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Introduction

Organic light-emitting diode (OLED) technology is becoming increasingly attractive due to its great potential for ultra-high definition (UHD) displays.¹⁻⁵ As a key factor in the performance of OLED devices, external quantum efficiency (η_{EQE}) is described as the ratio between the number of emitted photons and number of injected carriers. In most cases, the η_{EQE} of OLED devices can be expressed as the product of several contributing terms:^{6,7}

$$\eta_{\rm EQE} = \gamma \times \eta_{\rm EUE} \times \Phi_{\rm F} \times \eta_{\rm out} \tag{1}$$

where the carrier balance factor (γ) and output coupling factor (η_{out}) are associated with the device design and fabrication, respectively, while exciton utilization efficiency (η_{EUE}) and fluorescent quantum yield ($\Phi_{\rm F}$) are regarded as intrinsic properties of the emitters and are associated with corresponding excited-state processes. Spin statistics show that the

Ultrafast photophysics of an orange-red thermally activated delayed fluorescence emitter: the role of external structural restraint[†]

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The application of thermally activated delay fluorescence (TADF) emitters in the orange-red regime usually suffers from the fast non-radiative decay of emissive singlet states (k_{NR}^{S}), leading to low emitting efficiency in corresponding organic light-emitting diode (OLED) devices. Although k_{NR}^{S} has been quantitatively described by energy gap law, how ultrafast molecular motions are associated with the k_{NR}^{S} of TADF emitters remains largely unknown, which limits the development of new strategies for improving the emitting efficiency of corresponding OLED devices. In this work, we employed two commercial TADF emitters (**TDBA-Ac** and **PzTDBA**) as a model system and attempted to clarify the relationship between ultrafast excited-state structural relaxation (ES-SR) and k_{NR}^{S} . Spectroscopic and theoretical investigations indicated that S_1/S_0 ES-SR is directly associated with promoting vibrational modes, which are considerably involved in electronic–vibrational coupling through the Huang–Rhys factor, while k_{NR}^{S} is largely affected by the reorganization energy of the promoting modes. By restraining S_1/S_0 ES-SR in doping films, the k_{NR}^{S} of TADF emitters can be greatly reduced, resulting in high emitting efficiency. Therefore, by establishing the connection among S_1/S_0 ES-SR, promoting modes and k_{NR}^{S} of TADF emitters, our work clarified the key role of external structural restraint for achieving high emitting efficiency in TADF-based OLED devices.

recombination of injected electrons and holes leads to 25% singlet and 75% triplet states in OLED emitting layers, respectively,^{8,9} while $\eta_{\rm EUE}$ gives the fraction of excited states that can decay to the ground state radiatively. Since $T_1 \rightarrow S_0$ decay is spin-forbidden, $\eta_{\rm EUE}$ is largely determined by the quantum yield ($\Phi_{\rm RISC}$) of the reverse intersystem crossing (RISC, $T_1 \rightarrow S_0$, with rate constant of $k_{\rm RISC}$), which competes with other T_1 relaxation routes (radiative $k_{\rm R}^{\rm T}$ and non-radiative $k_{\rm NR}^{\rm T}$, Fig. S1†):^{10,11}

$$\eta_{\rm EUE} \propto \Phi_{\rm RISC} = \frac{k_{\rm RISC}}{k_{\rm RISC} + k_{\rm R}^{\rm T} + k_{\rm NR}^{\rm T}}$$
(2)

Enormous efforts have been made towards designing thermally activated delayed fluorescence (TADF) emitters with minimized singlet-triplet energy gap ($\Delta E_{\rm ST}$) and enhanced spin-orbit coupling (SOC) to enable thermal conversion of T₁ \rightarrow S₁, which can potentially push $\eta_{\rm EUE}$ to ~100%.¹²⁻¹⁵ Since the $k_{\rm RISC}$ of TADF emitters is usually on a time scale of 10³-10⁵ s⁻¹, $\eta_{\rm EUE}$ is generally associated with slow dynamics of TADF emitters, which has been intensively investigated.^{14,16-18}

In addition to the efficient utilization of current-generated triplet states, the $\Phi_{\rm F}$ of TADF emitters greatly affects the $\eta_{\rm EQE}$ of the corresponding OLED devices, which describes the ratio of singlet (S₁) states that can be radiatively relaxed to the S₀ state, *i.e.*, competing plausible relaxation channels for the S₁ state (Fig. S1[†]):¹⁹⁻²¹

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$$\Phi_{\rm F} = \frac{k_{\rm R}^{\rm S}}{k_{\rm P}^{\rm S} + k_{\rm NP}^{\rm S} + k_{\rm ISC}} \tag{3}$$

In addition, $\Phi_{\rm F}$ includes a contribution from the S₁ state directly generated by injected carriers ($\Phi_{\rm PF}$, prompt fluorescence) and converted from the T₁ state ($\Phi_{\rm DF}$, delayed fluorescence):

$$\Phi_{\rm F} = \Phi_{\rm PF} + \Phi_{\rm DF} \tag{4}$$

For organic TADF emitters, $k_{\rm ISC}$ is usually slow $(10^7-10^8 \text{ s}^{-1})$,^{16,22} for which the presence of rapid non-radiative decay is a key factor that can significantly reduce the $\Phi_{\rm F}$ of TADF emitters. In a weak coupling regime, the rate constant of the S₁ state non-radiative decay $(k_{\rm NR}^{\rm S})$ with energy gap $(\Delta E_{\rm S_1-S_0})$ and electronic coupling (*C*) can be described as²³⁻²⁵

$$k_{\rm NR}^{\rm S} = \frac{C^2 \sqrt{2\pi}}{\hbar \sqrt{\hbar \omega_{\rm M} \Delta E_{\rm S_1 - S_0}}} \exp\left\{-\frac{\Delta E_{\rm S_1 - S_0}}{\hbar \omega_{\rm M}} \left[\ln\left(\frac{\Delta E_{\rm S_1 - S_0}}{l \lambda_{\rm M}}\right) - 1\right]\right\}$$
(5)

