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Evidence on the $O_2(^1\Delta_g)$ Dimol-Sensitized Luminescence in Solution

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Only recently has the investigation of singlet oxygen dimol in the solution phase become possible. Using an ultrasensitive intensified charge-coupled detector, Chou et al. have simultaneously observed photosensitized $O_2(^1\Delta_g)$ dimol and O_2 ($^1\Sigma^+{}_g \rightarrow {}^3\Sigma^-{}_g$) visible emission spectra in solution.[1] Krasnovsky and Neverof[2−4] have reported the $O_2(^1\Delta_g)$ dimol-sensitized luminescence of various dyes based on steady-state experiments. Subsequently, Krasnovsky and Foote[5] applied a time-resolved method which incorporated the $O_2(^1\Delta_g)$ dimol-sensitized tetra-*tert*-butylphthalocyanine (PC) luminescence to study the relaxation dynamics of the $O_2(^1\Delta_g)$ dimol. However, evidence against the dimol-sensitized luminescence of PC and other dyes in solution has recently been reported by Gorman et al.[6] Their data are only consistent with a two-step mechanism which involves the $O_2(^1\Delta_g)$ sensitizing the acceptor to its triplet state (e.g., ^{3}PC) followed by the second-step energy transfer from $^1\Delta_g$, producing the excited singlet PC.

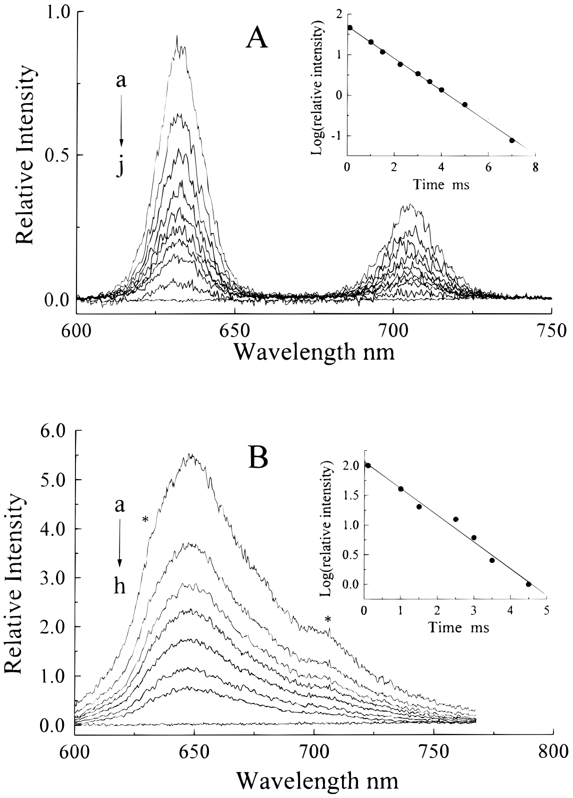

Figure 1. (A) Spectral evolution of the PH (2.0×10^{-4} M) sensitized $^1O_2$ dimol emission obtained at various delay times of (a) 50 μs, (b) 1 ms, (c) 1.5 ms, (d) 2.25 ms, (e) 3 ms, (f) 3.5 ms, (g) 4.0 ms, (h) 5.0 ms, (i) 7.0 ms, and (j) 30 ms. Insert: Logarithmic plot of the 637-nm emission intensity versus various delay times (solid circle) and its best least-squares fitted line (solid line). (B) Spectral evolution of the delayed NBA fluorescence obtained at various delay times of (a) 50 μs, (b) 1 ms, (c) 1.5 ms, (d) 2.5 ms, (e) 3.0 ms, (f) 3.5 ms, (g) 4.5 ms, and (h) 30 ms. * denotes the $^1O_2$ dimol emission. Insert: Logarithmic plot of the 675-nm emission intensity versus various delay times (solid circle) and its best least-squares fitted line.

