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Communication

New Direct Approach for Determining the Reverse Intersystem Crossing Rate in Organic Thermally Activated Delayed Fluorescent (TADF) Emitters

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ABSTRACT: We developed a new optical method to determine the rate of reverse intersystem crossing (k_{rISC}) in thermally activated delayed fluorescent (TADF) organic chromophores using time-resolved transient absorption spectroscopy. We successfully correlated the k_{rISC} of the TADF-chromophores with device performance. Specifically, we focused on the external quantum efficiency (η_{EQE}) and the stability of the device at high brightness levels. It is believed that by obtaining a large k_{rISC} one may reduce the possibility of triplet−triplet annihilation (TTA) and increase the long-term stability of organic light emitting diodes (OLEDs) devices at high brightness levels (η_{EQE} roll-off). In this contribution, we investigate the photophysical mechanism in a series of TADF-chromophores based on carbazole or acridine derivatives as donor moieties, and triazine or benzonitrile derivatives as the acceptor moieties. We found a relationship between large k_{rISC} values and high η_{EQE} values at low operating voltages for the TADF-chromophores investigated. In addition, those chromophores with a larger k_{rISC} illustrated a smaller η_{EQE} roll-off (higher stability) at high operating voltages. These features are beneficial for superior OLEDs performing devices. Contrarily, we found that if a chromophore has a $k_{rISC} \leq 10^5 s^{-1}$ its η_{EQE} is ≤5%. Such a small k_{rISC} suggests that there is no TADF effect operating in these organic systems and the molecule is not efficient in harvesting triplet excitons. Emission lifetime-based methodologies for determining the k_{rISC} were included for comparison but failed to predict the devices performance of the investigated TADF-chromophores to the same extent of our proposed methodology.

Organic light emitting diodes (OLEDs) based on chromophores with thermally activated delayed fluorescence (TADF) characteristics have captivated the attention of the scientific community as a potential replacement for their organometallic phosphors counterparts.[1−6] This is due to improvements including the devices' processability and ease of fabrication, synthetic flexibility for optical tuning, and cost-efficiency.[1,7,8] In addition, these TADF-based OLEDs are able to emulate the high internal quantum efficiencies ($\eta_{IQE} \approx 100$) offered by their Phosphors-OLED counterparts.[1,4,9] However, the key challenge hampering their commercialization is their poor device efficiency at high brightness levels, an effect known as efficiency roll-off.[10,11]

The high η_{IQE} has been ascribed to the conversion of nonemissive triplets into emissive singlets ($T_1 \rightarrow S_1$) in a reverse intersystem crossing process (rISC), which is made possible by the small energy gap between the singlet−triplet manifolds (ΔE_{ST}).[2,12] The field has primarily used steady-state measurements and microsecond spectroscopy to illustrate and calculate their k_{rISC}, under the premise that it may help to predict device performances.[1,7,13,14] Specifically, it is believed that obtaining a high k_{rISC} is critical for reducing the triplet−triplet annihilation (TTA) mechanism that causes η_{EQE} roll-off.[3,13,15] However, these indirect methods require a combination of selected tools and do not exclude the parallel coexistence of phosphorescence in the TADF-chromophore or the influence of the host material if the measurements are conducted in solid state.[3,16−20]

New methodologies applied to this problem, such as nanosecond transient absorption spectroscopy (ns TAS), can provide a powerful tool to examine the photophysical properties of organic chromophores with TADF characteristics. It is interesting to note that while there have been reports of studies investigating the quenching effect of molecular oxygen (O_2) in the emissive properties of highly efficient and well-known TADF systems, there have not been any detailed ns TAS O_2 quenching studies of these promising materials.[21,22] O_2 has been used for decades as a fundamental molecule for excited state sensitization.[21,23−25] The ns TAS is a time-resolved spectroscopic technique that can detect and resolve the dynamics of nonemissive intermediates contributing to the excited state of these chromophores in relatively long time scales (>10 ns).[26−34] These nonemissive conformers are detected as positive Δ absorption bands, namely excited state absorption (ESA).[21,30,33,35−37] By coupling O_2 with the ns

