Organic Light-Emitting Diodes



Blocking Energy-Loss Pathways for Ideal Fluorescent Organic Light-Emitting Diodes with Thermally Activated Delayed Fluorescent Sensitizers

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Organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence-sensitized fluorescence (TSF) offer the possibility of attaining an ultimate high efficiency with low roll-off utilizing noble-metal free, easyto-synthesize, pure organic fluorescent emitters. However, the performances of TSF-OLEDs are still unsatisfactory. Here, TSF-OLEDs with breakthrough efficiencies even at high brightnesses by suppressing the competitive deactivation processes, including direct charge recombination on conventional fluorescent dopants (CFDs) and Dexter energy transfer from the host to the CFDs, are demonstrated. On the one hand, electronically inert terminalsubstituents are introduced to protect the electronically active core of the CFDs; on the other hand, delicate device structures are designed to provide multiple energy-funneling paths. As a result, unprecedentedly high maximum external quantum efficiency/power efficiency of 24%/71.4 lm W⁻¹ in a green TSF-OLED are demonstrated, which remain at 22.6%/52.3 Im W^{-1} even at a high luminance of 5000 cd m⁻². The work unlocks the potential of TSF-OLEDs, paving the way toward practical applications.

Outstanding properties of materials with thermally activated delayed fluorescence (TADF) have triggered a new insight into the next-generation organic semiconductors for organic light-emitting diodes (OLEDs).^[1–4] What distinguishes TADF compounds from conventional organic materials is the small singlet–triplet energy gap (ΔE_{ST}), inducing efficient triplet-to-singlet spin-flip transition.^[5] Intriguingly, this so-called reverse intersystem crossing process (RISC) has aroused many fascinating properties, rendering materials with TADF suitable not only for next-generation emitters but also for ideal hosts in OLEDs with the latter being believed to be more adequate for practical applications owing to their unique technological merits.^[6–8]

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The dilemma for materials with TADF as emitters is a small $\Delta E_{\rm ST}$ intrinsically accompanied by small radiative decay rates $(k_r, \text{ typically } 10^5 - 10^7 \text{ s}^{-1})$, invoking instability and efficiency roll-off at high current density.^[9,10] This tradeoff can be broken by delivering the singlet energy of TADF to conventional phosphorescent or fluorescent dyes through the more efficient Förster resonance energy transfer (FET).^[11] With the TADF-sensitized phosphorescence (TSP) technology, ultimate efficiencies have been achieved with a large critical current density $(J_{1/2})$, which, however, cannot avoid the utilization of noble heavy metal atoms. Commonly, the commercial applications of OLED technology require high brightness levels approaching 5000 cd m⁻², given the predicted per-m² manufacturing cost of large area illumination as well as the limited aperture ratio of the high-resolution displays.^[12] Also, as the next challenging

target in organic semiconductors, an electrically pumped organic laser requires current densities ~10⁶ times larger than current display applications.^[12] Theoretically, TADF-sensitized fluorescent (TSF) OLEDs may offer prospects in realizing ultimate efficiencies with even lower efficiency roll-off, higher color-purity and longer term-stabilities than TSP-OLEDs. Strategies to realize TSF using materials with TADF as the sensitizing host or the assistant dopant have been proposed by our group and Prof. Adachi and co-workers separately, realizing dual enhancement of electroluminescence efficiency and operational stability.^[13–16] However, the performances of TSF-OLEDs are still far from satisfaction. How to unlock the full potential of TSF-OLEDs is still unrevealed.

Here, we demonstrate ultimately efficient TSF-OLEDs even at high brightnesses by blocking the competitive deactivations processes. On one hand, electronically inert terminal-substituents are introduced to substantially shield the electronically active core of the should be changed to conventional fluorescent dopants (CFDs) from contact with adjacent molecules while not affecting their evaporability. On the other hand, dedicate device structures are exploited to provide multiple energy funneling paths involving one from high-energy interfacial exciplex to an intermediate TADF host and then to CFDs, promoting the singlet excitons ratio while reducing triplet one. The energy-loss paths, such as direct charge recombination on the fluorescent dopants (CFDs) and Dexter energy transfer from the host to the CFDs, are thereof blocked. The resulting





Figure 1. The energy loss paths are indicated by the red lines. FET is the Förster energy transfer while DET is the Dexter energy transfer.

TSF-OLEDs exhibit maximum external quantum efficiency (EQE_{max})/power efficiency (PE_{max}) of 24%/71.4 lm W⁻¹, which remain at 22.6%/52.3 lm W⁻¹ even at a high luminance of 5000 cd m⁻². Those results testify the validity of such strategy and may shed more light on developing more efficient TSF-OLEDs suitable for practical applications.

