Novel donor-spacer-acceptor compound as the multifunctional component of exciplexes for efficient organic light-emitting diodes

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ABSTRACT By connecting tercarbazole (3Cz) and triphenyltriazine (TRz) units with a diphenyl ether group, we designed and synthesized a new donor-spacer-acceptor structure molecule 9'-(4-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenoxy)phenyl)-9'H-9,3':6',9''-tercarbazole (3Cz-*o*-TRz) as the multifunctional component of exciplex emitters. As expected, the intermolecular charge-transfer transition is dominant for 3Cz-*o*-TRz because of the space-enough and conjugation-forbidden linkage of the diphenyl ether group, increasing the intrinsic characteristics of the 3Cz and TRz moieties in its single-molecule state. Accordingly, three common electron acceptors (4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PyMPm), 4,6-bis(3,5-di(pyridin-4-yl)phenyl)-2-methylpyrimidine (B4PyMPm), and (1,3,5-triazine-2,4,6-triyl)tris(benzene-3,1-diyl)tris(diphenylphosphineoxide) (PO-T2T)) and three common electron donors (4,4'-(cyclohexane-1,1-diyl)bis(*N,N*-di-*p*-tolylaniline) (TAPC), tris(4-(10*H*-phenoxazin-10-yl)phenyl)amine (TPA-PXZ), and *N*1-phenyl-*N*4, *N*4-bis(4-(phenyl(*m*-tolyl)amino)phenyl)-*N*1-(*m*-tolyl)benzene-1,4-diamine (*m*-MTDATA)) were chosen to construct six exciplex emitters with 3Cz-*o*-TRz. In the organic light-emitting diodes (OLEDs), the emission spectra of these exciplex emitters could be gradually modulated from 510 to 590 nm. In addition, TAPC:3Cz-*o*-TRz- and 3Cz-*o*-TRz:PO-T2T-based OLEDs achieved desirable performance with maximum external quantum efficiencies (EQEs) around 12%. Moreover, a simple tandem OLED containing TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T emitters realized optimal performance with an ultralow turn-on voltage of 2.4 V and a maximum EQE of 14.1%. These results indicate the great potential of the donor-spacer-acceptor structure compounds in developing exciplex emitters.

Keywords: exciplex, donor-spacer-acceptor structure, intermolecular charge-transfer, organic light-emitting diode, multifunctional component

INTRODUCTION

Since Goushi *et al.* [1] reported the exciplex-based organic light-emitting diodes (OLEDs) with external quantum efficiencies (EQEs) exceeding the 5% theoretical limit of conventional fluorescent OLEDs in 2012, exciplex-based OLEDs have aroused

great attention [2–9]. The exciplex is well known with an intermolecular charge-transfer (CT) transition between the highest occupied molecular orbital (HOMO) of an electron-donating molecule (D) and the lowest unoccupied molecular orbital (LUMO) of an electron-accepting molecule (A) [10]. With the frontier molecular orbitals (FMOs) located on different molecules, the intermolecular excited states would provide small exchange energies to exciplexes, resulting in extremely small singlet-triplet splittings (ΔE_{ST}). Thus, similar to single-molecule thermally activated delayed fluorescence (TADF) emitters, exciplex emitters can also improve the utilization of triplet excitons through the reverse intersystem crossing (RISC) process and achieve a theoretical internal quantum efficiency of 100% [11–14]. In addition, the D:A mixed exciplex emitters would naturally have good bipolar electrical conductivity, which optimizes device structures and decreases operating voltages [15–17]. Thus, developing high-performance exciplex emitters is important.

