

Intramolecular Through-Space Charge-Transfer Emitters Featuring Thermally Activated Delayed Fluorescence for High-Efficiency Electroluminescent Devices

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Abstract

Through-space charge-transfer (TSCT) emitters have been extensively explored for thermally activated delayed fluorescence (TADF), but arranging various donors and acceptors into rigid cofacial conformations for various efficient TSCT TADF emitters has still remained a challenge. Here we report for the first time a “fixing acceptor” design to reach various efficient TSCT TADF emitters. By chemically fixing the acceptor (benzophenone) with a rigid spiro structure and cofacially aligning various donors with the fixed acceptor, a series of efficient TSCT TADF emitters have been developed. Single-crystal structures and theoretical calculations have verified closely-packed cofacial donor/acceptor conformations and favorable TSCT in the emitters. The emitters afford sky-blue to yellow TADF emission in doped films, with high photoluminescent efficiencies of up to 0.92 and reverse intersystem crossing rates of

up to $1.0 \times 10^6 \text{ s}^{-1}$. Organic light-emitting diodes using the emitters afford sky-blue to yellow electroluminescence with high external quantum efficiencies of up to 20.9%. The work opens a new avenue toward a wide variety of efficient TSCT TADF emitters.

Keywords: donor-acceptor systems, charge transfer, through space, thermally activated delayed fluorescence, electroluminescence

1. Introduction

Charge-transfer emitters with thermally activated delayed fluorescence (TADF) have aroused huge research interest for their wide applications in light-emitting devices [1-3], photocatalysis [4], and biological imaging [5], et al. They exhibit fast reverse intersystem crossing (RISC) from non-emissive triplet states (T_1) to emissive singlet states (S_1), due to the small singlet-triplet energy gaps (ΔE_{ST}) ($< 0.2 \text{ eV}$) produced by spatial separation of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) [1, 6]. With advantages of triplet-harvesting and low-cost, they have demonstrated a bright prospect for the use in electroluminescence (EL) devices [2, 3].

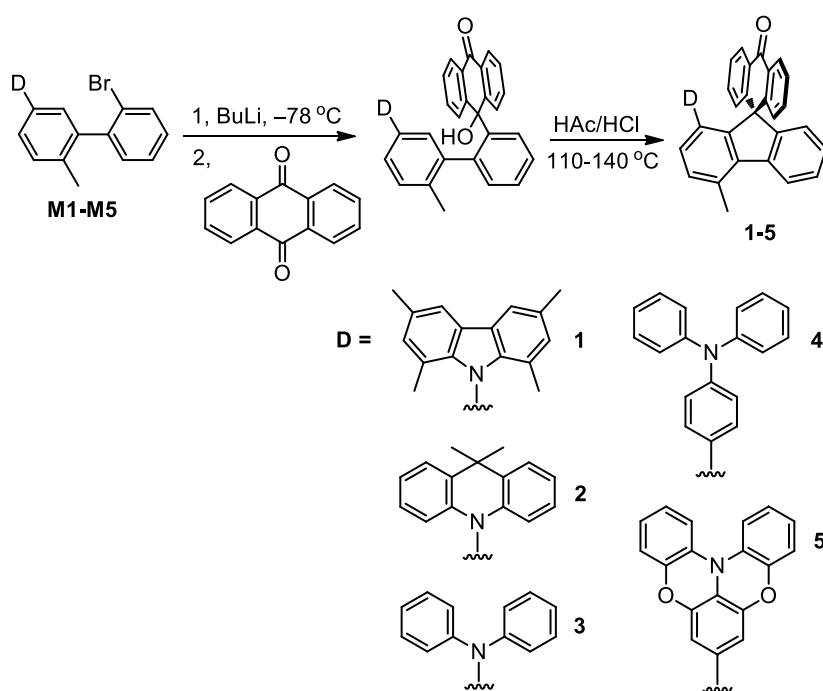
While through-bond charge-transfer TADF emitters have been widely developed by directly linking donor (D) and acceptor (A) units via chemical bonds or conjugated π -linkers and carefully twisting the D/A conformations [2, 3], through-space charge-transfer (TSCT) TADF emitters have recently attracted fast-growing interest [7]. In the simplest manner, TSCT systems can be developed by physically blending D and A molecules [6, 8, 9]. Such TSCT systems (also known as exciplex systems) can afford

