Nonexponential Luminescence Decay in Hexaureachromium(III)[1]

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Abstract: The decays of the sharp line phosphorescence ($^2E \rightarrow {}^4A_2$) and broad band fluorescence ($^4T_2 \rightarrow {}^4A_2$) emissions have been recorded at 77°K for $Cr(urea)_6{}^{3+}$ in crystalline and glassy environments. The ^2E lifetime of $Cr(urea)_6{}^{3+}$ is sensitive to environment and the double exponential decays observed in $[Cr(urea)_6](NO_3)_3$ and $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ are ascribed to multiple sites. No prompt fluorescence is detectable in any of the systems; both the fluorescence and phosphorescence from a single center exhibit the same lifetime. The multiexponential decay that prevails in rigid glass solutions of $Cr(urea)_6{}^{3+}$ disappears when the solvent becomes fluid.

Luminescence from hexacoordinated Cr(III) consists of broad fluorescence ($^4T_2 \rightarrow {}^4A_2$) and/or structured phosphorescence ($^2E \rightarrow {}^4A_2$). Although phosphorescence is the more common type of emission, fluorescence has been detected in a number of cases since it was first observed in $Cr(urea)_6{}^{3+}$.[2] Schlafer et al.[3] formulated a criterion for fluorescence emission, viz., the vibrationless level of $^4T_2$ must be below or be thermally accessible from ^2E (Figure 1). In most environments, $^4T_2$ is above ^2E and phosphorescence is the dominant emission, particularly at low temperatures. $Cr(urea)_6{}^{3+}$ and the closely related $Cr(antipyrene)_6{}^{3+}$ are of particular interest since the $^4T_2$-^2E separation in these species is very small and both phosphorescence and fluorescence are emitted under most conditions.

Fluorescence can be prompt, i.e., compete with intersystem crossing to ^2E, or be due to thermally induced back transfer from ^2E (delayed). Phosphorescence and delayed fluorescence decay at the same rate, whereas prompt fluorescence relaxes more rapidly. Dingle observed that $[Cr(urea)_6](NO_3)_3$ emission follows multiexponential decay kinetics at low temperatures and tentatively suggested that the faster component is prompt fluorescence.[4] An alternative interpretation has been advanced, wherein emission from nonequilibrated ^2E components is responsible for the dual lifetimes.[5]

Since the $^4T_2$ state is involved in Cr(III) photochemistry,[6] it is important to determine the $^4T_2$ lifetime and the intersystem crossing efficiency as a function of the $^4T_2$-^2E separation. Putative cases of prompt fluorescence, e.g., $Cr(CN)_6{}^{3-}$ and Cr^{3+}:MgO, have been found to arise from multiple chromophoric environments.[7,8] With the possible exception of $Cr(bipyr)_3{}^{3+}$,[9] $Cr(urea)_6{}^{3+}$ has been the only remaining example of prompt fluorescence. We now present evidence that negates this interpretation.

Experimental Section

For the measurement of lifetimes, a N_2 laser (Avco C-950) pumped Rhodamine 6G dye laser (λ 580 nm) was usually employed as the excitation source. The same results were obtained using a N_2 laser pumped 7-diethylamine-4-methylcoumarin dye laser (λ 454 nm) or the N_2 laser alone (λ 337 nm). The pulse width was always less than 10 nsec. The sample was placed in a cuvette in a glass dewar cooled either by direct immersion in liquid N_2 (77 K) or by cold N_2 vapor (85–300 K). The emission, filtered by 5 cm of a concentrated solution of chromium acetylacetonate, was passed through a 0.25 m Jarrell-Ash monochromator into a RCA C-31034 photomultiplier. A Q4283SA Centronic photomultiplier with poorer time resolution was substituted when high sensitivity was required. The signal from the photomultiplier was displayed on a 7904 Tekronix oscilloscope (7A19 or 7A11 amplifier). For time-resolved spectra the photomultiplier signal was fed to a P.A.R. Model 760 box-car integrator. The photomultiplier load resistors were varied from 50 Ω to 10 kΩ as dictated by the time response required. With the 50 Ω load, decays as short as 1 nsec were measurable. The spectral resolution that could be used depended upon the load resistor necessary for an adequate signal-to-noise ratio. For the lifetime measurements of line emission from $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ a 1-nm resolution was achieved, but for line emission for the other salts and glassy solutions the resolution was reduced to 5 nm. Lifetimes of the broad fluorescence emissions were recorded at 10 nm resolution. For the measurements of $I(0)$ as a function of temperature the emission monochromator band pass was intentionally increased to 60 nm. High-resolution steady-state emission spectra were obtained with a 0.75 m Jarrell-Ash monochromator, 9558 EMI photomultiplier, and P.A.R. Model HR8 lock-in amplifier combination, with excitation provided by a PEK 100 W Hg lamp and a 0.25 m Jarrell-Ash monochromator. For excitation spectra, the same apparatus was used but the Hg lamp was replaced with a PEK 75 W Xe lamp. The salts were recrystallized from water. In order to avoid dehydration, $Cr(urea)_6Cl_3 \cdot 3H_2O$ was kept in a sealed cuvette.

