High-efficiency blue thermally activated delayed fluorescence from donor–acceptor–donor systems via the through-space conjugation effect†

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The photophysical optimization of donor (D)–acceptor (A) molecules is a real challenge because of the intrinsic limitation of their charge transfer (CT) excited states. Herein, two D–A–D molecules featuring blue thermally activated delayed fluorescence (TADF) are developed, in which a homoconjugated acceptor 5,10-diphenyl-5,10-dihydroyphosphanthrene oxide (DPDPO2A) is incorporated to bridge four carbazolyl or 3,6-di-t-butyl-carbazolyl groups for D–A interaction optimization without immoderate conjugation extension. It is shown that the through-space conjugation effect of DPDPO2A can efficiently enhance intramolecular CT (ICT) and simultaneously facilitate the uniform dispersion of the frontier molecular orbitals (FMO), which remarkably reduces the singlet–triplet splitting energy (ΔE_ST) and increases FMO overlaps for radiation facilitation, resulting in the 4–6 fold increased rate constants of reverse intersystem crossing (RISC) and singlet radiation. The maximum external quantum efficiency beyond 20% and the state-of-the-art efficiency stability from sky-blue TADF OLEDs demonstrate the effectiveness of the “conjugation modulation” strategy for developing high-performance optoelectronic D–A systems.

1. Introduction

Organic donor-acceptor (D–A) molecules feature charge-transfer (CT) excited states and ambipolar characteristics, and therefore are widely used in optoelectronic applications, such as organic light-emitting diodes (OLEDs), organic solar cells (OSCs), photodetectors, memory devices, and so on. The electrical properties of D–A systems are readily modulated on the basis of the inherent relationship between molecules and D/A groups regarding electron gain and loss. In contrast, the photophysical properties of D–A molecules are more difficult to optimize due to the strong dependence of the excited-state characteristics on the intramolecular CT (ICT) interaction. For instance, thermally activated delayed fluorescence (TADF) materials emerge recently for OLED applications, which should have near-zero singlet–triplet splitting energy (ΔE_ST) to facilitate reverse intersystem crossing (RISC) for delayed fluorescence (DF). It is known that ΔE_ST is twice the electron exchange energy (J) expressed as:

$$\Delta E_{ST} = 2J = 2 \sum \int |\Psi_L(1)|^2 |\Psi_H(2)|^2 \left( \frac{e^2}{r_1 - r_2} \right) |\Psi_L(2)|^2 |\Psi_H(1)|^2 dr_1 dr_2$$

where $\Psi_H$ and $\Psi_L$ refer to the wave functions of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), respectively. On the other hand, according to Fermi’s golden rule, the transition probability (Γ) between the initial and final states can be described as:

$$\Gamma = \frac{2\pi}{\hbar} |\langle H \rangle|^2$$

and $\langle H \rangle = \langle |\Psi_I| \mu |\Psi_F| \rangle = \int \Psi_I \mu \Psi_F d\tau$ where $\mu$ is the dipole moment operator, electron charge and electron transition distance, respectively. On account of the CT singlet excited states (CT) for TADF molecules, their ΔE_ST and Γ are simultaneously in direct proportion to the HOMO–LUMO overlap integral $|\langle \Psi_H | \Psi_L \rangle|^2$, making the achievement of efficient DF become a real challenge.

Obviously, the conflict between ΔE_ST and Γ could be resolved by finding the best compromise for $|\langle \Psi_H | \Psi_L \rangle|^2$. Although it

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was shown that the moderate HOMO–LUMO overlap is an essential condition for improving the radiative efficiency of TADF molecules, the optimal frontier molecular orbital (FMO) distribution is still ambiguous, which limits the targeted molecular design. From another perspective, Adachi et al. demonstrated that the delocalization of the HOMO and the LUMO can enhance the radiative rate of CT compounds through increasing the oscillator strength of their 4ICT radiation despite small $\langle W^2_H \rangle \langle W^2_L \rangle$, which can be realized through either dendronizing the D group\textsuperscript{39} or increasing the density of D groups linked on the same $\pi$-bridge.\textsuperscript{10} The former more or less increases the synthesis complexity, whereas the latter leads to a remarkable bathochromic shift of the emission. Actually, because of the high sensitivity of emission color to the intensity of D–A interactions, the excited-state characteristics of blue TADF materials are even more difficult to modify.\textsuperscript{37,38}

