acceptor orbitals in a fashion reminiscent of arene complexes of third-row transition and main-group 14 elements.[8]

Finally, there is an interesting side aspect to the arylation reaction in that it provides a means of rendering f-metal halides soluble in aromatic hydrocarbons. This drastic change in the solubility is undoubtedly due to arene substitution. Since the metal–arene interaction is a weak one which will be dependent on the nature of the metal as well as the nucleophilicity of the arene, one can envision new sequestering techniques for f-block elements based on extraction procedures involving arene complexes.

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Supplementary Material Available: Table pertaining to data collection and refinement and a list of fractional coordinates (3 pages). Ordering information is given on any current masthead page.

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Fluorescence of Clay-Intercalated Methylviologen

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Methylviologen dichloride (MV) (1,1′-dimethyl-4,4′-dipyridinium dichloride or paraquat) is widely used as an effective electron relay in the process of sacrificial water photoreduction,[1] in conjunction with a variety of catalysts, such as colloidal platinum,[2] hydrogenase enzyme,[3] or ruthenium dioxide.[4] We have recently reported that a system consisting of tris(2,2′-bipyridyl)ruthenium(II) (Ru(bpy)$_3^{2+}$), MV, and a sacrificial electron donor, triethanolamine, in the presence of the clays, montmorillonite,[5,6] or hectorite,[7] when illuminated by visible light, produces hydrogen, albeit in low yield. It has been shown that MV intercalates into the sheets of these expandable smectites[6,8] with a basal spacing of 12.6 Å. Very recently, Ege et al.[9] have reported the catalytic hydrogen production in a clay/Pt/poly(vinyl acetate) film containing propylviologen sulfonate. The luminescence of colloidal suspensions of Ru(bpy)$_3^{2+}$ intercalated into these same smectites has been reported previously.[10-13] Its fluorescence is quenched by MV.[11] The elucidation of the effect of structure and composition of these complexes and of the function of each component on the photochemical processes may be assisted by a variety of spectroscopic studies. With this in mind we investigated the fluorescence behavior of MV. To the best of our knowledge fluorescence from MV at ambient temperatures has not been reported previously. However, fluorescence of MV^{2+} could be observed when it was incorporated into the lamellae of colloidal hectorite and montmorillonite suspensions. No fluorescence could be detected in the case of nontronite. Time-resolved fluorescence measurements as well as the fluorescence intensity variation with the ratio MV^{2+}/clay suggest different types of binding sites for MV^{2+} adsorbed on the clay colloidal particles.

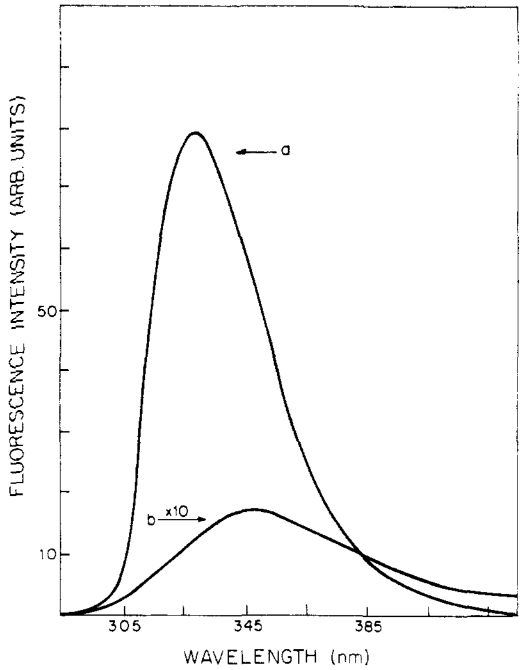

Figure 1. Corrected fluorescence spectra (λ_{ex} = 285 nm, excitation and emission band-pass, 3 nm) of methylviologen dication (MV^{2+}), 5 × 10^{-6} M, (a) in montmorillonite (0.25 g/L) and (b) in aqueous solution, pH 7. Spectra were measured on a Perkin-Elmer Model 44A spectrophotofluorimeter equipped with a DCSU-2 corrected spectral unit. The spectrum (b) in aqueous solution was recorded at a sensitivity which was 10× greater than that for spectrum a.

Excitation at 285 nm of a sample of MV^{2+} (5.0 × 10^{-6} M) in a colloidal suspension of montmorillonite (0.25 g/L) resulted in the fluorescence spectrum shown in Figure 1a (maximum at 330 nm). The fluorescence spectrum of MV^{2+} in an aqueous solution of the same concentration could be observed but was barely detectable (Figure 1b), the maximum occurring at 345 nm.[14] On incorporation into clay, the absorption spectral maximum of MV was 280 nm, which was shifted from that found in water (257.5 nm). It is known that MV^{2+} is readily incorporated into the interlamellar space of swollen clays.[6,16] It has been shown by infrared spectroscopy that MV^{2+} adopts a planar conformation when incorporated into montmorillonite.[8] The interlamellar space was previously determined to be 2.95 Å,[6] a value corroborating previous work[16,17,23] and requiring MV^{2+} to adopt a planar

