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Solvent Effect on the Nonradiative Deactivation of the Excited State of Tris(2,2′-bipyridyl)ruthenium(II) Ion

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Synopsis. Emission quantum yields and lifetimes of the $[Ru(bpy)_3]^{2+}$ ion were measured in various solvents at 25 °C. Nonradiative rate constants (k_{nr}) were calculated from these data. A plot of k_{nr} *vs.* the Gutmann's acceptor number was found to be linear. This result can be explained in terms of the contributions of charge transfer to solvent (CTTS).

The well-known luminescence of the tris(2,2′-bipyridyl)ruthenium(II) ion, $[Ru(bpy)_3]^{2+}$, has been extensively studied. It has been generally accepted that the luminescence at 77 K arises from a charge transfer to ligand (CTTL) excited state.[1] Houten and Watts,[2,3] however, studied effects of ligand and solvent deuteration on the luminescence quantum yields and lifetimes in aqueous solution between 0 and 100 °C. They concluded that in this temperature range charge transfer to solvent (CTTS) configurations contribute to the luminescence in addition to the CTTL configuration. This conclusion suggests that complex-solvent interactions in fluid solutions are important in the deactivation processes of the CTTL excited state. So it is surprising that there have been few photophysical and systematic studies of the $[Ru(bpy)_3]^{2+}$ complex in organic solvents. In this paper the author reports the emission quantum yields and lifetimes measured in various solvents and also some information on the contributions of CTTS to the nonradiative deactivation of the CTTL excited state.

Experimental

Tris(2,2′-bipyridyl)ruthenium(II) chloride pentahydrate, $[Ru(bpy)_3]Cl_2 \cdot 5H_2O$, was prepared according to the method described in the literature.[4] Found: C, 48.88; H, 4.51; N, 11.67%. Calcd for $C_{30}H_{34}O_5N_6RuCl_2$: C, 49.32; H, 4.69; N, 11.50%. All solvents were reagent grade and used without further purification. Absorption and emission spectra were measured with a Hitachi 124 double-beam spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, respectively. Emission quantum yields were determined at the excitation wavelength of 436 nm by the modified Parker and Rees method[5] using fluorescein purified by the reported procedures[6] in 0.1 mol dm^{-3} NaOH (yield, 0.90) or $[Ru(bpy)_3]Cl_2$ in aerated aqueous solution (yield, 0.028[7]) as the standards. Lifetimes were measured using an apparatus with a pulsed nitrogen laser as the exciting light source. All samples were prepared immediately prior to use and the complex solutions were nitrogen-saturated for 15—20 min. All measurements were carried out at 25 °C.

Results and Discussion

The absorption maxima in the visible CTTL band of the $[Ru(bpy)_3]^{2+}$ ion show only slighter shifts than the emission maxima upon changes of solvents (Table 1). However, the efforts to relate the tendency in the spectral shifts with solvent parameters such as dielectric constants were unsuccessful, although it was seen that both absorption and emission spectra shifted to red in alcohols having a longer carbon-carbon bond chains. The latter observation has been reported by Meisel *et al.*[8]

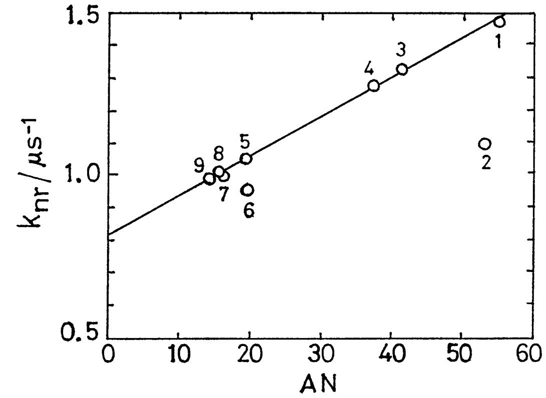

Fig. 1. Plot of k_{nr} *vs.* acceptor number(AN) for $[Ru(bpy)_3]Cl_2$ in various solvents at 25 °C. Solvent: 1, water; 2, acetic acid; 3, methanol; 4, ethanol; 5, acetonitrile; 6, dimethyl sulfoxide; 7, *N,N*-dimethylformamide; 8, benzonitrile; 9, pyridine.