Results

$[Cr(urea)_6](NO_3)_3$. The relative intensities of the 14196 and 14217 cm^{-1} lines, as recorded under steady illumination at 77 K, vary with excitation wave length (Figure 2). Although the differences are small, they are reproducible. The corresponding excitation spectra for the two lines are also different (Figure 3).

The 77 K emission decays were monitored in the region of the sharp line phosphorescence (704 nm) and broad band fluorescence (781 nm). Spectral resolution was lower in the pulsed than in the steady-state measurements; the 14196 and 14217 cm^{-1} lines were not resolved. In both the fluorescence and phosphorescence regions, nonexponential decay is obtained and the time evolution of the emission can be fitted to a double exponential function

$$I(t) = I_0(\alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2}) \qquad (1)$$

with $\tau_1 = 0.28$ μsec and $\tau_2 = 1.0$ μsec. α_1/α_2 is about ¼ and is slightly dependent upon the wavelength monitored. There are no additional decay components with $0.28\ \mu sec > \tau > 1.0$ nsec.

In the fluorescence region, $I(0)$ increases threefold as the temperature is raised from 77 to 150 K.

$[Cr(urea)_6]Cl_3 \cdot 3H_2O$. There are many lines in the emission spectrum of this crystal at 5 K.[5] The emission decays were monitored at wavelengths corresponding to many of these lines as well as in the fluorescence region (789 nm). The decays are nonexponential at all emission wavelengths, but the intensity-time profile varies markedly with the emission wavelength. At 698, 730, 741, 748, and 789 nm, a double decay is recorded (Figure 4a), but at 704, 709, 714,

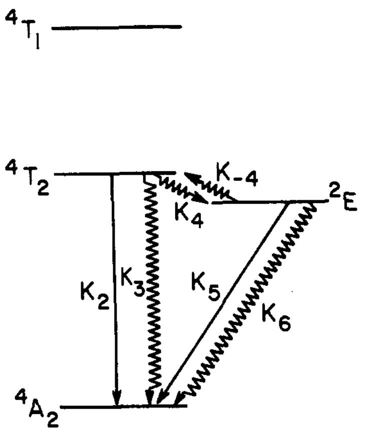

Figure 1. Energy levels and rate constants.

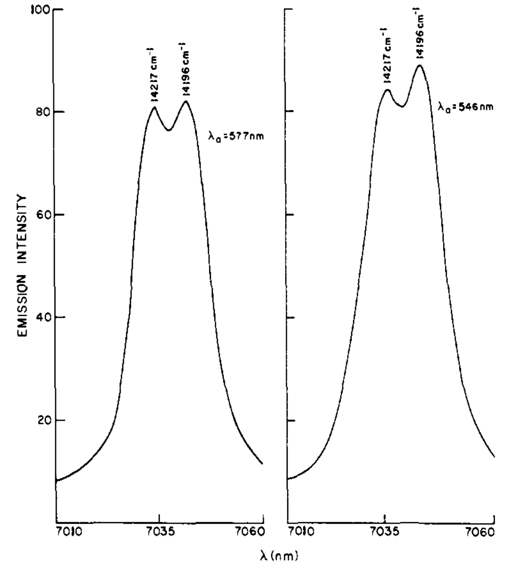

Figure 2. $^2E \rightarrow {}^4A_2$ emission spectra of $[Cr(urea)_6](NO_3)_3$ at 77 K for different excitation wavelengths.

