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Technical Note

A Low-Cost Test Method for Accurate Detection of Different Excited-State Species with a Lifetime Span over 5 Orders of Magnitude in One Time Window

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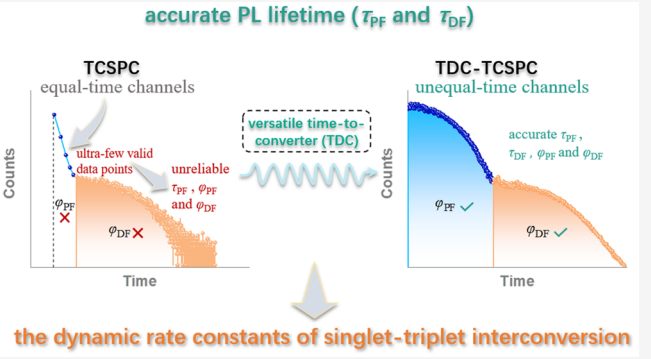
ABSTRACT: Accurate quantification on the quantum yields (φ) of both the prompt fluorescence (PF) and the delayed fluorescence (DF) species is quite essential for the clarification of molecular design rationales for thermally activated delayed fluorescence (TADF) luminogens. Currently, most φ_{PF} and φ_{DF} data of TADF fluorophores were acquired through time-correlated single-photon counting (TCSPC) lifetime measurement systems. However, because of their equal-time-channel working manner, so far all the commercially available TCSPC systems cannot render accurate measurement on φ_{PF} of TADF materials due to the lack of enough valid data points in the faster decay region of the corresponding photoluminescence (PL) decay curves. Although an intensified charge coupled device (ICCD) system equipped with a streak camera or an optical parametric oscillation laser has been proven to be a powerful tool for accurate determination of φ_{PF} and φ_{DF} of TADF fluorophores, the ultrahigh cost of these ICCD systems makes them inaccessible to most users. Herein, by replacing the timing module of a commercial TCSPC system with a low-cost and versatile time-to-digital converter (TDC) module, we developed a modified TCSPC system that can work in an unequal-time-channel manner. The resultant TDC-TCSPC system can not only concurrently determine the accurate lifetime of PF and DF species whose lifetime span even exceeds 5 orders of magnitude in just one time window but also render accurate measurements on φ_{PF} and φ_{DF} of TADF fluorophores. The reliability of the TDC-TCSPC method was verified through TCSPC- and ICCD-based comparative experiments on **ACMPS**, a known TADF fluorophore. Our results not only can provide a low-cost and convenient test method for accurate determination of key experimental data of TADF materials but also will facilitate deeper understanding of the molecular design principles for high-performance TADF materials.



INTRODUCTION

Owing to their enormous applicative potential in organic light-emitting diodes,[1] photocatalysis,[2] photodynamic therapy,[3] bioimaging,[4] energy storage,[5] and organic lasers,[6] thermally activated delayed fluorescence (TADF) materials comprising not only nanosecond-scaled prompt fluorescence (PF) but also microsecond- or even millisecond-scaled delayed fluorescence (DF) have drawn great attention recently.[7] To decipher the design rationales of high-performance TADF materials, two key experimental data on both the PF and the DF components, namely photoluminescence (PL) lifetimes (τ_{PF} and τ_{DF}) and quantum yields (φ_{PF} and φ_{DF}), are indispensable, because based on these data, the relevant rate constants of the singlet−triplet interconversion processes can be quantitatively determined, through which the exciton conversion dynamics can be clarified.[8−11]

Currently, through time-correlated single-photon counting (TCSPC),[12−14] the mainstream transient PL characterization technique, the accurate τ_{PF} and τ_{DF} values of a TADF fluorophore can be determined by choosing different time ranges.[15−21] Yet the accurate determination of φ_{PF} and φ_{DF} remains a difficult task. As depicted in eqs 1−4

$$\varphi_{PF} + \varphi_{DF} = \varphi_{PL} \quad (1)$$

$$f_{PF} + f_{DF} = 1 \quad (2)$$

$$\varphi_{DF} = \varphi_{PL} f_{DF} \quad (3)$$

$$\varphi_{PF} = \varphi_{PL} f_{PF} \quad (4)$$

the φ_{PF} and φ_{DF} of a TADF fluorophore can be determined once its total φ_{PL} and relative proportion of the PF and DF components (f_{PF} and f_{DF}) are acquired. While the total φ_{PL} of

