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Diluted exciplex concentrations in organic light emitting diodes for blue-shifted spectra and improved efficiency[†]

Jiakui Yan,^a Bizheng Dong,^a Yabo Xu,^a Bo Zhao, ^b*^a Fangming Jin,*^b Hua Wang ^{ac} and Wenlian Li^d

In this work, the effects of different ratios of the donor/acceptor and spacer host materials on exciplex organic light emitting diode (OLED) based DMAC-DPS:PO-T2T were explored, and an obvious spectral blue-shift and improved efficiency were achieved. It is noted that adjusting the ratios of the donor/acceptor and inserting spacer materials can regulate the distance between exciplex molecules to suppress concentration quenching. As a result, a 30–40 nm blue-shift and a high external quantum efficiency (EQE) of ~10% were achieved in all OLEDs and the maximum current efficiency, power efficiency and EQE of 35.4 cd A^{-1} , 33.7 lm W^{-1} and 13.4% were obtained in 70% concentration mCP spacer. The improved exciton utilization derived from multiple reverse intersystem crossing processes and efficient energy transfer were responsible for the high efficiency.

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1. Introduction

Organic light emitting diodes (OLEDs) have received more and more attention due to their huge potential application in solid state displays and lighting. The emitters used in OLEDs could be divided into three classes in general: traditional fluorescent materials, phosphorescent materials and thermally activated delayed fluorescence (TADF) materials.¹⁻³ Among them, the TADF materials have become the focus in recent years because of the advantages of high efficiency with $\sim 100\%$ internal quantum efficiency (IQE),⁴ low cost with pure fluorescent materials⁵ and green/sustainable development without heavy metals.⁶ A series of high efficiency TADF emitters with blue, green, orange and red emissions had been explored in the past decade.⁷⁻¹⁰ TADF emitters show monomolecular emission with intramolecular charge transfer¹¹ and the achievement of high efficiency is derived from efficient reverse intersystem crossing (RISC) of triplet excitons due to the small singlet-triplet energy

level splitting $(\Delta E_{\rm ST})$.¹² Besides, a kind of bimolecular emission¹³ in OLEDs, which is known as the exciplex emission,¹⁴ occurring due to the interaction between the donor and acceptor has also attracted attention.

An exciplex is formed from the intermolecular charge transfer excited state emission between the highest occupied molecular orbital (HOMO) energy level of donor materials and the lowest unoccupied molecular orbital (LUMO) energy level of acceptor materials,¹⁵ which exhibit intrinsic small $\Delta E_{\rm ST}$ due to the spatially separated HOMO and LUMO in two different molecules of donors and acceptors, respectively.¹⁶ So, similar to the TADF emitter, the exciplex could also achieve triplet exciton harvesting through the RISC process and improve the luminous efficiency, even 100% IQE.¹⁷ Besides, the exciplex shows pure fluorescence emission without heavy metals and the molecular design/synthesis of donor/acceptor materials is easier than that of TADF emitters due to its functionalized action. Therefore, exciplex emission also plays an important role in OLEDs and we could obtain the exciplex emission easily by mixing donor and acceptor materials with a 1:1 ratio.¹⁸ Almost all high efficiency exciplexes, from blue, green to yellowgreen emissions, adopted a mixed structure. Liu et al. reported a blue exciplex of 4,4'-bis(9-carbazolyl)-2,2'-dimethylbiphenyl: ((1,3,5-triazine-2,4,6-triyl) tris(benzene-3,1-diyl))tris(diphenylphosphine oxide) (CDBP:PO-T2T) with a 480 nm emission peak, while the external quantum efficiency (EQE) reaches 13.0%.¹⁹ Liang et al. developed an electron acceptor of 1-phenyl-1H-benzo[d]imidazole(1,3,5-triazine) (PIM-TRZ) based benzimidazole-triazine to fabricate a series of green exciplexes with

^a Key Laboratory of Interface Science and Engineering in Advanced Materials of Ministry of Education, Taiyuan University of Technology, Taiyuan, 030024,

P. R. China. E-mail: zhaobo01@tyut.edu.cn

^b School of Electrical Engineering, Anhui Polytechnic University, Wuhu, 241000, P. R. China. E-mail: jinfangming@126.com

