Research Article

Synergetic Insulation and Induction Effects Selectively Optimize Multiresonance Thermally Activated Delayed Fluorescence

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Multiresonance (MR) emitters featuring narrowband emissions and theoretically 100% exciton harvesting are great potential for organic light-emitting diode (OLED) applications. However, how to functionalize MR molecules without scarifying emission color purity is still a key challenge. Herein, we report a feasible strategy for selective optimization of MR molecules, which is demonstrated by a blue MR emitter tCBNDASPO substituted with a diphenylphosphine oxide (DPPO) group. Compared to its DPPO-free parent molecule, tCBNDASPO preserves narrowband feature with full widths at half maximum (FWHM) values of 28 nm in film and 32 nm in OLEDs and achieves 40% increased photoluminescence (92%) and electroluminescence quantum efficiencies (28%). It is showed that insulation effect of P=O effectively confines the singlet excited state on MR core to keep emission color purity, and its induction effect enhances singlet radiation and triplet-to-singlet conversion. This synergism for selective optimization is based on rational linkage between MR core and functional groups.

1. Introduction

For high-resolution photonic applications, emission color purity is one of the most important properties of luminescent materials and devices, which requires narrow full width at half maximum (FWHM) of emission peak [1]. Organic molecules feature relatively broadband emission characteristic of multiple vibrational transitions [2]. It is known that flexible moieties and intramolecular charge transfer (ICT) between donor (D) and acceptor (A) groups can significantly increase vibrational levels and widen spectral profiles, rendering FWHM > 100 nm [3]. In contrast, polycyclic aromatic hydrocarbon, such as anthracene and pyrene, shows advantageous FWHM values within 50 nm, owing to their highly rigid structures and locally excited (LE) first singlet states (1LE) [4]. Nevertheless, fluorescent characteristics and simple electrical properties of hydrocarbons limit their performance for photonic applications, e.g., organic light-emitting diodes (OLEDs) [5–12]. In recent years, thermally activated delayed fluorescence (TADF) featured pure-organic materials rapidly emerged for OLED applications, owing to the merits of 100% theoretical internal quantum efficiency (IQE, \( \eta_{\text{IQE}} \)), low cost, and high sustainability [13–16]. Singlet-triplet splitting energies (\( \Delta E_{\text{ST}} \)) of TADF molecules are nearly zero, so that nonradiative triplet excitons can be upconverted to radiative singlet excitons, through reverse intersystem crossing (RISC). Because \( \Delta E_{\text{ST}} \) is directly proportional to overlap integral of frontier molecular orbitals (FMO), D-A structure is most widely adopted [17, 18]. As consequence, the charge transfer-featured first singlet excited states (1CT) of TADF materials render FWHM around 100 nm, leading to unsatisfied color purities of TADF OLEDs.

In 2016, Hatakeyama et al. reported a new class of TADF-featured polycyclic aromatics, namely, multiresonance (MR) TADF emitters, e.g., DABNA-1, whose FWHM values were ~30 nm [19, 20]. In MR molecules, instead of the D-A groups, resonance effects of electron withdrawing and donating atoms, e.g., boron and nitrogen, are used to separate FMOs [21–26]. Therefore, high structural rigidity and effective ICT can be integrated to realize narrowband TADF emission [23]. Through conjugation extension and functional modification, blue [27–33], green [34–39], yellow [40, 41], and red [42] TADF emitters were developed, whose device efficiencies were
comparable to those of the most efficient counterparts, e.g., the maximum external quantum efficiencies (EQE, $\eta_{\text{EQE}}$) $>$20%. Modifying MR core with the electroactive D and A groups can markedly improve device performance but simultaneously induce bathochromic shifts and increased FWHM (>40 nm). It shows that conjugated bonding with the D/A groups induces the combined conjugation and induction effects on MR cores, which deepen potential energy surfaces of the first singlet excited states ($S_1$), respectively, due to the additional vibrational levels contributed by the D/A groups and the involvement of intergroup charge transfer components in the $S_1$ states (Scheme 1) [43].