The TSF process is illustrated in **Figure 1**. Ideally, the tripletto-singlet spin-flip transition happens on the TADF material through efficient RISC process, and then the formed singlet energy will be transferred to the CFDs through the long-range FET.^[13] As indicated by the red arrows, direct charge recombination on the CFDs as well as Dexter energy transfer (DET) from the triplet of the host to that of the CFDs are the two paths to loss. Extremely low CFD concentrations (<1 wt%) are usually adopted to reduce the loss paths, which, however, increase the device fabrication difficulty in controlling accurate and constant doping concentration and the effect is limitedly referred from the low device efficiencies.^[17]

In terms of direct recombination on CFDs, energy level tuning of the host and the dyes to achieve Langevin recombination can efficiently reduce this problems. For the Dexter interaction in the emitting layers (EMLs), unfortunately, the close proximity of the host materials and dyes mixed together increases the likelihood of such deactivation process. Technically, DET happens when the excited electron is transferred from the excited state of D (D*) to the ground state of the acceptor (A) via a nonradiative path. It has been established that the DET rate (k_{DET}) decreases as exp($-2r_{\text{DA}}/L$), where r_{DA} is the donor-acceptor separation relative to their van der Waals radii, L. This means that k_{DET} is significantly influenced by the intermolecular distances, which drops to negligibly small values as the intermolecular distance increases more than on the order of one or two molecular diameters.^[18,19] Besides, DET also requires the overlap of the molecular orbitals of neighboring molecules since electron exchange process is involved.^[20] Therefore, only donors in close proximity to acceptors may transfer their energy by the Dexter mechanism.

Reasonably, increasing the intermolecular distance may efficiently reduce the DET process. One way to increase intermolecular distances through molecule design is the adoption of the electronically inert terminal substituents. Owing to their large steric effect, inert units can sterically shield the electronically ADVANCED MATERIALS www.advmat.de

active cores of CFDs, not only increasing the intermolecular distance but also reducing the orbital overlap of neighboring molecules. Therefore, efficiently suppressed DET can be anticipated. Additionally, given that FET is long-range dipole–dipole interaction in the order of several nms, not requiring orbital overlap,^[20] it can be anticipated that steric bulk units on the CFDs only shows limited influence on the Förster interaction, which is the prerequisite for efficient TSF process. It should be noted that too large terminal units may affect the evaporability of the CFDs, rendering them only suitable for solution-processed OLEDs, not beneficial for high efficiencies.^[21] Therefore, the size of the terminal substituents should be wisely tuned to be suitable for highly efficient evaporated devices.

The CDFs testified in this work are presented in **Figure 2a**. All those dyes involve N^9, N^9, N^{10}, N^{10} -tetraphenylanthracene 9,10-diamine (PAD) as the luminophores, where anthracene unit was chosen due to its large conjugation rigid planar, benefiting to increase the k,s. Different size terminal-substituents, methyl, tert-butyl, and 2-phenylpropan-2-yl units, which are intrinsically electronically inert moieties, were adopted to be attached on the 9- and 10-position of the diamine units. The larger the size of the terminal units, the more significant sterical effect can be anticipated. Here the terminal substituents are attached on the diamine units rather than directly on the anthracene units to avoid the significant influence on geometrical and electronic properties of the dyes. Also, the terminal units chosen here do not influence the evaporability of the CFDs as they can be purified by the sublimation.

All the materials were featured with the crystal structures as shown in Figure 2b from both side- and plan-views. All dyes show twisted structures with the dihedral angles between the phenyl planes being 54.89°, 61.2°, 46.74°, and 69.65° for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively, indicating that the terminal-substituents show slight influence on the molecular structures. The distance from the center of the anthracene planes to the farthest atoms of the terminal-substituents were also measured to be 6.821, 8.180, 9.253, and 10.507 Å for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively, suggesting that the molecular sizes are gradually increased. Therefore, it can be anticipated that the distances between the anthracene cores and the neighboring molecules are gradually increased from PAD to PhtBuPAD.

The geometrical and electronic properties of the CFDs were simulated using density functional theory (DFT) with the most popular functional, B3LYP, to study the structure–property relationship of the fluorescent dyes. As illustrated in Figure 2c, the lowest unoccupied molecule orbitals (LUMOs) of all dyes are located on the anthracene units while the highest occupied molecule orbitals (HOMOs) distributions are extended to the diamine units owing to their strong electron-donating properties. Notably, no energy level distributes on the terminal-substituents, proving that those units only act as electronically inert moieties surrounding the electronically active PAD cores for all CFDs with different sterical effect. The DFT calculations for the lowest excited triplet states of these dyes revealed that the spin-density distributions also resided on the electronically active PAD units, surrounded by the terminal units.