tiny ΔE_{ST} values (\sim meV) due to the almost complete spatial separation of HOMO and LUMO orbitals, which are highly favorable for TADF [6, 10-15]. However, they usually afford low luminescent efficiencies, due to weak TSCT and pronounced non-radiative decay losses, resulting from loose packing and random orientations of the D/A molecules [16, 17]. To solve this challenge, the D/A molecules have been held close by non-conjugated σ -linkers [18-24]. Nevertheless, these D- σ -A TSCT systems still show relatively low luminescent efficiencies because of the lack of control over the relative orientations of the D and A units.

Recent researches have proved that cofacial D/A alignments are favored for developing efficient TSCT emitters [25-38], which can reinforce TSCT and promote radiative decay of charge-transfer states [35, 37]. Very recently, Jiang and Liao et al. have unveiled that fixation of the cofacial D/A conformation is critically important for developing efficient TSCT emitters, which can remarkably suppresses non-radiative decay of charge-transfer states by restricting the rotation or vibration of the D/A units [39]. The fixation has been achieved by chemically fixing the 9,10-dihydroacridine type D units and confining the D/A units into rigid cofacial conformations [39-46]. By this design, a series of highly efficient TSCT TADF emitters have been developed, which have proved high performances in EL devices [39-46]. Unfortunately, in this design, the D units are confined to be derivatives of 9,10-dihydroacridine [39-46], which imposes some restrictions on donor variation and further molecular engineering. It has still remained challenging to develop various efficient TSCT TADF emitters.

Herein, we report for the first time a “fixing acceptor” design to reach various

efficient TSCT TADF emitters. As shown in Scheme 1, TSCT emitters 1-5 are developed by chemically fixing the A unit (benzophenone) and confining the D/A units into closely-packed cofacial conformations. The A unit is fixed with a spiro-structure derived from a carbonyl group of the A precursor. The D units are facilely varied with different structures and electron-donating strengths, which are 1,3,6,8-tetramethyl-9*H*-carbazole (Me₄CAZ), 9,9-dimethyl-9,10-dihydroacridine (DMAC), diphenylamine (DPA), triphenylamine (TPA), and benzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine (BOP) for 1-5, respectively. Single-crystal *X*-ray structures and theoretical calculations have verified closely-packed cofacial D/A conformations and favorable TSCT in 1-5. In doped films, 1-5 afford strong sky-blue to yellow TADF emission, with high photoluminescent efficiencies (Φ_{PL}) of up to 0.92 and RISC rates (k_{RISC}) of up to $1.0 \times 10^6 \text{ s}^{-1}$. Organic light-emitting diodes (OLEDs) using 1-5 as the emitters show sky-blue to yellow EL with high external quantum efficiencies (*EQEs*) of up to 20.9%.



Scheme 1. Synthetic routes to TSCT emitters 1-5.

2. Results and discussion

Scheme 1 outlines the general synthetic route to 1-5. The rigid spiro-structure in a fluorene linker is utilized to fix benzophenone as the A unit. The D-containing compounds M1-M5 firstly reacted with *n*-butyllithium to form the phenyllithium reagents, which then reacted with one carbonyl group of the A precursor (anthraquinone) to afford the tertiary alcohol intermediates including both D and A units. By intramolecular Friedel-Crafts cyclization reactions in the tertiary alcohol intermediates, 1-5 were prepared with total yields of 40–64%. A key design is to direct the cyclization to occur at the ortho-position of the D unit by blocking the other cyclization site with a methyl group. Scheme S1 outlines the synthetic routes to the key intermediate compounds M1-M5. M3 was prepared by a Cu(I) catalyzed Ullman reaction between 2'-bromo-6-methyl-[1,1'-biphenyl]-3-amine (S1) and aniline, while M1, M2, M4 and M5 were synthesized by Pd(II) catalyzed Buchwald-Hartwig or Suzuki reactions between 2'-bromo-5-iodo-2-methyl-1,1'-biphenyl (S2) and D units or boronic acid derivatives of D units. Detailed synthesis procedures to S1, S2, M1-M5 and 1-5 are presented in Supporting Information. It is worth mentioning that the synthetic route reported here can apply to not only various D units but also different A precursors that carry a carbonyl group serving as the spiro-fixing site.

