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Blue OLEDs with narrow bandwidth using CF_3 substituted bis((carbazol-9-yl)phenyl)amines as emitters: structural regulation of linker between donor and acceptor in chromophores

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Abstract

Three new donor-acceptor (D-A) chromophores decorated with bis(trifluoromethyl)-substituted phenyl group as acceptor and bis(4-(9*H*-carbazol-9-yl)phenyl)amine as donor unit, namely 1,4-naphthyl-CF_3 (**1**), 1,5-naphthyl-CF_3 (**2**) and Ph-CF_3 (**3**), were designed and synthesized. Their photophysical and electrochemical characteristics, and corresponding theoretical calculations were investigated. They showed blue emissions with high photoluminescence quantum yields (PLQY). Doped organic light-emitting diodes (OLEDs) based on them were fabricated, which exhibited strong blue electroluminescence with emission peaks at 453, 446 and 440 nm and full width at half maximum (FWHM) of 69, 65 and 65 nm, respectively, Their Commission International del'Eclairage (CIE) coordinates correspond to (0.169, 0.158), (0.176, 0.134) and (0.163, 0.099). Besides, the maximum current efficiencies (CEs) of 2.8, 5.0 and 4.9 cd A^{-1}; power efficiencies (PEs) of 2.9, 5.4 and 5.2 lm W^{-1}; external quantum efficiencies (EQEs) of 2.3, 2.3 and 3.4% were achieved for 1,4-naphthyl-CF_3 (**1**), 1,5-naphthyl-CF_3 (**2**) and Ph-CF_3 (**3**) doped devices D1, D2 and D3, respectively. This study clearly showed that the optoelectronic properties of these organic small molecules can be regulated by rational design of molecular structures, and their emission wavelengths could be finely tuned within the blue region.

Key words

Blue OLEDs, Donor-acceptor structures, Narrow bandwidth, Structural regulation

1. Introduction

During the past decades, OLEDs has attracted intensive attention since the pioneering work by Tang *et al* in 1987.[1] Efficient emitters for the three primary red, green and blue colors have attained substantial developments and their optimized OLEDs have shown remarkable advantages like high luminescent efficiency, large-area display, flexible panel production, wide-viewing angle, low power consumption and so on.[2-5] Tuning the OLED emission wavelength to the blue region especially the deep blue color has been of particular significance because such light color finds useful applications in full-color OLEDs displays and white light illumination sources.[6-8]

Blue emitters, especially deep blue emitters with CIE y coordinate value smaller than 0.1, are particularly scarce and challenging due to the high energy gap of the emitters.[9-11] Although it is of great challenge, many efforts have been expended to achieve the blue emission. For example, transition metal complexes as emitters that are used to afford the blue phosphorescence, have drawn intense interest, because they can approach ideal 100% internal quantum efficiency by utilizing both singlet and triplet excitons.[12-14] Other kinds of molecules, such as AIEgens,[15, 16] “hot exciton” fluorophores,[17, 18] thermally activated delayed fluorescence (TADF) materials,[11, 19-24] hybridized local and charge transfer (HLCT) materials,[25, 26] are also investigated to realize blue emissions. However, the above-mentioned materials have some shortcomings which limit their practical application. For example, phosphorescent metal complexes are

commonly air-/moisture- sensitive, environmentally toxic, and expensive. AIEgens, “hot exciton” fluorophores, TADF and HLCT materials need the special skeletons with a certain pattern of distributed HOMO and LUMO, causing the fine regulation of the emission wavelength difficult. Therefore, it is still desirable to find alternative and accessible ways to develop efficient, stable, pure- and deep-blue materials.