We report here the evidence of $O_2(^1\Delta_g)$ dimol-sensitized luminescence in solution. In this study 1*H*-phenalen-1-one (PH) was chosen as a sensitizer which has been reported to produce the $O_2(^1\Delta_g)$ state with a near unit efficiency.[8,9] Nile Blue A perchlorate (NBA) was used as an energy acceptor of which the maximum of the S_0−S_1 vibronic band ($\lambda_{max} \sim 635$ nm) coincidentally overlaps with the $^1O_2$ dimol $(^1\Delta_g)_2$ (0,0) $\rightarrow$ $(^3\Sigma^-{}_g)_2$ (0,0) 637-nm emission in $CDCl_3$, fulfilling the fundamental requirement of the $O_2(^1\Delta_g)$ dimol-sensitization mechanism.[7] In this study, an ultrasensitive sub-millisecond time-resolved detection system has been developed.[10] This system is based on an intensified charged coupled detector coupled with a modulated Ar^+ square pulse to reduce the power-dependent photochemical production of $^1O_2$ quenchers in halogenated solvents.[11−15] A typical time-resolved spectral evolution of the PH-sensitized $^1O_2$ dimol 0,0 and 0,1 vibronic bands in $CDCl_3$ is depicted in Figure 1A. The decay monitored at 637 nm follows first-order kinetics, and the lifetime was calculated to be 2.3 ± 0.2 ms. Similar to our previous studies of the $^1O_2$ dimol emission in CCl_4,[10] the decay rate of the $^1O_2$ dimol emission in $CDCl_3$ is laser-intensity dependent. However, under the same laser intensity, its decay is twice as fast as that of the O_2 ($^1\Delta_g$ (0) $\rightarrow$ $^3\Sigma^-{}_g$ (0)) 1275-nm emission. These results can be rationalized by the dimol formation and decay pathways c, d, and l shown in Scheme 1.Accordingly, the $^1O_2$ dimol emission response function, $I_{dim}(t)$, can be expressed as

$$I_{dim}(t) = (k_D k_{ac}/k_{-ac})[^1\Delta g]_0^2 e^{-2k_p t} \qquad (1)$$

where k_D is the radiative decay rate of the $O_2(^1\Delta_g)$ dimol. Equation 1 clearly shows that the time-dependent dimol concentration reflects the slow and limiting annihilation of two $^1\Delta_g$ molecules, which corresponds to twice the decay rate of the $^1\Delta_g$ species, $2k_p$,[16] consistent with the experimental results.

By adding NBA to the same solution prepared to obtain Figure 1A, a new emission band maximum at ~650 nm appears and its time-dependent spectral evolution is shown in Figure 1B. Due to its spectral resemblance, the assignment of this delayed emission to the NBA fluorescence is unambiguous. The plot of integrating the emission intensity in the region 670−680 nm versus various delay times is fitted well by a single-exponential

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(16) The $O_2(^1\Delta_g)$ decay rate, k_p, in the kinetic expression for eq 1 as well as mechanisms 1−3 has implicitly involved the laser-intensity-dependent quenching term.