Based on the above calculations, it is reasonable to draw the conclusion that the electronically inert terminal-substituents

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Figure 2. a) The molecule structures of the dyes. b) The single-crystal structures of the fluorescent dyes observed from the side-view and the plan-view. c) The calculated geometrical structures of the dyes as well as the HOMO and LUMO as well as the triplet spin density distributions.

appended to diamines units only exert the sterical effect to substantially shield the electronically active core of the dyes from contact with adjacent molecules. Thus, the terminal units not only increase intermolecular distance between the luminophores of the dyes and the neighboring molecules but also reduce their orbital overlaps, which, are the prerequisite for efficient intermolecular electron exchange interactions. Therefore, the Dexter interactions can be greatly suppressed by the terminal-substituents. Since the shielding effect is related with the size of the terminal units, it can be anticipated that from







Figure 3. a) The absorption and emission spectra of the dyes in toluene solutions with concentration of 10-5 mol L⁻¹. b) The CV curves of the dyes in dichloromethane. c) The emission spectra of the DPEPO: 20 wt% TADF: with or without 3 mol% dye films. d) The PL transient decay curves of the 4CzTPN-Ph in the DPEPO: 20 wt% TADF: with or without 3 mol% dye films observed at 590 nm. The insert scheme is the energy transfer progress in the doped films and the molecule structure of 4CzTPN-Ph.

PAD to PhtBuPAD, as the terminal size gradually increased, the Dexter interactions can also be gradually suppressed.

The calculated HOMO and LUMO energy levels of the molecules were also shown in Figure 2c, exhibiting that the energy levels of other emitters are slightly shallower than those of PAD due to the enhanced electron-donating ability of the side groups by the introduction of the terminal-substituents. Additionally, the singlet and triplet energies were also calculated using timedependent DFT (TD-DFT) with B3LYP basis. The singlet energy of PAD is relatively higher than other dyes resulted from its relatively larger energy gap, indicating that the enhanced electrondonating ability of the side groups reduce the molecular energy gaps. The triplet energies were calculated to be 1.60, 1.57, 1.58, and 1.58 eV for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively. The large ΔE_{STS} of those dyes facilitate to achieve the high photoluminance quantum yields (ϕ_{PLS}) of the dyes by suppressing the intersystem crossing (ISC) process.

The photophysical properties of the emitters were investigated in toluene with concentration of 10^{-5} mol L⁻¹ as shown in **Figure 3**a. Intriguingly, all emitters show almost the same absorption spectrum, derived from the same electronically active cores which were not disturbed by the terminal-substituents appended to diamines units. Furthermore, compared to PAD with an emission peak at 510 nm, other emitters show slightly red-shifted emission with emission peaks of 531 nm for MePAD and 526 nm for tBuPAD and PhtBuPAD, inconsistent with the calculated results. The $\phi_{\rm PL}$ s were also measured in toluene to be 0.89, 0.80, 0.80, and 0.83 for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively. The slight reduction in $\phi_{\rm PL}$ s of other emitters than that of PAD may be attributed to the rotation of the terminal units which induces more relaxation process in the solution. The PL transient decay curves of the emitters were also measured and shown in **Table 1** with lifetimes (τ s) of 10.96, 12.64, 13.29, and 13.16 ns for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively. The $k_{\rm r}s$ of the dyes can also be calculated with the equation of $k_{\rm r} = \phi_{\rm PL}/\tau$, which are all in the range of 10⁸ s⁻¹, much higher than most of the TADF emitters with $k_{\rm r}s$ of usually in the range of 10⁵–10⁷ s⁻¹.

The cyclic voltammetry (CV) oxidation curves of the dyes were illustrated in Figure 3b, showing that the electrochemical properties of the dyes were significantly influenced by the terminal units. Compared to that of PAD, the oxidation potentials of the MePAD and tBuPAD are relatively lower, derived from the strong electron-donating properties of the methyl and tertbutyl units. Notably, the oxidation potential of PhtBuPAD is higher than those of MePAD and tBuPAD, indicating that the electron donating properties of the alkyl group are diluted by the phenyl units which can disperse the rich electrons. The HOMO energy levels of the emitters can be calculated to be 5.24, 5.15, 5.0, and 5.25 eV respectively for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively, determined from their anodic oxidation potentials. The LUMO energy levels were calculated by

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 Table 1. Properties of the fluorescent emitters.

Emitters	Emission ^{a)} [nm]	$\phi_{PL}{}^{a)}$	S ₁ ^{a)} [eV]	Τ ₁ ^{b)} [eV]	E _g ^{a)} [eV]	HOMO ^{c)} [eV]	LUMO ^{c)} [eV]	τ [ns]	kr [× 10 ⁸ s ^{−1}]
PAD	510	0.89	2.43	1.60	2.42	5.24	2.82	10.96	8.1
MePAD	531	0.80	2.34	1.57	2.40	5.15	2.75	12.64	6.3
tBuPAD	526	0.80	2.36	1.58	2.42	5.0	2.58	13.29	5.9
PhtBuPAD	526	0.83	2.36	1.58	2.42	5.25	2.83	13.16	6.3

a) Measured in toluene solution with concentration of 10⁻⁵ mol L⁻¹; ^b)Calculated using DFT with B3LYP basis; ^c) Measured in dichloromethane.

the HOMO values and the energy gaps ($E_{\rm g}$ s) obtained from the onsets of the absorption spectra of these emitters, which are listed in Table 1.