Organic small molecules as a kind of traditional chromophores have always attracted many interests because of their merits in molecular diversity, mass production, tunable energy gap, and low cost. Recently, donor-acceptor (D-A) type structure endowing the materials with bipolar properties which can facilitate the hole/electron injection and transport,[27-29] has been extensively investigated.[30] On the other hand, the trifluoromethyl-related group has been demonstrated to be a good acceptor in the D-A type blue materials,[31-34] and triarylamine is also a powerful and common donor for constructing blue emitting materials due to its sufficiency in electron and high emission efficiency.[35, 36] The functional material combining these two kinds of donor and acceptor would be a good candidate for designing efficient deep blue emitters. The linker between the donor and acceptor units also play an important role in the emission property of emitters.[15, 37] Herein, we designed and synthesized three deep blue chromophores, namely 1,4-naphthyl-CF_3 (**1**), 1,5-naphthyl-CF_3 (**2**) and Ph-CF_3 (**3**) (Scheme 1A), by incorporating 2,4-bis(trifluoromethyl)-substituted phenyl group as acceptor, bis(4-(9*H*-carbazol-9-yl)phenyl)amine as donor unit, and a different linker between the donor and acceptor part. The OLEDs employing these emitters (**1**-**3**) as the dopants all exhibited the pure blue luminescence with emission peak at 453, 446 and 440 nm; FWHM of 69, 65

and 65 nm; and CIE coordinates of (0.169, 0.158), (0.176, 0.134) and (0.163, 0.099), respectively. This study clearly showed that the photoluminescence of **1**-**3** can be readily regulated by molecular structural design, and particularly the emission wavelength of the designed fluorophores can be finely tuned within the blue region.