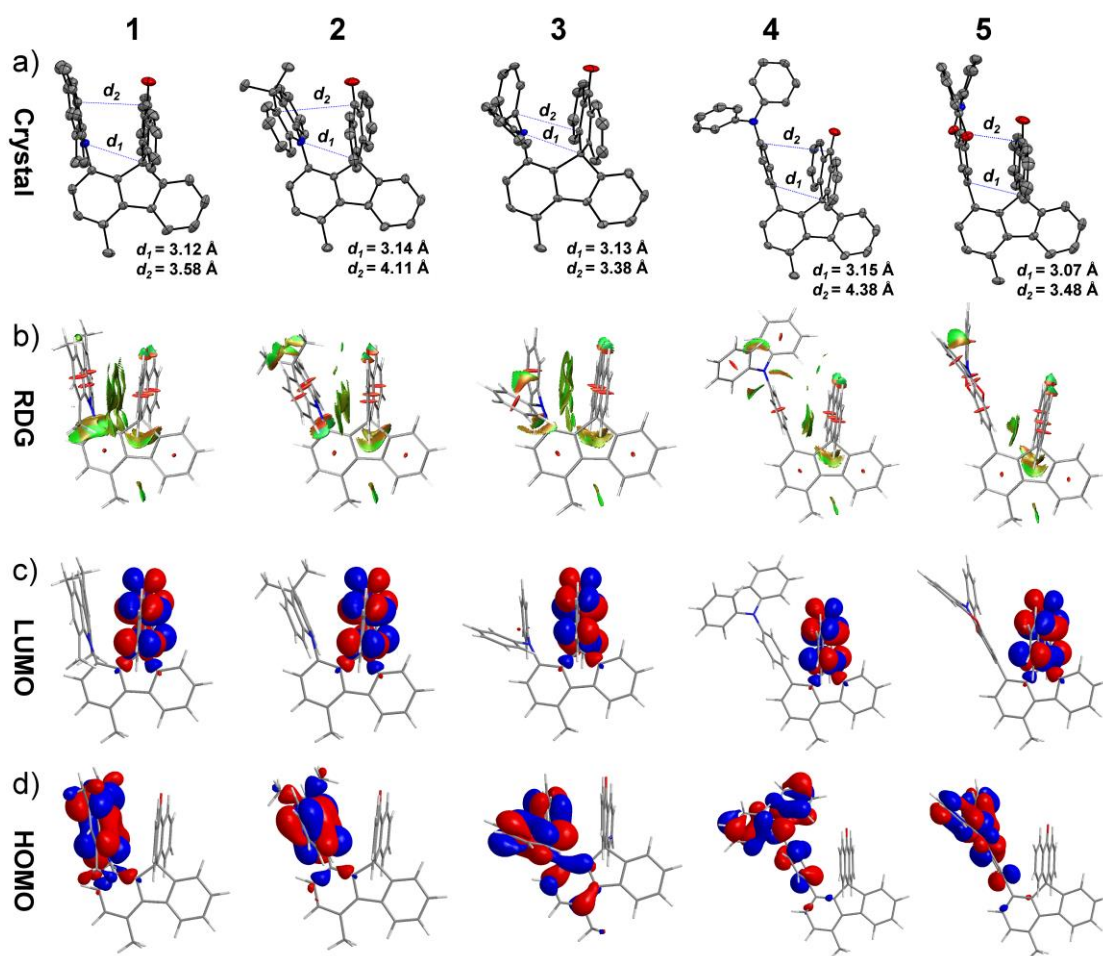


Figure 1. a) Single-crystal structures. b) Reduced density gradient (RDG) isosurfaces, c) LUMO and d) HOMO plots on the optimized S_0 states.

