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The Inductive-Effect of Electron Withdrawing Trifluoromethyl for Thermally Activated Delayed Fluorescence: Tunable Emission from Tetra- to Penta-Carbazole in Solution Processed Blue OLEDs

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The non-conjugated inductive-effect of trifluoromethyl (CF₃) is found to be a new acceptor instead of other conjugated moieties. Two blue emissive compounds 4CzCF₃Ph and 5CzCF₃Ph are synthesized by a simple catalyst free C-N coupling reaction. Solution-processed TADF devices based on 5CzCF₃Ph dopant exhibits significantly higher efficiency (11.8 cd/A, 5.2%) than 4CzCF₃Ph (1.03 cd/A, 0.67%) due to smaller ΔE_{ST} for efficient RISC.

Organic light-emitting diodes (OLEDs) have aroused intensive scientific and industrial interests for decades due to their potential applications in full color flat-panel displays and solid-state lightings.¹⁻³ According to spin statistics, the ratio of singlet and triplet excitons in an OLED is 1:3.⁴ Therefore, the internal quantum efficiency (IQE) of conventional fluorescent OLEDs is limited to 25% due to the utilization of only singlet excitons. Additionally, phosphorescent OLEDs based on triplet heavy metal complexes can achieve a maximum 100% of IQE by simultaneously harvesting both singlet and triplet excitons through intersystem crossing (ISC). However, the high cost of noble metal-based phosphorescent emitters as well as the lack of highly efficient stable pure blue phosphors spurs the exploration of new alternates.⁵

Very recently, tremendous efforts have been made to develop metal-free organic molecules which can utilize triplet excitons through efficient up-conversion, such as the mechanism of triplet-triplet annihilation (TTA) and thermally activated delayed fluorescence (TADF).⁶ The maximum IQE for TADF can reach 100% due to the efficient reverse intersystem crossing (RISC) from triplet to singlet state. Thus, a small energy gap between the lowest singlet and triplet state (ΔE_{ST}) is essential for TADF emitters to ensure the occurrence of RISC. The emission process for efficient TADF materials is dominated

by intramolecular charge transfer (ICT) transitions *via* triplet excitons, which requires the effective separation between the highest occupied natural transition orbitals (HONTO) and lowest unoccupied natural transition orbitals (LUNTO) at both singlet and triplet excited state.^{7,8} Therefore, to meet the requirements of ICT and smaller ΔE_{ST} , the simultaneous comprising of electron-donating and electron-withdrawing components through twisted structure is unavoidably necessary for the judicious molecular design of TADF materials. In general, electron-donating units include aryl amines like carbazole,^{5,8-14} diphenylamine¹¹ and triphenylamine,^{12,15,16} or phenoxazine,^{5,7,10,17,18} phenothiazine,¹⁹ etc. as well as their derivatives. On the other hand, various conjugated electron-withdrawing molecular building blocks have been extensively demonstrated for organic TADF materials, including triazine,^{7,10,17} oxadiazoles,^{15,18} dicyanobenzenes,^{9,13,14} sulfones,¹¹ benzophenones,⁵ thioxanthone,¹² heptazine,¹⁶ cyanopyridine,⁸ carbonyl⁵ etc. However, electron-withdrawing moieties based on non-conjugated elements have never been reported.

Herein, we have for the first time introduced electron-withdrawing trifluoromethyl (CF₃) as acceptor unit to TADF material through the electron-inductive-effect instead of other reports on conjugated-effect. CF₃ is a strong electron-withdrawing group which has been widely applied as alkyl substituent for ligands of phosphorescent heavy metal complexes in OLEDs.²⁰ Two blue emissive trifluoromethylbenzene containing compounds (4CzCF₃Ph and 5CzCF₃Ph) were designed and synthesized through our previously presented simple one-step catalyst free C-N coupling reaction by using multi-fluoro-substituted trifluoromethylbenzene and carbazole as the starting materials.^{8,21} Their optoelectronic properties can be largely tuned from *tetra*- to *penta*-carbazole substitution. Solution-processed devices based on 5CzCF₃Ph as a TADF dopant exhibited significantly higher efficiency than 4CzCF₃Ph due to lower ΔE_{ST} for efficient reverse ISC.