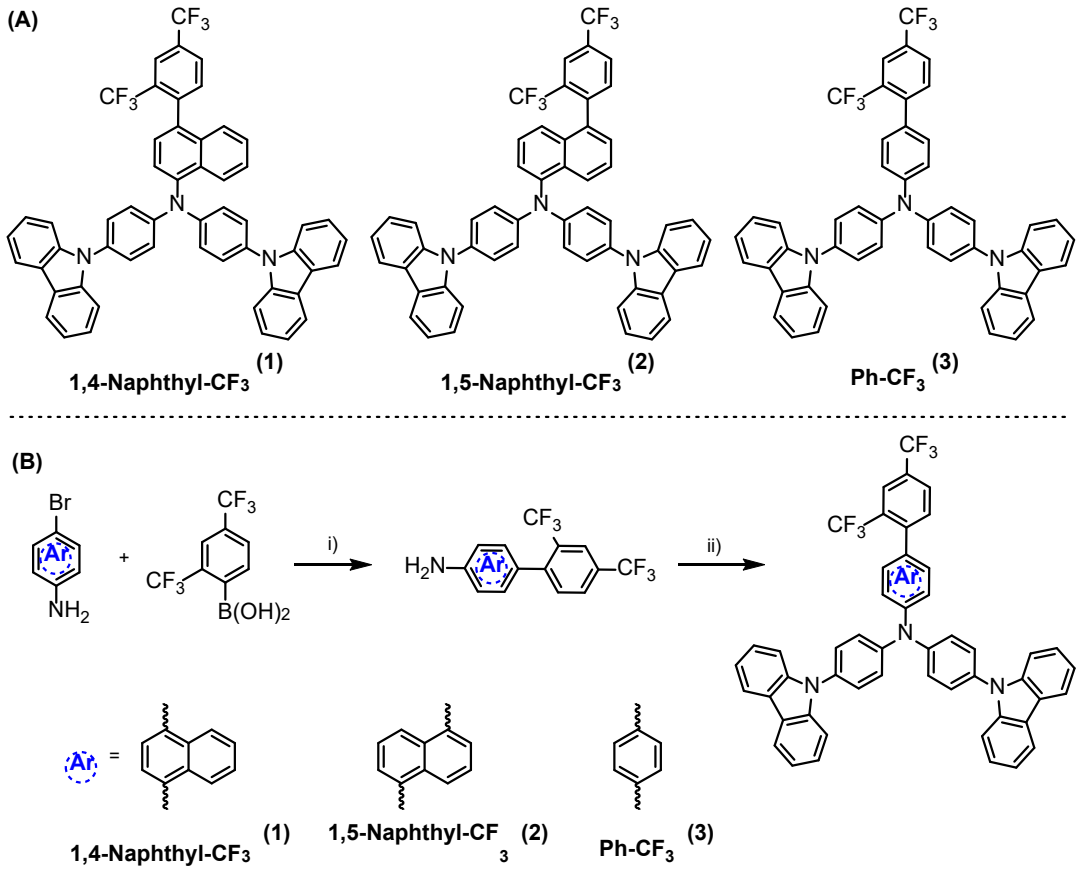
2. Results and discussion

2.1 Synthesis and characterization

The molecular structures of **1**-**3** are illustrated as shown in Scheme 1A, where the differences of them are the central arylene linkage and the bonding sites. These structures were successfully synthesized in 40-75% total yields via a two-step synthetic procedure as described in Scheme 1B. The CF_3-substituted amine intermediates were prepared by a Suzuki cross coupling reaction of (2,4-bis(trifluoromethyl)phenyl)boronic acid with the corresponding bromo-amines, and the donor part was subsequently attached to it by a Pd-catalyzed Buchwald−Hartwig reaction. The title compounds **1**-**3** were characterized by NMR spectroscopy (^{1}H, ^{13}C and ^{19}F NMR) and high resolution mass spectrometry, testifying the well-defined chemical structures and good purities. The detailed procedures for the synthesis and characterization data are given in the supporting information.

We tested the thermal stability of these compounds by the thermogravimetric analysis (TGA) under a N_2 atmosphere. As shown in Figure S1, the decomposition temperature (T_d) at 5% loss of the initial weight was 374, 391 and 405 °C for **1**-**3**, respectively,

exhibiting good thermal stabilities and demonstrating that these chromophores would be sufficiently stable in the device fabrication process via evaporation and vapor deposition.



Scheme 1 Chemical structures (A) and synthetic routes (B) for 1,4-naphthyl-CF_3 (**1**), 1,5-naphthyl-CF_3 (**2**), and Ph-CF_3 (**3**). Conditions: i) $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (2 equiv), EtOH/H_2O/Toluene, N_2, 110 °C, 12 h; ii) 9-(4-bromophenyl)-9*H*-carbazole (2.5 equiv), $Pd_2(dba)_3$ (5 mol%), $^tBu_3P$-HBF_4 (10 mol%), ^{t}BuONa (3 equiv), Toluene, N_2, 120 °C, 12 h.

2.2 Photophysical and thermal properties

The photophysical properties of the three CF_3-substituted D-A chromophores were characterized using UV-visible absorption and photoluminescence (PL) measurements, and the results are presented and summarized as shown in Figure 1 and Table 1. The

maximum absorption peak in toluene solution appears at 321, 322 and 329 nm for **1**-**3**, respectively, indicating a strong intramolecular π-π* electronic transition. It is noted that **1** and **2** shared similar absorption spectra in toluene, suggesting that the bonding site of the central unit does not affect much of the electronic transition. However, in the neat film state, the maximum absorption peak redshifted to 331, 352 and 347 nm for **1**-**3**, respectively. The emission peak of the PL spectra at 469, 463 and 461 nm with a relatively narrow FWHM of 63, 63 and 71 nm was recorded for **1**-**3** in toluene solution, respectively. A slight blueshift in the emission spectra was observed when the central motif was switched from naphthyl to phenyl group due to the decrease of the conjugation. As shown in Figures 1A-C, compared to the solution state, the PL emission spectra in neat film state were roughly the same. However, when they were doped in 4,4'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP), a blueshift was observed with the PL peaks of 459, 444 and 430 nm for **1**-**3** as shown in Figure 1D. As summarized in Table 1, they showed photoluminescence quantum yield (PLQY) of 66.9, 36.3 and 84.9% in toluene for **1**, **2** and **3**, respectively. However, in neat film state, the PLQY was reduced to 28.8, 11.2 and 34.8%, indicating that these emitters may suffer from a common aggregation-caused quenching (ACQ) effect to some extent caused by the intermolecular π–π stacking. In addition, the lifetime (τ) of 6.24, 5.61 and 3.12 ns in toluene was recorded. Accordingly, we obtained the nonradiative decay rate constants (k_{nr}) and the radiative rate constants (k_r) in solution. Compound **3** has the highest k_r and the lowest k_{nr} among the three chromophores, as a result of the highest PLQY and a relatively shorter lifetime which were observed.