724, 737, and 745 nm, a risetime preceded the decay (Figure 4b). The data in both the fluorescence and phosphorescence regions (698, 704, and 789 nm) were fitted to eq 1 with τ_1 = 2.0 μsec and τ_2 = 80 μsec. Although the lifetimes are wavelength invariant, α_1/α_2 depends not only in magnitude, but in sign as well, upon the emission wavelength. An additional component with a decay time ~50 nsec is present, but this may be an artifact, e.g., scattered light.

As the temperature is increased from 77 to 200 K, α_1/α_2 is nearly constant, but $I(0)$ of the fluorescence signal increases by a factor of 17.

Time-resolved spectra (Figure 5) depend somewhat upon time (0.5 μsec vs. 5 μsec) in the fluorescence region at 157 K.

Other Crystals. The 77 K decays of $[Cr(urea)_6](ClO_4)_3$ and $[Cr(urea)_6]I_3$ are exponential in both the fluorescence and phosphorescence regions and the lifetime in each case is independent of the emission wavelength. For $[Cr(urea)_6](ClO_4)_3$, $I(0)$ is increased threefold in the temperature range 77-100 K, while for $[Cr(urea)_6]I_3$, $I(0)$ is enhanced by a factor of 10 in the range 77-200 K. The risetimes of phosphorescence were not detectable and are <1 nsec.

Glass Solutions. The 77 K emission decay from $Cr(urea)_6{}^{3+}$ in a H_2O, methanol, ethylene glycol (1:2:1 v/v) glass is nonexponential, but in contrast to the crystal data, decays cannot be fitted to eq 1. The number of components is so large that no meaningful analysis is possible. The major components have lifetimes smaller than 200 nsec. Furthermore, the decay profile is dependent on the emission wavelength; the contribution of the faster decays is larger in the fluorescence region.

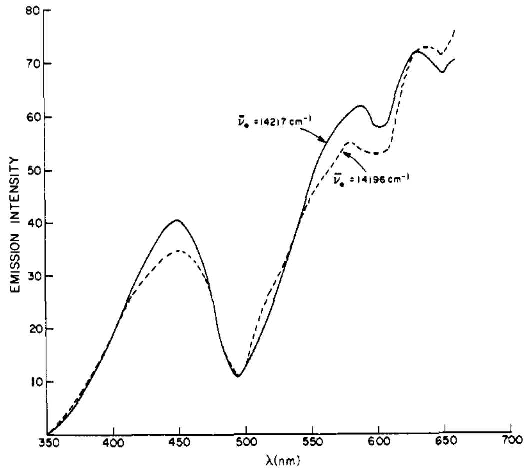

Figure 3. $^4T_2 \leftarrow {}^4A_2$ excitation spectra of $[Cr(urea)_6](NO_3)_3$ at 77 K for the monitored lines as indicated.

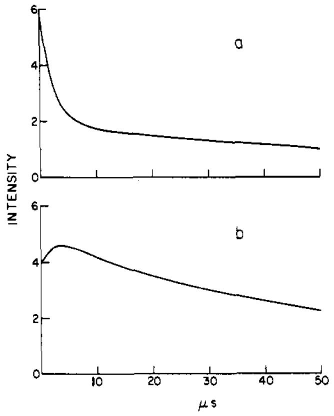

Figure 4. Decay profiles (77 K) of $[Cr(urea)_6]Cl_3{\cdot}3H_2O$ monitored at different wavelengths: (a) 698 nm, (b) 704 nm.

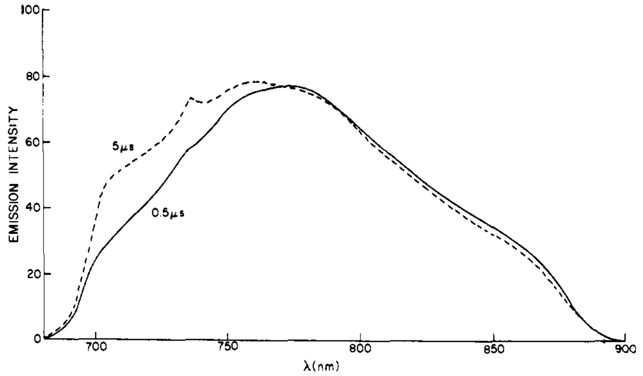

Figure 5. Time resolved spectra (157 K) of $[Cr(urea)_6]Cl_3{\cdot}3H_2O$ determined at the indicated times after pulsed excitation. The time window was 0.1 μsec.

