



The effect of dark states on the intersystem crossing and thermally activated delayed fluorescence of naphthalimide-phenothiazine dyads

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Abstract

A series of 1,8-naphthalimide (NI)-phenothiazine (PTZ) electron donor–acceptor dyads were prepared to study the thermally activated delayed fluorescence (TADF) properties of the dyads, from a point of view of detection of the various transient species. The photophysical properties of the dyads were tuned by changing the electron-donating and the electron-withdrawing capability of the PTZ and NI moieties, respectively, by oxidation of the PTZ unit, or by using different aryl substituents attached to the NI unit. This tuning effect was manifested in the UV–vis absorption and fluorescence emission spectra, e.g., in the change of the charge transfer absorption bands. TADF was observed for the dyads containing the native PTZ unit, and the prompt and delayed fluorescence lifetimes changed with different aryl substituents on the imide part. In polar solvents, no TADF was observed. For the dyads with the PTZ unit oxidized, no TADF was observed as well. Femtosecond transient absorption spectra showed that the charge separation takes ca. 0.6 ps, and admixtures of locally excited (³LE) state and charge separated (¹CS/³CS) states formed (in *n*-hexane). The subsequent charge recombination from the ¹CS state takes ca. 7.92 ns. Upon oxidation of the PTZ unit, the beginning of charge separation is at 178 fs and formation of ³LE state takes 4.53 ns. Nanosecond transient absorption (ns-TA) spectra showed that both ³CS and ³LE states were observed for the dyads showing TADF, whereas only ³LE or ³CS states were observed for the systems lacking TADF. This is a rare but unambiguous experimental evidence that the spin–vibronic coupling of ³CS/³LE states is crucial for TADF. Without the mediating effect of the ³LE state, no TADF is resulted, even if the long-lived ³CS state is populated (lifetime $\tau_{CS} \approx 140$ ns). This experimental result confirms the ³CS → ¹CS reverse intersystem crossing (rISC) is slow, without coupling with an approximate ³LE state. These studies are useful for an in-depth understanding of the photophysical mechanisms of the TADF emitters, as well as for molecular structure design of new electron donor–acceptor TADF emitters.

Introduction

Thermally activated delayed fluorescence (TADF) compounds are promising emitters to be used in organic light-emitting diodes (OLED) [1–12]. These emitters have the advantage of low cost and high harvesting efficiency of both the singlet and triplet excitons and thus a high quantum efficiency for the electroluminescence [13]. The TADF emission process involves the reverse intersystem crossing (rISC) from the triplet (T_1) state to the emissive singlet (S_1) state. A typical molecular structure motif for this kind of emitters is an electron donor–acceptor dyad, and the molecular geometry is usually orthogonal, i.e., the planes of the π -conjugation systems of the electron donor and acceptor are perpendicular to each other. As a result, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are spatially separated. This molecular geometry is beneficial to reduce the energy gap of the S_1/T_1 states, making the rISC possible. Because of the orthogonal molecular orbitals, the electron exchange energy (J) of the two unpaired electrons is small, which leads to a small energy gap ($2J$) of the S_1/T_1 states. Moreover, the orthogonal geometry is beneficial for the intersystem crossing (ISC) of the dyads, i.e., via the spin–orbit charge transfer ISC (SOCT-ISC) [14–18]. It can be considered as a generalization of the El-Sayed's rule for ISC. This SOCT-ISC may also enhance the rISC in OLED devices, in which the electron–hole recombination produces mainly the triplet state (the theoretical probability is 75%, by following the spin statistic rule) [1].

Compared to the application studies, the investigation of the photophysical mechanism of TADF emitters is far from mature [19–21]. Initially a two-state model was used for understanding of the photophysical processes of the electron donor–acceptor TADF emitters [9,22–26]. Soon it was realized this over simplified model is nonsufficient. For instance, the singlet/triplet charge-separated states ^1CS and ^3CS of these emitters are believed to undergo nonefficient slow interconversion, thus the poor rISC will not lead to efficient TADF. Later, a three-state model was proposed, i.e., the ^1CS , ^3CS , and a locally excited (^3LE) state should be involved in the TADF process. The rISC is facilitated by the ^3LE state, which shares a similar energy with the ^3CS state, e.g., the so called spin–vibronic coupling effect, and as a result, the rISC is fast and efficient, which can result in significant TADF [13,27–31]. It was also proposed that vibration facilitates the ISC in the TADF emitters [32,33]. However, the most popular optical spectroscopic methods previously used in this area, such as the very often used transient photoluminescence spectral measurement or the luminescence lifetime measurement, are unable to detect the dark states of the TADF emitters, i.e., the ^3LE and ^3CS states. Femtosecond transient absorption spectroscopy (fs-TA) was rarely used for the study of the photophysics of the TADF emitters [12,34–37],

since it suffers from the limitation of the time window of detection (up to a few ns). On the other hand, nanosecond transient absorption spectroscopy [38–44] and, more recently, time-resolved electron paramagnetic resonance (TREPR) spectroscopy [33,39,44–46] were also applied to study TADF mechanisms, but the examples are limited.

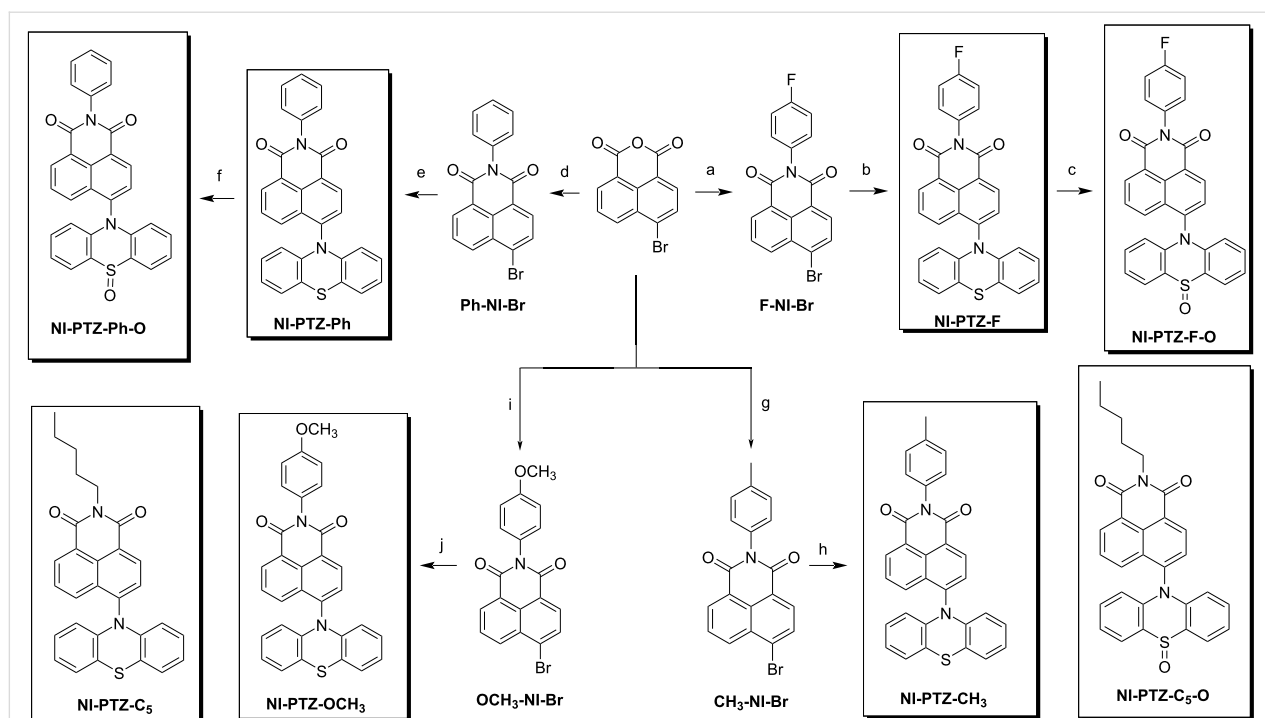
Therefore, much room is left for studies of the photophysical mechanism of the TADF emitters, especially to find experimental evidence of the spin–vibronic coupling effect, i.e., the involvement of the dark states, such as ^3LE and ^3CS states, in the TADF process of the electron donor–acceptor emitters.

In order to address the above challenge, herein we prepared a series of electron donor–acceptor dyads, based on naphthalimide (NI) as electron acceptor and phenothiazine (PTZ) as electron donor. The two units are connected by a C–N single bond, and they adopt orthogonal geometry due to conformational restriction. In order to tune the energy of the excited states, and to probe the effect of the energy ordering of the transient species involved in the TADF photophysical process, the electron-donating strength of the PTZ moiety is lowered by oxidation of the sulfur atom to the corresponding sulfoxide. Conversely, the electron-accepting capability of the NI unit is varied by introducing different aryl substituents, which contain both electron-donating and -withdrawing moieties. Although we reported **NI-PTZ** analogous dyads recently, they were not studied by fs-TA spectroscopy and the molecular structures are different from the current dyads [39,47]. The photophysical processes of the dyads were studied by steady state UV–vis absorption spectroscopy, transient photoluminescence spectroscopy, nanosecond/femtosecond transient absorption spectroscopy, electrochemistry, as well as DFT/TDDFT computations. We observed experimental evidence for the spin–vibronic coupling effect in the TADF photophysical processes of the electron donor–acceptor emitters.

Results and Discussion

Molecular design and structure confirmation

PTZ is a commonly used electron donor with strong electron-donating ability ($E_{\text{OX}} = +0.18$ V, vs Fc/Fc^+) [48], while the NI chromophore is an electron acceptor ($E_{\text{RED}} = -1.72$ V, vs Fc/Fc^+) [49]. By directly connecting the NI and PTZ unit through a C–N single bond, the π -conjugation plane of the NI and PTZ units adopts a perpendicular geometry which is beneficial for SOCT-ICS (Scheme 1). Previously we observed TADF with an analogue of **NI-PTZ-C₅** (the difference of the molecular structures is the alkyl chain, we called that analogue **NI-PTZ-N** here) [39]. In order to study the effect of tuning the energy and the ordering of the excited states on the photophysi-



Scheme 1: Synthesis of the compounds. Conditions: (a) 4-fluoroaniline, acetic acid, N_2 , reflux, 7 h, yield: 72%; (b) phenothiazine, sodium *tert*-butoxide, dry toluene, tri-*tert*-butylphosphine tetrafluoroborate, $Pd(OAc)_2$, 120 °C, 8 h, yield: 15%; (c) H_2O_2 (30%), CH_3COOH , 40 °C, 1 h, yield: 76%; (d) aniline, acetic acid, N_2 , reflux, 7 h, yield: 89%; (e) similar to step (b), yield: 52%; (f) similar to step (c), yield: 82%; (g) *p*-toluidine, acetic acid, N_2 , reflux, 7 h, yield: 83%; (h) similar to step (b), yield: 80%; (i) *p*-anisidine, acetic acid, N_2 , reflux, 7 h, yield: 75%; (j) similar to step (b), yield: 22%.

cal properties of the dyad, especially the ISC and TADF properties, we introduced electron-donating and -withdrawing aryl substituents on the NI unit (NI-PTZ-F, NI-PTZ-Ph, NI-PTZ-CH₃, NI-PTZ-OCH₃), and the electron-donating ability of the PTZ unit was modified by oxidation of the sulfur atom to the sulfoxide (NI-PTZ-F-O, NI-PTZ-Ph-O, NI-PTZ-C₅-O). The advantage of the oxidation approach is that almost only the energy of the ¹CS and ³CS states is changed, while other factors are kept intact to a large extent [46,50]. For instance, for the LE state, the electron exchange energy (*J*) for the unpaired electrons of the CS states (the energy gap of the ¹CS/³CS state is 2*J*), the energy gap of the ¹LE/³LE states of the NI moiety are not changed by the unique molecular structure modification method [51]. This approach is useful for studying molecules showing complicated, entangled photophysical processes upon photoexcitation, for instance the electron donor–acceptor type of TADF emitters [44,46]. Recently, we reported NI-PTZ analogous dyads, however, their molecular structures are different from the current dyads, and the photophysical properties were tuned by variation of the distance between the NI and the PTZ units, or by oxidation of the PTZ unit [47]. In the current dyads, we used different strategies.

