Luminescence Spectroscopy as a Probe of Binding State Differences between Enantiomeric and Racemic Poly(pyridyl)-ruthenium(II) Chelates intercalated in Smectite Clays

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Luminescence spectral studies (steady state and dynamic) indicate clear differences between the binding states of enantiomeric and racemic forms of poly(pyridyl)-ruthenium(II) complexes intercalated in Na-hectorite clay, even at low loadings of the exchanging sites.

We have recently reported that the u.v.–visible absorption spectral profiles of enantiomeric and racemic poly(pyridyl)-ruthenium(II) chelates cease to be identical when these cationic forms are ion-exchanged into montmorillonite clay.[1] Remarkably, such differences in spectral behaviour persist even when only a small fraction (<5%) of the exchangeable sites are loaded with the Ru^{II} chelate. This surprising result, which has been ascribed to differences in the binding states of the adsorbed enantiomeric and racemic forms,[1] is of considerable interest in the light of recent reports on the resolution of

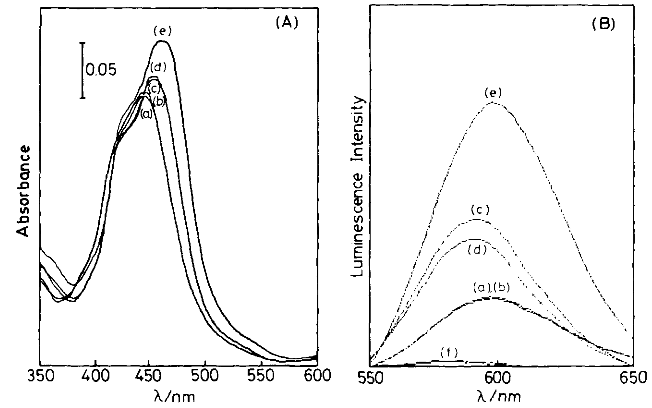

Figure 1. Absorption (A) and emission (B) spectra of enantiomeric and racemic forms of Ru(bpy)$_3^{2+}$ (2×10^{-5} M) in water [Λ- (trace a); Δ,Λ- (trace b)] and in 1 g dm^{-3} Na-hectorite [Λ- (trace c); Δ- (trace d); Δ,Λ- (trace e)]. Racemic Ru(bpy)$_3^{2+}$ was prepared by pre-mixing aqueous solutions of the Δ- and Λ-Ru(bpy)$_3^{2+}$ enantiomers and the same colloidal Na-hectorite dispersion was used to prepare all clay-containing samples. Absorption spectra were recorded against suitable references and emission slits spectra were obtained using 5 nm excitation and emission slits and an excitation wavelength of 460 nm. All samples were air-saturated. The emission spectrum of the blank clay dispersion (1 g dm^{-3} Na-hectorite) is shown in trace f of spectrum (B).

organic and inorganic racemates on chirally modified clay supports.[2—8] In seeking a better understanding of the sorption behaviour of metal complexes within the smectite clay interlayer, we have recently begun a systematic investigation of the luminescence characteristics of such metal chelate–clay adducts. We now report our observation that enantiomeric and racemic forms of RuL$_3^{2+}$ [L = 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen)] exhibit dramatic differences in their luminescence profiles upon intercalation in Na-hectorite clay. However, as shown below, the trends in luminescence intensity differences between enantiomeric and racemic forms are not the same for the seemingly analogous Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$, indicating that the environments of the two complexes may be different in the adsorbed state.

Absorption and emission spectral data on racemic Ru(bpy)$_3^{2+}$ intercalated in Na-montmorillonite and Na-hectorite have previously been reported.[9—12] The latter clay was selected for the present study owing to the substantially larger intensity of emission from Ru(bpy)$_3^{2+*}$–hectorite over that measured for Ru(bpy)$_3^{2+*}$–montmorillonite.[11] Figure 1 shows the absorption (A) and emission (B) profiles of 2×10^{-5} M Λ- and Δ,Λ-Ru(bpy)$_3^{2+}$ in water (traces a and b, respectively), and of 2×10^{-5} M Λ-, Δ-, and Δ,Λ-Ru(bpy)$_3^{2+}$ in an aqueous dispersion containing 1 g dm^{-3} Na-hectorite (traces c, d, and e respectively).† A comparison of traces a and b indicates that the absorption and emission spectra of the enantiomeric and racemic forms are the same in water, with $\lambda_{max.}$ (abs.) 452 nm and $\lambda_{max.}$ (emiss.) 597 nm. However, as is evident from Figure 1, the spectral profiles of the corresponding clay-containing samples exhibit substantial differences. Thus, while Λ,Δ-Ru(bpy)$_3^{2+}$–hectorite has an absorption maximum at 469 nm, and an emission maximum at 596 nm (these results are in good agreement with published data[11]), the corresponding values for the adsorbed enantiomers are 461 and 590 nm, respectively. The most striking feature of these spectra, however, is the dramatic difference in luminescence intensity between the enantiomeric and racemic forms, the value for the latter being nearly twice as large as that found, for example, with the Δ-enantiomer (compare traces d and e).‡ The somewhat larger emission intensity recorded for Λ-Ru(bpy)$_3^{2+*}$–hectorite (trace c), over that found for Δ-Ru(bpy)$_3^{2+*}$–hectorite (trace d), is attributed to the lower optical purity of the Λ-complex [90% enantiomeric excess (e.e.) for Λ- *vs.* 97% e.e. for Δ-Ru(bpy)$_3^{2+}$].