As the temperature is increased, the decay becomes more exponential and at 180 K when the glass melts, one single decay with τ = 25 nsec is observed at 700 and 800 nm. In fluid solutions, the concentration was kept below 10^{-3} M to avoid crystallite formation.

At 77 K, the $Cr(antipyrene)_6{}^{3+}$ decay curves are concentration dependent,[10] but no such concentration effect was found for $Cr(urea)_6^{3+}$ in the range 3×10^{-3}-1.5×10^{-1} *M*, with a 1 nsec time resolution. The absence of a concentration effect persists down to 10^{-4} *M*, but the system response time was only 100 nsec in the more dilute solutions.

Discussion

If the $^4T_2$ state is populated by a δ function impulse, the time evolution of the $^4T_2$ and ^2E states is described by the equations

$$[^4T_2] = \frac{[^4T_2]_0}{\lambda_2 - \lambda_1}[(\lambda_2 - k_T)e^{-\lambda_1 t} + (-\lambda_1 + k_T)e^{-\lambda_2 t}] \quad (2)$$

$$[^2E] = \frac{k_4[^4T_2]_0}{\lambda_2 - \lambda_1}[e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (3)$$

where $\lambda_{1,2} = \frac{1}{2}[(k_E + k_T) \mp \{(k_T - k_E)^2 + k_4k_{-4}\}^{1/2}]$

$$k_T = k_2 + k_3 + k_4$$

$$k_E = k_5 + k_6 + k_{-4}$$

(k_2-k_6 are defined in Figure 1.) The fluorescence and phosphorescence intensities are $I_F = k_2[^4T_2]$ and $I_P = k_5[^2E]$, respectively. If the fluorescence and phosphorescence spectra overlap, the resultant intensity variation can still be fitted by eq 1 using the same two decay constants, $\lambda_2 = 1/\tau_1$ and $\lambda_1 = 1/\tau_2$. The resulting profiles are exemplified by the actual decay curves shown in Figure 4. Either a double decay or a risetime followed by a decay will obtain depending upon the relative contributions of I_F and I_P.

At low temperatures, where $k_{-4} \simeq 0$, the fluorescence and phosphorescence lifetimes are $\tau_F = 1/(k_2 + k_3 + k_4) = 1/\lambda_2$ and $\tau_P = 1/(k_5 + k_6) = 1/\lambda_1$; all fluorescence is "prompt". As the temperature is increased and delayed fluorescence becomes detectable, λ_2 can no longer be equated to a simple prompt fluorescence lifetime, but the delayed fluorescence and phosphorescence both decay with the same lifetime ($1/\lambda_1$). Although it is customary to use eq 1 to analyze double decays it is evident that the "lifetimes", τ_1 and τ_2, can be rather complicated functions of the several relaxation rate constants.

Under the circumstances considered here, the excitation pulse width and detection system response time are sufficiently short to permit the use of eq 2 and 3 and hence of eq 1. α_1/α_2 in eq 1 depends upon the rate constants, k_2-k_6 and on the spectral overlap of the fluorescence and phosphorescence. At $t = 0$, $I(0) = I_0(\alpha_1 + \alpha_2)$. $I(0)$ is determined by extrapolation of the decay profile to $t = 0$. $I(0)$ varies as $k_2[^4T_2]_0$ and its magnitude will depend upon the time scale of the measurement. In the present work $I(0)$ corresponds to the emission intensity ~0.01 μsec after pulsed excitation. Since neither the $^4T_2 \rightarrow {}^4A_2$ radiative rate, k_2, nor the absorbed light intensity change much with temperature, $I(0)$ should be nearly constant with temperature if prompt fluorescence is the source of the $t = 0$ intensity. On the contrary, a marked thermal enhancement of $I(0)$ is to be expected only if delayed fluorescence is a major source of intensity at $t = 0$, in the fluorescence region.

