CLAY-ORGANIC INTERCALATES

Tuesday June 22, 2004

Clay-Organic Intercalates Poster Session	
5:00p	**EFFECTIVE LUMINESCENCE QUENCHING OF TRIS(2,2'-BIPYRIDINE)-RUTHENIUM(II) BY METHYLVIOLOGEN ON CLAY BY THE AID OF POLY(VINYLPYRROLIDONE).** Norishige Kakegawa[*1], and Makoto Ogawa[2] [1]Depertment of Earth and Planetary Science, Graduate School of Science, University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-0033, Japan; [2]Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

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EFFECTIVE LUMINESCENCE QUENCHING OF TRIS(2,2'-BIPYRIDINE)-RUTHENIUM(II) BY METHYLVIOLOGEN ON CLAY BY THE AID OF POLY(VINYLPYRROLIDONE)

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Intercalation of organic guest species into smectites is a way of constructing ordered inorganic-organic assembly with unique microstructures controlled by host-guest and guest-guest interactions. Organic dye-smectite intercalation compounds have been studied to understand the nature of the host-guest systems to construct novel photofunctional supramolecular systems.

Tris(2,2-bipyridine)ruthenium(II) (abbreviated as $[Ru(bpy)_3]^{2+}$) is one of the photoactive species studied most extensively because of its unique combination of chemical stability, capability of photosensitizing redox reactions, and photophysical. Photoprocesses of $[Ru(bpy)_3]^{2+}$ in heterogeneous media have been investigated extensively in order to construct functional supramolecular systems, which mimic natural photosynthetic. Along this line, photoprocesses of $[Ru(bpy)_3]^{2+}$ intercalated in smectites, have been studied far. Electron transfer quenching of $[Ru(bpy)_3]^{2+}$ adsorbed on clays in aqueous suspensions by transition metal ions, nitrobenzene, dimethylaniline on smectites have been reported. On the other hand, methylviologen (abbreviated as MV^{2+}) did not quench the excited $[Ru(bpy)_3]^{2+}$ on the clay, since the intercalation of the two cationic species results in segregation, where they are intercalated in the different gallery spaces.

In this study, electron transfer quenching of $[Ru(bpy)_3]^{2+}$ by methylviologen in aqueous clay suspension in the presence of poly(vinylpyrrolidone) (abbreviated as PVP) was investigated. The photoprocesses of the intercalated $[Ru(bpy)_3]^{2+}$ in the interlayer space of a swelling mica with PVP have already been reported. The co-intercalated PVP was forced to surround $[Ru(bpy)_3]^{2+}$ in close contact in the statically limited interlayer spaces to cause luminescence shifts and suppression of self-quenching. This result suggested that two cationic species ($[Ru(bpy)_3]^{2+}$ and exchangeable sodium ion) were intercalated in the same interlayer space of the swelling mica without segregation. Motivated by the result, the co-adsorption of $[Ru(bpy)_3]^{2+}$ and MV^{2+} on clays in aqueous suspensions in the presence of PVP was investigated. The added PVP in a clay aqueous suspension depressed the flocculation of $[Ru(bpy)_3]^{2+}/MV^{2+}$-clay.

Effective quenching of the excited $[Ru(bpy)_3]^{2+}$ in aqueous clay suspension by MV^{2+} in the presence of PVP was shown by the steady state luminescence and luminescence life times. The quenching behavior in suspensions containing different amounts of clays suggested that the intraparticle reaction was dominant. The homogeneous distribution of the adsorbed $[Ru(bpy)_3]^{2+}$ and MV^{2+} on clays was also shown by the quenching behaviors. When the clay with larger particle size was used as host, the quenching of the excited $[Ru(bpy)_3]^{2+}$ occurred effectively. The adsorption of poly(vinylpyrrolidone) on clay resulted in the co-adsorption of the tris(2,2-bipyridine)ruthenium(II) and methylviologen without segregation.