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The Sensitization of Rare Earth Ion Luminescence in Dilute Solutions by [1]Benzopyrano[3,4-*c*]pyridine-4,5(3*H*)-dione Derivatives

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Synopsis. Luminescence spectra and lifetimes are presented for the rare earth ions sensitized by [1]benzopyrano-[3,4-*c*]pyridine-4,5(3*H*)-dione derivatives in dilute solutions. It is to be noted that, among the benzopyranopyridine derivatives investigated, 2-phenyl-[1]benzopyrano[3,4-*c*]pyridine-4,5(3*H*)-dione brings about the most efficient sensitization for the luminescence of europium and terbium ions. Some discussions are made of the energy-transfer processes from these excited benzopyranopyridine derivatives to terbium ions.

Although the phenomenon of intramolecular energy transfer in β-diketone chelates of rare earth ions is well known,[1] the process of intermolecular energy transfer between organic compounds and rare earths has been discussed only recently.[2] This note will give the luminescence characteristics of europium and terbium ions sensitized by 2-phenyl-[1]benzopyrano[3,4-*c*]pyridine-4,5(3*H*)-dione (PBPP), 2-*p*-methoxyphenyl-[1]-benzopyrano[3,4-*c*]pyridine-4,5(3*H*)-dione (*p*-MBPP), and 7-methoxy-2-phenyl-[1]benzopyrano[3,4-*c*]pyridine-4,5(3*H*)-dione (MPBPP) in 1:1 (v/v) ethanol–methanol solutions.

Experimental

Three benzopyranopyridine derivatives, europium nitrate hexahydrate and gadolinium nitrate hexahydrate, and terbium acetate hemihydrate and gadolinium acetate anhydrate were prepared by the methods described by Sakurai *et al.*,[3] Dawson *et al.*,[4] and Witt *et al.*[5] respectively. The luminescence and excitation spectra were measured using the Hitachi Model MPF-2A fluorescence spectrophotometer. Measurements of the lifetimes of the rare earth ion luminescence sensitized by benzopyranopyridine derivatives were made with a photomultiplier located at a 90° angle from the exciting intense ultraviolet beam from a xenon lamp. The flash light given by this lamp had a life-duration of less than 50 μs.

Results and Discussion

The spectra observed at room temperature are presented in Fig. 1. The degree of enhancement in the rare earth ion luminescence at a certain fixed wavelength, *i.e.*, 613 nm for europium and 544 nm for terbium ions, sensitized by donors (benzopyranopyridine derivatives), are shown in Table 1 in terms of the enhancement factor obtained by dividing the relative intensity of the luminescence of the rare earth ions in the presence of the donors by that in their absence, the concentration of the donors being 2.0×10^{-4} M, and that of the acceptors (rare earth salts), 4.5×10^{-3} M. It should be noted that, among the donors investigated, PBPP brings about the most efficient sensitization for the luminescence of europium and terbium ions.

The presence of an acceptor causes a blue shift to the fluorescence and excitation bands of a benzopyranopyridine derivative (Figs. 1 and 2). This result indicates that there is a weak interaction between benzopyranopyridine derivatives and the rare earth ions. Since the excitation spectrum of the rare earth luminescence overlaps appreciably with that of the benzopyranopyridine derivative–rare earth mixed system, a direct excitation of the rare earth should also occur (Fig. 2). However, such an excitation would be

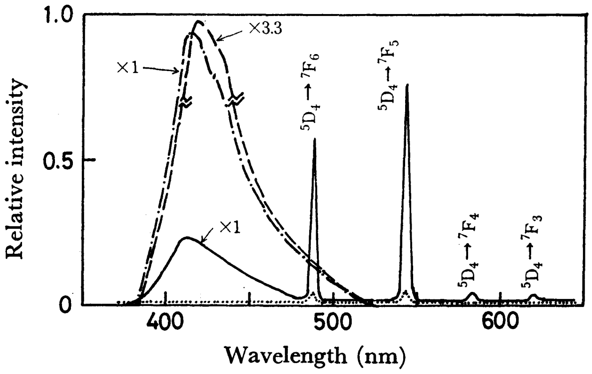

Fig. 1. Luminescence spectra of PBPP (8×10^{-5} M) alone (---), PBPP (8×10^{-5} M)–gadolinium acetate (9×10^{-4} M) system (-•-), PBPP (8×10^{-5} M)–terbium acetate (9×10^{-4} M) system (—), and terbium acetate (9×10^{-4} M) alone (···).

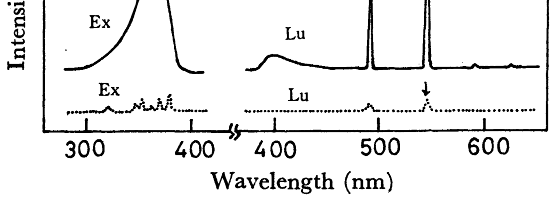

Fig. 2. Excitation (Ex), fluorescence (Fl), and phosphorescence (Ph) spectra of PBPP alone (---) and PBPP–gadolinium acetate system (-•-) at 77 K and Ex and luminescence (Lu) spectra of PBPP–terbium acetate system (—) at 77 K and terbium acetate alone (···) at room temperature. Ex spectra; for the emissions as indicated by arrows. Fl, Ph, and Lu spectra; excitation at 370 nm.

