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Notes

Characterization of the Luminescent *Cu(CN)$_2$Br^{2-} Exciplex

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Introduction

The efficient luminescence from certain Cu(I) complexes has been the subject of intense studies, particularly within the context of assigning the optical transitions involved.[2,3] On the one hand, the copper(I) transitions resulting in luminescence have been ascribed to metal-to-ligand charge transfer (MLCT), where the electron is transferred from the copper(I) center to the unoccupied π^* orbital of the ligand,[4−10] or to charge transfer to solvent (CTTS), where the electronic charge moves to the solvent[11−13] molecule from the central atom. On the other hand, a metal-centered transitions of the types $3d^{10} \rightarrow 3d^94s$ and $3d^{10} \rightarrow 3d^94p$ on Cu(I) are considered[14−17] as another source of light emission. The common feature of all of the emissions is the pronounced Stokes shift, which especially in the case of the halocuprate(I) complexes in aqueous solutions is rather large.[3]

Recently we demonstrated that coordinatively-unsaturated *Cu(CN)$_2^-$, formed upon UV irradiation in aqueous solutions of dicyanocuprate(I), associates with halide ions to create a longer-lived, more highly luminescent species assigned as an exciplex.[18] However, since halo ligands also coordinate to the metal center in the ground state, with a stepwise formation constant that is about an order of magnitude smaller than that for the excited-state reaction,[18,19] the luminescence characteristics were explained by a mechanism involving both ground- and excited-state equilibrium reactions. We have observed that there is a dependence of lifetime on both the concentration and the nature of halo ion. At ambient temperature, the longest luminescence lifetime, ~200 ns, was observed for the Cu(CN)$_2^-$−Br$^-$ system in aqueous solutions at 5 M ionic strength, providing favorable conditions for characterizing the mixed-ligand inorganic exciplex. In this work, the absorption and emission spectra of the equilibrated, aqueous Cu(CN)$_2^-$−Br$^-$ system have been investigated, as well as the luminescence quenching dynamics, using steady-state and time-resolved photochemical techniques, in order to elucidate the nature of the luminescent exciplex, *Cu(CN)$_2$Br^{2-}, formed following absorption of the photon.

Experimental Section

Reagent grade NaBr, NaClO$_4$ (Reanal), and 1,1′-dimethyl-4,4′-bipyridinium dichloride (MV^{2+} = methylviologen, Aldrich) were used as received for the preparation of stock solutions from which solutions of desired bromide, MV^{2+} concentration, and ionic strength were prepared. Weighed samples of crystalline potassium dicyanocuprate(I), synthesized by the method described elsewhere,[19,22] were added to the argon bubble-degassed solutions. Glycerol−water mixtures (X_{glycerol} = 0, 0.15, 0.3), prepared from double-distilled, ion-exchanged water and reagent grade glycerol (Reanal), were used for the solvent media. The absorption spectra were recorded using a 0.01-cm quartz cuvette, while the emission spectra and time-resolved photochemical experiments were performed on 3-mL reaction mixtures in a 1-cm quartz cuvette.

Absorption spectra were obtained using a Zeiss SPECORD M40 spectrophotometer connected to an IBM/AT-compatible PC. Luminescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B spectrofluorophotometer. Luminescence quantum yields were determined by the quinine sulfate method.[23]

Time-resolved spectra, luminescence lifetimes, and transient absorbances were determined by a laser flash photolysis system described elsewhere.[12]

Results and Discussion

Absorption and Emission Spectra. Figure 1 shows a characteristic change in the UV region as the bromide ion concentration is varied for a series of difference absorption spectra between pairs of samples, both containing bromide at identical concentrations but only one having the dicyanocuprate(I) complex at a fixed concentration, 1.6×10^{-3} M, in glycerol−water solvent mixture ($X_{\mathrm{glycerol}} = 0.3$). The disappearance of the dicyanocuprate(I) peaks at 222 and 234 nm is concomitant with the formation of absorption bands at 226 and 238 nm. The structure of the spectrum which emerges with increasing bromide ion concentration is rather similar to that of Cu(CN)$_2$Cl^{2-} [18] in the range 220−250 nm; hence, the growing absorption peaks are assigned as the spin- and symmetry-allowed d $\rightarrow \pi^*$ MLCT transition in mixed-ligand bromodicyanocuprate(I) complex. It should be noted that these spectral changes are identical to those obtained in aqueous solution at 5 M ionic

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(1) On leave from Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, U.K.