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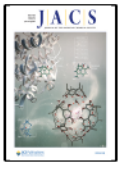

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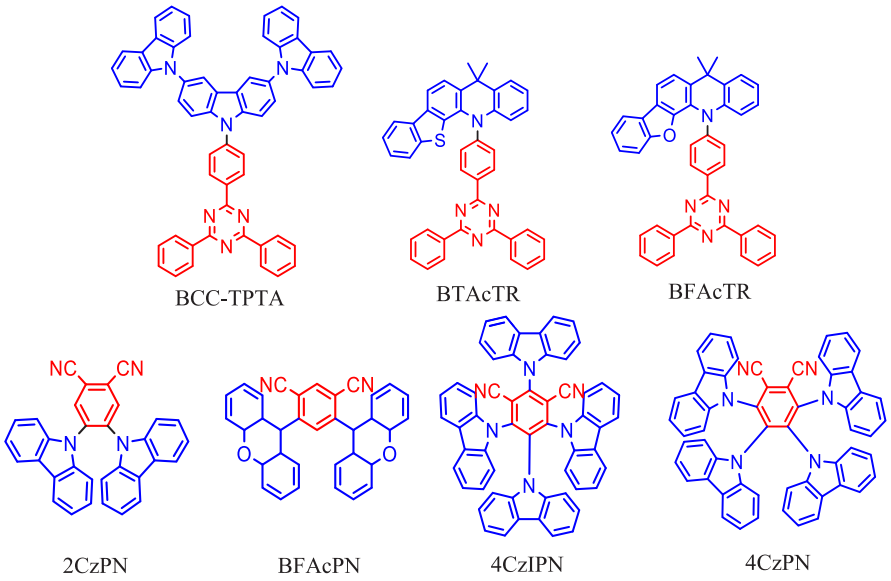

Figure 1. Molecular structure of the investigated TADF-active chromophores.

TAS technique, we aim to identify and characterize the ESA bands with O_2 sensitivity, which in these time scales, should be observed in a significant ESA decay lifetime lengthening attributed to triplets. In this publication, we present the first results of ns TAS spectroscopy to determine the k_{rISC} in organic chromophores with TADF characteristics by direct triplet state characterization. A series of chromophores with diverse molecular structures were investigated to demonstrate our methodology (Figure 1). Emission lifetime-based methodologies for estimating the k_{rISC} were included for comparison.

To demonstrate our ns TAS methodology, the well-known 2CzPN and BCC-TPTA were used as standards (Figure 2A; Figure 2B). For the 2CzPN system, two ESA bands were detected. These bands have been previously reported and attributed to triplet state conformations.[28,38] As we previously reported for BCC-TPTA, we did not detect long-lived ESA bands that are consistent with triplet density.[21] This was true despite detecting fast decaying ESA (singlets) for BCC-TPTA by the fs transient absorption technique (Figure S11). This is because our ns TAS technique operates at time scales longer than the time scales in where typical singlets conformation occurs, allowing us to discriminate between transient singlet and transient triplet conformations. In contrast to the BCC-TPTA chromophore, similar long-lived ESA bands to those obtained for the 2CzPN system were found for the remaining investigated chromophores. Therefore, oxygen sensitization experiments were carried out to further characterize the relaxation pathways of these long-lived ESA bands, namely triplets.