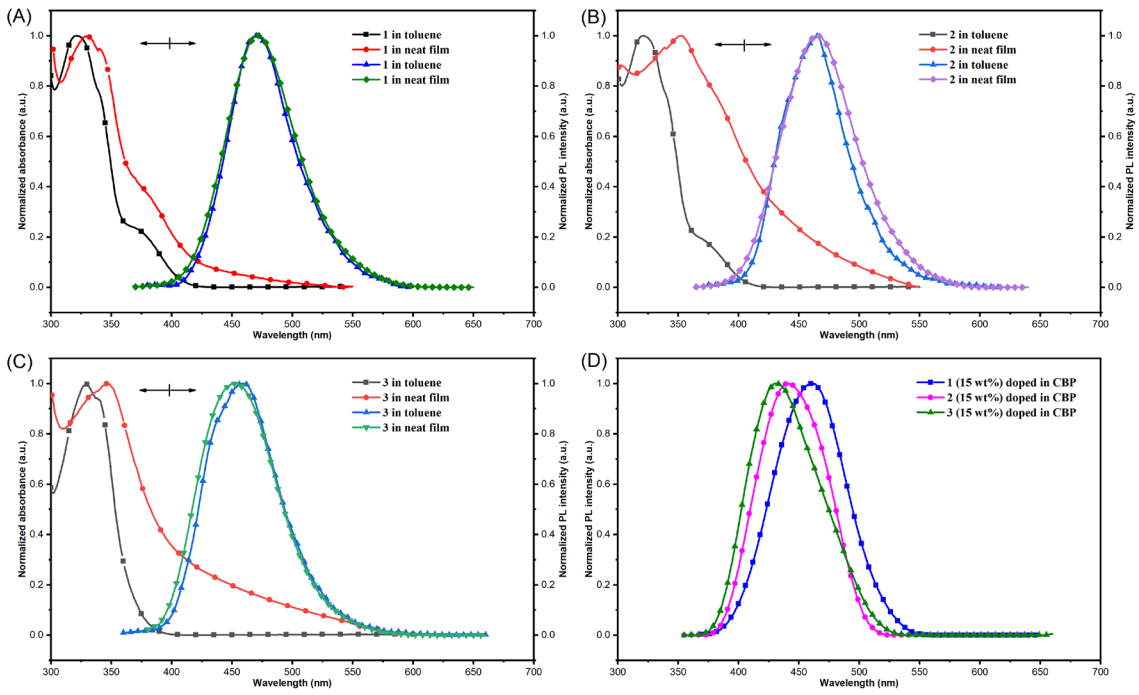


Figure 1 The UV-vis absorption and PL spectra for **1** (A), **2** (B) and **3** (C) in toluene solution and neat film at 298 K. D: PL spectra for **1-3** measured in doped CBP film (15 wt%).

Table 1. Photophysical properties for **1-3**

Emitter	λ_{max}^{abs} (^{a}/^{b} nm)	λ_{max}^{PL} (^{a}/^{b} nm)	Φ^{em} (^{a}/^{b} %)	τ^{em} (ns)^{a}	k_r/k_{nr} (10^8 s^{-1})^{c}	HOMO (^{d}/^{e} eV)	LUMO (^{d}/^{f} eV)
1	321/331	469/474	66.9/28.8	6.24	1.07/0.53	-5.14, -5.24	-1.67, -2.21
2	322/352	463/464	36.3/11.2	5.61	0.64/1.14	-5.14, -5.23	-1.66, -2.18
3	329/347	461/454	84.9/34.8	3.12	2.72/0.49	-5.16, -5.26	-1.59, -1.93

[a] Measured in toluene solution (10 μM). [b] Measured in neat film. [c] Calculated by the equation $\Phi^{em} = k_r\tau^{em} = k_r/(k_r + k_{nr})$. [d] Energy levels estimated from the DFT calculation results. [e] Energy levels estimated from CV curves. [f] Calculated from the equation LUMO = HOMO + E_g^{opt}, where E_g^{opt} is the optical energy band gap estimated from UV-vis spectra.