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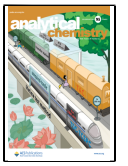
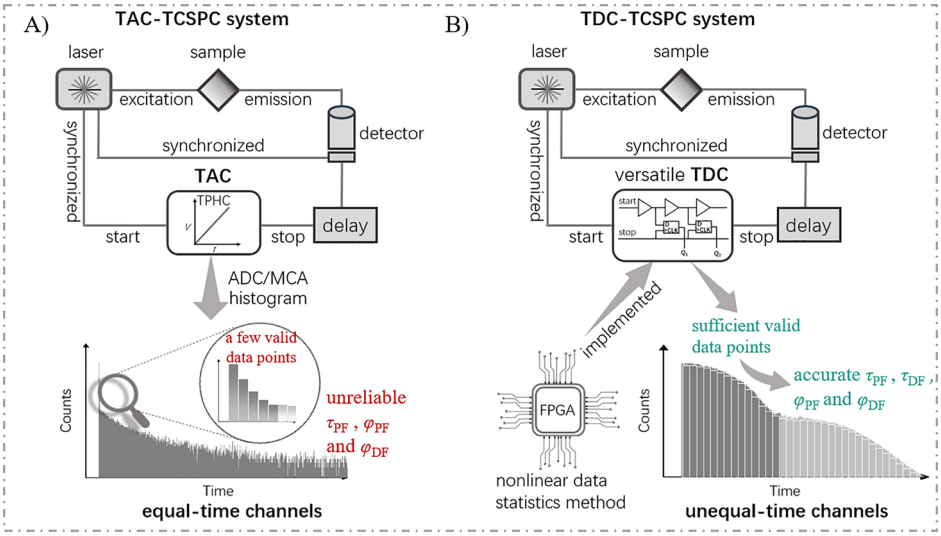


Scheme 1. Comparison of Working Schematic of Commercial TAC-TCSPC Systems (A) and the TDC-TCSPC System Reported Here (B) in PL Decay Measurements[a]



[a]TAC: time-to-amplitude converter; TPHC: time-to-pulse height conversion; ADC: analog-to-digital converter; MCA: multi-channel analyzer; TDC: time-to-digital converter; FPGA: field programmable gate array.

a TADF fluorophore can be readily determined, the precise demerging of φ_{PF} and φ_{DF} from the total φ_{PL}, i.e., the acquisition of accurate f_{PF} and f_{DF} data, either from the integration area data of the PF and the DF components (S_{PF} and S_{DF}) in the whole PL decay profile[22] or from the pre-exponential factor (α) and lifetime (τ) values of the PF and the DF components (eqs 5 and 6),[23] is still a difficult task.

$$f_{PF} = \frac{\alpha_{PF}\tau_{PF}}{\sum \alpha_i \tau_i} = \frac{S_{PF}}{S_{PF} + S_{DF}} \quad (5)$$

$$\varphi_{PF} = \frac{\varphi_{PL} S_{PF}}{S_{PF} + S_{DF}} \quad (6)$$

The reason is that the commercial TCSPC-based systems generally work under an equal-time-channel measurement manner. Once the time window is extended to submillisecond to ensure the accurate determination of α_{DF} and τ_{DF}, the short-lived PF components will inevitably suffer from an ultralow measurement resolution, leading to not only quite unreliable S_{PF} but also significantly overestimated τ_{PF} values.[24,25]

To address this problem, a test method capable of accurately determining either the S_{PF} and S_{DF}, or the α_{PF}, τ_{PF}, α_{DF}, and τ_{DF} values in just one time window is required. Recently, it has been demonstrated that when a streak camera or an optical parametric oscillation (OPO) laser is integrated into an intensified charge coupled device (ICCD), with the aid of the unequal-time-channel working manner of an ICCD, the resultant device can be used to accurately quantify the S_{PF} and S_{DF} in one time range, and hence, the φ_{PF} and φ_{DF} values of a TADF fluorophore can be precisely demerged.[26] Note that the span of the time range can even be extended to 10 orders of magnitude (10^0–10^{10} ns).[27] However, since neither streak camera (~$300,000-$500,000) nor OPO laser (~$100,000) is inexpensive, to date only few research groups can afford to use this ICCD-based transient PL characterization method.[28,29] Therefore, it is highly desirable to develop a low-cost test method that enables the concurrent determination of S, or α and τ of different excited-state species in just one time window, even though the lifetime values of these species are distinctly different.