(2) Parker, W. L.; Crosby, G. A. *J. Phys. Chem.* **1989**, *93*, 5692.

(3) Knotter, D. M.; Blasse, G.; van Vliet, J. P. M.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 2196.

(4) Blasse, G.; McMillin, D. R. *Chem. Phys. Lett.* **1980**, *70*, 1.

(5) Blaskie, M. W.; McMillin, D. R. *Inorg. Chem.* **1980**, *19*, 3519.

(6) Kirchoff, J. R.; Gamache, R. E., Jr.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 238.

(7) Gamache, R. E., Jr.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141.

(8) Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. *Inorg. Chem.* **1987**, *26*, 3167.

(9) Crane, D. R.; Di Benedetto, J.; Palmer, C. E. A.; McMillin, D. R.; Ford, P. C. *Inorg. Chem.* **1988**, *27*, 3698.

(10) Crame, D. R.; Ford, P. C. *Inorg. Chem.* **1993**, *32*, 2391.

(11) Stevenson, K. L.; Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472.

(12) Stevenson, K. L.; Berger, R. M.; Grush, M. M.; Stayanoff, J. C.; Horváth, A.; Horváth, O. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 215.

(13) Horváth, O.; Fendler, J. H.; Stevenson, K. L. *Inorg. Chem.* **1993**, *32*, 227.

(14) Pedrini, C. *Phys. Status Solidi B* **1978**, *87*, 273.

(15) Chermette, H.; Pedrini, C. *J. Chem. Phys.* **1981**, *75*, 1869.

(16) Horváth, A.; Zsilák, Z.; Papp, S. *J. Photochem. Photobiol. A: Chem.* **1989**, *50*, 129.

(17) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1986**, *108*, 7211.

(18) Horváth, A.; Stevenson, K. L. *Inorg. Chem.* **1993**, *32*, 2225.

(19) Horváth, A.; Stevenson, K. L. *Inorg. Chim. Acta* **1991**, *186*, 61.

(20) Gordon, S.; Hart, E. *J. Am. Chem. Soc.* **1964**, *86*, 5343.

(21) Tuttle, T. R., Jr.; Golden, S. *J. Phys. Chem.* **1980**, *84*, 2457.

(22) Horváth, A.; Horváth, O.; Stevenson, K. L. *J. Photochem. Photobiol. A: Chem.* **1992**, *68*, 155.

(23) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.

0020-1669/94/1333-5351$04.50/0

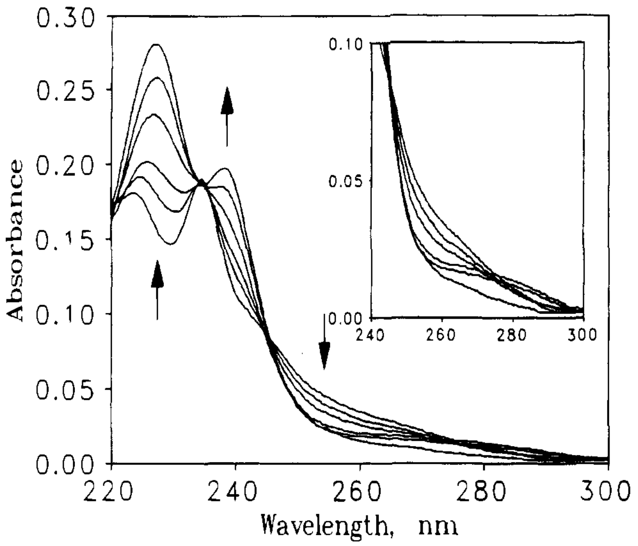

Figure 1. UV absorption spectra of copper(I) complexes in an $X_{\mathrm{glycerol}} = 0.30$ glycerol–water solvent mixture, for 1.6×10^{-3} M $\mathrm{Cu(CN)_2^-}$ and 0, 0.2, 0.4, 1, 2, 3 M $\mathrm{Br^-}$.

