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Coordination Chemistry of Solid Eu^{3+} Salts with Vaporized Organic Solvents by Fluorescence Technique and Characteristic of Deposited Solid from Liquid Thin Films for Solid–Vapor Interaction Studies

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1. Introduction

This study investigated how the fluorescence spectrum of $EuCl_3 \cdot 6H_2O$ in solid state changes in the presence of organic solvent such as methanol (MeOH) and *N, N*–dimethylformamide (DMF). Difference spectra and 2 dimensional correlation spectra (2D COS) obtained from fluorescence spectra were used to determine base components of the fluorescence bands, and band intensities were obtained using deconvolution procedure with curve fitting technique. Spectral changes observed were analyzed in terms of relative intensities of component bands in $^5D_0 \rightarrow {}^7F_1$, or in $^5D_0 \rightarrow {}^7F_2$ transition (*i*band/f1 and *i*band/f2) and intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ band to the $^5D_0 \rightarrow {}^7F_1$ one (f2/f1).

Solid–vapor interactions differ from those in solution. Molecular loosening is required for vapor to diffuse to the reactive site of the solid. For this reason, thin films of solid are ideal for solid–vapor interaction studies. An important part of this study is devoted to the formation of solid thin films obtained from methanol solutions climbing a vertical glass substrate. The solid thin film produced was less than 5 μm thick and offers a lot of potential in solid–gas interaction studies.

2. Results and Discussions

The fluorescence spectral changes of solid $EuCl_3 \cdot 6H_2O$ in the presence of MeOH and DMF vapors were successfully analyzed using relative intensities of bands. In the solid states under both vapors, the *i*band/f1 ratios largely changed depending on the kind of organic ligand vapor in spite of the magnetic dipole character of $^5D_0 \rightarrow {}^7F_1$ transition which is insensitive to the ligand environment. Each vaporized solvent gives unique characteristics to the spectrum of $EuCl_3 \cdot 6H_2O$ in solid state. The solid $EuCl_3 \cdot 6H_2O$ exhibited large increase in the f2/f1 and accompanied large changes in relative intensities of bands in both $^7F_1$ and $^7F_2$ regions upon the deliquescence under the MeOH vapor, but exhibited small change on the deliquescence under the DMF vapor. These indicate phase change itself does not cause large spectral changes.

$EuCl_3 \cdot 6H_2O$ methanol solutions produced four solid films with patterns of an isotropic radial, a fanlike, a concentric circle and the presence of finger instability. The fluorescence spectrum of each solid films showed that each solid pattern is potentially different from each other. The climbing liquid thin films of maleimide methanol solution also produced four uniform solid films of different thickness and patterns. The characteristics of the solid film produced by evaporation of liquid thin climbing film shows that these solid films can be used for solid–vapor interaction studies.

3. Conclusions

Fluorescence spectra of solid $EuCl_3 \cdot 6H_2O$ under DMF and MeOH vapor solvents showed considerable spectral changes in $^5D_0 \rightarrow {}^7F_1$ region which were not observed in the corresponding liquid solutions. Significant spectral changes were observed on deliquescence under MeOH vapor, but small under DMF vapor.

Solid thin films were successfully prepared by evaporation of liquid thin climbing films of $EuCl_3 \cdot 6H_2O$ and maleimide methanol solutions. The characteristerics of the solid thin films were unique to experimental conditions employed.

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