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LETTERS

Determination of Triplet Quantum Yields from Triplet−Triplet Annihilation Fluorescence

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A new method for measuring triplet quantum yields is described and demonstrated. In this self-calibrated technique, one compares intensities of prompt fluorescence and delayed triplet−triplet annihilation fluorescence from the solution-phase sample of interest. This approach differs from other methods in that it requires no reference compounds, energy-transfer partners, or absolute measurements of triplet state energy, sample concentration, optical density, excitation energy, or emission intensity. Instead, the triplet quantum yield is determined from the emission time profile, using data from a single sample. Results from this method agree with published values to within ca. 0.02, even in the unfavorable case of a weakly fluorescent sample.

Introduction

One of the most common fates of an optically excited organic molecule is intersystem crossing to populate its triplet state. The triplet quantum yield, which describes the probability of this process, is therefore a centrally important parameter in molecular photophysics.[1] Although various experimental methods for measuring triplet quantum yields are in widespread use, all of them rely either on comparisons with reference compounds or on the absolute values of separately measured parameters. For example, in energy-transfer methods, triplet states of the sample compound quantitatively transfer their energy to co-dissolved acceptor species, whose concentration is then measured by induced absorption or, in the case of $^1\Delta_g$ oxygen, by near-infrared luminescence. These methods require a calibration donor species of known triplet quantum yield, and they can be inaccurate if the efficiency of transfer is not as high as presumed.[2] Another comparative method measures the ratio of triplet−triplet absorptions in separate sample and reference solutions and deduces the sample's triplet quantum yield from that ratio, provided that the relative triplet−triplet absorptivities of the two species are already known.[3] Thermal lens, photoacoustic, and transient grating methods avoid the need for a co-dissolved reference compound, but the triplet quantum yield must be extracted using independent knowledge of the triplet state energy.[4,5] All of the standard methods thus combine more than one critical measurement and consequently suffer from experimental complexity and error accumulation.

We present here a novel, simpler method for triplet quantum yield determinations that requires just one emission measurement on a sample containing only the species of interest. Our method works by assessing the relative populations of excited singlet and triplet states from the intensity of prompt fluorescence relative to that of delayed fluorescence arising from triplet−triplet annihilation. Because this kinetic method is internally self-referenced, no calibrations, reference species, prior knowledge, or absolute measurements are needed. The method's uncertainties appear to be comparable or superior to those of current standard methods.

Description of the Method

According to Kasha's Rule,[6] optical emission from normal organic compounds in solution is dominated by the two longest-lived excited electronic states: the lowest excited singlet (denoted here $^1A^*$) and the lowest triplet ($^3A^*$). The triplet

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TABLE 1: Processes Following Encounters of Two Triplet State Molecules

statistical weight	encounter complex	after dissociation	after internal conversion	after ^{1}A* radiationless decay	^{3}A* states quenched	^{1}A* states produced
1/9	^{1}(AA)*	$^1A^{**} + {}^1A$	$^1A^* + {}^1A$	$\Phi_T\,{}^3A^* + (2 - \Phi_T)\,{}^1A$	$(2 - \Phi_T) \times 1/9$	$1 \times 1/9$
3/9	^{3}(AA)*	$^3A^{**} + {}^1A$	$^3A^* + {}^1A$	$^3A^* + {}^1A$	$1 \times 3/9$	0
5/9	^{5}(AA)*	$^3A^* + {}^3A^*$	$^3A^* + {}^3A^*$	$^3A^* + {}^3A^*$	$0 \times 5/9$	0
				Totals:	$\frac{(5 - \Phi_T)}{9}$	1/9

quantum yield, Φ_T, is defined as the fraction of $^1A^*$ species that undergo radiationless decay to form $^3A^*$. Fluorescence emission from $^1A^*$ to the ground state has a characteristic spectrum for each compound and a typical duration in the nanosecond range. $I_\mathrm{f}^\mathrm{prompt}$, the detected intensity of this emission after pulsed excitation, can be time-integrated to give $N_\mathrm{f}^\mathrm{prompt}$, the total prompt fluorescence signal

$$N_\mathrm{f}^\mathrm{prompt} = \int I_\mathrm{f}^\mathrm{prompt}\,\mathrm{d}t = \alpha[{}^1A^*]_0\Phi_\mathrm{f} \qquad (1)$$

Here, α is a constant representing instrumental sensitivity, $[{}^1A^*]_0$ is the total concentration of excited singlet states, and Φ_f is the singlet's fluorescence quantum yield. We note that an experimental value for $N_\mathrm{f}^\mathrm{prompt}$ is normally available as the area under a prompt fluorescence trace, even if the detection system is not able to time-resolve that emission.