Since TCSPC-based instruments are readily accessible, once they are endowed with an unequal-time-channel working manner, a low-cost yet accurate measurement method for φ_{PF} and φ_{DF} is expected to be acquired. Excitingly, in 2007, Wahl et al. disclosed that when an appropriate time-to-digital converter (TDC) module was introduced into a TCSPC system, the resultant instrument can run repeatedly and continuously over multiple events, through which not only picosecond timing can be realized, but also the measurable time span can even be extended to any length.[30] Inferred from these discoveries, we conjectured that if an unequal-time-channel working manner can be implemented in TDC-modified TCSPC systems, the accurate quantification of S_{PF} and S_{DF} of a TADF fluorophore in just one time window may be realized. Nevertheless, although firms such as Horiba, PicoQuant, Hamamatsu, and Edinburgh Instruments have already issued some TCSPC systems bearing certain TDC accessories,[31−34] all these TDC modules are merely designed to promote faster data acquisition and cannot work in an unequal-time-channel manner due to the lack of appropriate hardware and software.

Herein, through replacing the relevant timing module of a commercial TCSPC system with an appropriate functional TDC accessory, we developed a low-cost yet accurate quantification method for φ_{PF} and φ_{DF} of TADF fluorophores in just one time window. It is noteworthy that theoretically, once a femtosecond laser equipped with a chirped pulse amplification module is used as the excitation source of this TDC-TCSPC system, distinct excited-state species whose lifetime span even exceeds 9 orders of magnitude (10^{-2}–10^8 ns) can be detected in just one time window. The reliability of the proposed method was confirmed through TCSPC- and ICCD-based comparative experiments using a known TADF compound as the research model. Our results not only can provide a low-cost and convenient method for acquiring key experimental data of TADF materials but will also facilitate

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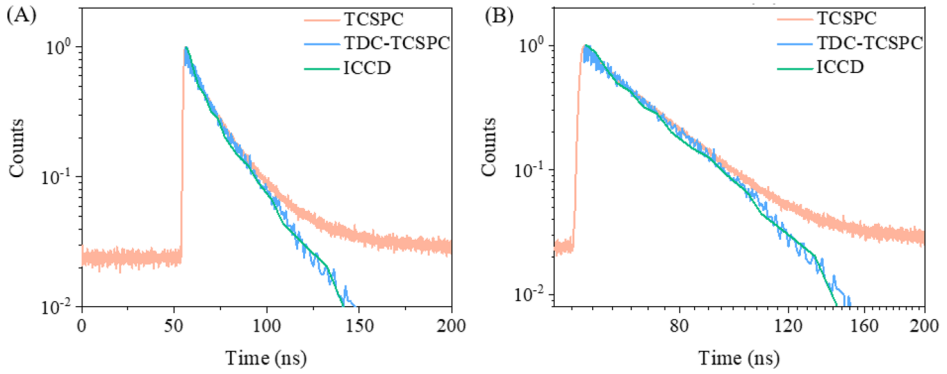

Figure 1. PL decay curves of the **ACMPS**-based sample obtained from TCSPC, TDC-TCSPC, and ICCD systems in a time range of 0−200 ns in single-log form (A) and double-log form (B). The corresponding ICCD-based curves were plotted on the basis of data extracted from a relevant literature report[36] using Origin software.

deeper understandings of the molecular design principles for high-performance TADF materials.