where $\omega_{\rm M}$ and $\lambda_{\rm M}$ represent the frequency and reorganization energy contribution of the promoting vibrational mode, while *l* is the number of involved vibrational modes. By assuming *l* = 1, eqn (5) can be simplified to the famous energy gap law with the molecule-specific parameter γ as^{21,25-27}

$$k_{\rm NR}^{\rm S} \propto \exp\left(-\frac{\gamma \Delta E_{\rm S_1-S_0}}{\hbar \omega_{\rm M}}\right)$$
 (6)

which indicates that $k_{\rm NR}^{\rm S}$ increases exponentially with the reduction of the $S_1 \rightarrow S_0$ energy gap ($\Delta E_{\rm S_1-S_0}$), leading to challenges in the design of long-wavelength TADF emitters with high $\Phi_{\rm F}$.²⁸⁻³¹ As a result, reported TADF emitters in the blue to green regime largely exhibit considerably high $\Phi_{\rm F}$,³²⁻³⁴ while the $\eta_{\rm EQE}$ of the corresponding OLED devices are primarily affected by RISC. In contrast, the small $\Delta E_{\rm S_1-S_0}$ of orange–red TADF emitters leads to fast $k_{\rm NR}^{\rm S}$ competing with the radiative decay of the S₁ state, resulting in a low $\Phi_{\rm F}$ and subsequently an unsatisfactory $\eta_{\rm EQE}$ for OLED devices, although up to 100% $\eta_{\rm EUE}$ can be expected *via* efficient RISC.^{19,28,35-37}

Recently, enormous efforts have been made towards developing long-wavelength TADF-based OLED devices with a high $\eta_{\rm EOE_1}^{28,35}$ in which the low $\Phi_{\rm F}$ of TADF emitters is usually regarded as the main obstacle.28,38-40 Therefore, one can expect opportunities to further improve the η_{EQE} of TADF-based longwavelength OLED devices by somehow effectively slowing down the $k_{\rm NR}^{\rm S}$ rate.⁴¹⁻⁴⁴ Recently, Kwon and co-workers reported an acceptor-donor-acceptor (ADA) type TADF emitter (PzTDBA, Scheme 1) and realized >30% of the η_{EQE} of orange-red OLED devices.45 Although the excited-state mechanism that is responsible for the high η_{EOE} is still ambiguous, the reported ~100% $\Phi_{\rm F}$ of **PzTDBA** in doping films indicates that nonradiative decay of the S₁ state is nearly terminated, which seems to violate the well-known energy gap law (eqn (6)). Therefore, understanding the underlying ultrafast photophysics that is associated with the slow k_{NR}^{S} of **PzTDBA** might provide inspiration for designing high-performance TADF emitters in the long-wavelength regime.



Scheme 1 Illustrated chemical structure of investigated TADF emitters: (a) TDBA-Ac, D-A type; (b) PzTDBA, A-D-A type. The charge donors and acceptors are displayed in blue and red, respectively.

In this work, the ultrafast photophysics of an orange-red TADF emitter (PzTDBA, ADA-type) and its DA-type analogue (TDBA-Ac, deep-blue) was investigated using femtosecond transient absorption (fs-TA), time-resolved fluorescence (tr-FL) and theoretical vibrational analysis.46 Compared with the onestep D-A twisting of the TDBA-Ac emitter, PzTDBA exhibits two-step S₀/S₁ excited-state structural relaxation (ES-SR), *i.e.* fast D-A twisting and slow planarization of the Pz group. The promoting vibrational modes associated with the S₀/S₁ ES-SR motions of the TDBA-Ac and PzTDBA emitters were theoretically identified, which dominate the electronic-vibrational coupling (EVC) of the S_1 state. Meanwhile, promoting modes contribute to fast k_{NR}^{S} through the corresponding reorganization energy contribution (λ_M). In doping films, the S₀/S₁ ES-SR motions of PzTDBA are suppressed by external structural restraint, which greatly slows down $k_{\rm NR}^{\rm S}$ and leads to ~100% $\Phi_{\rm F}$. Our work established the connection among the S₀/S₁ ES-SR, promoting modes and S1 state non-radiative decay and indicated the key role of medium rigidity in improving the emitting efficiency of TADF emitters, which should provide inspiration for the future development of TADF emitters.

Results and discussion

Low-lying excited states and steady state spectra

Fundamental photophysics of **TDBA-Ac** and **PzTDBA** emitters were first investigated in solvents with different polarities (Table S1[†]). In OLED devices, TADF emitters are usually doped in a wide-bandgap organic semiconductor as the host. To avoid multi-photon excitation of the host in fs-TA experiments, we prepared doping films (2 wt%) of TADF emitters by employing polystyrene (PS) as the host, and the polarity of the PS medium ($\varepsilon = 2.6-2.7$, $\Delta f = 0.03$) was determined to be comparable with toluene (Fig. S2[†]).^{47,48} The UV/Vis absorption and fluorescence spectra of the **TDBA-Ac** and **PzTDBA** emitters in various solutions and films (2 wt%) can be seen in Fig. 1 and S3.[†] The TD-DFT (M06-2X/6-311G^{**}, PCM = toluene) calculated vertical lowlying singlet and triplet states (S₁–S₃, T₁–T₃) are listed in Table S2[†] with the visualized distribution of frontier orbitals (HOMO-2 to LUMO+2) shown in Table S3.[†] The lowest-lying S₁



Fig. 1 The steady UV/vis absorption and fluorescence spectra of TDBA-Ac (a) and PzTDBA (b) in various solutions and PS doping films. Measured total fluorescence quantum yield ($\Phi_{\rm F}$), corresponding prompt ($\Phi_{\rm PF}$) and delayed ($\Phi_{\rm DF}$) contribution, as well as the related contribution of the delayed component ($\Phi_{\rm DF}/\Phi_{\rm F}$) of TDBA-Ac (c) and PzTDBA (d).

states of **TDBA-Ac** and **PzTDBA** are dominated by the H \rightarrow L transition, corresponding to the charge transfer state (noted as $^{1}CT_{DA}$) with low oscillator strength, which can be seen as weak absorption of **TDBA-Ac** (400–450 nm) and **PzTDBA** (420–540 nm). Upon UV excitation, solvatochromism was observed for **TDBA-Ac** and **PzTDBA**, indicating that the fluorescence emission originated from the lowest-lying $^{1}CT_{DA}$ state.^{49,50} Intriguingly, ~1000 cm⁻¹ (**TDBA-Ac**) and ~1400 cm⁻¹ (**PzTDBA**) blueshifted emissions were observed in PS doping films compared to in toluene (comparable polarity), indicating the presence of multifaceted interactions, which are discussed below.