^c College of Textile Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China

^d State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033, P. R. China

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di-[4-(N,N-ditolvl amino)-phenyl]cyclohexane (TAPC), 4,4',4"tris(N-carbazolyl) triphenylamine (TCTA) and 9,9',9"-triphenyl-9H,9H',9H"-[3,3':6',3"]-tercarbazole (Tris-Cz) as donors, and finally high maximum EQEs of 21.7%, 19.1% and 18.6% were realized, respectively.²⁰ Tian et al. utilized the combination of a novel electron donor 4,4,8,8,12,12-hexaphenyl-8,12-dihydro-4H-benzo[9,1]quinolizino[3,4,5,6,7- defg]acridine (DEX) and a PO-T2T acceptor to form a green exciplex at 520 nm with an EQE of 11.2%.²¹ Hu et al. achieved a highly efficient yellow exciplex with an emission peak at 566 nm and an EQE of 9.7% by using triazatruxene-based molecules Tr-Tol as the donor and 2,4,6-tris(3-(1H-pyrazol-1-yl)phenyl)-1,3,5-triazine (3P-T2T) as the acceptor, respectively.²² However, the average efficiency level of exciplexes is lower than those of phosphorescent and TADF emitters and the spectra also present some shift with the change of mixed ratio or operation voltage.23 Hence, the luminous mechanism needs to be explored further and the luminous efficiency needs to be improved in exciplex OLEDs. Generally speaking, the donor/acceptor mixed ratio in the exciplex emitting layer (EML) is mostly 1:1, and we consider that the exciplex concentration, in comparison with the dopant concentration in a host-guest doping system OLED, may have a significant impact on exciplex emission behavior.

Herein, we try to dilute the exciplex to reduce the exciplex concentration by adjusting the acceptor ratio or inserting a spacer into the exciplex EML, and explore the influence on the exciplex OLED performance. In detail, the exciplex of bis[4-(9,9dimethyl-9,10-dihydroacridine)phenyl]sulfone (DMAC-DPS): PO-T2T is chosen as the reference, which is a highly efficient exciplex possessing TADF characteristics. By reducing the ratio of PO-T2T or inserting a spacer of bis(2-(diphenylphosphino)phenyl)ether oxide/m-bis(N-carbazolyl)benzene DPEPO/mCP into the exciplex, we diluted the exciplex concentration successfully. As a result, a large range of spectral variations (30-40 nm) from yellow-green to sky-blue emissions was realized and the exciplex OLED efficiency was also enhanced with the diluted exciplex concentration with a maximum current efficiency, power efficiency and EQE of 35.4 cd A^{-1} , 33.7 lm W^{-1} and 13.4% in a 70% concentration mCP spacer.

2. Experimental section

All of the OLEDs were fabricated on indium tin oxide (ITO) coated glass substrates with a sheet resistance of 10 Ω sq⁻¹. The ITO substrates were cleaned first with acetone, deionized water and acetone and then treated with ultraviolet-ozone for 15 min, and then the ITO substrates were loaded into a high vacuum chamber (approximately 3×10^{-4} Pa) for subsequent deposition. After finishing the deposition of the organic layers, an Al cathode was deposited at the end with a shadow mask, which defined the device area as 3×3 mm². Photoluminescence (PL) spectra were recorded with a FluoroMax-4 fluorescence spectrometer (HORIBA Jobin Yvon). The transient PL decay profiles of the films were recorded using an Edinburgh Instrument FLS980 spectrometer equipped with an EPL-375 ps pulsed

diode laser under a nitrogen atmosphere. The photoluminescence quantum yield (PLQY) was determined using an FLS980 fluorescence spectrometer. Electroluminescence (EL) spectra were recorded using a PR-655 spectra scan spectrometer with computer control. The current–voltage–luminance curves were recorded using a measuring system of a Keithley 2400 power supply combined with a BM-7A luminance colorimeter. The EQE was calculated from the current density–voltage–luminance curve and EL spectra data. All of the organic materials were procured commercially and used without further purification.