EXPERIMENTAL SECTION

To validate the accuracy of the test method proposed here, **ACMPS** (structure and synthetic route shown in Scheme S1), a known TADF compound was selected as the research model, because its transient PL decay characters have been investigated exhaustively *via* an ICCD-based instrument.[35,36] **ACMPS** was subject to three times recrystallization followed by vacuum sublimation to render high purity. The film sample of 10 wt %**ACMPS** in DPEPO matrix (bis[2-(diphenylphosphino)phenyl]ether oxide, supplied by Luminescence Technology Corporation), was fabricated through spin-casting from a corresponding 10 mg mL^{-1} chloroform solution on a quartz substrate at 500 r min^{-1} for 10 s followed by 1500 r min^{-1} for 30 s.

All the transient PL measurements were conducted under a vacuum condition. The TCSPC-based measurements were performed on a Jobin Yvon Horiba FluoroHub-B using a 370 nm nanoLED as the excitation source (a 400 nm high-pass filter was used to eliminate the interference from the excitation source, and the monitored emission wavelength was 470 nm). The TDC-TCSPC-based measurements were conducted on a TDC-modified fluorophotometer assembled in our laboratory, in which a versatile TDC module (model: FF4) was inserted between the laser and the detector of a commercial Jobin Yvon Horiba FluoroMax-4, and a passively Q-switched diode-pumped picosecond laser (L355-10-300, pulse width: 100 ps) was employed as the excitation source (monitored emission wavelength: 470 nm). It is worth mentioning that these two accessories cost only about $40,000.

RESULTS AND DISCUSSION

Instrumental Modification Rationale. As shown in Scheme 1, for a conventional TCSPC instrument using time-to-amplitude converter (TAC) as the timing module, when the sample was excited by a laser, a "Start" signal will be sent to the TAC to promote timing, which will not stop until the "Stop" signal arrives. Through time-to-pulse height conversion (TPHC) technology, a linear analog voltage that is proportional to the interval between the "Start" and "Stop" signals can be generated in the TAC module, and it will be further digitized and stored by an analog-to-digital converter (ADC) and a multichannel analyzer (MCA) integrated in TAC, respectively. Eventually, a histogram of PL photon time distribution equivalent to the PL decay can be generated in the MCA. Note that as the range of both analog voltage and digitization in an ADC is limited, the measurable time span of a TAC will largely depend on its own structure and function. Besides, a linear time statistical method is often used in ADC-integrated TAC. As a consequence, most of the commercial TCSPC-based PL lifetime characterizing instruments only operate in an equal-time-channel manner, and their time channel number is less than 16000.

Nevertheless, for TADF materials bearing not only ns-scaled PF species but also μs-scaled DF species, to investigate their PL decay properties, a relatively wide time window is necessary. Empirically, for a TADF fluorophore whose DF lifetime is 10 μs, the time window for PL lifetime measurement needs to be no less than 100 μs. Assuming that even the maximum time channel number of 16000 is used, the highest resolution for each channel is only ca. 6 ns, which is too large to render satisfactory resolution for the ns-scaled PF species in either S_{PF} or τ_{PF} measurement. Theoretically, this hard nut can be cracked either by substantially increasing the number of time channels or by introducing a nonlinear time statistics method. Taking into consideration that apart from technical limitations, blindly increasing the number of time channels will not only prolong the data acquisition time, reduce the signal noise ratio (SNR), but also make the samples prone to photobleaching, endowing TCSPC systems with an unequal-time-channel working manner should be a better solution.

Excitingly, after years of development, a time-digital converter (TDC) is now able to accurately measure the time interval between the "Start" and the "Stop" pulse signals. Besides, with the aid of powerful field programmable gate array (FPGA) technology, quite flexible data statistical manners can be implemented in the TDC. Therefore, we speculated that if a TDC implemented by FPGA (Figure S3) bearing a logarithmic time statistical manner can be integrated into TCSPC systems, in the nanosecond and submicrosecond time regions, the intervals between two adjacent time channels can be greatly shortened, so that much more valid experimental data can be obtained in the faster decay region, an effective test region for the short-lived species, thus greatly improving the test resolution of the short-lived species.