The presence of triplet states causes additional, much weaker emission that spectrally matches the prompt fluorescence but persists far longer. This is "P-type" delayed fluorescence emitted from singlet excited states formed through triplet−triplet annihilation.[7] As listed in Table 1, encounters of two triplet molecules can give complexes having singlet, triplet, or quintet spin states, with relative statistical weights of 1, 3, and 5, respectively. Dissociation of the singlet complex produces one ground-state molecule plus another in a highly excited singlet state that quickly converts to $^1A^*$, the fluorescent state. As this is the only bimolecular path for producing $^1A^*$ from triplets, the rate of $^1A^*$ production is $^1/_9$ of the triplet−triplet encounter rate. A fraction Φ_T of those $^1A^*$ molecules revert to $^3A^*$. The second line of Table 1 shows that each triplet complex deactivates one $^3A^*$ molecule. Finally, because molecular quintet states are normally energetically inaccessible,[8] the quintet encounter complexes dissociate to their starting species, causing no population changes. Net quenching of $^3A^*$ through thecombination of these processes occurs at $(5 - \Phi_\mathrm{T})/9$ times the triplet−triplet encounter rate. The key result from this analysis, which should be valid for most organic compounds, is that the kinetic ratio of $^1A^*$ production to $^3A^*$ removal is $(5 - \Phi_\mathrm{T})^{-1}$.

Because the $^3A^*$ lifetime normally exceeds that of $^1A^*$ by orders of magnitude, singlets formed by triplet−triplet annihilation decay much faster than they are formed. We can therefore invoke the steady-state approximation to obtain

$$[{}^1A^*]_t = \frac{k_\mathrm{TT}^\mathrm{enc}}{9k_\mathrm{S}}[{}^3A^*]_t^{\,2} \qquad (2)$$

where k_S is the singlet state's total decay constant and $k_\mathrm{TT}^\mathrm{enc}$ is a parameter representing the effective rate constant for encounters between triplets. This leads to the following expression for $I_\mathrm{f}^\mathrm{delayed}$, the detected intensity of delayed fluorescence

$$I_\mathrm{f}^\mathrm{delayed} = \alpha\frac{k_\mathrm{TT}^\mathrm{enc}}{9}\,\frac{k_\mathrm{rad}}{k_\mathrm{S}}[{}^3A^*]_t^{\,2} = \alpha\frac{k_\mathrm{TT}^\mathrm{enc}}{9}\,\Phi_f[{}^3A^*]_t^{\,2} \qquad (3)$$

Here, k_rad is the radiative rate constant of the singlet state. We can now obtain an expression for Q, the experimental ratio of integrated prompt fluorescence signal to initial delayed fluorescence intensity, as

$$Q \equiv \frac{N_\mathrm{f}^\mathrm{prompt}}{I_\mathrm{f}^\mathrm{delayed}(0)} = \frac{9}{\Phi_\mathrm{T}\,k_\mathrm{TT}^\mathrm{enc}\,[{}^3A^*]_0} \qquad (4)$$

where we have applied the relation $[{}^3\mathrm{A}^*]_0 = \Phi_\mathrm{T}[{}^1A^*]_0$ for the maximum triplet concentration. Note that Q has dimensions of time.

To determine Φ_T from Q using eq 4, one needs the value of $k_\mathrm{TT}^\mathrm{enc}[{}^3A^*]$. This can be obtained from a kinetic analysis of the delayed fluorescence, combined with the relation between triplet encounters and quenching found from Table 1. Triplet-state population decay may include both a second-order component (from triplet−triplet annihilation only) and a first-order component (from a combination of unimolecular decay and pseudo-first-order processes such as quenching by oxygen, impurities, etc.). Using k_TT^q to denote the rate constant for second-order quenching, and k_1 for the apparent first-order rate constant, we can write the following differential rate law

$$\frac{\mathrm{d}[{}^3A^*]}{\mathrm{d}t} = -k_1[{}^3A^*]_t - k_\mathrm{TT}^\mathrm{q}[{}^3A^*]_t^{\,2} \qquad (5)$$