Scheme 1 illustrates the synthetic routes for 4CzCF₃Ph and 5CzCF₃Ph. Both compounds can be synthesized through a

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simple one-step catalyst-free aromatic nucleophilic substitution reaction by using *tetra*- or *penta*-fluorotrifluoromethylbenzene as the electrophile and carbazole as the nucleophile. The yield for 4CzCF₃Ph was as high as 80%, which reduced to 40% for 5CzCF₃Ph due to the distinct steric hindrance of bulk carbazole substitution at all aryl positions in trifluoromethylbenzene. It should be noted that by using the relatively low-cost multi-fluorobenzene (*tetra*- or *penta*-) which was activated through the electron-withdrawing CF₃ as electrophile for the C-N coupling reaction, the synthetic methodology in this work is superior to normal metal catalyzed Ullman reactions,²² due to the lack of *tetra*- and *penta*-halogenated trifluoromethylbenzene (Br or I) as well as the very low yields especially upon *tetra*- and *penta*-carbazole substitution.

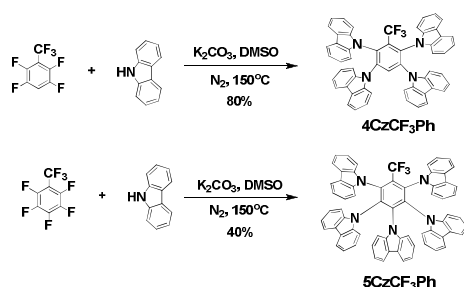
Both compounds exhibited good thermal stability owing to their rigid bulky molecular structure. The decomposition temperatures (T_d , corresponding to 5% weight loss) determined from thermogravimetric analysis (TGA) for 4CzCF₃Ph and 5CzCF₃Ph are 417 and 455°C, respectively. (Figure S1, Supporting Information). The melting temperature (T_m) for 4CzCF₃Ph is as high as 303°C. Unfortunately, the glass transition temperatures (T_g) for both compounds have not been detected.

The UV-vis absorption and photoluminescence (PL) spectra of the new compounds were studied in both dichloromethane solution and film state, and the key data were summarized in Table 1. As shown in Figure 1, from their absorption spectra, two strong bands at 290 and 335 nm can be observed. The absorption at ~290 nm can be ascribed to $n-\pi^*$ transition of carbazole, while the 335 nm bands belongs to the $\pi-\pi^*$ transition which was significantly enhanced by intensity at film state. In addition, the longer wavelength absorption (over 350 nm) of intramolecular charge transfer transition from the electron-donating carbazole to electron-withdrawing trifluoromethylbenzene was also increased by intensity and red-shifted at film state compared in solution. 4CzCF₃Ph exhibited blue emission with λ_{max} at 440 nm in CH₂Cl₂ and 445 nm at film state. However, 5CzCF₃Ph displayed an obvious red-shifted emission, with λ_{max} at 481 nm in CH₂Cl₂ and 495 nm

compounds. Furthermore, the PL quantum yield (Φ) for 4CzCF₃Ph in toluene was measured to be 13 and 14% at ambient and oxygen free conditions, respectively. However, the values for 5CzCF₃Ph increased to 24 and 43%. The singlet (E_s) and triplet energy (E_T) were determined by the highest-energy vibronic sub-band of the 77 K fluorescence and phosphorescence spectra, respectively (Figure 2). The two compounds exhibited nearly the same E_T values, with 2.78 eV for 4CzCF₃Ph and 2.80 eV for 5CzCF₃Ph. However, significantly higher E_s of 3.02 eV was observed for 4CzCF₃Ph, which reduced to 2.82 eV for more carbazole containing 5CzCF₃Ph. Therefore, relatively lower singlet-triplet energy gap (ΔE_{ST}) of 0.02 eV allowing for efficient reverse ISC was achieved in 5CzCF₃Ph compared to 0.24 eV of 4CzCF₃Ph, suggesting 5CzCF₃Ph might be a better TADF material. As can be seen from the above mentioned results, the photophysical properties between 4CzCF₃Ph and 5CzCF₃Ph can be largely tuned by increasing only one electron-donating carbazole unit to the central phenyl ring.

From the ground state highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) distributions (Figure 3), the LUMO are mainly localized through the electron-withdrawing trifluoromethylbenzene moiety for both compounds. However, slight difference was observed on the distribution of HOMO, which was delocalized through the peripheral *tetra*-carbazole and the central phenyl ring for 4CzCF₃Ph and only peripheral *penta*-carbazole for 5CzCF₃Ph.