Table 1. Effects of Solvent Composition and Ionic Strength (μ) on Luminescence Quantum Yield (ϕ_L) and Lifetime (τ) Measured at Ambient Temperature[a] ($[\mathrm{Br^-}] = 1.5$ M)

X_{glycerol}	μ (M)	$10^3\phi_L$	τ (ns)
0.00	5.0	1.25	190
0.15	1.5	0.80	480
0.15	5.0	4.40	950
0.30	5.0	6.10	1510

[a] Uncertainty is ±5% for ϕ_L and ±3% for τ.

strength. However, the weak absorption band appearing as a shoulder in the 265–300-nm range develops at high bromide ion concentration only, when the addition of NaBr also accompanies the enhancement in the ionic strength. This medium effect suggests that the transition which produces the luminescent molecular entity is CTTS in nature.

The steady-state luminescence measurements display a rather large Stokes shift (280–480 nm); the excitation spectrum matches the absorption band in the 265–300-nm range, while the emission maximum appears at 480 nm. The luminescence quantum yield and the lifetime show solvent and ionic strength dependence, as indicated in Table 1.

Time-Resolved Emission and Absorption Spectra. The time-resolved luminescence experiments also revealed a significant sensitivity to the bromide ion concentration and the solvent composition. For example, as shown in Table 1, the lifetime increases 10-fold in a glycerol–water ($X_{\mathrm{glycerol}} = 0.3$) solvent mixture at 5 M ionic strength compared to that observed in pure water at 5 M ionic strength.

In a 1.5 M NaBr solution ($X_{\mathrm{glycerol}} = 0.15$) of dicyanocuprate(I) ($[\mathrm{Cu(I)}] = 1.0 \times 10^{-3}$ M) 266-nm laser excitation (15 ns, 20 mJ) resulted in the formation and decay of several intermediates with different spectra and lifetimes. Figure 2 shows the transient absorption spectra recorded 100 ns and 5 μs after the laser pulse in the 300–860-nm range. The coincidence of the absorption band peaking at 700 nm with that of the published normalized spectrum of the hydrated electron[20,21] suggests that the solvated electron is one of the primary products of the photoexcitation. Addition of electron scavengers such as $\mathrm{NO_3^-}$, $\mathrm{MV^{2+}}$, or $\mathrm{O_2}$ to the solution decreases the absorption and increases the decay rate at 700 nm, supporting the assignment of the red absorption band. Hence the primary photochemical reactions can be regarded as which are analogous to the reactions

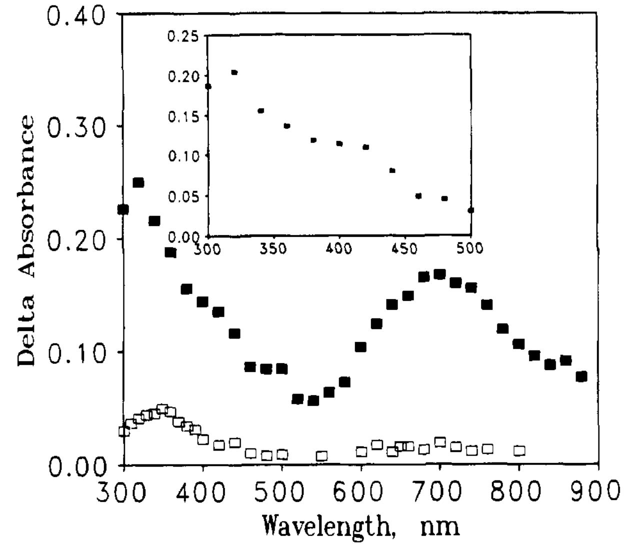

Figure 2. Transient absorption spectra recorded 100 ns (■) and 5 μs (□) after a 266-nm laser pulse in glycerol–water solvent mixture ($X_{\mathrm{glycerol}} = 0.15$); $[\mathrm{Cu(I)}] = 10^{-3}$ M, and $[\mathrm{Br^-}] = 1.5$ M. Inset: transient absorption spectrum obtained by subtracting the spectra of e_{solv}^- and $^{\bullet}\mathrm{Br_2^-}$ from the overall spectrum detected 100 ns after the laser excitation.