Such concurrent first- and second-order decay has the following analytic solution

$$[{}^3A^*]_t = [{}^3A^*]_0\frac{1 - \beta}{e^{k_1 t} - \beta} \qquad (6)$$

The dimensionless parameter β in this expression equals the fraction of initial decay that occurs through the second-order channel

$$\beta = \frac{k_\mathrm{TT}^\mathrm{q}[{}^3A^*]_0}{k_1 + k_\mathrm{TT}^\mathrm{q}[{}^3A^*]_0} \qquad (7)$$

By solving eq 7 for k_TT^q and using the relation $k_\mathrm{TT}^\mathrm{q} = (5 - \Phi_\mathrm{T})k_\mathrm{TT}^\mathrm{enc}/9$, we obtain

$$k_\mathrm{TT}^\mathrm{enc}[{}^3A^*]_0 = \left(\frac{9}{5 - \Phi_\mathrm{T}}\right)\frac{k_1\beta}{1 - \beta} \qquad (8)$$

Substituting this into eq 4 leads to a final result for Φ_T

$$\Phi_\mathrm{T} = \frac{5}{1 + Q\left(\dfrac{k_1\beta}{1 - \beta}\right)} \qquad (9)$$

TABLE 2: Experimental Parameters and Triplet Quantum Yields (Φ_T) Calculated from the Kinetic Traces in Figure 1

sample	N_f^{prompt} (10^{-6} V−s)	$I_f^{delayed}(0)$ (10^{-3} V)	k_1 (s^{-1})	β	$k_1\beta/(1-\beta)$ (s^{-1})	k_A (s^{-1})	Φ_T (this work)	Φ_T (prior)
TPP	4.250	14.3	–	–	–	20 170	0.71 ± 0.03	0.69,[a] 0.70[b]
Zn-TPP	4.622	21.3	1530	0.929	20 020	–	0.93 ± 0.02	0.92,[a] 0.93[b]
C_{70}	3.301	39.3	–	–	–	46 980	1.01 ± 0.02	0.994[c]
C_{70}	1.532	6.83	–	–	–	19 200	0.94 ± 0.05	0.994[c]

[a] Reference 11. [b] Reference 12. [c] Reference 10.

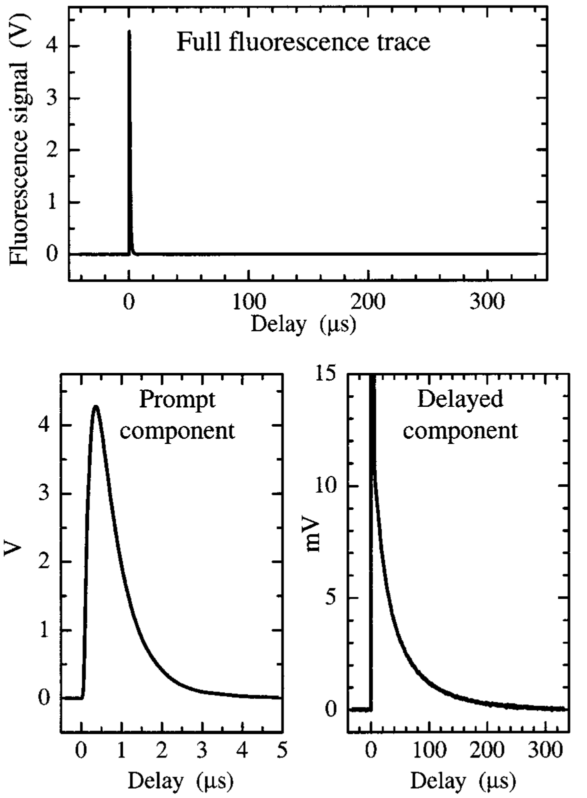

Figure 1. Time-resolved emission traces measured at 654 nm from a sample of TPP in degassed toluene excited at 532 nm. The top frame shows the emission signal over its full range of amplitude and time. The frames below show: (left) the prompt component on a faster time scale, reflecting the instrument response function; and (right) the weak delayed component on a more sensitive amplitude scale.

Note that k_{TT}^{enc} no longer appears; it was only a canceling parameter in this derivation.

To find the triplet quantum yield using our method, one records fluorescence intensity from a sample solution following pulsed excitation. The apparatus requires a time resolution high enough to show the kinetics of triplet decay, which typically occurs on the microsecond scale. It is not necessary to resolve the large prompt fluorescence signal, because the numerator of Q is just the integral under its trace. The denominator of Q is the zero-delay intercept of the much weaker delayed fluorescence trace. Finally, the entire delayed fluorescence trace is fit to the form given by eqs 3 and 6. This provides values for β and the first-order decay constant, k_1.