We will now examine, in terms of the foregoing discussion, the possible source of the multiple decays: prompt fluorescence and phosphorescence; phosphorescence from nonthermalized ^2E components; or, as we believe, phosphorescence and/or delayed fluorescence from $Cr(urea)_6^{3+}$ in different environments.

$^4T_2$ Prompt Fluorescence. At 5 K, the time-dependent behavior of the 14196 and 14217 cm^{-1} lines in the $[Cr(urea)_6](NO_3)_3$ emission is very different.[4,5] The 14196 cm^{-1} line exhibits a 40 μsec risetime and a 240 μsec decay time. The 14217 cm^{-1} line decays in a double exponential fashion, but the same two lifetimes prevail.[5] According to Dingle,[4] 14217 cm^{-1} is the 0-0 transition of $^4T_2 \rightarrow {}^4A_2$, i.e., prompt fluorescence, and 14196 cm^{-1} comes from $^2E \rightarrow {}^4A_2$. In this analysis 40 μsec is the $^4T_2$ lifetime at 5 K, and the risetime of $^2E \rightarrow {}^4A_2$ represents the slow feeding of ^2E by $^4T_2$. However, this is ruled out by the variation of the emission spectrum with excitation wavelength; the relative intensities of 14196 and 14122 are definitely different at 546 and 577 nm (Figure 2). In addition, the thermal enhancement of $I(0)$ is characteristic of delayed rather than prompt fluorescence and shows that the delayed fluorescence is emitted at times much smaller than 40 μsec, the purported decay time of $^4T_2$.

The effect of temperature on the $I(0)$ of $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ is even more striking and prompt fluorescence cannot be a significant contribution to the nonexponential decay in this system.

Finally, when delayed fluorescence is detectable, prompt fluorescence should persist at low temperatures, yet no broad fluorescence band is emitted by any $[Cr(urea)_6]X_3$ salt at 4-5 K.[4,5]

Emission from Nonthermalized ^2E Components. In addition to confirming Dingle's $[Cr(urea)_6](NO_3)_3$ results, Yersin, Otto, and Gliemann found a nonexponential decay in $[Cr(urea)_6]Br_3$.[5] They suggested an alternate explanation for the multiple decay, viz., the two decay constants correspond to transitions from the split components of ^2E. In $[Cr(urea)_6](NO_3)_3$ the 14217 and 14196 cm^{-1} lines were assigned as $^2E_a \rightarrow {}^4A_2$ and $^2E_b \rightarrow {}^4A_2$. The persistence of the two transitions at 5 K is to be expected only if thermalization is absent. Formally, eq 2 and 3 still apply, but the concentrations of $^4T_2$ and ^2E are now replaced by ^2E_a and ^2E_b. This interpretation does not explain the double decay of the 77 K broad fluorescence from $[Cr(urea)_6](NO_3)_3$ and $[Cr(urea)_6]Cl_3 \cdot 3H_2O$, nor is it consistent with the excitation wavelength variation of the relative 14196 and 14217 cm^{-1} intensities. Furthermore, nonthermalization of ^2E components is not observed in other complexes (vide infra).

Multiple Sites in $[Cr(urea)_6]X_3$ Crystals. The change in the emission spectrum with excitation wavelength (Figure 2) and of the excitation spectrum with emission wavelength (Figure 3) point strongly to a third interpretation of the decay results wherein multiple sites are involved. In this picture each center is excited, either directly or by energy transfer, and independently emits phosphorescence and delayed fluorescence. A double decay simply means that the ^2E lifetime is different in each site. A risetime then indicates $^2E \rightarrow {}^2E$ energy transfer from a short-lived species to one with a longer lifetime. Suppose that the energy transfer is A → B, then depending upon the relative intensities of directly excited and transferred B emission and on the spectral overlap of the A and B emissions, the decay profiles will resemble Figures 4a or 4b. If only B emission is monitored, a risetime will be observed when A → B transfer is significant. However, overlapping A and B emission can obscure this effect.

The effect of temperature on $I(0)$ is now readily understood, for only the phosphorescence and delayed fluorescence are monitored at $t > 10$ nsec.

