorescent materials.

The photophysical properties of emitter 1 were explored in dichloromethane, film and exhibited in Figure 2a and Table 1, S1. In the solution of dichloromethane, the ${}^{1}\pi \rightarrow \pi^{*}$ transition of carbazole moiety in emitter 1 corresponds to the weak absorption band in the wavelength of 275-350 nm. The strong absorption in the wavelength of 220-275 nm is probably attributed to the ${}^{1}\pi \rightarrow \pi^{*}$ transitions of naphthalene unit.^[2a] The emitter shows intensive violet/deep-blue fluorescent emission with a peak of 390 nm in dichloromethane under the excitation of 305 nm. The emission of emitter in the film was slightly red shift to 400 nm under the same excitation wavelength. The slight red shift (20 nm) of the emission was attributed to agglomeration of molecules in solid states. It should be noted that the large torsion angles in the molecule guarantee the weak intermolecular interactions and suppress the π - π interactions in solid state, resulting in the highly efficient violet/deep-blue fluorescence. The calculated electron



Figure 1. The intermolecular packing of 1 by CH- π interactions between adjacent molecules in crystals, and the torsion angles between carbon atoms **Table 1**. Photophysical and electrochemical properties for emitter **1**.



Figure 2. (a) UV-visible absorption, photoluminescence spectra of **1** at 298 K (in CH₂Cl₂ and film); (b) Calculated electron cloud distributions of HOMO/LUMO of **1**.

cloud distributions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 1 were shown in Figure 2b.^[6] The electron cloud of HOMO distribute over almost the entire molecule, while the electron cloud of LUMO mainly distribute in the two naphthalene moieties, which is consistent with the fact that the electron density of carbazole is much higher than that of naphthalene. The Φ_{PL} of the emitter is quite high up to 0.72 in dichloromethane, and the lifetime of the emitter is 5.81 ns in CH₂Cl₂. The emission exhibited narrow FWHM (48 nm). In the neat film, the Φ_{PL} of the emitter is also as high as 0.65, and the lifetime of the emitter is 6.02 ns. The emission spectrum shows much narrower FWHM (39 nm). The short lifetime of the excited states indicate the nature of fluorescence. We noted that the high Φ_{PL} of the emitter in neat film may have positive effect on the performance of electroluminescence induced by the less extent of aggregation induced quenching. The cyclic voltammetry in CH₂Cl₂ was carried out to investigate the electrochemical property of compound. As shown in Figure S1, the compound shows reversible oxidation wave and the oxidation potential was calculated to be 0.80 V. The carbazole oxidation should be responsible for this positive oxidation potential.[3a] The energy levels of the highest occupied molecular orbital and the lowest unoccupied molecular orbitals of compound based on the cyclic voltammetry are estimated to be -5.60 and -2.42 eV, respectively.

To evaluate the electroluminescence performance, the violet/deep-blue emitter was further used to prepare the electroluminescent device. As depicted in Figure S2a, the non-doped violet/deep-blue OLEDs were fabricated with the structures of indium-tin-oxide (ITO) (180 nm)/molybdenum trioxide (MoO₃) (3 nm)/ di-(4-(N,N-di-p-tolyl-amino)-phenyl)cyclohexane (TAPC) (40 nm)/ 4,4',4"-tris(carbazol-9-yl)triphenylamine (TCTA) (10 nm)/emitter **1** (x nm)/ 2,2',2"-

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Compound	$\lambda_{em}[nm]$	FWHM [nm]	τ [ns]	$arPhi_{ m PL}$	[eV]	[eV]	[eV] ^{c)}		
1	390 (CH ₂ Cl ₂)	48 (CH ₂ Cl ₂)	5.81 (CH ₂ Cl ₂)	0.72 (CH ₂ Cl ₂)	0.80	3.18	-5.60/-2.42		
	400 (film)	39 (film)	6.02 (film)	0.65 (film)					

^{a)}At a concentration of 1.0×10^{-5} mol/L in CH₂Cl₂ or neat film, $\lambda_{ex} = 305$ nm; ^{b)}In CH₂Cl₂; ^{c)}HOMO (eV) = -e($E_{onset}^{ox} + 4.8$), $E_g = 1240/\lambda$, LUMO (eV) = $E_g + HOMO$.