Figure 1a depicts the single-crystal X-ray structures of 1-5. The crystallographic data are summarized in Table S1. The D units and the spiro-fixed A units in 1-5 all display closely-packed cofacial configurations. The shortest distances between the non-hydrogen atoms of the D and A units are as short as 3.07–3.15 Å, indicating close D/A interactions. Figure S1 illustrates intramolecular π - π stacking interactions. For 1-5, the D and A units stack to each other with the centroid-to-centroid distances and dihedral angles of the two stacking rings at 3.3–3.8 Å and 10–29° (Figure S1 and Table S2), respectively, which indicates strong or considerable face-to-face π - π stacking

interactions [35, 39].

Theoretical calculations were conducted with density functional theory (DFT) (See ESI). Figure 1b-d show the calculation results of the ground-states (S_0). On the optimized S_0 states, the closely-packed D/A units exhibit considerable non-covalent van der Waals interactions, as revealed by the reduced density gradient (RDG) isosurfaces (Figure 1b and Figure S2), which agree with the π - π stacking interactions between the D and A units [35, 39]. The HOMOs of 1, 2, 4 and 5 distribute predominantly over the D units, while the HOMO of 3 distributes over the diphenylamine unit, extending to the connected phenyl ring of the fluorene linker (Figure 1c). The LUMOs of 1-5 are all concentrated on the spiro-fixed benzophenone units (Figure 1d), with nearly no distributions on the fluorene linkers, due to the interrupted conjugation by the spiro-carbons. It is shown that the HOMOs and LUMOs of 1-5 exhibit nearly no overlaps on the fluorene linkers, which minimizes through-bond charge-transfer. In contrast, the HOMOs and LUMOs largely overlap through the space due to the close cofacial D/A packing, which facilitates TSCT [35, 39]. Figure S3 depicts the natural transition orbital (NTO) analysis based on time-dependent DFT (TDDFT) calculations. For the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions, the hole and particle orbitals are predominantly delocalized over the D units and the spiro-fixed benzophenone units, respectively, which confirms the TSCT character of the S_1 and T_1 states. The calculated ΔE_{ST} values of 1-5 are as small as 8–27 meV (Table S3), which agrees with the almost complete spatial separation of HOMOs and LUMOs. The S_1 and T_1 states were further optimized with the TDDFT method. The relaxed S_1 and T_1 geometries show better cofacial D/A

alignments than the S_0 geometries (Figure S4), as revealed by the shorter distances and more parallel alignments (except 3) between the D and A units (Table S2), due to the Coulomb attractive interactions on excited-states [39].

Figure S5 shows the absorption and photoluminescence (PL) spectra of 1-5 in toluene solution. Table S4 summarizes the photophysical characteristics. In addition to the strong absorption bands (below 350 nm for 1-4 and below 400 nm for 5) that arise from the D/A-centered $^1\pi-\pi^*/^1n-\pi^*$ transitions, 1-5 exhibit weak charge-transfer absorption bands at around 380 nm for 1-4 and 410 nm for 5 (Figure S5a). The emergence of charge-transfer absorption indicates strong electronic coupling between the D and A units on ground states, due to the marked D/A overlap [39, 40, 45]. In the toluene solution, 1-5 afford green to orange emission centered at 514, 548, 524, 522 and 571 nm (Figure S5b), respectively. The different emission energies for 1-5 result from the different electron-donating strengths of the D units, as shown by electrochemical measurements (*vide infra*). The gradual red-shift of the emission by increasing the solvent polarity agrees with the charge-transfer character of the emission (Figure S6). In degassed toluene solution, 1-5 afford Φ_{PL} below 0.10 (Table S4), which suggests considerable non-radiative decay losses in the fluid solution, presumably caused by vibrations or rotations of the unfixed D units (especially for 3 and 4 with rotary phenyl rings) [29, 43]. 1-3 show both prompt and delayed components in the transient PL decays (Figure S7 and Table S4), reflecting the TADF feature of the emission, whereas 4 and 5 do not show delayed components, presumably because the T_1 states are mostly consumed by non-radiative deactivations before being converted

to the S_1 states. 1-5 all display aggregation-induced emission phenomena, as revealed by the remarkable enhancement of PL intensity upon increasing the water fraction in the mixed THF/H₂O solution (Figure S8), due to suppressed vibrations or rotations of molecular fragments in aggregation states [24, 25].

