

## Intermolecular Energy Transfer from Phenanthrene to Europium in Aqueous Micellar Solution

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Energy transfer from the first triplet state of phenanthrene to the  $^5D_1$  and  $^5D_0$  states of the tris(dipicolinato)-europium(III) anion in aqueous micellar solution has been demonstrated unambiguously by excited kinetic measurements.

Micellar assemblies provide convenient microheterogeneous systems in which ions and molecules may be held in close proximity so that the dynamics of energy transfer may be studied and perhaps exploited. Intramolecular energy transfer from ligand molecules to the metal ion in lanthanide complexes is well known.<sup>1</sup> Whilst theoretical arguments<sup>2</sup> and high pressure studies<sup>3</sup> suggest that the transfer is from the triplet state of the donor to an approximately isoenergetic state of the lanthanide ion, the mechanism of the analogous intermolecular transfer in fluid solution is less clear. One reliable method of demonstrating the states involved in energy transfer is to show the identity of the decay time of the donor state and the rise time of the acceptor state under a range of experimental conditions. For an organic triplet donor state and a lanthanide acceptor state it is difficult to achieve this demonstration in practice by luminescence decay measurements since the phosphorescence quantum yield of the donor triplet state is very small and it may occur in the same spectral region as the emission from the acceptor lanthanide ion state. Thomas<sup>4</sup> did not observe energy transfer from micellar phenanthrene to the europium aquo ion whilst Fendler<sup>5</sup> was unable to observe the triplet directly whilst showing energy transfer from micellar naphthalene to the terbium aquo ion.

In this communication we use a combination of transient absorption spectroscopy, luminescence spectroscopy, oxygen

quenching studies, and the suitable photophysical and chemical properties of the tris(dipicolinato)europium(III),  $[\text{Eu}(\text{PDC})_3]^{3-}$ , to show the mechanism unambiguously.

The system, for a typical experiment, consisted of an aqueous solution (room temperature, pH 6.3) of  $[\text{Eu}(\text{PDC})_3]^{3-}$  ( $1.3 \times 10^{-2} \text{ M}$ ), cetyltrimethylammonium bromide ( $2.9 \times 10^{-2} \text{ M}$ ), and phenanthrene ( $3.2 \times 10^{-4} \text{ M}$ ). Oxygen was removed by repeated freeze-pump-thaw cycles. Under these conditions single phenanthrene molecules will be largely inside the cetyltrimethylammonium micelles and a significant proportion of the  $[\text{Eu}(\text{PDC})_3]^{3-}$  anion total concentration will be associated with the positively charged micellar surface. Excitation with *ca.* 0.1 J of 347 nm radiation in 10 ns from a ruby laser initially excites the phenanthrene singlet state which decays in a time short compared with the laser pulse, both by prompt fluorescence and by intersystem crossing to populate the first excited triplet state,  $T_1$ . The decay of this triplet state (which was exponential over more than four lifetimes with little noise and well distributed residuals) was monitored by the transient ( $T_1 \rightarrow T_2$ ) absorption at 490 nm to give a rate constant  $k_T = 9.1 \pm 0.3 \times 10^4 \text{ s}^{-1}$ .

The sensitised emission from the  $^5D_1$  state of the  $[\text{Eu}(\text{PDC})_3]^{3-}$  anion following the laser pulse was monitored at 540 nm ( $^5D_1 \rightarrow ^7F_1$ ) and it decays exponentially (over more than five lifetimes) with a rate constant  $k_1 = 8.5 \pm 0.3 \times 10^4 \text{ s}^{-1}$ . In the absence of the phenanthrene the emission from the  $^5D_1$  state is very weak with  $k_1 = 9.6 \times 10^5 \text{ s}^{-1}$ . This latter value is typical of directly excited europium complexes in aqueous solution. It is clear that the uniquely (under these conditions)

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long-lived  $^5D_1$  emission is due to pumping from the phenanthrene triplet decay. The slightly smaller decay rate constant for the sensitised emission than for the transient absorption may reflect the mobility of the phenanthrene within the micelle. The expected  $3.0 \times 10^{-7}$  s rise time for the  $^5D_1$  emission could not be directly observed owing to stray light and electrical noise during the first microsecond following the laser pulse. Since the phenanthrene triplet energy closely matches the energy of the  $^5D_2$  state of  $[\text{Eu}(\text{PDC})_3]^{3-}$  it is likely that the initial transfer to the europium centre occurs to this state which, however, relaxes non-radiatively too quickly for significantly emission to be detected.

The rise time of the emission from the  $^5D_0$  state of  $[\text{Eu}(\text{PDC})_3]^{3-}$  is also exponential with a rate constant  $k_{\text{ET}} = 1.16 \pm 0.08 \times 10^5 \text{ s}^{-1}$ , this emission being monitored at 616 nm ( $^5D_0 \rightarrow ^7F_2$ ). The emission subsequently decays on a millisecond timescale, characteristic of well shielded  $\text{Eu}^{3+}$  complex ions in solution.

The comparability of the three measured rate constants shows conclusively that the energy transfer process is: Phenanthrene triplet  $\rightarrow \text{Eu}(^5D_1)$  and  $\rightarrow \text{Eu}(^5D_0)$ . Further evidence is provided by the quenching of the triplet upon

admission of  $\text{O}_2$  to the system. It is observed that the changes in the rate constants for the pumped  $^5D_1$  emission and  $^5D_0$  rise time parallel the shortened lifetime of the phenanthrene triplet. These rate constants become  $k_{\text{T}} = 3.9 \pm 0.2 \times 10^5 \text{ s}^{-1}$  (transient triplet absorption),  $k_1 = 4.3 \pm 0.5 \times 10^5 \text{ s}^{-1}$  ( $^5D_1$  decay), and  $k_{\text{ET}} = 3.8 \pm 0.2 \times 10^5 \text{ s}^{-1}$  ( $^5D_0$  rise time). Copies of the original rise/decay curves were provided for the referees and are available from the authors.

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## References

- 1 W. M. Watson, R. P. Zerger, J. T. Yardley, and G. D. Stucky, *Inorg. Chem.*, 1975, **14**, 2675; H. Richter-Lustig, A. Ron, and S. Speiser, *Chem. Phys. Lett.*, 1982, **85**, 576; B. Alpha, J.-M. Lehn, and G. Mathis, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 266.
- 2 D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836.
- 3 A. V. Hayes and H. G. Drickamer, *J. Chem. Phys.*, 1982, **76**, 114.
- 4 M. Almgren, F. Grieser, and J. K. Thomas, *J. Am. Chem. Soc.*, 1979, **101**, 2021.
- 5 J. R. Escabi-Perez, F. Nome, and J. H. Fendler, *J. Am. Chem. Soc.*, 1977, **99**, 7749.