In recent years, a new strategy has been proposed to improve the efficiency of exciplex emitters by introducing bipolar donor-acceptor structure compounds as the constituting components [18–20]. In general, donor-acceptor structure molecules can form a CT transition by excitation, which would separate positive and negative charges. Thus, the donor and acceptor moieties in the donor-acceptor structure molecules are expected to possess more spatially separated charges than those without CT formation, which would lead to the formation of exciplexes [19]. To date, the electroluminescence (EL) performance of exciplex emitters has been significantly improved by employing donor-acceptor structure components [21–25]. However, current donor-acceptor structure molecules are purposefully developed for the emitters or hosts of OLEDs. They normally exhibit sole donor-dominated or acceptor-dominated properties because of the strong conjugation between the electron-donating and electron-accepting groups [26–29]. In 2015, Zhang *et al.* [30] attempted to use the typical donor-acceptor structure compound 10,10'-(sulfonylbis(4,1-phenylene))bis(9,9-dimethyl-9,10-dihydroacridine) (DMAC-DPS) to construct exciplex emitters as the D and A components. The maximum EQEs of these exciplex emitters are fairly lopsided in the OLEDs, i.e., 9.1% with DMAC-DPS as the D component and 1.6% with DMAC-DPS as the A component. These results indicate that DMAC-DPS is donor-dominated and can only be used as the D

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component to construct efficient exciplex emitters. Therefore, current donor-acceptor structure molecules obviously have their inherent limitation. As the components of exciplex emitters, the ideal donor-acceptor structure molecules should simultaneously maintain the intrinsic characteristics of electron-donating and electron-accepting moieties in the single-molecule state.

In this work, we designed and synthesized a new molecule, 9'-(4-(4,6-diphenyl-1,3,5-triazine-2-yl)phenoxy)phenyl)-9'*H*-9,3':6',9''-tercarbazole (3Cz-*o*-TRz), by using a donor-spacer-acceptor structure. In this molecule, the electron-donating group tercarbazole (3Cz) is connected with the electron-accepting group triphenyltriazine (TRz) through the diphenyl ether group. The former contributes to the separation of FMOs by appending secondary donor groups on a central carbazole to enlarge the delocalization of HOMOs, and the latter is a rigid planar acceptor moiety with a small steric hindrance, which can promote intermolecular interactions. With a space-enough and conjugation-forbidden diphenyl ether linkage, the intramolecular interaction between the 3Cz and TRz is efficiently suppressed [31]. Thus, 3Cz-*o*-TRz is supposed to maintain the intrinsic characteristics of the 3Cz and TRz moieties in the single-molecule state and serve as the multifunctional component of exciplex emitters. As expected, the photophysical properties of 3Cz-*o*-TRz were mainly characterized by its constituent moieties and the intermolecular CT transition, and 3Cz-*o*-TRz can be used as the D and A components to construct exciplex emitters. Correspondingly, three common electron acceptors, including 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PyMPm), 4,6-bis(3,5-di(pyridin-4-yl)phenyl)-2-methylpyrimidine (B4PyMPm), and (1,3,5-triazine-2,4,6-triyl) tris(benzene-3,1-diyl)tris(diphenylphosphineoxide) (PO-T2T), and three common electron donors, including 4,4'-(cyclohexane-1,1-diyl)bis(*N,N*-di-*p*-tolylaniline) (TAPC), tris(4-(10*H*-phenoxazin-10-yl)phenyl)amine (TPA-PXZ), and *N*1-phenyl-*N*4,*N*4-bis(4-(phenyl(*m*-tolyl)amino)phenyl)-*N*1-(*m*-tolyl)benzene-1,4-diamine (*m*-MTDATA), were selected to blend with 3Cz-*o*-TRz to form six exciplex emitters. These exciplexes achieved the modulation of the emission spectra with the peaks varied from 510 to 590 nm. Among them, 3Cz-*o*-TRz:PO-T2T with 3Cz-*o*-TRz as the D component and TAPC:3Cz-*o*-TRz with 3Cz-*o*-TRz as the A component achieved nearly identical performance in the OLEDs with a maximum EQE around 12%. Moreover, a simple tandem OLED simultaneously containing TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T in the emissive layer (EML) further realized optimal performance with an ultralow turn-on voltage of 2.4 V and a maximum EQE of 14.1%. These results prove that the donor-spacer-acceptor structure molecules could be an ideal candidate to construct exciplexes as the D or A component and open new possibilities for the structure design of the corresponding OLEDs.