The suppressed DET by the terminal-substituents can be directly testified by the PL transient decay curves of the mixed films of bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO): 20 wt% 2,3,5,6-tetrakis(3,6-diphenylcarbazol-9-yl)-1,4-dicyanobenzene (4CzTPN-Ph) with and without 3 mol% CFDs, observed at the emission peak of the orange TADF emitter, 4CzTPN-Ph.^[1] The singlet energy of 4CzTPN-Ph is reported to be about 2.2 V with an emission spectra peaked at 577 nm.^[1] Given that the lower singlet energy of 4CzTPN-Ph than CFDs, the energy transfer between the singlet excitons is avoided. Therefore, the only energy transfer process in the system is the DET from the triplet of 4CzTPN-Ph to that of the dyes. Figure 3c shows the emission spectra of the doped films, exhibiting only the emission from 4CzTPN-Ph. The PL decay curves of 4CzTPN-Ph in the doped films with or without CFDs were measured and illustrated in Figure 3d, the lifetimes of the prompt parts (τ ps) remain the same, indicating that no singlet excitons of 4CzTPN-Ph involved in the energy transfer process in the system. Contrarily, compared with that of the film without CFDs, the lifetimes of the delayed parts (τ ds) of the films with dyes were reduced, assigned to the DET from the TADF material to the CFDs, which induces an additional triplet exciton decay process.

The intrinsically decay curves of triplet after removing the excitation source can be written as^[22]

$$d[T_1]/d[t] = -(k_{\rm nr}^{\rm T} + k_{\rm RISC})[T_1] + k_{\rm ISC}[S_1]$$
(1)

where k_{nr}^{T} stands for the nonradiative decay rates of the triplet. k_{RISC} is the RISC rates while k_{ISC} represents the ISC rates.

When a DET process is introduced, the decay curves of T_1 can be expressed as

$$d[T_1]/d[t] = -(k_{\rm nr}^{\rm T} + k_{\rm DET} + k_{\rm RISC})[T_1] + k_{\rm ISC}[S_1]$$
(2)

where the k_{DET} stands for the DET rates from the TADF triple to that of the fluorescent dyes. According to those two equations, the DET process will quicken the decay process of triplet excitons of the TADF material, leading to relatively shorter lifetimes. Additionally, as can be seen from Figure 3d, the smaller the size of the terminal units of the dyes, the shorter the τ_{d} s of the films were observed. According to Equation (2), the shorter τ_{d} indicates the larger k_{DET} . The films doped dyes with relatively larger terminal-substituents show the longer τ_{d} s and thus the smaller k_{DET} s, evidencing that the large terminal-substituents can suppress Dexter interactions.

The electroluminance (EL) performances of the CFDs were examined with the device structures of indium tin oxide (ITO)/4,4'-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline) (TAPC, 30 nm)/tris(4-(9H-carbazol-9-yl)phenyl)amine (TCTA, 10 nm)/ 10,10'-(sulfonylbis(4,1-phenylene)) bis(10H-phenoxazine) (PXZ-DPS): 0.5 mol% CFDs (30 nm)/9,10-bis(4-(2-phenyl-1H-benzo[d] imidazol-1-vl)phenvl) anthracene (BPBiPA, 40 nm)/LiF (0.5 nm)/ Al (150 nm) as is shown in Figure 4a (Device Type I). Here, PXZ-DPS was chosen as the TADF sensitizing host, possessing a small $\Delta E_{\rm ST}$ of 0.08 eV with an emission peak at 508 nm.^[23] Though the small ΔE_{ST} renders PXZ-DPS an efficient RISC efficiency, its k_r is only about 1.7×10^7 s⁻¹, nearly two orders lower than that of the CFDs. As can be seen from Figure S1 of the Supporting Information, significant overlaps between the emission spectrum of PXZ-DPS and the absorption spectra of the dyes are observed, indicating efficient energy transfer. As elucidated by the energy level of the devices (Figure 4a), due to the relatively deeper LUMO energy level of PXZ-DPS than those of dyes, electrons from the adjacent electron-transporting layer will be preferentially injected into the PXZ-DPS host, and then combined with the holes injected from TCTA layer owing to the small energy barriers. Therefore, direct charges recombine on the dyes can be avoided, also evidenced by the measured electroluminescence decay curves of the devices, as illustrated in Figure S2 of the Supporting Information, where no spike was observed after the voltage being turned off, indicating no charge trapping on the dyes.^[13]