The introduction of more electron-donating carbazole in 5CzCF₃Ph destabilizes and rises the molecular orbitals. Thus, the calculated HOMO levels of 5CzCF₃Ph (5.40 eV) is higher than 4CzCF₃Ph (5.48 eV). From the calculation on the spin density distribution, HONTO and LUNTO triplet excited state for 4CzCF₃Ph were well controlled and mainly located at electron-donating carbazole moiety as well as the central phenyl ring. However, obvious disparity on the distribution of triplet excited states were observed for 5CzCF₃Ph, with HONTO delocalized mainly at the central phenyl and partially at peripheral electron-donating carbazole, while LUNTO mainly at the electron-withdrawing CF₃ substituted central phenyl ring. The partial separation of HONTO and LUNTO triplet excited state between the electron donating and accepting moieties



Scheme 1 Synthetic routes for the new compounds 4CzCF₃Ph and 5CzCF₃Ph.

at film state, respectively. Besides, the microsecond delayed transient decay time for 4CzCF₃Ph and 5CzCF₃Ph in degassed toluene were measured to be 9.31 and 15.33 μ s, respectively (Figure S2), indicating potential TADF characters for both

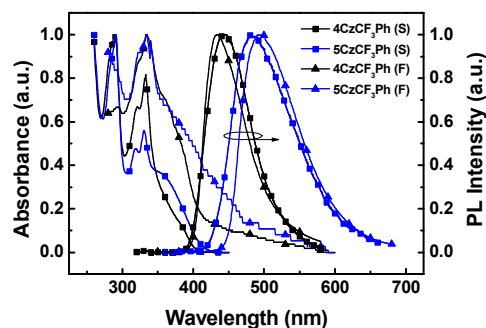


Fig. 1 Normalized UV-vis absorption and PL spectra of 4CzCF₃Ph and 5CzCF₃Ph in CH₂Cl₂ solution (S) and at thin films (F).

Table 1 Physical data for 4CzCF₃Ph and 5CzCF₃Ph

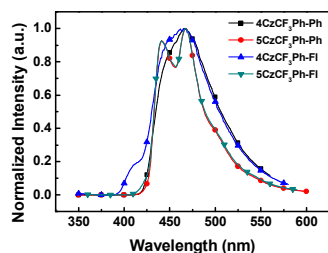
Compound	$T_d/T_g/T_m$ (°C)	λ_{abs}^a (nm)	λ_{max}^a (nm)	λ_{max}^b (nm)	E_g^c (eV)	E_s^d (eV)	E_T^d (eV)	HOMO/LUMO ^e (eV)	HOMO/LUMO ^f (eV)	τ^g (μ s)
4CzCF ₃ Ph	417/-/303	288,321,332	440	445	2.98	3.02	2.78	-5.48/-1.71	-5.60/-2.62	9.31
5CzCF ₃ Ph	455/-/-	290,319,330	481	495	2.82	2.82	2.80	-5.40/-1.88	-5.57/-2.75	15.33

^a Measured in CH₂Cl₂ solution at room temperature. ^b Measured at film state. ^c Optical bandgap was calculated from the absorption edge of spectra. ^d Singlet and Triplet energy was calculated from low temperature (77 K) fluorescence and phosphorescence spectra, respectively. ^e Values from DFT calculations. ^f HOMO was measured by CV, LUMO calculated from the difference between optical bandgap and HOMO. ^g Lifetime measured in degassed toluene solution.

for 5CzCF₃Ph indicates a smaller ΔE_{ST} , which is the distinct key role for the emission process of a TADF material.^{7,8} Thus, the oxygen-sensitive PL quantum yield, the stronger ICT at triplet state, and the smaller ΔE_{ST} as well as the microsecond scale emission lifetime indicates 5CzCF₃Ph as a typical TADF material.

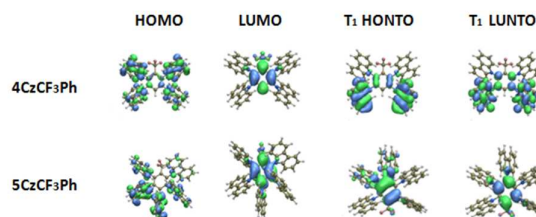
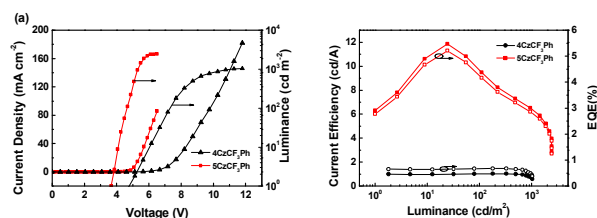
The electrochemical properties for 4CzCF₃Ph and 5CzCF₃Ph were measured by cyclic voltammetry (CV). Both compounds showed quasi-reversible oxidation and irreversible reduction behavior (Figure S3). Their HOMO levels determined from the onset of oxidation curves were 5.60 and 5.57 eV for 4CzCF₃Ph and 5CzCF₃Ph, respectively. From the difference between HOMO and optical bandgaps, the LUMO levels were calculated to be 2.62 and 2.75 eV, respectively. And the experimental data are in good agreement with the theoretical results.

