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Quadratic nonlinear optical properties of ruthenium(II)–bipyridine complexes in crystalline powders

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Quadratic nonlinear optical properties for the crystalline powders of two types of ruthenium–bipyridine [Ru(bipy)$_3$] complexes were investigated. The nonlinear optical processes markedly depended on the molecular structures of the ruthenium complexes. Second harmonic generation (SHG) and very weak two-photon emission were observed for the alkylated ruthenium–bipyridine compexes with two long alkyl chains attached via amide bonds (RuC$_n$B), whereas only two-photon emission was observed for Ru(bipy)$_3$. The existence of two amide bonds in one bipyridine ligand for RuC$_n$B complexes most probably enhanced the molecular hyperpolarizability as compared with Ru(bipy)$_3$. The SHG intensity from RuC$_n$B complexes increased in the order RuC$_{18}$B < RuC$_{12}$B ≃ RuC$_{16}$B. The order of SHG intensity from RuC$_n$B was ascribed to the difference in size of each crystalline powder estimated by X-ray diffraction methods.

Keywords: Second harmonic generation (SHG), two-photon emission, ruthenium–bipyridine complexes, nonlinear optical properties

INTRODUCTION

Photonic technology based on photons instead of present-day electrons in electronics is greatly welcomed due to ultra-fast and parallel operations.[1] Nonlinear optical effects, including optical harmonic generation, electro-optic modulation, optical bistability and so on, are very important phenomena that will be important in realizing future photonic devices. Organic compounds have attracted much interest in view of their optical nonlinear susceptibility being larger than that of inorganic compounds.[2] For second-order optical nonlinearity such as second harmonic generation (SHG), intramolecular charge-transfer transitions of organic compounds without inversion symmetry cause large quadratic optical nonlinearities. Organic compounds having electron donors and acceptors at each end of the conjugate system have been investigated extensively.[3] Stilbene, azobenzene and polyenes with amino and nitro moieties are the best examples.[4]

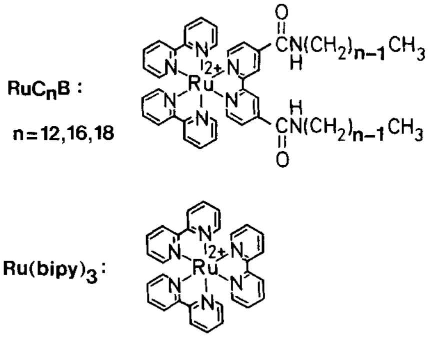

Figure 1 Structures and abbreviations of the compounds employed in the present experiment.

Metal complexes have hardly been investigated so far for their optical nonlinearity. Only a few examples were reported with respect to SHG from metal complexes[5,6] The present authors recently found that a ruthenium(II)–bipyridine complex showed SHG in a Langmuir–Blodgett (LB) film.[7] The ruthenium complex had a large molecular hyperpolarizability (70×10^{-30} esu). A metal-to-ligand charge-transfer transition (MLCT) contributed to the strong SHG from the ruthenium complex. Laser-induced modulation of SHG intensity from the ruthenium metal complex became possible by the formation of excited state with UV laser pulses.[8] We now report SHG from several ruthenium complexes in crystalline powders. The effects of alkyl chain length and ligand on quadratic nonlinear optical properties are discussed.

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EXPERIMENTAL

The structures of the materials employed in this experiment are shown in Fig. 1. The crystalline powders were prepared from methanol solutions. The samples for SHG measurement were prepared by putting the crystalline powders between two glass slides. The particle size of the crystalline powders was estimated to be less than 5 μm from optical microscopic observation. A Nd–YAG laser (1064 nm, 10 ns, 100 mJ cm^{-2}) served as an excitation source. The luminescence from a sample was detected by a photomultiplier (Hamamatsu R-928) after passing through a copper(II) sulfate aqueous solution, IR-cut filters and a monochromator. The data were stored by a computer-controlled storage scope (Iwatsu TS-8123).

X-ray measurements were performed by powder diffraction methods at the Center of Advanced Instrumental Analysis, Kyushu University.

