Ladder-like energy-relaying exciplex enables 100% internal quantum efficiency of white TADF-based diodes in a single emissive layer

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Development of white organic light-emitting diodes based on purely thermally activated delayed fluorescence with a single-emissive-layer configuration has been a formidable challenge. Here, we report the rational design of a donor-acceptor energy-relaying exciplex and its utility in fabricating single-emissive-layer, thermally activated delayed fluorescence-based white organic light-emitting diodes that exhibit 100% internal quantum efficiency, 108.2 lm W$^{-1}$ power efficiency, and 32.7% external quantum efficiency. This strategy enables thin-film fabrication of an 8 cm × 8 cm thermally activated delayed fluorescence white organic light-emitting diodes (10 inch$^2$) prototype with 82.7 lm W$^{-1}$ power efficiency and 25.0% external quantum efficiency. Introduction of a phosphine oxide-based acceptor with a steric group to the exciplex limits donor-acceptor triplet coupling, providing dual levels of high-lying and low-lying triplet energy. Transient spectroscopic characterizations confirm that a ladder-like energy relaying occurs from the high-lying triplet level of the exciplex to a blue emitter, then to the low-lying triplet level of the phosphine oxide acceptor, and ultimately to the yellow emitter. Our results demonstrate the broad applicability of energy relaying in multicomponent systems for exciton harvesting, providing opportunities for the development of third-generation white organic light-emitting diode light sources.
Considerable effort has recently been devoted to developing high-efficiency, white organic light-emitting diodes (WOLEDs) with compact design and large-area processing capability\(^1\)-\(^3\). Thermally activated delayed fluorescence (TADF), based on purely organic emitters, enables theoretical 100% internal quantum efficiency for both singlet and triplet exciton harvesting\(^4\)-\(^6\). A single-emissive layer (EML) design, comprising blue/yellow emitters or red/green/blue emitters, can simplify WOLED device structure effectively and can meet the demands of large-scale production, quality control, and low cost\(^8\)-\(^9\). However, competition in exciton confinement between various color emitters makes it challenging to control emission color and device efficiency synchronously (Fig. 1)\(^10\),\(^11\). As an additional constraint, charge-transfer excited states of TADF dyes are highly sensitive to host-dopant interactions\(^12\)-\(^14\) and interfacial effects\(^15\). Indeed, there are few reports of high-efficiency, purely TADF-based WOLEDs, among which multiple emissive layers are required to modify exciton allocation by spatially separating two or three host-dopant systems of different emission colors\(^16\)-\(^18\).

High-efficiency WOLEDs with single-EML layout requires precise optimization of optical transition and energy transfer (ET) in a multi-emitter-doped host\(^19\). However, the narrow single-triplet splitting energy (\(\Delta E_{CT}\)) of TADF emitters limits energy-level regulation. The singlet-triplet energy gap between the blue and yellow TADF emitters, e.g., bis[4-(9,9-dimethyl-9,10-dihydroacridine)phenyl]sulfone (DMAC-DPS, \(S_1/T_1 \approx 2.8\) eV)\(^20\) and 2,3,5,6-tetrakis(3,6-di-tert-butylcarbazol-9-yl)-1,4-dicyanobenzene (4CzTPNBu, \(S_1/T_1 \approx 2.2\) eV)\(^4\), is approximately 0.6 eV, leading to nonradiative deactivation of excitons during energy transfer\(^21\)-\(^23\).

Presently, the performance of single-EML, TADF-based WOLEDs is not comparable to that of their phosphorescent counterparts\(^24\),\(^25\). We reason that a host matrix with dual levels of high-lying and low-lying triplet energy, which match the energy levels of blue and yellow TADF emitters, may improve performance\(^23\),\(^26\). In contrast, single-molecule-based hosts cannot offer two triplet excited states, due to fast internal conversion to the lowest triplet state (\(T_1\)). Therefore, an exciplex host based on a bimolecular donor–acceptor (D–A) system is likely to provide two different triplet states upon appropriate D–A coupling\(^27\),\(^28\).

