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# Facilitating intrinsic delayed fluorescence of conjugated emitters by inter-chromophore interaction†

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Delayed fluorescence (DF) is a unique emitting phenomenon of great interest for important applications in organic optoelectronics. In general, DF requires well-separated frontier orbitals, inherently corresponding to charge transfer (CT)-type emitters. However, facilitating intrinsic DF for local excited (LE)-type conjugated emitters remains very challenging. Aiming to overcome this obstacle, we demonstrate a new molecular design strategy with a DF-inactive B,N-multiple resonance (MR) emitter as a model system. Without the necessity of doping with heavy atoms, we synthesized a co-facial dimer in which an excimer-like state ( $S_{exc}$ ) was expected to facilitate efficient reverse intersystem crossing (RISC,  $T_1 \rightarrow S_{exc}$ ) and intrinsic DF. Benefiting from greatly enhanced SOC and reduced  $\Delta E_{ST}$ , the proof-of-concept emitter Np-2CzB exhibited  $k_{RISC}$  up to  $6.5 \times 10^5 \text{ s}^{-1}$  and intrinsic DF with >35% contribution ( $\Phi_{DF}/\Phi_F$ ) in dilute solution. Further investigation indicated that  $S_{exc}$  state formation relies on an optimized co-facial distance ( $d = \sim 4.7 \text{ \AA}$ ), strong inter-chromophore interaction ( $J_{coul} > 450 \text{ cm}^{-1}$ ) and a rigid structure ( $T_{S_1 \rightarrow S_0} < 350 \text{ cm}^{-1}$ ). Although our strategy was demonstrated with a B,N-MR emitter, it can be applicable to many LE-type conjugated emitters without intrinsic DF. By triggering potential DF emission, many classic emitters might play a more important role in optoelectronics.

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## Introduction

The thermally activated delayed fluorescence (TADF) of organic emitters refers to long-lived fluorescent emission occurring with a lifetime similar to phosphorescence, which is usually facilitated by efficient reverse intersystem crossing (RISC) from a populated triplet to a fluorescent singlet state.<sup>1-3</sup> In the area of photophysics, TADF is actually a rather traditional concept. For instance, the unusually strong DF of C<sub>70</sub> was successfully observed under appropriate conditions,<sup>4</sup> while the DF of Cy-5 dye was demonstrated to be feasible with remarkable back isomerization of the T<sub>1</sub> state.<sup>5</sup> Benefitting from the pioneering work of Adachi *et al.*, TADF emitters received intensive attention for application in the development of electroluminescent devices.<sup>6-8</sup>

In devices, the recombination of injected electrons and holes creates 25% singlet and 75% triplet excitons, in which the TADF mechanism is a feasible way of harvesting generated dark triplet excitons.<sup>9,10</sup> For organic light-emitting diode (OLED) devices, efficient triplet harvesting is regarded as a primary factor for achieving qualified external quantum efficiency ( $\eta_{EQE}$ ), which can usually be expressed as a product of several contributing terms:<sup>11,12</sup>

$$\eta_{EQE} = \gamma \times \eta_{EUE} \times \Phi_F \times \eta_{out} \quad (1)$$

in which the exciton utilizing efficiency ( $\eta_{EUE}$ ) is directly determined by the efficient harvesting of triplet excitons. Furthermore, organic emitters featuring TADF emission have been demonstrated to be beneficial for pursuing electrically pumped organic lasers (EPOLs), as efficient RISC can greatly release the accumulation of dark triplet excitons, which are not capable of producing stimulated emission in most cases.<sup>13-16</sup> In addition to application to OLEDs and EPOLs, TADF emission has received attention in the area of bio-imaging.<sup>17-20</sup> By using DF emission, time-gated imaging can inherently eliminate interference from short-lived endogenous fluorescence and scattered light, which is very helpful for improving the accuracy and S/N ratio of imaging on a cellular level.<sup>21,22</sup>

However, for the majority of organic emitters, acquiring TADF emission remains challenging. In order to convert a T<sub>1</sub>

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population to the  $S_1$  state, the RISC transition should be fast enough to compete kinetically with radiative and non-radiative  $T_1 \rightarrow S_0$  decay.<sup>23–26</sup> According to Fermi's golden rule, the RISC rate ( $k_{\text{RISC}}$ ) is related to spin-orbit coupling (SOC) matrix elements and the  $S_1$ - $T_1$  energy gap ( $\Delta E_{\text{ST}}$ ):<sup>2,27,28</sup>

$$k_{\text{RISC}} \propto \left| \frac{\langle \Psi_{T_1} | \hat{H}_{\text{SO}} | \Psi_{S_1} \rangle}{\Delta E_{\text{ST}}} \right|^2 \quad (2)$$

For the charge-transfer (CT)-type emitters, a minimized  $\Delta E_{\text{ST}}$  is induced by well-separated frontier orbitals (FOs) between electron donor and acceptor.<sup>29–31</sup> Meanwhile, the local-excited (LE) nature of the low-lying triplet states leads to greatly different electronic configurations of the initial and final states of the RISC transition.<sup>32–35</sup> As the result, a moderate SOC, *i.e.*  $\langle \Psi_{T_1} | \hat{H}_{\text{SO}} | \Psi_{S_1} \rangle$ , can be guaranteed. Combining the minimized  $\Delta E_{\text{ST}}$  and moderate SOC,  $k_{\text{RISC}}$  of  $10^4$ – $10^6$  s<sup>-1</sup> can be reached for CT-type TADF emitters.<sup>6,36,37</sup> Although CT-type emitters usually exhibit TADF with a several orders of magnitude slower decay rate ( $k_{\text{DF}}$ ,  $10^3$ – $10^5$  s<sup>-1</sup>) than prompt fluorescence ( $k_{\text{PF}}$ ,  $10^7$ – $10^9$  s<sup>-1</sup>), the corresponding  $k_{\text{RISC}}$  can still ensure a maximized  $\eta_{\text{EQE}}$  (up to  $\sim 100\%$ ) in OLED devices.<sup>38–40</sup>

However, for organic emitters with the  $S_1$  state dominated by LE ( $\pi \rightarrow \pi^*$ ) excitation, *i.e.* most conjugated emitters with a rigid polycyclic aromatic framework, an efficient RISC transition is usually inherently blocked. Firstly, the SOC Hamiltonian can be approximately described as:<sup>41,42</sup>

$$\hat{H}_{\text{SO}} \approx \sum_i^{N_e} \zeta(r_i) \hat{\mu}_L \hat{\mu}_S \quad (3)$$

For conjugated aromatic emitters, both  $S_1$  and  $T_1$  states are dominated by identical ( $\pi \rightarrow \pi^*$ ) electronic configurations, leading to a near-zero magnetic moment resulting from orbital angular momentum ( $\mu_L$ ) and subsequent weak SOC.<sup>43–45</sup> Moreover, the LE nature of the  $S_1$  state leads to a considerable overlap integral of the FOs, resulting in a large  $\Delta E_{\text{ST}}$ . Therefore, for most conjugated emitters, intrinsic TADF is difficult to achieve.

For instance, with typical conjugated frameworks, multiple resonance (MR) emitters have received enormous attention since the first report by Hatakeyama *et al.* in 2016.<sup>46–50</sup> As B,N-doped conjugated chromophores, B,N-MR emitters exhibit an LE-type ( $\pi \rightarrow \pi^*$ )  $S_1$  state and low-frequency mode dominated vibronic coupling, leading to a high fluorescence quantum yield ( $\Phi_{\text{F}}$ ) and color purity.<sup>51–54</sup> However, many reported B,N-MR emitters were recognized as TADF-inactive in dilute solution ( $k_{\text{RISC}} = 10^3$ – $10^4$  s<sup>-1</sup>) due to weak SOC and large  $\Delta E_{\text{ST}}$ , leading to a nearly negligible contribution from intrinsic TADF, *i.e.*  $\Phi_{\text{DF}}/\Phi_{\text{F}} < 5\%$ .<sup>46,55,56</sup> Plenty of efforts have been made to overcome the inherent barrier, such as heavy atom (S, Se, *etc.*) doping<sup>57–59</sup> and long-range CT mixing in the  $S_1$  state, by which the  $k_{\text{RISC}}$  of B,N-MR emitters were promoted to  $10^5$ – $10^6$  s<sup>-1</sup>.<sup>60</sup>

On the other hand, it was found that the RISC of many TADF-inactive B,N-MR emitters can be greatly boosted in doped films with a specific host, such as DABNA-1 in mCBP and TBN-TPA in 2,6-DCzppy.<sup>46,61</sup> The underlying mechanism for this intriguing phenomenon was successfully uncovered by Chou and co-workers.<sup>62</sup> In doped films, the  $S_1$  state of B,N-MR emitters can

form an exciplex-like state with the host. As a result, the greatly changed electronic configuration of the emitting state (exciplex) leads to enhanced SOC, while  $\Delta E_{\text{ST}}$  can be accordingly reduced as the exciplex is energetically lower than the  $S_1$  state. The landmark work of Chou *et al.* greatly inspired us to explore a new strategy for facilitating the intrinsic TADF of conjugated emitters. As an analog of the guest-host interaction, the intramolecular excimer-like state facilitated by delicate interchromophore interaction might lead to similarly enhanced SOC and reduced  $\Delta E_{\text{ST}}$ , resulting in greatly boosted  $k_{\text{RISC}}$  without the presence of a specific host, *i.e.* intrinsic TADF. More importantly, as a host is no longer included, this strategy may be useful for many conjugated emitters in addition to specific types of emitters. It is worth noting that the strategy of interchromophore interaction has been employed to improve the  $\eta_{\text{EQE}}$  of small-molecule (first-generation) OLED by the formation of excimer-like states,<sup>63–65</sup> while controllable interchromophore interaction by rational molecular design has recently been used for emission switching that can rapidly respond to external stimuli in aggregated states.<sup>66</sup> However, to the best of our knowledge, intrinsic TADF enabled by interchromophore interaction has rarely been reported.