The results of the emission quantum yields listed in Table 1 may be explained this way. If CTTS actually contributes to the CTTL excited state, it may safely be said that the higher electron-attractive power a solvent has (that is, the more electrophilic a solvent is), the more easily the charge transfers to the solvent. Such a state is unlikely to be stable and thus would lead to a fast nonradiative deactivation. Taking account of the fact that the so-called Gutmann's acceptor number[9] adequately fits the solvent properties described above, the nonradiative rate constant for the CTTS deactivation, k_{CTTS}, can be considered to be proportional to the acceptor number (AN). Hence the following expression:

$$k_{nr} = k_{nr}^{\circ} + k_{CTTS} = k_{nr}^{\circ} + k'[AN],$$

can be derived, where k_{nr}, k_{nr}°, and k' denote the total nonradiative rate constant, the nonradiative rate constant independent of CTTS, and a rate constant dependent on AN, respectively. The value of k_{nr} can be calculated from the emission quantum yields (Q) and measured lifetimes (τ_m) by the equation, $k_{nr}=\tau_m^{-1}-k_r$, where k_r is the radiative rate constant calculated from Q/τ_m. The results are also tabulated in Table 1. The plot of k_{nr} *vs.* the acceptor number, AN, is illustrated in Fig. 1, which clearly shows a linear dependence of k_{nr} on AN with a slope of 0.012

TABLE 1. ABSORPTION AND EMISSION SPECTRAL DATA, EMISSION QUANTUM YIELDS, LIFETIMES, AND SOLVENT PARAMETERS FOR $[Ru(bpy)_3]Cl_2$ IN VARIOUS SOLVENTS AT 25 °C

Solvent	Ab[a] λ_{max}/nm	Em[b] λ_{max}/nm	Q[c]	τ_m[d]/μs	k_{nr}/μs^{-1}	AN	Dielectric constant[e]	R/%[f]
Methanol	449	609	0.045 ± 0.002	0.72 ± 0.03	1.33	41.3	32.6	38
Acetonitrile	450	611	0.059 ± 0.002	0.89 ± 0.03	1.06	19.3	38.0	23
Ethanol	450	608	0.052 ± 0.004	0.74 ± 0.02	1.28	37.1	24.3	36
Acetic anhydride	451	611	0.075 ± 0.003				20.7	
Acetic acid	451	619	0.065 ± 0.003	0.85 ± 0.05	1.10	52.9	6.13	26
Ethylene glycol	452	611	0.070 ± 0.003				40.75	
Water	452	628	0.042 ± 0.002	0.65 ± 0.02	1.47	54.8	78.3	45
1-Pentanol	452	610	0.059 ± 0.003				13.9	
DMF[g]	453	628	0.068 ± 0.006	0.93 ± 0.04	1.00	16.0	36.1	18
Benzyl alcohol	454	610	0.078 ± 0.002				13.1	
1-Octanol	454	628	0.061 ± 0.002				10.34	
1-Decanol	454	630	0.056 ± 0.002					
Pyridine	454	619	0.087 ± 0.003	0.92 ± 0.05	0.99	14.2	12.3	18
DMSO[h]	454	630	0.077 ± 0.005	0.96 ± 0.02	0.96	19.3	46.6	15
Benzonitrile	454	609	0.073 ± 0.002	0.92 ± 0.02	1.01	15.5	25.2	19

a) Absorption maxima. b) Emission maxima. c) Excited at 436 nm. d) Excited at 337 nm. e) Ref. 10. f) See text. g) *N*,*N*-Dimethylformamide. h) Dimethyl sulfoxide.

μs^{-1} except in the case of the acidic solvent, acetic acid. Using the value of the intercept, 0.82 μs^{-1} ($= k^{\circ}_{nr}$), the percentages, R, for the contributions of CTTS to the total nonradiative rate constant can be evaluated (Table 1). As was expected, in a solvent with a large acceptor number such as water, about half of the CTTL excited state of the $[Ru(bpy)_3]^{2+}$ ion deactivate through the contributions of CTTS, whereas in solvents such as *N*,*N*-dimethylformamide, benzonitrile, and pyridine the percentages are only about 20%. Unfortunately the experiments in other solvents could not be carried out because of the solubility problem or the lack of the knowledge of the acceptor number, but the general features obtained in this work seem to be unchanged.

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