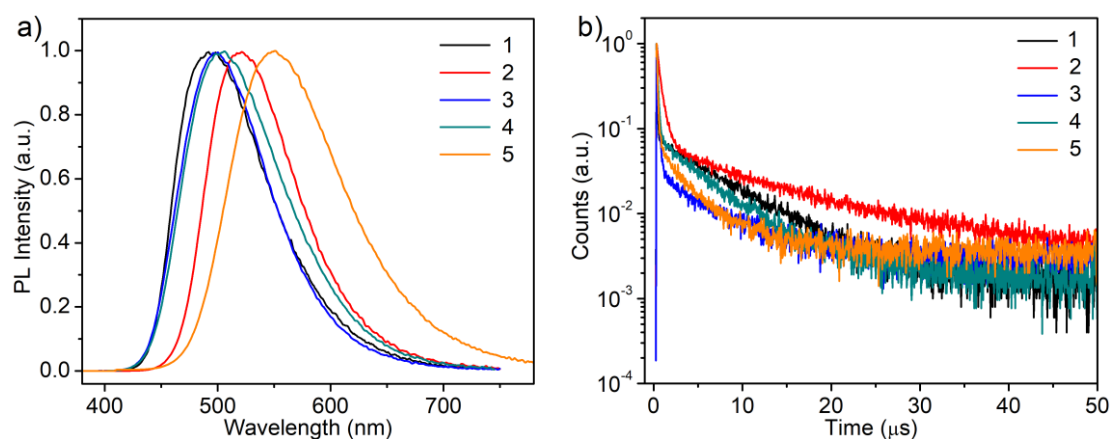


Figure 2. a) PL spectra and b) transient PL decay curves of 1-5 in 30 wt.% doped DPEPO films.

Table 1. Summary of emission characteristics and excited-state energy levels of 1-5 in 30 wt.% doped DPEPO films.

	PL λ (nm)	ϕ_{PL}	τ_{p} (ns)	τ_{d} (μ s)	$E_{\text{S}}/E_{\text{T}}/\Delta E_{\text{ST}}$ (eV)
1	493	0.92	64	6.8	2.79/2.76/0.02
2	520	0.80	457	10.9	2.67/2.60/0.07
3	497	0.82	130	5.9	2.77/2.76/0.01
4	504	0.89	132	5.3	2.79/2.76/0.03
5	550	0.52	99	3.3	2.61/2.58/0.03

Figure 2a shows the PL spectra of 1-5 in 30 wt.% doped bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) films. Table 1 summarizes the

emission characteristics. In the doped films, 1-5 afford sky-blue to yellow charge-transfer emission centered at 493, 520, 497, 504 and 550 nm, respectively, with high Φ_{PL} values of 0.80–0.92 for 1-4 and a moderate Φ_{PL} of 0.52 for 5 (Table 1). The remarkable enhancement of Φ_{PL} in doped films in comparison with the solution results from further suppression of intramolecular vibrations/rotations in the solid state [35, 39]. Figure S9 shows the low-temperature fluorescence and phosphorescence spectra of the doped films. From the onsets of the fluorescence and phosphorescence spectra, singlet (E_{s}) and triplet (E_{t}) energies were respectively calculated (Table 1). 1-5 afford ΔE_{ST} values at 10–70 meV, which are sufficiently small for rapid RISC. Figure 2b shows the transient PL decay curves. 1-5 all show distinct prompt and delayed components in the transient PL decays, with prompt (τ_{p})/delayed (τ_{d}) lifetimes at 64 ns/6.8 μs , 457 ns/10.9 μs , 130 ns/5.9 μs , 132 ns/5.3 μs and 99 ns/3.3 μs , respectively. The delayed components are remarkably suppressed at low temperature (Figure S10), which confirms the TADF nature of 1-5. Table S5 summarizes the calculated rate constants of the emission in the doped films. 1-5 show radiative decay rates of singlet state ($k_{\text{r,s}}$) at $0.7\text{--}3.3\times 10^6\text{ s}^{-1}$, which are within the normal range reported for TSCT emitters [35, 37, 39-43, 45]. 1-4 show non-radiative decay rates of singlet state ($k_{\text{nr,s}}$) at $1.8\text{--}7.3\times 10^5\text{ s}^{-1}$, whereas yellow-emitting 5 exhibits a much larger $k_{\text{nr,s}}$ of $2.0\times 10^6\text{ s}^{-1}$, in accordance with the energy gap law. Notably, 1-5 exhibit high k_{RISC} values at $9.9\times 10^5\text{ s}^{-1}$, $2.3\times 10^5\text{ s}^{-1}$, $3.3\times 10^5\text{ s}^{-1}$, $6.1\times 10^5\text{ s}^{-1}$ and $7.1\times 10^5\text{ s}^{-1}$, respectively, indicating their high capability of converting triplets to singlets for emission.