In principle, a common exciplex comprises a donor and an acceptor with comparable excited energy levels and strong D–A coupling, lowering \(S_1\) and \(T_1\) levels of the exciplex below those of the donor and the acceptor. In contrast, an exciplex design featuring a large triplet energy gap between the donor and the acceptor limits donor–acceptor triplet coupling (Fig. 1)\(^29\). This leads to dual triplet levels of the exciplex with an energy difference of 0.6 eV. Therefore, a facile triplet energy transfer process may occur, namely the \(S_f/T_2\) of the exciplex host \(\rightarrow\) the \(S_f/T_1\) of blue emitter \(\rightarrow\) the \(T_2\) of the exciplex host \(\rightarrow\) the \(T_1\) of yellow emitter. As an added benefit, the exciplex host with near-zero \(\Delta E_{CT}\) can provide additional triplet-singlet conversion and enhance singlet-exciton utilization in the blue-TADF emitter.

As a proof of concept, we designed and synthesized two exciplex hosts, mCP:pDPBITPO and mCP:DpPBITPO, with \(T_2\) and \(T_1\) energy levels of 3.0 and 2.5 eV, based on a high-triplet-energy donor, 1,3-bis(carbazol-9-yl)benzene (mCP, \(T_1 \approx 3.0\) eV) and low-triplet-energy phosphine oxide (PO) acceptors (5-(2-(4-(diphenylphosphoryl)phenyl)-benzimidazol-1-yl)-1,3-phe-nylene)bis(diphenylphosphino oxide) (pDPBITPO) and (5-(1-(4-(diphenylphosphoryl)phenyl)-benzoimidazol-2-yl)-1,3-phe-nylene)bis(diphenylphosphino oxide) (DpPBITPO) (\(T_1 \approx 2.5\) eV as the average of DMAC-DPS and 4CzTPNBu) (Fig. 2a). Our experimental results show that these two exciplexes promote energy transfer relaying in their DMAC-DPS and 4CzTPNBucodoped films. A single-EML design based on mCP:pDPBITPO and mCP:DpPBITPO exciplex yielded TADF WOLEDs with a maximum external quantum efficiency (\(\eta_{EQE}\)) of 32.7% and a maximum power efficiency of 108.2 lm W\(^{-1}\), comparable to that of fluorescent lamps.

## Results

### Exciplex host design

The key molecular design of DpPBITPO and DpPBITPO involves electron-accepting phenylbenzimidazole encapsulated by three diphenylphosphino oxide (DPO) moieties to provide suitable frontier molecular orbital energy levels and to reduce intermolecular charge-transfer interactions with mCP (Fig. 2a). Furthermore, the single-crystal structure of DpPBITPO reveals a twisted configuration of the phenylbenzimidazole group due to steric hindrance of the DPO moiety (Supplementary Fig. 1). This leads to improved triplet-state structural relaxation, reduced \(T_1\) energy level, and enlarged \(\Delta E_{ST}\). Density functional theory (DFT) simulations show locally excited \(T_1\) states of mCP, pDPBITPO and DpPBITPO (Supplementary Fig. 2 and Supplementary Table 1). \(T_1\) energy gaps between the donor and the two acceptors reach \(~0.8\) eV, which is adequate to restrain D–A triplet exciton interactions. As a result of suppressed triplet D–A electronic coupling, high-lying triplet (\(T_2\)) and \(T_1\) states of the exciplexes are localized at mCP and PO acceptors, respectively. Moreover, the energy gaps between the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of mCP and PO acceptors reach \(~0.6\) eV (Fig. 2b and Supplementary Figs. 3). This suggests strong driving forces of D–A charge transfer upon excitation, giving rise to charge-transfer \(S_1\) states. Effective spin-orbital coupling between the