The T_1 state of **TDBA-Ac** was identified as a local excited state on the acceptor (noted as ${}^{3}LE_A$) while the T_1 excitation of **PzTDBA** was localized on the donor (${}^{3}LE_D$), which allows direct $T_1 \rightarrow S_1$ RISC (${}^{3}LE_{D/A} \rightarrow {}^{1}CT_{DA}$).^{51,52} Meanwhile, the T_2 states of **TDBA-Ac** and **PzTDBA** were recognized as charge transfer states (${}^{3}CT_{DA}$). With identical orbital wavefunction to the ${}^{1}CT_{DA}$ state, the corresponding $T_2 \rightarrow S_1$ RISC (${}^{3}CT_{DA} \rightarrow {}^{1}CT_{DA}$) is forbidden.^{51,52} By further confirming the CT/LE nature of lowlying singlet/triplet states through natural transition orbital (NTO) analysis (Fig. S4 and S5†) and hole–electron analysis (Table S4†),^{53,54} the $T_1 \rightarrow S_1$ (${}^{3}LE_{D/A} \rightarrow {}^{1}CT_{DA}$) transition was assigned as the accessible RISC channel that is responsible for the delayed fluorescence of **TDBA-Ac** and **PzTDBA**.

The thermally accessible $\Delta E_{\rm ST}$ is critical for RISC, while estimating $\Delta E_{\rm ST}$ through the vertical excitation energy of S₁ and T₁ states was reported to be unreliable.⁵⁵ Thus, we further optimized the S₁ and T₁ geometry of the **TDBA-Ac** and **PzTDBA** emitters to estimate adiabatic $\Delta E_{\rm ST}^*$. As listed in Table 1, **TDBA-Ac** and **PzTDBA** exhibit $\Delta E_{\rm ST}^*$ of ~0.3 eV and ~0.26 eV in lowpolarity media (CHX and TOL, $\Delta f < 0.02$), respectively, facilitating RISC for harvesting T₁ states with moderate $\langle S_1 | \hat{H}_{SO} | T_1 \rangle$. However, increasing to medium polarity (in DCM, $\Delta f = 0.22$) leads to enlarged ΔE_{ST}^* (>0.33 eV) for **TDBA-Ac** and **PzTDBA** with nearly unchanged $\langle T_1 | \hat{H}_{SO} | S_1 \rangle$, which might explain the reduced RISC rate (k_{RISC}). Note that the vertical (ΔE_{ST}) and adiabatic (ΔE_{ST}^*) singlet-triplet energy gap does not have a certain magnitude relationship as it depends on multiple factors, such as the different ES-SR in the S₁/T₁ states and steepness of the corresponding potential energy surface (PES), which are simplified as schematic diagrams (Fig. S6†). The total Φ_F and corresponding prompt/delayed (Φ_{PF}/Φ_{DF}) contribution of **TDBA-Ac** and **PzTDBA** were further measured in different solutions

Table 1 TDDFT calculated vertical (*E*) and adiabatic (*E**) excitation energy of the lowest-lying (S₁, T₁) states and corresponding energy gaps (ΔE_{ST} , ΔE_{ST}^*) of TDBA-Ac and PzTDBA in different mediums using PCM as the model; SOC matrix elements for ISC ($\langle S_1 | \hat{H}_{SO} | S_1 \rangle$) and RISC ($\langle T_1 | \hat{H}_{SO} | S_1 \rangle$) were calculated by using the linear response approach

	TDBA-Ac			PzTDBA		
	CHX	TOL	DCM	CHX	TOL	DCM
$E(S_1)/eV$	3.617	3.626	3.667	3.130	3.142	3.207
$E(T_1)/eV$	3.250	3.251	3.252	3.015	3.014	3.010
$\Delta E_{\rm ST}/{\rm eV}$	0.367	0.375	0.415	0.115	0.128	0.197
$E^*(S_1)/eV$	3.474	3.482	3.509	2.792	2.804	2.861
$E^{*}(T_{1})/eV$	3.173	3.173	3.174	2.539	2.538	2.531
$\Delta E_{\rm ST}^*/{\rm eV}$	0.301	0.309	0.335	0.253	0.266	0.330
$\langle S_1 \hat{H}_{SO} T_1 \rangle / cm^{-1}$	0.338	0.339	0.294	0.016	0.018	0.058
$\langle T_1 \hat{H}_{SO} S_1 \rangle / cm^{-1}$	0.341	0.341	0.341	0.053	0.052	0.058

and PS doping films. As illustrated in Fig. 1c, TDBA-Ac exhibits nearly solvent-independent $\Phi_{\rm F}$ (30–50%). With increasing solvent polarity, the solvation of the ¹CT_{DA} (S₁) state and unchanged energy level of the ${}^{3}LE_{A}(T_{1})$ state resulted in reduced $\Delta E_{\rm ST}$, ^{50,56} which is consistent with the observed increasing of the $\Phi_{\rm DF}$ contribution ($\Phi_{\rm DF}/\Phi_{\rm F}$, Fig. 1c). Upon optical excitation, S₁ \rightarrow T₁ \rightarrow S₁ is the only feasible channel for delayed fluorescence, \$^{17,38,57}\$ and increased $\Phi_{
m DF}/\Phi_{
m F}$ might correspond to higher $\Phi_{\rm ISC}$ and $\Phi_{\rm RISC}$. In contrast, the $\Phi_{\rm F}$ of **PzTDBA** rapidly decreased from 37% in non-polar CHX to undetectably low in polar mediums, which implies different relaxation of the photogenerated S₁ state. Intriguingly, TDBA-Ac and PzTDBA exhibit nearly 100% $\Phi_{\rm F}$ and an evenly divided contribution of $\Phi_{\rm PF}$ and $\Phi_{\rm DF} \left(\Phi_{\rm DF} / \Phi_{\rm F} \approx 50\% \right)$ in PS doping films, indicating that the S₁ state decay is dominantly radiative, while all ISC-generated T₁ states can be harvested through subsequent RISC. Considering the importance of $\Phi_{\rm F}$, resolving the photophysics behind the fully radiative relaxation of orange-red PzTDBA in doping film would be of high interest.