TABLE 1. ENHANCEMENT FACTORS FOR VARIOUS RARE EARTH ION SYSTEMS AND TRIPLET ENERGY LEVELS[a)] OF THE DONORS ALONE AND THE DONOR–GADOLINIUM NITRATE MIXED SYSTEMS

Donor	Excitation wavelength (nm)	Enhancement factor		Triplet level[a)]	
		Eu^{3+} (613 nm)	Tb^{3+} (544 nm)	Donor alone (cm^{-1})	Gd^{3+} (cm^{-1})
PBPP	370	40	70	21300	21500
p-MBPP	370	27	32	21200	21400
MPBPP	370	20	55	21100	21600

a) The phosphorescence maxima of the donors.

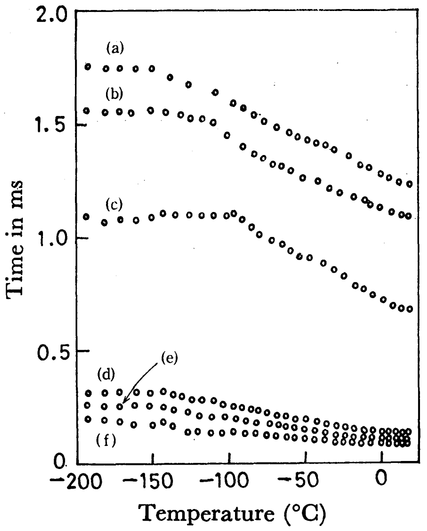

Fig. 3. The lifetimes of terbium ${}^5D_4$—${}^7F_5$ for the *p*-MBPP–Tb (a), PBPP–Tb (b), and MPBPP–Tb (c) systems, and those of the europium ${}^5D_0$—${}^7F_2$ for the *p*-MBPP–Eu (d), PBPP–Eu (e), and MPBPP–Eu (f) systems.

inefficient, because the excitation bands for the luminescence of rare earth ions are weak and very narrow.

As is shown in Fig. 1, the fluorescence intensity of PBPP at room temperature decreases when rare earth ions are present. It is impossible to excite gadolinium ions by energy transfer from either the lowest excited singlet or triplet state of the PBPP, since no transitions in the visible or near-infrared regions exist in the case of gadolinium ions. It can be seen from Fig. 2 that the intensity ratio of the phosphorescence to the fluorescence of the donor at 77 K is much increased by the presence of gadolinium ions. Accordingly, the decrease (about 70%) in fluorescence intensity in the presence of gadolinium ions at room temperature is due to the enhancement in the intersystem crossing (from the lowest excited singlet state to the lowest excited triplet state) of the donor caused by gadolinium ions. The fact that the fluorescence intensity of the donor at room temperature is weakened to about 10% by the presence of terbium (III) ions must be due to the combined effect of the increase in the intersystem crossing of the PBPP caused by terbium ions, with that of the energy transfer from the PBPP to the terbium ions. The excitation of terbium ions by the direct transfer of energy from the lowest excited singlet states of the donors is energetically feasible, but this process would be inefficient because the intersystem crossing of the donors would be enhanced by terbium ions in almost the same degree as by gadolinium ions.

The triplet energy levels of the donors alone and those of the donor–Gd systems at 77 K are listed in Table 1. When the gadolinium ions are present, the triplet levels show a blue shift. The triplet levels of all the donor–Gd systems are nearly 21500 cm^{-1} above the ground energy levels of the donors. The resonance level (${}^5D_4$)[6)] of terbium ions is 20430 cm^{-1} above the ground level (${}^7F_6$). The ${}^5D_4$ level of terbium ions is, therefore, readily populated by the energy transfer from the triplet state of the donor. Consequently, the luminescence is due to the transition to the ${}^7F$ manifold levels from the ${}^5D_4$ levels of terbium ions. In addition, the intensity ratio of the phosphorescence to the fluorescence decreases with an increase in the concentration of terbium when the donor concentration is kept constant at 77 K, until finally it becomes impossible to observe the phosphorescence spectra of the donors (Fig. 2). From the facts described above, it may be concluded that an energy transfer can be expected from the lowest triplet energy levels to terbium ion levels.

The line emissions due to the transitions from the ${}^5D_0$ levels of europium and the ${}^5D_4$ levels of terbium ions sensitized in the mixed systems were so intense that measurements of the lifetimes could be made easily. The observed lifetimes are presented in Fig. 3. Among the mixed systems of the [1]benzopyrano[3,4-*c*]pyridine-4,5(3*H*)-dione derivatives and rare earth ions so far investigated, the duration of the luminescence of the *p*-MBPP–Tb system was found to be the longest.

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