A commonly used electron donor for the construction of electron donor–acceptor TADF molecules is carbazole. However,

since our aim was to study the TADF photophysics with model TADF emitters, the use of phenothiazine (PTZ) instead of carbazole presents a few advantages. First, upon connection of the electron acceptor (i.e., the NI unit) to the N atom of phenothiazine, a more restricted geometry is achieved than using carbazole. This is beneficial for the orthogonal geometry and thus TADF is ensured. Second, as compared with carbazole, the use of phenothiazine in the construction of TADF emitters offers an additional dimension to tune the photophysical properties, i.e., the phenothiazine unit can be oxidized to the sulfoxide, thus tuning the energy states ordering between the ¹CS, ³CS, and ³LE states. Moreover, the advantage of this molecular structure design is the ability to change only one factor (such as the CS state energy), while keeping other factors intact to a large extent (e.g., the LE state energy). This is an important advantage for the study of complicated photophysical mechanisms involved in TADF processes.

The syntheses of the dyads are based on the known derivatization chemistry of NI and PTZ chromophores, which are coupled through a Buchwald–Hartwig coupling reaction (another NI-PTZ paper) [39]. The oxidation of the PTZ unit was readily performed by treatment with H_2O_2 as oxidant (Scheme 1). All compounds were obtained with satisfactory yields and the molecular structures were fully characterized by

^1H NMR, ^{13}C NMR, and HRMS spectra (Experimental section).

UV-vis absorption and fluorescence emission spectra

The UV-vis absorption spectra of the compounds were studied (Figure 1 and Figure S29 in Supporting Information File 1). For the compounds without an oxidized PTZ unit, there are characteristic absorption bands in the 300–375 nm range, which are attributed to the NI moiety, i.e., originating from the $S_0 \rightarrow {}^1\text{LE}$ transition (Figure 1a). Moreover, in the range of 375–570 nm, there is a weak, broad absorption band centered at 460 nm, similar to the analogue **NI-PTZ-C₅** [39], which is assigned to the $S_0 \rightarrow {}^1\text{CS}$ transition [52–54]. In addition, the aromatic ring attached to the NI unit changing it from an electron-pulling group to an electron-pushing group, leads to a blue shift of the absorption peak of the CS and the absorbance decreases (Figure S30 in Supporting Information File 1). For the oxidized molecules, the $S_0 \rightarrow {}^1\text{CS}$ transition absorption peak is blue shifted to 360–420 nm (Figure 1b). These results indicate that upon oxidation of the PTZ unit, the electronic coupling between the donor and acceptor is reduced [55].

The fluorescence spectra of the compounds are studied (Figure 2 and Figure S31 in Supporting Information File 1). For the compounds with native PTZ unit, like **NI-PTZ-F**, there are broad, structureless fluorescence bands centered at ca. 620 nm in cyclohexane (CHX) and HEX, which are attributed to the CS state emission. Moreover, the fluorescence of the compounds is strongly quenched and red-shifted in polar solvents, as compared to that in CHX and HEX. The higher polarity solvents can stabilize the CS state, and the energy of CS state will decrease.

As a result, the emission band will be red-shifted and the fluorescence intensity will be greatly reduced. The results infer that the emissive S_1 state has a substantial CS character [56]. Thus, the assignment of the emissive S_1 state to a CS state is reasonable.

Upon oxidation of the PTZ moiety, the degree of fluorescence quenching in polar solvents became less significant than that of the compounds with a native PTZ unit (Figure 2e and 2f) [57]. Moreover, it is noted that the CS emission wavelength of **NI-PTZ-F-O** and **NI-PTZ-Ph-O** is different from a 4-diphenylamino-substituted NI [58]. These results indicate that the ${}^1\text{CS}$ state of these two dyads involves the oxidized PTZ unit as a whole electron donor, not only the N atom of the PTZ unit [59,60]. Further, the **NI-PTZ-F-O** and **NI-PTZ-Ph-O** compounds adopt an orthogonal geometry, and the N atom in the PTZ unit is not in π -conjugation with NI moiety due to a conformational restriction [55]. Thus, it is not the ordinary intramolecular charge transfer (ICT) state that affects the fluorescence of these two dyads. Indeed, the highly solvent polarity dependent fluorescence emission intensity, and wavelength are different from the 4-amino NI derivatives, which are much less solvent polarity-dependent [59,61].

Since a TADF molecule is characterized by a stronger fluorescence under nitrogen atmosphere and a substantial quenching under air or oxygen atmosphere [22], the fluorescence spectra of the dyads containing native PTZ unit under different atmospheres were studied (Figure 3a–d and Figure S32a in Supporting Information File 1). The results show that the fluorescence intensity of the dyads is stronger under a N_2 atmosphere, but is significantly quenched under air atmosphere. The fluorescence

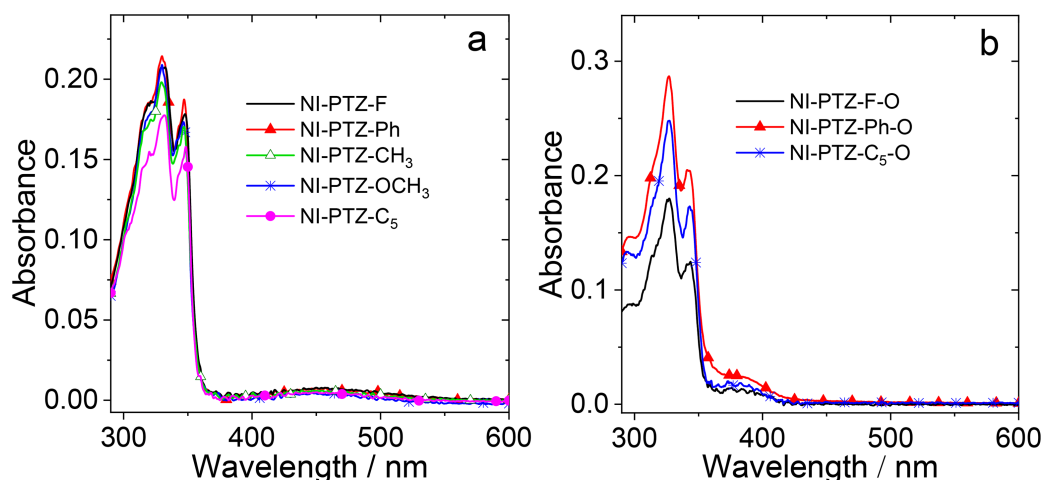
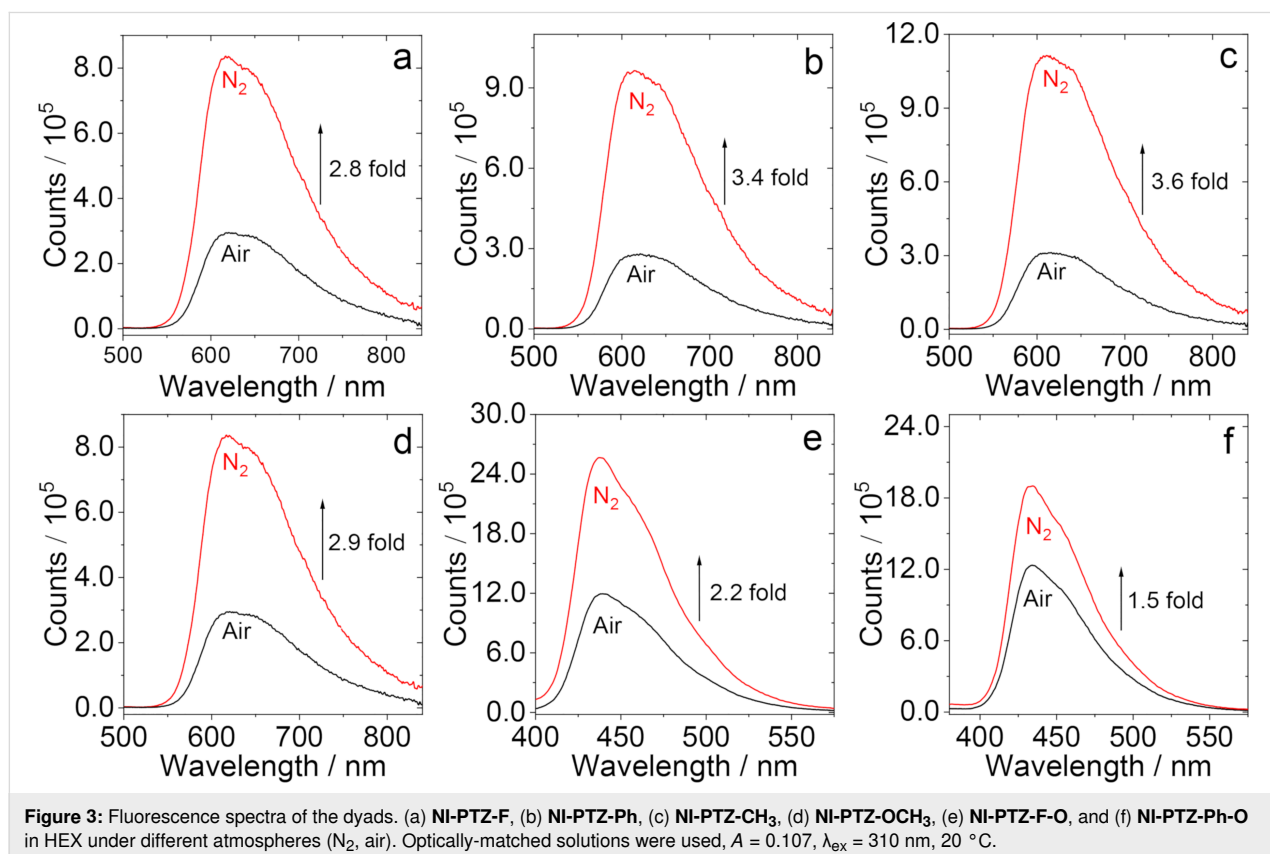
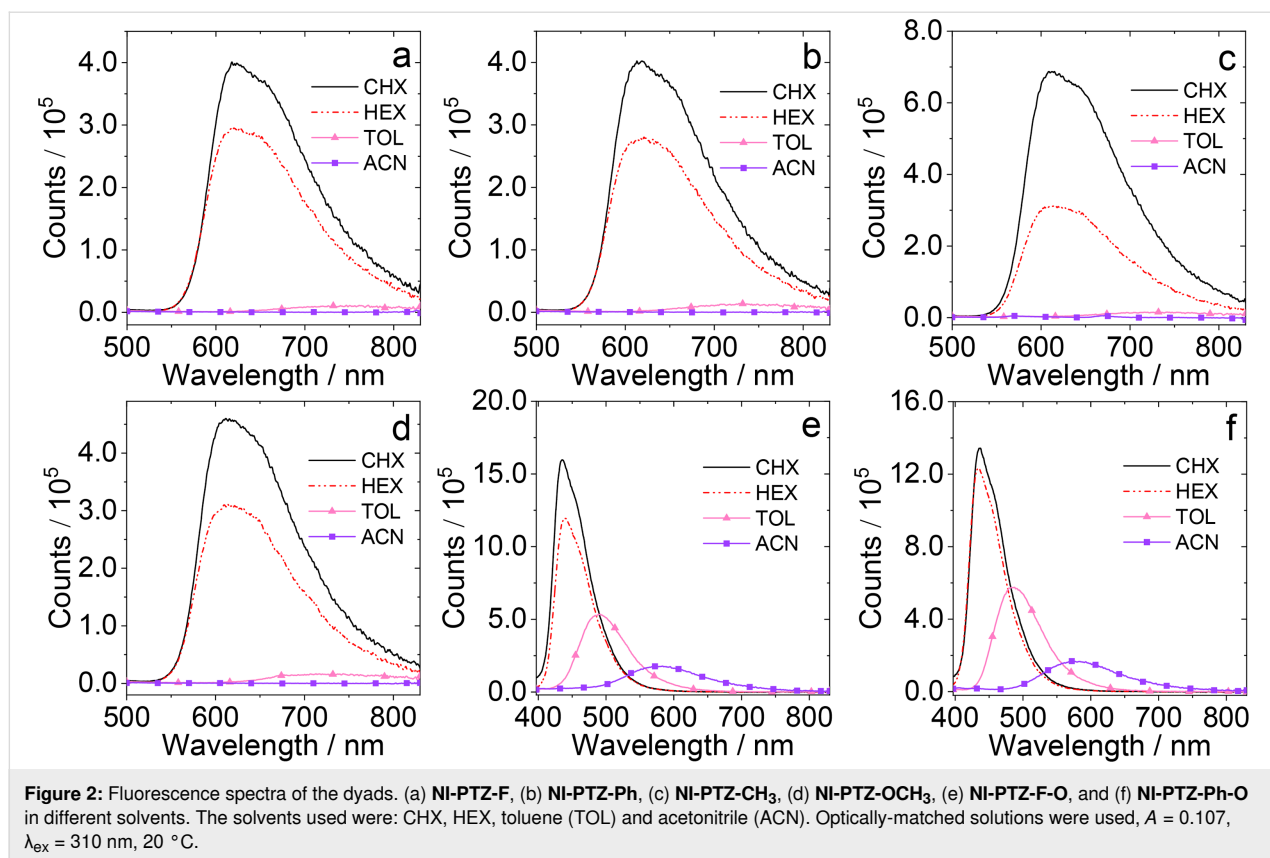