tr-FL and excited-state relaxation

The time-resolved fluorescence (tr-FL) measurements of **TDBA Ac** and **PzTDBA** were further performed by time-correlated single-photon counting (TCSPC) upon excitation at $\lambda_{ex} =$ 400 nm.

The resulting traces were fitted as the sum of prompt ($\tau_{\rm PF}$) and delayed ($\tau_{\rm DF}$) components (Fig. S7, S8[†] and Table 2). Combining with measured $\Phi_{\rm PF}$ and $\Phi_{\rm DF}$, the rate constants for ISC (S₁ \rightarrow T₁, $k_{\rm ISC}$) and RISC (T₁ \rightarrow S₁, $k_{\rm RISC}$) as well as corresponding $\Phi_{\rm ISC}$ and $\Phi_{\rm RISC}$ were estimated (Table 2). With calculated SOC matrix elements ($\langle S_1 | \hat{H}_{\rm SO} | T_1 \rangle$ and $\langle T_1 | \hat{H}_{\rm SO} | S_1 \rangle$), we attempted to reproduce the experimentally extracted values of $k_{\rm ISC}$ and $k_{\rm RISC}$ using the thermal vibration correlation function (TVCF)^{16,54,58} and semi-classical Marcus^{59,60} approaches. However, as shown in Table S5,[†] TVCF and Marcus approaches failed to describe $k_{\rm ISC}$ and $k_{\rm RISC}$, which might be attributed to the ignorance of non-Condon effects, such as Herzberg–Teller coupling and spin–vibronic coupling.^{61–63} Meanwhile, we noticed that calculation errors for the $k_{\rm ISC}$ of **PzTDBA** are much more significant than for **TDBA-Ac**, which might imply higher structural flexibility of **PzTDBA** and will be discussed in detail below. By further estimating the experimental values of $k_{\rm R}^{\rm S}$, $k_{\rm NR}^{\rm S}$ and $k_{\rm NR}^{\rm T}$ (Table 2), the quantitative contribution of the plausible relaxation channels was calculated for the S₁ and T₁ states.

As visualized in Fig. 2, the S_1 relaxation of **TDBA-Ac** is dominated by the slightly increased ISC with increased solvent polarity, while the ISC-generated T_1 states can be converted to S_1 with nearly identical Φ_{RISC} , which leads to the nearly unchanged Φ_F of **TDBA-Ac** in CHX (0.53), TOL (0.49) and DCM (0.47). In contrast, although ISC still dominates the S_1 decay of **PZTDBA** in CHX and TOL, the generated T_1 states largely decay nonradiatively to S_0 rather than thermally converting to S_1 *via* RISC, for which a low Φ_F was observed in CHX (0.37) and TOL (0.13). In high-polarity DCM, the S_1 decay of **PZTDBA** is predominately occupied by the non-radiative path to S_0 , leading to an undetectable Φ_F (<0.01), which might be attributed to the exponentially increased k_{NR}^S described by band-gap law with the reducing of the $S_1 \rightarrow S_0$ energy gap ($\Delta E_{S_1-S_n}$).

Intriguingly, **TDBA-Ac** and **PzTDBA** exhibit nearly identical pattern of S₁ and T₁ decay in PS doping films, which is largely differed with observation in solutions. The S₁ decay of **TDBA-Ac** and **PzTDBA** in PS doping films are dominated by equally divided radiative decay (S₁ \rightarrow S₀) and ISC (S₁ \rightarrow T₁), while ISCgenerated T₁ states can be further converted to S₁ through efficient RISC ($\Phi_{RISC} > 0.9$). Due to negligible role of nonradiative path in both S₁ (<5%) and T₁ (<10%) state decay, **TDBA-Ac** and **PzTDBA** exhibit unexpectedly high Φ_{F} in PS doping films, which agrees with the reported high η_{EQE} of corresponding OLED devices.^{45,46} However, such high Φ_{F} (0.95) of

Table 2 Measured photophysical data for the TDBA-Ac and PzTDBA emitters in N2-saturated solutions and PS doping films

	TDBA-Ac				PzTDBA			
	^a CHX	^a TOL	^a DCM	^b PS	^a CHX	^a TOL	^a DCM	^b PS
$\tau_{\rm PF}/\rm ns$	6.72	21.35	36.15	14.12	8.70	23.95	13.62	38.25
$\tau_{\rm DF}/\mu s$	0.15	0.14	0.48	1.21	0.10	0.29	0.23	1.10
$\Phi_{\rm F}$	0.53	0.49	0.47	0.90	0.37	0.13	< 0.01	0.95
$\Phi_{ m PF}$	0.23	0.16	0.11	0.44	0.03	0.03	< 0.01	0.50
$\Phi_{ m DF}$	0.30	0.33	0.36	0.46	0.34	0.10	0	0.45
$f_{\Phi_{\rm ISC}}$	0.57	0.67	0.78	0.51	0.93	0.78	0	0.47
${}^{g}\Phi_{\mathrm{RISC}}$	0.39	0.39	0.43	0.82	0.35	0.10	0	0.90
$k_{\rm PF}/10^7 {\rm s}^{-1}$	14.88	4.69	2.77	7.14	11.49	4.17	7.35	2.63
$dk_{\rm R}^{\rm S}/10^6 {\rm s}^{-1}$	33.48	7.70	3.05	31.43	3.10	1.13	_	13.16
$k_{\rm NR}^{\rm S}/10^6 {\rm s}^{-1}$	30.29	7.82	3.16	3.49	5.28	8.02	73.46	0.69
$^{d}k_{\rm ISC}/10^{7} {\rm s}^{-1}$	8.50	3.14	2.15	3.65	10.66	3.25	_	1.25
$k_{\rm DF}/10^6 {\rm s}^{-1}$	3.57	3.54	1.01	0.74	3.63	0.43	_	0.86
$^{d}k_{\rm RISC}/10^{5}~{\rm s}^{-1}$	18.75	17.57	4.98	6.69	13.42	0.52	_	8.20
$dk_{\rm NR}^{\rm T}/10^5 {\rm s}^{-1}$	31.50	32.55	9.60	4.49	35.91	4.24	_	4.53