In this work, we demonstrate a new strategy for facilitating the intrinsic TADF of conjugated emitters by interchromophore interaction. With a TADF-inactive B,N-MR emitter (CzB) as a model system, CzB dimers (BiPh-2CzB and Np-2CzB) with different linkers were synthesized. The fs-TA spectra indicated the formation of an excimer-like state ( $S_1 \rightarrow S_{\text{exc}}$ ,  $\sim 250$  ps) in the  $S_1$  state decay of a proof-of-concept emitter Np-2CzB, leading to efficient RISC ( $T_1 \rightarrow S_{\text{exc}}$ ) with  $k_{\text{RISC}}$  up to  $6.5 \times 10^5$  s<sup>-1</sup> and intrinsic TADF with  $\Phi_{\text{DF}}/\Phi_{\text{F}} > 35\%$  in dilute solution ( $10^{-5}$  M). Further investigation indicated that the  $S_{\text{exc}}$  formation of Np-2CzB is associated with at least three factors: (1) a suitable interchromophore distance ( $d \approx 4.7$  Å); (2) strong electronic coupling for excimer formation ( $J_{\text{coul}} > 450$  cm<sup>-1</sup>); and (3) a rigid co-facial geometry ( $I_{S_1 \rightarrow S_0} < 350$  cm<sup>-1</sup>). The formed  $S_{\text{exc}}$  state leads to a nearly degenerate  $S_{\text{exc}}/T_1$  state ( $\Delta E_{\text{ST}} < 20$  meV) and enhanced SOC due to the very different electronic configurations of the  $S_{\text{exc}}$  state, which all contribute to the intrinsic TADF of the proof-of-concept emitter Np-2CzB. Please note that the strategy described in this work should not be limited to B,N-MR emitters. In terms of the underlying photophysics, it can be generalized to any organic conjugated emitters with an  $S_1$  state dominated by LE ( $\pi \rightarrow \pi^*$ ) excitation.

## Results and discussion

### Molecular design

Here we aim to develop a new strategy which can potentially facilitate the intrinsic TADF of conjugated emitters by interchromophore interaction and the corresponding formed excimer-like state ( $S_{\text{exc}}$ ). We selected the B,N-MR emitter CzB, *i.e.* 2,6-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)boron, as a model chromophore, which was demonstrated to be lacking intrinsic TADF in solution ( $k_{\text{RISC}} = \sim 1.5 \times 10^4$  s<sup>-1</sup>).<sup>67,68</sup> It is well known that an excimer can usually form between chromophores with co-facial geometry, while the co-facial distance ( $d$ ) might be the



primary factor for the formation of an  $S_{\text{exc}}$  state.<sup>69–72</sup> Therefore, we designed two co-facial CzB dimers with different linkers. Please note that dimerization of B,N-MR frameworks has been widely employed in co-planar geometry to extend conjugation and in a helicene structure for chiroptical responses,<sup>73–75</sup> but co-facial dimerization of B,N-MR emitters to facilitate an  $S_{\text{exc}}$  state has rarely been reported.

As shown in Scheme 1, we employed biphenyl (Biph) and naphthalene (Np) as covalent linkers to construct co-facial CzB dimers with different co-facial distances ( $d$ ). By using Suzuki coupling (ESI, Section S1†), CzB units were covalently linked to neighboring  $\alpha$  sites of Biph and Np linkers, leading to dimers named Biph-2CzB and Np-2CzB, respectively. Preliminary DFT calculation confirmed the co-facial geometry of two CzB units in both Biph-2CzB and Np-2CzB (Table S1†). The co-facial distance ( $d_{\text{B-B}}$ ) in the  $S_0$  state was estimated to be 5.4 Å and 4.9 Å in Biph-2CzB and Np-2CzB, respectively, which are significantly larger than the corresponding distance between neighboring  $\alpha$  sites on Biph (3.9 Å) and Np (3.6 Å) due to the non-parallel configuration of the two CzB units. The key role of geometry in inter-chromophore interaction will be discussed in the following sections.

### Delayed fluorescence

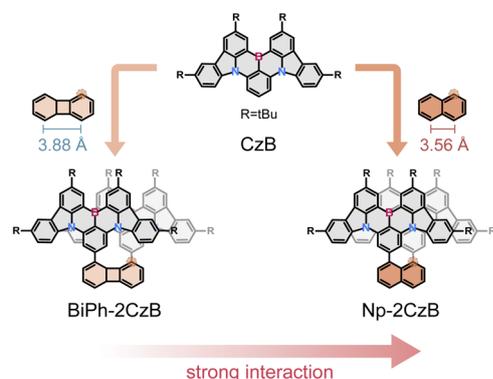
The steady-state UV/Vis absorption and fluorescence spectra of synthesized CzB, Biph-2CzB and Np-2CzB were measured in  $N_2$ -saturated DCM solution ( $10^{-5}$  M) and PMMA doped films ( $0.2 \text{ mg g}^{-1}$ ). As shown in Fig. 1a and b, Biph-2CzB exhibited fluorescence emission at 500 nm, which is nearly identical to the measured emission spectra of CzB, indicating the absence of inter-chromophore interaction in Biph-2CzB. Meanwhile, an extra-broad emission peak centered at 540 nm was observed for Np-2CzB (Fig. 1c), overlapping with CzB monomer emission at 500 nm. By measuring the concentration-dependent absorption spectra (Fig. S5†) and solvent-polarity-dependent fluorescence spectra (Fig. S6†) of Np-2CzB, the participation of intermolecular interaction and long-range CT states can be ruled out. Thus, the observed broad emission of Np-2CzB at 540 nm was preliminarily assigned to the emission of the expected  $S_{\text{exc}}$  state. We further examined the potential TADF activity of

synthesized CzB, Biph-2CzB and Np-2CzB emitters. By measuring the fluorescence spectra in air- (triplet states are quenched) and  $N_2$ -saturated DCM solution, both CzB (Fig. 1d) and Biph-2CzB (Fig. 1e) were recognized as TADF inactive. However, pronounced TADF was observed for Np-2CzB (Fig. 1f), and the fluorescence spectra in  $N_2$ -saturated solution were substantially stronger than in an air-saturated solution. Intriguingly, the observed TADF (green line in Fig. 1f) exhibited a single peak at 540 nm, different from the double-peak shape (500 nm and 540 nm) of the fluorescence spectra of Np-2CzB, indicating that TADF is associated only with the  $S_{\text{exc}}$  state.

To quantify the contributions of the PF and DF components, we estimated the total fluorescence quantum yield ( $\Phi_{\text{F}}$ ) and the contributions of PF and DF components, *i.e.*  $\Phi_{\text{PF}}$ ,  $\Phi_{\text{DF}}$  and  $\Phi_{\text{F}} = \Phi_{\text{PF}} + \Phi_{\text{DF}}$ . As shown in Fig. 1g–i and Table 1, CzB exhibits a  $\Phi_{\text{F}}$  of  $\sim 100\%$  with a low DF contribution in both DCM solution ( $\Phi_{\text{DF}}/\Phi_{\text{F}} = 0.11$ ) and PMMA doped films ( $\Phi_{\text{DF}}/\Phi_{\text{F}} = 0.01$ ), which is consistent with the typical LE ( $\pi \rightarrow \pi^*$ ) character of the  $S_1$  state.<sup>76–78</sup> Furthermore, although Biph-2CzB is much less fluorescent ( $\Phi_{\text{F}} < 0.5$ ) than CzB, its DF contributions in DCM solution ( $\Phi_{\text{DF}}/\Phi_{\text{F}} = 0.10$ ) and PMMA doped films ( $\Phi_{\text{DF}}/\Phi_{\text{F}} = 0.02$ ) are very consistent with the corresponding values for CzB, indicating similar RISC and different  $S_1$  state relaxation channels, such as faster non-radiative decay and slower radiative decay of Biph-2CzB compared with CzB. Intriguingly, Np-2CzB exhibited a considerable DF contribution ( $\Phi_{\text{DF}}/\Phi_{\text{F}} = 0.37$ ) in DCM solution, indicating an efficient RISC channel predominantly associated with  $S_{\text{exc}}$  emission at 540 nm. We further measured the fluorescence decay traces of CzB, Biph-2CzB and Np-2CzB in DCM solution (Fig. 2) and PMMA doped films (Fig. S7†) to investigate the relaxation channels of the corresponding low-lying singlet and triplet states. As shown in Fig. 2a, CzB exhibited a PF lifetime of  $\tau_{\text{PF}} = 6.30$  ns and a barely observable DF component in DCM solution, which is comparable with the measured  $\tau_{\text{PF}} = 9.00$  ns of Biph-2CzB. Although a long-lived tail can be observed in the fluorescence decay traces of CzB and Biph-2CzB in DCM solution, its low contribution ( $< 10$  photon counts compared with  $10^4$  counts at the maximum) resulted in difficulty in the quantitative fitting of  $\tau_{\text{DF}}$ . Thus, the lack of intrinsic TADF was confirmed for CzB and Biph-2CzB, corresponding to the reported slow RISC of CzB ( $k_{\text{RISC}} = 1.5 \times 10^4 \text{ s}^{-1}$ ) in solution.<sup>67,68</sup>