As illustrated in Figure 4b and Figure S3 of the Supporting Information, when observed at the emission peaks of the dyes, the PL transient decay curves of the PXZ-DPS: x mol% dye films show clearly delayed components, evidencing the TSF process in the films. Besides, the lifetimes of the delayed parts are gradually decreased with the dye concentration increasing, owing to the enhanced FET from the TADF to the fluorescent dyes. The same trend was also observed in the EL decay curves of the devices with increasing dye concentrations (Figure S2, Supporting Information). The emission spectra of the TSF-OLEDs are shown in Figure 4c, where the emissions of the dyes with terminal units show slightly redshift compared with that of PAD, corresponding to the spectra obtained with PL excitation. The half-peak widths are 87, 76, 73, and 80 nm for devices with PAD, MePAD, tBuPAD, and PhtBuPAD, respectively. Contrarily, the device with PXZ-DPS as the emitter was also fabricated, showing a half-peak width of 105 nm, wider than that of the TSF-OLEDs. The relatively narrow spectrum of TSF-OLEDs render them suitable for display applications, where high color-purity is required.

The device efficiencies with dopant concentration of 0.5 mol% are shown in Figure 4d, proving that the larger the



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Figure 4. a) The TSF-OLED structures of **Device Type I** and some of the molecule structures. b) The PL decay curves of the host: PhtBuPAD doped films. c) The EL-spectrum of the TSF-OLEDs. d) The EQE-brightness curves of the TSF-OLEDs based on different dyes. e) The normalized EQE_{max} and the ϕ_{PL} s versus the dopant concentrations.

terminal-substituents of CFDs, the higher the device EQE_{max} can be obtained. The ϕ_{PL} s of the doped films were measured to be 0.77, 0.85, 0.85, and 0.86 for PAD, MePAD, tBuPAD, and PhtBuPAD, respectively. The much lower device efficiencies of PAD based device than that of PhtBuPAD can be partly attributed to the relatively lower ϕ_{PL} of PAD than that of PhtBuPAD.

However, this cannot explain the inferior efficiencies based on MePAD and tBuPAD since their ϕ_{PL} s are similar to that of PhtBuPAD. Considering no direct charge recombination on the dyes, we believe the difference of the device efficiencies is owing to the influence of the Dexter interactions in the EMLs. As discussed above, the terminal-substituents of the dyes can

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suppress the DET process in the devices and the suppression effect greatly depends on size of the units. The sizes of the terminal units from PAD to PbtBuPAD are gradually increased, leading to enhanced suppression effect, and thus their device efficiencies show the same trend.

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To further reveal the influence of the terminal-substituents on device performances, the EQE_{max} of the devices and the ϕ_{PI} s of the doped films with the gradually increased dopant concentrations were measured and the normalized values were summarized in Figure 4e. For all dyes, the concentration influence on the $\phi_{PL}s$ is quite limited. Contrarily, the EQE_{max} of the devices are gradually reduced with the dye concentration increasing. Ruling out the influence of $\phi_{PL}s$, it is reasonable to make the conclusion that the reduction in EQE_{max} is due to the enhanced DET derived from the increased dopant concentration, which shortens the intermolecular distances. Additionally, it seems that the larger the terminal units, the slower the reduction rate in EQE_{max} with dopant concentration increasing, further proving that large terminal substituents can suppress the DET and thus the exciton loss. However, though dyes with large terminal units can suppress DET, EQE_{max} of only 13.7% was achieved, still much lag behind the phosphorescent or the TADF OLEDs.

Further efficiency promotion may be realized by introducing a wide-energy-gap host to dilute the TADF materials to suppress the aggregation-caused quenching effect.^[14] A new bipolar wide-energy-host, 3-(3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9-phenyl-9H-carbazole (PhCzTrz) was developed to dilute PXZ-DPS to suppress exciton annihilation. Owing to the deep LUMO and HOMO energy levels of PhCzTrz, which were 2.93 and 6.15 eV, respectively, exciplex emission was observed from PhCzTrz and TCTA mixed films as is shown in Figure S4 of the Supporting Information, exhibiting efficient TADF properties as indicated by the delayed part of the decay curve. But there is no exciplex formed between PhCzTrz and 3,3-di(9Hcarbazol-9-yl)biphenyl (mCBP). Based on this, two kinds of TSF-OLEDs (Device Type II and III) were fabricated for comparison as shown in Figure 5a,b. Also, it was demonstrated that interfacial exciplex at the interface of PhCzTrz/TCTA layers was formed in Device Type III as shown in Figure S5 (Supporting Information).