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**Fig. 1 Proposed energy-relaying mechanism.** Exciton allocation in single-emissive-layer, TADF WOLEDs comprising a D–A exciplex host, a blue emitter, and a yellow emitter. Inefficient energy transfer occurs from the exciplex host to the blue emitter and subsequently to the yellow emitter, due to a large energy gap between the blue and yellow emitters (-0.6 eV). The proposed exciplex, based on a high triplet donor and a low triplet acceptor, generates a large triplet gap between a high-lying \(T_2\) and a low-lying \(T_1\). This design enables efficient ladder-like (-0.3 eV ladder spacing) triplet energy transfer from \(T_2\) \(\rightarrow\) blue emitter \(\rightarrow\) \(T_1\) \(\rightarrow\) yellow emitter. ET, IC, ISC, and RISC refer to energy transfer, internal conversion, intersystem crossing, and reverse ISC, respectively.
locally excited triplet state and the charge-transfer $S_1$ state substantially facilitates reverse intersystem crossing (RISC), as evident in the cases of mCP:pDPBITPO and mCP:DpPBITPO (ref. 30). Moreover, PO acceptors are superior to conventional low-triplet-energy acceptors with exposed $T_1$ states, such as TPBI ($T_1 = 2.7$ eV) and BPhen ($T_1 = 2.6$ eV), due to prevention of collision-induced quenching at the $T_1$ state by peripheral DPPO groups.

Estimated by $0 \rightarrow 0$ transitions in emission spectra, the $T_1$ energy levels (2.48 eV) of pDPBITPO and DpPBITPO match well with 4CzTPNBu (2.2 eV), while featuring triplet gaps that are 0.54 eV lower than mCP ($T_1 = 3.02$ eV). Meanwhile, the $S_1$
energy levels of the PO acceptors are 3.2 eV, similar to mCP (S1 = 3.5 eV). The deep-blue emissions from co-evaporated mCP:PO acceptor films exhibit a bathochromic shift of 30 nm, corresponding to Gibbs free energy for charge separation beyond 0.2 eV, indicating exciplex formation through D–A electronic coupling (Fig. 2c; Supplementary Figs. 4 and 5; Supplementary Table 2) (ref. 29). The D–A vibrational coupling leads to structureless phosphorescence spectra of mCP:DpPBITPO and mCP:DpPBITPO. The main peaks at 415 nm correspond to the 0 → 0 triplet transition of mCP, namely the mCP-centered T2 → S0 transitions. Therefore, the T2 levels of the exciplexes (∼3.0 eV) support efficient energy transfer to DMAC-DPS. Furthermore, the tails of the phosphorescence spectra from 500 to 650 nm overlap with those of the PO acceptors, which can be ascribed to either the T1 → S0 transitions of the exciplexes or to triplet leakage to the T1 state of the PO acceptors39. Compared to T1 states located at the PO acceptor, mCP-induced T2 states are closer to S1 states, supporting RISC transitions. In the case of weak D–A triplet exciton interactions and mCP-centralized HOMOs, these T2 states dominate the triplet population. Furthermore, D–A vibrational coupling restrains vibrational perturbation of potential energy surfaces and further alleviates internal conversion from the T2 to T1 states (Fig. 2d), closely resembling rigid, intramolecular charge-transfer systems31. Despite the decreased photoluminescence quantum yields (ϕPL) of the exciplexes (<15%) (Supplementary Table 2), the PO acceptor-induced T1 states can serve as intermediate states to promote triplet energy transfer to 4CzTPNBu.

**Photophysical investigation on the energy-relaying process.**

The DMAC-DPS (30 wt%) and 4CzTPNBu (5 wt%) singly doped sky-blue and yellow exciplex films (100 nm) showed ∼30% and ∼65% increased ϕPL, respectively (Fig. 2e; Supplementary Table 2). These values are still far below the intrinsic values of the dopants (∼95%), due to either triplet leakage to the T1 of the PO acceptors (for DMAC-DPS) or the large energy gap-induced inefficient energy transfer (for 4CzTPNBu). For the doubly doped films of mCP:PO acceptor:30% DMAC-DPSx% 4CzTPNBu (x = 0.5–5), they all achieved ϕPL values above 90%, approximately the sum of the singly doped films.