3. Results and discussion

3.1 Small ratio acceptor

The exciplex donor and acceptor materials used in this work are DMAC-DPS and PO-T2T, respectively, which are a TADF donor and a common acceptor.^{24,25} In general, DMAC-DPS represents a highly efficient blue TADF emitter, which could also be used as a donor material due to the intramolecular donor unit.²⁶ The molecular structures of DMAC-DPS and other organic materials used here are shown in Fig. 1. Besides, the mixed ratio between the donor and acceptor in the exciplex EML is 1:1 commonly. Therefore, we consider that the exciplex concentration could reach the highest value at a ratio of 1:1, which could sufficiently lead to the formation of the exciplex. First, we try to change the mixed ratio, even a very small ratio, which is similar to that of the host–guest doped system, to dilute the exciplex concentration by reducing the acceptor molecule amount of PO-T2T.

The device structure based on the DMAC-DPS:PO-T2T exciplex is designed as follows: ITO/MoO₃ (3 nm)/N,N''-bis-(1naphthl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (30 nm)/ TCTA (10 nm)/DMAC-DPS:x% PO-T2T (25 nm)/1,3,5-tris(Nphenyl-benzimidazol-2-yl)benzene (TPBi) (45 nm)/LiF (1 nm)/ Al (100 nm), x = 50, 5, 1, 0.5 and 0. The device of 50% concentration has a common donor/acceptor ratio of 1:1, while that from 5% to 0.5% is in the decreased direction of the exciplex concentration due to the insufficient number of acceptor molecules. The 0% concentration device is a reference, which is a non-doped blue device with intrinsic DMAC-DPS emission. As shown in Fig. S1 (ESI⁺), all of the devices presented a low turn-on voltage below 3 V and high luminance, which indicated the excellent charge injection, transport and recombination. The EL performance with efficiency curves and spectra are shown in Fig. 2. The device of 50% concentration (1:1 ratio) achieved a moderate efficiency with a maximum current efficiency (CE), power efficiency (PE) and EQE of 16.8 cd A^{-1} , 17.8 lm W^{-1} and 5.6%, respectively. However, the device efficiencies were improved with the reduced PO-T2T concentration with maximum CEs and EQEs of 17.0/24.2/ 24.8 cd A⁻¹ and 6.1/10.0/10.8% at concentrations of 5/1/0.5%, respectively. As mentioned above, the DMAC-DPS is a blue TADF material, so the intrinsic RISC process on DMAC-DPS would contribute to the efficiency improvement at a low PO-T2T concentration through the energy transfer from DMAC-DPS to



the exciplex of DMAC-DPS:PO-T2T with more triplet exciton collection and utilization.²⁷ The reference device of 0% concentration with pure DMAC-DPS emission showed the maximum CE, PE and EQE of 21.6 cd A^{-1} , 25.2 lm W^{-1} and 10.3%, respectively. The exciplex concentration of DMAC-DPS:PO-T2T was diluted with a reduced acceptor PO-T2T amount, which increased the distance of the "exciplex molecule". Therefore, the improvement of device efficiency could also be attributed to the suppressed exciton concentration quenching by spatial

separation of the exciplexes.²⁸ More interestingly, the EL spectra shown in Fig. 2c exhibited a spectral blue shift from 512 nm (50%) to 488 nm (0.5%). The corresponding Commission Internationale de I'Eclairage (CIE) coordinates in Fig. 2d also gave an obvious shift from the green zone to blue zone due to the reduced PO-T2T concentration. In a previous report, the spectral shift could be explained as the effect of polarity of the exciplex,²⁹ which could be regarded as the molecule with a separated charge, and the charge separation induces strong



Fig. 2 The device structure and performance with different concentrations of the PO-T2T acceptor. (a) Device structure schematic diagram. (b) Current efficiency–luminance-EQE curves. (c) The EL spectra under 6 V. (d) The CIE coordinate exhibition of the EL spectra.