Obviously, the negative influences of vibrational linkages on emission color purities of MR chromophores significantly limit functionalization and further performance improvement of MR TADF materials. So, a rational molecular design strategy should be based on avoiding the involvement of electron-withdrawing/donating groups in the $S_1$ states but simultaneously utilizing their induction effects to optimize ICT in MR core. In this sense, insulating linkage provides a feasible way to combine color purity preservation and efficiency improvement, because it can (i) interrupt conjugation interactions with functional groups, therefore excluding them from the $S_1$ state [44], and (ii) provide additional induction effect to accurately modulate ICT [45, 46] within MR chromophores (Scheme 1). Herein, as a proof of concept, we develop a blue MR TADF emitter named tCBNDA, and a functional group of diphenylphosphine oxide (DPPO) (Figure 1(a) and Scheme S1). Owing to induction effect of P=O linkage [47], the DPPO group is completely excluded from the $S_1$ state. Simultaneously, induction effect of the P=O group extends the lowest unoccupied molecular orbital (LUMO) of tCBNDA, increasing FMO overlap and thereby singlet oscillator strength ($f_S$). As expected, in addition to the identical single-molecular photoluminescence (PL) spectrum with the unchanged FWHM value of 28 nm, PL quantum yield ($\phi_{\text{PL}}$) of tCBNDA is improved by ~30% to 92%, owing to its 17-fold increased singlet radiation rate constant ($k^S_{\text{rad}}$) and more than halved triplet nonradiation rate constant ($k^T_{\text{nr}}$). Consequently, tCBNDA-based blue OLEDs achieved the excellent color purity and the state-of-the-art $\eta_{\text{EQE}}$ up to 28.0%, which was 40% higher than that of tCBNDA-based analog. Different from previous report [48], the comparison between MR emitters with/without phosphorylation clearly indicates synergism of insulation and induction effects on EL performance enhancement, which provides an effective way for selective functional extension and optimization of MR systems.

2. Results

2.1. Structures and Gaussian Simulation Results. Chemical structures of tCBNDA and tCBNDA$^+$ were fully characterized with NMR and mass spectra and elemental analyses (see experimental section in supporting information). A direct borylation method [49] was used to inset boron atom at ortho-position between 3,6-di(tert-butyl)carbazole (tCz) and one diphenylamine (DPA) (Scheme S1). Density functional theory (DFT) calculation shows that due to its planar and conjugated structure, whole carbazole is fused in B-N framework (Figures S1-S5). As a result, the highest occupied molecular orbitals (HOMO) of tCBNDA and tCBNDA$^+$ are identical, indicating the exclusion of DPPO from direct D-A interactions. Furthermore, DPPO substitution induces the decreases of the HOMO and LUMO energy levels by only 0.05 and 0.07 eV, which are consistent with the same experimentally measured values of -5.7 and -3.0 eV for tCBNDA and tCBNDA$^+$ (Figure S8 and Table S1). Nonetheless, the electron-withdrawing effect of P=O induces appropriate extension of the lowest unoccupied molecular orbital (LUMO) to nitrogen atom of diphenylamine of tCBNDA$^+$, thereby increasing probability of FMO overlap. Despite its negligible influences on occupied molecular orbitals, induction effect of P=O makes the LUMO+1 and the LUMO+2 shift from MR core to DPPO.

Natural transition orbital (NTO) investigation indicates that the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ excitations of tCBNDA and tCBNDA$^+$ are predominantly contributed by