As it can be observed for 2CzPN in Figure 2E, a lengthening in its ESA relaxation dynamics was obtained when the measurements were conducted in O_2-free environments. A similar monoexponential decay constant of ~1.7 μs ($k_{Triplet}$ = 5.8 × 10^5 s^{-1}) was obtained for both ESA bands regardless of the solvent used. It is important to note that the lengthening in these ESA bands (triplets) lifetimes correlate well with the lengthening in the long-lived emissive lifetime of 2CzPN (Figure 3A) and with the significant quantum yield enhancement after purging oxygen (Φ_{TADF}). The Φ_{TADF} is quantified by the difference in Φ of the chromophore before and after purging oxygen. This Φ_{TADF} value is widely used to determine the k_{rISC} in emission lifetime-based methodologies.[13,17,22] We need to highlight that the ESA decay rate of 2CzPN is magnitudes higher than the reported rates of phosphorescence (K_P) in chromophores with TADF characteristics determined at low temperatures.[3] One can expect that this rate (K_p) will not get any larger at high temperatures. Therefore, we can rule out the possibility of room-temperature phosphorescence.

In the case of BTAcTr, there are two ESA bands (see Figure 2C) present. The **ESA 2** band showed a higher sensitivity to the presence of O_2.[25,39] A lengthening in the monoexponential decay of ~310 ns ($k_{Triplet}$ = 3.2 × 10^6 s^{-1}) was obtained for the **ESA 2** conformation in toluene (Figure 2G) and 183 ns ($k_{Triplet}$ = 5.6 × 10^6 s^{-1}) in chloroform (Figure S7) after purging oxygen. The lengthening in these ESA band lifetimes of BTAcTr correlates well with its Φ_{TADF} and with the lengthening in its long-lived emissive lifetime (Figure 3B). Similar behavior was obtained for the BFAcTr system in chloroform (Figure S7). A lengthening in the monoexponential decay with a time constant of 244 ns ($k_{Triplet}$ = 4.2 × $10^6 s^{-1}$) was obtained for the **ESA 2** band in O_2-free environments. Under these circumstances, we can attribute the **ESA 2** band to triplet state conformations. This assignment became more evident when a lack of ESA bands is observed by the ns TAS for BFAcTr in toluene solution (Figure S6). This lack of ESA bands correlates well with the BFAcTr lack of a long-lived emissive component when toluene is used as the solvent (Figure 3C). In the case of BFAcPN (Figure 2D), multiple ESA bands were detected with **ESA 2** and **ESA 3** showing a similar decay profile and time decay of ~1.1 μs ($k_{Triplet}$ = 9.1 × 10^5 s^{-1}) regardless of the solvent used. As with the 2CzPN, BTAcTr, and BFAcTr systems, the ESA band lifetime lengthening of BFAcPN in O_2-free environments correlates well with its Φ_{TADF} and with the lengthening in its long-lived emissive lifetime.

Despite the fact that O_2 is a fairly nondiscriminatory excited-state quencher, the overwhelming evidence obtained from multiple spectroscopic techniques connects the Φ_{TADF} (Table S4) of these systems with (1) an increase in their long-lived ESA band lifetime and (2) an increase in their long-lived