RESULTS AND DISCUSSION

Luminescence spectra from the crystalline powders of Ru(bipy)$_3$ and RuC$_{16}$B excited by 1064 nm laser pulses are shown in Fig. 2. Strong red emission with a maximum at 600 nm (B) was observed for Ru(bipy)$_3$. On the other hand, monochromatic light at 532 nm (A) and very weak emission with a maximum at 620 nm were observed for RuC$_{16}$B. Ru(bipy)$_3$ and RuC$_n$B are known to show red luminescence with peaks at 600 and 620 nm, respectively, upon excitation of their absorption band. The temporal profiles of the emission from the two compounds were totally different as shown in Fig. 3. The emission from Ru(bipy)$_3$ has a long temporal profile with a lifetime of about 600 ns. The emission from RuC$_{16}$B consisted of a very short-lived component (10 ns), which is equivalent to the incident laser pulse width, and of a long-lived (600 ns) and a very weak one. The time profiles and spectra of emission from RuC$_{12}$B and RuC$_{18}$B were similar to that of RuC$_{16}$B. The emission intensities from both Ru(bipy)$_3$ at 600 nm and RuC$_{16}$B at 532 nm and 620 nm increased quadratically with the incident laser power at 1064 nm, as shown in Fig. 4. These results strongly suggest that the luminescence from Ru(bipy)$_3$ at 600 nm and from RuC$_{16}$B at 620 nm was caused by two-photon excitation. Both Ru(bipy)$_3$ and RuC$_{16}$B compounds have an absorption at 532 nm so that the very strong laser pulses at 1064 nm are considered to excite both compounds via two-photon absorption to the lowest excited state. The emission from RuC$_{16}$B at

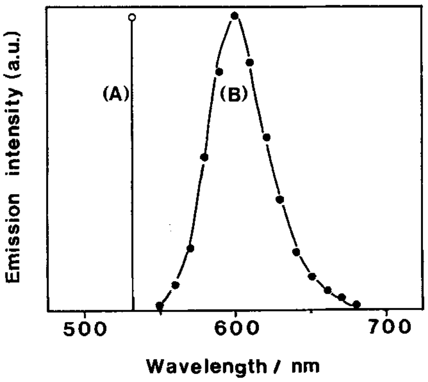

Figure 2 Emission spectra from crystalline powders of (A) RuC$_{16}$B and (B) Ru(bipy)$_3$ upon Nd–YAG laser irradiation at 1064 nm.

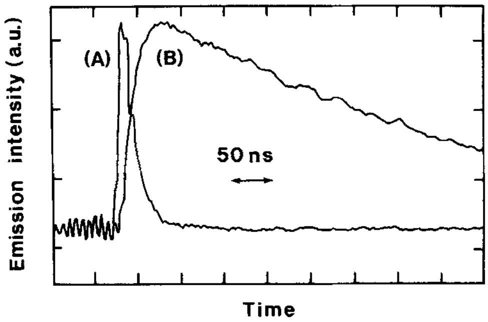

Figure 3 Temporal profiles of the luminescence from crystalline powders of (A) RuC$_{16}$B at 532 nm and (B) Ru(bipy)$_3$ at 600 nm on Nd–YAG laser irradiation at 1064 nm.

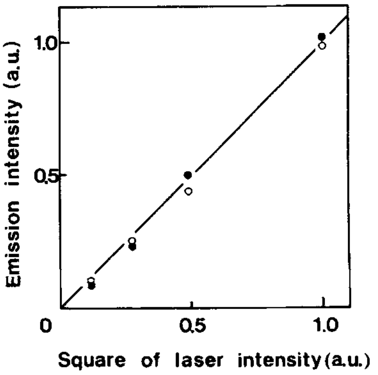

Figure 4 Effects of excitation laser intensity at 1064 nm on the emission from RuC$_{16}$B at 532 nm (closed circles) and Ru(bipy)$_3$ at 600 nm (open circles).

