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金-1,2-ジ-(4-ピリジル)-エチレン錯体の構造と発光特性

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Structures and emission properties of gold-1, 2-di-(4-pyridyl)-ethylene complexes

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1. Introduction

Gold complexes, in particular Au(I) complexes exhibit intense luminescence in the visible region. Their luminescence may originate from ligands in particular geometry around gold atoms or can be related to the presence of gold(I)-gold(I) attractive interactions (so called aurophilic interactions)[1]. Specifically, luminescence may involve transitions between orbitals of only the metal centers, transitions in orbitals of the ligands, or transitions involving orbitals of both metal and ligands (charge transfer transitions). Au(I) has a d^{10} closed shell configuration and the ground state is $^1S_0$, while excited states are $^3D_2$, $^3D_1$,$^3D_0$, and $^1D_0$. The only permitted electronic transition is $^1D_0 \rightarrow {}^1S_0$, the rest of transitions are forbidden according to the spin rule. Many luminescence Au(I) complexes though exhibit phosphorescence due to the spin-orbit coupling and other effects such as relativistic effects.

Complexes with aurophilic interactions have strong tendency for aggregation and depending on the ligand they can form various two- and three-dimensional (2, 3D) structures and polymeric chains.

We are interested in the 2D assembly of aurophilic complexes using Au surface as a template. We attempt to compare the luminescence properties of surface-grown thin films with the traditional solvothermal-grown complexes. As a ligand we used 1, 2-di-(4-pyridyl)-ethylene (BPE) and 4,4'-bipyridine (4BP). The detailed structures of the resulting crystals have been analyzed with the use of scanning tunneling microscope (STM) (thin films), and X-ray diffraction for the bulk crystals. Luminescence properties have been investigated using fluorescence microscopy, spectrophotometry, and STM tip-induced luminescence [2]. In addition, bulk Raman and tip-enhanced Raman spectroscopy have been used to understand chemical composition of the complexes. In this presentation, we will discuss relationship between structure and emission properties of these new Au-bipyridines complexes.

2. Experimental

Surface-grown thin films were prepared by dipping a Au/mica substrate into ethanolic solution containing 1, 2-di-(4-pyridyl)-ethylene, and 0.1M HCl for time ranging from few hour to several days. The bulk crystal, having a salmon-pink color, was obtained by heating the mixture of $HAuCl_4$, HCl and BPE at 170 °C.

3. Results and Discussion

The fluorescence images of a pure BPE in a solid-state, and its complex with Au are shown in Figure 1(a) and (b), respectively. Upon excitation with λ_{ex} = 330-380 nm, the complex showed a blue emission, markedly different from the original green emission of the pure ligand.

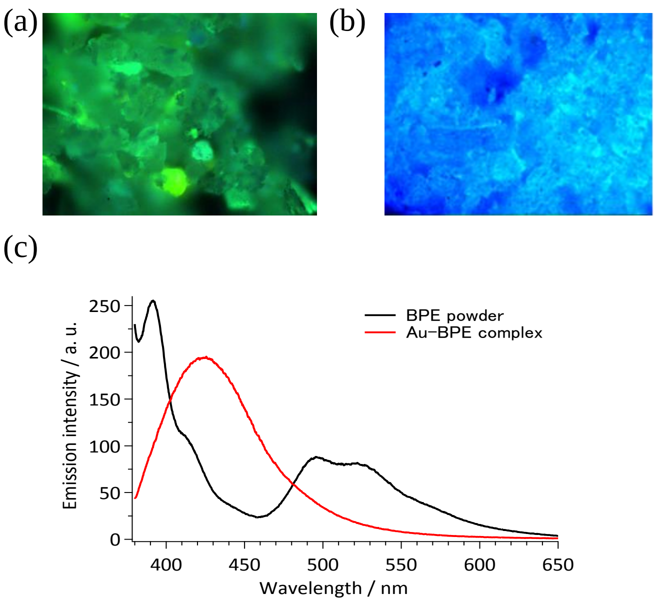

Fig. 1. Emission images of (a) BPE powder, and (b) Au-BPE complex (λ_{ex} = 330-380 nm); (c) emission spectra of (a), and (b) in the solid-state (λ_{ex} = 330 nm).

The emission spectrum of BPE is shown in Fig. 1(c) (black curve). The excitation of BPE results in structured emission in the range of 380-600 nm, which is attributed to phosphorescence [3]. The emission spectrum changes drastically upon complex formation (a red-curve in Fig. 1(c)). It shows only one broad emission peak with maximum at ~ 424 nm. The emission may be attributed to fluorescence, enhanced upon nitrogen atom coordination, or to the charge transfer from ligand to metal (LMCT) [4]. Raman spectrum of the crystal was observed to be slightly red-shifted in comparison to the spectrum observed for a pure BPE.

Raman spectrum of the surface-grown crystal shows, in addition to vibration modes of BPE, low frequency vibrational modes at ~78 and 120 cm^{-1}, that can be assigned to Au-Au and Au-Cl stretching frequencies. STM images reveal formation of a stripe phase. We propose that the stripe phase is composed of protonated BPE in coordination with Au and Cl, and the bright chains correspond to the aurophilic Au···Au contacts. The stability of these crystals comes in part from the hydrogen bonding involving N-H, and partially from Au-Au aurophilic interactions, and Coulombic interactions between H···Cl moieties.

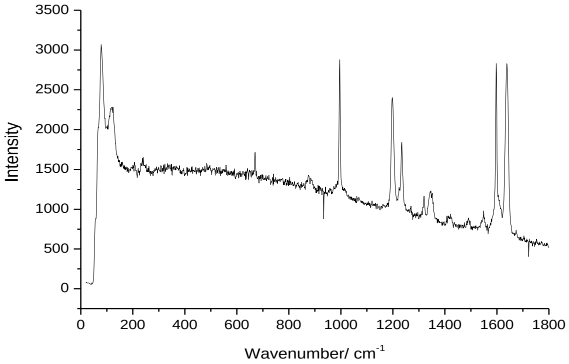

Fig. 2. Raman spectrum of the surface-grown BPE complex.

References :

[1] H. Schmidbaur ab, A. Schier, Chem. Soc. Rev., **2012**, 41, 370-412.

[2] I. Rzeznicka, T. Yamada, M. Kawai, *Surf. Sci.* **2011**, 605, 2032-2037.

[3] S. Hotchandani, A.C. Testa, J. Photochem. Photobiol. A: Chem., **1991**, 55, 323-328.

[4] J Luo, M Hong, R Wang, R Cao, L Han, Z Lin, *Eur. J. Inorg. Chem.*, **2003**, 2705-2710.