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Dimers with thermally activated delayed fluorescence (TADF) emission in non-doped device[†]

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Two novel TADF molecules, with donor#1- σ -donor#2- π -acceptor (D1- σ -D2- π -A) conformation, were designed and synthesized through-bond charge transfer (TBCT) and through-space charge transfer (TSCT). These two materials differ only in the D1 groups with triphenylamine for **SFCCN** and 10-phenyl-10*H*-phenoxazine for **SFCCNO**. Due to the unconjugated linkage, both materials showed very similar emission to that from D2- π -A TBCT effect in dilute solution. **SFCCNO** can form dimers at the aggregation state and exhibit intermolecular D1/A TSCT emission because of the planar D1 conformation. Therefore, a non-doped device based on **SFCCNO** exhibited efficiencies of 12.9% at 100 cd m⁻² and 10.4% at 1000 cd m⁻², which are much higher than the **SFCCN** based device.

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Introduction

In recent years, through the constant efforts of research groups across the world, thermally activated delayed fluorescence (TADF) emitter-based organic light-emitting diodes (OLEDs) have gained tremendous achievements.^{1–4} A basic description of the TADF mechanism is as follows: in a TADF emitter, the single energy (S₁) and triplet energy (T₁) levels are strongly coupled, which allows intersystem crossing (ISC) between the two levels.^{5,6} In this regard, the TADF emitter has much smaller energy difference between the S₁ and T₁ (ΔE_{ST}) levels than typical organic molecules, which enables reverse intersystem crossing (RISC) to occur. This strategy can provide a new up-conversion avenue to harvest the additional 75% triplets and thus achieve 100% internal quantum efficiency (IQE) in theory.^{7–9}

According to TADF designed strategy, the alignment of electron donor (D)/acceptor (A) and the charge transfer (CT) process between them are very important, and normally, the HOMO dispersed at the donor and LUMO located on the acceptor should have a small overlap to obtain a small $\Delta E_{\rm ST}$.^{10,11}

In many reports, the D/A blocks were linked in one conjugated molecule with twisted configuration to minimize the $\Delta E_{\rm ST}$ and gave a covalent through-bond charge transfer (TBCT) emission.^{12,13} This is a typical paradigm for achieving TADF, but recently, researchers have found that through-space charge transfer (TSCT) model can be an alternative.^{14–17} A representative TSCT model is D/A complex, or known as exciplex, which constitutes a small $\Delta E_{\rm ST}$ corresponding to the intermolecular spatial CT process¹⁸ (Scheme 1a). Chemists have further been trying to merge D/A blocks together in one molecule with an unconjugated linkage, and an intramolecular spatial CT would lead to TADF emission if there is a short D/A distance in space (Scheme 1b and c). These new approaches undoubtedly enrich the structural diversity of TADF materials.¹⁹

In this study, a new configuration called D1- σ -D2- π -A for TADF is constructed to exhibit intermolecular CT emission at the aggregation state.^{20,21} The two target molecules, SFCCN and SFCCNO, have very similar structure except that the latter one has one more electron-donating oxygen to strengthen the donor strength of D1 (SFCCN: D1 = triphenylamine; SFCCNO: D1 = oxygen-bridged triphenylamine; D2 = carbazole, A = 4,6-diphenyl-1,3,5-triazine). As shown in Scheme 1d, the intramolecular electronic interaction between D1 and A are intercepted because: (i) the TBCT path is blocked by the unconjugated spiro-carbon, (ii) the intramolecular TSCT path is also impossible due to the long D1/A distance and unfavorable D1/A conformation.²²⁻²⁵ By contrast, D2/A coupling is conspicuous for the conjugative D2– π –A linkage and the distance between them is shorter than that of D1/A in this special molecular design. However, the CT emission from D1 to A of SFCCNO can be

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Scheme 1 (a) Charge transfer in two different molecules; (b) charge transfer in a single molecule; (c) charge transfer in two molecules with the same structure; (d) CT emissions in different states between SFCCN and SFCCNO; route 1 = Intramolecular through-bond charge transfer (TBCT) emission; route 2 = Blocked intra-TBCT path in solution for long distance in D1/A; route 3 = Inter-molecular through-space charge transfer (TSCT) emission in aggregation state.

clearly observed as compared to the referential pristine **SFCCN** film. Non-doped TADF OLEDs were constructed and the **SFCCNO** based device exhibits external quantum efficiencies (EQEs) of 12.9% at 100 cd m⁻² and 10.4% at 1000 cd m⁻². Our novel non-heterodimeric emissive system has a comparable device performance to those OLEDs using conventional D/A complexes with dimeric inter-TSCT emission.^{26–29}