However, as shown in Fig. 2b, Np-2CzB exhibited bi-exponential fluorescence decay in DCM solution ( $\tau_{\text{PF1}} = 5.6$  ns and  $\tau_{\text{PF2}} = 49.4$  ns) and PMMA doped films ( $\tau_{\text{PF1}} = 5.2$  ns and  $\tau_{\text{PF2}} = 49.1$  ns). More specifically, emission at 500 nm is dominated by fast decay ( $\tau_{\text{PF1}} = \sim 5.6$  ns), assigned to the  $S_1$  state lifetime, which is consistent with the measured  $\tau_{\text{PF}}$  of CzB and Biph-2CzB. Meanwhile, slow decay ( $\tau_{\text{PF2}} = \sim 49$  ns) is associated with  $S_{\text{exc}}$  at 540 nm, which agrees with the prolonged lifetime of the excimer-like states in reported cases.<sup>79–82</sup>

Please note that the observed  $\tau_{\text{PF2}}$  must be distinguished from the TADF of Np-2CzB, which was observed with a lifetime of  $\sim 2.5 \mu\text{s}$  ( $\tau_{\text{DF}}$ , Fig. 2c) in DCM solution and is associated with  $S_{\text{exc}}$  emission at 540 nm. With the measured fluorescence quantum yield ( $\Phi_{\text{PF}}$ ,  $\Phi_{\text{DF}}$ ) and lifetime ( $\tau_{\text{PF}}$ ,  $\tau_{\text{DF}}$ ), we calculated the decay rate of each relaxation channel (ESI, Section S2†), *i.e.*



Scheme 1 Molecular design of co-facial CzB dimers with biphenylene (BiPh) and naphthalene (Np) as covalent linkers.



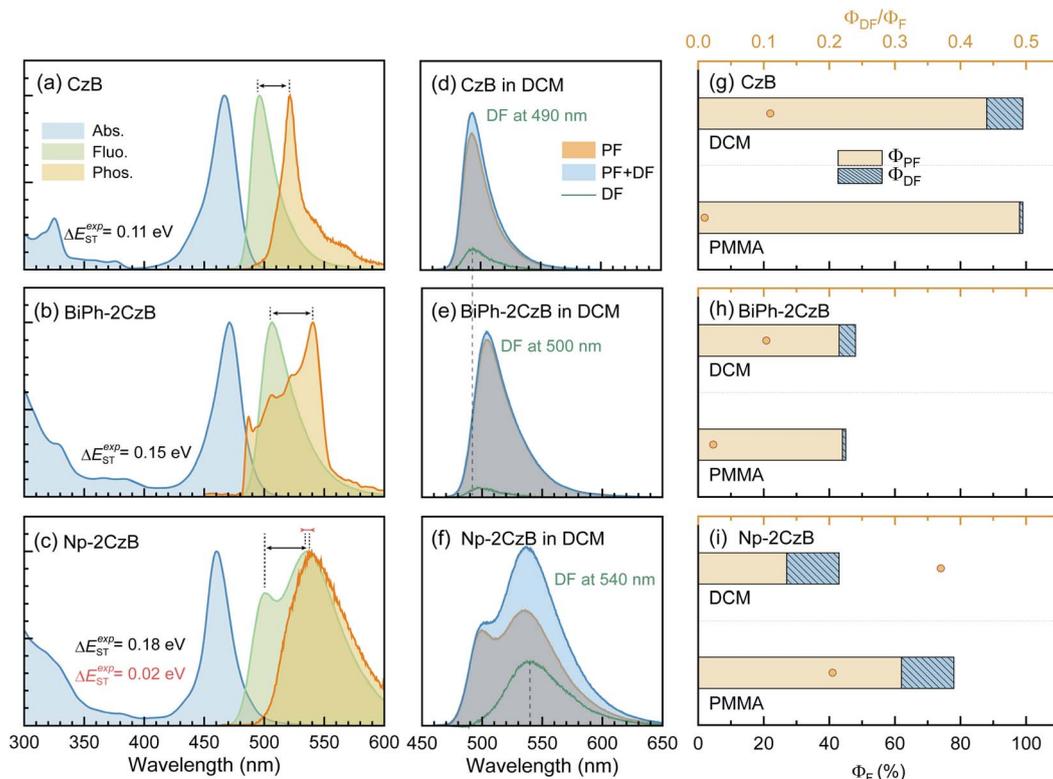


Fig. 1 Measured absorption, fluorescence and phosphorescence (50 ms gated) spectra of CzB (a), BiPh-2CzB (b) and Np-2CzB (c) in  $N_2$ -saturated DCM solution ( $1 \times 10^{-5}$  M); comparison of fluorescence spectra of CzB (d), BiPh-2CzB (e) and Np-2CzB (f) in air- (gray bands) and  $N_2$ - (blue bands) saturated DCM solution ( $1 \times 10^{-5}$  M), the differential spectra (green lines) correspond to the DF component, measured fluorescence quantum yield ( $\Phi_F$ ,  $\Phi_{PF}$ ,  $\Phi_{DF}$ ) and relative contribution of delayed fluorescence ( $\Phi_{DF}/\Phi_F$ ) of CzB (g), BiPh-2CzB (h) and Np-2CzB (i) in  $N_2$ -saturated DCM solution ( $1 \times 10^{-5}$  M) and PMMA doped films (0.2 mg  $g^{-1}$ ).

$k_r^S$ ,  $k_{nr}^S$ ,  $k_{ISC}$  and  $k_{RISC}$ . As listed in Table 1, CzB exhibits highly efficient radiative decay to the  $S_0$  state ( $k_r^S = 1.4 \times 10^8$   $s^{-1}$ ), which is one or two orders of magnitude faster than the corresponding  $k_{nr}^S$  and  $k_{ISC}$ , leading to close-to-unity  $\Phi_F$ . Please note that we can barely observe the DF components of CzB and Biph-2CzB in DCM solution (Fig. 2a), for which  $k_{RISC}$  cannot be calculated. However, a  $k_{RISC}$  of  $1.5 \times 10^4$   $s^{-1}$  was reported for CzB in dilute solution,<sup>67,68</sup> which is half of our measured value ( $k_{RISC} = 2.9 \times 10^4$   $s^{-1}$ ) of CzB in PMMA doped films. Meanwhile, Biph-2CzB exhibited very similar RISC dynamics to CzB, *i.e.*

unobservable RISC in DCM solution and  $k_{RISC} = 4.9 \times 10^4$   $s^{-1}$  in PMMA doped films. However, unlike CzB, the  $k_{nr}^S$  value ( $\sim 5.2 \times 10^7$   $s^{-1}$  in DCM solution) of Biph-2CzB was fast enough to be competitive with  $k_r^S$  ( $\sim 4.8 \times 10^7$   $s^{-1}$  in DCM solution), leading to  $\Phi_F < 0.5$ . Since the band gaps of CzB and Biph-CzB are similar to each other, the observation that the  $k_{nr}^S$  of Biph-CzB is nearly 50 times faster than that of CzB might be attributed to specific vibrational modes with a pronounced Huang-Rhys factor ( $S_k$ ) and reorganization energy contribution ( $\lambda_k$ ) to the  $S_1 \rightarrow S_0$

Table 1 Photophysical parameters of CzB, BiPh-2CzB and Np-2CzB measured in DCM solution and PMMA doped films

		$\Phi_{PF}$	$\Phi_{DF}$	$\tau_{PF}$ (ns)	$\tau_{DF}$ ( $\mu$ s)	$k_r^{S_a}$ ( $10^7$ $s^{-1}$ )	$k_{nr}^{S_b}$ ( $10^6$ $s^{-1}$ )	$k_{ISC}^c$ ( $10^6$ $s^{-1}$ )	$k_{RISC}^d$ ( $10^5$ $s^{-1}$ )
CzB	DCM	0.88	0.11	6.30	—	14.0	1.41	17.6	0.15 <sup>e</sup>
	PMMA	0.98	0.01	6.80	35.2	14.4	1.46	1.49	0.29
BiPh-2CzB	DCM	0.43	0.05	9.00	—	4.78	51.8	11.6	—
	PMMA	0.44	0.01	9.90	20.6	4.40	53.8	2.22	0.49
Np-2CzB	DCM	0.27	0.16	5.60 <sup>f</sup>	2.50	0.55	7.25	7.53	6.45
				49.4 <sup>g</sup>					
	PMMA	0.62	0.16	5.20 <sup>f</sup>	1.25	1.26	3.56	4.18	1.01
				49.1 <sup>g</sup>					