![Scheme 1: Influence of functionalization on emission properties of multiresonance (MR) emitters and design proposal of “insulating induction” strategy. The incorporation of the functional groups (FG) in the first singlet states ($S_1$) renders potential surface deepening (PSD) and emission bathochromic shift and widening, due to involving in more vibrational levels. The insulating linkage between MR core and FG prevents the $S_1$ extension. Therefore, the $S_1$ state is confined on MR core through vibrational limitation (VL), inducing recovered narrow emission band.](image-url)
HOMO→LUMO transitions (weights > 90%) (Figure 1(b) and S2-S3). Thus, the $S_1$ and $T_1$ energy levels and $\Delta E_{ST}$ values of tCBNDA and tCBNDASPO are around 3.0, 2.6, and 0.43 eV, with negligible differences within 0.02 eV. Compared to tCBNDA, LUMO extension in tCBNDASPO leads to slightly increased overlap integrals of FMO wave functions ($\langle \Psi_H | \Psi_L \rangle$) and electron cloud densities ($\langle \Psi_H | \rho | \Psi_L \rangle$) but markedly shortened centroid-centroid distances of FMOs ($d_{H-L}$) at the ground ($S_0$), $S_1$ and $T_1$ states (Figure S4). As a result, the singlet oscillator strength ($f_S$) of tCBNDASPO reaches to 0.2929, which is 0.0021 larger than that of tCBNDA. More importantly, the $S_1$ state of tCBNDASPO is completely localized on its tCBNDA core. It indicates that although nonplanar DPPO could introduce additional vibrational levels, its steric hindrance actually restrains vibration of its linked phenyls, and insulation effect of P=O excludes it from excited-state transitions. In this case, valid vibrational levels involved in radiation are still thoroughly contributed by tCBNDA core (Scheme 1). Such vibrational limitation (VL) would support the consistence between tCBNDA and tCBNDASPO in emission profiles. Although the same FMO locations of the $S_1$ and $T_1$ excitations make spin-orbital coupling vanished, the second triplet ($T_2$) states of tCBNDA and tCBNDASPO provide a feasible channel for effective RISC (Figures S5-S7).

2.2. Photophysical Properties. In accord with time-dependent DFT (TDDFT) results, electronic spectra of tCBNDA and tCBNDASPO in dilute dichloromethane solutions (10 $^6 \text{mol L}^{-1}$) consist of exactly the same absorption bands, corresponding to $\pi \rightarrow \pi^*$ (<300 nm), $n \rightarrow \pi^*$ (300-400 nm), and charge-transfer (~450 nm) transitions (Figure 2(a) and Table S1). It indicates that DPPO is indeed not involved in the singlet excitation of tCBNDASPO. Moreover, experimentally estimated $f_S$ of tCBNDASPO is as high as 0.3738, over 0.3417 of tCBNDA. PL spectra of these two molecules in dilute solutions completely overlap, corresponding to blue emissions with peak wavelengths at 467 nm. The solvatochromic properties of tCBNDA and tCBNDASPO are also the same (Figure S9). Therefore, DPPO does not significantly change ICT in the latter. As consequence, FWHM values of tCBNDA and tCBNDASPO in dilute dichloromethane are identical and as small as 28 nm, which are even smaller than 33 nm of DABNA-1 [19] without functionalization.

In neat films, emission peaks of tCBNDA and tCBNDASPO slightly shift to 470 nm (Figure 2(a) and Table S1). However, FWHM of tCBNDA neat film markedly increases to 47 nm, due to its planar structure induced aggregation. In contrast, tCBNDASPO neat film still preserves a small FWHM of 32 nm, owing to its asymmetric structure and steric hindrance of DPPO.
tCBNDA and tCBNDAPO are further dispersed in a host matrix 4,6-bis(diphenylphosphoryl)dibenzofuran (DBFDPO) [50] to form vacuum-evaporated films of DBFDPO:x% MR emitters. It is showed that concentration dependence of PL spectra for these two MR emitters is different (Figure S10). FWHM of DBFDPO:x% tCBNDA is linearly proportional to x%, reflecting serious self-aggregation tendency (Figure S11). Furthermore, \( \phi_{PL} \) of tCBNDA-based films reaches the highest value of 72% at a low x = 7, then rapidly decreases to 29% at x = 20. In contrast, FWHM of DBFDPO:x% tCBNDAPO (32 nm) is independent on x. tCBNDAPO simultaneously endows its films with the highest \( \phi_{PL} \) of 92% at x = 20. It indicates that steric hindrance of DPPO effectively suppresses self-aggregation and alleviates intermolecular interaction-induced quenching.