As alternatives, D–A–D and D–A–A type molecules seem promising, owing to their advantage of accurate ICT modulation.\textsuperscript{39,60} The D–A–D structure could be regarded as the combination of two D–A units with doubled but dispersed D and A groups. Lee et al. constructed a D–A–D dyne through the single-bond conjugation of two isophthalonitrile acceptors, which resulted in the LUMO delocalization, 1.5-fold photoluminescence quantum yield (PLQY, $\phi_{\text{PL}}$) and twofold external quantum efficiency (EQE, $\eta_{\text{EQE}}$) of its devices, however, accompanied by a remarkable emission red shift ($\sim$50 nm).\textsuperscript{61} In contrast, through incorporating $P=O$ as the insulating acceptor, we realized a pure-blue D–A–D TADF dye, but its HOMO and LUMO were still localized on single D/A groups.\textsuperscript{62} Obviously, the conjugation between D–A units should be precisely modulated to optimize electronic interplays.\textsuperscript{63} In this sense, systems based on homojunction would be the desired alternatives, whose through-space conjugation effect on intramolecular electronic communications is between the through-bond conjugation and insulating effects.\textsuperscript{44} Therefore, they could not only support sufficient D–A interactions, but also avert inmoderate conjugation extension, and are “ideal” for developing high-efficiency blue TADF dyes (Scheme 1).

It is noteworthy that the lengths of homoconjugated units are commonly larger than diphenylene, which would weaken D–A interactions, if used as $\pi$-linkers.\textsuperscript{65} In such a case, a homoconjugated acceptor is desired, since it can directly combine with D groups to provide strong enough ICT effects and simultaneously suppress excessive intramolecular electronic interactions. As a proof of concept, in this contribution, we incorporate a homoconjugated phosphine oxide (PO) acceptor 5,10-diphenyl-5,10-dihydrophosphanthrene oxide (DPDPO2A) into D–A–D systems $9,9',9''$-oxo-[5,10-diphenyl-5,10-dihydrophosphanthrene-2,3,7,8-tetrayl]tetakis(9H-carbazole) oxides (4CzDPDPO2A) and $9,9',9''$-oxo-[5,10-diphenyl-5,10-dihydrophosphanthrene-2,3,7,8-tetrayl]tetakis(3,6-di-tert-butyl-9H-carbazole) oxides (4BCzDPDPO2A), collectively named 4ArRPPO2A and 4ArRPPO2A with completely localized HOMOs and LUMOs, the homoconjugated DPDPO2A acceptor dramatically facilitates intramolecular electronic interplays, providing HOMOs and LUMOs uniformly dispersed on D and A groups, respectively, which shortens the centroid distances and increases the overlap integrals between the HOMOs and the LUMOs, accompanied by enhanced ICT effects. As a result, the doped films of 4CzDPDPO2A and 4BCzDPDPO2A reveal pure-blue and sky-blue emissions with 4–6 fold increased rate constants of prompt fluorescence (PF, $k_{\text{PF}}$) and singlet radiation ($k^S$) and 2–4 fold increased DF rate constants ($k_{\text{DF}}$), as well as dramatically improved RISC efficiencies ($\phi_{\text{RISC}}$) of 85 and 94%, respectively. As expected, 4CzDPDPO2A and 4BCzDPDPO2A achieve photoluminescence (PL, $\phi_{\text{PL}}$) and electroluminescence (EL, $\eta_{\text{EQE}}$) quantums efficiencies of 65 and 81% and 11.5 and 23.7%, respectively, which are 2–10 times higher in comparison to 4ArPPPO2A and 4ArRPPO2A, making them favorable among the blue TADF dyes reported to date. This work demonstrates a facile strategy to optimize the electronic effect in D–A molecules through conjugation modulation, which provides a new way to overcome the bottlenecks of their optoelectronic applications.

2. Results and discussion

2.1. Design and structures

We choose our previously reported blue TADF molecules o2ArPO as the D–A unit, whose simple D–$\pi$–A structures consist of Cz/tBCz and diphenylphosphine oxide (DPPO) as D and A groups, respectively.\textsuperscript{66} Although their HOMOs are uniformly dispersed on the Cz/tBCz groups, their LUMOs are localized on the single phenyls. Despite the pure-blue emissions, the limited D–A interactions result in relatively low $\phi_{\text{PL}}$ and $\eta_{\text{EQE}}$, less than 50 and 10%, respectively, for o2ArPO. From the D–$\pi$–A structures of o2ArPO to the D–A–D structures, when two P=O groups are used to simultaneously link two Cz/tBCz substituted phenyls at ortho positions, the cyclic DPDPO2A acceptor with the feature of through-space conjugation and the homoconjugated 4ArRPPO2A are formed; when the single P=O group is used as an insulating linkage between two D–A units, 4ArRPPO2A and