$$\begin{tikzcd}
\mathrm{Cu(CN)_2^-} + h\nu \arrow[r] \arrow[d, shift right, "+\mathrm{Br^-}"'] & \mathrm{Cu(CN)_2} + e_{\mathrm{solv}}^- & (1) \\
\mathrm{Cu(CN)_2Br^{2-}} + h\nu \arrow[r] \arrow[u, shift right, "-\mathrm{Br^-}"'] & \mathrm{Cu(CN)_2Br^-} + e_{\mathrm{solv}}^- & (2)
\end{tikzcd}$$

that occur in solutions of dicyanocuprate(I) and chloride ion.[19,22] The quantum yield, ϕ_e, for solvated electron formation was estimated by comparing the peak electron transient absorbances with that obtained from an aqueous solution of dicyanocuprate(I) under normal conditions.[22] This procedure resulted in $\phi_e = 0.12 + 0.02$ in a solvent mixture ($X_{\mathrm{glycerol}} = 0.15$) at 1.5 M bromide ion concentration. At 700 nm, the absorbance appears to undergo a pseudo-first-order decay, due to the efficient electron scavenging by copper(I) complexes,[12,22] to a very small residual absorption after several microseconds. This behavior is different from that detected in the range 300–400 nm, as indicated by the rapid and slow decay at 360 nm in Figure 3. In the time-resolved spectrum taken 5 μs after the laser pulse (see Figure 2), after the solvated electron has disappeared, one can see an absorption band peaking at 360 nm and a very weak but rather wide band in the 600–800-nm range, suggesting the formation of $^{\bullet}\mathrm{Br_2^-}$, which has a very similar spectrum.[24,25] From the shape of the decay curve (Figure 3), it appears that $^{\bullet}\mathrm{Br_2^-}$ is formed in a very short period (within 1 μs) after the laser pulse, a behavior which cannot be explained by the thermal reaction between the bromide ion and the copper(II) species formed in the primary photochemical reaction. It is reasonable to suppose, however, that $^{\bullet}\mathrm{Br_2^-}$ forms in the coordination sphere after the second bromide ion attaches to the copper atom and an electron transfers to the d^9 orbital of the metal center.

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(24) Gordon, L. H. Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution. *NSRDS-NBS* **1981**, *69*, 52–53.

(25) A recent study demonstrated that the $^{\bullet}\mathrm{I_2^-}$ radical can be formed by photoexcitation of iodocuprate(I) complexes.[13] The appearance of this species was attributed to the reduction of the copper(II) complex produced in the primary photochemical reaction: $\mathrm{CuI_3^-} + 2\mathrm{I^-} \rightarrow \mathrm{CuI_3^{2-}} + \mathrm{I_2^-}$. An estimation of the rate constant for radical formation based on the transient absorption yielded a value of $(4.4 \pm 2.6) \times 10^7$ $\mathrm{M^{-1}\,s^{-1}}$ at 1 M NaI. Such a fast redox reaction can also be expected between the excited triiodocuprate(I) and the iodide ion.

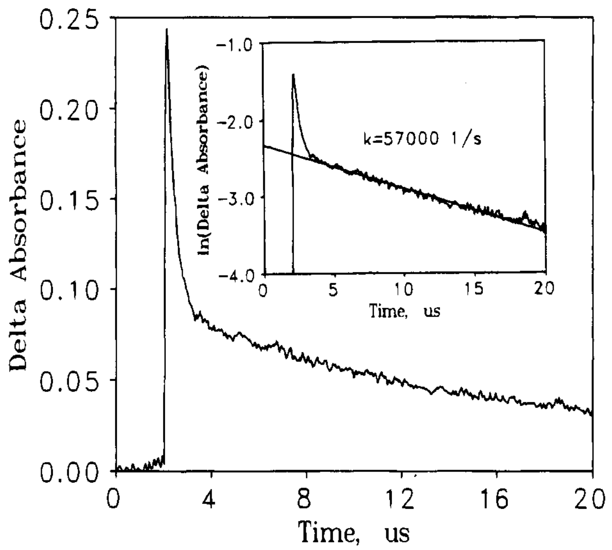

Figure 3. Transient absorption spectrum at 360 nm (same conditions as in Figure 2). Inset: ln(absorbance) and the decay constant of the longer-lived intermediate.