^{*a*} Concentration of 10⁻⁵ M. ^{*b*} Doping concentration of 2 wt%. ^{*c*} Calculated by $k_{\rm PF} = 1/\tau_{\rm PF}$ and $k_{\rm DF} = 1/\tau_{\rm DF}$. ^{*d*} Rate constants $k_{\rm R}^{\rm S}$, $k_{\rm ISC}$, $k_{\rm RISC}$ and $k_{\rm NR}^{\rm T}$ were calculated using the method described by Adachi *et al.*^{10,19} ^{*e*} Calculated using $k_{\rm NR}^{\rm S} = k_{\rm PF} - k_{\rm R}^{\rm S} - k_{\rm ISC}$. ^{*f*} Calculated using $\Phi_{\rm ISC} = k_{\rm ISC}/(k_{\rm ISC} + k_{\rm R}^{\rm S} + k_{\rm NR}^{\rm S})$. ^{*g*} Calculated using $\Phi_{\rm RISC} = \Phi_{\rm DF}/(1 - \Phi_{\rm PF})$.



Fig. 2 Visualized contribution of ISC ($S_1 \rightarrow T_1$), radiative (R, $S_1 \rightarrow S_0$) and non-radiative (NR, $S_1 \rightarrow S_0$) decay of S_1 state for TDBA-Ac (a) and PzTDBA (b) in various solutions and PS doping films. Contribution of RISC ($T_1 \rightarrow S_1$) and non-radiative (NR, $T_1 \rightarrow S_0$) decay of T_1 state for TDBA-Ac (c) and PzTDBA (d) in various solutions and PS doping films, radiative decay of T_1 state was ignored due to low contribution.

PzTDBA observed in PS doping film seems to be inconsistent with the energy gap law, implying unique photophysics by which non-radiative decay of S_1 state can be greatly suppressed.

fs-TA and structural relaxation

The fs-TA signal upon UV excitation ($\lambda_{ex} = 320 \text{ nm}$) of **TDBA-Ac** and **PzTDBA** in CHX solution and PS doping film were recorded by broadband probe ($\lambda_{probe} = 350-750 \text{ nm}$) with delay times up to 7.0 ns, and the temporal resolution of fs-TA was measured to be ~90 fs. As shown in Fig. S9 and S10,† the measured fs-TA signals of **TDBA-Ac** and **PzTDBA** are contributed by negative ground-state bleaching (GSB) in the $\lambda_{probe} = 350-400 \text{ nm}$ regime, and the positive excited-state absorption (ESA) band extended in the longer wavelength region up to $\lambda_{probe} = 750 \text{ nm}$.

Upon UV excitation, high-lying S_n states can be populated, followed by rapid internal conversion (IC, $S_n \rightarrow S_1$) to the longlived S_1 state, which explains the dramatically reshaped ESA in the 1 ps delay time.^{64,65} For the subsequent delay times of 1 ps to 1 ns, fs-TA evolution visualizes wavepacket motion that highly depends on the topology of S_1 PES.^{41,66-68} For instance, the role of the excited-state structural relaxation (ES-SR) in the S_1 state decay of DA- and DAD/ADA-type TADF emitters has been intensively reported.⁶⁹⁻⁷³ Suffering from the poor structural sensitivity of UV/Vis fs-TA, S_1/S_0 ES-SR usually leads to minimized alternation of the ESA shape, which is consistent with the observed fs-TA of **TDBA-Ac** and **PzTDBA** for 1 ps to 1 ns delay times.^{41,74}

For characterizing S_1/S_0 ES-SR, the geometries of **TDBA-Ac** and **PzTDBA** in the S_0 , S_1 and T_1 states were optimized using DFT and TD-DFT approaches. The resulting structures are

illustrated in Table S6,† while total reorganization energies $(\lambda_{S_0 \to S_1} \text{ and } \lambda_{S_1 \to S_0})$ were calculated for evaluating the ES-SR of the TDBA-Ac and PzTDBA emitters together with the root of the mean squared displacement (RMSD_{S_1/S_0}) between the S₀ and S₁ states (Fig. S11[†]). As listed in Table 3, the calculated values of $\lambda_{S_n \to S_n}$, $\lambda_{S_n \to S_n}$ and RMSD_{S1/Sn} indicate a more pronounced ES-ER of PzTDBA in the S1 state than TDBA-Ac, which obviously cannot be attributed to structural extension (DA to ADA structure) as the total reorganization energy and RMSD are not additive. To evaluate the contribution of each of the molecular fragments of the TDBA-Ac and PzTDBA emitters to the ES-SR, several critical structural parameters were defined, as illustrated in Fig. S12[†] and measured (Table 3) for the S_0 and S_1 states. Upon vertical excitation, TDBA-Ac and PzTDBA initially remain in So geometry in the Franck-Condon (FC) region, following by ES-SR until reaching the global minimum of S1 PES, i.e. optimized S1 geometry. For TDBA-Ac, S1/S0 ES-SR featured a slight increase in the D-A twisting angle β from 89.82° (S^{FC}₁) to 92.00° (S^T₁), while the dihedral angles of the Ac (α) and TDBA (γ) framework bending remained nearly unchanged in the S₁ state decay. In contrast, ADA-type PzTDBA exhibits higher flexibility than that of TDBA-Ac. In addition to the fast motion of the D-A twisting (S_1^{FC}) angle (β) from 79.72°/79.06° to 89.02°/91.43° (S_1^T) , framework planarization of the center donor (Pz) was observed as the dihedral angle (α) increased from 164.57° (S_1^T) to 180.00° (S_1^{TP}). The simultaneous S_0 - S_1 state changing of α and β angles may correspond to a two-step S₁/S₀ ES-SR (S₁^{FC} \rightarrow S₁^T \rightarrow S_1^{TP}), which has been widely reported,^{75,76} *i.e.* fast D–A twisting $(S_1^{FC} \rightarrow S_1^T)$ followed by slow framework planarization $(S_1^T \rightarrow S_1^T)$ S_1^{TP}). Target analysis was further performed to acquire