![Scheme 1 Molecular design of D–A–D systems. Two D–A type molecules can be combined to form (i) a uniform D–A–D system based on through-bond conjugation, (ii) a united D–A–D system based on through-space conjugation or (iii) a separated D–A–A–D system based on insulating linkage.](Image)
4ArPPODPO with nonconjugated D–A–D structures are formed. The D/A ratios in 4ArPPOPO and 4ArDPDPO2A are equal, but the D–A interaction intensity in each D–A unit of 4ArPPODPO is comparable to that in 4ArDPDPO2A (Scheme S1†). Actually, the basic structure of these molecules is the same as that of a P=O-based acceptor substituted with four carbazole-based donors (Scheme S2†). In this case, the only structural difference between 4ArDPDPO2A, 4ArPPOPO and 4ArPPODPO is the conjugation extent, which should be the main reason leading to their diverse photophysical properties.

The single-crystal structure of 4CzDPDPO2A indicates a nearly coplanar DPPO2A ring with a large dihedral angle of ~140°, which should be ascribed to the strong intramolecular hydrogen bonds between P=O groups and H atoms at both-side ortho positions with H⋯O distances less than 3 Å (Fig. 1b). The intramolecular hydrogen bonds also give rise to the cis configuration of DPPO2A with coplanar P=O groups, in which two same-side phenyls reveal the intramolecular π–π interaction with a centroid–centroid distance of ~3.8 Å. Similarly, the ortho-substitution enables intramolecular π–π interactions between adjacent Cz groups with a centroid–centroid distance of ~3.7 Å. More importantly, the distance between two C=C bonds in the 1,4-diphosphinine oxide unit is 2.84 Å, which is short enough for the p-orbital overlap.67 These intramolecular interplays not only result in the planar phosphanthrene ring with potential homoconjugation, but also enhance the molecular rigidity to increase fPL.

Although the crystals of 4tBCzDPDPO2A cannot be obtained, on account of the negligible intramolecular steric hindrance for 3,6-tert-butyls of the peripheral tBCz groups, the configurations of 4ArDPDPO2A would be similar, which is further demonstrated by the density functional theory (DFT) simulation (Fig. S2–S4†). In contrast, due to the C–P bond rotation of their P=O linkers, the structures of 4ArPPOPO and 4ArPPODPO are
more flexible, twisted and asymmetrical, which not only induces differences between two D–A units in spatial orientation, but also suppresses intermolecular interactions.\textsuperscript{21,68} As a result, the thermal stability of 4ArDPDPO2A is remarkably higher than that of 4ArPPOPO and 4ArPPODPO, but all the materials reveal a stable amorphous phase in the solid state (Fig. S5\textsuperscript{†}). Because 4ArDPDPO2A, 4ArPPOPO and 4ArPPODPO are comparable regarding intermolecular interactions, it is rational to attribute their optical properties to their single molecule characteristics.

2.2. DFT and TDDFT simulations

DFT and time-dependent DFT (TDDFT) calculations were performed to figure out the frontier molecular orbital (FMO) distributions and the excitation characteristics. As depicted in Fig. 2a, the HOMOs of 4ArDPDPO2A are almost equally dispersed on their four Cz/tBCz groups, accompanied by minor contributions from phosphanthrene rings. Their HOMO+1s and HOMO+2s also reveal similar distributions [Fig. S2 and S3\textsuperscript{†}]. Meanwhile, the LUMOs, LUMO+1s and LUMO+2s of 4ArDPDPO2A are uniformly dispersed on their DPDPO2A groups. It should be noticed that for the LUMOs and LUMO+1s, the electronic wave functions of p-orbitals of sp\textsuperscript{2}-hybrid C atoms at two sides of P atoms are effectively and directly overlapped without the incorporation of orbitals from P atoms, convincingly evidencing through-space conjugation between the “P=O-separated” phenylenes in phosphanthrene rings (Fig. S4\textsuperscript{†}). In contrast, the HOMOs and LUMOs of 4ArPPOPO and 4ArPPODPO are basically localized at one-to-two Cz/tBCz groups on one side of the molecules and the phenyls linked with P=O groups. Furthermore, FMOs of 4ArPPODPO are more centralized than those of 4ArPPOPO, due to the stronger D–A interactions in the former. Therefore, as expected, in contrast to insulating linkage, the homoconjugated acceptors in D–A–D molecules can dramatically facilitate FMO delocalization, as shown in Fig. 2b and 2c.

![Fig. 2](image-url)
especially leading to uniform HOMO dispersion on all D groups at both sides of the acceptors.