<sup>a</sup> Calculated with  $k_r^S = \Phi_{PF}/\tau_{PF}$ . <sup>b</sup> Calculated with  $k_{nr}^S = k_{PF} - k_r^S - k_{ISC}$ ,  $k_{PF} = 1/\tau_{PF}$ . <sup>c</sup> Calculated with  $k_{ISC} = k_{PF}\Phi_{ISC} = k_{PF} \times \Phi_{DF}/\Phi_F$ . <sup>d</sup> Calculated with  $k_{RISC} = (k_{PF} + k_{DF})/2 - [(k_{PF} + k_{DF})^2/2 - k_{PF}k_{DF}(1 + \Phi_{DF}/\Phi_{PF})]^{0.5}$ . <sup>e</sup> Collected from values reported in ref. 64. <sup>f</sup>  $\tau_{PF}$  of  $S_1$  state, *i.e.* CzB monomers in Np-2CzB. <sup>g</sup>  $\tau_{PF}$  of  $S_{exc}$  state.



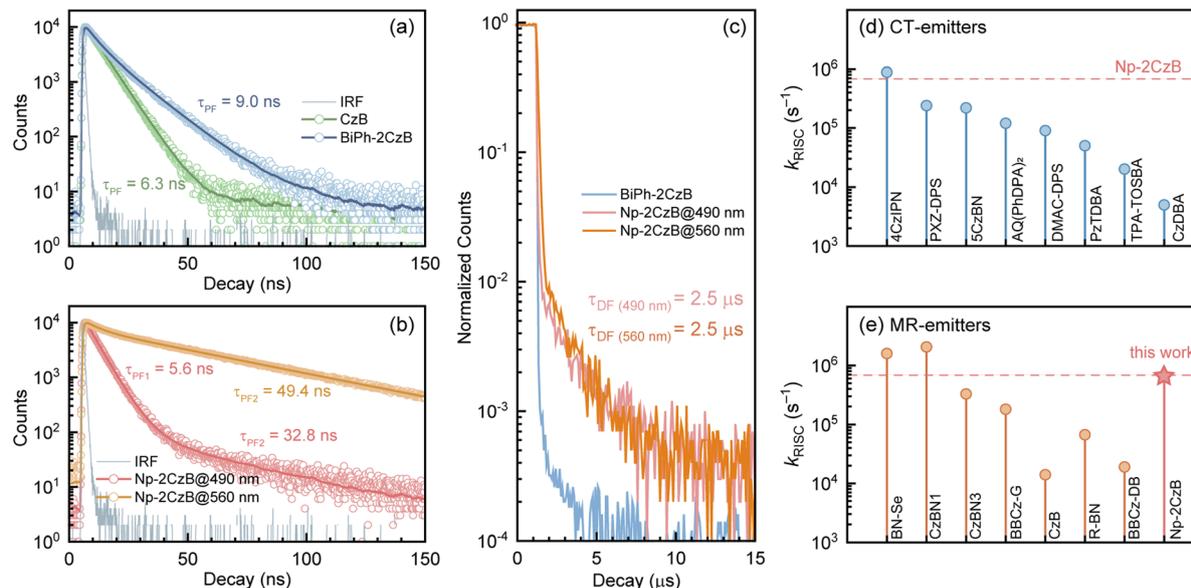


Fig. 2 (a) The PF decay traces of CzB and Biph-2CzB in DCM solution; (b) the PF decay traces of Np-2CzB at emission wavelengths of 490 nm and 560 nm in DCM solution; (c) the DF decay traces of Biph-2CzB and Np-2CzB in DCM solution, in which the DF component of Biph-2CzB was unobservable; (d) reported  $k_{RISC}$  values of several typical CT-type TADF emitters in dilute solution; (e) comparison between the measured  $k_{RISC}$  value of our proof-of-concept emitter Np-2CzB with several reported B,N-MR emitters in dilute solution.

transition, which was described as the band-gap law in a weak coupling regime.<sup>24,25,31</sup>

Furthermore, the observed DF contribution ( $\Phi_{DF}/\Phi_F = 0.37$ ) and  $\sim 2.5$   $\mu$ s DF lifetime of Np-2CzB correspond to a surprisingly high  $k_{RISC} = 6.5 \times 10^5$  s<sup>-1</sup> in DCM solution. Quantitatively, the estimated  $k_{RISC} = 6.5 \times 10^5$  s<sup>-1</sup> in DCM solution is nearly 50 times faster than the reported  $k_{RISC}$  of CzB ( $1.5 \times 10^4$  s<sup>-1</sup>), which is also comparable to reported selenium-doped B,N-MR emitters with symmetric (BN-SeSe,  $k_{RISC} = 2.0 \times 10^6$  s<sup>-1</sup>) and asymmetric (BN-Se,  $k_{RISC} = 1.6 \times 10^6$  s<sup>-1</sup>) frameworks.<sup>57,59</sup> As illustrated in Fig. 2d and e, the measured  $k_{RISC}$  of Np-2CzB is higher than those of many well-known CT-type TADF emitters and recently reported B,N-MR emitters in dilute solution; the details can be found in Tables S2 and S3.†

We then attempted to explore the plausible origin of the efficient RISC of Np-2CzB in dilute solution. As described in eqn (2),  $k_{RISC}$  is highly dependent on  $\Delta E_{ST}$  and the corresponding SOC matrix element  $\langle \Psi_{T_1} | \hat{H}_{SO} | \Psi_{S_1} \rangle$ .<sup>28,43,83</sup> To estimate  $\Delta E_{ST}$ , we measured the phosphorescence spectra of CzB, Biph-2CzB and Np-2CzB in DCM solution at 77 K (Fig. 1a–c), in which the PF component was screened by 50 ms time-gating. Combined with the corresponding fluorescence spectra,  $\Delta E_{ST}$  of 0.11 eV (CzB) and 0.17 eV (Biph-2CzB) were estimated, which are much smaller than the TDDFT calculated values (Fig. S8†) and usually regarded as a thermally accessible gap at room temperature.<sup>37,84</sup> Therefore, the RISC channels of CzB and Biph-2CzB might be mainly blocked by a low SOC matrix element, and were calculated as  $0.044$  cm<sup>-1</sup> and  $0.005$  cm<sup>-1</sup>, respectively, using the linear-response method. As both  $S_1$  and  $T_1$  states of CzB feature an identical LE ( $\pi \rightarrow \pi^*$ ) electronic configuration, the magnetic moment resulting from orbital angular momentum ( $\mu_L$ ) can be extremely low, leading to the TADF-inactive character of CzB

and Biph-2CzB. For Np-2CzB, although  $\langle \Psi_{T_1} | \hat{H}_{SO} | \Psi_{S_1} \rangle$  was also calculated to be low ( $< 0.1$  cm<sup>-1</sup>), the  $\langle \Psi_{T_1} | \hat{H}_{SO} | \Psi_{S_{exc}} \rangle$  associated with RISC ( $T_1 \rightarrow S_{exc}$ ) can be much higher due to the dramatically changed electronic configuration of the  $S_{exc}$  state, which explains the observed fact that the TADF of Np-2CzB is associated only with  $S_{exc}$  emission. Due to the limitation of electronic structure calculation of an excimer-like state, directly calculating the SOC matrix element involving the  $S_{exc}$  state remains challenging, but we still believe that the greatly enhanced SOC may be the main reason for the intrinsic TADF of Np-2CzB. Meanwhile, as the  $S_{exc}$  state is energetically lower than the  $S_1$  state of Np-2CzB, the resulting  $\Delta E_{ST}$  ( $T_1 \rightarrow S_{exc}$ )  $< 0.02$  eV may also contribute to the observed  $k_{RISC}$  of  $6.5 \times 10^5$  s<sup>-1</sup> in DCM solution.

### Inter-chromophore interaction

We successfully observed the intrinsic TADF of Np-2CzB, which is associated with the  $S_{exc}$  state facilitated by inter-chromophore interaction. The formation of the  $S_{exc}$  state relies on interaction between a chromophore ( $M^*$ ) with a localized  $S_1$  state and the neighboring chromophore (M) on the  $S_0$  state, *i.e.*  $|^1(S_1S_0)\rangle = (1/2)^{0.5} [|M^*M\rangle \pm |MM^*\rangle]$ .<sup>85,86</sup> For Np-2CzB, the formed  $S_{exc}$  state exhibited red-shifted emission and efficient RISC ( $k_{RISC} = 6.5 \times 10^5$  s<sup>-1</sup>) in DCM solution. However, Biph-2CzB exhibited nearly identical emission to CzB, indicating very weak inter-chromophore interaction. We performed reduced density gradient (RDG) analysis for Biph-2CzB and Np-2CzB (Fig. 3a and b).