EXPERIMENTAL SECTION

General methods

All raw materials and reagents were purchased from commercial suppliers and used without further purification. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded by using a Bruker Advance-400 spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. Density functional theory (DFT) calculation was performed by using the Gaussian 09

program package with the B3LYP/6-31g (d) basis set. Thermogravimetric analysis (TGA) was performed using a TA SDT 2960 instrument under a nitrogen atmosphere. Cyclic voltammetry (CV) was conducted in *N,N*-dimethylformamide using a CHI660E electrochemical analyzer. The ultraviolet (UV)-visible absorption spectra were obtained using a Hitachi UV-Vis spectrophotometer U-3900, and the transient photoluminescence (PL) spectra were recorded using a Hitachi fluorescence spectrometer F-4600. PL decays were measured using an Edinburgh Instruments F980 spectrometer.

OLEDs fabrication and characterization

Indium tin oxide (ITO) glasses with a sheet resistance of 15 Ω per square were used as substrates for device fabrication. Before the device was fabricated, the glasses were first cleaned with acetone, ethanol, and deionized water and then placed in a drying oven at 120°C for 2 h. The glasses were treated with UV-ozone for 30 min and then placed into a thermal deposition instrument with a high pressure of 5×10^{-4} Pa. All organic layers were deposited onto the glass substrate at a general rate of 1–2 $\text{\AA s}^{-1}$. In general, the deposited rates of LiF and Al were controlled at 0.1 and 10 $\text{\AA s}^{-1}$, respectively. The optical and electrical data of the devices were respectively recorded with a PR655 Spectscan and Keithley 2400 Source Meter under ambient atmosphere simultaneously. The current efficiency (CE), power efficiency (PE), and EQE were calculated with the data of current, luminance, and emission, assuming a Lambertian distribution.

RESULTS AND DISCUSSION

The synthetic scheme of 3Cz-*o*-TRz is depicted in Scheme 1. First, the electron-donating segment 3Cz was synthesized in high yields from the Buchwald-Hartwig coupling reaction between carbazole and carbazole derivative, followed by a deprotection reaction with tetrabutylammonium fluoride. Meanwhile, the electron-withdrawing unit 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine reacted with the 4-bromophenol to produce TRz-*o*-PhBr via Williamson reaction. Target compound 3Cz-*o*-TRz was then synthesized between the 3Cz and TRz-*o*-PhBr segments via the Buchwald-Hartwig coupling reaction, and its chemical structure was further confirmed by the NMR and mass spectra (shown in Figs S1–S5).

The thermal properties of 3Cz-*o*-TRz were measured using TGA and differential scanning calorimetry under a nitrogen atmosphere to evaluate its thermal stability. As shown in Fig. S6, 3Cz-*o*-TRz has excellent thermal stability with a decomposition temperature (T_d , corresponding to 5% weight loss) of 508°C. Meanwhile, no glass transition was observed in the testing range of 25 to 300°C. Therefore, 3Cz-*o*-TRz has enough thermal stability to be used in thermal evaporation.

The complete separation of FMOs is indispensable for the donor-spacer-acceptor structure molecules to serve as multifunctional components of exciplexes. Thus, theoretical calculations were applied on 3Cz-*o*-TRz to simulate its geometrical structure and molecular orbital distributions. The ground state (S_0) was optimized by using DFT with a B3LYP/6-31G* basis set. As shown in Fig. 1, the HOMO and LUMO of 3Cz-*o*-TRz were completely delocalized on the 3Cz and TRz moieties, respectively. Such ideal separated HOMO and LUMO should be attributed to the diphenyl ether spacer, which distinctly suppresses the conjugation between the 3Cz and TRz groups. Fur-

Scheme 1 Synthetic procedure of 3Cz-*o*-TRz.