The HOMO energy levels of the compounds are basically in accord with their D groups whose HOMO values are equal to \(-5.4 \text{ eV}\) for Cz and \(-5.2 \text{ eV}\) for tBCz (Fig. 2a, S2, S3 and Table S1). Differently, the LUMOs of 4ArDPDPO2A are remarkably deeper than those of 4ArPPOPO and 4ArPPODPO by 0.15 and 0.25 eV, respectively, which reflects the stronger electron-withdrawing effect of the DPDP2O2A group. Furthermore, it is noteworthy that the HOMO–LUMO energy gaps of 4ArDPDPO2A are 0.1 and 0.2 eV smaller than those of 4ArPPOPO and 4ArPPODPO, respectively, which is perfectly consistent with the results of cyclic voltammetry (CV) analysis (Fig. S6 and Table S2). The measured HOMO energy levels of 4ArDPDPO2A are about 0.05 eV smaller than those of their analogues, while the HOMO energy levels of 4ArPPOPOP and 4ArPPOPDPO are equivalent. Therefore, in comparison to 4ArPPOPOP and 4ArPPOPDPO, respectively, which is perfectly consistent with the results of cyclic voltammetry (CV) analysis (Fig. S6 and Table S2).

The overlap integrals \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) and the centroid distances \(d(\Psi_i^H - \Psi_l^L)\) of the FMOs for the 4ArDPDPO2A, 4ArPPOPO and 4ArPPOPDPO are gradually decrease from \(-3.3, -3.1\) to \(-3.0 \text{ eV}\). It is rational that the larger steric hindrance of two ortho-DPO groups in 4ArPPOPO and 4ArPPOPDPO provides a more twisted configuration and further reduces the ICT effect, leading to their highest LUMO energy levels. Besides the stronger electron-withdrawing effect of DPDP2O2A acceptors, the deepest LUMOs and HOMOs of 4ArDPDPO2A should be actually attributed to the strongest ICT interactions between their DPDP2O2A and Cz/tBCz groups. This is further evidenced by their smallest experimental HOMO–LUMO energy gaps of \(-2.8 \text{ eV}\), which is as much as 0.2 and 0.3 eV smaller than those of 4ArPPOPO and 4ArPPOPDPO, respectively. Consequently, the incorporation of homoc conjugated DPDP2O2A as the acceptor can indeed improve the ICT effect, owing to its through-space conjugation effect facilitated D–A interactions.

Natural transition orbital (NTO) analysis of singlet and triplet excitations was performed to identify the excited-state characterisitics (Fig. 2b and S7). \(99,100\) For 4ArDPDPO2A, similar to the FMO locations of their ground states (S0), the “holes” are uniformly dispersed on their four D groups, accompanied by minor contributions from phenylenes of DPDP2O2A rings, while the “particles” are mainly distributed on their DPDP2O2A groups, manifesting their CT-predominant first singlet excited states (S1). In contrast, the S1 states of 4ArPPOPOP and 4ArPPOPDPO are completely localized with the “holes” on single D groups and the “particles” on single phe nylenes linked with P=O groups. The significantly delocalized S1 states of 4ArDPDPO2A undoubtedly originate from the through-space conjugation effect of DPDP2O2A for the uniformity of D–A interactions in whole molecules. The insulating P=O linkages in 4ArPPOPOP and 4ArPPOPDPO in turn impede the electronic communications between two D–A units, resulting in their locally confined S1 states. It is noteworthy that comparable to their insulated analogues, the S1 energy levels of 4ArDPDPO2A (\(-3.0 \text{ eV}\)) are only slightly lower by 0.1 eV, still corresponding to blue emissions, which manifests the limited influence of the homoconjugated linkage on emission color. On the other hand, for S0 \(\rightarrow\) T1 excitations, all the molecules reveal LE T1 states with the “holes” and “particles” localized on their Cz groups, which benefits the RISC transitions from the T1 to the S0. \(71\) Although the planar geometry of the DPDP2O2A acceptor is a requirement, its homoconjugation is the main reason for the preserved excited-state energy levels and enhanced ICT effect of 4ArDPDPO2A.