2.3 Theoretical calculations

To better understand the optoelectronic properties of these D-A structures at the molecular level, we performed the density functional theory (DFT) calculations using Gaussian 09 suite of programs at the B3LYP/6-31G(d) level.[38] The distributions and energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for **1**-**3** are shown in Figure 2 and Table 1. All the three compounds were observed with highly twisted conformation from the optimized geometry. As shown in Figure 2, the HOMO levels of these structures were mainly located on the bis-carbazolyl amine unit and partly on the adjacent phenyl group, while the LUMO levels were mostly distributed on the CF_3-substituted phenyl group and its adjacent phenyl or naphthyl group. Thus, the HOMO and LUMO distributions overlapped slightly on the middle benzene unit between CF_3-substituted phenyl group and bis-carbazolyl amine moiety. The partial overlap of the frontier orbitals may promote the radiative decay and result in efficient luminescence.[39] Furthermore, **1** and **2** share a very similar feature both in the HOMO and LUMO distributions and levels from DFT estimation, which may be responsible for the closely similar UV-vis absorption spectra observed in toluene solution (Figures 1A-B). In addition, the energy gap between HOMO and LUMO of **3** (3.57 eV) is larger than that of **1** (3.47 eV) and **2** (3.48 eV), which is consistent with the higher energy emission of **3** in the PL spectrum (Figure 1).

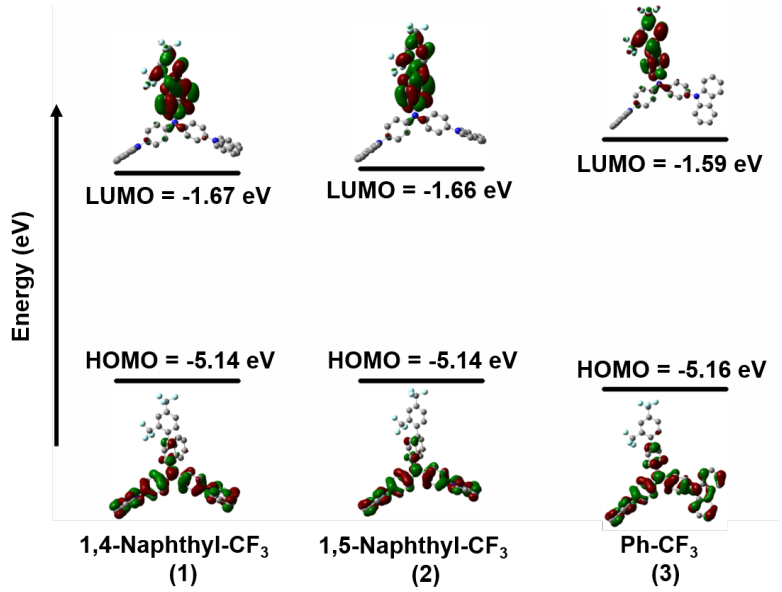


Figure 2 HOMO and LUMO energy levels and distributions for the optimized geometry of **1**-**3**.

2.4 Electrochemical properties

The cyclic voltammetry (CV) has been performed to investigate the electrochemical properties of the three fluorophores with ferrocene as the internal standard under a N_2 atmosphere. From Figure S2, reversible oxidation waves were observed for these D-A chromophores with an oxidation peak at 1.27, 1.33 and 1.34 V, which can be ascribed to the oxidation of the bis(4-(9*H*-carbazol-9-yl)phenyl)amine motifs. The HOMO was then estimated from the electrochemically determined oxidation potential versus that of ferrocene, and the LUMO was estimated from the electrochemically determined HOMO plus the optical band gap evaluated from the onset wavelength of UV-vis absorption. As shown in Table 1, the HOMO/LUMO energy levels for **1**-**3** were -5.24/-2.21, -5.23/-2.18, -5.26/-1.93 eV, respectively, which favorably agrees with the results estimated from the DFT calculations.