Table 1. Emission kinetic data of Δ-,Λ-, and Δ,Λ-Ru(phen)$_3^{2+*}$–hectorite (clay 1.0 g dm^{-3}).[a]

Complex (conc./M)	A_1	τ_1/ns	A_2	τ_2/ns
Δ- (3.4×10^{-5})	0.107	44	0.076	547
Λ- (3.4×10^{-5})	0.110	49	0.073	547
Δ,Λ- (3.4×10^{-5})[b]	0.132	42	0.068	461

[a] Simulation studies were carried out with the decay function $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. All data were recorded for fresh solutions. [b] Δ and Λ were premixed (to form Δ,Λ) prior to adsorption onto the clay.

Luminescence studies have also been carried out on adsorbed Δ-, Λ-, and Δ,Λ-Ru(phen)$_3^{2+}$, and these results also indicate differences in binding states of enantiomeric and racemic forms.§ Most significantly, the peak emission intensity of the adsorbed racemate is *ca.* 60% lower than that of the pure enantiomers. This trend is the opposite of that found with Ru(bpy)$_3^{2+}$, indicating thereby that the environments of the two complexes may be different in the intercalated state. We have also carried out preliminary flash excited luminescence studies on our Ru(phen)$_3^{2+}$-containing samples. While Δ-, Λ-, and Δ,Λ-Ru(phen)$_3^{2+*}$ exhibited identical first order decay kinetics (τ 470 ns) in water, the emission decay profiles of the corresponding adsorbed chelates were more complex. These curves could be satisfactorily simulated with a double exponential decay function,¶ and values of the fitting parameters are presented in Table 1. The important point which we wish to highlight here is that the excited state of the adsorbed racemate decays more rapidly (increased ratio of $A_1:A_2$ and lower value of τ_2) than those of the pure enantiomers, a result consistent with our steady state emission data.

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† Ca-hectorite was obtained from the Clay Minerals Repository, University of Missouri, and converted into the easily dispersible Na$^+$-exchanged form as described in ref. 11. The cation exchange capacity (c.e.c.) of the clay was *ca.* 1 mequiv./g. The loading level of the Ru^{II} complexes was *ca.* 4% of the clay's c.e.c. (2×10^{-5} M Ru^{II}; 1 g dm^{-3} Na-hectorite), and complete sorption of the complexes on clay was checked through high speed (18 000 r.p.m.) centrifugation of the samples followed by spectral analysis of the supernatant. Perchlorate salts of the enantiomeric Ru^{II} complexes were used in the present set of experiments. Elemental analyses were in good agreement with the formulation Ru(bpy)$_3$(ClO$_4$)$_2$·H$_2$O. Δ,Λ-Ru(bpy)$_3^{2+}$ was prepared by mixing aqueous solutions of the Δ- and Λ-Ru(bpy)$_3^{2+}$ enantiomers. The spectral results obtained with the above racemate were similar to those observed with an authentic sample of Δ,Λ-Ru(bpy)$_3$(ClO$_4$)$_2$.

‡ While the spectra in Figure 1 were recorded for air-saturated solutions, additional experiments were conducted on deoxygenated solutions. The effect of deoxygenation on emission intensities was only marginal for the clay-containing solutions,[9] whereas the expected emission yield enhancement was observed for Ru^{II} complexes dissolved in water.

§ Δ,Λ-Ru(phen)$_3^{2+}$–hectorite was prepared by pre-mixing the Δ- and Λ-isomers prior to sorption on clay.

¶ Complex decay profiles could be due to the possible heterogeneity of clay sites (G. Villemure, C. Detellier, and A. G. Szabo, *J. Am. Chem. Soc.*, 1986, **108**, 4658) and/or self quenching of excited states.[11]

In conclusion, the novel emission spectral studies reported further substantiate our recent claim that there exist subtle differences between the intercalation modes of enantiomeric and racemic RuL_3^{2+} complexes in clays, even at loading levels as low as 5% of the clay's cation exchange capacity. Our studies reveal a striking difference in the peak emission intensities between the two forms of adsorbed chelates, a corresponding difference in excited state lifetime, and detectable shifts in the emission maximum, similar in magnitude to that noted previously in absorption spectral studies.

We thank Mr. D. Kotkar for assistance. Flash excited luminescence studies were carried out by Ms. T. Guin in Professor M. Chowdhury's laboratory at the Indian Association for the Cultivation of Science, Calcutta. This work was supported by IEL Ltd.

Received, 3rd November 1986; Com. 1560

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