Figure 1: UV-vis absorption spectra of (a) **NI-PTZ-F**, **NI-PTZ-Ph**, **NI-PTZ-CH₃**, **NI-PTZ-OCH₃**, and **NI-PTZ-C₅** and (b) **NI-PTZ-F-O**, **NI-PTZ-Ph-O**, and **NI-PTZ-C₅-O** in *n*-hexane (HEX), $c = 1.0 \times 10^{-5}$ M, 20 °C.



intensity under N_2 atmosphere is 2–4 times higher than that under an air atmosphere. However, for the dyads with an oxidized PTZ unit (Figure 3e and 3f and Figure S32b in Supporting Information File 1), the fluorescence intensity is less dependent on the atmosphere. Moreover, we suggest that the reduced luminescence of the oxidized molecules in air may be caused by the quenching effect of oxygen to the S_1 state. According to this experimental phenomenon, we preliminarily speculate that the dyads with a native PTZ unit may have TADF property, but not for the oxidized molecules.

To confirm the above speculation, the fluorescence decay traces of the dyads were studied in detail (Figure 4 and Figure S33 in Supporting Information File 1). The fluorescence decay traces of the dyads containing native PTZ units in HEX show an obvious double exponential feature. For example, the lifetime of **NI-PTZ-F** is 24 ns (96.3%)/1.2 μ s (3.7%) under N_2 atmosphere (Figure 4a). The short-lived component can be attributed to the prompt fluorescence of $^1CS \rightarrow S_0$, while the long-lived component is the delayed fluorescence, via the rISC process. In addition, the lifetime of the long-lived component of the compound under air atmosphere is greatly shortened, which also verifies that these compounds have TADF properties. Moreover, with our derivatization approach, the geometry and

electron-donating ability of the PTZ unit are unchanged, but the electron-accepting ability of the NI part is changed by introducing different aryl substituents at the nitrogen of the NI unit. We found the magnitude of the long-lived components of the TADF emitters is changed (Figure 4a–d). Interestingly, the dyads with the oxidized PTZ unit do not have long-lived components (Figure 4e and 4f), and their fluorescence lifetimes are basically the same in nitrogen and air atmosphere and the lifetimes are on a nanosecond scale, indicating that the oxidized molecules do not have TADF properties. We reported NI-PTZ analogous dyads recently, however, the delayed fluorescence lifetimes were much longer (2.0–14.4 μ s) as compared to the current dyads [47]. TADF emitters with shorter delayed fluorescence lifetimes are suitable for fabrication of OLED devices, to suppress the efficiency roll-off effect.

The photophysical data of all compounds are compiled in Table 1. The fluorescence quantum yields (Φ_F) of the compounds were measured with an optical integration sphere and were in the range of 2–4% for the dyads with PTZ unoxidized and oxidized. It is interesting to note that the fluorescence quantum yields of the dyads are low, and similar to the native NI ($\Phi_F = 0.5\%$ in HEX), but much lower than for 4-diphenyl-amino-substituted NI ($\Phi_F = 75\%$ in HEX) [58]. We propose that

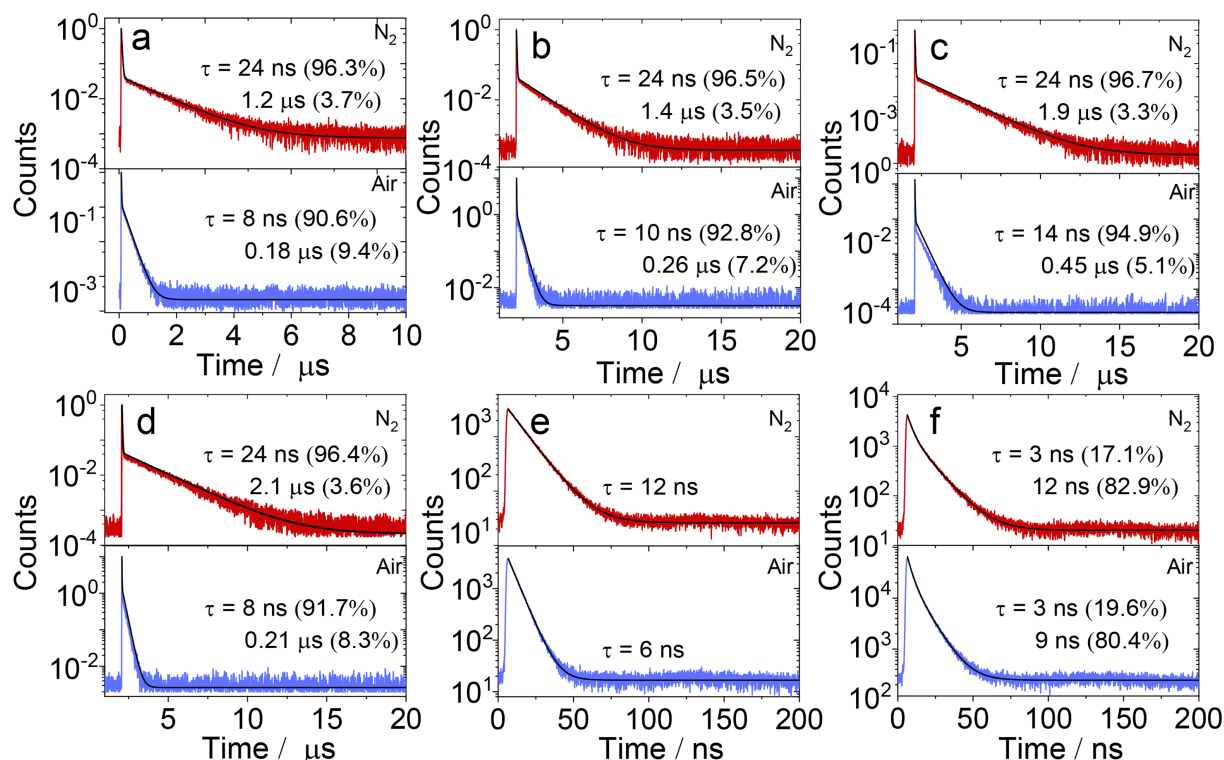


Figure 4: Fluorescence lifetime of (a) **NI-PTZ-F**; (b) **NI-PTZ-Ph**; (c) **NI-PTZ-CH₃**; (d) **NI-PTZ-OCH₃** ($\lambda_{em} = 610$ nm, $c = 1.0 \times 10^{-5}$ M) and (e) **NI-PTZ-F-O**; (f) **NI-PTZ-Ph-O** ($\lambda_{em} = 440$ nm, $c = 2.0 \times 10^{-5}$ M) in different atmospheres (N_2 , air). Excited with a picosecond pulsed laser ($\lambda_{ex} = 340$ nm), in HEX, 20 °C.

Table 1: Photophysical parameters of the compounds.

Compounds	$\lambda_{\text{abs}}(\text{nm})^a$	ϵ^b	$\lambda_{\text{em}}(\text{nm})^c$	$\tau_F(\text{ns})^d$	$\Phi_F(\%)^e$	k_r^f	k_{nr}^g
NI-PTZ-F	333	2.1	620	8 (90.6%) 180 (9.4%)	3.5	3.9 0.01	1.2 0.06
NI-PTZ-Ph	330	2.1	619	10 (92.8%) 260 (7.2%)	3.5	3.2 0.01	1.0 0.04
NI-PTZ-CH₃	329	2.0	611	14 (94.9%) 450 (5.1%)	3.5	2.4 0.0	0.7 0.02
NI-PTZ-OCH₃	330	2.1	611	8 (91.7%) 210 (8.3%)	4.1	4.7 0.02	1.2 0.05
NI-PTZ-C₅	332	1.8	611	9 (94.4%) 240 (5.6%)	2.6	2.7 0.01	1.1 0.04
NI-PTZ-F-O	329	2.0	440	6	3.5	5.8	1.6
NI-PTZ-Ph-O	330	2.1	434	3 (19.6%) 9 (80.4%)	4.1	2.7 3.7	3.3 1.1
NI-PTZ-C₅-O	332	1.8	433	6	2.6	4.3	1.6

^aMaximal UV–vis absorption wavelength in HEX, $c = 1.0 \times 10^{-5}$ M, 20 °C; ^bMolar absorption coefficient at absorption maxima in HEX, $\epsilon: 10^4 \text{ M}^{-1} \text{ cm}^{-1}$; ^cemission wavelength in HEX; ^dfluorescence lifetime under air atmosphere in HEX, $\lambda_{\text{ex}} = 340 \text{ nm}$; ^efluorescence quantum yields determined in HEX, $\lambda_{\text{ex}} = 310 \text{ nm}$; ^fradiative decay rate constant. $k_r = \Phi_F/\tau_F$, in 10^6 s^{-1} ; ^gnon-radiative decay rate constant. $k_{nr} = (1-\Phi_F)/\tau_F$, in 10^8 s^{-1} .

there is an efficient non-radiative decay channel for the S_1 state of these dyads, especially for the dyads with the oxidized PTZ unit. ISC is one possible relaxation pathway, because the orthogonal geometry of the dyads is beneficial for SOCT-ISC. Previously we have shown that SOCT-ISC occurs for the analogue of **NI-PTZ-C₅** [39].

In order to study the ISC efficiency of the dyads, we measured the singlet oxygen quantum yield (Φ_Δ) of the dyads in solvents with varying polarity (Table 2). For the dyads containing unoxidized PTZ, the Φ_Δ is less than 20% in non-polar solvents, and Φ_Δ becomes negligible in polar solvents. It should be noted that given the lowest transient species was not a ^3LE state, instead a CS state, no formation of $^1\text{O}_2$ should be observed (see below Figure 8 and Figures S36 and S37 in Supporting Information File 1). For the dyads with the oxidized PTZ unit, however, the

Φ_Δ are much higher, especially in polar solvents. These results indicate that the lowest state of these dyads is the ^3LE state, and the ISC yields are close to unit (see below Figure 9 and Figure S38 in Supporting Information File 1). However, these results do not necessarily mean that the ISC of the dyads containing a native PTZ unit is poor, it can be that the lowest transient state of these dyads is a CS state. We confirmed this is the case for the dyads of **NI-PTZ-F**, etc.