$$^*Cu(CN)_2Br^{2-} + Br^- \rightarrow Cu(CN)_2^{2-} + {}^{\bullet}Br_2^- \qquad (3)$$

This is in agreement with our proposed mechanism for exciplex formation in the $Cu(CN)_2^- - X^-$ systems (X = Cl, Br, I),[18] namely, reaction of the excited species with halide ion resulting in a decrease in luminescence lifetime. On the basis of our estimate of the rate constant for this reaction, 7×10^5 M^{-1} s^{-1}, in aqueous solution at 5 M ionic strength, the rapid appearance of $^{\bullet}Br_2^-$ can be explained. The decay of the absorbance at 360 nm, following the first rapid stage, obeys pseudo-first-order kinetics with a rate constant of 5.7×10^4 s^{-1}.

The development of $^{\bullet}Br_2^-$, however, cannot be followed due to the superposition of a very strong transient absorption peaking at 320 nm and associated with another very short-lived intermediate. We have estimated the spectrum of this species by subtracting the absorption spectra of e_{solv}^- (100 ns after the laser pulse) and $^{\bullet}Br_2^-$ (the values extrapolated to 100 ns using absorptions detected 5 μs after the laser pulse and the decay constant of $^{\bullet}Br_2^-$, 5.7×10^4 s^{-1}) from the overall spectrum obtained 100 ns after the laser pulse. The procedure revealed a very strong absorption band peaking at 320 nm and a weaker shoulder at 420 nm. The fast decay of the 395-nm absorbance obeys first-order kinetics with a lifetime of 480 ± 20 ns, which is identical to that of the luminescence (Figure 4, Table 1). This coincidence and the very rapid development of the absorption after the laser pulse (peaking in the same or shorter period than that of the solvated electron) suggest that we obtained the spectrum of the luminescent excited species. Since the luminescent $^*Cu(CN)_2Br^{2-}$ complex can be formed either by direct excitation of the bromodicyanocuprate(I) or by reaction between the ground-state bromide ion and the excited dicyanocuprate(I), this species can be regarded as the precursor of $^{\bullet}Br_2^-$. Considering the quantum yield for solvated electron formation, the molar absorbance of $^{\bullet}Br_2^-$ and e_{solv}^-, and the efficiency of the exciplex reaction with the bromide ion (about 20%[22,26]), we obtain a rather high value for exciplex formation quantum yield, $\phi_{exc} = 0.4$. Using this result, we estimated the molar absorbance of the luminescent species: $\epsilon_{320nm} = 7200 \pm 800$ M^{-1} cm^{-1} and $\epsilon_{420nm} = 3800 \pm 500$ M^{-1} cm^{-1}. These rather large molar absorbances suggest that the transitions are spin- and symmetry-allowed.

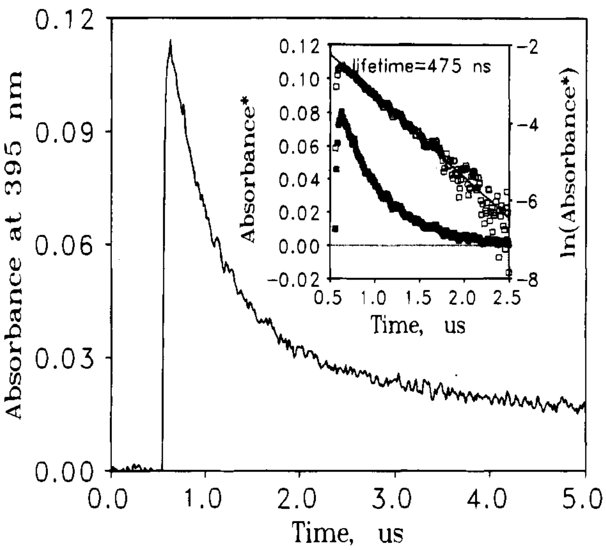

Figure 4. Transient absorption spectrum at 395 nm (same conditions as in Figure 2). Inset: absorbance corrected for the absorbance of the longer-lived species ($^{\bullet}Br_2^-$) and the decay constant of the short-lived intermediate.