The existing of the interfacial exciplex greatly modulates the charge recombination ways in the devices. As elucidated by the device energy levels, electrons from the adjacent electron-transporting layer will be injected into the deep LUMO energy level of PhCzTrz in both devices. However, the situation for holes is different. In Device Type II, the holes from the mCBP layer will be preferentially injected into the HOMOs of PXZ-DPS but some still will be injected into the PhCzTrz, directly forming PhCzTrz excitons, especially under high voltage. The accumulated holes on the PXZ-DPS changes the internal electric field distributions, shifting its LUMO to a deeper level.^[24] Electrons thereafter become accessible from PhCzTrz to PXZ-DPS, forming PXZ-DPS excitons. Only TSF process from PXZ-DPS to the dyes can be anticipated, as shown in Figure 5c. In terms of Device Type III, the electrons on PhCzTrz will be quickly transferred to the TCTA/emitting layers interfaces to combine with the holes in the TCTA layer to form low energy interfacial exciplex excitons. The interfacial exciplex acts like exciton

sources, from where the energy will be transferred either to the intermediate TADF material and then to the CFDs, or directly to the CFDs, as illustrated in Figure 5d, constituting multiple energy funneling paths.

The concentration of PXZ-DPS and PhtBuPAD in the devices were optimized 30 wt% and 2 mol%, respectively. Both device showed relatively higher efficiencies than the one with only PXZ-DPS as the host, due to the suppressed annihilations induced by PXZ-DPS itself. Remarkably, a EQE_{max} of 24% with a PE_{max} of 71.4 lm W^{-1} was observed for Device Type III. To the best of our knowledge, this is the highest values for the TSF-OLEDs reported so far. Also, the efficiency roll-off of the devices was extremely small, with EQE/PE remaining at 22.6% and 52.3 lm W^{-1} even at the brightness level of 5000 cd m⁻², suitable for practical applications. Contrarily, Device Type II showed inferior performances with the EQE_{max}/PE_{max} of only 19.0%/48.1 lm W⁻¹ and relatively more significant efficiency roll-off. Since the current density of both devices is almost the same, the influence of the charge balance on device performances is negligible (Figure S6, Supporting Information). Also, no spike was observed for the EL decay curves of both devices after the voltage was turned-off, proving no direct charge recombination on the dyes. Therefore, the main difference derived from interfacial exciplex.

In Device Type II, only sensitizing path from PXZ-DPS to dyes exists. Also, the formation of the PhCzTrz excitons adds an additional energy loss through DET from triplet states of PhCzTrz to dyes as shown in Figure 5c, especially under high current density, which may account for the relatively high efficiency roll-off. Contrarily, when interfacial exciplex formed, the formation of the wide-energy-gap host excitons can be suppressed. As illustrated in Figure 5d, on one hand, as competing processes, the high RISC rate of the exciplex can suppress the DET from the exciplex triplet to the fluorescent dyes. On the other hand, the enhanced Förster energy transfer from the exciplex to the TADF material can greatly promote the ratio of the singlet excitons (>25%) of the TADF material while suppressing the triplet ones (<75%), which also suppresses DET from TADF triplet to that of the fluorescent dyes. Therefore, the exciton loss through DET can be greatly reduced with the second-order funneling path, benefiting the device efficiencies.

Direct sensitizing process from the interfacial exciplex to the fluorescent dyes can be demonstrated by the EL decay curves of the fluorescent devices without PXZ-DPS as shown Figure S7 (Supporting Information). For the fluorescent device with interfacial exciplex, the decay lifetime is shorter than that of the exciplex devices but higher than the devices without interfacial exciplex, demonstrating the direct energy-funneling from the exciplex to the dopant, which also enhances TSF process and suppresses exciton loss through Dexter interactions. Besides, clear overshoot was observed after the voltage was turned off in the device without interfacial exciplex, attributing to the charge trapping on the dye. Contrarily, there is no direct charge trapping on the dyes when interfacial exciplex exists, indicating that interfacial exciplex facilitates to reduce charge recombination on the fluorescent dyes. Those results greatly show the vital importance of the formation of the interfacial exciplex, not only achieving multiple energy funneling but also modulation charge recombination in the emitting layers. Here, it is





Figure 5. a,b) The energy level diagrams of **Device Type II and III.** c,d) The energy funneling mechanisms in **Device Type II and III.** e) The EQEbrightness curves of **Device Type II and III.** f) The EQE_{max}-dopant concentration relationships of **Device Type III** with different CFDs.

worth noting that triplet fusion for anthracene derivatives has also been employed to promote the device efficiencies.^[25] However, the contribution of triplet fusion can be negligible for the devices here due to the low doping concentrations as well as the suppressed formation of the triplet states on the anthracene derivatives.