Electrochemistry study

In order to obtain the energy of the CS state, the electrochemistry of these compounds was studied (Figure 5). A reversible oxidation wave at +0.29 V (vs Fc/Fc^+) was observed for **NI-PTZ-F**, which is attributed to the oxidation of the PTZ part. Moreover, a reversible reduction wave was observed at −1.78 V (vs Fc/Fc^+) due to the reduction of the NI unit. For all the dyads

Table 2: Singlet oxygen quantum yields (Φ_Δ , in %) in different solvents.^a

Compounds	CHX	HEX	TOL	DCM	ACN
NI-PTZ-F	12	18	0	— ^b	— ^b
NI-PTZ-Ph	14	18	1	— ^b	— ^b
NI-PTZ-CH₃	15	17	0	— ^b	— ^b
NI-PTZ-OCH₃	14	23	2	— ^b	— ^b
NI-PTZ-C₅	17	19	1	— ^b	— ^b
NI-PTZ-F-O	25	30	50	100	100
NI-PTZ-Ph-O	23	26	46	100	90
NI-PTZ-C₅-O	28	36	48	100	96

^aThe $E_T(30)$ values of the solvents are 30.9 (CHX), 31.0 (HEX), 33.9 (TOL), 40.7 (DCM), and 45.6 (ACN), respectively, in kcal mol^{-1} . Singlet oxygen quantum yield (Φ_Δ) with $\text{Ru}(\text{bpy})_3[\text{PF}_6]_2$ as standard ($\Phi_\Delta = 0.57$ in DCM) in different solvents; $\lambda_{\text{ex}} = 340 \text{ nm}$; ^bnot observed.

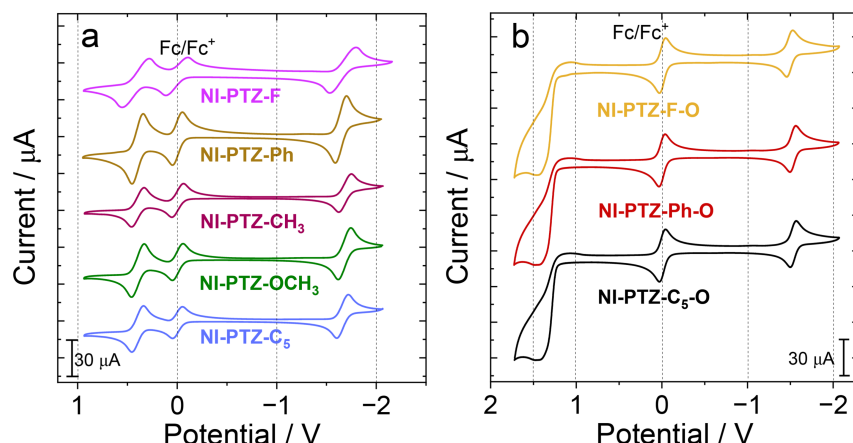


Figure 5: Cyclic voltammograms of the compounds. (a) **NI-PTZ-F**; **NI-PTZ-Ph**; **NI-PTZ-CH₃**; **NI-PTZ-OCH₃**; **NI-PTZ-C₅** in deaerated DCM and (b) **NI-PTZ-F-O**; **NI-PTZ-Ph-O**; **NI-PTZ-C₅-O** in deaerated ACN. Ferrocene (Fc) was used as internal reference (set as 0 V in the cyclic voltammograms), 0.10 M Bu₄NPF₆ as supporting electrolyte, scan rates: 100 mV/s, *c* = 1.0 × 10^{−3} M, 20 °C.

containing a native PTZ unit, the oxidation potentials are virtually the same. However, the reduction potential changes to some extent, which is consistent with our molecular design to keep the donor part unchanged and modify the NI part by introducing different electron-pushing and withdrawing aryl substituents at the nitrogen atom of the NI unit. For **NI-PTZ-F-O**, an irreversible oxidation wave at +1.38 V (vs Fc/Fc⁺) was observed, which may due to the weak electron-donating ability of the PTZ part after oxidation, and there was still a reversible reduction potential at −1.53 V (vs Fc/Fc⁺). Slightly cathodically shifted reduction waves were observed for other dyads containing an oxidized PTZ unit, i.e., **NI-PTZ-Ph-O** and **NI-PTZ-C₅-O**.

The redox potentials of the compounds are collected in Table 3. The Gibbs free energy changes (ΔG_{CS}) for charge separation (CS) as well as the energy of the charge transfer states (E_{CS}) were calculated using the Rehm–Weller equation (Equations 1–3) and the obtained values are listed in Table 4 [62–64].

$$\Delta G_{CS} = e(E_{OX} - E_{RED}) - E_{00} + \Delta G_S \quad (1)$$

$$\Delta G_S = \frac{e^2}{4\pi\epsilon_S\epsilon_0 R_{CC}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A} \right) \left(\frac{1}{\epsilon_{REF}} - \frac{1}{\epsilon_S} \right) \quad (2)$$

$$E_{CS} = e[E_{OX} - E_{RED}] + \Delta G_S \quad (3)$$

It should be noted that the E_{00} values used in the analysis is the S_1 state energy, not the T_1 energy, because we have shown that the CS is fast in this kind of compact dyads, and the precursor

Table 3: Electrochemical redox potentials of the compounds.^a

Compounds	$E_{(OX)}/V$	$E_{(RED)}/V$
NI-PTZ-F^b	+0.29	−1.78
NI-PTZ-Ph^b	+0.35	−1.69
NI-PTZ-CH₃^b	+0.33	−1.75
NI-PTZ-OCH₃^b	+0.33	−1.74
NI-PTZ-C₅^b	+0.34	−1.72
NI-PTZ-F-O^c	+1.38	−1.53
NI-PTZ-Ph-O^c	+1.38	−1.56
NI-PTZ-C₅-O^c	+1.37	−1.56

^aCyclic voltammetry in N₂-saturated solvents containing 0.10 M Bu₄NPF₆, a Pt electrode as the counter electrode, glassy carbon electrode as the working electrode, ferrocene (Fc/Fc⁺) as the internal reference (set as 0 V in the cyclic voltammograms), and Ag/AgNO₃ couple as the reference electrode; ^bmeasured in DCM; ^cmeasured in ACN.

of the CS is the ¹LE state [58]. From Table 4, it is found that the ΔG_{CS} of these compounds are negative in all solvents, indicating that the charge separation process is thermodynamically allowed in these solvents and the CS state energy of the dyads calculated by the redox potentials are slightly higher than the experimental values in HEX (the fluorescence, Figure 2). For the unoxidized molecules, with increasing solvent polarity, the CS state energy decreases sharply. From HEX to ACN, the CS state energy level decreases by ca. 0.7 eV. Note, we did not determine the electron exchange energy (*J*) concerning the unpaired electrons in the CS state (the energy gap of the ¹CS/³CS states is 2*J*). However, since the dyads have orthogonal geometry, the energy gap of the ¹CS/³CS states should be small, on a <0.1 eV scale [39,58]. For the dyads with oxidized PTZ moieties, the CS state energy is higher than that of the unoxidized molecules, and it is also decreased with increasing solvent polarity.

Table 4: Gibbs free energy changes of the charge separation (ΔG_{CS}) and energy of charge separation states (E_{CS}) of the compounds in different solvents.^a

Compounds	ΔG_{CS} (eV)				E_{CS} (eV)			
	HEX	TOL	DCM	ACN	HEX	TOL	DCM	ACN
NI-PTZ-F^b	−0.23	−0.39	−0.83	−0.95	2.38	2.22	1.78	1.66
NI-PTZ-Ph^c	−0.26	−0.42	−0.86	−0.98	2.35	2.19	1.75	1.63
NI-PTZ-CH₃^d	−0.29	−0.40	−0.84	−0.96	2.34	2.23	1.79	1.67
NI-PTZ-OCH₃^e	−0.25	−0.41	−0.85	−0.97	2.37	2.21	1.78	1.66
NI-PTZ-C₅^f	−0.26	−0.41	−0.86	−0.98	2.37	2.21	1.77	1.65
NI-PTZ-F-O^g	−0.02	−0.18	−0.63	−0.75	3.22	3.06	2.62	2.49
NI-PTZ-Ph-O^h	−0.01	−0.17	−0.62	−0.74	3.25	3.06	2.65	2.52
NI-PTZ-C₅-Oⁱ	−0.02	−0.18	−0.63	−0.75	3.24	3.08	2.64	2.51

^aCyclic voltammetry in deaerated solutions containing 0.10 M Bu₄NPF₆, a Pt electrode as counter electrode, a glassy carbon electrode as working electrode, and Ag/AgNO₃ couple as the reference electrode; ^b E_{00} = 2.61 eV; ^c E_{00} = 2.61 eV; ^d E_{00} = 2.63 eV; ^e E_{00} = 2.63 eV; ^f E_{00} = 2.62 eV; ^g E_{00} = 3.24 eV; ^h E_{00} = 3.26 eV; ⁱ E_{00} = 3.26 eV. E_{00} (E_{00} = 1240/ λ) is the singlet state energy of the compounds, λ is the wavelength of the crossing point of normalized UV–vis absorption spectra and fluorescence emission spectra.

The T₁ state of NI was determined as 2.25 eV (phosphorescence method) [65], and the T₁ state of the PTZ unit was determined as 2.45 eV (phosphorescence method) [66]. These energy levels are close to the CS states (Table 4), and thus, in HEX and TOL, the three states ¹CS, ³CS, and ³LE share a similar energy, and TADF may be resulted. For the dyads with the oxidized PTZ unit, the E_{CS} state of the **NI-PTZ-F-O**, **NI-PTZ-Ph-O**, and **NI-PTZ-C₅-O** was increased by ca. 0.8 eV. Thus, we do not expect TADF for these three dyads, especially in HEX. In polar solvents, such as ACN, no TADF was observed.

Thermal stability analysis (thermogravimetry analysis, TGA)

The thermal stability of TADF emitters is very important for the application in OLED devices. Therefore, the compounds were investigated by thermogravimetric analysis (TGA) and the results are shown in Figure 6 and Figure S34 in Supporting Information File 1. The thermal decomposition temperature (temperature at 5% thermal weight loss) of each compound were determined as follows: **NI-PTZ-F** (422 °C), **NI-PTZ-Ph** (375 °C), **NI-PTZ-CH₃** (436 °C), **NI-PTZ-OCH₃** (432 °C), **NI-PTZ-F-O** (371 °C), **NI-PTZ-Ph-O** (362 °C), **NI-PTZ-C₅** (436 °C), **NI-PTZ-C₅-O** (373 °C). The results show that the thermal stability of these compounds is excellent, and the thermal stability of dyads containing unoxidized PTZ units is better than those containing oxidized PTZ units.