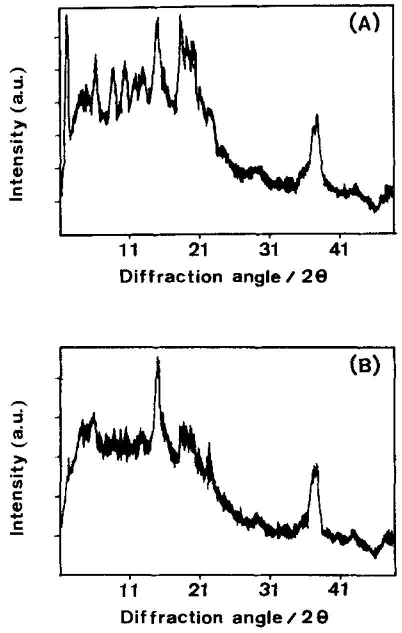

Figure 5 X-ray powder diffraction patterns for (A) $RuC_{16}B$ and (B) $RuC_{18}B$.

532 nm was due to SHG.[7,8] Noncentrosymmetric molecular structure and crystal structure are necessary for SHG. $Ru(bipy)_3$ is considered to have a pseudo-centrosymmetric molecular structure, because the three identical bipyridine ligands combine with ruthenium metal via octahedral coordination. $Ru(bipy)_3$ has the same probability for transition of the electrons from the ruthenium atom to each of the three bipyridine ligands. The molecular structure of RuC_nB, on the other hand, seems to be noncentrosymmetric, because one of the three bipyridine ligands has two amide bonds at the 4,4′-positions, which results in an anisotropic transition. The RuC_nB type is expected to have a much larger molecular hyperpolarizability than $Ru(bipy)_3$ due to a vectorial electron transition from the ruthenium atom to the bipyridine ligand with amide bonds.[7] The reason why SHG is observed only for RuC_nB compounds can be explained in this way.

The SHG intensity from RuC_nB was about 500 times smaller than that of urea, partly because of the imperfect alignment of the permanent dipole moment in RuC_nB powders. The SHG intensity from RuC_nB species depended strongly on the alkyl chain length. It became larger in the order $RuC_{16}B \simeq RuC_{12}B > RuC_{18}B$. The SHG intensity from $RuC_{16}B$ and $RuC_{12}B$ is about five times higher than that of $RuC_{18}B$. It is expected that the order of SHG intensity from RuC_nB is controlled by the crystalline structures and sizes. The X-ray powder diffraction patterns are shown in Fig. 5 for $RuC_{16}B$ and $RuC_{18}B$. The diffraction angle and intensity for $RuC_{12}B$ are almost the same as those of $RuC_{16}B$. The diffraction patterns are similar among these three compounds but the intensity is different. The crystalline structure of these RuC_nB derivatives is thus assumed to be almost the same. The X-ray diffraction intensities for $RuC_{16}B$ are much higher than those for $RuC_{18}B$ at all peaks suggesting the difference in the size of the crystals. In general, the SHG intensity should increase quadratically with increase in the size of crystalline powders if the size of the crystalline powders is shorter than a coherent length for SHG. In the present experiment, the size of the crystalline powders is less than about 5 μm, which is comparable with the coherent length of $RuC_{18}B$, which was estimated by SHG measurement of LB films.[7] These data suggest that the variation of SHG intensity among RuC_nB compounds can be ascribed to the size of the crystalline powders.

CONCLUSION

$Ru(bipy)_3$, having three identical bipyridine ligands, showed only two-photon emission upon excitation with 1064 nm laser pulses. For RuC_nB species which have two amide bonds in one of the three bipyridine ligands, both SHG and very weak two-photon emission were observed under the same conditions. Amide bonds in RuC_nB having an electron-withdrawing nature facilitate a vectorial electronic transition from ruthenium atom to a bipyridine ligand resulting in a large molecular hyperpolarizability. The SHG intensity of RuC_nB complexes decreased in the order $RuC_{16}B \simeq RuC_{12}B > RuC_{18}B$. It can be ascribed to the difference in size of the crystalline powders.

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