Experimental section

The molecule (3,3'), (4,4') and 5 were synthesized according to our previous work.^{16,30}

3'-(9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazol-3-yl)-10-phenyl-10*H*-spiro[acridine-9,9'-fluorene] (SFCCN)

A mixture of 3-bromo-9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazole (1.30 g, 2.35 mmol), 10-phenyl-3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-spiro[acridine-9,9'-fluorene] (1.50 g, 3.25 mmol), (molecule 4 and 5) Pd(PPh₃)₄ (136 mg) and Na₂CO₃ (1.24 g, 11.74 mmol, water 12.5 mL) in THF (50 mL) was heated to reflux under argon and stirred for 24 hours. The reaction mixture was then dissolved in ethyl acetate and washed thrice with water (3 × 30 mL). The combined organic layer was dried with Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether (PE)/dichloromethane (DCM) (7:3 v/v) as an eluent to obtain a white product and weighed (1.72 g, 83%). ¹H NMR (600 MHz, Chloroform-*d*) δ 9.06 (d, *J* = 8.6 Hz, 2H), 8.85 (d, *J* = 1.4 Hz, 4H), 8.47 (s, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.14 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 1.8 Hz, 2H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.73 (t, J = 7.8 Hz, 2H), 7.68–7.57 (m, 10H), 7.54–7.53 (m, 3H), 7.50–7.46 (m, 2H), 7.42–7.43 (m, 1H), 7.37 (d, J = 7.0 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 6.95 (t, J = 1.5 Hz, 2H), 6.62 (t, J = 1.0 Hz, 2H), 6.53 (d, J = 1.6 Hz, 2H), 6.39 (d, J = 1.2 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 171.83, 170.93, 156.92, 155.09, 141.58, 141.47, 141.37, 141.13, 140.91, 139.90, 139.92, 139.88, 139.24, 136.15, 135.02, 134.17, 132.68, 131.23, 131.09, 130.71, 129.03, 128.73, 128.50, 128.46, 127.88, 127.80, 127.64, 127.23, 126.66, 126.39, 125.97, 125.86, 124.87, 124.34, 123.94, 120.60, 120.54, 120.00, 119.08, 118.76, 114.66, 110.21, 110.11, 56.67. MS (EI) m/z: 879.271 [M⁺]. Calcd for C₆₄H₄₁N₅:880.067.

3-(9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazol-3yl)spiro[fluorene-9,9'-quinolino[3,2,1-*kl*]phenoxazine] (SFCCNO)

A mixture of 3-bromo-9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazole (1.50 g, 2.71 mmol), 3-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)spiro[fluorene-9,9'-quinolino[3,2,1-*kl*]phenoxazine] (1.78 g, 3.25 mmol),(molecule 4' and 5) Pd(PPh₃)₄ (157 mg) and Na₂CO₃ (1.44 g, 13.55 mmol, water 12.5 mL) in THF (50 mL) was heated to reflux under argon and stirred for 24 h. Then the reaction mixture was dissolved in ethyl acetate and washed thrice with water (3 × 30 mL). The combined organic layer was dried with Na₂SO₄, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using PE/DCM (7:3 v/v) as an eluent to obtain a white product and weighed (2.01 g, 85%). ¹H NMR (600 MHz, Chloroform-*d*) δ 9.04 (d, *J* = 18.9 Hz, 2H), 8.82 (d, *J* = 7.3 Hz, 4H), 8.54 (s, 1H), 8.29 (d, *J* = 24.9 Hz, 1H), 8.19 (d, *J* = 20.9 Hz, 1H), 8.02 (s, 1H), 7.85 (d, *J* = 34.8 Hz, 4H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.62 (m, 10H), 7.44 (d, J = 21.9 Hz, 2H), 7.39–7.29 (m, 2H), 7.19 (m, 1H), 7.06 (m, 4H), 6.82 (t, J = 7.6 Hz, 1H), 6.77 (m, 1H), 6.67 (t, J = 7.9 Hz, 2H), 6.25 (d, J = 42.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 171.82, 170.90, 148.54, 146.78, 141.53, 140.90, 137.12, 136.13, 135.04, 133.94, 132.68, 131.15, 130.70, 130.52, 129.32, 129.29, 129.02, 128.72, 127.19, 126.65, 126.42, 123.97, 123.78, 123.44, 122.96, 120.63, 120.28, 118.98, 117.60, 116.94, 115.32, 114.22, 110.12, 56.90. MS (EI) m/z: 893.284 [M +]. Calcd for C₆₄H₃₉N₅O: 894.050.