Femtosecond transient absorption (fs-TA) spectra

In order to study the CS, charge recombination (CR), and ISC of the compounds, the femtosecond transient spectra were

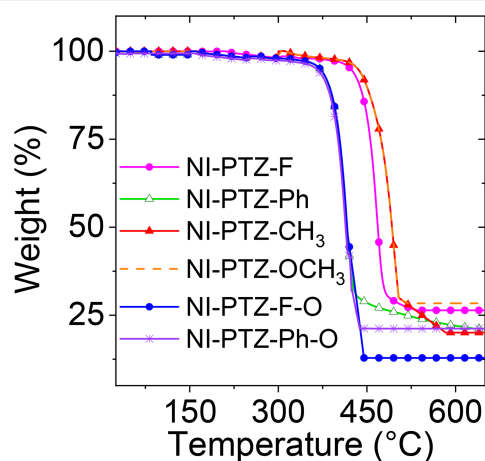


Figure 6: Thermogravimetric analysis curves of **NI-PTZ-F**, **NI-PTZ-Ph**, **NI-PTZ-CH₃**, **NI-PTZ-OCH₃**, **NI-PTZ-F-O**, and **NI-PTZ-Ph-O**. Temperature range: 25–800 °C, heating rate: 10 °C/min in N₂ atmosphere.

studied (Figure 7). Taking the **NI-PTZ-F** as an example, the transient absorption spectra measured in HEX and the evolution associated difference spectra (EADS), obtained by global fitting based on sequential kinetic model, are presented (Figure 7a and 7b). The first transient species (black line in Figure 7b) is attributed to a localized singlet excited state of ¹NI* by comparison with the reported spectra of NI [58]. Within 155 fs, the system evolves to the second spectrum (blue line), for which both a sharp peak centered at 404 nm and a broad band in the range 600–750 nm were observed, which is identified as a relaxation of the ¹NI* state and the evolution towards a CS state. Then, within about 599 fs, the system evolves to the third spectrum, which shows a sharp absorption

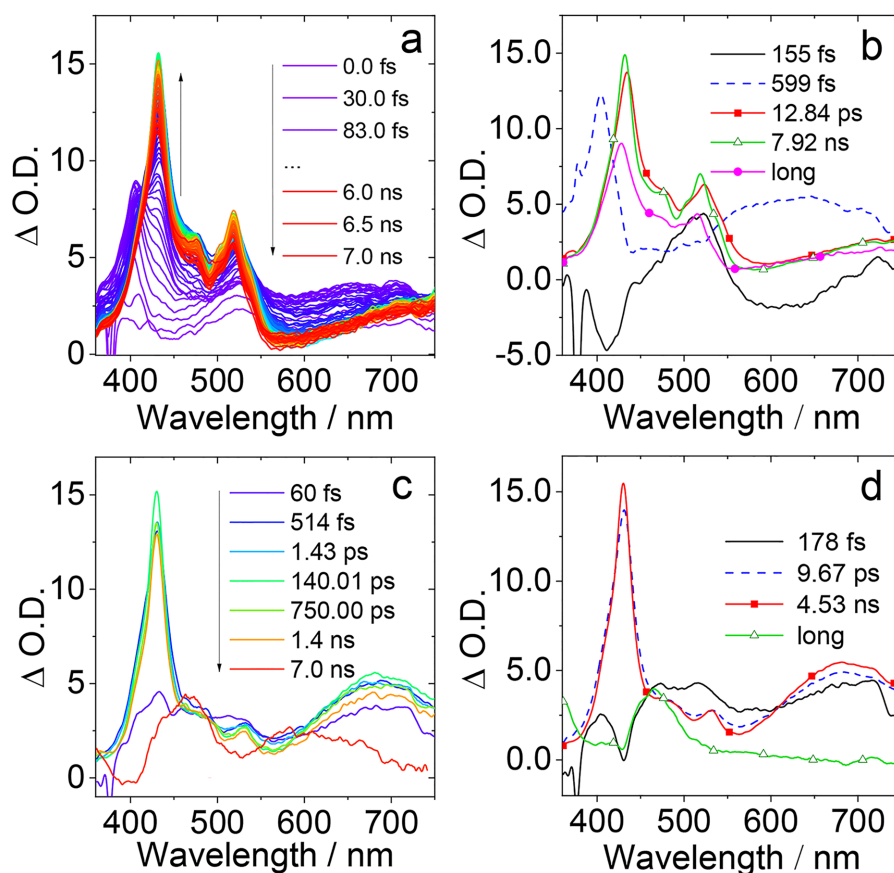


Figure 7: Femtosecond transient absorption spectra of **NI-PTZ-F**. (a) Transient absorption spectra and (b) the EADS obtained with global analysis in HEX. Femtosecond transient absorption spectra of **NI-PTZ-F-O**. (c) Transient absorption spectra and (d) relative EADS obtained with global analysis in ACN. $\lambda_{\text{ex}} = 340$ nm.

band centered at 433 nm and 522 nm, corresponding to the absorption of $\text{NI}^{\bullet}$ and $\text{PTZ}^{+\bullet}$, thus being a CS state. Then, within 12.84 ps, another spectrum is developed, which has still the characteristics of the CS state, however, the intensity of the two bands increases and both peaks blue-shift by about 3 nm, indicating a vibrational relaxation of the CS state and thus, we propose the geometry and solvent relaxation takes ca. 12.84 ps. At the same time, in this process, the triplet features of ^3LE start to appear (460 nm). Since the relaxed CS state and CR evolve within 7.92 ns, this is in agreement with the TADF luminescence studies (ca. 8 ns, Figure 4a), thus the decay of the ^1CS state in aerated solution takes ca. 7.92 ns. Then, the system evolves to the final spectrum (magenta), which is characterized by the features of ^3LE and CS states, and it is in good agreement with the ns-TA results (see below Figure 8a). Moreover, we propose that the precursor of the ^3CS state is the ^3LE state. While in ACN (Figure S35a and S35b in Supporting Information File 1), the fluorescence lifetime is not observed, we speculate that the lifetime of ^1CS state is too short, and finally within 8.08 ps, a ^3CS state has been formed, with some characteristic absorption peaks of $\text{NI}^{\bullet}$ (430 nm) and $\text{PTZ}^{+\bullet}$ (502 nm). Al-

though we reported **NI-PTZ** analogous dyads recently, the fs-TA spectroscopy was not used to study their photophysical processes [47].

Femtosecond transient spectra of **NI-PTZ-F-O** were also studied (Figure 7c and 7d). The solubility of **NI-PTZ-F-O** in HEX is poor, which leads to a poor transient spectral signal (Figure S35c and S35d in Supporting Information File 1) and we did not obtain the EADS, CS, CR, and other time constants exactly. In ACN, the first transient species (black line in Figure 7d) can be recognized as a localized singlet excited state of $^1\text{NI}^*$ by comparison with the spectra reported for the parent NI [58]. Within about 178 fs, the blue line, which has two sharp peaks at 430 nm and 530 nm and a wide peak at 600–750 nm, indicates the beginning of ^1CS state formation. Then, within 9.67 ps, there is a vibrational relaxation of the charge separated (CS) state (red line in Figure 7d). Later in about 4.53 ns, the triplet features of ^3LE appear with a characteristic absorption peak of $^3\text{NI}^*$ at 463 nm and this process can be ascribed to SOCT-ISC (green line in Figure 7d). This postulation is supported by the nanosecond transient spectra (see below).

Nanosecond transient absorption (ns-TA) spectra

In order to study the lowest-lying transient species of the dyads formed upon photoexcitation, the ns-TA spectra of **NI-PTZ-F** in HEX were studied (Figure 8a). Upon pulsed laser excitation, a positive absorption band centered at ca. 430 nm was observed, which is inconsistent with the characteristic triplet state absorption of the NI unit (460 nm) [39], while this positive absorption band is closer to that of $\text{NI}^{\bullet-}$, which was determined at ca. 430 nm [58]. Therefore, this absorption band is assigned to the NI radical anion. The excited state absorption (ESA) band centered at 460 nm is attributed to the ^3NI state. Moreover, another positive absorption band centered at ca. 510 nm is attributed to absorption of $\text{PTZ}^{+\bullet}$ [39]. Therefore, we propose that the lowest T_1 state of **NI-PTZ-F** is an admixture of ^3CS and ^3LE states. This is in agreement with the fs-TA spectral studies (Figure 7a and 7b). Similar ns-TA spectra were observed for other dyads without an oxidized PTZ unit (Figure S36 in Supporting Information File 1).

In order to study the solvent-dependency of the dyads containing native PTZ units, the ns-TA spectra of **NI-PTZ-F** in HEX, TOL, DCM, and ACN as solvents were studied (Figure 8). With increasing of the solvent polarity, the CS state energy will decrease, yet the ^3LE state energy will be intact to a large extent [58]. The results showed that in HEX, both ^3LE and CS states were observed. Herein, we assign the CS state to ^3CS , not ^1CS , based on lifetimes. Note, even if the ^1CS state (emission state) is populated via rISC, it is unlikely to be detected in ns-TA spectra due to its transient character (the lifetime of this state is

short, its concentration is too low to be detected by ns-TA spectroscopy) [67,68]. The monoexponential decay kinetics indicate that the ^3LE and ^3CS state are in good equilibrium, i.e., the spin–vibronic coupling, which is critical for the TADF [27,28,31,33,46].

In polar solvents, however, the ^3NI state signal in the ns-TA spectra diminished, but the $\text{NI}^{\bullet-}$ and $\text{PTZ}^{+\bullet}$ signals were persistent (Figure 8b, 8c, and 8d). Moreover, the transient species lifetimes decreased to 140 ns in ACN. In polar solvents, the CS state energy becomes lower, therefore, only the ^3CS state was observed. In this case, we assume the spin–vibronic coupling becomes weaker, accordingly, no TADF is resulted, even when the ^3CS state is populated. Similar results were found for other unoxidized compounds (Figure S37 in Supporting Information File 1). A theoretical model predicts that without the spin–vibronic coupling, the rISC is nonefficient and the TADF will be inhibited [27,28,46]. Therefore, our results represent a solid experimental evidence for the spin–vibronic coupling model of the TADF.

The ns-TA spectra of oxidized molecules were also studied (Figure S38 in Supporting Information File 1) in HEX. For **NI-PTZ-F-O**, the ESA bands centered at 360 nm and 460 nm were observed, which is attributed to the ^3NI state. Moreover, the ESA bands are similar to those observed for **F-NI-Br** and **NI-Br** [39]. Therefore, we propose that the low T_1 state of **NI-PTZ-F-O** is a ^3LE state. Similar results were found for other oxidized molecules. With the increase of the solvent polarity, the energy of the CS state decreases. Therefore, the

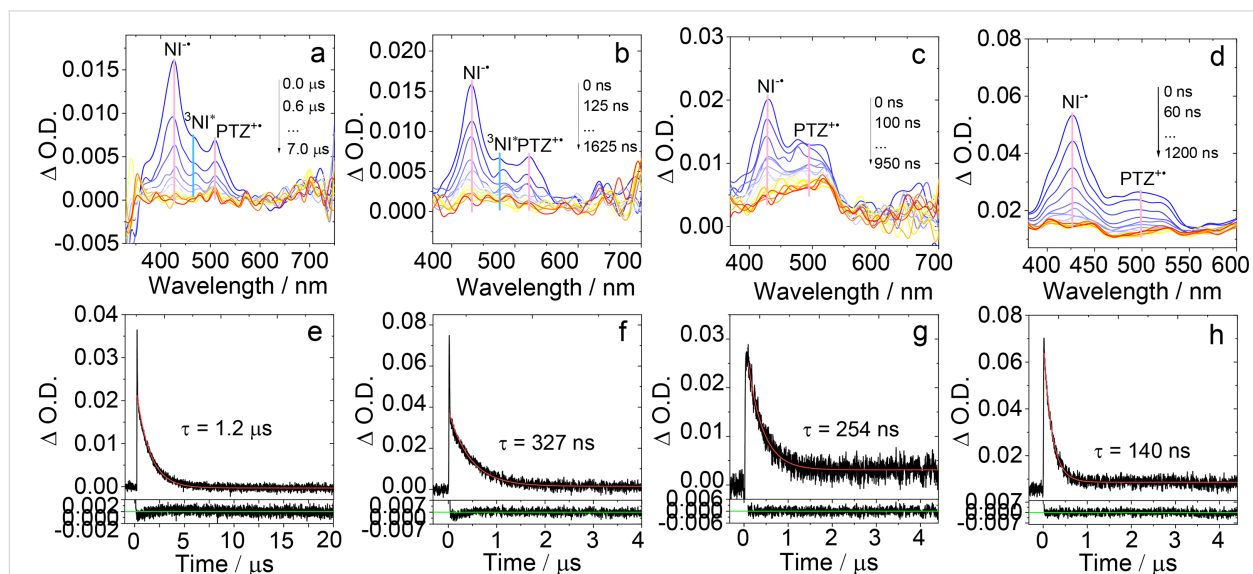


Figure 8: Nanosecond transient absorption spectra of **NI-PTZ-F** in deaerated solvents of (a) HEX ($c = 2.0 \times 10^{-5}$ M), (b) TOL ($c = 2.0 \times 10^{-5}$ M), (c) DCM ($c = 1.0 \times 10^{-4}$ M), and (d) ACN ($c = 1.0 \times 10^{-4}$ M). The corresponding decay traces are (e) HEX ($c = 2.0 \times 10^{-5}$ M), (f) TOL ($c = 2.0 \times 10^{-5}$ M), (g) DCM ($c = 1.0 \times 10^{-4}$ M), and (h) ACN ($c = 1.0 \times 10^{-4}$ M) at 430 nm. $\lambda_{\text{exc}} = 355$ nm, 20 °C.

ns-TA spectra of the compounds were studied (Figure 9) in ACN. We found that the transient absorption feature of the dyads with an oxidized PTZ unit does not change, i.e., a ^3LE state was observed even in ACN. This is supported by the ns-TA spectra of the reference compounds in ACN. Experimentally, no TADF was observed for these dyads. These results confirmed the critical role of the spin–vibronic coupling, i.e., the ^3LE mediate $^3\text{CS} \rightarrow ^1\text{CS}$ rISC in TADF [27]. The photochemical properties of each compound in different solvents are summarized in Table 5.