Additionally, other dyes were also demonstrated in the device structure of **Device Type III**, showing EQE_{max}/PE_{max} of 18.6%/54.0, 20.8%/61.9, and 22.7%/66.8 lm W⁻¹ for PAD, MePAD, and tBuPAD, respectively, as can be seen from **Table 2** and Figure S8 (Supporting Information). Those performances are much higher than those of the TSF-OLEDs with only PXZ-DPS as the host, proving the superiority of the devices with multiple energy funneling paths. The EQE_{max}-dye concentration relationship was also examined in such device structures as revealed in Figure 5f. The same conclusion can also be drawn that the larger

size of the terminal substituents can suppress the excitons loss through DET. Moreover, comparing with the trend of the device with only PXZ-DPS as the hosts, the EQE_{max} reduction rate is much slower, also evidencing that the exciton loss was further reduced in the devices with multiple energy funneling paths.

In conclusion, we have shown that to boost the TSF-OLED performances, the exciton loss paths must be blocked. The CFDs with their electronically active cores shielded by the electronically inert terminal-substituents as well as the device structures with multiple energy funneling paths were exploited, reducing charge recombination on the CFDs and suppressing the Dexter interactions in the emitting layers. All those efforts maximally suppress the exciton loss, leading to TSF-OLEDs with breakthrough EQE of 24.0% with extremely low efficiency roll-off. Additionally, unlike previous work adopting extremely low dopant concentration (<1 wt%) to reduce DET, high dopant

Table 2. Device performances of the TSF-OLEDs.

Emitter	Voltage [V]			EQE [%]			РЕ [lm W ⁻¹]			CIE ^{d)}
	10 cd m ⁻²	1000 cd m ⁻²	5000 cd m ⁻²	Max	1000 cd m ⁻²	5000 cd m ⁻²	max	1000 cd m ⁻²	5000 cd m ⁻²	
PAD ^{a)}	2.56	3.22	4.13	18.6	18.5	17.0	54.0	51.2	36.9	(0.36,0.57)
MePAD ^{a)}	2.54	3.16	4.0	20.8	20.7	19.5	61.9	58.9	44.0	(0.37,0.58)
tBuPAD ^{a)}	2.57	3.12	3.91	22.7	22.5	21.5	66.8	65.8	49.8	(0.36,0.58)
PhtBuPAD ^{a)}	2.55	3.11	3.90	24.0	23.8	22.6	71.4	68.5	52.3	(0.36,0.58)
PhtBuPAD ^{b)}	2.94	3.55	4.25	19.3	18.7	17.4	48.5	47.2	36.5	(0.36,0.58)
PhtBuPAD ^{c)}	2.51	3.07	3.70	13.7	13.3	12.9	41.6	41.0	33.7	(0.36,0.58)

a) Device structure III; ^{b)} Device structure I; ^{c)} Device structure II; ^{d)} The Commission Internationale de L'Eclairage (CIEs) were obtained under the voltage of 5 V.

concentration (3–5 wt%) can be used by using CFDs with steric terminal units, reducing the device fabrication difficulties and paving their way toward practical applications. We can presume that such concept can be used to fabricate highly efficient full-color fluorescent OLEDs. Furthermore, with a fluorescent laser dye, light amplification in an organic solid-state film with the aid of TADF-sensitized approach has also been observed.^[26] Our results here may shed more potential about the TSF-OLEDs technique in current-injection organic semiconductor lasers.

Experimental Section

Materials: DPEPO, 4CzTPN-Ph, TAPC, and TCTA were purchased from Xi'an Polymer Light Technology Co. Ltd. (Xi'an, Shanxi province, China). PXZ-DPS, BPBiPA were synthesized according to reported procedures.

Synthesis of Fluorescent Dyes: The following general procedure for the synthesis of CDFs was used. Diphenylamine (1.02 g, 6.0 mmol), di-p-tolylamine (1.19 g, 6.0 mmol), bis (4-(tert-butyl)phenyl)amine (1.69 g, 6.0 mmol), or bis (4-(2-phenylpropan-2-yl)phenyl)amine (2.44 g, 6.0 mmol) was added to a stirred solution of 9,10-dibromoanthracene (1.01 g, 3.0 mmol) and potassium carbonate (2.48 g, 18.0 mmol) in toluene (30 mL). With stirring, a solution of palladium(11) acetate (40.4 mg, 0.18 mmol) and tri-tert-butylphosphine (133.6 mg, 0.66 mmol) in 30 mL of toluene was then added. The reaction mixture was stirred and refluxed for 10h. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over Mg₂SO₄, and concentrated in vacuo. Column chromatography of the residue solid (eluent: chloroform/ hexane = 1/4) afforded the target compounds with the yield of over 80%.

 N^9, N^9, N^{10}, N^{10} , N^{10} , L^{10} , $CDCl_3$): δ (ppm) = 8.47 (dd, 4H), 7.42 (dd, 4H), 7.23 (t, 8H), 7.12 (d, 8H), 6.86 (t, 4H). High-resolution mass spectrometry (*m*/*z*): [M+H]⁺ calculated for $C_{38}H_{28}N_2$, 513.23; found, 513.24. Elemental analysis (calculated, found for $C_{38}H_{28}N_2$): C (89.03%, 89.01%), H (5.51%, 5.50%), N (5.46%, 5.49%).