(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) (50 nm)/ lithium fluoride (LiF) (1 nm)/ aluminum (Al) (100 nm). In this device, ITO was used as the anode, and MoO₃ was used as hole injection layer (HIL). TAPC layer and TPBi layer were used as hole transport layer (HTL) and electron transport layer (ETL), respectively. TCTA was used as exciton-blocking layer, and the non-doped emitter 1 was used as light-emitting layer (EML). The 15 nm of neat film of emitter 1 was selected to investigate the device performance. The energy levels and the illustration of device structure of the violet/deep-blue OLED are depicted in Figure S2. From the energy level diagram of OLED (Figure **S2b**), the HOMO/LUMO levels of the emitter match with those of the TCTA and TPBi, indicating a good carrier trapping in this emitter layer,^[7] which is helpful for achieving high EL performance. As depicted in Figure 2a, the emitter 1-based OLED show excellent violet/deep-blue fluorescence with emission peak at 410 nm with narrow FWHM of 62 nm. This is also well verified from the 1931 Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.04) corresponding to the deep-blue region (Inset in Figure 2b). It is also found that the normalized EL spectra are overlapped quite well at various applying voltages from 4 V to 7 V, implying that the EL spectra is independent of the applying voltages and the fluorescence is only originated from the aggregation state of emitter 1.[2a] Notably, the

EL emission is slightly red shift to that of the neat film, which is maybe the more compact stacking under the deposition of vacuum evaporation. Form EQE-current density (EQE-J) curve in Figure 2b, current efficiency-luminance-power efficiency (CE-L-PE) curves and current density-voltage-luminance (J-V-L) curves in Figure 3, the emitter 1-based violet/deep-blue device also realizes acceptable EL performance. For example, the turnon voltages is only 3.4 V, and the maximum luminance, CE, PE and EQE are 1326 cd/m², 0.36 cd/A, 0.27 lm/W, and 1.79%, respectively. It is noted that the efficiency roll-off is quite small over the whole operation progress. Although this preliminary device performance is not high, which could be attributed to the less efficient device structure which do not well limit electron and hole carrier in emitting layer, inducing a low exciton utilization rate. Compared to the previously reported deep-blue OLEDs based on the carbazole/anthracene derivative with ethyl group,^[3c] the emission wavelength of the reported device is about 440 nm with 1931 CIE coordinates of (0.18, 0.17) and peak EQE of $\sim 2\%$. So the compound designed herein have slightly longer alkyl chain (butyl group) have great influence on the emission property and lead to shorter emission wavelength (violet/deepblue emission). From the spectral properties of electroluminescence, thses indicate the emitter 1 still have huge



Figure 2. The EL spectra (a) and *EQE-J* curve (b) of violet/deep-blue OLED based on **1**. Inset: EL photograph (up) and1931 CIE coordinate (down) of device at 6 V.

Table 2. EL data for the violet/deep-blue-emitting devices.



Figure 3. The *CE-L-PE* curves (a), *J-V-L* curves (b) of violet/deep-blue OLED based on 1.



^{a)}Current density is 100 mA cm⁻²; ^{b)}Luminance is 1 cd m⁻²

potential application in the development of violet/deep-blue OLEDs.

In summary, a novel highly efficient violet/deep-blue fluorescent emitter was developed by linking carbazole and naphthalene with large torsion angles. Owing to the large torsion angles between carbazole and naphthalene moiety, the π - π interactions in solid state was suppressed, ensuring the highly efficient violet/deep-blue fluorescence. The designed emitter shows bright violet/deep-blue emission at wavelength of 400 nm with high Φ_{PL} up to 0.65 in neat film, and the FWHM of emitter is narrow (39 nm). The maximum emission peak, luminance and EQE for violet/deep-blue electroluminescence with 1931 CIE coordinates of (0.16, 0.04) are 410 nm, 1326 cd/m² and ~ 2%, respectively. The further exploration of this deep-blue fluorescent material toward high-performance deep-blue electroluminescence is going on in our laboratory.

Acknowledgments

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Supplementary data

Supplementary data (details of the compound synthesis, NMR, and the device fabrication and testing) associated with this article can be found in **Supporting Information**.

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Highlights

- Highly efficient violet/deep-blue fluorescent carbazole derivative is designed.
- The large torsion angles results in the violet/deep-blue fluorescence.
- Violet/deep-blue OLED with λ_{EL} of 410 nm and 1931 CIE coordinate of (0.16, 0.04).

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