Table 1 The EL performances of the DMAC-DPS:PO-T2T exciplex with a reduced acceptor PO-T2T concentration

λ (nm)	V _{on} (V)	CE/PE/EQE cd $A^{-1} lm^{-1} W^{-1} / \%$		
		Maximum	$1000 \text{ cd } \text{m}^{-2}$	CIE (x, y) at 6 V
512	2.7	16.8/17.8/5.6	12.8/10.5/5.0	(0.29, 0.52)
504	2.7	17.0/17.3/6.1	16.4/14.1/5.1	(0.24, 0.43)
492	2.5	24.2/28.2/10.0	14.4/11.2/7.2	(0.21, 0.37)
488	2.5	24.8/28.8/10.8	14.2/11.3/4.8	(0.20, 0.35)
480	2.7	21.6/25.2/10.3	14.9/11.5/5.0	(0.18, 0.31)
	λ (nm) 512 504 492 488 480	$\begin{array}{c c} \lambda \ (nm) & V_{on} \ (V) \\ \hline 512 & 2.7 \\ 504 & 2.7 \\ 492 & 2.5 \\ 488 & 2.5 \\ 480 & 2.7 \\ \end{array}$	$\begin{array}{c c} & & & & \\ \hline \lambda \ (nm) & V_{on} \ (V) & & \\ \hline & & \\ \hline 512 & 2.7 & 16.8/17.8/5.6 \\ 504 & 2.7 & 17.0/17.3/6.1 \\ 492 & 2.5 & 24.2/28.2/10.0 \\ 488 & 2.5 & 24.8/28.8/10.8 \\ 480 & 2.7 & 21.6/25.2/10.3 \\ \hline \end{array}$	$\begin{array}{c c} & \underline{\operatorname{CE/PE/EQE cd A^{-1} lm^{-1} W^{-1}/\%} \\ \hline \lambda \ (nm) & V_{on} \ (V) & \underline{\operatorname{Maximum}} & 1000 \ cd \ m^{-2} \\ \hline 512 & 2.7 & 16.8/17.8/5.6 & 12.8/10.5/5.0 \\ 504 & 2.7 & 17.0/17.3/6.1 & 16.4/14.1/5.1 \\ 492 & 2.5 & 24.2/28.2/10.0 & 14.4/11.2/7.2 \\ 488 & 2.5 & 24.8/28.8/10.8 & 14.2/11.3/4.8 \\ 480 & 2.7 & 21.6/25.2/10.3 & 14.9/11.5/5.0 \\ \hline \end{array}$

interactions between exciplexes, which result in a blue shift.³⁰ The summary of EL performances is listed in Table 1.

3.2 Spacer insertion

In this section, we try to dilute the exciplex concentration by inserting different types of spacers based on the DMAC-DPS:PO-T2T exciplex EML mentioned above. The device structure is as follows: ITO/MoO₃ (3 nm)/NPB (30 nm)/TCTA (10 nm)/ DMAC-DPS: PO-T2T (1:1): x% DPEPO or mCP (25 nm)/PO-T2T (10 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm), and the mixed ratio of the donor and acceptor is 1:1. The spacers are selected as DPEPO or mCP, while the DPEPO has a wide energy gap with a HOMO of 6.8 eV and a LUMO of 2.6 eV, a high triplet energy of 2.98 eV and a relatively low hole/electron mobility of 1.4 imes $10^{-9}/7.0 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.^{31}$ More importantly, the DPEPO would not form exciplexes with DMAC-DPS and PO-T2T. So the introduction of DPEPO into the DMAC-DPS:PO-T2T exciplex EML would just dilute the exciplex concentration, and not interact with the donor or acceptor. The current densityvoltage-luminance (J-V-L) characteristics of the DMAC-DPS: PO-T2T (1:1): x% DPEPO device are displayed in Figure S2. The current density presented an obvious decrease with an

increase in the DPEPO concentration, which is derived from the wide energy gap and low carrier mobility of DPEPO. The injection and transport of carriers would be blocked with the increase of the DPEPO amount in the EML, which leads to the reduction of current density under the same voltage.

