EXCITED-STATE CHIRAL DISCRIMINATION IN AQUEOUS SOLUTIONS OF LANTHANIDE(III): 2,6-PYRIDINEDICARBOXYLATE COMPLEXES*

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Addition of resolved-Ru(phenanthroline)$_3^{2+}$ to aqueous solutions of racemic complexes of Ln(2,6-pyridinedicarboxylate)$_3^{3-}$ (where Ln = Eu(III) and Tb(III) results in efficient quenching of lanthanide emission. The terbium complex is quenched more than the europium complex illustrating the importance of electronic overlap. The emission is also circularly polarized indicating that the quenching mechanism is enantioselective. Comparison with previous data allows for the identification of the enantiomer in excess, and, thus, of the favored enantioselective energy transfer pair.

Although chiral discriminatory interactions involving diastereomeric pairs of optically active molecules has been observed and recognized since the time of Pasteur, there have only been a very few observations of such differences involving excited electronic states[1-9] (for a review see ref.[10]). Furthermore, these latter observations have more often simply reflected differences between R–R and R–S molecular ground state conformations through monitoring of an excited state process, such as contact quenching, or short-range sensitization of a chemical reaction by a photo-excited chiral molecule. Recently, chiral discrimination directly involving the differential diastereomeric interactions of excited states has been observed by monitoring the time dependence of the measured differential circularly polarized emission[11]. This study involved the quenching of excited Tb(2,6-pyridinedicarboxylate = DPA)$_3^{3-}$ by resolved Ru(1,10-phenanthroline = phen)$_3^{2+}$. In the work reported here, we report further on this phenomenon including data for the chiral quenching of Tb(DPA)$_3^{3-}$ and Eu(DPA)$_3^{3-}$. Analysis of this data allows one to determine the quenching rate constant, and the identity of the dominant enantiomer present in solution.

EXPERIMENTAL AND RESULTS

Lanthanide(III) ions are known to form tris-terdendate complexes with D_3 symmetry with 2,6-pyridinedicarboxylic acid (DPA) in aqueous solutions under basic conditions. Since the lignad is achiral, both enantiomers (Λ) and (Δ) are formed in equal

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amounts, and the solution can be described as a racemic equilibrium. At room temperature $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ complexes are inert on the luminescent time-scale, and, thus, one is able to measure the CPL from a non-racemic excited state by using circularly polarized light as the excitation source[12]. In some cases, one is also able to disturb the racemic equilibrium by adding chiral non-coordinating environment compounds (Pfeiffer-effect). In these cases, using unpolarized radiation, one can also measure CPL from $Tb(DPA)_3^{3-}$, but in this case the measurement reflects non-racemic ground state concentrations of the two enantiomers.

As reported previously[11], when a small amount of resolved $Ru(phen)_3^{2+}$ is added to an aqueous solution of $Tb(DPA)_3^{3-}$, circular polarization is observed in the luminescence from Tb(III). The spectra obtained are completely inverted when (+)-$Ru(phen)_3^{2+}$ is used instead of (−)-$Ru(phen)_3^{2+}$, and are identical to published spectra for the $Tb(DPA)_3^{3-}$ complex. This indicates that this species is intact under these conditions. Unlike other studies in which chiral species have been added to racemic $Tb(DPA)_3^{3-}$ solutions with little or no observed quenching, addition of the $Ru(phen)_3^{2+}$ complex is accompanied by a large decrease in $Tb(DPA)_3^{3-}$ luminescence. As expected, the magnitude of the observed CPL as reflected in the dissymmetry ratio, $g_{em} = \Delta I/(I/2)$, also changes as a function of (−)-$Ru(phen)_3^{2+}$ concentration.

Total emission intensity and g_{em} are plotted as a function of (−)-$Ru(phen)_3^{2+}$ concentration in Fig. 1 for $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ solutions. Tb(III) luminescence and circular polarization are monitored at 543·5 nm within the $^7F_5 \rightarrow {}^5D_4$ transition, and Eu(III) emission and circular polarization are monitored at 615 nm corresponding to a peak wavelength in the $^7F_2 \rightarrow {}^5D_0$ transition. Stern–Vollmer plots for the quenching of the $Tb(DPA)_3^{3-}$ and $Eu(DPA)_3^{3-}$ solutions are presented in Fig. 2.