The calculated RDG scattering diagram of Np-2CzB exhibited several spikes in the low-density and low-gradient region (highlighted by the dashed box in Fig. 3b), indicating the



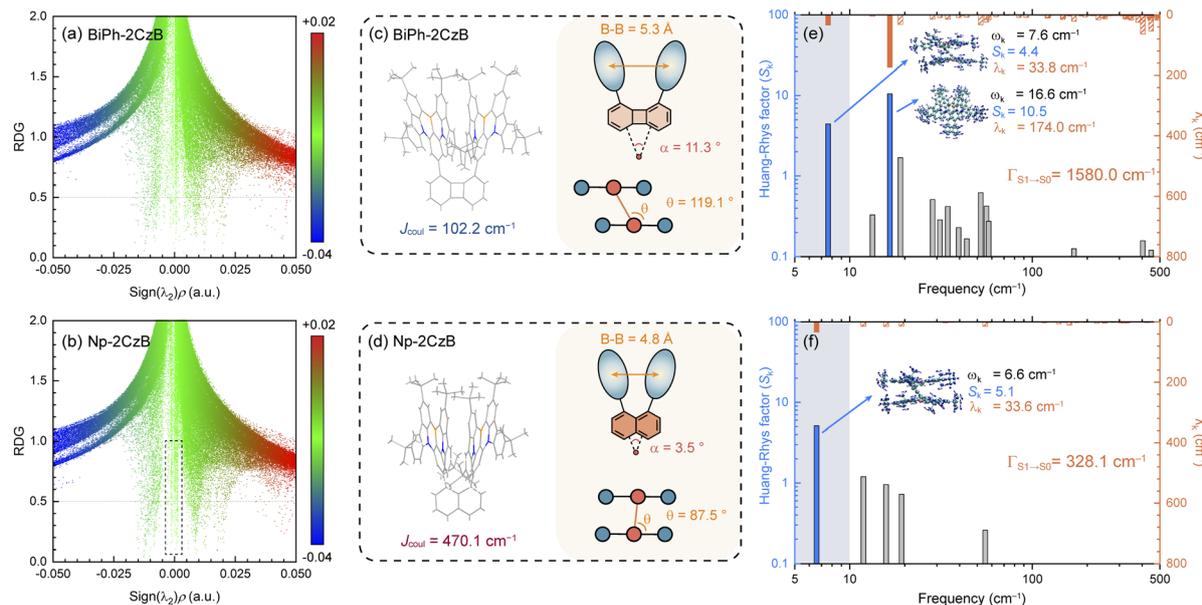


Fig. 3 Calculated reduced density gradient (RDG) scattering diagrams based on the  $S_1$  state geometry of BiPh-2CzB (a) and Np-2CzB (b); the TDDFT (B3LYP/6-31g\*) optimized geometry of BiPh-2CzB (c) and Np-2CzB (d); calculated Huang–Rhys factor ( $S_k$ ) and reorganization energy contribution ( $\lambda_k$ ) of each vibrational mode of BiPh-2CzB (e) and Np-2CzB (f) for the  $S_1 \rightarrow S_0$  transition.

presence of pronounced inter-chromophore interaction, which can also be visualized by the corresponding RDG iso-surface displayed in Fig. S9.† However, such features can barely be observed on the RDG scattering diagram and iso-surface of BiPh-2CzB, implying the absence of inter-chromophore interaction, which is consistent with its observed fluorescence spectra being similar to CzB. We further attempted to explore the structural and energetic origin of the different inter-chromophore interactions within the two CzB dimers with different linkers.

Firstly,  $S_{exc}$  formation relies on co-facial geometry with a suitable co-facial distance ( $d = 3.0\text{--}5.0 \text{ \AA}$ ),<sup>87–89</sup> for which we optimized the  $S_1$  state structure of BiPh-2CzB and Np-2CzB by the TDDFT approach; the corresponding structural parameters are listed in Table 2. As illustrated in Fig. 3c and d, Np-2CzB exhibited a co-facial (B–B) distance of  $d = 4.8 \text{ \AA}$  in the  $S_1$  state, which is  $0.5 \text{ \AA}$  shorter than that of BiPh-2CzB ( $d = 5.3 \text{ \AA}$ ). Meanwhile, the  $S_1$  state geometry of Np-2CzB exhibited a dihedral angle of  $\alpha = 3.5^\circ$  and a slipping angle of  $\theta = 87.5^\circ$  between the two CzB units. As a result, Np-2CzB exhibited improved co-facial configuration in the  $S_1$  state compared to BiPh-2CzB ( $\alpha = 11.3^\circ$ ,  $\theta = 119.1^\circ$ ), *i.e.* the two CzB units are more spatially overlapped in Np-2CzB than in BiPh-2CzB, leading to a favorable configuration for  $S_{exc}$  formation. Furthermore, the calculated  $S_0$  and  $S_1$  state geometries also revealed the different  $S_1/S_0$  excited-state structural relaxation (ES-SR) of BiPh-2CzB and Np-2CzB. As listed in Table 2, BiPh-2CzB exhibited pronounced CzB twisting ( $\beta_1/\beta_2$ ) and bending ( $\gamma_1/\gamma_2$ ) angles with up to 30% change between  $S_1$  and  $S_0$  states, which might lead to two-step  $S_1/S_0$  ES-SR, as we reported previously.<sup>31,55</sup> Intriguingly, the twisted  $S_1/S_0$  ES-SR of Np-2CzB ( $\sim 7\%$   $S_1/S_0$  changing) is less pronounced than that of BiPh-2CzB. Meanwhile, the two CzB

units in Np-2CzB exhibited a significantly planarized (bending angles  $\gamma_1/\gamma_2 = 5.1^\circ$ ) feature in the  $S_1$  state compared to CzB ( $\gamma = 18.5^\circ$ ) or BiPh-2CzB ( $\gamma_1/\gamma_2 = 11.3^\circ/15.7^\circ$ ), which might also contribute to the  $S_{exc}$  state formation of Np-2CzB. Furthermore, the formation of an  $S_{exc}$  state also relies on appreciable inter-chromophore electronic coupling ( $J$ ), which has been widely discussed in the framework of the exciton theory.<sup>90–92</sup> In general, electronic coupling includes contributions from Coulomb ( $J_{coul}$ ) and charge transfer terms ( $J_{CT}$ ), while  $S_{exc}$  state formation is known to require considerable  $J_{coul}$  and weak CT coupling.<sup>70,93</sup> The low value of  $J_{CT}$  in both BiPh-2CzB and Np-2CzB can be

Table 2 The DFT/TDDFT calculated geometric parameters, electronic coupling ( $J_{coul}$ ) and reorganization energy ( $\Gamma_{S_1 \rightarrow S_0}$  and  $\Gamma_{S_0 \rightarrow S_1}$ ) of CzB, BiPh-2CzB and Np-2CzB

	BiPh-2CzB		Np-2CzB		CzB	
	$S_0$	$S_1$	$S_0$	$S_1$	$S_0$	$S_1$
$\alpha$ ( $^\circ$ ) <sup>a</sup>	11.2	11.3	4.8	3.5		
$\theta$ ( $^\circ$ ) <sup>b</sup>	118.5	119.1	91.3	87.5		
$J_{coul}$ ( $\text{cm}^{-1}$ )	102.2		470.1			
B–B ( $\text{\AA}$ ) <sup>c</sup>	5.4	5.3	4.9	4.8		
$N_1\text{--}N_1$ ( $\text{\AA}$ ) <sup>c</sup>	5.2	5.1	4.7	4.7		
$N_2\text{--}N_2$ ( $\text{\AA}$ ) <sup>c</sup>	5.2	5.1	4.7	4.7		
$\beta_1/\beta_2$ ( $^\circ$ ) <sup>d</sup>	41.7/45.6	30.0/31.9	52.1/52.1	48.4/48.4		
$\gamma_1/\gamma_2$ ( $^\circ$ ) <sup>e</sup>	16.6/13.7	11.3/15.7	9.3/9.3	5.1/5.1	19.9	18.5
$\Gamma_{S_1 \rightarrow S_0}$ ( $\text{cm}^{-1}$ )	1579.9		328.1		480.6	
$\Gamma_{S_0 \rightarrow S_1}$ ( $\text{cm}^{-1}$ )	1661.8		423.2		410.4	

<sup>a</sup> Dihedral angle between two CzB units. <sup>b</sup> Slipping angle of two CzB units. <sup>c</sup> Distance between two CzB units. <sup>d</sup> Twisting angle of two CzB units with BiPh/Np linker. <sup>e</sup> Bending angle of two CzB units.



ensured by their barely observable solvatochromism (Fig. S6<sup>†</sup>), while  $J_{\text{coul}}$  can usually be estimated with:<sup>85,93,94</sup>

$$J_{\text{coul}} = \frac{1}{4\pi\epsilon_0} \frac{\mu^2(\cos \alpha - 3 \cos^2 \theta)}{d^3} \quad (4)$$