The EL performance with efficiency curves and spectra with different DPEPO dopant concentrations of 0, 30%, 50% and 70% are displayed in Fig. 3. The device of 0% DPEPO showed a pure DMAC-DPS:PO-T2T exciplex emission with an emission peak at 540 nm, and the maximum CE, PE and EQE were 23.3 cd A^{-1} , 24.4 lm W^{-1} and 7.2%, respectively. Then, with the increase of DPEPO concentration from 30% to 70%, the device EQE presented an improvement from 7.8% to 9.4%. Similar to the section of the small ratio PO-T2T acceptor, the improvement of efficiency could also be derived from the reduced exciplex concentration quenching with the increased molecular distance of exciplexes due to the introduction of DPEPO. Besides, to our more surprise, a large spectral blue shift of about 30 nm was observed as shown in Fig. 3c. The emission peaks were fixed at 540 nm, 532 nm, 524 nm and 508 nm at concentrations of 0%, 30%, 50% and 70%, respectively. The CIE coordinates shown in Fig. 3d also exhibited a shift from the



Fig. 3 The device structure and performance with the DPEPO dopant. (a) Device structure schematic diagram. (b) Current efficiency–luminance–EQE curves. (c) The EL spectra under 6 V. (d) The CIE coordinate exhibition of the EL spectra.

yellow zone to the green zone. The blue shift of the exciplex EL spectra ($h\nu_{\rm max}$) could be explained by the following reasons: it results from the increase of the distance between the donor and acceptor with the enhanced DPEPO content. Based on eqn (1), the increased average distance between the donor and acceptor leads to an increased distance between the electrons and holes in the exciplex charge transfer state, which leads to an improved Coulomb potential energy $E_{\rm C}(r)$ (approaching zero). Thus, the energy of the exciplex charge transfer state increases with the separation of the donor and acceptor (Formula (2)), resulting in the formation and emission of higher energy exciplexes, which lead to the blue shifted spectra.^{32,33}

$$E_{\rm c}(r) = -\frac{e^2}{4\pi r\varepsilon_0 \varepsilon} - eFr \tag{1}$$

$$h\nu_{\rm max} \approx I_{\rm D} - A_{\rm A} - E_{\rm C}$$
 (2)

Here, *e* is the electron charge, *F* is the electric field, and ε_0 and ε are the permittivity of the vacuum and medium, respectively. *I*_D and *A*_A are the donor's ionization potential and the electron affinity of the acceptor. The EL performance of different DPEPO concentrations doped into the DMAC-DPS:PO-T2T exciplex EML is summarized in Table 2.

The steady PL spectra curves of the DMAC-DPS:PO-T2T film with different DPEPO doping concentrations of 0, 30%, 50% and 70% are shown in Fig. 4. It can be seen that the PL emission peak also presents a blue shift with the increase in the concentration of DPEPO, which is consistent with the trend of EL spectra.

Next, another spacer, mCP with different concentrations, was doped into the DMAC-DPS:PO-T2T exciplex EML based on the same device structure. The concentrations were designed to be 10%, 30%, 50% and 70%, respectively. However, different from DPEPO, which has no interaction with the donor or acceptor, mCP is a hole transport material with a strong electron donating ability and would also form an exciplex with PO-T2T. The exciplex of mCP:PO-T2T presents a highly efficient blue emission with a peak at 475 nm.³⁴ So the introduction of mCP into the EML would result in two exciplexes of mCP:PO-T2T and DMAC-DPS:PO-T2T. The EL efficiency and spectra are shown in Fig. 5. An obvious efficiency improvement was observed with the increase of the mCP concentration, and the EQEs were 9.5%, 12.4%, 12.6% and 13.4% at concentrations of 10%, 30%, 50% and 70%, respectively. The maximum CE and

 Table 2
 The EL performances of the DMAC-DPS:PO-T2T exciplex with different DPEPO concentrations

	2	V	<u>CE/PE/EQE</u> cd $A^{-1} lm^{-1} W^{-1}/\%$		CIF(r, y)
	/nm)	$(V)^{v_{on}}$	Maximum	$1000 \text{ cd } \text{m}^{-2}$	at 6 V
0% DPEPO 30% DPEPO 50% DPEPO 70% DPEPO	540 532 524	2.7 3.0 3.0	23.3/24.4/7.2 24.4/23.2/7.8 25.9/26.5/9.3	20.7/16.1/6.4 20.7/14.8/6.6 22.0/15.3/6.6	(0.36, 0.56) (0.33, 0.53) (0.30, 0.51) (0.25, 0.41)



Fig. 4 The steady PL spectra of DMAC-DPS:PO-T2T: x% DPEPO films with concentrations of 0, 30%, 50% and 70%, respectively.