PL decays of tCBNDA- and tCBNDAPO-based films consist of ns-scale prompt fluorescence (PF) and μs-scale delayed fluorescence (DF) components (Figures S12 and S13). It is showed that DBFDPO matrix can effective restrain concentration quenching. Therefore, PF (\( \tau_{PF} \)) and DF (\( \tau_{DF} \)) lifetimes are in reverse proportion to x%
(Table S2). Nevertheless, emission lifetimes of tCBNDA are more dependent on x%, in accord with its stronger intermolecular interactions. Compared to neat film, τPF and τTF of DBFDPO:7% tCBNDA are markedly increased by 2.5 folds, respectively. In contrast, DBFDPO:20% tCBNDAASPO reveals 1.4 folds and 0.3 fold increased τPF and τTF, respectively. It is known that triplet-involved DF with longer lifetime should suffer from more serious quenching. However, compared to its PF, when x ≥ 20, DF of DBFDPO:x% tCBNDAASPO is unexpectedly less sensitive to doping concentration, reflecting highly efficient RISC and reduced triplet quenching.

DF intensities of tCBNDA- and tCBNDAASPO-based films are in reverse proportion to temperature (Figures S14 and S15), corresponding to transition from T1-originated phosphorescence (pH) to the S1 state with markedly larger allowedness through thermally activation. Temperature-dependent time-resolved emission spectra (TRES) show the same tendencies (Figures S16 and S17). PF, DF, and pH spectra of tCBNDA and tCBNDAASPO are nearly overlapped, corresponding to near-zero ΔE_ST values of 0.07 and 0.05 eV, respectively (Figure 2(b) and Table S1). TRES of DBFDPO:x% MR emitters indicate that DF components are in reverse proportion to x%, since the sensitivity of triplet states to concentration quenching (Figure S18). Furthermore, compared to neat film, DF component of DBFDPO:7% tCBNDA is more significantly enhanced than its PF component. Therefore, triplet involved processes, e.g., Dexter energy transfer (DXT) and triplet quenching, are main factors influencing emission properties of tCBNDA-based films. In contrast, both PF and DF components of DBFDPO:20% tCBNDAASPO are increased. Nevertheless, its DF increase ratio is markedly smaller than that of DBFDPO:7% tCBNDA. Since PLQY values of tCBNDAASPO-based films are always larger than those of tCBNDA-based analogs (Table S2), the shorter lifetimes of the former should be ascribed to faster singlet radiation and more efficient RISC.

Rate constants (k) and efficiencies (ϕ) of key TADF transitions were estimated to figure out effects of PO substitution on electronic characteristics of MR molecules (Figure 2(d) and Table S2). It is showed that ratio of PF (ϕPF) and DF (ϕDF) efficiencies is ~2:1 for DBFDPO:20% tCBNDAASPO, on the contrary to ~1:3 for DBFDPO:7% tCBNDA. Especially, in accord with their f_s values (insets of Figure 2(d)), singlet radiative rate constant (k_S^T) of DBFDPO:20% tCBNDAASPO reaches to 1.4×10^8 s^-1, which is more than 17 folds of that of DBFDPO:7% tCBNDA. Although rate constant of intersystem crossing (ISC) (k ISC) for DBFDPO:20% tCBNDAASPO is twice of that of DBFDPO:7% tCBNDA, and RISC rate constant (k_RISC) of the former is a half of the latter, the dynamic predominance of ISC for these two films is the same. However, it is noted that k_S^T/k ISC ratio of DBFDPO:20% tCBNDAASPO is 2 as ~8 folds of that of DBFDPO:7% tCBNDA (0.27). In addition, despite their comparable RISC quantum efficiencies (ϕ_RISC) of ~95%, η_RISC/ISC quantum efficiency (ϕ ISC) ratio of the former is more than 3 (ϕ ISC = 31%), owing to overwhelming advantage of its k S^T to k ISC, which can largely reduce ISC-RISC cycles [51]. On the contrary, ϕ_RISC/ϕ ISC ratio of the latter is only 1.3. More efficient triplet-to-singlet conversion further reduces triplet quenching of DBFDPO:20% tCBNDAASPO, whose triplet nonradiative rate constant (k_T^T) is only one-third of that of DBFDPO:7% tCBNDA. Therefore, compared to tCBNDA, tCBNDAASPO makes its film remarkably superior in singlet radiation and triplet harvesting.