Computational investigations

The optimized ground state geometry of the dyads at the DFT-B3LYP/6-31G (d) level of theory determined with Gaussian 09

shows that the dihedral angles between the PTZ and NI moieties are close to 90° , which is beneficial for SOCT-ISC (Figure 10). Thus, the $^1\text{LE} \rightarrow ^1\text{CS} \rightarrow ^3\text{LE} \rightarrow ^3\text{CS}$ is facilitated, as well as the rISC processes, i.e., $^3\text{CS} \rightarrow ^3\text{LE} \rightarrow ^1\text{CS}$, thus the TADF becomes possible. Moreover, we found that the PTZ unit in the dyads adopts a puckered geometry (i.e., nonplanar geometry). This is known for the PTZ moiety [69,70]. We also optimized the geometry of the dyads at the S_1 and T_1 states (Tables S1 and S2 in Supporting Information File 1). In gas phase or nonpolar solvents, the dihedral angles between the NI and the PTZ moiety are in the range of $73\text{--}90^\circ$, close to that of the S_0 state. However, the PTZ unit adopts a planar geometry, especially for the S_1 and T_1 states optimized in polar solvents. It is known that the $\text{PTZ}^{+\bullet}$ adopts a planar geometry [69,70]. These results indi-

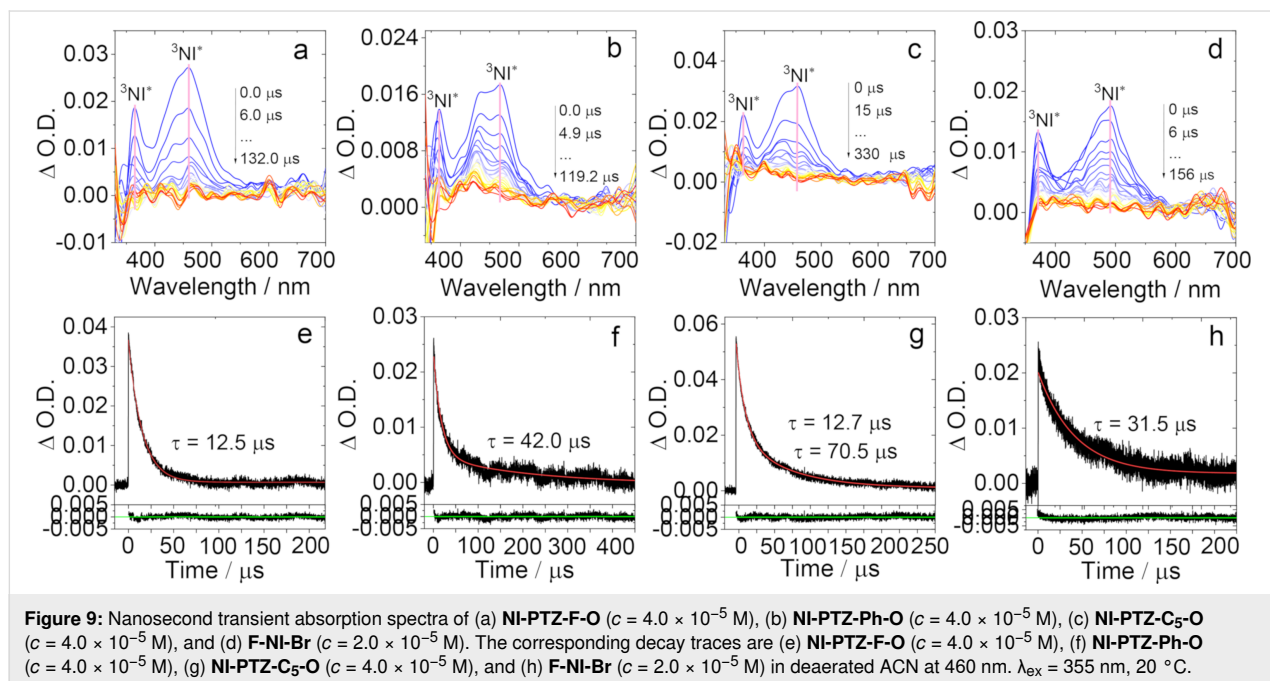


Figure 9: Nanosecond transient absorption spectra of (a) **NI-PTZ-F-O** ($c = 4.0 \times 10^{-5}$ M), (b) **NI-PTZ-Ph-O** ($c = 4.0 \times 10^{-5}$ M), (c) **NI-PTZ-C₅-O** ($c = 4.0 \times 10^{-5}$ M), and (d) **F-NI-Br** ($c = 2.0 \times 10^{-5}$ M). The corresponding decay traces are (e) **NI-PTZ-F-O** ($c = 4.0 \times 10^{-5}$ M), (f) **NI-PTZ-Ph-O** ($c = 4.0 \times 10^{-5}$ M), (g) **NI-PTZ-C₅-O** ($c = 4.0 \times 10^{-5}$ M), and (h) **F-NI-Br** ($c = 2.0 \times 10^{-5}$ M) in deaerated ACN at 460 nm. $\lambda_{\text{ex}} = 355$ nm, 20°C .

Table 5: Summary of photochemical properties of the compounds.

Compounds	TADF property		The last-observed transient species (fs-TA)		The lowest-lying transient species (ns-TA)	
	HEX	ACN	HEX	ACN	HEX	ACN
NI-PTZ-F	yes	— ^a	$^3\text{CS}, ^3\text{LE}$	^3CS	$^3\text{CS}, ^3\text{LE}$	^3CS
NI-PTZ-Ph	yes	— ^a	— ^b	— ^b	$^3\text{CS}, ^3\text{LE}$	^3CS
NI-PTZ-CH₃	yes	— ^a	— ^b	— ^b	$^3\text{CS}, ^3\text{LE}$	^3CS
NI-PTZ-OCH₃	yes	— ^a	— ^b	— ^b	$^3\text{CS}, ^3\text{LE}$	^3CS
NI-PTZ-C₅	yes	— ^a	— ^b	— ^b	$^3\text{CS}, ^3\text{LE}$	^3CS
NI-PTZ-F-O	no	no	— ^a	^3LE	^3LE	^3LE
NI-PTZ-Ph-O	no	no	— ^b	— ^b	^3LE	^3LE
NI-PTZ-C₅-O	no	no	— ^b	— ^b	^3LE	^3LE

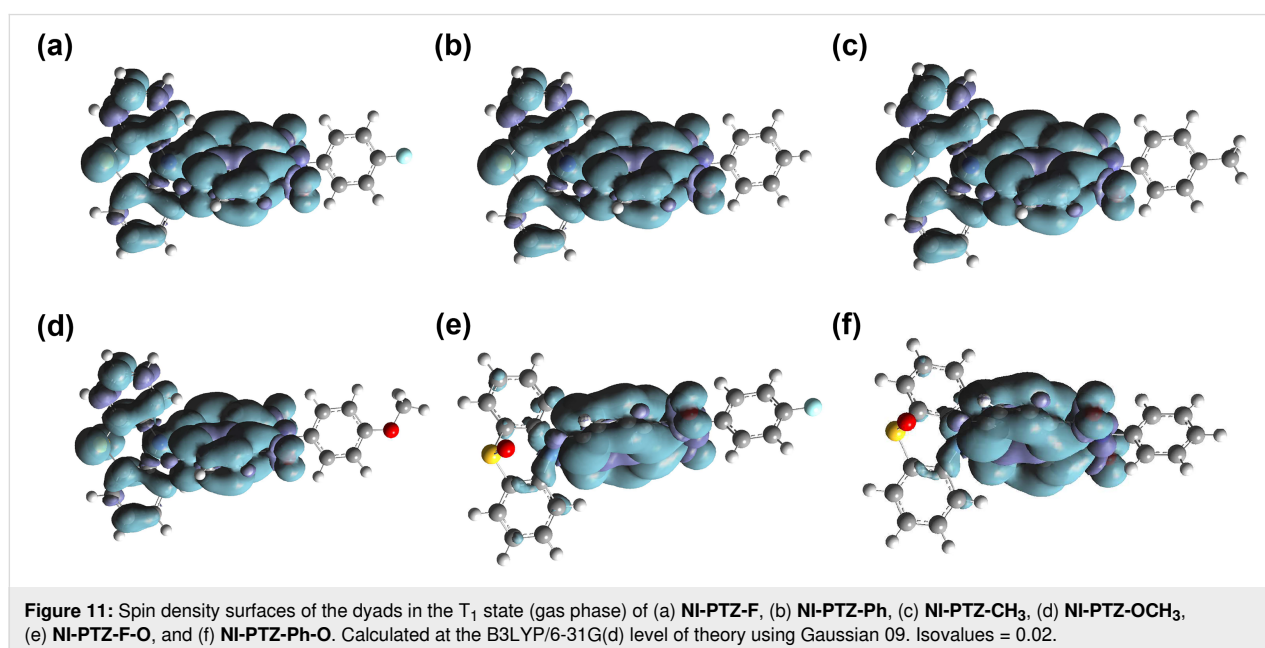
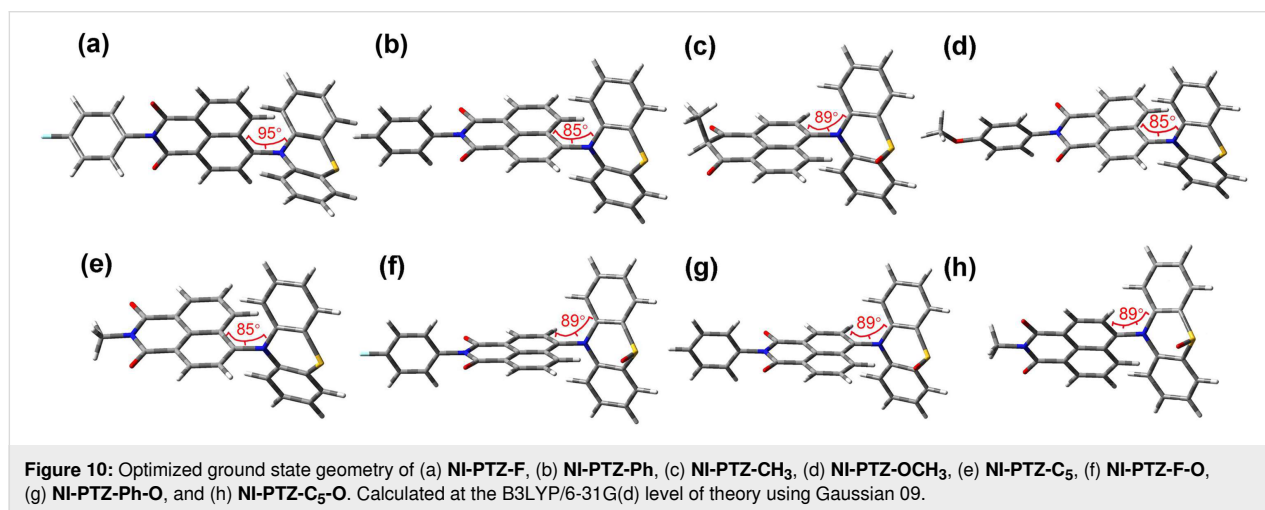
^aNot observed; ^bnot measured.