The overlap integrals \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) and the centroid distances \(d(\Psi_i^H - \Psi_l^L)\) of the FMOs for the 4ArDPDPO2A, 4ArPPOPO, and 4ArPPOPDPO are remarkably larger \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) as large as 0.8, accompanied by negligible \(d(\Psi_i^H - \Psi_l^L)\). However, \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) values of 4ArDPDPO2A reach 0.43, which is 2 and 4 fold those of 4ArPPOPO and 4ArPPOPDPO. Especially, \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) values of 4ArDPDPO2A are extremely small and are equal to 2.8 Å, which is extraordinary for D–A systems and only one seventh of those of 4ArPPOPO and 4ArPPOPDPO. Such small \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) values undoubtedly benefit from the uniformly and symmetrically dispersed HOMOs and LUMOs of 4ArDPDPO2A due to the through-space conjugation effect of DPDP2O2A. Similarly, in comparison to their analogues, 4ArDPDPO2A reveal remarkably larger \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) and smaller \(d(\Psi_i^H - \Psi_l^L)\). It is noteworthy that compared to 4ArPPOPO, the more centralised FMOs in more twisted 4ArPPOPDPO by the steric effect dramatically decrease their \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) and \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\), and enlarge their \(d(\Psi_i^H - \Psi_l^L)\) and \(d(\Psi_i^H - \Psi_l^L)\), which is the origin of the conflict between \(\Delta E_{ST}\) and \(\Gamma\) for the insulating D–A–D systems. Obviously, as expected, the employment of homoconjugated DPDP2O2A can realize the best compromise \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) through simultaneous ICT enhancement due to the electronic effect and FMO delocalization due to the spatial effect.

In consequence, among these molecules, 4ArDPDPO2A simultaneously achieve comparable S1 energy levels, the smallest \(\Delta E_{ST}\) and the largest \(\left\langle \Psi_i^H|\Psi_l^L \right\rangle\) (Table S2), which are ascribed to their strongest ICT effects and the uniformly delocalized FMOs, respectively. Therefore, it is convincing that the homoconjugated acceptor-based D–A–D systems would be one of the alternatives with efficient blue TADF emission.

2.3. Optical properties

It is known that the emission color of CT molecules is strongly dependent on the solvent polarity, namely so-called “solvatochromism”, which is ascribed to the large polarity difference between their S0 and S1 states. \(74\) Accordingly, the PL spectra of these PO materials are measured in different solvents (Fig. 3a). In high-polarity solvents, the emissions from all the materials are remarkably red-shifted, manifesting their effective ICT interactions. Nevertheless, it is noted that the bathochromic shifts for 4ArDPDPO2A are the biggest, being 130 nm for the maxima, which is 30 and 40 nm larger than those for 4ArPPOPO and 4ArPPOPDPO, respectively. As a result, along with the increase of solvent polarity \(\beta\), the Stokes shift \(\delta\) of
4ArDPDPO2A increases more sharply than their analogues, which is quantitatively evidenced by the bigger slopes for the former (Fig. 3b). Consistent with theoretical simulation results, by virtue of the through-space conjugation effect, the ICT intensities in 4ArDPDPO2A are the strongest among these molecules, whereas the smallest red shifts for 4ArPPDPO are in accord with their weakest ICT interactions restrained by their twisted configurations. Therefore, with respect to the ICT effect, the linkages in multiple D–A systems are equally important, besides the electronic effects for D and A groups.

The ground-state dipole moment (μ₀) of the molecules is evaluated by DFT calculations (Table S1†). The μ₀ of 4ArDPDPO2A is ~4.5–5.1 Debye, which is about 2 Debye smaller than that of 4ArPPPO due to the thoroughly symmetrical and coplanar DDPO2A groups in the former. In the same way, the additional P=O and the twisted configuration provide the biggest μ₀ for 4ArPPDPO. According to the Lippert–Mataga relationship, the singlet excited-state dipole moment (μe) is estimated [Fig. 3b and Table S1†]. Because of the reverse order for their ICT intensity, the μe differences between 4ArDPDPO2A and their analogues decrease. Nevertheless, the μe of ArDPDPO2A which is ~9 Debye is still 1.5–3.5 Debye smaller than that of their analogues, and even 1.2 and 6.2 Debye smaller than those of their D–A units, respectively, which should be attributed to the uniformly dispersed FMOs on the S1 states of ArDPDPO2A. The small μe of TADF emitters would facilitate their RISC through ΔEST reduction by the host field effect, while their small μe is beneficial to suppress dipole–dipole interaction induced quenching. In this sense, ArDPDPO2A would be superior in simultaneous TADF improvement and quenching suppression.

The electronic absorption spectra of all the compounds in dilute chloroform solutions (10⁻⁶ mol L⁻¹) contain three bands around 230, 285 and 340 nm, corresponding to π → π* transitions of phenyl and Cz groups and n → π* transitions of the latter, respectively (Fig. 4a and b). More importantly, different from the absorption tails for 4ArPPPO and 4ArPPDPO around 350 nm, 4ArDPDPO2A reveal additional and distinct CT absorption bands centered at 360 and 375 nm, respectively, further displaying their homoconjugation-enhanced ICT.