2.3. Electroluminescence Performance. η_{PL} over 90%, bipolar modification and good film formability (Figure S19) of tCBNDAASPO make device structural simplification feasible. Therefore, a four-material-based simple trilayer structure of ITO/MoO3 (6 nm)|mCP (50 nm)|DBFDPO:x% MR emitters (25 nm)|DBFDPO (40 nm)|LiF (1 nm)|Al was adopted to fabricate OLEDs through vacuum evaporation, in which mCP is 1,3-bis(9H-carbazol-9-yl)benzene as hole transporting layers, and DBFDPO simultaneously serves as host in emissive layer (EML) and electron-transporting layer (Figure 3(a)). The doping concentration (x%) was tuned to achieve the optimal device performance (Figures S20 and S21). All the devices revealed narrowband blue emissions peaked at 472 nm, corresponding to Commission Internationale de l’Eclairage (CIE) coordinates of 0.12 and 0.17-0.23 (Table S3). In accord with optical results, increasing x% induced electroluminescence (EL) red shift and FWHM increase by 4 nm for tCBNDA-based devices, respectively, corresponding to a maximum CIEy increase of 0.06. On the contrary, tCBNDAASPO-based devices displayed unchanged EL peak wavelengths and FWHM values of 32 nm, corresponding to a negligible CIEy variation within 0.01. At x = 7 and 20, emission color purities of tCBNDA- and tCBNDAASPO-based blue OLEDs were almost the same (Figure 3(b)).

The dependence of volt-amperes characteristics on x% was not distinct, revealing the predominance of DBFDPO host in carrier transportation of EMLs (Figures S17 and S21 and Table S1). However, at the same voltages, current densities (j) of tCBNDAASPO-based devices were lower than those of tCBNDA-based analogs, while luminance of the former was higher than that of the latter. It means DPO substitution improved carrier flux balance and recombination. Simultaneously, tCBNDA-based devices achieved the best performance at relative low x, e.g., the highest efficiencies of 29.3 cd A^-1 for current efficiency (CE, η_CE) and 27.0 lm W^-1 for power efficiency (PE, η_P) at x = 10 and 20.2% for η_EQE at x = 7 (Figure 3(c) and S20 and Table S1). It indicates self-aggregation of tCBNDA worsens concentration quenching in its devices, which further increased roll-offs. In contrast, tCBNDAASPO-based devices achieved the best performance at markedly higher x% (Figure S21). At x = 20, tCBNDAASPO endowed its device with the state-of-the-art maximum efficiencies of 40.4 cd A^-1, 40.9 lm W^-1, and 28.0%, which were largely improved by 40%-50% in comparison to the best results of tCBNDA. At 100 nits, EL efficiencies of DBFDPO:20%
tCBNDASPO still remained 29.8 cd A\(^{-1}\) and 20.6%, which were still beyond the highest values of tCBNDA-based devices. Obviously, the advantage of tCBNDASPO in more efficient RISC and triplet quenching reduction effectively alleviated triplet quenching, leading to markedly reduced EQE roll-offs.

EL performances of representative functionalized MR-TADF emitters are summarized in Figure 3(e) and Table S4. It is showed that EL emissions from most of them shifted to green, yellow, or orange with increased CIE\(\gamma\) > 0.2. In comparison, tCBNDASPO realizes the combination of CIE\(\gamma\) preservation and \(\eta_{EQE}\) improvement, reaching the top-rank levels of MR-TADF emitters.