The weakly populated bands at 500 nm, observed in the time-resolved contours of mCP:PO acceptor exciplexes due to the phosphorescence from the PO acceptors, could be dramatically enhanced upon doping of 30% DMAC-DPS (Fig. 3a). The triplet energy was transferred from DMAC-DPS to PO acceptors at about 70 ns, followed by the appearance of dominant phosphorescence bands at 150 ns. For mCP:PO acceptor:5% 4CzTPNBu, we only observed blue bands from the exciplexes within 50 ns. The absence of phosphorescence bands indicates that PO acceptors do not participate in triplet energy transfer to 4CzTPNBu due to forbidden T2 → T1 transitions of the exciplexes. The time-resolved emission spectra (TRES) of mCP:PO acceptor:30% DMAC-DPS:0.5% 4CzTPNBu films were measured to examine the exact energy transfer process (Fig. 3b). In the time range of 100–500 ns, along with the decrease of the bands assigned to DMAC-DPS (∼470 nm), the bands that peaked at ∼500 nm gradually became dominant, which could be attributed to phosphorescence from the PO acceptors. After the coexistence of the phosphorescent and yellow bands during this time range, the yellow bands remained while the phosphorescence bands vanished. Furthermore, despite the low 4CzTPNBu concentration (0.5%), the DF lifetimes (τDF) of blue bands of DMAC-DPS singly doped films (x = 0) decreased from 1 to 0.5 μs while the τDF values of yellow bands decreased to 0.7 μs (Fig. 3c; Supplementary Table 2). With a large distance between the dopants, energy transfer depends largely on the intermediate T1 energy levels of the PO acceptors for exciton migration from blue to yellow dopants.

Apart from the ultrafast intensity rise (6 ns) in yellow bands (insets in Fig. 3c), we recorded appreciable and nearly synchronous rises in both phosphorescent and yellow bands within 100–500 ns. DMAC-DPS with high-lying excited states supports additional energy transfer to the T1 state of the PO acceptor and then 4CzTPNBu. These synchronous rises further suggest coordination of the exciplex and DMAC-DPS in facilitating energy transfer to 4CzTPNBu. Therefore, upon excitation, a fast, singlet energy transfer occurs, and the triplet energy can be immediately transferred from the exciplexes to DMAC-DPS and then to the T1 energy levels of the PO acceptors within 100–500 ns (Fig. 3d). Almost instantly, the PO acceptors provide the triplet-exciton migration and energy transfer to 4CzTPNBu. As a result, energy harvesting is improved by energy relaying that occurs between blue and yellow dyes, namely mCP:PO acceptor → DMAC-DPS → PO acceptor → 4CzTPNBu.

**WOLED performance.** Based on the high ϕPL values of dual-doped exciplex films and the excellent electrical performance of the PO acceptors and their exciplexes (Supplementary Fig. 3; Supplementary Tables 1 and 2), we further constructed two trilayer TADF-based WOLEDs (W1 and W2) with doubly doped, single-emissive layers (Fig. 4a; Supplementary Fig. 6). Through concentration tuning of 4CzTPNBu, we achieved color modulation from pure white to warm white with a color rendering index beyond 80 and with high chromatic stability (Fig. 4b; Supplementary Figs. 7 and 8; Supplementary Table 3). Commission Internationale de l’Eclairage (CIE) coordinates and correlated color temperatures were (0.31, 0.35)/6582 K for the pure white device and (0.44, 0.47)/3474 K for the warm white device. Their chromatic purity compared well with a standard daylight source (Illuminant D65) and an incandescent light (Illuminant A).

For the mCP:DpPBITPO-based device W1, we achieved maximum efficiencies of 98.4 lm W−1 and 30.6%. mCP:DpPBITPO-derived W2 generated a power efficiency of 108.2 lm W−1, an external quantum efficiency of 32.7% and a device lifetime of 233 h at half-initial luminance (Fig. 4c; Supplementary Figs. 9–11). Device degradation is mainly due to photo- and electro-decomposition of DMAC-DPS (Supplementary Figs. 12 and 13). So, using another more stable blue TADF emitter 4,5-bis(carbazol-9-yl)-1,2-dicyanobenzene (2CzPN) instead of DMAC-DPS (Supplementary Fig. 14), device lifetime can be doubled (Supplementary Fig. 11). Based on a 30% out-coupling ratio of an indium tin oxide glass, we derived 100% internal quantum efficiencies (ηIQE) for both W1 and W2. Large-size WOLEDs are hard to fabricate due to stringent requirements on defect control and device homogeneity. We next fabricated TADF WOLED prototypes with lateral dimensions of 8 cm × 8 cm and efficiencies of 82.7 lm W−1 and 25.0% (Fig. 4d, Supplementary Fig. 15). Our approach is applicable to conventional acceptors. For example, devices W3 and W4, based on two commercial TPBI and BPhen acceptors, achieved maximum efficiencies of 71.3 lm W−1 and 22.6% (Fig. 4c, Supplementary Table 3). In addition, our strategy enabled phosphorescent and hyperfluorescent WOLEDs with respective external quantum efficiencies of 32.4% and 13.7% (Supplementary Fig. 16).