By using TDDFT calculated geometric parameters ( $\alpha$  angle,  $\theta$  angle and inter-chromophore distance  $d$ ) and transition dipole moment  $\mu$ , the inter-chromophore  $J_{\text{coul}}$  of Np-2CzB was estimated as 470.1  $\text{cm}^{-1}$ , which is more than 4.5 times the calculated  $J_{\text{coul}}$  for Biph-2CzB (102.2  $\text{cm}^{-1}$ ) and consistent with the reported  $J_{\text{coul}}$  value for excimer formation in  $\pi$ -stacked dimers of perylene bisimide (PBI), *i.e.* Bis-PBI 1 ( $J_{\text{coul}} = 678.0 \text{ cm}^{-1}$ ) and Bis-PBI 3(S) ( $J_{\text{coul}} = 545.0 \text{ cm}^{-1}$ ), in which two PBI chromophores are covalently linked by spacer moieties.<sup>95,96</sup>

Finally, with suitable co-facial geometry and electronic coupling, the formation of the  $S_{\text{exc}}$  state can still be disrupted by vibrational motion and  $S_1/S_0$  ES-SR of the  $S_1$  state, for which we further performed vibrational analysis on BiPh-2CzB and Np-2CzB. By performing vibrational analysis, we estimated the total internal reorganization energy of the  $S_1 \rightarrow S_0$  transition ( $T_{S_1 \rightarrow S_0}$ ), which can be employed to generalize the  $S_1/S_0$  ES-SR. It can be seen that the  $T_{S_1 \rightarrow S_0}$  of BiPh-2CzB (1579.9  $\text{cm}^{-1}$ ) is almost 5 times that of CzB (480.6  $\text{cm}^{-1}$ ) (Fig. S10<sup>†</sup>), indicating the highly flexible structure of BiPh-2CzB in the  $S_1$  state, which can potentially disrupt the formation of the  $S_{\text{exc}}$  state. In contrast, the  $T_{S_1 \rightarrow S_0}$  of Np-2CzB (328.1  $\text{cm}^{-1}$ ) is even lower than that of CzB, indicating a rigid structure without pronounced vibrational motion in the  $S_1$  state, which might also be critical for  $S_{\text{exc}}$  formation. We further calculated the Huang–Rhys factor ( $S_k$ ) and reorganization energy contribution ( $\lambda_k$ ) of each vibrational mode and attempted to find the key modes that can promote or disrupt  $S_{\text{exc}}$  formation.

It is known that vibrational modes with considerable  $S_k$  (*i.e.* promoting modes) are heavily involved in the vibronic coupling of the  $S_1$  state, while the  $\lambda_k$  of promoting modes is associated with either  $S_1/S_0$  ES-SR or the vibrational motion of the  $S_1$  state,<sup>97–100</sup> which can disrupt  $S_{\text{exc}}$  formation. As shown in Fig. 3e, the  $T_{S_1 \rightarrow S_0}$  of BiPh-2CzB is mainly contributed by two promoting modes in the low-frequency regime, *i.e.* mode 1 ( $S_k = 4.4$ ) at  $\omega_k = 7.6 \text{ cm}^{-1}$  with  $\lambda_k = 33.8 \text{ cm}^{-1}$  and mode 2 ( $S_k = 10.5$ ) at  $\omega_k = 16.6 \text{ cm}^{-1}$  with  $\lambda_k = 174.0 \text{ cm}^{-1}$ . As illustrated in Fig. S11,<sup>†</sup> mode 1 corresponds to the twisting motion of two CzB units along with a Biph linker, associated with the fluctuation of  $\beta_1/\beta_2$  and  $\theta$  angles with respect to the equilibrium position in the  $S_1$  state. Meanwhile, mode 2 corresponds to bending of the CzB units, *i.e.* the fluctuation of  $\gamma_1/\gamma_2$  angles. Intriguingly, for Np-2CzB, mode 1 was found to be identical to that of BiPh-2CzB (Fig. 3f), but mode 2 of Np-2CzB at  $\omega_k = 15.8 \text{ cm}^{-1}$  was one order of magnitude lower at  $\lambda_k$  (15.1  $\text{cm}^{-1}$ ) than that of BiPh-2CzB, indicating that the bending motion of CzB units is greatly suppressed in the  $S_1$  state of Np-2CzB. Thus, we deduced that the bending mode ( $\omega_k = \sim 16 \text{ cm}^{-1}$ ) of CzB can potentially disrupt  $S_{\text{exc}}$  formation in co-facial dimers, while reducing the  $\lambda_k$  of such a mode might be critical for formation of the  $S_{\text{exc}}$  state.

The vibrational analysis can also explain the excitation ( $\lambda_{\text{ex}}$ )-dependent emission of Np-2CzB in DCM solution (Fig. 4a) and PMMA doped films (Fig. 4b). By performing multi-Gaussian

fitting on the emission spectra of Np-2CzB (Fig. S12 and S13<sup>†</sup>), the contributions of  $S_1$  and  $S_{\text{exc}}$  state emission can be quantified. For convenience, we defined the indicator  $\delta = A_{\text{exc}}/A_{S_1}$ , in which  $A_{\text{exc}}$  and  $A_{S_1}$  stand for the peak areas of  $S_{\text{exc}}$  and  $S_1$  emission spectra, respectively. In DCM solution, the  $\delta$  indicator exhibits pronounced  $\lambda_{\text{ex}}$ -dependence, *i.e.* visible excitation ( $\lambda_{\text{ex}} > 410 \text{ nm}$ ) resulting in  $S_{\text{exc}}$  dominated emission ( $\delta > 12$ ), while  $S_{\text{exc}}$  might be disrupted ( $\delta < 6$ ) upon UV excitation ( $\lambda_{\text{ex}} < 350 \text{ nm}$ ). As illustrated in Fig. 4c, the UV excitation populated high-lying singlet states ( $S_n$ ,  $n > 1$ ) can rapidly decay to a vibrationally hot  $S_1$  state. As a result, the excessive vibrational energy (probably on the bending mode of CzB units) can disrupt  $S_{\text{exc}}$  formation, leading to reduced  $\delta$  values, while a cold  $S_1$  state populated by visible excitation leads to a more favourable condition for  $S_{\text{exc}}$  formation with reduced vibrational motion in the  $S_1$  state. However, in PMMA doped films, the vibrational motion of the corresponding mode might be greatly confined, leading to  $\lambda_{\text{ex}}$ -independent emission. Meanwhile, due to external structural restraint on  $S_1/S_0$  ES-SR, the CzB units in the  $S_1$  state might not be fully relaxed to an optimal configuration (bending angles  $\gamma_1/\gamma_2 = 5.1^\circ$ ) that is favorable for  $S_{\text{exc}}$  formation. As a result, the  $S_{\text{exc}}$  emission remains at a low level ( $\delta < 8$ ) upon all tested  $\lambda_{\text{ex}}$ . Vibrational analysis and  $\lambda_{\text{ex}}$ -dependent emission spectra of Np-2CzB further confirmed that  $S_{\text{exc}}$  formation in Np-2CzB can be disrupted by the bending mode of CzB units, which is strongly coupled with the  $S_1 \rightarrow S_0$  transition. However, the formation dynamics of the  $S_{\text{exc}}$  state in Np-2CzB still remains unknown, because of which we performed fs-TA measurement on CzB, BiPh-2CzB and Np-2CzB in both DCM solution and PMMA doped films.

### Excited-state dynamics

To further resolve the excited-state relaxation of CzB, BiPh-2CzB and Np-2CzB emitters, especially to explore the formation dynamics of the  $S_{\text{exc}}$  state, the fs-TA response of the corresponding emitters in both DCM solution and PMMA doped films were recorded upon UV excitation.