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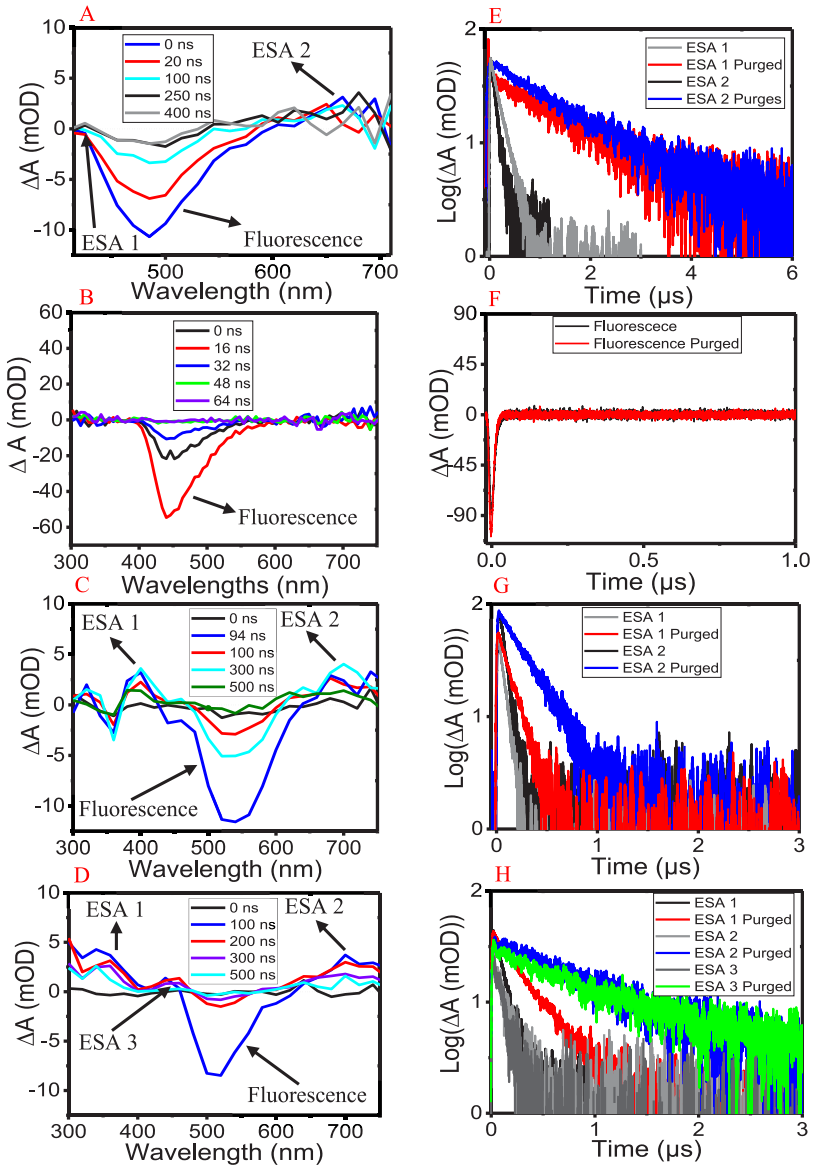

Figure 2. Time-resolved absorption spectra of 2CbzPN (A), BCC-TPTA (B), BTAcTr (C), and BFAcPN (D). ESA decay relaxation profiles of 2CbzPN (E), BCC-TPTA (F), BTAcTr (G), and BFAcPN (H).

emissive lifetime. Under these circumstances and time scales, it becomes evident that purging oxygen from the solution resulted in mostly unquenched triplet excited states that may contribute to the long-lived emissive lifetime of the investigated chromophores, as it was recently reported for some of these, and others, TADF-active systems.[22] Consequently, these results strongly suggest that at least part of the nonemissive triplet density is converted into emissive singlets through the rISC mechanism. Here, we proposed quantifying the amount of nonemissive triplets converted into emissive singlets, namely the k_{rISC}, by multiplying the deactivation rates of these ESA bands ($k_{Triplets}$) in O_2-free environments by the Φ_{TADF} factor (eq 1):