It is interesting that the maximum ηIQE values of W1 and W2 are larger than the sum of the corresponding singly doped blue and yellow devices (Supplementary Figs. 17 and 18). We further doped 30% DMAC-DPS in the emissive layer of the yellow device...
ladder-like, high-efficiency white-emitting systems and multicomponent white-emitting systems and add value to the design may offer fundamental insight into energy transfer in trilayer device provides a sustainable, cost-effective approach to more, the realization of purely TADF-based WOLEDs in a simple these exciplex hosts leads to 100% exciton harvesting. Further-

(Supplementary Fig. 19). Incorporation of DMAC-DPS dramatically improved the efficiencies by ~40%. Furthermore, we fabricated an mCP:DpPBITPO-based WOLED with dual emissive layers, in which DMAC-DPS and 4CzTPNBu were spatially separated to interrupt triplet energy transfer from DMAC-DPS to DpPBITPO to 4CzTPNBu. This reduced maximum efficiencies to 9.3%, due to triplet leakage to the T1 levels of DpPBITPO in the emissive-layer TADF WOLEDs with

Discussion
Our work suggests a general approach to realizing single-

Methods
Preparation of PO acceptors. We designed and synthesized two phosphine oxide acceptors (pDpPBITPO and DpPBITPO). These acceptors were fully characterized by 1H NMR, 13C NMR, 31P NMR, MS, elemental analysis, and single-crystal (if available) X-ray diffraction analysis (Supplementary Figs 21–26).

General procedure of the cyclization reaction. In an argon atmosphere, aromatic aldehyde (1 mmol) and arylamine (1 mmol) were dissolved in DMF (5 mL). The resulting solution was heated to 80 °C. A saturated aqueous Na2S2O5 solution (1 mL) was then added to the mixture and stirred for 20 h at 80 °C. After cooling to room temperature, the mixture was poured into water. The precipitate was filtered and the solid was then washed with water and dried under vacuum to afford white powder in 71% yield.1H NMR (TMS, CDCl3, 400 MHz): 7.889 (d, J = 7.6 Hz, 1H), 7.712 (d, J = 7.8 Hz, 1H), 7.388 (t, J = 7.6 Hz, 1H), 7.337 (td, J = 7.8 Hz, 1.2 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.259 ppm (d, J = 8.0 Hz, 1H); 13C NMR (TMS, CDCl3, 100 MHz): 149.900, 141.878, 137.911, 135.705, 133.655, 130.916, 129.751, 128.253, 127.122, 123.642, 123.131, 123.843, 122.730, 119.244, 109.037 ppm; HRMS (MALDI-TOF) m/z [M + H+] 596.873; elemental analysis (%) for C29H19Br2N2: C 45.03, H 2.18, N 5.55; found: C 45.03, H 2.18, N 5.55.

2-(4-Bromophenyl)-1-(3,5-dibromophenyl)-1H-benzo[d]imidazole (DpPBITBr). The precursor was filtered and the solid was then washed with water and dried under vacuum to afford white powder in 71% yield.1H NMR (TMS, CDCl3, 400 MHz): 7.889 (d, J = 8.0 Hz, 1H), 7.712 (d, J = 8.4 Hz, 2H). 7.454 (d, J = 8.8 Hz, 4H), 7.388 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H), 7.259 ppm (d, J = 8.0 Hz, 1H); 13C NMR (TMS, CDCl3, 100 MHz): 149.900, 141.878, 137.911, 135.705, 133.655, 130.916, 129.751, 128.253, 127.122, 123.642, 123.131, 123.843, 122.730, 119.244, 109.037 ppm; HRMS (MALDI-TOF) m/z [M + H+] 596.873; elemental analysis (%) for C30H18Br2N2: C 46.45, H 2.18, N 5.55; found: C 46.45, H 2.18, N 5.55.