In the 5 K lifetime measurements of Yersin, Otto, and Gliemann,[5] the 14196 and 14217 lines in $[Cr(urea)_6](NO_3)_3$ were resolved; the 14217 cm^{-1} decay profile resembled Figure 4a while the 14196 cm^{-1} decay exhibited a risetime in accord with the energy transfer model. In our measurements at 77 K the two lines were not resolved and the absence of a risetime is due to overlapping emission.

The lines with decay profiles of the Figure 4b type (risetime) are the most intense in the 5 K emission spectrum of

$[Cr(urea)_6]Cl_3{\cdot}3H_2O$.[5] Either these sites are more numerous or the lines are intensified by energy transfer.

The change in the broad fluorescence spectrum with time (Figure 5) is additional evidence against emission from the same center. If the short- and long-lived fluorescence components arise from single center prompt and delayed fluorescence, respectively, the fluorescence spectra should be the same for both components.

The $^4T_2$–^2E separation in $Cr(urea)_6{}^{3+}$ is rather sensitive to the environment. Both the emission spectra and intensity ratios of fluorescence to phosphorescence vary with the counterion in crystals[11] and the composition of the solvent mixture in solution.[12] Although crystal structures have not been reported for all of the crystals studied here, several structures of the $[M(urea)_6]X_3$ type have been completed[13-15] and these contain features that bear on the multiple site interpretation. The $M(urea)_6{}^{3+}$ moieties determine the structure and the anions are distributed "interstitially". Even a large anion such as $ClO_4{}^-$ fits loosely in the triangular channels. This situation leads to considerable disorder and the M^{3+} site symmetry in $[Al(urea)_6](ClO_4)_3$ changes with temperature.[14,15] ESR measurements in Cr^{3+} doped $[Al(urea)_6](ClO_4)_3$ indicate two nonequivalent Cr^{3+} sites above 25°, but six nonequivalent sites below room temperature.[16] $[Cr(urea)_6](NO_3)_3$ exists in two monoclinic phases with a transition temperature of 100°.[15] In hydrated salts, the arrangement of water molecules would likely lead to nonequivalent $Cr(urea)_6{}^{3+}$ sites.

The very marked nonexponentiality in glassy systems also indicates the sensitivity of the decay rates to environment, and it is not surprising to find multiple decays in $[Cr(urea)_6](NO_3$, $[Cr(urea)_6]Cl_3{\cdot}3H_2O$, and $[Cr(urea)_6]Br_3$.[5] In fact, it is more difficult to understand the single exponential decay in $[Cr(urea)_6](ClO_4)_3$ and $[Cr(urea)_6]I_3$. Either all the sites in these two crystals decay in nearly the same way, or efficient energy transfer to one predominant emitting site prevails.

Parenthetically, the possibility of multiple sites requires caution in the assignment of ^2E splittings. For example, a 69-cm^{-1} interval in the $[Cr(urea)_6]I_3$ emission spectrum was ascribed to the ^2E splitting.[17] However, the temperature variation of the intensities departed markedly from a Boltzmann distribution. These "components" may well originate in different sites.

It is of interest to compare the emission decay behavior in glassy solutions of $Cr(CN)_6{}^{3-}$ and $Cr(urea)_6{}^{3+}$. In both systems, the nonexponentiality disappears when the solvent becomes fluid. However, in glassy $Cr(CN)_6{}^{3-}$, nonexponentiality is observed only upon excitation of the low-energy tail of the $^4T_2 \leftarrow {}^4A_2$ bands, while all wavelengths excite nonexponential decay in $Cr(urea)_6{}^{3+}$. Apparently, the lifetime of the $Cr(urea)_6{}^{3+}$ complex is more sensitive to environment than is that of $Cr(CN)_6{}^{3-}$.

Conclusion

The nonexponential decays in $Cr(urea)_6{}^{3+}$ are due to emission from complexes in different environments and the prompt fluorescence lifetime must be less than 10^{-9} sec. The short $^4T_2$ lifetime in $Cr(urea)_6{}^{3+}$ is mirrored by the results in other Cr(III) systems and is probably due to a large value for k_4. Apparently the $^4T_2 \rightsquigarrow {}^2E$ intersystem crossing is very fast ($<10^{-9}$ sec) whenever $^4T_2$ is above ^2E, and all observed fluorescence is delayed.

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References and Notes

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