Steady-state EL spectra of tCBNDA and tCBNDASPO were similar to PL spectra of their films, except for slight red shifts (Figure 4(a)). However, comparison on time-resolved PL and EL spectra indicates that DF component of DBFDPO:7% tCBNDA was predominant in PL process.
But, in EL process, it was significantly reduced, at the same time of remarkable PF increasing (Figure 4(b)). On the contrary, PF and DF components of EL emission from DBFDPO:20% tCBNDASPO were simultaneously enhanced. It is showed that $J$ of the devices was roughly in direct proportion to the doping concentrations of tCBNDA and tCBNDASPO (Figures S20 and S21). Therefore, due to the deeper LUMOs and shallower HOMOs of these two MR emitters than those of DBFDPO, direct carrier capture and recombination would be dominant in EL mechanism. Different to spin-forbidden triplet photo-excitation, electro-generated triplet excitons are formed directly through carrier recombination. Therefore, triplet concentration in devices follows spin statistics, which is larger than photo-excited triplets. Higher $k_{nr}^{T}$ and multiple ISC-RISC cycles of tCBNDA induced more serious triplet quenching and decreased EL DF components. For the same reason, owing to its halved $k_{nr}^{T}$, overwhelming thermodynamic advantage of RISC, and extremely high $k_{r}^{S}$ at the level of $10^{8}$ s$^{-1}$, tCBNDASPO dramatically improved triplet harvesting in its devices, indicating the importance of functionalization for exciton utilization enhancement.

### 3. Discussion

In summary, a DPPO-modified blue MR emitter named tCBNDASPO is developed to demonstrate a feasible strategy for selectively improving TADF performance without sacrificing narrowband emission feature. The insulation and induction effects of the P=O group are combined to, respectively, confine the $S_{1}$ state on MR core and enhance key TADF transitions. Therefore, tCBNDASPO achieves preserved FWHM values (28 nm in film and 32 nm in device), 30% increased $\phi_{PL}$ (> 90%), 17-fold increased $k_{r}^{S}$ ($10^{8}$ s$^{-1}$), halved $k_{nr}^{T}$, and doubled $\phi_{ISC}/\phi_{RISC}$ ratio. Based on a trilayer simple structure, tCBNDASPO endowed its blue OLEDs with desired high color purity and the state-of-the-art $\eta_{EQE}$ up to 28.0%. Therefore, linkage between MR frameworks and functional groups is crucial for selective optimization and purposeful system extension of MR-TADF materials.

### 4. Materials and Methods

Additional synthesis, Gaussian simulation results, electrochemical, photophysical and morphological properties,
device performance, and NMR spectra are included in the Supplementary Materials.

Data Availability

All other data are available from the authors upon reasonable request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Authors’ Contributions

H. X. conceived the idea. J. B., S. C., L. Q., N. Z., and C. D. performed the synthesis and device fabrication. J. B., J. Z., and S. C. performed the measurement. All the authors discussed the data and wrote the paper together. Jinkun Bian and Su Chen contributed equally to this work.

