Coumarinium–Europium Energy Transfer: Efficient Triplet Migration between Two Cations[1]

By PETER G. TARASSOFF and NICOLAE FILIPESCU*
(*Department of Chemistry, The George Washington University, Washington, D. C.* 20052)

Summary Intermolecular triplet energy transfer from the coumarinium cation to the tripositive europic ion was demonstrated.

EFFICIENT intermolecular transfer of triplet excitation energy from organic sensitizers to nonchelated lanthanide-ion acceptors has been demonstrated in fluid solution[2] and in rigid matrix.[3] The rates of individual radiative and radiationless processes and the dependence of the transfer efficiency on the donor–acceptor separation distance have been studied in frozen mixed solutions of aromatic carbonyl compounds and either Eu^{3+} or Tb^{3+} ions. The validity of conclusions derived from photokinetic and statistical treatments[2–4] of spectroscopic data depends on the initial assumption that there is no association between the sensitizer and acceptor and that both are randomly dispersed throughout the rigid glass. However, complex formation between polar carbonyl donors and tervalent rare-earth ions cannot be ruled out, especially at the high concentrations required for experiments in rigid matrix.

We present spectroscopic evidence for efficient energy transfer from the π,π^* triplet of the protonated-coumarin cation to the Eu^{3+} ion in a frozen solution of mixed alkylsulphonic acids. The probability of donor–acceptor complexation in this case is very remote because of their mutual electrostatic repulsion.

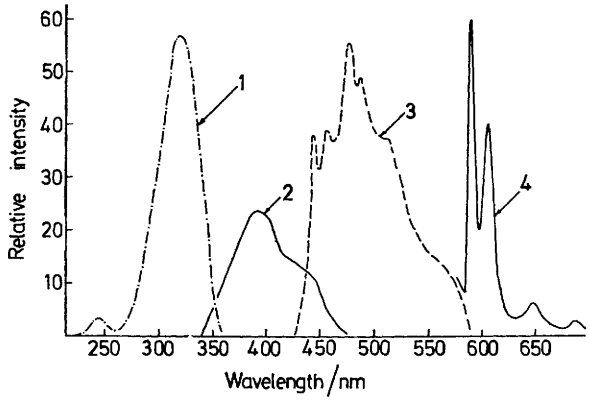

FIGURE. Emission and excitation spectra of 10^{-4} M coumarin in alkanesulphonic acid glass at 77 K: 1-excitation spectrum of emission monitored at 500 nm; 2 and 3-fluorescence and phosphorescence of coumarinium ion, excited at 340 nm, respectively; 4-sensitized Eu^{3+} emission from a sulphonic-acid glass, at liquid nitrogen temperature, containing 10^{-2} M coumarin and 5×10^{-2} M $EuCl_3$ excited with u.v. light at 340 nm (on a different relative intensity scale). The spectra, recorded on a Hitachi-Perkin Elmer MPF-2A spectrometer, were not corrected for photomultiplier response or excitation-source output.

The coumarinium ion is a suitable triplet-energy donor for Eu^{3+}, since its T_1 level is properly located with respect to the ^5D resonance levels of Eu^{3+}, and since it undergoes efficient intersystem crossing as shown by its intense phosphorescence ($\phi_p = 0{\cdot}84$).[5] We have also established that the europic ion retains its narrow-band characteristic emission in the strongly acidic media needed for the protonation of coumarin.

The emission and excitation spectra of coumarinium ion in a clear rigid solution of alkylsulphonic acids at 77 K are shown in the Figure. The protonated coumarin emits a broad fluorescence centred around 390 nm with a quantum yield $\phi_f = 0{\cdot}12$ and a structured, much more intense, blue-green $\pi^* \rightarrow \pi$ phosphorescence ($\phi_p = 0{\cdot}84$) in the 430—540 nm region, with a lifetime of 2·4 s. The $0 \rightarrow 0$ band in the $T_1 \rightarrow S_0$ emission places the lowest triplet around 22,300 cm^{-1}, appropriately above the $^5D_0$ (17,300 cm^{-1}) and $^5D_1$ (19,000 cm^{-1}) levels of the Eu^{3+} ion. Comparison of both u.v. absorption and emission spectra of coumarin in neutral organic solvents with those in sulphuric or alkylsulphonic acid established that coumarin is completely protonated in undiluted acid solution.[5] We tested numerous acidic solvents before we found a suitable one, a mixture of methane sulphonic and propanesulphonic acids, 3 : 1 (v/v). This solvent mixture completely protonated coumarin, readily dissolved europic chloride up to 10^{-1} M concentrations, yielded rare-earth-ion solutions stable for several days before any precipitation became noticeable, and produced a clear glass on freezing in liquid nitrogen.

Curve 4 in the Figure shows the narrow-band emission characteristic of infra-4f luminescence corresponds to transitions $^5D_0 \rightarrow {}^7F_0$ (580 nm), $^5D_0 \rightarrow {}^7F_1$ (608 nm), $^5D_0 \rightarrow {}^7F_2$ (650 nm), and $^5D_0 \rightarrow {}^7F_3$ (680 nm). When another sulphonic-acid solution, containing only 5×10^{-2} M $EuCl_3$ but no coumarin, was excited under identical conditions at 340 nm, there was no detectable emission. This established the sensitizer role of the coumarinium ion. The overall quantum yield for the sensitized europic-ion emission shown in the Figure was 0·31 relative to a Rhodamine B standard. The detailed photokinetic and statistical treatment of the coumarinium–Eu^{3+} system will be reported elsewhere.

We thank the Energy Research and Development Administration for support.

(*Received*, 31*st December* 1974; *Com.* 1580.)

---

[1] From the Ph.D. dissertation of P.G.T. at George Washington University, 1974.

[2] N. Filipescu and G. W. Mushrush, *J. Phys. Chem.*, 1968, **72**, 3516, 3522.

[3] F. L. Minn, G. W. Mushrush, and N. Filipescu, *J. Chem. Soc.* (*A*), 1971, **63**; G. W. Mushrush, F. L. Minn, and N. Filipescu, *J. Chem. Soc.* (*B*), 1971, 427.

[4] F. L. Minn and N. Filipescu, *J. Chem. Soc.* (*A*), 1970, 1016.

[5] N. Filipescu, S. K. Chakrabarti, and P. G. Tarassoff, *J. Phys. Chem.*, 1973, **77**, 2276.