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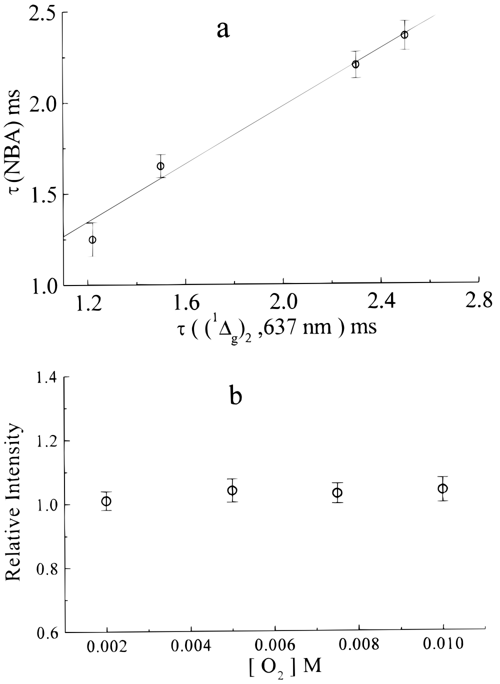
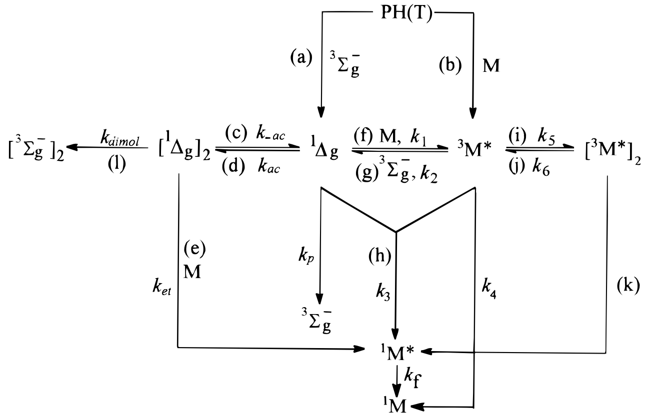


Figure 2. (a) Lifetime of the delayed NBA fluorescence versus that of the $(^1\Delta_g)_2$ (0,0) → $(^3\Sigma^-{}_g)_2$ (0,0) 637-nm emission at various excitation laser intensities (364 nm, 15−80 mW). (b) Delayed NBA emission intensity (normalized in the aerated solution) as a function of the added oxygen concentration.

Scheme 1



decay dynamics, and the lifetime was calculated to be 2.2 ± 0.2 ms. Figure 2a plots the dependence of the delayed NBA fluorescence decay dynamics with those of the dimol 637-nm emission for several sets of experiments under various laser intensities. The slope was calculated to be 0.90 ± 0.12, indicating that both $^1O_2$ dimol emission and delayed NBA fluorescence undergo the same decay dynamics.[17] We have also performed a series of experiments by varying oxygen concentrations from 2.05 × 10^{-3} [18,19] to 1.03 × 10^{-2} M. The results shown in Figure 2b indicate that the NBA emission intensity, within the experimental error, is nearly independent of the added oxygen above the aerated concentration.

Three possible mechanisms may account for the occurrence of the delayed NBA emission in this study, which are all congenial with the observed decay dynamics. To help the following discussion we adopted the scheme originally applied by Gorman et al.[6] with a slight modification to depict the relaxation dynamics of the sensitized NBA emission (see Scheme 1). The time-dependent delayed NBA fluorescence response function derived from mechanisms (1) the dimol sensitization process (c−e), (2) two-step $^1\Delta_g$ sensitization (f−h), and (3) the T−T annihilation process (i−k) can be expressed as $F_1(t)$, $F_2(t)$, and $F_3(t)$, respectively, shown as follows:

$$F_1(t) = \frac{k_r k_{ac} k_{et}[M][^1\Delta_g]_0^2}{k_f k_{-ac}} e^{-2k_p t} \qquad F_2(t) = \frac{k_r k_3 k_1 [M][^1\Delta_g]_0^2}{k_f k_2 [^3\Sigma_g^-]} e^{-2k_p t}$$

$$F_3(t) = \frac{k_r k_5 k_1^2 [M]^2 [^1\Delta_g]_0^2}{k_f k_2^2 [^3\Sigma_g^-]^2} e^{-2k_p t}$$

where k_r is the radiative lifetime of ^{1}NBA*.[20] As has been pointed out by Gorman et al.,[6] varying oxygen concentration above the air-saturated condition would cause (a) no effect, (b) inversely proportionality to [O_2], and (c) inversely proportionality to the square of [O_2] for mechanisms 1−3, respectively. Although the decay dynamics can be well explained by all three proposed mechanisms,[21] the nearly oxygen concentration-independent NBA emission can only be rationalized by mechanism 1.