Table 3 DFT and TD-DFT (M06-2X, 6-311G**, PCM = toluene) calculated optimal geometric parameters of TDBA-Ac and PzTDBA in the S ₀	, S ₁
and T_1 states, as well as the calculated total reorganization energy and RMSD associated with the S_1 state ES-SR ^a	

	TDBA-Ac			PzTDBA			
	*α (°)	**β (°)	***γ (°)	*α (°)	**β ₁ /β ₂ (°)	*** \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	
S ₀ geometry	176.50	89.82	11.36	164.57	79.72/79.06	11.56/10.99	
S_1 geometry	175.45	92.00	12.12	180.00	89.02/91.43	11.65/11.37	
T_1 geometry	176.57	90.82	4.77	180.00	88.60/91.33	11.40/11.40	
$\lambda_{S_n \to S_n}$ (cm ⁻¹)	1161			2790			
$\lambda_{S_1 \rightarrow S_0} (cm^{-1})$	1273			2552			
$RMSD_{S_{*}/S_{*}}(Å)$	0.053			0.241			

^{*a*} *Bending dihedral angle of donor (Ac/Pz); **donor-acceptor twisting angle; ***bending dihedral angle of acceptor (TDBA).

quantitative information on S_1/S_0 ES-SR that may play a key role in the S_1 state relaxation. By including three or four sequential decay processes, measured fs-TA data can be well-reproduced by the displayed decay-associated spectra (DAS) of each decay components and concentration evolution of each transient species (Fig. 3), while species-associated spectra (SAS) can be seen in Fig. S13 and S14.[†] The initial decay $(A \rightarrow B)$ with 300–400 fs time constant was accompanied by considerable ESA reshaping, corresponding to rapid IC $(S_n \rightarrow S_1)$. The fs-TA was subsequently dominated by S_1/S_0 ES-SR until the wavepacket reached the global minimum of S_1 PES. For **PzTDBA**, highlighted two-step S_1/S_0 ES-SR $(B \rightarrow C \rightarrow D,$ *i.e.* $S_1^{FC} \rightarrow S_1^T \rightarrow S_1^{TP})$ predicted by calculated S_0 and S_1 geometries was observed, featuring a slight ESA reshaping. The



Fig. 3 The decay-associated spectra (DAS) extracted from the fs-TA data of TDBA-Ac in CHX solution (a) and PS doping film (b) as well as PzTDBA in CHX solution (c) and PS doping film (d). Fitted concentration evolution of TDBA-Ac (e) and PzTDBA (g) in CHX solution (dashed lines) and PS doping film (solid lines). Promoting vibrational modes of TDBA-Ac (f) and PzTDBA (h) with large contribution to the HR factors. Calculated HR factors and reorganization energy contribution of each vibrational mode of TDBA-Ac (i) and PzTDBA (j) for the $S_1 \rightarrow S_0$ transition in CHX solution. The dominant modes displayed in (f) and (h) are highlighted correspondingly.

observed fast (4.8 ps in CHX, $S_1^{FC} \rightarrow S_1^{T}$) and slow (334 ps in CHX, $S_1^{T} \rightarrow S_1^{TP}$) steps correspond to D–A twisting (β_1/β_2 angles) and Pz planarization (α angle), respectively.

For **TDBA-Ac**, one-step S_1/S_0 ES-SR was observed (7.2 ps, $S_1^{FC} \rightarrow S_1^T$) in the PS doping film, corresponding to the D–A twisting (β angle), which is comparable with the fast S_1/S_0 ES-SR step of **PzTDBA**. However, S_1/S_0 ES-SR of **TDBA-Ac** was unobservable in CHX, which might be attributed to a less pronounced $S_0 \rightarrow S_1$ structural change than for **PzTDBA**, *i.e.* nearly unchanged β angle in the S_0 (89.82°) and S_1 (92.00°) states.

Intriguingly, the extracted time constants of D–A twisting $(S_1^{FC} \rightarrow S_1^T, 14.0 \text{ ps})$ and Pz planarization $(S_1^T \rightarrow S_1^{TP}, 636 \text{ ps})$ of **PzTDBA** in the PS doping film are 2–3 times slower than corresponding S_1/S_0 ES-SR steps in CHX (Fig. 3g and S15†), implying a higher potential barrier for S_1 PES, which is consistent with our fs-TA observations for multiple-resonance emitters.⁷⁷ Moreover, slow S_1 isomerization of azo-benzene embedded in polymer films was reported previously, attributing to external structural restraint from polymer micronetworks.⁷⁸

As discussed above, the fluorescence emission of **PzTDBA** was strongly quenched ($\Phi_{\rm F} = 0.37$ in CHX) in solutions due to the presence of fast non-radiative decay, while a high $\Phi_{\rm F}$ (>0.95) in the PS doping film may be feasible if non-radiative $S_1 \rightarrow S_0$ decay can be greatly suppressed. Our fs-TA data revealed higher S_1/S_0 ES-SR barriers of **PzTDBA** in PS doping films than in CHX, which might imply the presence of an underlying association between S_1/S_0 ES-SR and the non-radiative decay of the S_1 state, *i.e.* restrained S_1/S_0 ES-SR leads to suppressed non-radiative decay. Conversely, $k_{\rm NR}^{\rm S}$ was described to be highly correlated with promoting vibrational modes by the energy gap law (eqn (5)).^{21,23} Thus, we attempted to unveil the underlying relationship among the S_1/S_0 ES-SR, promoting modes and non-radiative decay of the S_1 state.