As shown in Fig. S14,<sup>†</sup> the fs-TA spectra of CzB exhibited pure decay without reshaping of the fs-TA spectra at a probe wavelength of  $\lambda_{\text{pr}} = 350\text{--}750 \text{ nm}$ . With minimized  $S_1/S_0$  ES-SR (Table 2),  $S_1$  state decay is dominated by the radiative channel, leading to close-to-unity  $\Phi_{\text{F}}$  (Table 1). For BiPh-2CzB, pronounced  $S_1/S_0$  ES-SR leads to highly efficient ( $k_{\text{nr}}^S \approx 5 \times 10^7 \text{ s}^{-1}$ ) non-radiative  $S_1 \rightarrow S_0$  decay. However, the fs-TA spectral shape of BiPh-2CzB (Fig. S15<sup>†</sup>) remains nearly unchanged in a time window up to 7 ns, indicating that fs-TA in the UV/Vis regime is insensitive to  $S_1/S_0$  ES-SR of these emitters. Thus, observation of  $S_1/S_0$  ES-SR dynamics relies on quantitative fitting of fs-TA. Intriguingly, the fs-TA spectra of Np-2CzB exhibit a negative band at  $\lambda_{\text{pr}} = \sim 465 \text{ nm}$  in both DCM solution and PMMA doped films (Fig. S16<sup>†</sup>), which is clearly blue shifted in comparison with CzB ( $\lambda_{\text{pr}} = \sim 475 \text{ nm}$ ) and BiPh-2CzB ( $\lambda_{\text{pr}} = \sim 478 \text{ nm}$ ). Considering that the observed negative band is comprised of ground state bleaching (GSB) and stimulated emission (SE) of the  $S_1$  state, the blue-shifted negative fs-TA band of Np-2CzB can be explained by the lack of an SE ( $S_1$ )



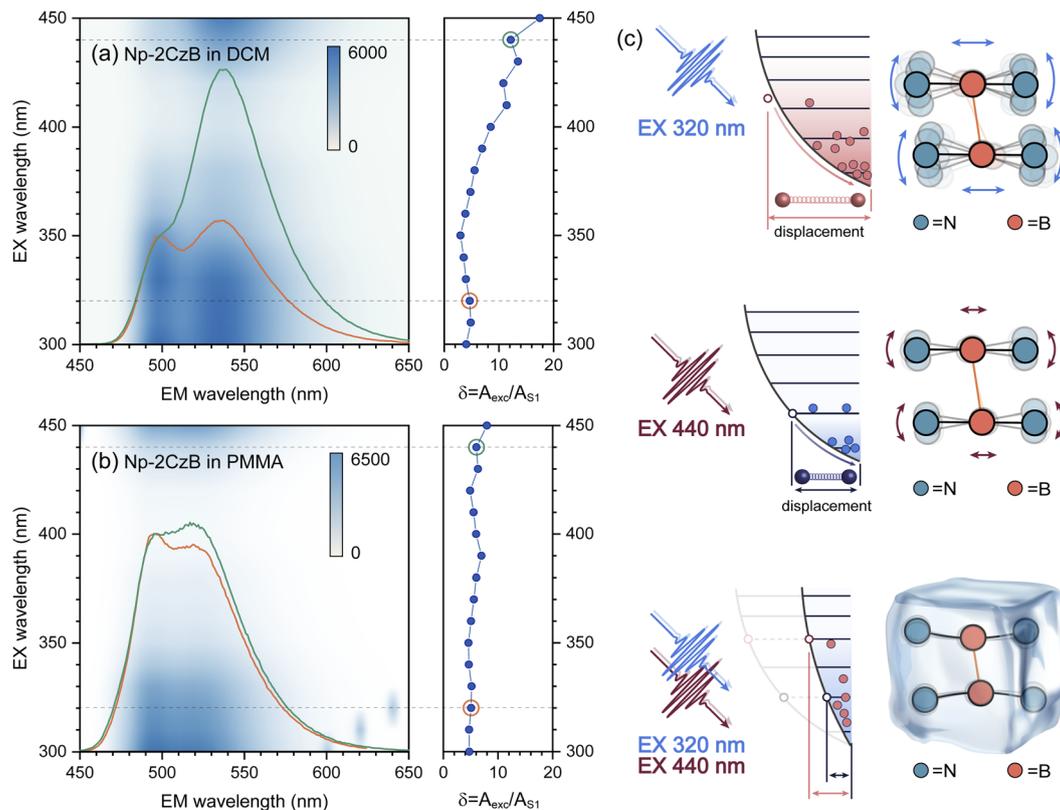


Fig. 4 The measured excitation–emission spectra of Np-2CzB in DCM solution (a) and PMMA doped films (b); corresponding excitation dependence of the contribution ratio ( $A_{\text{exc}}/A_{S_1}$ ) of  $S_{\text{exc}}$  and  $S_1$  emission, as well as emission spectra upon excitation at 320 nm (orange lines) and 440 nm (green lines); (c) illustrative sketch of  $S_{\text{exc}}$  emission upon 320 nm (upper) and 440 nm excitation (middle) in solution and in PMMA doped films (bottom).

band, while the replaced  $S_{\text{exc}}$  state might not be capable of having an SE.

Target analysis was further performed to acquire quantitative information about the excited-state relaxation of BiPh-2CzB and Np-2CzB, in which formation of an  $S_{\text{exc}}$  state might be entangled with  $S_1/S_0$  ES-SR motion. By including two or three sequential processes, the measured fs-TA data can be well reproduced by the extracted decay-associated spectra (DAS, Fig. 5a–d and S17†) of each decay process and the concentration evolution of each transient species (Fig. 5e, f and S18†).

For CzB, an ultrafast process ( $S_1^{\text{FC}} \rightarrow S_1'$ ,  $\tau_1$ ) might correspond to the slight  $S_1/S_0$  ES-SR revealed by TDDFT calculation, which becomes slower ( $\sim 6.4$  ps) in PMMA doped film than in DCM solution ( $\sim 2.0$  ps) due to external structural restraint. The subsequent process ( $\sim 5$  ns) accompanied by the  $S_1$  state SE at  $\sim 490$  nm corresponds to the  $S_1$  state lifetime ( $S_1 \rightarrow S_0$ ,  $\tau_{S_1}$ ), which is comparable to the measured fluorescence lifetime ( $\tau_{\text{PF}}$ ).

For BiPh-2CzB, target analysis revealed two-step relaxation with 2–3 times slower time constants in PMMA doped films than in DCM solution, corresponding to two-step  $S_1/S_0$  ES-SR, as previously reported.<sup>31,55</sup> As discussed in the sections above,  $S_1/S_0$  ES-SR of BiPh-2CzB features simultaneous changing of CzB twisting ( $\beta_1$  and  $\beta_2$  angles) and their own bending motion ( $\gamma_1$  and  $\gamma_2$  angles). The fast step of  $S_1/S_0$  ES-ER ( $\tau_1 = 1\text{--}4$  ps)

corresponds to CzB twisting along with the biphenyl linker (noted as  $S_1^{\text{FC}} \rightarrow S_1'$ ), while the slow step ( $\tau_2 = 150\text{--}350$  ps) might originate from the bending motion of CzB frameworks ( $S_1^{\text{T}} \rightarrow S_1^{\text{TB}}$ ). Furthermore, the structurally relaxed  $S_1$  state ( $S_1^{\text{TB}}$ ) exhibits decay with  $>7$  ns time constants, which is comparable to the measured  $\tau_{\text{PF}} = 9$  ns, corresponding to the  $S_1$  state lifetime ( $\tau_{S_1}$ ). The corresponding DAS of  $\tau_{S_1}$  feature a pronounced negative peak at  $\lambda_{\text{pr}} = 475\text{--}480$  nm, contributed by the GSB and SE of relaxed  $S_1^{\text{TB}}$ . Meanwhile, the  $\tau_{S_1}$  of BiPh-2CzB is also similar to the  $\tau_{\text{PF}}$  ( $\sim 7$  ns) of CzB. Therefore, it is clear that the  $S_1$  state of BiPh-2CzB is dominated by CzB units without interchromophore interaction. Since the  $S_1/T_1$  states of CzB units are dominated by similar  $\pi \rightarrow \pi^*$  character, the RISC of  $T_1 \rightarrow S_1$  is actually forbidden, leading to TADF-inactive BiPh-2CzB.

In comparison, Np-2CzB exhibited very different excited-state dynamics. In DCM solution, two-step relaxation of the initially populated  $S_1^{\text{FC}}$  of Np-2CzB was observed (Fig. 5b). Although the fast step ( $\tau_1 = 2.9$  ps) can be assigned to  $S_1/S_0$  CzB twisting ( $S_1^{\text{FC}} \rightarrow S_1'$ ), the slow step ( $\tau_2 = 240$  ps) can hardly be attributed to  $S_1/S_0$  ES-ER as it became faster ( $\sim 180$  ps) in PMMA doped films. With external structural restraint in doped films, the promoting modes that can disrupt  $S_{\text{exc}}$  formation, such as the bending mode of CzB units in Np-2CzB, can be further suppressed. As a result, unlike  $S_1/S_0$  ES-ER,  $S_{\text{exc}}$  formation can be even faster in PMMA doped films than in solution, which is