Figure S11 shows the cyclic voltammograms measured in solution. 1-5 show

similar electrochemical reductions and LUMO levels (around -2.70 eV) but different electrochemical oxidations and HOMO levels ($-5.23 \sim -4.99$ eV) (Table S6), because they use the same A unit and different D units. The Me4CAZ, DPA and TPA donors have similar electron-donating strengths, which lead to similar HOMO levels (around -5.2 eV) and emission energies for 1, 3 and 4 (Figure 2a). The DMAC and BOP donors have increased electron-donating strengths, which lead to destabilized HOMO levels (-5.14 and -4.99 eV, respectively) and decreased emission energies for 2 and 5 (Figure 2a). As shown by thermal gravity analysis (Figure S12), 1-5 all possess high thermal stability, with 5% weight loss temperatures at 401 , 385 , 384 , 417 and 444 °C, respectively.

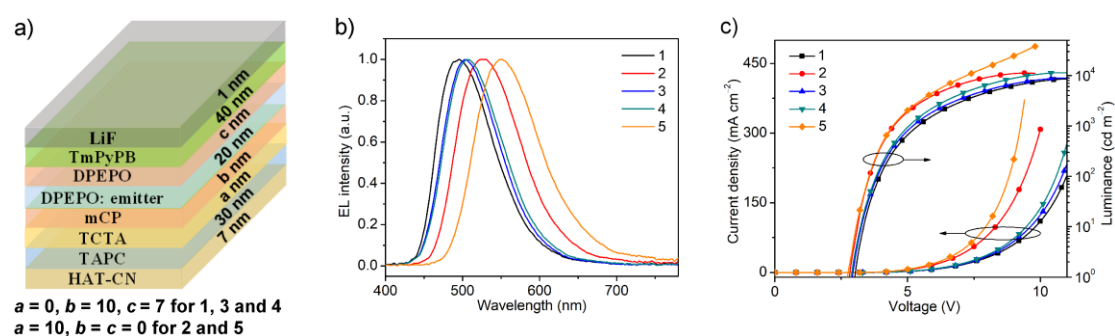


Figure 3. a) Device structures, b) EL spectra and c) current-density and luminance versus driving voltage curves of OLEDs using 1-5 as the emitters.

To evaluate their application potential in EL devices, 1-5 were employed as emitters in vacuum-evaporated OLEDs. Figure 3a illustrates the device structures, which are indium-tin-oxide (ITO)/HATCN (7 nm)/TAPC (30 nm)/mCP (10 nm)/PPF: 30 wt.% emitter (20 nm)/PPF (7 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) for

sky-blue to blue-green-emitting 1, 3 and 4, and ITO/HATCN (7 nm)/TAPC (30 nm)/TCTA (10 nm)/PPF: 30 wt.% emitter (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm) for green to yellow-emitting 2 and 5. Scheme S2 illustrates the energy-level diagrams of the devices as well as the chemical structures of the used materials. Here, 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN) and 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) function as the hole-injection and transport layers, respectively; 1,3-di(9*H*-carbazol-9-yl)benzene (mCP) or 4,4',4''-tris-(9*H*-carbazol-9-yl)-triphenylamine (TCTA) serve as the electron/exciton-blocking layer; 2,8-bis(diphenylphosphoryl)dibenzo[b,d]furan (PPF), an analog of DPEPO, serves as not only the host but also the hole/exciton-blocking layer; 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) and LiF serve as the electron-transport and injection layers, respectively. Figure 3b shows the EL spectra. The OLEDs based on 1-5 afforded sky-blue to yellow EL with the emission peaks at 494, 527, 503, 507 and 550 nm, respectively, and Commission Internationale de l'Eclairage (CIE) coordinates at (0.20, 0.42), (0.31, 0.56), (0.22, 0.48), (0.24, 0.50) and (0.41, 0.55), respectively.