In order to investigate the device performance of the newly designed two compounds of 4CzCF₃Ph and 5CzCF₃Ph, solution-processed TADF devices were fabricated with the structure of ITO/PEDOT:PSS (40 nm)/mCP:4CzCF₃Ph or 5CzCF₃Ph (10 wt%, 40 nm)/TmPyPB (60 nm)/LiF (0.8 nm)/Al (100 nm). Among, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and LiF was used as the hole- and electron-injecting materials, respectively, 1,3,5-tri(m-pyrid-3-ylphenyl)benzene (TmPyPB) acted as the electron transporting material. The widely used high triplet (2.9 eV) host 1,3-bis(*N*-carbazolyl)benzene (mCP)²³ doped with 10 wt% of 4CzCF₃Ph (Device A) or 5CzCF₃Ph (Device B) were spin-coated as the emissive layer. The luminance-voltage-current density (*L-V-J*) characteristics, efficiency *versus* luminance curves and

**Fig. 2** Normalized fluorescence (FL) and phosphorescence (Ph) spectra in toluene at 77 K.

the electroluminescence (EL) spectra of the two devices are shown in Figure 4 and S4. The key device data are summarized in Table 2. Device A based on 4CzCF₃Ph exhibited blue emission with λ_{max} at 464 nm, which was bathochromic to 484 nm in device B with 5CzCF₃Ph as dopant. The red-shifted emission behavior is consistent with their photoluminescence.

5CzCF₃Ph based device B exhibited significantly better EL performance than device A. A lower turn on voltage of 3.9 V, maximum luminance of 2436 cd cm⁻², maximum current efficiency of 11.8 cd A⁻¹ and external quantum efficiency of 5.2% were achieved in 5CzCF₃Ph containing device B. These values for 4CzCF₃Ph based device A was 4.8 V, 1032 cd cm⁻², 1.03 cd A⁻¹ and 0.63%, respectively. The lower turn-on voltage of device A might be ascribed to the slightly higher HOMO levels of 5CzCF₃Ph which allowed for lower hole-injection barrier directly from PEDOT:PSS (5.2 eV)²⁴ to the TADF dopant in the emissive layer. Besides, the significantly higher device efficiency for 5CzCF₃Ph can be mostly attributed to its remarkably smaller ΔE_{ST} for efficient reverse ISC to better utilize the triplet excitons in the devices.

**Fig. 3** Ground state HOMO and LUMO, triplet excited state HONTO and LUNTO distributions of 4CzCF₃Ph and 5CzCF₃Ph from theoretical calculation.**Fig. 4** (a) *L-V-J* characteristics, (b) current efficiency and external quantum efficiency (EQE) *versus* luminance (*L*) curves of device A and B.**Table 2** Electroluminescence characteristics of the devices

Device	Dopant	V_{on}^a (V)	L_{max}^b (cd m ⁻²)	η_c^c (cd A ⁻¹)	η_{ext}^d (%)	CIE ^e (x,y)
A	4CzCF ₃ Ph	4.8	1032	1.03	0.67	(0.17,0.18)
B	5CzCF ₃ Ph	3.9	2436	11.8	5.2	(0.21,0.33)

^a Turn-on voltage. ^b Maximum luminance. ^c Maximum current efficiency. ^d Maximum external quantum efficiency. ^e Recorded at 8V

In conclusion, the non-conjugated trifluoromethyl has been found as a new electron-withdrawing building block for TADF materials. Two blue emitter 4CzCF₃Ph and 5CzCF₃Ph have been

designed and synthesized through a simple one-step catalyst free C-N coupling reaction by using low-cost starting materials. From both experimental and theoretical investigations, we have found that by variation on the number of carbazole substituent (from *tetra-* to *penta-*) in trifluoromethylbenzene, tunable optoelectronic properties can be achieved. Solution processed blue emitting devices by using 4CzCF₃Ph and 5CzCF₃Ph as TADF dopant, exhibited maximum current efficiency of 11.8 and 1.03 cd A⁻¹, respectively. The significantly better EL performance of 5CzCF₃Ph can be contributed to its relatively smaller ΔE_{ST} which promotes more efficient reverse ISC. Besides previous electron-deficient units such as heterocyclic aromatic rings or sulfone or carbonyl based electron-conjugated-effect, the electron-inductive-effect of non-conjugated units also provides an extra electron-withdrawing approach for TADF materials.

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