Consequently, in this work, a TDC module with a logarithmic time statistical manner was screened out (model: FF4), and subsequently integrated into a commercially available TCSPC lifetime measurement system to render an

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Table 1. Lifetime Fitting Results of TRPL Profiles Obtained by TCSPC or TDC-TCSPC Systems

	0−200 ns				0−100 μs[a]			
	τ_1	τ_2	$\tau_{avg.}$	χ^2	τ_1	τ_2	$\tau_{avg.}$	χ^2
TDC-TCSPC	3.7 ns (33%)	17.8 ns (67%)	13.3 ns	1.12	1.8 μs (61%)	6.2 μs (39%)	3.5 μs	1.20
TCSPC[b]	5.4 ns (33%)	19.1 ns (67%)	13.9 ns	1.40	1.9 μs (40%)	7.1 μs (60%)	3.4 μs	1.11

[a]Only tail-fitting was conducted on the TRPL profiles of the long-lived DF components in this time window. [b]The fitting results in time range of 0−200 ns and 0−100 μs were derived from two separate TRPL experiments.

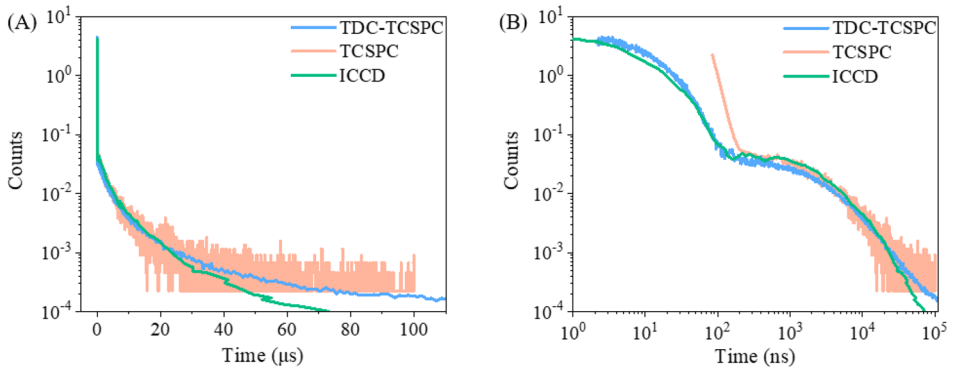

Figure 2. PL decay curves of the **ACMPS**-based sample obtained from TCSPC, TDC-TCSPC, and ICCD systems in a time window of 0−100 μs in single-log form (A) and double-log form (B). The corresponding ICCD-based curves were plotted using data extracted from a relevant literature report[36] using Origin software.

unequal-time-channel working manner. Besides, to obtain a relatively small instrument response factor (IRF) to ensure reliable measurement for the short-lived PL species, and to render a relatively high SNR to ensure reliable measurement for the long-lived PL species, a high-energy picosecond laser (ca. 1 μJ per pulse, 280 ps duration) was employed as the excitation source.

Comparative TRPL Studies on ACMPS. To validate the reliability of the TDC-TCSPC method we proposed here, comparative measurements should be conducted using TCSPC, TDC-TCSPC, and ICCD-based methods. However, since both streak camera and OPO laser are quite costly, currently, we are unable to conduct ICCD-based experiments due to the lack of corresponding instruments. Consequently, only TCSPC and TDC-TCSPC measurements were performed on a 10 wt %**ACMPS** doped film using DPEPO as the host matrix, while the corresponding ICCD-based TRPL profile of the very similar sample was extracted from the literature[36] using Origin software for comparative studies.

When the time range was set as 0−200 ns, a test window suitable for conventional fluorophore whose PL lifetime is of nanosecond scale, the PL decay profile obtained from TDC-TCSPC measurement is almost completely consistent with that extracted from the ICCD-based literature report.[36] Note that both decay profiles show biexponential behaviors that possibly originate from the intermolecular interactions or various molecular conformations in a rigid environment.[37] However, it is slightly different from the TCSPC-based one, because the latter has its baseline significantly elevated (Figure 1). Nevertheless, further biexponential fitting results revealed that the PL decay curves of **ACMPS** show analogous lifetime characters, regardless of whether the test method was TDC-TCSPC or TCSPC [τ_1: 3.7 ns (33%) vs 5.4 ns (33%); τ_2: 17.8 ns (67%) vs 19.1 ns (67%); $\tau_{avg.}$: 13.3 ns vs 13.9 ns; see Table 1]. Although we failed to acquire reliable fitting results for the ICCD-based curve due to the lack of corresponding experimental data, the nearly identical PL decay profiles exported from TDC-TCSPC-based and ICCD-based measurements clearly verified the consistency of these two test methods. While the poor overlap of the PL decay profile derived from TCSPC with TDC-TCSPC in the longer time range of 80−200 ns could be observed, it should be ascribed to the interference from the long-lived DF signals in the TCSPC method. Therefore, for luminogens containing not only short-lived PF species ($\tau \sim$ ns), but also long-lived DF species ($\tau >$ 1 μs), all three above-mentioned methods, i.e., TCSPC, TDC-TCSPC, and ICCD, can enable reliable and consistent lifetime measurements on the short-lived PF species, but the TCSPC method will suffer from the interference from the long-lived DF species, which inevitably brings about some test error.