Vibrational analysis and non-radiative decay

The energy gap law (eqn (5)) clearly describes how promoting vibrational modes affect k_{NR}^{S} through their vibrational frequency (ω_{M}) and reorganization energy (λ_{M}), while promoting modes are vibrational modes that are considerably involved in the EVC of the S₁ state through a pronounced Huang-Rhys (HR) factor (S_{k}).^{24,79,80} We further calculated the S_{k} and λ_{k} contribution of each of the vibrational modes involved in the S₁ \rightarrow S₀ transition (Fig. 3i and j), in which the promoting modes associated with the k_{NR}^{S} of **TDBA-Ac** and **PzTDBA** are illustrated in Fig. 3f and h, respectively.

As shown in Fig. 3j and h, three promoting modes were identified for the $S_1 \rightarrow S_0$ transition of **PzTDBA** due to considerable S_k . The modes at 410 cm⁻¹ (ω_M^{DA-1}) and 421 cm⁻¹ ($\omega_M^{DA-2}_M$) correspond to symmetric and asymmetric D–A twisting and exhibit considerable reorganization energy contributions ($\lambda^{DA-1}_M = 174 \text{ cm}^{-1}$ and $\lambda_M^{DA-2} = 350 \text{ cm}^{-1}$), which are associated with the fast S_1/S_0 ES-SR step observed on fs-TA of **PzTDBA**, *i.e.* $S_1^{FC} \rightarrow S_1^T$ with the D–A twisting motion. For **TDBA-Ac** (Fig. 3i and f), the corresponding S_1/S_0 ES-SR of D–A twisting is associated with

promoting modes at $\omega_{\rm M}^{\rm DA-1} = 247 \text{ cm}^{-1}$ and $\omega_{\rm M}^{\rm DA-2} = 387 \text{ cm}^{-1}$ with substantially lower $\lambda_{\rm M}^{\rm DA-1}$ (45.9 cm⁻¹) and $\lambda_{\rm M}^{\rm DA-2}$ (132 cm⁻¹), which is consistent with its rigid structure predicted theoretically, *i.e.* less pronounced S₁/S₀ ES-SR than **PzTDBA**.

Meanwhile, $S_1 \rightarrow S_0$ decay of **PzTDBA** features a promoting mode at $\omega_M^D = 32.8 \text{ cm}^{-1}$ with a surprisingly high HR factor ($S_k = 6.12$) and considerable reorganization energy ($\lambda_M^D = 201.1 \text{ cm}^{-1}$), corresponding to the bending motion of the Pz framework, which is clearly associated with the observed slow S_1/S_0 ES-SR step of **PzTDBA**, *i.e.* $S_1^T \rightarrow S_1^{TP}$. Intriguingly, this particular mode was also observed for **TDBA-Ac** at $\omega_M^D =$ 11.6 cm⁻¹ with a much lower HR factor ($S_k = 0.15$) and a two orders of magnitude lower reorganization energy contribution ($\lambda_M^D = 1.70 \text{ cm}^{-1}$) than that of **PzTDBA**, indicating that it was excluded from the $S_1 \rightarrow S_0$ decay of **TDBA-Ac**. As a result, the second S_1/S_0 ES-SR step ($S_1^T \rightarrow S_1^{TP}$) was absent from the fs-TA signal of **TDBA-Ac**.

Furthermore, we investigated the influence of medium polarity on the promoting modes of the **TDBA-Ac** and **PzTDBA** emitters. As shown in Fig. S16,[†] for **PzTDBA** in DCM solution, an extra promoting mode at 15.4 cm⁻¹ was observed with considerable S_k but ignorable λ_k , which might be less associated with the non-radiative decay of S₁ state **PzTDBA**. In contrast, a promoting mode at 12.4 cm⁻¹ was observed for **TDBA-Ac** with considerable S_k (8.71) and λ_k (108.23 cm⁻¹) in DCM solution, which is very different from the case of **TDBA-Ac** in low-polarity solvents, indicating that the S₁/S₀ ES-SR of **TDBA-Ac** (DA-type) is more evidentially coupled with charge transfer than **PzTDBA** (ADA-type).

As discussed above, the one- (TDBA-Ac, $S_1^{FC} \rightarrow S_1^{T}$) and twostep (**PzTDBA**, $S_1^T \rightarrow S_1^{TP}$) S_1/S_0 ES-SR are directly associated with promoting vibrational modes that are considerably involved in the EVC of the S₁ state through their HR factor. Meanwhile, promoting modes contribute to the k_{NR}^{S} of the S₁ state through corresponding λ_M , which implies that S_1/S_0 ES-SR can significantly affect k_{NR}^{S} (and subsequently Φ_{F}) through the promoting vibrational modes (Fig. 4). For instance, the one-step S₁/S₀ ES-SR of TDBA-Ac is associated with vibrational modes with low S_k and λ_M , while the promoting modes associated with the two-step S_1/S_0 ES-SR of PzTDBA have much higher S_k and $\lambda_{\rm M}$. As a result, the non-radiative channel plays a minor role in the S₁ decay of structurally rigid TDBA-Ac, while the emission of structurally flexible PzTDBA is severely hampered by the fast non-radiative decay of the S1 state. Furthermore, the two-step S_1/S_0 ES-SR motions of PzTDBA are greatly suppressed in the PS doping films due to the external structural restraint, for which the S1 non-radiative decay associated with the promoting modes might be correspondingly weakened, leading to the greatly improved $\Phi_{\rm F}$ of **PzTDBA** in the doping films. In this sense, the external structural restraint for S_1/S_0 ES-SR motions might be critical for achieving a high η_{EQE} for TADF-based OLED devices.