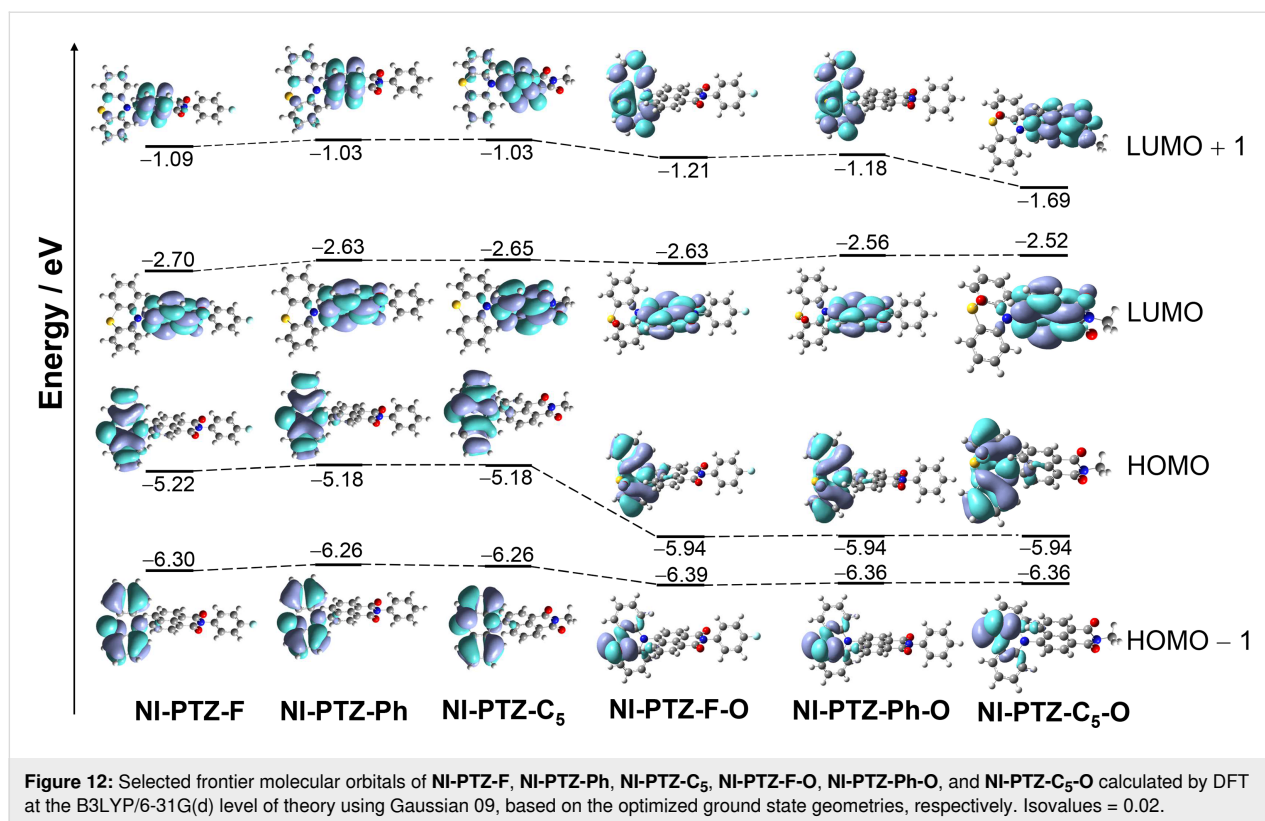
cate that the S_1 and T_1 states of the dyads containing a native PTZ unit are in the CS state. For the dyads containing an oxidized PTZ moiety, however, the PTZ moiety always adopts a puckered geometry, indicating the S_1 and T_1 states of these dyads are LE states, not CS states. These results infer that the T_1 state of the dyads with the oxidized PTZ is a ^3LE state, not a ^3CS state, even in polar solvents, such as ACN. These results are supported by the ns-TA spectral observations.

The spin density surface of the T_1 state of the dyads were also computed (Figure 11 and Table S3 in Supporting Information File 1). For the dyads containing a native PTZ moiety, the T_1 state density is delocalized on the NI and PTZ moieties. Since these two moieties have different T_1 state energies (2.25 and 2.45 eV, respectively), the T_1 state should be a ^3CS state, not an

equilibrium of $^3\text{PTZ}/^3\text{NI}$ state. In polar solvents (e.g., ACN), literally the same results were observed. These results are in agreement with the ns-TA spectral studies (Figure 8 and Figures S36 and S37 in Supporting Information File 1). For the dyads containing oxidized PTZ moieties, however, the T_1 state is always confined on the NI moiety. These results infer that the T_1 state of the dyads with the oxidized PTZ is a ^3LE state, not a ^3CS state, even in polar solvents, such as ACN. These results are fully supported by the ns-TA spectral observations (Figure 9 and Figure S38 in Supporting Information File 1).

The frontier molecular orbitals (MOs) were studied (Figure 12 and Figure S39 in Supporting Information File 1). For all the dyads, the HOMOs are confined on the PTZ or the oxidized PTZ moieties, whereas the LUMOs are localized on the NI





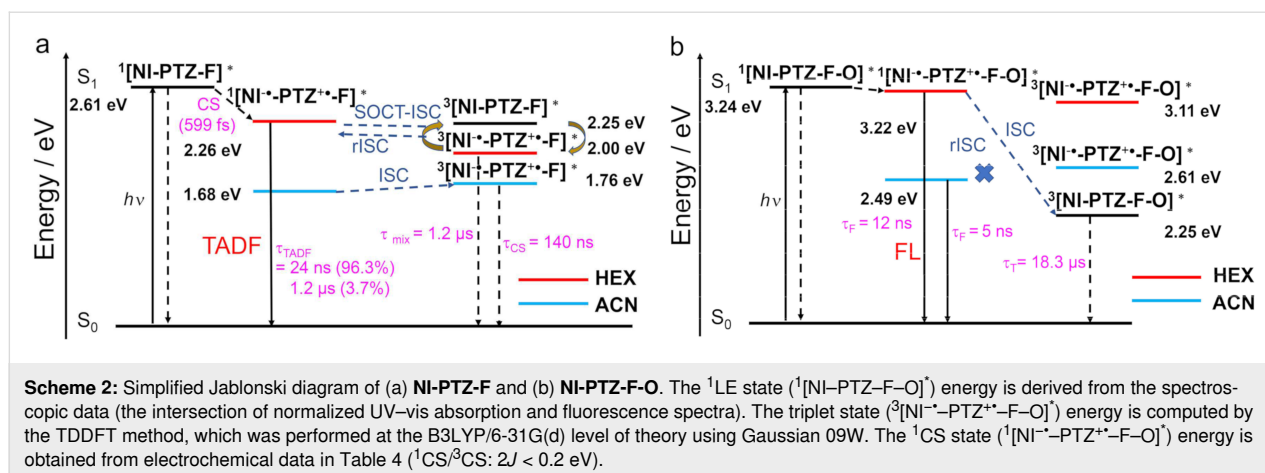
moieties. Interestingly, for the dyads containing a native PTZ moiety, the HOMO energy is slightly varied by up to 0.04 eV, which is attributed to the electron-withdrawal or donating feature of the aryl substituent attached to the nitrogen atom of the NI moieties. Interestingly, although there is no distribution of LUMO on the aryl moiety, the LUMO energy of the dyads are varied by up to 0.12 eV. These subtle variations of the molecular orbital energy impose effects on the photophysical property of the dyads, such as the delayed fluorescence lifetime of the TADF emissions. Of note, upon oxidation of the PTZ moiety in the dyads, the HOMO energy decreases substantially by up to 0.8 eV, whereas the LUMO energy changed by less than 0.2 eV. Thus, the HOMO/LUMO energy gap increases upon oxidation of the PTZ moiety. This is supported by the blue-shifted fluorescence of the dyads with the oxidized PTZ moieties as compared to the dyads containing the native PTZ moiety (Figure 2). Since the NI moiety is intact, the ³CS state becomes much higher than the ³LE state and we postulate the TADF will vanish for these dyads. This conclusion is fully supported by the experimental observations. These studies show that our strategy of tuning the energy ordering of the ¹CS, ³LE, and ³CS states by changing the electron-donating and withdrawal-capability of the PTZ and NI moieties is successful.

The photophysical processes of the dyads are summarized in Scheme 2. For **NI-PTZ-F**, the ¹CS, ³CS, and ³LE states share

similar energies. Thus, TADF was observed. The efficient spin–vibronic coupling of the ³CS/³LE states was supported by ns-TA spectral studies, in which both the ³CS and ³LE states were observed, and the two transient species decay with the same kinetics. In polar solvents, however, the CS state energy decreases sharply, yet, the ³LE state energy does not change, thus, although a long-lived ³CS state was found in ACN ($\tau_{\text{CS}} = 140$ ns), no TADF was observed. This is a solid experimental evidence that spin–vibronic coupling is essential for TADF, and the ³CS → ¹CS rISC is slow, without the coupling with the intermediate ³LE state. The conventionally used transient luminescence spectral method is unable to supply such in-depth mechanistic insights into the TADF mechanism. For the dyads with the oxidized PTZ units, however, the CS state energy is increased by up to 0.8 eV, yet the ³LE state energy does not change. Thus the spin–vibronic coupling between the ³LE and ³CS is weak and no TADF was observed for this dyad only a long-lived ³LE state was observed in the ns-TA spectra. These studies are useful for studying the complex photophysical processes involved in the TADF of electron donor–acceptor dyads, and for molecular structure design of new electron donor–acceptor TADF emitters.

Conclusion

In summary, we prepared a series of naphthalimide (NI)–phenothiazine (PTZ) electron donor–acceptor dyads, to make an



in-depth study of the photophysical mechanism of the thermally activated delayed fluorescence (TADF) of the electron donor–acceptor emitters. In order to tune the photophysical properties, we changed the electron-donating and the electron-withdrawal capability of the PTZ and NI moieties, respectively. From the UV–vis absorption and fluorescence emission spectra, we observed changes of $S_0 \rightarrow ^1\text{CS}$ absorption bands, which showed the tuning effect. For the dyads containing a native PTZ unit, TADF was observed, and with changing the aryl substituents at the NI unit, the prompt and delayed fluorescence lifetimes changed as well. In polar solvents, no TADF was observed. Moreover, we did not observe TADF in the dyads with oxidized PTZ units. Femtosecond transient absorption spectra show the charge separation takes ca. 0.6 ps, and the formation of the admixture of ^3LE and $^1\text{CS}/^3\text{CS}$ states was observed (in *n*-hexane). The decay of the ^1CS state and charge recombination (CR) in aerated *n*-hexane takes ca. 7.92 ns. While for the dyads with an oxidized PTZ unit, ^1CS state formation takes ca. 178 fs and the CR takes 4.53 ns to give the ^3LE state (in acetonitrile). Nanosecond transient absorption (ns-TA) spectra show that both ^3CS and ^3LE states were observed for the scenario where TADF occur, whereas only the ^3LE state or the ^3CS state were observed for the systems lacking TADF. This is a rare but unambiguous experimental evidence that the spin–vibronic coupling of $^3\text{CS}/^3\text{LE}$ states is crucial for TADF. Without the mediating effect of the ^3LE state, no TADF will be resulted, even if the long-lived ^3CS state is populated (lifetime $\tau_{\text{CS}} \approx 140$ ns). This experimental result confirms the $^3\text{CS} \rightarrow ^1\text{CS}$ reverse intersystem crossing (rISC) is slow, without coupling with an approximate ^3LE state. Thermogravimetric analysis (TGA) shows that the thermal decomposition temperature of these compounds is higher than 360 °C, and the thermal stability is excellent. From the above studies, TADF properties of such compounds can be studied with conventional spectroscopic methods (the UV–vis absorption and fluorescence emission spectra, etc.), and herein we also demonstrated

that transient absorption spectra (femtosecond/nanosecond transient absorption spectra) can be used to study the TADF properties, for instance by monitoring the dark states. In addition, we show that the TADF properties of these dyads can be tuned by changing the electron-donor (**NI-PTZ-F-O**, **NI-PTZ-Ph-O**) or electron-acceptor (**NI-PTZ-F**, **NI-PTZ-Ph**, **NI-PTZ-CH₃**, **NI-PTZ-OCH₃**). We found that the energy gaps between the three states (^1CS , ^3CS and ^3LE states), which can be judiciously controlled by molecular design, play an important role in the occurrence of TADF. These studies not only contribute to the in-depth understanding of the photophysical mechanism of TADF emitters, but also provide more molecular systems for the molecular structure design of new electron donor–acceptor TADF emitters.