Results and discussion

Synthesis and characterization

The detailed synthetic routes of the target molecules **SFCCN** and **SFCCNO** are depicted in Scheme 2. Intermediates 3 and 3' were synthesized by a two-step continuous reaction under the same conditions. Correspondingly, intermediates 4 and 4' were synthesized *via* the Miyaura borylation reaction. Resultantly, **SFCCN** and **SFCCNO** were successfully obtained in good quantity through the Suzuki–Miyaura coupling reaction with 3-bromo-9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazole and respective intermediate reagents. The molecules **SFCCN** and **SFCCNO** were fully characterized by ¹H NMR, ¹³C NMR and MALDI-TOF with their spectral detail mentioned in the ESI[†] (Fig. S1–S6).

Thermal property

Thermogravimetric analysis (TGA) was performed to study the thermal stability of **SFCCN** and **SFCCNO**. As shown in Table 1, the decomposition temperatures (T_d , at 5% weight-loss) are 554 and 491 °C for **SFCCN** and **SFCCNO**, respectively, which indicate that both materials have good thermal stability. Moreover, they have relatively high glass transition temperature (T_g) of 264 and 212 °C, respectively (Fig. S7 and S8, ESI†).

Photophysical properties

The photophysical properties of **SFCCN** and **SFCCNO** were recorded at room temperature in toluene solution (10^{-5} M) . Phosphorescence spectra were measured at a low temperature using the same solvent. **SFCCN** and **SFCCNO** show very similar

Table 1 Physical properties of SFCCN and SFCCNO

	$T_{\rm d}/T_{\rm g}^{\ a} \left(^{\circ} {\rm C}\right)$	$\lambda_{\max}^{b}(nm)$	HOMO/LUMO (eV)	$\Delta E_{\mathrm{ST}}^{c}$ (eV)
SFCCN	554/264	421	-5.15/-2.09	0.23
SFCCNO	491/212	420	-5.11/-2.04	0.24

 a $T_{\rm d}$ obtained from TGA measurements and $T_{\rm g}$ obtained from DSC measurements. b PL spectra measured in a toluene solution. c $\Delta E_{\rm ST}$ estimated from the experimental S₁ and T₁ energies.

fluorescence spectra with an emission peak at 431 and 428 nm, respectively (Fig. 1a). Apart from that, another TADF compound called SFCC, synthesized in our previous work, with the same backbone also exhibited a very similar peak at 434 nm.¹⁶ This was not a coincidence but indicated that the TBCT emission mainly originated from the conjugated D2-A interaction while the D1/A TSCT interaction can be ignored because of the unconjugated linkage and long distance between them. However, in the aggregation state, the fluorescence spectra for SFCCNO (512 nm) showed a significant red-shift as compared to the SFCCN (458 nm) (Fig. 1b). The PL spectrum (493 nm) of the SFCCN: SFCCNO (1:1) mixed film is also shown in Fig. S9 (ESI[†]). Thus, we preliminarily hypothesize that SFCCNO has an additional oxygen to strengthen the electron donating capability in D1, which might contribute to an apparent redshift in the photoluminescence process (intermolecular TSCT emission from D1 to A), and the details will be discussed below. Besides, fluorescence spectra of bis[2-(diphenylphosphino)phenvl] ether oxide (DPEPO) films doped with SFCCN and SFCCNO (5 wt% to 30 wt%) are shown in Fig. S10 in ESI.[†] Photoluminescence quantum yields (PLQYs) of SFCCNO in the DPEPO host matrix under nitrogen atmosphere were measured. As the interaction between SFCCNO molecules is strictly suppressed by the low doping ratio, 5 wt% SFCCNO-doped film exhibits a low PLQY of 56% due to the low radiative local excited states. With an increase in the doping ratio, more effective intermolecular TSCT transition becomes the critical radiative decay channel and a PLQY of 81% was observed for 30 wt% SFCCNO doped film. More importantly, the SFCCNO neat film still exhibits a comparable PLQY of 71%, which indicates that intermolecular TSCT transition would significantly suppress



Scheme 2 Synthetic routes to target molecules SFCCN & SFCCNO.