Since the TCSPC measurement results indicated the existence of long-lived DF species in **ACMPS**, to acquire the lifetime of the DF component, the time range was further extended to 0−100 μs. As illustrated in Figure 2A, when being plotted in a single-log form that mainly shows the decay character of long-lived species, the three transient PL curves nearly resemble each other. Consistently, the TDC-TCSPC-based and TCSPC-based PL decay curves show quite comparable tail-fitting results [τ_1: 1.8 μs (61%) vs 1.9 μs (40%); τ_2: 6.2 μs (39%) vs 7.1 μs (60%); $\tau_{avg.}$: 3.5 μs vs 3.4 μs, see Table 1]. Hence, when a time window of 0−100 μs is used, all three methods can provide reliable and consistent lifetime measurement results for the long-lived DF species of **ACMPS**. Nevertheless, once these curves were plotted in a double-logarithmic way to clearly manifest not only the short-lived excited species with ns-scaled τ but also the long-lived excited species whose $\tau$is up to the μs scale, the ICCD-based and TDC-TCSPC-based curves are also similar, but the TCSPC-based one is quite different in the region of 0−200 ns (Figure 2B), which should be ascribed to the rather low resolution of the TCSPC technique in its ns-scaled measurement channels.

Therefore, although TCSPC, TDC-TCSPC, and ICCD all can provide convincing PL decay measurements on different excited-state species with a large lifetime span over 5 orders of

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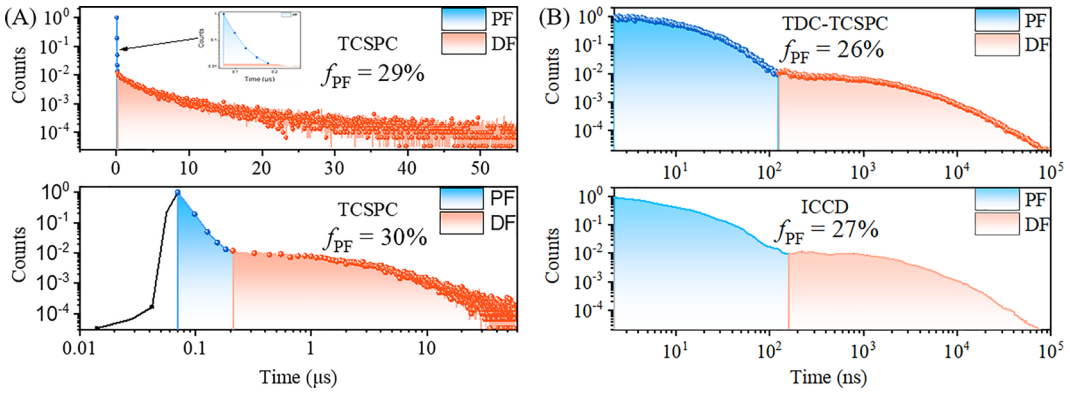

Figure 3. Calculation results on f_{PF} of **ACMPS** according to the corrresponding $S_{PF}/(S_{PF} + S_{DF})$ values of PL decay curves obtained from (A) TCSPC system and (B) TDC-TCSPC and ICCD systems. The corresponding ICCD-based curves were plotted using data extracted from a relevant literature report[36] using Origin software.