$$k_{rISC} = k_{Triplet} * \Phi_{TADF} \quad (1)$$

Rates of 3.5×10^6 s^{-1}, 9.8×10^6 s^{-1}, 4.1×10^7 s^{-1}, and 7.2×10^7 s^{-1} were obtained for 2CzPN, BFAcPN, BFAcTr, and BTAcTr, respectively (Table 1). These k_{rISC} magnitudes seem to concur to some extent with the quantum chemical simulations (QCS) presented here (Supporting Information) and with those published by Brédas.[5] We used the k_{rISC} determined by our methodology and correlated them with their device performance under the same device architectures. We obtained a proportional relationship between the k_{rISC} and η_{EQE} (Figure 4), with TADF chromophores with the larger k_{rISC} showing higher η_{EQE}. Specifically, η_{EQE} of 9%, 14.1%, 20.4%, and 21.8% for 2CzPN, BFAcPN, BFAcTr, and BTAcTr systems were reported, respectively. To further validate our methodology, we used it to determine the k_{rISC} of some well-known TADF chromophores from the limited transient absorption data published in the literature. A relationship between the k_{rISC} and the η_{EQE} was obtained for systems such as 4CzIPN and 4CzPN. Specifically, a k_{rISC} of 2.2×10^7 s^{-1} and 7.0×10^6 s^{-1} correlating well with η_{EQE} values of 19.3% and 17.8% were observed, respectively.[2,41] It is interesting to note that if the chromophore (*o*-CzBN, *m*-CzBN, *p*-CzBN) possess a $k_{rISC} \leq 10^5$ s^{-1}, an $\eta_{EQE} \leq 5\%$ is obtained (Table S2). These results suggest the minimum k_{rISC} that a TADF chromophore

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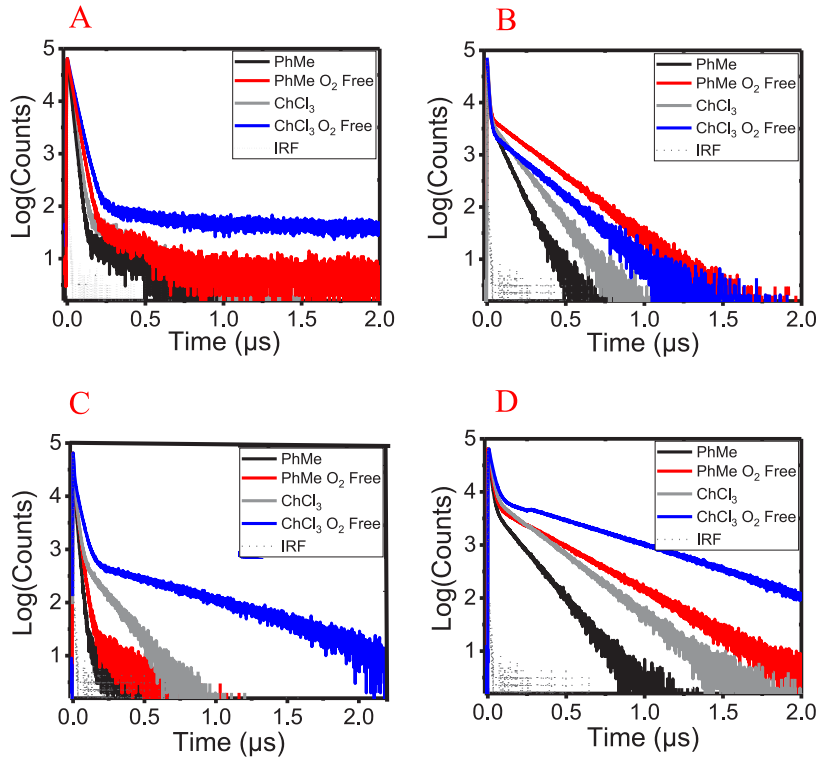

Figure 3. Emissive lifetime characterization of 2CbzPN (A), BTAcTr (B), BFAcTr (C), and BFAcPN (D).

Table 1. k_{rISC} Comparison and Device Performances Summary of the TADF-Active Systems[a]

Chromophore	k_{rISC} 10^7 s^{-1} (Our-Method)	EQE_{MAX}	k_{rISC} 10^7 s^{-1} (Emission lifetime-based)
BTAcTr	7.2	21 [40]	7.65
BFAcTr	4.6	20.4 [40]	1.03
4CzIPN	2.2	19.3 [2,41]	1.4[42]
4CzPN	0.70	17.8 [2,41]	0.047
BFAcPN	0.98	14.1[Sup.Info]	1.45
2CzPN	0.35	9 [2]	0.060

[a]EQE_{MAX} = maximum EQE value at low operating voltages.