Luminescence Quenching and Electron Scavenging. On the basis of the relatively long lifetime of emission, it is reasonable to regard the light emission process as phosphorescence; i.e., the luminescence originates from a triplet excited state. In order to confirm this assignment, oxygen was used as a quencher. A series of solutions ($X_{glycerol} = 0.15$) were prepared containing the copper(I) complex at 2×10^{-4} M, bromide ion at 1.5 M, and varying concentrations of oxygen. This was achieved by mixing in various ratios two reaction mixtures: one argon-saturated (deoxygenated) and the other saturated with oxygen under atmospheric pressure. Since oxygen can act in the excited sample both as an electron scavenger and as a triplet quencher, we measured the decay constant of the solvated electron and the luminescence lifetime on the same sample. The results of these measurements clearly indicate that the oxygen is a very efficient quencher of luminescence because the value of $k_q[O_2] = (9.5 \pm 0.5) \times 10^5$ s^{-1} is very close to that for electron scavenging, $k_e[O_2] = (1.5 \pm 0.1) \times 10^6$ s^{-1}, which is diffusion-controlled, confirming the triplet nature of the luminescent exciplex.

In another experiment, methylviologen was used to quench the exciplex luminescence in a reaction which occurs via electron transfer from the excited species. Efficient quenching was indicated by a significant shortening in the luminescence lifetime with increasing [MV^{2+}]. The development of $^{\bullet}MV^+$ absorbance peaking at 395 nm and in the 550–650-nm range was also observed; however, this change is expected from the concerted effect of luminescence quenching and the solvated electron scavenging

$$^*Cu(CN)_2Br^{2-} + MV^{2+} \rightarrow Cu(CN)_2Br^- + {}^{\bullet}MV^+ \qquad (4)$$

$$e_{aq}^- + MV^{2+} \rightarrow {}^{\bullet}MV^+ \qquad (5)$$

The rate constants for these reactions were estimated by measuring the lifetimes of the luminescence and the solvated electron at various concentrations of methylviologen. The results indicate that methylviologen is very efficient in the quenching reaction, yielding $k_q = (6 \pm 1) \times 10^9$ M^{-1} s^{-1}. The electron-scavenging rate constant ($k_s = 1.3 \times 10^{10}$ M^{-1} s^{-1}) is

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[26] Unpublished results.

smaller than in pure aqueous solution[22,27] due to the greater viscosity of the glycerol–water solvent mixture than of the water.

Conclusions

Transient absorption spectroscopy and quenching studies confirm the triplet nature of the luminescent species $^*Cu(CN)_2Br^{2-}$, created either by direct excitation of the ground-state bromodicyanocuprate or by coordination of the bromide ion to the central atom in the excited dicyanocuprate(I). This triplet excited molecule would be favorable for formation of $^{\bullet}Br_2^-$ in the coordination sphere after the second ligand attaches to the metal center and an electron transfers to the d^9 orbital of the copper atom. The quenching experiments also illustrate that, on the one hand, $^*Cu(CN)_2Br^{2-}$ can act both as an electron donor, when methylviologen is used as quencher, and as an electron acceptor, in a reaction with the bromide ion at high concentration, and, on the other hand, it can transfer energy to another molecule. The rather large Stokes shift and the sensitivity of luminescence to the solvent suggest that the geometric relaxation of the excited state is a very important factor in influencing the lifetime.

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(27) Farrington, J. A.; Ebert, M.; Land, E. J.; Flechter, K. *Biochim. Biophys. Acta* **1973**, *314*, 372.