Table 2. Summary of EL performances of OLEDs using 1-5 as the emitters.

	V_{on} (V) ^a	η_{c} (cd A ⁻¹) ^b	EQE (%) ^c	L_{max} (cd m ⁻²)	EL λ (nm)	CIE (x, y)
1	3.0	50.4/43.9/32.9	20.9/18.2/13.7	8600	494	(0.20, 0.42)
2	2.8	52.4/52.0/43.9	16.1/16.0/13.5	11000	527	(0.31, 0.56)
3	2.9	49.4/47.7/36.5	17.7/17.3/13.3	8800	503	(0.22, 0.48)
4	2.9	56.3/54.2/43.9	20.0/19.1/15.6	11000	507	(0.24, 0.50)
5	2.7	43.5/43.2/38.5	13.2/13.1/11.7	39000	550	(0.41, 0.55)

^a Voltage to reach 1 cd m⁻². ^b Current efficiencies at the maximum, 100 cd m⁻² and 1000

cd m⁻². ^c *EQEs* at the maximum, 100 cd m⁻² and 1000 cd m⁻².

Figure 3c shows the current-density and luminance versus voltage curves. Table 2 summarizes the device performances. The OLEDs based on 1-5 showed low turn-on voltages below 3.0 V and high peak current efficiencies/*EQEs* at 50.4 cd A⁻¹/20.9%, 52.4 cd A⁻¹/16.1%, 49.4 cd A⁻¹/17.7%, 56.3 cd A⁻¹/20.0% and 43.5 cd A⁻¹/13.2%, respectively. The *EQEs* follow the trend of Φ_{PL} in the doped films (Table 1). Figure S13 shows the *EQE* versus luminance curves. At 100/1000 cd m⁻², the *EQEs* remained at 18.2%/13.7%, 16.0%/13.5%, 17.3%/13.3%, 19.1%/15.6% and 13.1%/11.7% for devices based on 1-5, respectively. The devices based on 1, 3 and 4 showed relatively large efficiency roll-offs (Table 2). Efficiency roll-offs in TADF OLEDs are usually ascribed to triplet-triplet/triplet-polaron annihilations in the emissive layers [47]. The high k_{RISC} values of 1-5 indicate that they can efficiently consume triplets for emission, alleviating triplet-triplet/triplet-polaron annihilations [48-51]. By broadening the recombination zones with optimized device structures, the efficiency roll-offs would be suppressed [35, 36]. The high device efficiencies indicate that 1-5 are promising functional materials for high-performance EL devices.

3. Conclusion

We reported a “fixing acceptor” design for efficient TSCT TADF emitters. By chemically fixing the A unit (benzophenone) and cofacially aligning various D units with the fixed A unit, TSCT TADF emitters 1-5 were developed. Single-crystal

structures and theoretical calculations verified closely-packed cofacial D/A conformations and favorable TSCT in 1-5. In doped films, 1-5 afforded high Φ_{PL} of up to 0.92 and k_{RISC} of up to $1.0 \times 10^6 \text{ s}^{-1}$. OLEDs using them as emitters showed high $EQEs$ of up to 20.9%. The work has demonstrated that fixing the acceptor can afford efficient TSCT TADF emitters. In principle, the “fixing acceptor” design allows facile variation of donor and feasible variation of acceptor as long as the acceptor precursors carry a carbonyl group that serves as the spiro-fixing site (such as thioxanthen-9-one sulfone and its derivatives). Varying the fixed acceptor is currently ongoing in our lab. The work opens a new avenue toward a wide variety of efficient TSCT TADF emitters, which are promising functional materials for high-performance EL devices.

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Conflict of interest

The authors declare no conflict of interest.

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