Under conditions for which β is nearly zero, there is negligible triplet−triplet annihilation, and our method is not appropriate. This limit can usually be avoided by increases in sample concentration or excitation energy. (Although sequential multiphoton absorption may reduce the apparent value of Φ_T in some samples, such errors will generally occur at intensities higher than are needed to measure delayed fluorescence.) Equation 9 also becomes invalid when β approaches 1, corresponding to negligible first-order decay relative to triplet−triplet annihilation. However, in this strong-annihilation limit, the triplet state population assumes the familiar form

$$[^3A^*]_t = [^3A^*]_0\left(\frac{1}{1+k_At}\right) \qquad (10)$$

where k_A is a parameter that can easily be determined by kinetic fitting of the delayed fluorescence data. The value of Φ_T can then be found from k_A and Q using the following expression

$$\Phi_T = \frac{5}{1+Qk_A} \qquad (11)$$

Implementation and Results

We have tested this method on several samples for which reliable triplet quantum yields have already been reported. Degassed toluene solutions in 1-cm cuvettes were excited at 532 nm by 8-ns pulses from a Nd:YAG laser. The excitation energies were in the range of 1−3 mJ. Fluorescence emission was focused onto the entrance slit of a small monochromator (ISA Triax 190) set to the peak of the emission spectrum. Mounted at the exit slit was a silicon photodiode detector whose output was ac-amplified before being recorded by a digitizing oscilloscope (Tektronix TDS-430A). The response time of this detection system was limited to 700 ns. To overcome the limited dynamic range of the oscilloscope's analog-to-digital converters, different settings of vertical sensitivity and sweep speeds were used to separately record the prompt and delayed emissions. We averaged several hundred emission traces in the oscilloscope to improve the signal-to-noise ratio.

Three samples were used: free base tetraphenylporphyrin (TTP), its zinc complex (Zn-TPP), and the fullerene C_{70}. We included the fullerene sample because it challenges our method in two ways. First, C_{70} has a low fluorescence quantum yield of 5×10^{-4},[9] making delayed fluorescence relatively difficult to detect. Second, in contrast to the porphyrins, C_{70} gives not just "P-type" delayed fluorescence from triplet−triplet annihilation, but also "E-type" delayed fluorescence from $S_1 \leftarrow T_1$ thermal activation.[10] Although these two forms of delayed fluorescence are spectrally identical, the intensity of the thermally activated component depends linearly, rather than quadratically, on the triplet concentration. We therefore needed to perform a more complex kinetic analysis to accurately determine β and k_1 from the delayed fluorescence trace, even though the thermally activated component contributed less than 20% of the delayed emission from our room-temperature C_{70} sample.

In Figure 1, we plot the fluorescence trace measured for the TPP sample. The upper frame, which covers the full voltage and time ranges needed for our analysis, is dominated by the intense burst of prompt fluorescence emission. This prompt component is shown on a much expanded time scale in the lower left frame. The shape of this trace is just the instrument response function, and its integral provides the numerator of the parameter Q. The lower right frame of Figure 1 shows the weak delayed fluorescence measured with greatly increased vertical sensitivity.

Table 2 lists parameters found from our data on test samples, along with the deduced values of Φ_T. Under our experimental conditions, Zn-TPP showed a mixture of first- and second-order triplet-state decay, but the decays of TPP and C_{70} were almost entirely second-order. We list two C_{70} runs, with high and low excitation energies, to illustrate the robustness of the method. The low-energy C_{70} run represents a very unfavorable situation, because delayed fluorescence was suppressed both by the low fluorescence quantum yield of C_{70} and by the small initial concentration of triplet states. In addition, analysis of the delayed signal was complicated by the contribution from thermally activated fluorescence, as discussed above. Despite the greater uncertainties caused by these effects, the deduced Φ_T value agrees adequately with that from the high-energy run. We also note that all of our triplet yield values match previously published reports within estimated experimental errors, which were 0.02 or 0.03 except in the low-energy C_{70} case.

In summary, the kinetics-based triplet quantum yield method described here should be applicable to a large number of compounds that emit detectable fluorescence and undergo triplet−triplet annihilation in fluid solution. This method enjoys the unique advantages of requiring no absolute instrumental calibrations, reference samples, energy-transfer species, or knowledge of other photophysical parameters. We expect that it will prove a useful tool for future photophysical studies.

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