According to the energy difference of 8.66 kcal/mol[23] between T_1 of NBA and the $O_2(^1\Delta_g)$ state, k_1/k_2 in mechanisms 2 and 3 is calculated to be 4.45 × 10^{-7} at 298 K. Assuming that pathways e, h, and i are diffusion-controlled processes, the intensity ratio for the sensitized NBA fluorescence originating from mechanism 2 versus that from mechanism 1 can be expressed as $F_2/F_1 = (k_1 k_{-ac})/(k_2 k_{ac}[^3\Sigma^-{}_g])$. Taking k_{ac} to be a bimolecular diffusion-controlled rate (1.34 × 10^{10} M^{-1} s^{-1}) in $CDCl_3$, and a lower limit of k_{-ac} of 2.6 × 10^{10} s^{-1},[24] F_2/F_1 was then calculated to be 0.87 × 10^{-4} in oxygenated $CDCl_3$, indicating that >99% of the emission intensity originates from mechanism 1, if both processes exist simultaneously. On the other hand, the ratio of the emission intensity between mechanism 3 and 2 is calculated to be ≪1. Therefore, both experimental results and theoretical derivation are mutually consistent, concluding that mechanism 1 may play a key role to account for the sensitized delayed NBA emission, giving evidence to support the dimol-sensitization mechanism proposed by Khan and Kasha three decades ago.[7]

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Supporting Information Available: Detailed kinetic derivations for eq 1 and mechanisms 1−3 (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[17] The correlation shown in Figure 2a is based on the decay of delayed NBA emission versus the unquenched (no NBA added) $O_2(^1\Delta_g)$ dimol emission. However, a slope of 0.90 ± 0.12 indicates that the added NBA has a negligible quenching effect on the $O_2(^1\Delta_g)$ dimol, hence the $O_2(^1\Delta_g)$ emission. The quenching rate of NBA has been determined to be 2.6 × 10^6 M^{-1} s^{-1} in $CDCl_3$.

[18] The value of oxygen solubility in $CDCl_3$ is taken to be the same as that in $CHCl_3$.[21]

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[20] The lifetime and quantum yield of the prompt NBA emission were measured to be 3.2 × 10^{-9} s and 0.92, respectively, in $CDCl_3$. Consequently, the radiative decay rate, k_r, of 2.9 × 10^8 $s^{-1}$was deduced.

[21] There is another possible mechanism incorporating radiative transfer of $O_2(^1\Delta_g)$ dimol energy to NBA. To check this possibility we have performed a series of experiments by exciting the sample at different portions of the sample cuvette. The results show negligible difference for the delayed NBA emission intensity. Therefore, it is unlikely that the delayed fluorescence results from the radiative transfer of the $O_2(^1\Delta_g)$ dimol energy to NBA. On the other hand, it has been recently shown by Scurlock and Ogilby[22] that the dimol dissociates to yield singlet sigma oxygen. Therefore, another possible mechanism depicted as follows has to be considered:

$$(^1\Delta g)_2 \rightarrow (^1\Sigma^+{}_g) + (^3\Sigma^-{}_g) \xrightarrow{\text{NBA}} {}^3\text{NBA} \xrightarrow{^1\Delta g} {}^1\text{NBA}^* \rightarrow \text{NBA} + h\nu$$

In this sequence of reactions, three $^1\Delta g$ molecules are consumed to produce the NBA fluorescence: two in the formation of the dimol and a third to form ^{1}NBA* from ^{3}NBA. Therefore, the intensity of the NBA emission should be proportional to $[^1\Delta g]_0^3$, which is inconsistent with our experimental results.

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[23] The near-infrared luminescence spectra of a frozen, glassy solution of NBA in ethanol at 77 K showed a weak emission with a peak maximum at ∼920 nm (τ ∼ 300 μs). This emission was absent under fluid conditions at room temperature and was thus tentatively ascribed to the phosphorescence spectrum of NBA.

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