Figure 1 (a) LUMO distributions, (b) HOMO distributions, (c) ground geometry of the S_0 state, and (d) the optimized structure of the excited state of 3Cz-*o*-TRz.

thermore, the centroid distance between the HOMO and LUMO of 3Cz-*o*-TRz was theoretically estimated at 26.4 Å, which is large enough to suppress the spatial CT transition. In specific, the dihedral angle of diphenyl ether changed from 34° at S_0 to 89° at the adiabatic excited states, indicating that positive and negative charges would be more separated at the excited states. Meanwhile, the oscillator strength of 3Cz-*o*-TRz was estimated to be only 0.013, further proving the separation of its FMOs. Relatively isolated donor and acceptor moieties in 3Cz-*o*-TRz would remarkably increase the intrinsic characteristics from the 3Cz and TRz groups in the single-molecule state, ensuring that 3Cz-*o*-TRz could serve as the D or A component to construct exciplexes.

The photophysical properties of 3Cz-*o*-TRz and two eigen derivatives of 3Cz and TRz groups (9'-phenyl-9*H*-9,3':6',9''-tercarbazole (3Cz-Ph) and 2,4,6-triphenyl-1,3,5-triazine (TriPh-

TRz)) were investigated to gain an in-depth evaluation of 3Cz-*o*-TRz in the single-molecule state and neat film. Fig. 2a displays the UV-visible absorption and PL spectra of three compounds in dilute toluene solution at room temperature. The absorption of 3Cz-*o*-TRz (with the maximum absorption at 341 nm) is almost composed of those of 3Cz-Ph and TriPh-TRz, suggesting that only local excited (LE) transition absorptions exist. Meanwhile, the PL spectrum of 3Cz-*o*-TRz is nearly consistent with that of 3Cz-Ph. These results indicate that 3Cz-*o*-TRz only exhibits the intrinsic characteristics of the 3Cz and TRz groups in the single-molecule state. Fig. 2b shows the fluorescent spectra of 3Cz-*o*-TRz in PMMA with different doping concentrations. With the increasing doping concentrations of 3Cz-*o*-TRz in PMMA, the relative intensity of LE emission decreased by degrees, whereas a new fluorescence peaked at 445 nm gradually appeared. As shown in Fig. 2c, the LE emission in neat 3Cz-*o*-TRz film

Figure 2 (a) Absorption and PL spectra of 3Cz-o-TRz, 3Cz-Ph, and TriPh-TRz in dilute toluene solution; (b) fluorescent spectra of 3Cz-o-TRz distributed in PMMA with various concentrations; (c) fluorescent spectra of spin-coated films of 3Cz-Ph, TriPh-TRz, 1:1 mixture of 3Cz-Ph and TriPh-TRz and 3Cz-o-TRz; (d) fluorescence and phosphorescence spectra of 3Cz-o-TRz films at 77 K; (e) structure of eigen derivatives used in the experiment.

completely disappeared, and only a broad and structureless emission peaked at 450 nm, which is consistent with the emission of the 3Cz-Ph:TriPh-TRz blend. Therefore, the new emission could be attributed to the intermolecular CT transition between 3Cz-o-TRz molecules under aggregation state, which further confirms that 3Cz-o-TRz could maintain the intrinsic characteristics of the donor and acceptor moieties. The low-temperature fluorescence and phosphorescence spectra of 3Cz-o-TRz in neat film were then obtained to estimate its lowest singlet (S_1) and triplet (T_1) energy levels under aggregation state. On the basis of the onset positions of the fluorescence and phosphorescence spectra shown in Fig. 2d, the S_1 and T_1 energy levels were respectively calculated to be 2.88 and 2.84 eV. The singlet-triplet splitting (ΔE_{ST}) of 3Cz-o-TRz under aggregation state was accordingly estimated to an extremely small value of 0.04 eV, indicating its potential TADF characteristic. In addition, the relatively high T_1 level of 2.84 eV would be conducive to the confinement of the excitons on the exciplexes for 3Cz-o-TRz-based exciplex emitters [32].