PE were also achieved at a concentration of 70% with 35.4 cd A^{-1} and 33.7 lm W^{-1} , respectively. Meanwhile, the EL spectra shown in Fig. 5b exhibited a blue shift gradually with the enhanced mCP concentration in the DMAC-DPS:PO-T2T exciplex with emission peaks at 528 nm, 520 nm, 512 nm and 504 nm at concentrations of 10%, 30%, 50% and 70%, respectively. More importantly, the emission spectra exhibit smooth curves with one single peak without other emission shoulders. Besides, the PL spectra with different mCP concentrations shown in Fig. 6a also present a similar tendency to EL spectra. So we consider that the emission with various mCP concentrations is still the exciplex emission with spectral movement, even at a high mCP concentration of 70%. This indicates that a large spectral blue shift could be realized in exciplex emission through the increased exciplex molecular distance by a simple small ratio acceptor or spacer insertion.

In this section, the device of 70% mCP concentration showed the highest EL efficiency with a maximum CE, PE and EQE of 35.4 cd A⁻¹, 33.7 lm W⁻¹ and 13.4%, respectively. The highest efficiency can be explained by the following reasons: first, the exciplex concentration of DMAC-DPS:PO-T2T is diluted with the increase in the mCP concentration, which also increased the distance of the "exciplex molecule". Therefore, exciton concentration quenching could be suppressed by spatial separation of the exciplexes. Second, the formation of two exciplexes and the energy transfer between them also contributed to the high efficiency, which is showed in Fig. 5d. mCP:PO-T2T (Exciplex 1) is a blue exciplex with an exciplex photon energy of 2.64 eV^{35} and DMAC-DPS:PO-T2T (Exciplex 2) is a lower energy exciplex (2.40 eV^{35}) with a yellow-green emission. So the energy transfer from Exciplex 1 to Exciplex 2 could happen and the energy transfer efficiency was enhanced with an increase in the concentration of mCP. Third, both Exciplex 1 and Exciplex 2 exhibited TADF behavior as in previous reports.^{24,29} Therefore, the multiple RISC process with highly efficient triplet exciton harvesting could be achieved in this system. That means, there existed multiple RISCs in the ternary two exciplex system for triplet exciton utilization, which is responsible for high device efficiency. The EL performances of this section are summarized in Table 3.

To illustrate the energy transfer between the two exciplexes further, the steady state PL spectra and transient PL decay



Fig. 5 The EL performance and luminous mechanism with the mCP dopant. (a) Current efficiency–luminance–EQE curves. (b) The EL spectra under 6 V. (c) The CIE coordinate exhibition of EL spectra. (d) Energy transfer and luminous mechanism within two exciplexes.



Fig. 6 The film PL spectra of DMAC-DPS:PO-T2T: x% mCP. (a) Steady PL spectra. (b) Transient PL decay lifetime curves. (Monitored at the emission peaks of PL spectra).

Table 3 The EL performances of the DMAC-DPS:PO-T2T exciplex with different mCP concentrations

		V	${\rm CE/PE/EQE}{\rm cd^{-1}}{\rm A^{-1}}{\rm lm^{-1}}{\rm W^{-1}/\%}$		CIE(x, y)
	λ (nm)	$(V)^{V_{on}}$	Maximum	1000 cd m^{-2}	at 6 V
0% mCP	540	2.7	23.3/24.4/7.2	20.7/16.1/6.4	(0.36, 0.56)
10% mCP	528	2.8	28.6/27.2/9.5	26.8/21.0/8.6	(0.32, 0.54)
30% mCP	520	2.9	34.3/32.6/12.4	29.2/22.0/10.6	(0.30, 0.52)
50% mCP	512	3.0	34.7/33.2/12.6	29.6/22.1/10.7	(0.27, 0.48)
70% mCP	504	3.1	35.4/33.7/13.4	29.4/21.9/10.8	(0.26, 0.45)