To directly verify the influence of the external structural restraint on the S₁ non-radiative decay of **PzTDBA**, we measured temperature-dependent emission spectra of **PzTDBA** in polyethylene oxide (PEO) doping films (Fig. S18†). With a glass transition temperature (T_{g}) of 220 K, PEO provides a "softer"



Fig. 4 Simplified energetic diagram illustrating two-step ES-SR ($S_1^{FC} \rightarrow S_1^T$ and $S_1^T \rightarrow S_1^{TP}$) of **PzTDBA** in low-polarity solution (orange line, TOL), high-polarity solution (cyan line, DCM) and PS doping film (red line). The double arrows represent the potential barriers of D–A twisting ($S_1^{FC} \rightarrow S_1^T$) and Pz planarization ($S_1^T \rightarrow S_1^{TP}$).

microenvironment than PS ($T_g = 373$ K) and can be further "softened" by increasing the temperature.^{81,82} As a TADF emitter, **PzTDBA** was expected to be more fluorescent at higher temperatures due to faster RISC. However, we observed clear fluorescence quenching with increasing temperature in the 297–347 K range, indicating that non-radiative decay was enhanced in the medium with reduced external structural restraint, which is consistent with our analysis described above.

Note that we cannot perform vibrational analysis for TADF emitters with the presence of the external structural restraint, but we speculate that the λ_M of the promoting modes of **PzTDBA** might be greatly reduced due to the external structural restraint, in agreement with slowed S_1/S_0 ES-SR motions in the doping films, especially the Pz bending mode (ω_M^D) associated with the slow S_1/S_0 ES-SR step ($S_1^T \rightarrow S_1^{TP}$) might be terminated. As a result, S_1^T instead of S_1^{TP} might dominate the emission of **PzTDBA** in the PS doping films (see Fig. 4), which explains the observed blue-shifted emission in the PS doping film compared with the case in toluene solution, which has comparable polarity to the PS medium. Meanwhile, the emission of **PzTDBA** in solutions mainly originates from S_1^{TP} due to the accessible barrier of $S_1^T \rightarrow S_1^{TP}$, which thus suffers from the plague of non-radiative decay (Fig. 4).

Last but not least, in addition to the S_1 state, we noticed that **TDBA-Ac** and **PzTDBA** exhibit a suppressed non-radiative decay channel of the T_1 state in the PS doping films compared to in solutions (Fig. 2c and d), which inspired us to consider the role of T_1/S_0 ES-SR in the non-radiative decay of the T_1 state. As shown in Fig. S17,† **TDBA-Ac** exhibits several vibrational modes with considerable S_k in the region <100 cm⁻¹, but the low λ_M implies that ES-SR may not be strongly associated with non-radiative $T_1 \rightarrow S_0$ decay. In contrast, the promoting modes of

PzTDBA at 32.9 cm⁻¹ and 421/410 cm⁻¹ contribute considerable λ_{M} , while pronounced T_1/S_0 ES-SR was indicated (Table 3), including Pz bending and D-A twisting. Therefore, it might be plausible that the non-radiative $T_1 \rightarrow S_0$ decay is similarly associated with two T_1/S_0 ES-SR motions, because the non-radiative $T_1 \rightarrow S_0$ decay of **PzTDBA** was strongly suppressed in the PS doping film due to the external structural restraint. However, unlike S_1 relaxation, without direct spectroscopic evidence of T_1/S_0 ES-SR in different media, verifying this hypothesis requires further investigation.

Conclusions

To summarize, we performed a comprehensive investigation of the photophysics of two TADF emitters, TDBA-Ac (DA-type, blue light) and PzTDBA (ADA-type, orange-red light), using fs-TA, tr-FL and theoretical approaches. Compared with the one-step $S_1/$ $S_0 \text{ ES-SR} (S_1^{\text{FC}} \rightarrow S_1^{\text{T}})$ of **TDBA-Ac**, the S_1 state decay of **PzTDBA** is dominated by two steps, S_1/S_0 ES-SR ($S_1^{FC} \rightarrow S_1^T \rightarrow S_1^{TP}$), while greatly slowed S₁/S₀ ES-SR motions of PzTDBA were observed in the PS doping films due to the external structural restraints. Vibrational analysis indicated that the S₁/S₀ ES-SR motions are directly associated with the promoting modes that are considerably involved in the EVC of the S_1 state through their own S_k , while the promoting modes contribute to fast k_{NR}^{S} via λ_{M} . In doping films, the external structural restraint leads to suppressed S₁/S₀ ES-SR and reorganization energy contribution of the promoting modes, resulting in slowed k_{NR}^{S} and a highly fluorescent S1 state that is favorable for OLED application. With TDBA-Ac and PzTDBA as model systems, we established the connection among the S_0/S_1 ES-SR, promoting modes and k_{NR}^S of TADF emitters, which indicated the key role of the external

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structural restraint in obtaining high $\Phi_{\rm F}$ TADF emitters. Our work also provides a new direction for OLED design, and it might be necessary to take the rigidity of host materials used for the emitting layer into consideration to avoid emission quenching through fast non-radiative decay associated with the S₁/S₀ ES-SR of TADF emitters, especially for TADF emitters with a relatively small band gap, which might be a useful reference for future OLED application.

Data availability

All experimental and calculational data are available from the corresponding author upon reasonable request.

Author contributions

Yixuan Gao: conceptualization, methodology, investigation, data curation, formal analysis, visualization, and writing – original draft; Yaxin Wang: methodology, data curation, formal analysis, and validation; Zilong Guo: investigation, visualization, project administration, and supervision; Yan Wan: methodology and resources; Zheng Xue and Yandong Han: resources and project administration; Wensheng Yang: supervision, resources, and funding acquisition; Xiaonan Ma: conceptualization, formal analysis, funding acquisition, supervision, and writing – review and editing.

Conflicts of interest

The authors declare no competing financial interest.

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