1-(4-Bromophenyl)-2-(3,5-dibromophenyl)-1H-benzo[d]imidazole (DpPBITBr). The precursor was filtered and the solid was then washed with water and dried under vacuum to afford white powder in 71% yield.1H NMR (TMS, CDCl3, 400 MHz): 7.889 (d, J = 8.0 Hz, 1H), 7.712 (d, J = 8.4 Hz, 2H), 7.676 (d, J = 1.6 Hz, 1H), 7.644 (d, J = 1.6 Hz, 2H), 7.395 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.337 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.244-7.175 ppm (m, 3H); 13C NMR (TMS, CDCl3, 100 MHz): 147.946, 144.887, 137.911, 135.705, 133.655, 130.916, 129.751, 128.253, 127.122, 123.642, 123.131, 123.843, 122.730, 119.244, 109.037 ppm; HRMS (MALDI-TOF) m/z [M + H+] 596.873; elemental analysis (%) for C30H18Br2N2: C 46.45, H 2.18, N 5.55; found: C 46.45, H 2.18, N 5.55.
141.754, 135.966, 134.279, 134.031, 132.437, 131.971, 129.887, 127.821, 123.335, 122.678, 122.055, 121.942, 119.321, 109.379 ppm; HRMS (MALDI-TOF) m/z: [M + H]+ 506.875; elemental analysis (%) for C19H11Br3N2: C 45.01, H 2.19, N 5.53; found: C 45.02, H 2.19, N 5.56.

**General procedure of phosphorylation.** In an argon atmosphere, bromide (1 mmol), NaOAc (3.3 mmol), Pd(OAc)2 (0.15 mmol) and diphenylphosphine (3.3 mmol) were dissolved in DMF (10 mL). The mixture was heated to 130°C and kept at this temperature for 36 h under stirring. After cooling to room temperature, the reaction was quenched with water (20 mL). The solution was then extracted with CH2Cl2 (3 × 20 mL). The organic layers were combined and dried with anhydrous sodium sulfate. The solvent was removed in vacuo, and the residue was purified by flash column chromatography to afford phosphine oxide derivatives.

(5-(2-(4-(Diphenylphosphoryl)phenyl)-1H-benzo[d]imidazol-1-yl)-1,3-phenylene)bis(diphenylphosphine oxide) (pDPBITPO), prepared from pDPBITBr to afford white powder in 67% yield. 1H NMR (TMS, CDCl3, 400 MHz): 7.878-7.757 (m, 4H), 7.723 (dd, J1 = 8.0 Hz, J2 = 11.6 Hz, 2H), 7.653 (dd, J1 = 8.0 Hz, J2 = 11.6 Hz, 4H), 7.584-7.518 (m, 5H), 7.518-7.418 (m, 15H), 7.418-7.343 (m, 8H), 7.343-7.291 (m, 1H), 7.258 (t, J = 7.6 Hz, 1H), 7.065 ppm (d, J = 8.0 Hz, 1H); 13C NMR (TMS, CDCl3, 100 MHz): 149.765, 141.950, 136.643, 136.531, 136.472, 136.338, 135.668, 135.555, 135.386, 134.038, 133.941, 133.847, 133.802, 132.789, 132.618, 132.535, 131.878, 131.581, 131.274, 131.226, 131.199, 131.178, 131.053, 130.763, 130.711, 130.660, 130.548, 130.200, 129.148, 128.474, 128.355, 127.924, 127.859, 127.796, 127.754, 127.632, 123.410, 122.848, 119.402, 109.656 ppm; 31P NMR (TMS, CDCl3, 160 MHz): 28.195, 27.637 ppm; HRMS (MALDI-TOF) m/z: [M + H]+ 871.323; elemental analysis (%) for C55H41N2O3P3: C 75.86, H 4.75, N 3.22; found: C 75.88, H 4.76, N 3.25.
pump pulse. The gate width was 2 ns.

temperature. Excitation (wavelength: 350 nm) was performed with femtosecond scattered light from the sample and a blank substrate. The emission scans, with the emission monochromator scanning over the Rayleigh light in the two spectra are equal to the number of photons absorbed by the sample. The quantum yield was calculated using an F900 software wizard.