Fig. 1 The fluorescence spectra of SFCCN and SFCCNO (a) in toluene solution and (b) as a neat film; (c and d) UV-Vis absorptions (300 K) in CH₂Cl₂, fluorescence spectra (77 and 300 K) and phosphorescence spectra (77 K) of SFCCN and SFCCNO in toluene.

the concentration quenching effect. We further measured UV-Vis absorption (300 K) in CH₂Cl₂, fluorescence spectra (77 and 300 K) and phosphorescence spectra (77 K) in toluene for **SFCCN** and **SFCCNO**, respectively, as shown in Fig. 1c and d. $\Delta E_{\rm ST}$ of **SFCCN** (0.23 eV) and **SFCCNO** (0.24 eV) were obtained accordingly and their physical properties are summarized in Table 1. Besides, Fig. 2 shows the transient PL decay spectra of **SFCCN** (30 wt%) and **SFCCNO** (30 wt%) in the film state with two decay processes in nanosecond and microsecond scales. It

can be seen that the delay times of 30 wt% doped **SFCCN** and 30 wt% doped **SFCCNO** were 0.3 μ s and 5.8 μ s, respectively. **SFCCNO** showed nearly 20 times delay effect compared to the **SFCCN**. Fig. S11 (ESI[†]) shows the transient PL decay spectra of **SFCCNO** neat film and doped **SFCCNO** at a lower concentration. The **SFCCNO** neat film exhibits an obvious delay time of 2.1 μ s, which is much longer than the 5% doped **SFCCNO** (0.02 μ s). It is then confirmed that more obvious TADF properties can be obtained under increased doping ratio.



Fig. 2 Transient photoluminescence spectra of DPEPO: SFCCN (30 wt%) and DPEPO: SFCCNO (30 wt%) in film state.

Electrochemical properties

From cyclic voltammetry (CV) tests along with the optical bandgaps calculated from the UV-vis spectra, the HOMO/LUMO energy levels were estimated to be -5.15/-2.09 eV and -5.11/-2.04 eV for **SFCCN** and **SFCCNO**, respectively (Table 1 and Fig. S12, ESI†). These HOMO values indicate that the introduction of oxygen can merely slightly enhance the donor strength. Thus, the electron-donating ability of the two donors should be different. Besides, the stronger electron-donating strength of 10-phenyl-10*H*-phenoxazine in **SFCCNO** might not be the real cause for the unexpected fluorescence red-shift in the film state.

Theoretical calculations

We found the answer through DFT calculations (finished at PBE0/def2-SVP and TD-PBE0/def2SVP level with Grimme's D3BJ empirical dispersion correction). Only **SFCCNO** can form a dimer by the stacking of the donor moiety from one and the acceptor moiety from the other molecule. It is mainly because oxygen introduction can planarize the D1 group, which facilitates face-to-face D/A spatial interaction and forms TSCT. The hole is distributed on the donor group and the electron is distributed on the acceptor group for both the adiabatic S₁ and T₁ states, as shown in Fig. 3. The small hole-electron centroid distance and the large hole-electron spatial separation lead to large red shift of the emission wavelength (Table S1, ESI[†]). Besides, more DFT calculations and the frontier orbital levels of **SFCCN** and **SFCCNO** in their ground state are all shown in Tables S2 and S3 and Fig. S13 (ESI[†]), respectively.

Electroluminescence properties

To evaluate the TADF materials and further confirm the conjecture, we fabricated a doped OLED device with the following structure: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)/ mCP (10 nm)/DPEPO: **SFCCN/SFCCNO** (X wt%, 20 nm)/DPEPO

(5 nm)/TmPyPB (40 nm)/Liq (2 nm)/Al (120 nm) (Fig. 4a). The molecular structures of other materials applied in this device are shown in Fig. 4b. Here, indium tin oxide (ITO) and Al acted as the anode and cathode, respectively. Dipyrazino [2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolatolithium (Liq) were the hole- and electron-injecting layers. Di[4-(N,N-ditolyl-amino)-phenyl] cyclohexane (TAPC) and tris(4-(9H-carbazol-9-yl) phenyl) amine (TCTA) were employed as the hole transport layer with favorable hole mobility. 1,3-Bis(Ncarbazolyl)benzene (mCP) was used as the electron-blocking layer for efficient exciton utilization. DPEPO was applied as the host due to its high triplet energy. 1,3,5-Tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) was the electron-transporting layer. 5 nm DPEPO acted as the exciton-blocking layer to confine the excitons, which helped control the charge recombination. The device performances of two TADF emitters at low concentration (5 wt%) to high concentration (30 wt%) are all shown in Table S4 (ESI⁺). As expected, at the concentration of 5 wt%, both devices exhibited the same emission at 460 nm, wherein the dimer cannot be formed at such a low concentration. However, in 30 wt% doped devices, the EL emission peaks at 516 nm for SFCCNO (with 12.9% EQE) and 472 nm for SFCCN (with 10.0% EQE) are obtained, which confirmed what we speculated. Also, Fig. S14 (ESI⁺) exhibits progressive red-shifts of EL spectra under concentrations varying from 3 to 30 wt%.