The CV characterization of 3Cz-o-TRz was performed to evaluate its HOMO and LUMO energy levels. As shown in Fig. S7, from the onsets of the oxidation and reduction curves, the HOMO and LUMO energy levels of 3Cz-o-TRz were estimated to be -5.86 and -3.05 eV, respectively, which are nearly identical to the results of 3Cz and TRz [33]. As shown in Fig. S8, various common D and A materials with appropriate FMOs energy levels were selected to construct exciplex emitters with 3Cz-o-TRz.

Fig. 3 displays the PL spectra of the varied blended films based on 3Cz-o-TRz with a ratio of 1:1. Among them, the 4,4'-N,N'-dicarbazolylbiphenyl (CBP):3Cz-o-TRz-blended film exhibited the intrinsic emission of 3Cz-o-TRz, which peaked at 425 nm. This result can be ascribed to the fact that CBP possesses deeper HOMO and shallower LUMO energy levels [17] than 3Cz-o-TRz and no exciplex can form between CBP and 3Cz-o-TRz. By contrast, by mixing 3Cz-o-TRz with three D materials, 3Cz-o-TRz:TAPC, 3Cz-o-TRz:TPA-PXZ, and 3Cz-o-TRz:*m*-MTDATA exhibited significantly red-shifted PL spectra with peaks at 510,

Figure 3 PL spectra of 3Cz-o-TRz-based blend films (1:1) (a) with various D materials and (b) with various A materials; (c) transient fluorescence decays of the 3Cz-o-TRz:PO-T2T, TAPC:3Cz-o-TRz mixed film at 488 nm.

530, and 580 nm, respectively. Similarly, 3Cz-o-TRz:B3PyMPM, 3Cz-o-TRz:B4PyMPM, and 3Cz-o-TRz:PO-T2T, in which 3Cz-o-TRz was mixed with three A materials, also exhibited red-shifted PL spectra peaked at 465, 475, and 510 nm, respectively. These results distinctly indicate that 3Cz-o-TRz could serve as both D and A components to construct various exciplexes.

Whether or not these 3Cz-o-TRz-based exciplexes possess effective TADF characteristics was explored. 3Cz-o-TRz:PO-T2T with 3Cz-o-TRz as the D component and TAPC:3Cz-o-TRz with 3Cz-o-TRz as the A component were selected as the representatives to investigate their transient fluorescence decay. As shown in Fig. 3c and Table S1, the PL decay curves of both exciplexes contained a prompt fluorescence and a delayed fluorescence. In addition, the delayed components of the two exciplexes were evidently stronger than that of pure 3Cz-o-TRz, indicating the more efficient RISC process of these exciplexes, which would benefit the exciton utilization in the OLEDs [34]. Accordingly, we further measured the PL quantum yields (PLQYs) of 3Cz-o-TRz:PO-T2T and TAPC:3Cz-o-TRz under air atmosphere. Their absolute PLQYs were 68% for TAPC:3Cz-o-TRz and 66% for 3Cz-o-TRz:PO-T2T.

Subsequently, the EL performance of these six 3Cz-o-TRz-based exciplex emitters was evaluated. The OLEDs based on the exciplex emitters with 3Cz-o-TRz as the A component were fabricated with a structure of ITO/TAPC (or TPA-PXZ or m-MTDATA) (40 nm)/TAPC (or TPA-PXZ or m-MTDATA):3Cz-o-TRz (20 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al. Among them, ITO and LiF/Al worked as the anode and the cathode, respectively; the corresponding D material and 3,3'-(5'-(3-(pyridin-3-

yl)phenyl)-[1,1':3',1''-terphenyl]-3,3''-diyl)dipyridine (TmPyPB) were respectively used as the hole-transporting layer (HTL) and the electron-transporting layer (ETL). Meanwhile, the OLEDs based on the exciplex emitters with 3Cz-o-TRz as the D component were fabricated with a structure of ITO/TAPC (30 nm)/3Cz-o-TRz (10 nm)/3Cz-o-TRz:B3PyMPM (or B4PyMPM or PO-T2T) (20 nm)/B3PyMPM (or B4PyMPM or PO-T2T) (50 nm)/LiF (1 nm)/Al. In particular, a thin layer of 3Cz-o-TRz was introduced into the device to prevent the formation of exciplex between the HTL and the EML.