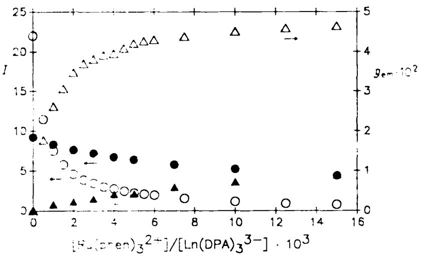

FIG. 1

Total emission intensities (circles) and dissymmetry ratios, g_{em} (triangles) for $Ru(phen)_3^{2+}$ added to aqueous solutions of $Tb(DPA)_3$ (open symbols) and $Eu(DPA)_3^{3-}$ (filled symbols). λ_{em}[Eu(III)] 612 nm; λ_{em}.[Tb(III)] 543·5 nm

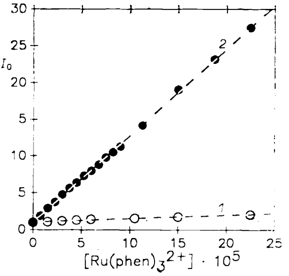

FIG. 2

Stern–Vollmer plots for the quenching of $Eu(DPA)_3^{3-}$ (1) and $Tb(DPA)_3^{3-}$ (2) by $Ru(phen)_3^{2+}$ (see text)

DISCUSSION

From the slope of the linear least-square fits to the data presented in Fig. 2 and the measured emission lifetimes, one can approximate the quenching rate constants (k_q) for the two systems; $k_q(Tb) = 1{\cdot}2 \,.\, 10^8$ and $k_q(Eu) = 9{\cdot}6 \,.\, 10^6$. The value for $Tb(DPA)_3^{3-}$ agrees with the time dependent CPL results where it was determined that the individual rate constants for quenching of the different enantiomers were approximately $1 \,.\, 10^8$ and $2 \,.\, 10^8$. The large differences in the rate constant for the Eu versus Tb complex, are understandable in terms of the difference in overlap between lanthanide emission and $Ru(phen)^{2+}$ absorption.

In a recent study[13], we have determined the absolute identity of the $Eu(DPA)_3^{3-}$ complex by comparison with the previously published spectra and crystal structure of $Eu(oxydiacetate)_3^{3-}$. In particular, a positive value for g_{em} at 612 nm has been associated with the Δ-enantiomer. Thus, we conclude that the spectra shown correspond to an excess of this isomer, and that the Λ-enantiomer is quenched more efficiently than the Δ isomer under the conditions of this experiment. Preliminary calculations suggest that this result is consistent with a model that ascribes the differential energy transfer to preferred intermolecular distances between the diastereomeric pairs.

REFERENCES

1. Goedeweeck R., De Schryver F. C.: Photochem. Photobiol. *39*, 515 (1984).
2. Goedeweeck R., Van der Aurweraer M., De Schryver F. C.: J. Am. Chem. Soc. *107*, 2334 (1985).
3. Ruttens F., Goedeweeck R., Lopez-Arbeloa F., De Schryver F. C.: Photochem. Photobiol. *42*, 341 (1985).
4. Lopez-Arbeloa F., Van der Aurweraer M., Ruttens F., De Schryver F. C.: J. Photochem. Photobiol., A *44*, 63 (1988).
5. Lopez-Arbeloa F., Goedeweeck R., Ruttens F., De Schryver F. C., Sisido M.: J. Am. Chem. Soc. *109*, 3068 (1987).
6. Lopez-Arbeloa F., Van der Aurweraer M., Andriessen R., De Schryver F. C.: J. Photochem. Photobiol., A *42*, 133 (1988).
7. Irie M., Yorozu T., Kayashi K.: J. Am. Chem. Soc. *100*, 2246 (1978).
8. Yoruzo T., Hayashi K., Irie M.: J. Am. Chem. Soc. *103*, 5480 (1981).
9. Rau R., Ratz R.: Angew. Chem. *95*, 552 (1983).
10. Rau H.: Chem. Rev. *83*, 535 (1983).
11. Metcalf D. H., Wu S., Hilmes G. L., Riehl J. P., Demas J. M., Richardson F. S.: J. Am. Chem. Soc. *111*, 3082 (1989).
12. Hilmes G. L., Riehl J. P.: Inorg. Chem. *24*, 1721 (1985).
13. Coruh N., Hilmes G. L., Riehl J. P.: Inorg. Chem. *27*, 3647 (1988).