185 2.5 Electroluminescence properties

186 In view of the excellent blue emitting properties of these CF_3-substitued D-A
187 chromophores, we used **1**-**3** as the emitters to study their electroluminescence (EL)
188 performance, and the associated doped OLED devices (D1-D3) were fabricated. Thermal
189 vacuum deposition was chosen to fabricate the devices due to the good thermal stabilities
190 of these chromophores. The device configuration consists of the following layers:
191 ITO/HATCN (20 nm)/TAPC (40 nm)/mCP (5 nm)/EML (20 nm)/TPBi (40 nm)/LiF (1
192 nm)/Al (100 nm) as described in Figure 3A and B,[40] where ITO (indium tin oxide) and
193 Al (aluminum) worked as the anode and cathode, HATCN (dipyrazino[2,3-*f*:2',3'-
194 *h*]quinoxaline-2,3,6,7,10,11-hexacarbonitrile) and LiF (lithium fluoride) as the hole and
195 electron injection layers (HIL/EIL), 4,4'-(cyclohexane-1,1-diyl)bis(*N*,*N*-di-*p*-
196 tolylaniline) (TAPC) as the hole transporting layer (HTL), 1,3-di(9*H*-carbazol-9-
197 yl)benzene (mCP) as the electron blocking layer (EBL)[41] and 1,3,5-tris(1-phenyl-1H-
198 benzo[*d*]imidazol-2-yl)benzene (TPBi) as the electron transporting layer (ETL). Here the
199 host is 4,4'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP). The electroluminescence data are
200 presented and summarized in Figure 4 and Table 2.

201 As shown in Figure 4A, when a proper voltage was applied, the three devices D1-D3
202 doped with CBP (15 wt%) exhibited blue electroluminescence, with the maximum peak
203 of EL spectra at 453, 446 and 440 nm and a relatively narrow FWHM of 69, 65, 65 nm,
204 respectively. These EL peaks were comparable to those in the PL spectra at film state
205 with the doping concentration of 15 wt% in CBP (Figure 1D), which were 459, 444 and
206 430 nm for **1**-**3**, respectively. As depicted in Table 2 and Figure S8, these devices D1-D3

exhibited CIE chromaticity coordinates of (0.169, 0.158), (0.176, 0.134) and (0.163, 0.099), respectively, exhibiting strong blue emissions. Especially, the D3 displays the deep blue luminescence with a CIE of (0.163, 0.099), in which the CIE y value is smaller than 0.1. These blue OLEDs showed low turn-on voltages (V_{on}, at a luminance of 1 cd m^{-2}) at the range of 3.2-3.3 V as given from Figure 4B.[42] The maximum luminance (L_{max}) of devices D1-D3 can reach 10640, 7621 and 6749 cd m^{-2}, respectively, which is superior to other blue OLEDs emitting the similar light.[43] Figures 4C-D show the EQE-*L* and CE & PE-*L* curves, in which maximum CEs of 2.8, 5.0, and 4.9 cd A^{-1}; PEs of 2.9, 5.4, and 5.2 lm W^{-1} were realized for **1-3** based devices D1, D2 and D3, respectively. The device D3 gave the highest quantum efficiency among the three doped blue OLEDs with a peak EQE of 3.4%, which is consistent with the trend of PLQY. Switching the central structure from phenyl to naphthyl led to the decrease of the EQE to 2.3% probably due to the more vibrational quenching caused by the increased conjugation structure. By using the same device architecture, the nondoped OLED devices D4-D6 based on **1-3** were also investigated (Table 2 and Figure S7). Compared with the devices doped with CBP, the EL spectra of these nondoped devices were slightly redshifted. Remarkably, similar EQEs in nondoped devices were achieved compared to that of the doped devices, indicating that this family of chromophores may have the potential to be used as the host materials.