The key performances of these OLEDs are illustrated in Fig. 4 and listed in Table 1. The EL spectra of six exciplex emitters all red-shifted relative to their PL spectra, which peaked at 524, 540, and 588 nm for TAPC:3Cz-o-TRz, TPA-PXZ:3Cz-o-TRz, and m-MTDATA:3Cz-o-TRz and at 516, 520, and 520 nm for 3Cz-o-TRz:B3PyMPM, 3Cz-o-TRz:B4PyMPM, and 3Cz-o-TRz:PO-T2T, respectively. Meanwhile, all the six devices exhibited relatively low turn-on voltages (at the brightness of 1 cd m^{-2}) around 2.6 V because of the good carrier injection and transport capabilities of exciplex emitters. Among the six exciplex emitters, m-MTDATA:3Cz-o-TRz exhibited the lowest efficiencies in the device. This result can be ascribed to the fact that the narrow bandgap of orange-red exciplex emitter greatly increases the non-radiative decays of excited states [35]. By contrast, the green OLEDs with TAPC:3Cz-o-TRz and 3Cz-o-TRz:PO-T2T as emitters achieved maximum CEs and EQEs of 39.3 and 37.2 cd A^{-1} and 12.1% and 11.8%, respectively, and remained at high values of 11.5% and 11.0% at a luminance of 1000 cd m^{-2} . These results are consistent with their PLQY results. With 3Cz-

Figure 4 (a) EL spectra, (b) EQE-luminance plots of donors:3Cz-*o*-TRz; (c) EL spectra, (d) EQE-luminance plots of 3Cz-*o*-TRz:acceptors.

Table 1 Summary of OLED performances

EML	$\lambda_{\max}$ (nm)	V_{on} (V)	$\text{CE}_{\max}$ (cd A ⁻¹)	$\text{EQE}_{\max}$ (%)	CE_{1000} (cd A ⁻¹)	EQE_{1000} (%)
TAPC: 3Cz- <i>o</i> -TRz	520	2.7	39.3	12.1	37.4	11.5
TPA-PXZ: 3Cz- <i>o</i> -TRz	540	2.6	33.8	10.1	33.0	9.9
<i>m</i> -MTDATA: 3Cz- <i>o</i> -TRz	588	2.5	2.4	1.1	2.3	1.0
3Cz- <i>o</i> -TRz: B3PyMPM	516	2.6	16.0	5.5	7.0	2.3
3Cz- <i>o</i> -TRz: B4PyMPM	520	2.6	20.0	6.2	16.0	5.0
3Cz- <i>o</i> -TRz: PO-T2T	516	2.6	37.2	11.8	34.5	11.0
TAPC:3Cz- <i>o</i> -TRz/3Cz- <i>o</i> -TRz:PO-T2T	516	2.4	43.8	14.1	35.6	11.5

o-TRz serving as either D or A component, the exciplex emitters could realize comparable EL performance with the maximum EQEs around 12%. These results successfully demonstrate that our donor-spacer-acceptor structure molecule 3Cz-*o*-TRz meets the requirements of the multifunctional component to construct exciplexes and efficient exciplex emitters as either D or A component.

Given their similar green EL emission, TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T were used to construct a simple tandem OLED to further demonstrate the superiority of 3Cz-*o*-TRz. The device configuration was ITO/TAPC (30 nm)/TAPC:3Cz-*o*-TRz

(10 nm)/3Cz-*o*-TRz (7 nm)/3Cz-*o*-TRz:PO-T2T (10 nm)/PO-T2T (60 nm)/LiF (1 nm)/Al. In this device, two individual emitters of TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T were stacked in series through a thin 3Cz-*o*-TRz interconnecting layer. The interconnecting layer not only prevents the formation of an undesired interfacial exciplex between TAPC and PO-T2T [36] but also avoids additional charge injection barriers in the EML. The corresponding device performance is illustrated in Fig. 5. The EL spectrum of the tandem OLED was consistent with the emission of TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T and exhibited no change with the increase in driving voltage.