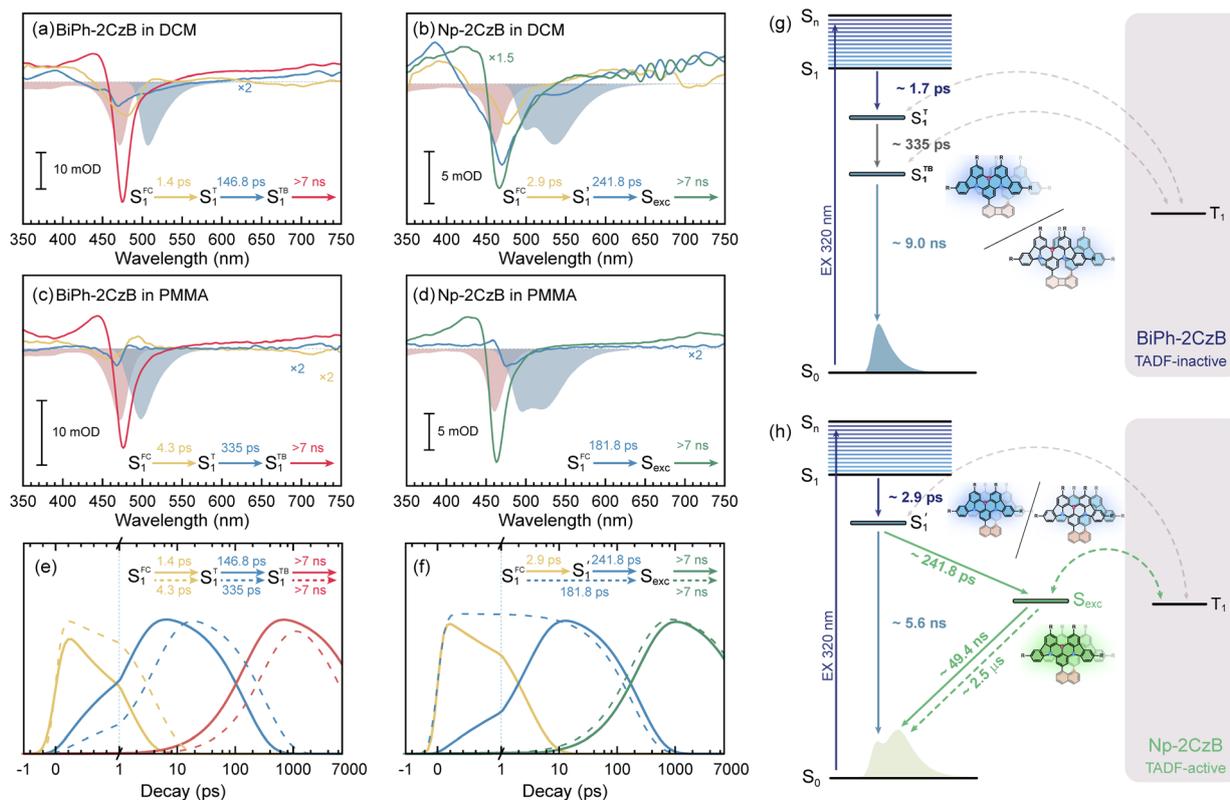


Fig. 5 Target analysis extracted decay-associated spectra (DAS) of fs-TA data of BiPh-2CzB (a) and Np-2CzB (b) in DCM solution, as well as BiPh-2CzB (c) and Np-2CzB (d) in PMMA doped films; the corresponding steady absorption (red filled bands) and fluorescence spectra (blue filled bands) overlap; concentration evolution of transient species extracted from the fs-TA of BiPh-2CzB (e) and Np-2CzB (f) in DCM solution (solid lines) and PMMA doped films (dashed lines); simplified excited-state relaxation path of BiPh-2CzB (g) and Np-2CzB (h).

what we observed for Np-2CzB. Therefore, the observed 180–240 ps process was assigned to the formation of the  $S_{exc}$  state ( $S_1' \rightarrow S_{exc}$ ), which is consistent with the reported formation time of an intramolecular excimer of  $\sim 250$  ps in sandwich-linked dicarbazolyl compounds (*m*-DCzPe) and of  $\sim 140$  ps in Ant-(SiMe<sub>2</sub>)<sub>n</sub>-Ant, in which two anthracene groups are linked by disilane.<sup>101,102</sup> Meanwhile, it is found that the corresponding DAS of further relaxation of  $S_{exc}$  features a negative peak at  $\lambda_{pr} = 460\text{--}465$  nm, *i.e.*  $\sim 700$  cm<sup>-1</sup> blue shifted compared to the corresponding peak of Biph-2CzB, which can be explained by the reduced SE ( $S_1$ ) signal due to the  $S_1 \rightarrow S_{exc}$  transition and the lack of SE for the  $S_{exc}$  state. Therefore, the observed long-lived species on fs-TA of can be largely attributed to the formed  $S_{exc}$  state.

Intriguingly, the  $S_1/S_0$  ES-SR associated with CzB bending motion was missing in the fs-TA of Np-2CzB, which can be explained by two aspects: (1) CzB bending in the  $S_1$  state takes place in a similar timescale to  $S_{exc}$  formation, because of which the two parallel processes cannot be distinguished from each other; (2) CzB bending might be too weak to be detected, which is consistent with the low contribution of reorganization energy ( $\lambda_k = 15.1$  cm<sup>-1</sup>) of the corresponding vibrational mode at  $\omega_k = 15.8$  cm<sup>-1</sup>. Actually, as discussed above, since the pronounced bending motion of CzB units might be able to disrupt  $S_{exc}$  formation, the greatly suppressed bending motion of  $S_1/S_0$  ES-

SR might be the key factor for  $S_{exc}$  formation in Np-2CzB. On the other hand, please note that although external structural restraint in PMMA doped films leads to the kinetically faster formation of the  $S_{exc}$  state, there might be a higher ratio at which Np-2CzB cannot fully relax to the optimized structure of the  $S_1$  state for  $S_{exc}$  formation. As a result, we observed a significantly higher DF ratio of Np-2CzB in DCM solution ( $\Phi_{DF}/\Phi_F = 0.37$ ) than in PMMA doped films ( $\Phi_{DF}/\Phi_F = 0.20$ ).

Unlike Biph-2CzB, the delocalized nature of the  $S_{exc}$  state ensures that its electronic configuration is very different from the LE ( $\pi \rightarrow \pi^*$ ) nature of the  $S_1$  and  $T_1$  states, leading to the greatly enhanced  $\langle \Psi_{S_{exc}} | \hat{H}_{SO} | \Psi_{T_1} \rangle$  of Np-2CzB. Meanwhile, the nearly degenerate excitation energy of the  $S_{exc}$  and  $T_1$  states leads to  $\Delta E_{ST} < 0.02$  eV. As a result, an efficient RISC channel ( $T_1 \rightarrow S_{exc}$ ) with  $k_{RISC} = 6.5 \times 10^5$  s<sup>-1</sup> can be facilitated, leading to intrinsic TADF with  $\tau_{DF} = 2.50$   $\mu$ s and  $\Phi_{DF}/\Phi_F = 0.37$  in DCM solution. Through co-facial dimerization, we successfully converted a TADF-inactive chromophore (CzB,  $k_{RISC} = 1.5 \times 10^4$  s<sup>-1</sup>) into a TADF-active emitter (Np-2CzB,  $k_{RISC} = 6.5 \times 10^5$  s<sup>-1</sup>) with  $\sim 50$  times promotion of  $k_{RISC}$ .

## Conclusions

To summarize, we demonstrated a general strategy of molecular design, which can potentially facilitate the intrinsic TADF of



conjugated emitters with LE ( $\pi \rightarrow \pi^*$ ) dominated  $S_1$  and  $T_1$  states. With a TADF-inactive B,N-MR emitter as a model system, we synthesized a co-facial dimer with suitable structure and electronic coupling, in which an excimer-like state ( $S_{\text{exc}}$ ) was facilitated with  $\sim 250$  ps formation time. Relying on enhanced SOC ( $S_{\text{exc}}-T_1$ ) and reduced  $\Delta E_{\text{ST}}$ , an intrinsic TADF with  $k_{\text{RISC}} = 6.5 \times 10^5 \text{ s}^{-1}$  and  $\Phi_{\text{DF}}/\Phi_{\text{F}} > 37\%$  was successfully demonstrated in dilute solution. Further investigation indicated that a suitable co-facial distance ( $d = \sim 4.7 \text{ \AA}$ ) and inter-chromophore electronic coupling ( $J_{\text{coul}} > 450 \text{ cm}^{-1}$ ) are essential for  $S_{\text{exc}}$  formation, while suppressing a key vibrational mode (CzB bending) can be critical to avoid disrupting the inter-chromophore interaction. For the majority of conjugated organic emitters, the lack of intrinsic TADF greatly limits their application in emerging areas such as OLED and EPOL devices. Although the present strategy was demonstrated with a B,N-MR emitter as a model system, we believe that it can be regarded as a general strategy for other types of organic emitter, as long as they feature a rigid conjugated framework and localized  $\pi \rightarrow \pi^*$  character of  $S_1$  and  $T_1$  states. By activating the intrinsic DF emission, many traditional organic emitters might play more important roles in a wide range of applications, for which our work might provide inspiration for the community.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Yixuan Gao: conceptualization, methodology, investigation, data curation, formal analysis, visualization, and writing – original draft; Yingman Sun: synthesis the compounds; Zilong Guo: investigation, visualization, project administration, and supervision; Guo Yu: participated in the discussion of the inter-chromophore interaction; Yaxin Wang: methodology, data curation, formal analysis, and validation; Yan Wan: methodology and resources; Yandong Han and Wensheng Yang: resources and project administration; Dongbing Zhao: supervision, resources, and funding acquisition; Xiaonan Ma: conceptualization, formal analysis, funding acquisition, supervision, and writing – review & editing.

## Conflicts of interest

The authors declare no competing financial interest.

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