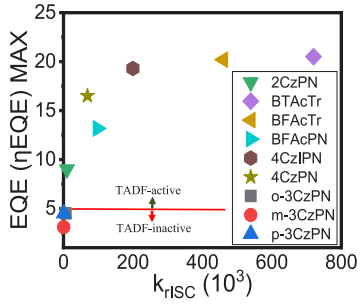

Figure 4. Correlating the device EQE with the k_{rISC}.

must possess to be able to harvest triplet excitons in the device via an rISC process and be a TADF-active emitter.

It is believed that TADF emitters with a large k_{rISC} may reduce the TTA mechanism responsible for the η_{EQE} roll-off in OLEDs.[1,3,15,26] In the case of the chromophores with triazine as acceptor, a reduced η_{EQE} roll-off was observed for BTAcTr (5%) while the higher η_{EQE} roll-off was observed for BCC-TPTA (76%); its lack of ESA bands suggests minimal triplet exciton conversion to singlet excitons.[21] In the case of the TADF chromophores with benzonitrile functionalities as the acceptor, reduced η_{EQE} roll-offs were found for 4CzIPN (6%), BFAcPN (8.5%), and 4CzPN (10%) in comparison with that of 2CzPN (55%).[2,41] These observations are also consistent with obtaining a large k_{rISC} and reducing the η_{EQE} roll-offs (Figure S2).

Emission lifetime-based methodologies for calculating the k_{rISC} were included for comparison.[13,17,22] Rates of 6.0×10^5 s^{-1}, 1.45×10^7 s^{-1}, 1.03×10^7 s^{-1}, and 7.65×10^7 s^{-1} were obtained for 2CzPN, BFAcPN, BFAcTr, and BTAcTr, respectively. Unlike the case for our methodology, no trends between the krISC determined by emission lifetime-based methodologies and the ηEQE were obtained. This was also true when the published emissive lifetime data for well-known TADF-chromophores were taken into consideration. It is interesting to note that $\eta_{EQE} \leq 5\%$, which implies TADF-inactive emitters,[38] were reported for some chromophores (*o*-CzBN and *p*-CzBN, Table S2) whose k_{rISC} determined by emission lifetime-based methods were within the same order of magnitude ($\geq 10^4$ s^{-1}) as with TADF-active emitters. Contrarily, our methodology showed that these TADF-inactive chromophores possess k_{rISC} ($\leq 10^5$ s^{-1}), highlighting the minimal k_{rISC} magnitude that a TADF chromophore must possess to be TADF-active. These observations were not achieved when traditional emission lifetime-based methods were employed.

In conclusion, we developed a new optical strategy for the direct determination of the k_{rISC} in organic chromophores with TADF characteristics. Our methodology allowed us to (a)

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directly characterize the triplet state dynamics for determining the k_{rISC} in organic TADF chromophores and (b) highlight the correlation of a large k_{rISC} with a high η_{EQE} value and its device stability for TADF-OLEDs at high operating voltages. We also illustrated the correlation of obtaining a $k_{rISC} > 10^5 s^{-1}$ for efficient TADF-active molecules. These structure−function relationships were not possible by using emission lifetime-based methodologies. This work may facilitate the excited-state characterization of organic chromophores with TADF characteristics and will help to discover top TADF candidates for superior OLEDs device performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c01225.

Additional experimental and computational details: (1) fluorescence quantum yield (Φ) measurements, (2) emission lifetime based methodology for determining the k_{rISC}, (3) Steady-State measurements, (4) experimental calculation of the ΔE_{ST}, (5) approach for determining the k_{rISC} and ΔE_{ST} via QCS, (6) detailed time-resolved ns TAS and TCSPC analysis, (7) fs TAS measurements for BCC-TPTA (PDF)

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Notes

The authors declare no competing financial interest.

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