Figure 5 (a) EL spectra at different voltages; (b) current density-luminance-voltage characteristics, (c) CE-luminance plots, and EQE-luminance plots of the tandem device.

Accordingly, the tandem device originated from the emission of TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T exciplexes. Compared with the OLEDs based on single exciplex emitters, the turn-on voltage of the tandem device further decreased to 2.4 V because the tandem OLED can successfully eliminate the charge injection barriers at the HTL/EML and ETL/EML interfaces, as shown in Fig. S9. Moreover, the series connection of two exciplex emitters could further avoid carrier leakage and improve the device efficiency [37,38]. Accordingly, the tandem OLED exhibited a maximum CE of 43.8 cd A⁻¹ and a maximum EQE of 14.1%, which improved by approximately 20% compared with those of TAPC:3Cz-*o*-TRz- and 3Cz-*o*-TRz:PO-T2T-based OLEDs. These results indicate that the appropriate design of device structure can evidently improve the EL performance of exciplex emitters.

CONCLUSION

A new donor-spacer-acceptor structure molecule, 3Cz-*o*-TRz, was developed using a diphenyl ether to connect the 3Cz and TRz segments. 3Cz-*o*-TRz can be used to construct exciplex emitters as either D or A component because it exhibits the intrinsic characteristics of 3Cz and TRz groups in the single-molecule state. Moreover, TAPC:3Cz-*o*-TRz with 3Cz-*o*-TRz as the A component and 3Cz-*o*-TRz:PO-T2T with 3Cz-*o*-TRz as the D component achieved uniform EL performance with the maximum EQEs of 12.1% and 11.8%, respectively. In addition, a simple tandem OLED formed by stacking TAPC:3Cz-*o*-TRz and 3Cz-*o*-TRz:PO-T2T in the EML realized improved performance with an ultralow turn-on voltage of 2.4 V and a maximum EQE of 14.1%. These results prove that the donor-spacer-acceptor

structure molecule not only serves as the multifunctional component to construct exciplex emitters but also has unique advantages in the design of device structures.

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Author contributions Zheng CJ and Zhang XH conceived and supervised the project. Yang HY and Shi YZ designed and synthesized the molecule. Yang HY, Zhang M, and Zhao JW prepared the device and performed the corresponding measurements and characterizations. Yang HY and Pu CP performed the data analysis. Yang HY wrote the paper with support from Zheng CJ. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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一种新型给体-间隔基-受体结构材料作为多功能组分实现高效激基复合物发光二极管

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摘要 为了实现高效的激基复合物发光二极管(OLED), 我们设计并合成了一种新型给体-间隔基-受体(D-Spacer-A)结构分子3Cz-o-TRz. 通过引入二苯醚基团作为间隔基, 可以有效地抑制3Cz-o-TRz分子内的电荷转移过程, 使其在单分子态下能够同时表现出给体和受体片段的本征特性, 从而能够作为多功能组分来构建激基复合物. 基于此, 3Cz-o-TRz分别与不同的受体材料和给体材料结合, 构建了六种激基复合物发光分子. 其中, 基于3Cz-o-TRz分别作为给体和受体组分所构建的激基复合物OLED器件均实现了最大外部量子效率(EQE)约为12%的性能. 并且, 通过串联激基复合物TAPC:3Cz-o-TRz和3Cz-o-TRz:PO-T2T为发光分子进一步提高了器件性能, 最大EQE可达14.1%. 我们的工作证明了具有D-Spacer-A结构的分子在构建激基复合物OLED中具有巨大潜力.