 $N^9, N^9, N^{10}, N^{10}, N^{10}$ -tetra-*p*-tolylanthracene-9,10-diamine (MePAD): ¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.16 (dd, 4H), 7.32 (dd, 4H), 6.98 (s, 16H), 2.24 (s, 12H). High-resolution mass spectrometry (*m*/*z*): [M+H]⁺ calculated for C₄₂H₃₆N₂, 569.29; found, 569.27. Elemental analysis (calculated, found for C₄₂H₃₆N₂): C (88.69%, 88.68%), H (6.38%, 6.37%), N (4.93%, 4.95%).

 $N^9, N^9, N^{10}, \dot{N}^{10}$ -tetrakis (4-(tert-butyl)phenyl)anthracene-9,10-diamine (tBuPAD): ¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.18 (s, 4H), 7.33 (s, 4H), 7.17 (s, 8H), 7.01 (s, 8H), 1.26 (s, 36H). High-resolution mass spectrometry (*m*/*z*): [M+H]⁺ calculated for C₅₄H₆₀N₂, 737.48; found, 737.45. Elemental analysis (calculated, found for C₅₄H₆₀N₂): C (87.99%, 87.97%), H (8.21%, 8.22%), N (3.80%, 3.81%).

 N^9, N^9, N^{10}, N^{10} -tetrakis (4-(2-phenylpropan-2-yl)phenyl) anthracene-9,10-diamine (PhtBuPAD): ¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.50 (m, 4H), 7.45 (m, 4H), 7.33 (m, 16H), 7.22 (m, 4H), 7.03 (m, 16H), 0.32 (t, 24H). High-resolution mass spectrometry (*m*/*z*): [M+H]⁺ calculated for C₇₄H₆₈N₂, 984.54; found, 984.53. Elemental analysis (calculated, found for C₇₄H₆₈N₂): C (90.20%, 90.17%), H (6.96%, 6.97%), N (2.84%, 2.86%).

Theoretical Calculations: The geometrical and electronic properties of dyes were performed with the Gaussian 09 program package. The calculation was optimized by means of B3LYP (Becke three parameters hybrid functional with Lee–Yang–Perdew correlation functionals) with the 6-31G(d) atomic basis set. The singlet and triplet states were calculated using TD-DFT calculations with B3LYP/6-31g(d). The molecular orbitals were visualized using Gaussview.

Optical Characterization of Organic Thin Films: Ultravioletvisible absorption spectra were recorded using an Agilent 8453 spectrophotometer. PL quantum efficiency was measured by an absolute PL quantum yield measurement system (C9920-02, Hamamatsu Photonics) in air atmosphere with an excitation wavelength of 360 nm. The PL spectrum and PL transient decay curves of the films were measured using a transient spectrometer (Edinburg FL920P).

Electrochemical Measurement: The CV measurement were performed with a Potentiostat/Galvanostat Model 283 (Princeton Applied Research) electrochemical workstation, using Pt as working electrode, platinum wire as auxiliary electrode, and a Ag/AgCl electrode as reference electrode standardized against ferrocene/ferrocenium. The oxidation potentials were measured in dichloromethane (CH₂Cl₂) solution containing 0.1 $\text{Mn-Bu}_4\text{NPF}_6$ as supporting electrolyte at a scan rate of 100 mV s⁻¹.

Device Fabrication and Measurement: Before device fabrication, the ITO glass substrates were precleaned carefully. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 5×10^{-5} Torr. The hole-injection and holetransporting material TAPC, exciton blocking material TCTA, and electrontransporting material BPBiPA were thermally evaporated at a rate of 1.0 Å s⁻¹. After the organic film deposition, 0.5 nm of LiF and 150 nm of aluminum were thermally evaporated onto the organic surface. All of the organic materials used were purified by a vacuum sublimation approach. The forward-viewing electrical characteristics of the devices were measured using a Keithley 2400 source meter. The electroluminescence spectra and luminance of the devices were obtained on a PR650 spectrometer. All the device fabrication and characterization steps were performed at room temperature under ambient laboratory conditions. For measurement of the transient electroluminescence characteristics, short-pulse excitation with a pulse width of 15 μs was generated using an Agilent 8114A pulse generator. The amplitude of the pulse was 9 V, and the baseline was -3 V. The period was 50 μ s, the delayed time was 25 μ s, and the duty cycle was 30%. The decay curves of the devices were detected using an Edinburg FL920P transient spectrometer.

[CCDC 1564531; 1564532; 1564534; 1564535 contain the supplementary crystallographic data for this paper. These data can

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be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fluorescent organic light-emitting diodes, high efficiency, multiple energy-funneling paths, terminal substituents, thermally activated delayed fluorescent sensitizers

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