Nevertheless, all the absorption bands are preserved in the spectra of the neat films, further indicating their limited intermolecular interactions (Fig. S8†). The absorption, fluorescence (FL) and phosphorescence (PH) spectra of these molecules in dilute toluene solutions were further measured to determine their intrinsic excited-state energy levels (Fig. S9†). In accord with TDDFT results, the intramolecular electronic and vibrational couplings facilitate red-shifts of PH spectra for these compounds by 30 nm in comparison to the carbazole molecule. As expected, the red-shifted fluorescence and preserved phosphorescence of 4ArDPDPO2A give rise to their near-zero ΔEST of 0.09 and 0.06 eV, respectively, which are remarkably lower by 0.07–0.23 eV in contrast to their nonconjugated analogues (Table S2†).

The vacuum-evaporated films of 4ArDPDPO2A, 4ArPPPO and 4ArPPDPO as dopants in the 4,6-bis(diphenylphosphoryl) dibenzofuran (DBFDPO) matrix were prepared to get an insight into the photophysical properties of the emissive layers (EML) in their OLEDs. The emitters can be homogenously dispersed in DBFDPO, resulting in a small Root-Mean-Square roughness around 1 nm (Fig. S11†). All the films reveal blue/sky-blue fluorescence. It is shown that in comparison to Cz-based analogues, the stronger electron-donating effect of the tBCz group results in moderate emission red shifts of ~10 nm (Fig. 4a and b). The FL peak wavelengths of 4ArDPDPO2A are 470 and 479 nm, respectively, corresponding to sky-blue emissions, which are only 15 and 10 nm larger than those of 4ArPPPO and 4ArPPDPO, respectively. Therefore, as designed, the emission bathochromic shifts of 4ArDPDPO2A should mainly originate from their enhanced ICT effect rather than the limited conjugation extension by DPDPO2A. The PH spectrum of the 4CzDPDPO2A-based film at 77 K shows the 0 → 0 transition at 480 nm, giving rise to a small ΔEST of 0.05 eV, which is only half of ~0.1 eV for its analogues (Table S3†). Therefore, compared to insulating linkages, homoconjugated DPPO2A can indeed effectively reduce ΔEST. The PH emission of the 4BCzDPDPO2A-based film peaking at 484 nm is almost overlapped with its FL, which further reduces its ΔEST to 0.03 eV. Nevertheless, 4BCzPPPO and 4BCzPPDPO also give ΔEST as small as 0.04 eV for their films. Since D groups are on both sides of D–A–D systems, D groups with stronger electron-donating
ability can enhance the local ICT interaction. In this sense, the comparable $\Delta E_{ST}$ values of 4CzDPDPO2A, 4tBCzPPOPO and 4tBCzPPODPO actually in turn manifest the effectiveness of through-space conjugation in ICT enhancement. Differently, despite the one more P==O acceptor in 4ArPPODPO, its $\Delta E_{ST}$ is equivalent to that of 4ArPPOPO, since their insulating linkages restrain D-A interactions in single D-A units rather than entire molecules. Nevertheless, all the molecules reveal typical TADF emissions combined with one short-lifetime PF component (Fig. S10†) and one long-lifetime DF component (Fig. 4c and d).

The rate constants ($k$) and efficiencies ($\phi$) of the key transitions during the TADF process are estimated according to the transient characteristics and $\phi_{PF}$ and $\phi_{DF}$ (Fig. 5 and Table S3†). The 4tBCzDPDPO2A-based film reveals an extremely high $k_{PF}$ at the level of $10^8 \text{s}^{-1}$, which is among the highest values for blue TADF dyes to date. The $k_{PF}$ of the 4CzDPDPO2A-based film also reaches $7 \times 10^7 \text{s}^{-1}$ which is about half of that of 4tBCzDPDPO2A, however, it is still 2–3 fold those of 4ArPPOPO and 4ArPPODPO. Furthermore, 4ArPDPDPO2A endow their films with an improved $k_{DF}$ of 2–3 $\times 10^7 \text{s}^{-1}$, which is 2–4 fold those of 4ArPPOPO and 4ArPPODPO. Obviously, the incorporation of the DPDPO2A acceptor in 4ArPDPDPO2A simultaneously facilitates their PF and DF processes, among which 4tBCzDPDPO2A with stronger D groups is more superior. In this sense, the ICT interaction would be the key influencing factor for the overall photophysical properties of these emitters.