curves of the DMAC-DPS:PO-T2T film with different mCP doping concentrations of 0, 30%, 50% and 70% are shown in Fig. 6. It can be seen that with the increase in the concentration of mCP, the position of the PL emission peak also presents a blue shift, which is consistent with the trend of EL spectra. And the lifetime shown in Fig. 6b exhibited a decrease with the increased mCP concentration. Different from DPEPO addition, there exist two exciplex RISC processes and one DMAC-DPS intrinsic RISC process with the addition of mCP as mentioned above. And the delayed fluorescence lifetimes had been reported previously as 3.1 µs,³⁶ 1.2 µs³⁷ and 1.8 µs³⁸ for DMAC-DPS, Exciplex 1 and Exciplex 2, respectively. At low mCP concentration, the process of RISC mainly includes DMAC-DPS and Exciplex 2, and the major lifetime is exhibited as Exciplex 2 due to the energy transfer from DMAC-DPS to Exciplex 2. However, as the mCP concentration increased, the strong RISC process of Exciplex 1 with a shorter lifetime begin to occupy the main role and the energy transfer from high energy Exciplex 1 to low energy Exciplex 2 also could happen. Therefore, the film of DMAC-DPS:PO-T2T: x% mCP showed a reduced lifetime with the enhanced concentration of mCP with enhanced multiple RISC channels and the energy transfer process. Besides, the PLQYs of the films also were obtained to be 38%, 58%, 60% and 69% at mCP concentrations of 0%, 30%, 50% and 70%, respectively. The improved PLQYs with the

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Fig. 7 The EL spectra of four representative concentration exciplex OLEDs under 4–8 V. (a) 50% PO-T2T. (b) 0.5% PO-T2T. (c) 70% DPEPO. (d) 70% mCP.

increased mCP concentrations also supported the high device efficiency.³⁹ Therefore, the suppressed exciton concentration quenching with the increased molecular distance improved PLQYs with multiple RISC channels and efficient energy transfer from a high energy exciplex to a low energy exciplex are responsible for the high EL efficiency.

We also noticed that a more serious roll-off appears with the small ratio PO-T2T (1% and 0.5%) and high concentration doped DPEPO/mCP (70%) device. With a small ratio PO-T2T (1% and 0.5%), the molecule of DMAC-DPS plays the main role, therefore, a serious roll-off occurs from the long triplet lifetime of the DMAC-DPS molecule, which results in triplet–triplet annihilation (TTA).⁴⁰ Because the triplet lifetime of the DMAC-DPS molecule (1.8 μ s) is shorter than that of the DMAC-DPS molecule (3.1 μ s), the roll-off could be prevented with a high concentration PO-T2T due to the sufficient formation of the DMAC-DPS:PO-T2T exciplex. Other than this, a higher concentration of the host material increases the distance between exciplex molecules, which makes the coupling between molecules become weaker. Therefore, the lower coupling efficiency at high voltages leads to a serious roll-off.⁴¹

To indicate the spectral stability further, four representative concentration devices of 50% PO-T2T, 0.5% PO-T2T, 70% DPEPO and 70% mCP under different voltages are shown in Fig. 7. It could be seen that the EL spectra of these OLED based exciplexes were very stable under different voltages from a wide range of 4–8 V, which means the emission properties remain the same without other impurities as the charge injection and recombination enhanced.

4. Conclusions

In summary, blue-shifted spectra and improved efficiency were realized in the exciplex OLED of DMAC-DPS:PO-T2T by simply diluting the exciplex concentration through small ratio acceptor PO-T2T doping or spacer insertion of DPEPO and mCP. As a result, a 30–40 nm blue-shift and a high EQE of $\sim 10\%$ were achieved in all OLEDs and the maximum CE, PE and EQE of 35.4 cd A⁻¹, 33.7 lm W⁻¹ and 13.4% were obtained in a 70% concentration mCP spacer. The suppressed exciton concentration quenching, improved PLQYs and efficient energy transfer are the main reasons for high OLED efficiency. So in this work, a simple method was exploited successfully to modulate the exciplex emission spectra and improve the EL efficiency. And we believe that the doped donor/acceptor or spacer insertion would be an efficient path for achieving highly efficient exciplex OLEDs.

Author contributions

Y. J. K. wrote the main manuscript and carried out most of the experiments and data analysis. D. B. Z. and X. Y. B. helped in measuring and collecting the experimental data. Z. B. and W. H. guided the progress of experiments and manuscript writing. J. F. M. and L. W. L. took part in the mechanism discussions. All authors reviewed the manuscript.

Conflicts of interest

There are no conflicts to declare.

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