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Table I. Intensity of Fluorescence of Methylviologen Dication with Different Concentrations of Clays

concn, g/L	% cec[a]	fluorescence[b] intensity
	Montmorillonite	
0.20	5.6	40
0.15	7.5	42
0.10	11	41
0.05	22	36
0.02	56	25
0.01	112	14
	Hectorite	
0.50	2.8	82
0.25	5.6	64
0.05	28	40

[a] % cec is the fraction of the clay-exchangeable cations which have been replaced by MV^{2+}. % cec was calculated by using the previously determined cation-exchange capacity of the clay (0.89 mequiv/g for montmorillonite and 0.72 mequiv/g for hectorite).[6] [MV^{2+}] = 5.0 × 10^{-6} M. [b] Given in arbitrary units. The intensity scales for the two clays were not identical. The quantum yields were 0.070 for hectorite and 0.014 for montmorillonite.

structure for intercalation. On the basis of above evidence, it may be reasonable to attribute the observation of fluorescence of MV^{2+} to a reduction of nonradiative deactivation processes when it is in such a planar configuration. We note that fluorescence from a strained MV derivative, 1,1′-ethylene-2,2′-dipyridinium dichloride (diquat dichloride), has been reported previously (ϕ_F = 0.04).[18] Similar steric arguments have been put forward to explain the strong increase of fluorescence of 2-*p*-toluidinyl-6-naphthalenesulfonate (TNS) when bound to proteins.[19] Clearly when MV^{2+} is intercalated into clays any external quenching by the chloride anion will be reduced. However, the iron content of the clays may act as possible quencher of MV^{2+} fluorescence.[12] We therefore measured the fluorescence of MV^{2+} in different clays having different iron content.[20] The measured intensities were 5 times larger in hectorite compared to montmorillonite whereas no fluorescence could be detected in samples with nontronite. The fluorescence spectral maximum was 328 nm in hectorite and 330 nm in montmorillonite. Quantum yields were 0.070 and 0.014 in the two clays, respectively. The relative iron content of these three swelling clays provides a satisfactory rational for the observed differences in fluorescence efficiency.

The effect of the ratio of MV^{2+}/clay on the fluorescence intensity was also investigated (Table I). In the case of hectorite there was a decrease in fluorescence intensity as the fraction of the clay-exchangeable cations replaced by MV^{2+} (percent cec; see Table I) increased (decreasing clay concentration). The same trend was observed for montmorillonite. The fluorescence enhancement with increasing clay concentration (up to 0.2 g/L) cannot be the result of stacking of MV^{2+} on the clay surface as has been shown to be the case for the radical cation MV$^{+\bullet}$.[21,22] Rather, it may be explained by one or both of two possibilities since there was no free MV^{2+} for cec < 90%.[23] There may be more than one binding site for MV^{2+} with the colloidal particles. A weak binding to the surface of the clay may be a site in which the MV^{2+} retains some internal flexibility and which is exposed to external quenchers. In such a location the MV^{2+} fluorescence would be reduced. The second site would be a preferential intercalation into the interlayer region of the clay where the MV^{2+} dication was rigidly bound. A similar interpretation has been proposed by Schoonheydt et al.[24] to explain the fluorescence behavior of Ru(bpy)$_3^{2+}$ adsorbed onto clay particles. Alternately self-quenching of fluorescence of MV^{2+} may be occurring at the higher percent cec as the sites become saturated with MV^{2+}.

Time resolved fluorescence measurements provide additional information on the binding processes.[25] The fluorescence decay of MV^{2+} in hectorite (0.05 g/L) obeyed double exponential kinetics with decay times of 3.51 and 1.57 ns. The fluorescence contribution of each component to the total spectrum was 0.72 and 0.28, respectively.[25] In the case of MV^{2+} and montmorillonite (0.5 g/L) the decay times were 1.13 and 0.37 ns with fractional fluorescences of 0.37 and 0.63, respectively. These results support the model of two different binding sites for MV^{2+} in the clays. The lower values in montmorillonite may be due to quenching by bound iron.

Experiments are under way to verify our interpretation, to further characterize the fluorescence of the adsorbed MV^{2+} into clays, and to exploit these observations to provide a better understanding of the structure and function of the system.

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Dehydrogenation of Isobutane by Oxygen-Deficient Cobalt/Oxygen Cluster Ions

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We report the gas-phase reactions of coordinated cobalt/oxygen cluster ions with isobutane using chemical ionization/fast-atom bombardment (CI/FAB) mass spectrometry.[1-3] In particular, the activation of hydrocarbon bonds in the alkane by metal/oxygen cluster ions of certain stoichiometries is reported, and the reactivity is discussed in terms of the structure of the reactive metal/oxygen cluster ions.

Metal cluster ions were formed by the bombardment of a metal foil with an energetic (8 keV) primary beam of fast xenon atoms. The sputtered metal cluster ions react with O$_2$ in the high-pressure (0.1-0.2 torr) ion source,[3] and the metal cluster product ions were analyzed in a reverse-geometry, double-focusing mass spectrometer[4] by collision techniques.[5] Three types of coordinated co-

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