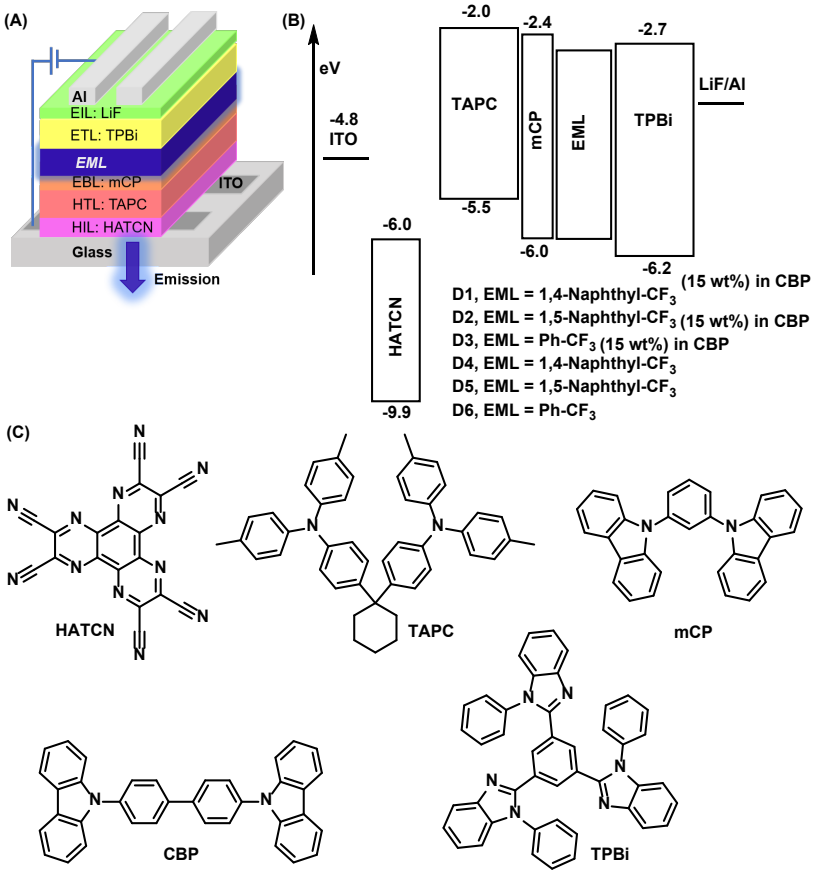


Figure 3 The architecture (A) and energy levels (B) of the devices; the chemical structures of the materials used in the devices (C).