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Supplementary Materials

Scheme S1: synthetic procedure of tCBNDASPO: (i) 3,6-tert-butyli-carbazole, K2CO3, Cul, 18-crown-6, DMI, 190 °C, 48 h; (ii) diphenylamine, t-BuOK, Pd2dba3, tri(tert-butyl)phosphine, toluene, 90 °C, 5 h; (iii) BBr3, toluene, 120 °C, 20 h; (iv) NBS, CH2Cl2, r.t., 30 min; (v) diphenylphosphine, Pd(OAc)2, NaOAc, DMF, 130 °C, 24 h; 30% H2O2, CH2Cl2, 0°C, 1 h. Figure S1: contours and energy levels of the first three frontier molecular orbitals of monomer of tCBNDA and tCBNDASPO simulated with the DFT method. Figure S2: contours of “hole” and “particle” of S0 → S1 and S0 → T1 excitations for tCBNDA simulated with the TD-DFT method. E0, ET, f, and σ refer to the energy levels of the S1 and the T1 states, singlet oscillator strength, and contribution weight. Figure S3: contours of “hole” and “particle” of S0 → S1 and S0 → T1 excitations for tCBNDASPO simulated with the TD-DFT method. E0, ET, f, and σ refer to the energy levels of the S1 and the T1 states, singlet oscillator strength, and contribution weight. Figure S4: centroid-centroid distances of FMOs (dH-L) and overlap integrals of FMO wave functions (⟨ψH|ψL⟩) and electron cloud densities (⟨ψ2H|ψ2L⟩) of tCBNDA and tCBNDASPO at the S0, S1, and the T1 states. Figure S5: contours of “hole” and “particle” of S0 → S2 and S0 → T2 excitations for tCBNDA simulated with the TD-DFT method. E0, ET, f, and σ refer to the energy levels of the S2 and the T2 states, singlet oscillator strength, and contribution weight. Figure S6: contours of “hole” and “particle” of S0 → S2 and S0 → T2 excitations for tCBNDASPO simulated with the TD-DFT method. E0, ET, f, and σ refer to the energy levels of the S2 and the T2 states, singlet oscillator strength, and contribution weight. Figure S7: Illustration of DF processes for tCBNDA and tCBNDASPO. VC and NR refer to vibrational coupling and nonradiation. Figure S8: cyclic voltammogram of tCBNDA and tCBNDASPO measured in DCM for oxidation and THF for reduction at room temperature with the scanning rate of 100 mV s-1 and tetra-n-butylammonium hexafluorophosphate as supporting electrolyte (0.1 mol L-1). Figure S9: electronic absorption and photoluminescence (PL) spectra of (a) tCBNDA and (b) tCBNDASPO in different solvents with diverse polarities. Figure S10: variation of PL spectra for DBFDPO:x% tCBNDA and DBFDPO:x% tCBNDASPO films. Figure S11: dependence of FWHM and PLQY values for DBFDPO:x% tCBNDA and DBFDPO:x% tCBNDASPO films. Figure S12: concentration dependence of PF (a) and DF (b) decay curves for DBFDPO:x% tCBNDA films. Figure S13: concentration dependence of PF (a) and DF (b) decay curves for DBFDPO:x% tCBNDASPO films. Figure S14: temperature dependence of DF decays for neat tCBNDA (a) and tCBNDASPO (b) films. Figure S15: temperature dependence of DF decays for DBFDPO:7% tCBNDA (a) and DBFDPO:20% tCBNDASPO (b) films. Figure S16: temperature dependence of time-resolved emission spectra (TRES) for neat tCBNDA (a) and tCBNDASPO (b) films. Figure S17: temperature dependence of time-resolved emission spectra (TRES) for DBFDPO:7% tCBNDA (a) and DBFDPO:20% tCBNDASPO (b) films. Figure S18: concentration dependence of time-resolved emission spectra (TRES) for DBFDPO:x% tCBNDA (a) and DBFDPO:x% tCBNDASPO (b) films. Figure S19: atom force microscopy (AFM) images of neat films and DBFDPO:7% tCBNDA and DBFDPO:20% tCBNDASPO films. Figure S20: (a) EL spectra (inset) and luminance-current density (J)-voltage curves of the devices with different tCBNDA doping concentrations of 5%, 7%, 10%, and 20%; (b) efficiencies vs. luminance relationships of the devices. Figure S21: (a) EL spectra (inset) and luminance-current density (J)-voltage curves of the devices with different tCBNDASPO doping concentrations of 10%, 20%, 30%, and 40%; (b) efficiencies vs. luminance relationships of the devices. Figure S22: 1H NMR spectrum of tCBNDA in CDCl3. Figure S23: 1H NMR spectrum of tCBNDASPO in CDCl3. Figure S24: 13C NMR spectrum of tCBNDA in CDCl3. Figure S25: 13C NMR spectrum of tCBNDASPO in CDCl3. Figure S26: 31PNMR spectrum of tCBNDASPO in CDCl3. Table S1: basic physical properties of tCBNDA and tCBNDASPO. Table S2: TADF characteristics of DBFDPO:x% tCBNDA and DBFDPO:x% tCBNDASPO films. Table S3: EL performance of DBFDPO:x% tCBNDA and DBFDPO:x% tCBNDASPO. Table S4: EL performance of representative functionalized MR-TADF emitters. (Supplementary Materials)

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