Considering RISC as the core transition for the DF process, the $k$ and $\phi$ of RISC ($k_{RISC}$ and $\phi_{RISC}$) are further evaluated. The $k_{RISC}$ of the 4tBCzDPDPO2A-based film is beyond $8 \times 10^4 \text{s}^{-1}$, which is 2 fold that of 4CzDPDPO2A and as high as 8 fold those of 4ArPPOPO and 4ArPPODPO, respectively. At the same time, 4tBCzDPDPO2A realizes the highest $\phi_{RISC}$ of 94%, which is beneficial to RISC for overcoming its inferior $k$ in contrast to intersystem crossing (ISC). On the other hand, the rate constants ($k_{S}^f$) of singlet radiation for 4ArPDPDPO2A-based films are as high as $2–3 \times 10^6 \text{s}^{-1}$, which is dramatically higher by 4–6 fold in comparison to 4ArPPOPO and 4ArPPODPO. Moreover, 4tBCzDPDPO2A also achieves the lowest rate constant of singlet nonradiation ($k_{NR}^S$). Nevertheless, the $k_{S}^f$ values of 4ArPDPDPO2A and 4ArPPODPO based films are comparable, which are 50% smaller than those of 4ArPPOPO. The highly rigid coplanar

![Image](56x476 to 539x729)

Fig. 4 Photophysical properties of 4ArDPDPO2A, 4ArPPOPO and 4ArPPODPO in the DBFDPO matrix. (a) Electronic absorption spectra in dilute CHCl$_3$ ($10^{-6} \text{ mol L}^{-1}$), room-temperature fluorescence (FL) and low-temperature time-resolved phosphorescence (PH) spectra in DBFDPO-hosted vacuum-evaporated films of 4CzDPDPO2A, 4CzPPOPO and 4CzPPODPO; (b) 4tBCzDPDPO2A, 4tBCzPPOPO and 4tBCzPPODPO; (c) transient emission spectra of 4CzDPDPO2A, 4CzPPOPO and 4CzPPODPO and (d) 4tBCzDPDPO2A, 4tBCzPPOPO and 4tBCzPPODPO.

![Image](56x476 to 539x729)

Fig. 5 Linear correlations between $\phi_{PL}$ of 4ArDPDPO2A, 4ArPPOPO and 4ArPPODPO and the rate constants ($k$) and efficiencies ($\phi$) of the key transitions involved in the TADF process.
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By contrast, the maximum EL efficiencies of 4CzDPDPO2A-based blue devices are reduced by about 50%, but its maximum hEQE of 11.5% is still favorable among pure-blue TADF diodes. Especially, most of the pure-blue TADF devices suffer from the serious roll-offs due to the high-energy excitons more sensitive to quenching effects. In contrast, 4CzDPDPO2A supports its devices with an hEQE of 11.0 and 9.0% at 100 and 1000 nits, corresponding to the impressive EQE roll-offs of 4 and 22%, respectively. In comparison to 4CzDPDPO2A, the maximum EL efficiencies of 4ArPPOPO and 4ArPPDPO based devices are further halved, accompanied by sharply worsened roll-offs which are more than 30 and 60% at 100 and 1000 nits, respectively.

It is noteworthy that the maximum hEQEs of these devices reveal a perfect linear dependence on the k and f of the TADF transitions for these emitters, which demonstrates the consistency between photophysical and EL performance modulation (Fig. S12†).

### Table 1  EL performance of blue OLEDs based on 4ArDPDPO2A, 4ArPPOPO and 4ArPPDPO

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Vm(V)</th>
<th>Lmax(cd m⁻²)</th>
<th>ηCE(cd A⁻¹)</th>
<th>ηPE(Lm W⁻¹)</th>
<th>ηEQE(%)</th>
<th>λEL/[CIE (x, y)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4CzDPDPO2A</td>
<td>4.3, 7.8, 10.8</td>
<td>11 020</td>
<td>20.2, 19.3, 15.9</td>
<td>14.8, 7.8, 4.6</td>
<td>11.5, 11.0, 9.0</td>
<td>460/0.17, 0.24</td>
</tr>
<tr>
<td>4CzPPOPO</td>
<td>5.3, 10.3, 15.8</td>
<td>1344</td>
<td>7.1, 3.1, 1.1</td>
<td>4.2, 0.9, 0.2</td>
<td>4.9, 2.1, 0.8</td>
<td>444/0.17, 0.18</td>
</tr>
<tr>
<td>4CzPPDPO</td>
<td>5.5, 16.0, —</td>
<td>157</td>
<td>1.6, 0.3, —</td>
<td>0.9, 0.1, —</td>
<td>1.1, 0.2, —</td>
<td>440/0.19, 0.19</td>
</tr>
<tr>
<td>4tBCzDPDPO2A</td>
<td>3.7, 7.3, 10.3</td>
<td>18 765</td>
<td>44.8, 41.8, 35.0</td>
<td>38.0, 18.0, 10.7</td>
<td>23.7, 22.2, 18.5</td>
<td>472/0.18, 0.30</td>
</tr>
<tr>
<td>4tBCzPPOPO</td>
<td>5.0, 9.5, 15.0</td>
<td>23 22</td>
<td>5.8, 4.3, 2.2</td>
<td>3.7, 1.4, 0.5</td>
<td>3.6, 2.6, 1.3</td>
<td>460/0.18, 0.23</td>
</tr>
<tr>
<td>4tBCzPPDPO</td>
<td>4.8, 9.3, 16.3</td>
<td>1761</td>
<td>7.0, 5.1, 1.3</td>
<td>4.6, 1.7, 0.2</td>
<td>4.0, 2.9, 0.7</td>
<td>460/0.19, 0.25</td>
</tr>
</tbody>
</table>