DFT calculations. DFT computations were performed with different parameters for structural optimization and vibrational analysis. The ground state conformation of DpPBITPO was established according to single-crystal data. Ground, singlet, and triplet states in vacuum were optimized by restricted and unrestricted formalisms of Beck’s three-parameter hybrid exchange functional32 and Lee, and Yang and Parr correlation functional33 B3LYP/6-31 G(d,p), respectively. Fully optimized stationary points were further characterized by harmonic vibrational frequency analysis to ensure a real, local minimum without imaginary vibrational frequency. Total energy changes were also calculated using zero-point energy for both the ground and triplet states. Contours were visualized using GaussianView 5.0. All computations were performed using a Gaussian 09 software package.

Device fabrication and testing. Before loading into a deposition chamber, the ITO substrate was cleaned with detergent and deionized water, dried in an oven at 120 °C for 4 h, and treated with oxygen plasma for 3 min. Devices were fabricated by evaporating organic materials at a rate of 0.1–0.2 nm/s onto the ITO substrate sequentially at a pressure below 4 × 10⁻⁷ Pa. Onto the electron-transporting layer, a layer of LiF with 1 nm thickness was deposited at a rate of 0.1 nm/s to improve electron injection. Finally, a 100-nm layer of Al was deposited at a rate of 0.6 nm/s as the cathode. The emission area of the devices was 0.09 cm², as determined by the overlapped area of the anode and the cathode. After fabrication, devices were immediately transferred to a glove box for encapsulation with glass coverslips using epoxy glue. EL spectra and CIE coordinates were measured using a PR655 spectrum colorimeter. Current–density–voltage and brightness–voltage curves of the devices were measured using a Keithley 4200 source meter and a calibrated silicon photodetector. All measurements were carried out at room temperature under ambient conditions. For each structure, four devices were fabricated in parallel to confirm performance repeatability. The data reported herein were those closest to the average results.

Photophysical measurement. Steady-state emission spectra were measured using an Edinburgh FPLS 920 fluorescence spectrophotometer. TADF dye-doped films (100 nm) were prepared by vacuum evaporation for optical analysis. Photoluminescence quantum yields (PLQY, φPL) of these films were measured through a LabSphere 1-M-2 (φ = 6°) integrating sphere coated with Benfect having efficient light reflection from 200 to 1600 nm, which was integrated with FPLS 920. The absolute φPL determination of the sample was performed with two spectral (emissor–detector, with a 1 cm monochromator scanning over the Rayleigh optical spectrum from the sample and a blank substrate. The first spectrum recorded the scattered light and the sample emission, and the second spectrum recorded the scattered light of the Benfect coating. Integration and subtraction of the scattered light in the two spectra are equal to the number of photons absorbed by the sample (Nabs), while integration of the sample emission is equal to the number of photons emitted (Nem). Then, absolute φPL can be estimated according to the equation of φPL = Nem/Nabs. Spectral correction (emission arm) was applied to raw data after background subtraction, and from these spectrally corrected curves, the quantum yield was calculated using an F900 software wizard.

Time-resolved photoluminescence measurements with nanosecond time resolution were acquired with a gated, intensifi ed CCD camera system (Andor iStar DH740 CCI-010) connected to a grating spectrometer (Andor SR303i) at room temperature. Excitation (wavelength: 350 nm) was performed with femtosecond laser pulses, generated by introducing 1 kHz pulses (pulse length: 80 fs) from a central Ti:sapphire laser source and a TOPAS optical parametric amplifier (Light Conversion). Time-resolved photoluminescence of the sample was obtained by stepping the intensified CCD gate delay relative to the pump pulse. The gate width was 2 ns.

Data availability Data that support the findings of this study are available from the corresponding authors upon request. The X-ray crystallographic coordinates for the DpPBITPO structure reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 2077630. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

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C.H. and R.D. contributed equally to this work. W.H., X.L., and H.X. conceived the projects. C.H., R.D., S.H., P.M., J.B., M.S., C.D., and Y.W. performed the experiments. C.H., R.D., S.H., H.X., X.L., and W.H. analyzed the data and wrote the paper. All authors commented on the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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