magnitude, the widely used traditional TCSPC technique cannot render accurate PF and DF lifetime data concurrently in just one time window. This will, however, bring about significant test errors when calculating φ_{PF} and φ_{DF}; both are quite important parameters for TADF materials. Taking **ACMPS** as an example, when the time range was set as 0−100 μs, the PL decay curve derived from traditional TCSPC measurements can be globally fitted with three components, *i.e.*, τ_1 = 17.2 ns (α_1 = 99.6%), τ_2 = 2.2 μs (α_2 = 0.3%), and τ_3 = 9.3 μs (α_3 = 0.1%). Obviously, here only the excited-state species with lifetime of 17.2 ns can be safely assigned to the PF component of **ACMPS**. However, this value is more than 20% larger than the accurate one measured in a time-window of 0−200 ns ($\tau_{avg.}$ = 13.9 ns, see Table 1). The reason is that when the time window is 0−100 μs, the time interval for two adjacent channels will be too large (in this case, 24.4 ns when the number of time channels is 4096) to render enough valid data points in the faster decay region (in this case, only five data points, see Figure 3A), leading to quite unreliable measurement results for the PF species. Moreover, the overestimated τ_{PF} obtained from the 0−100 μs time-windowed TCSPC measurement implies that the slope of this TRPL curve at the faster decay region should be smaller than the real value. As a consequence, on the basis of the 0−100 μs time-windowed TCSPC measurement results, the φ_{PF}, either calculated through the S_{PF} value according to eq 5 or calculated through the α_{PF} and τ_{PF} data from the global fitting on TRPL profile according to eq 6, should be overestimated. Specifically, upon precise demerging of S_{PF} and S_{DF} from the 0−100 μs TRPL profile, the f_{PF} of **ACMPS** was calculated to be 29%−30%; while according to the α and τ data derived from global fitting, the calculated f_{PF} was as high as 50%.

In contrast, both the ICCD and TDC-TCSPC systems are able to show high resolution for not only the short-lived PF species but also the long-lived DF species of a TADF fluorophore; hence, the S_{PF} and S_{DF} can be accurately determined, leading to reliable calculation of f_{PF} for a TADF fluorophore. In the case of **ACMPS**, by using the S_{PF} and S_{DF} data of the TDC-TCSPC-derived and ICCD-derived TRPL profiles (Figure 3B), quite analogous f_{PF} data were obtained (26% and 27% in sequence), indicative of the consistency of these two test methods. It is noteworthy that in line with our deduction, the f_{PF} data obtained through TDC-TCSPC and ICCD methods are both smaller than those obtained via TCSPC-based measurements. All these experimental findings indicated that TDC-TCSPC is a low-cost yet accurate test method for precisely demerging φ_{PF} and φ_{DF} from the total φ_{PL} of a TADF fluorophore.

In summary, by replacing the timing module of a commercial TCSPC system with a versatile TDC accessory, we developed a low-cost but accurate lifetime measurement method, namely, TDC-TCSPC, through which not only τ_{PF} and τ_{DF} with lifetime span of over 5 orders of magnitude can be accurately determined in just one time window, but also accurate S_{PF} and S_{DF} can be acquired. Therefore, the real φ_{PF} and φ_{DF} of a TADF fluorophore can be determined accurately. The reliability of this TDC-TCSPC-based test method was verified through comparative experiments using **ACMPS** as the research model. It is noteworthy that theoretically, once a femtosecond laser is used as the excitation source of this TDC-TCSPC system, distinct excited-state species whose lifetime span even exceeds 9 orders of magnitude (10^{-2}−10^{8} ns) can be detected in just one time window. Therefore, our results can provide a low-cost and convenient test method for obtaining key experimental data of not only TADF materials bearing μs-scaled long-lived excited-state species but also room-temperature phosphorescence (RTP) materials with ms-scaled lifetime and hence may facilitate deeper understanding of the molecular design principles for high-performance TADF and RTP materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.3c00319.

Synthetic route, ^{1}H NMR and ^{13}C NMR spectra of **ACMPS** TADF molecule, and the working process scheme of data acquisition for TAC timing and TDC timing (PDF)

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Author Contributions

⊥C. Li and Y. Luo contributed equally.

Notes

The authors declare no competing financial interest.

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