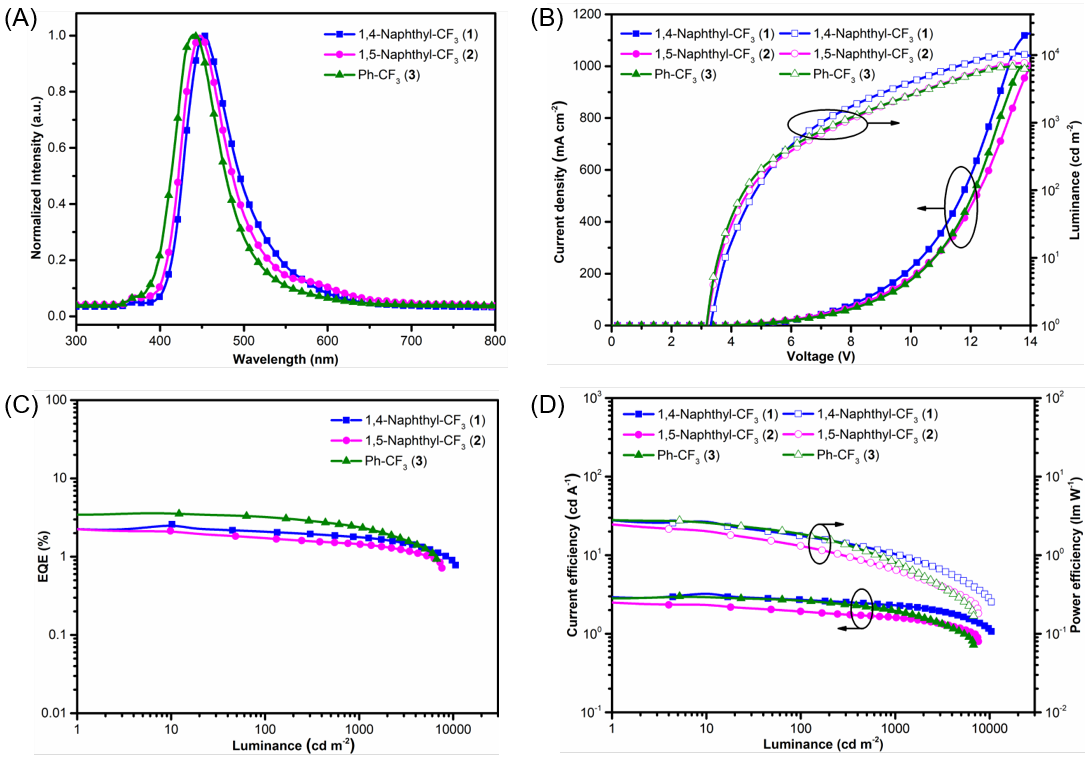


Figure 4 The performance of the three OLED devices. The EL spectra (A), current density-voltage-luminance (*J*-*V*-*L*) curves (B), EQE-luminance (C), and CE and PE vs luminance (D) for the doped devices D1-D3, respectively.

Table 2. The EL performance of doped (D1-D3) and nondoped (D4-D6) OLEDs devices

Device	λ_{max}^{EL} (nm)	FWHM (nm)	EQE[a] (%)	CE[b] (cd A^{-1})	PE[b] (lm W^{-1})	L_{max} (cd m^{-2})	V_{on} (V)[c]	CIE (x, y)
D1	453	69	2.3/2.1/1.8	2.8	2.9	10640	3.3	0.169, 0.158
D2	446	65	2.3/1.7/1.4	5.0	5.4	7621	3.2	0.176, 0.134
D3	440	65	3.4/3.2/2.4	4.9	5.2	6749	3.2	0.163, 0.099
D4	457	78	2.4/2.6/2.4	4.1	2.7	13080	4.4	0.166, 0.198
D5	447	75	2.2/2.2/2.0	3.0	2.3	7424	4.0	0.170, 0.163
D6	440	66	2.5/3.1/2.9	3.3	1.9	6659	4.9	0.167, 0.130

[a] Efficiency recorded at 1/100/1000 cd m^{-2}. [b] Maximum efficiency. [c] Turn-on voltage recorded at a luminance of 1 cd m^{-2}.

In order to further investigate the effect of the central linkage between the D and A parts, we prepared a compound (quinoline-CF_3, **4**) with quinoline as the central linker to connect the same D and A moieties. Compound **4** showed a photoluminescence peak at 516 nm and absorption peaks at 320 and 405 nm in toluene (Figure S10A). A doped OLED by using **4** as the emitter was also fabricated under the same architecture of D1 as depicted in Figure 3A, which emitted a blue-green light with a maximum EL peak at 517 nm and the CIE coordinate of (0.269, 0.497) (Figure S10E and S11). Introduction of *N*-heterocyclic quinoline motif as the central linker can significantly stabilize the LUMO level (-1.94 eV),[44] leading to a bathochromic shift both in solution PL and EL from the

OLED. The OLEDs based on our developed chromophores clearly demonstrate that the emission wavelength within the blue region could be finely tuned by changing the linker and bonding site. We believe that better blue emitters can be easily realized by combining the adopted molecular design strategy with other design strategies, such as by taking advantages of harvesting both singlet and triplet excitons.

3 Conclusion

In conclusion, we designed and synthesized three new D-A type CF_3-substituted bis((carbazol-9-yl)phenyl)amines by regulating the central motif, and their optoelectronic properties have been fully investigated. All the three emitters are demonstrated to exhibit strong blue light. Especially, the OLED device D3 using Ph-CF_3 (**3**) as the emitter exhibited a pure deep blue luminescence with the peak at 440 nm, FWHM of 65 nm and CIE coordinate of (0.163, 0.099), in which the CIE y coordinate value is notably smaller than 0.1. Our study here presents a viable organic synthesis strategy for achieving efficient deep blue emitters. By simplifying the conjugation or altering the bonding site of the linker, we realized the fine regulation of the emission wavelength within the blue region.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work.

Acknowledgements

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