Experimental

General methods

All the chemicals used in synthesis are analytical pure and were used as received without further purification. UV–vis absorption spectra were measured on a UV-2550 Shimadzu spectrophotometer. Fluorescence spectra were recorded with an FS5 spectrofluorometer (Edinburgh instruments Ltd., U.K.). Fluorescence quantum yields (Φ_F) were measured by an absolute photoluminescence quantum yield spectrometer (Quantaaurus-QY Plus C13534-11, Hamamatsu Ltd., Japan). Luminescence lifetimes of compounds were measured with an OB920 luminescence lifetime spectrometer (Edinburgh Instruments Ltd., U.K.). **NI-PTZ-F**, **NI-PTZ-Ph**, **NI-PTZ-CH₃**, **NI-PTZ-OCH₃**, and the oxidized molecules **NI-PTZ-F-O** were prepared according to the literature methods [11,39,43,71].

Synthesis of **NI-PTZ-F**

Compound **NI-PTZ-F** was synthesized by a modified literature method [39]. Under N_2 atmosphere, **F-NI-Br** (200 mg, 0.542 mmol), phenothiazine (130 mg, 0.650 mmol), $\text{Pd}(\text{OAc})_2$

(22 mg, 0.098 mmol), and sodium *tert*-butoxide (70 mg, 0.732 mmol) were dissolved in dry toluene (8 mL). Then, tri-*tert*-butylphosphine tetrafluoroborate (19 mg, 0.065 mmol) was added. The mixture was refluxed and stirred for 8 h under N₂. After cooling, water (20 mL) was added, and the mixture was extracted with ethyl acetate (3 × 30 mL). After separation, the combined organic layer was washed with water and brine (3 × 30 mL), respectively, dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/PE 1:5, v:v). Compound **NI-PTZ-F** was obtained as orange solid. Yield: 40 mg (15%); mp 136.2–137.2 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.87 (d, *J* = 7.63 Hz, 1H), 8.70 (d, *J* = 7.25 Hz, 1H), 8.60 (d, *J* = 8.51 Hz, 1H), 8.00 (d, *J* = 7.63 Hz, 1H), 7.77–7.81 (m, 1H), 7.29–7.35 (m, 4H), 7.11 (d, *J* = 7.51 Hz, 2H), 6.85–6.88 (m, 2H), 6.77–6.80 (m, 2H), 6.08 (d, *J* = 8.13 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 162.9, 158.1, 151.9, 142.6, 138.2, 138.2, 130.8, 130.3, 128.0, 127.6, 124.6, 123.5, 121.1, 117.5, 116.4, 111.8; HRMS–ESI (*m/z*): [M + H]⁺ calcd for C₃₀H₁₇FN₂O₂S, 489.0995; found, 489.1072.

Synthesis of NI-PTZ-Ph

NI-PTZ-Ph was synthesized by a reported method [11,71] similar to that of **NI-PTZ-F**. The crude product was purified by column chromatography (silica gel, DCM/PE 1:3, v:v). Compound **NI-PTZ-Ph** was obtained as orange solid. Yield: 243 mg (52%); mp 126.2–127.2 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.87 (d, *J* = 7.63 Hz, 1H), 8.70 (d, *J* = 7.13 Hz, 1H), 8.59 (d, *J* = 8.38 Hz, 1H), 7.99 (d, *J* = 7.63 Hz, 1H), 7.76–7.80 (m, 1H), 7.57–7.61 (m, 2H), 7.52 (d, *J* = 7.38 Hz, 1H), 7.35 (d, *J* = 7.25 Hz, 2H), 7.11 (d, *J* = 7.50 Hz, 2H), 6.77–6.87 (m, 4H), 6.09 (d, *J* = 7.76 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.1, 163.0, 143.7, 143.4, 138.8, 133.2, 133.0, 131.5, 130.5, 130.3, 130.2, 128.3, 128.0, 124.2, 122.1, 120.6, 115.8; HRMS–ESI (*m/z*): [M + H]⁺ calcd for C₃₀H₁₈N₂O₂S, 471.1089; found, 471.1159.

Synthesis of NI-PTZ-CH₃

NI-PTZ-CH₃ was synthesized with a method similar to that of **NI-PTZ-F**. The crude product was purified by column chromatography (silica gel, DCM/PE 1:3, v:v). The product was obtained as orange solid. Yield: 230 mg (80%); mp 100.2–101.5 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.87 (d, *J* = 7.63 Hz, 1H), 8.69 (d, *J* = 8.38 Hz, 1H), 8.58 (d, *J* = 8.50 Hz, 1H), 7.98 (d, *J* = 7.76 Hz, 1H), 7.75–7.79 (m, 1H), 7.38 (d, *J* = 8.01 Hz, 2H), 7.23 (d, *J* = 8.26 Hz, 2H), 7.10 (dd, *J*₁ = 1.50 Hz, *J*₂ = 1.50 Hz, 2H), 6.84–6.88 (m, 2H), 6.78–6.80 (m, 2H), 6.08 (dd, *J*₁ = 1.13 Hz, *J*₂ = 1.13 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.1, 163.7, 143.7, 138.8, 132.4, 132.2, 131.4, 130.5, 130.3, 130.2, 128.3, 127.1, 123.3, 120.6, 115.8,

21.3; HRMS–ESI (*m/z*): [M + H]⁺ calcd for C₃₁H₂₀N₂O₂S, 485.1245; found, 485.1325.

Synthesis of NI-PTZ-OCH₃

NI-PTZ-OCH₃ was synthesized by a method similar to that of **NI-PTZ-F**. The crude product was purified by column chromatography (silica gel, DCM/PE 1:5, v:v). The product was obtained as orange solid. Yield: 55 mg (22%); mp 123.2–124.3 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.87 (d, *J* = 7.63 Hz, 1H), 8.70 (d, *J* = 7.25 Hz, 1H), 8.58 (d, *J* = 8.51 Hz, 1H), 7.98 (d, *J* = 7.63 Hz, 1H), 7.75–7.79 (m, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.08–7.12 (m, 4H), 6.76–6.87 (m, 4H), 6.08 (d, *J* = 8.13 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.0, 163.7, 143.7, 143.4, 132.2, 131.4, 130.4, 129.5, 128.9, 128.6, 128.3, 127.1, 127.1, 123.3, 120.6, 115.8, 56.1; HRMS–ESI (*m/z*): [M + H]⁺ calcd for C₃₁H₂₀N₂O₃S, 501.1195; found, 501.1276.

Synthesis of NI-PTZ-F-O

Compound **NI-PTZ-F-O** was synthesized by a modified literature method [43]. Compound **NI-PTZ-F** (36 mg, 0.074 mmol) was dissolved in glacial acetic acid (5 mL), H₂O₂ (1.5 mL, 30%, 1.184 mmol) was added dropwise and the mixture was stirred at 40 °C for 1 h. Then, the reaction mixture was poured into water and the pH of the mixture was brought to 7 by the addition of saturated aqueous solution of Na₂CO₃. After cooling, water (10 mL) was added, and the mixture was extracted with ethyl acetate (3 × 20 mL). The organic layer was separated and washed with water and brine solution (3 × 20 mL), respectively. The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/MeOH 50:1, v:v) and the product was obtained as yellow solid. Yield: 28 mg (76%); mp 100.1–101.0 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.87 (d, *J* = 7.63 Hz, 1H), 8.70 (d, *J* = 7.26 Hz, 1H), 8.59 (d, *J* = 7.26 Hz, 1H), 8.00 (d, *J* = 7.26 Hz, 1H), 7.76–7.80 (m, 1H), 7.30 (d, *J* = 8.26 Hz, 4H), 7.11 (d, *J* = 7.51 Hz, 2H), 6.85–6.88 (m, 2H), 6.78–6.80 (m, 2H), 6.50 (d, *J* = 7.51 Hz, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.7, 163.4, 140.9, 140.3, 133.2, 133.1, 132.0, 130.6, 130.4, 130.3, 123.8, 123.6, 123.1, 116.8, 116.7, 116.5; HRMS–MALDI (*m/z*): [M + H]⁺ calcd for C₃₀H₁₇FN₂O₃S, 505.0944; found, 505.0973.

Electrochemical studies

The cyclic voltammetry curves were recorded with a CHI610D electrochemical workstation (CHI instruments, Inc., Shanghai, China) in N₂-purged saturated solutions containing 0.10 M Bu₄NPF₆ as a supporting electrolyte, a platinum electrode as counter electrode, a glassy carbon electrode as working electrode, and the Ag/AgNO₃ (0.1 M in ACN) couple as the refer-

ence electrode. Ferrocenium/ferrocene (Fc^+/Fc) redox couple was used as an internal reference.

Femtosecond transient absorption spectroscopy

Femtosecond transient absorption spectra (fs-TA) were acquired on a system based on a Ti:sapphire regenerative amplifier (Coherent Astrella). The system produces 40 fs pulses at 800 nm, with a repetition rate of 1 kHz. The instrument resolution is 100 fs. Excitation pulses at 340 nm were produced by a commercial parametric amplifier. The pump beam polarization was set to the magic angle with respect to the probe beam. The probe beam was obtained by focusing a small portion of the fundamental 800 nm beam on a 2 mm CaF_2 crystal, kept under continuous rotation to avoid damage. The pump-probe delay was introduced by sending the portion of the fundamental beam used for white light generation through a motorized translator. After focusing and overlapping the pump and probe beams at the sample position, the probe beam was directed through a spectrograph and to the detector. The sample was contained in a 1 mm quartz cuvette mounted on a movable stage, in order to avoid photodecomposition. The data were subdivided in two different time intervals and fitted using the Glotaran-Application 1.5.1 and Surface Explorer software. The number of kinetic components to be used for Global analysis was estimated by performing a preliminary singular values decomposition (SVD) analysis. All data were chirp-corrected before global fitting.

Nanosecond transient absorption spectroscopy

The nanosecond transient absorption spectra were measured on a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, Ltd., U.K.). The data (kinetic decay traces and the transient difference absorption spectra) were analyzed with the L900 software. All samples were deaerated with N_2 for ca. 15 min before measurement and excited with a nanosecond pulsed laser (OPO nanosecond pulsed laser). The wavelength is tunable in the range of 410–2500 nm.

Calculation study

The geometries of the compounds in their ground state were optimized using density functional theory (DFT) with the B3LYP functional and the 6-31G(d) basis set [72]. The excited state geometries of S_1 and T_1 were optimized with time-dependent TD-DFT (DFT) using the same functional and basis sets as in the ground state optimizations [73]. The spin density of the compounds were optimized using DFT with the B3LYP functional and 6-31G(d) basis set. The excitation energy of the compounds was calculated by TD-DFT at the B3LYP/6-31G(d) level of theory.

Supporting Information

Supporting Information File 1

General experimental methods, ^1H NMR, ^{13}C NMR, and HRMS spectra of the compounds as well as theoretical computation and photophysical data.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-19-79-S1.pdf>]

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