* At 1, 100 and 1000 cd m⁻². b The maximum luminance. c EL efficiencies at the maximum, 100 and 1000 cd m⁻². d EL peak wavelength.
on $k_{\text{PF}}$ and $k_{\text{DF}}$, the maximum $\eta_{\text{EQE}}$ is more sensitive to the variations of $k_F^2$ and $k_{\text{RISC}}$, as indicated by the larger slopes of their fitting lines. Therefore, as predicted, the simultaneous enhancement of the singlet radiation and triplet-to-singlet conversion is crucial to improve the EL performance of TADF emitters. Furthermore, in contrast to $\phi_{\text{PF}}$, the triplet-correlated $\phi_{\text{DF}}$ and $\phi_{\text{RISC}}$ are more influential to the maximum $\eta_{\text{EQE}}$, which is in accord with the statistical advantage and dominant contribution of triplet excitons for EL. Therefore, it is convincing that the success of 4ArDPDPO2A in TADF OLEDs originates from the superiority of homoconjugated acceptors in optimizing the photophysical properties of D–A–D systems via the through-space conjugation effect, namely simultaneously enhancing ICT and singlet radiation through FMO optimization.

The excellent EL performance of 4ArDPDPO2A manifests the great potential of homoconjugated D–A systems as TADF emitters, especially for blue OLEDs. Although the exciton utilization efficiencies (EUE) of 4ArDPDPO2A approach 100%, the homoconjugated TADF dye still has a huge space for development with respect to D–A combination and optimization.

3. Experimental section

3.1. Fabrication and characterization of OLEDs

Before loading into a deposition chamber, the ITO substrate was cleaned with detergents 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 layers at a rate of 0.1–0.2 nm s$^{-1}$ onto the ITO substrate sequentially at a pressure below 4 × 10$^{-4}$ Pa onto the electron-transporting layer, a layer of LiF with 1 nm thickness was deposited at a rate of 0.1 nm s$^{-1}$ to improve electron injection. Finally, a 100 nm-thick layer of Al was deposited at a rate of 0.6 nm s$^{-1}$ as the cathode. The emission area of the devices was 0.09 cm$^2$ as determined by the overlap area of the anode and the cathode. After fabrication, the devices were immediately transferred to a glove box for encapsulation with glass cover slips using epoxy glue. The EL spectra and CIE coordinates were measured using a PR655 spectrophotometer. The current–voltage–brightness and brightness–voltage curves of the devices were measured using a Keithley 4200 source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions. For each structure, four devices were fabricated in parallel to confirm the performance repeatability. The device results reported were the data most close to the average values.

4. Conclusions

We demonstrate the feasibility of optimizing the photophysical properties of D–A–D molecules via the through-space conjugation effect of homoconjugated acceptors. In contrast to insulating linkage and through-bond conjugation, through-space conjugation provides sufficient intramolecular electronic communication without immoderate conjugated extension. This feature makes it “ideal” for selectively adjusting optoelectronic properties. As evidenced by 4ArDPDPO2A, besides preserved blue emissions, the employment of homoconjugated DPDPO2A groups uniformly delocalizes FMOs for simultaneous ICT and $\langle \psi_f^2|\psi_s^2 \rangle$ enhancement, giving rise to their dramatically increased $k_{\text{RISC}}$ and $k_F^2$ by 4–6 times. The comprehensively optimized TADF transitions endow 4BCzDPDPO2A with $\phi_{\text{PF}}$ and $\eta_{\text{EQE}}$ reaching 81 and 23.7%. This work not only develops a new kind of blue TADF emitter, but also indicates the significance of conjugation optimization for D–A systems, which would accelerate their realistic applications in diverse optoelectronic devices.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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