Then, we finally fabricated non-doped devices by only changing the emissive layer. The EQE of the non-doped device based on **SFCCN** dramatically decreased to 3.8% because of serious concentration quenching effect. Remarkably, the non-doped device based on **SFCCNO** had an obviously higher efficiency, which exhibited a maximum EQE of 13.0% and maximum current efficiency of 41.0 cd A^{-1} (Table 2). The device performance comparison between the doped and non-doped OLEDs is shown in Fig. 4c and d. In the aggregation state, **SFCCNO** dimeric CT emission is formed with two functional moieties



Fig. 3 Calculated hole and electron distribution of the adiabatic S1 and T1 states of SFCCN, SFCCNO and SFCCNO dimer.



Fig. 4 (a) Energy level diagrams of devices; (b) chemical structures of other materials applied in the OLED devices; (c) EQE-luminance characteristics of the doped and non-doped devices; (d) PE-current density characteristics of the doped and non-doped devices.

 Table 2
 Electroluminescence performance of the doped and non-doped devices

	Doping ratio (%)	V^{a}_{on} (V)	Peak ^b (nm)	$\begin{array}{c} {\rm CE}^c \\ ({\rm cd} \ {\rm A}^{-1}) \end{array}$	EQE^{d} (%)	$\operatorname{CIE}^{b}(X, Y)$
SFCCN	30	3.8	472	15.1	10.0/7.3/3.1	(0.16, 0.23)
	100	3.8	472	8.0	3.8/3.4/2.0	(0.20, 0.26)
SFCCNO	30	3.7	516	36.5	12.9/12.5/8.8	(0.29, 0.48)
	100	3.6	520	41.0	13.0/12.9/10.4	(0.32, 0.55)

^{*a*} Driving voltage at 0.2 mA cm⁻². ^{*b*} Measured at a current density at 5 mA cm⁻². ^{*c*} Maximum current efficiency. ^{*d*} Maximum EQE, at 100 cd m⁻² and at 1000 cd m⁻².

approaching each other. Furthermore, the device had low efficiency roll-off in which the EQE merely drops from 12.9% to 10.4% for device luminance increasing from 100 cd m^{-2} to 1000 cd m^{-2} . The emission is not from the TADF molecule itself but from the intermolecular TSCT species, which is very similar

Table 3	Summary of related TA	DF OLEDs based on	exciplex emitters
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Emitters	$\lambda_{\mathrm{PL}} \left(\mathrm{nm} \right)$	ϕ_{film} (%)	$V_{\rm ON}$ (V)	EQE _{max} (%)	Ref.
SFCCNO	520	71	3.6	13.0	This work
CDBP:POT2T	476	51	2.5	13.0	31
CPF:POT2T	/	41	2.2	9.5	32
mCP:POT2T	472	/	/	8	33
TCTA/3P-T2T	554	/	2.0	7.8	34
<i>m</i> -MTDATA: PBD	540	20	/	2	35
TCTA: Bphen	464	/	2.6	2.61	36
DPNC: Bphen	580	/	4.0	3.3	37
ТСТА: ВЗРУМРМ	490	36	/	0.93	38

to exciplex emission. The difference is that the dimeric emission in our case is based on the same molecules, whereas exciplex needs at least two kinds of materials. The comparison between **SFCCNO** and representative traditional exciplexes are displayed in Table 3. It can be seen that the PLQY of SFCCNO dimer (71%) is the highest among all the D/A exciplexes, and the SFCCNO based device also has one of the highest EQE.

Conclusions

In summary, we designed and synthesized two novel TADF molecules, SFCCN and SFCCNO, based on a new configuration called D1- σ -D2- π -A. Because two materials have identical "D2– π –A" TBCT segments, they exhibited nearly the same photoluminescence in solution, but an abnormal red shift in the fluorescence of SFCCNO in the film state was observed. The oxygen bridge could increase the electron-donating ability in D1 moiety of SFCCNO, but it is not the main reason for this phenomenon. The planar conformation of 10-phenyl-10H-phenoxazine could form face-to-face interaction with the planar triazine acceptor in different molecules of SFCCNO, which is the main reason for the red shift. This dimeric inter-TSCT emission from D1 to A in the aggregation state did not exist in SFCCN film. In the non-doped devices, SFCCNO as an emitter exhibited an EQE of 12.9% at 100 cd m⁻² and an EQE of 10.4% at 1000 cd m⁻², which is much higher than that of SFCCN. This kind of dimeric TADF emission, which is much similar to the two-component exciplex emission, proves a new emission behavior in aggregation state.

Conflicts of interest

There are no conflicts to declare.

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