PROCEEDINGS OF SCIENCE

Development of Liquid Scintillator containing Zirconium Complex for Neutrinoless Double Beta Decay Experiment

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An organic liquid scintillator containing a zirconium complex has been developed for a new neutrinoless double beta decay experiment. In order to produce a detector that has good energy resolution (4% at 2.5 MeV) and low background (0.1 counts/(t·year) and that can monitor tonnes of target isotope, we chose a zirconium β-diketone complex having high solubility (over 10 wt.%) in anisole. However, the absorption peak of the diketone ligand overlaps with the luminescence of anisole. Therefore, the light yield of the liquid scintillator decreases in proportion to the concentration of the complex. To avoid this problem, we synthesized a β-keto ester complex introducing -OC_3H_7 or -OC_2H_5 substituent groups in the β-diketone ligand, and a diethyl malonate complex. Those shifted the absorption peak to around 245 nm and 210nm, respectively, which are shorter than the emission peak of anisole (275 nm). However, the shift of the absorption peak depends on the the scintillation solvent. Therefore we have to choose an adequate solvent for the liquid scintillator. The best performance will be obtained by pure anisole scintillator containing a tetrakis diethyl malonate zirconium.

We also synthesized a Zr-ODZ complex, which has a high quantum yield (30%) and good emission wavelength (425 nm) with a solubility 5 wt.% in benzonitrile. However, the absorption peak of the Zr-ODZ complex was around 240 nm. Therefore, it is better to use the scintillation solvent which has shorter luminescence wavelength than that of benzonitrile.

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1. Liquid scintillator containing zirconium complex

To use ^{96}Zr for the $0\nu\beta\beta$ experiment, we have developed the liquid scintillator containing a zirconium acetylacetone complex (Zr(acac)$_4$). However, the scintillation light decreased in proportion to the concentration of the complex. To avoid this problem, we must shift the absorption peak of the complex to a shorter wavelength. The simplest way to do this is to introduce substituent groups such as -OC$_3$H$_7$ and -OC$_2$H$_5$ in the β-diketone ligand. We synthesized tetrakis (isopropyl acetoacetate) zirconium ($Zr(CH_3CCOCHCOOCH(CH_3)_2)_4$: Zr(iprac)$_4$) and tetrakis (ethyl acetoacetate) zirconium ($Zr(CH_3CCOCHCOOCH_2CH_3)_4$: Zr(etac)$_4$). The molecular masses of these complexes are 711.92 and 665.81, respectively.

We measured the solubility of these complexes in anisole and they were over 10 wt.%. We also measured the absorbance spectrum and obtained the left side figures of Fig. 1. The absorption peaks of Zr(iprac)$_4$ and Zr(etac)$_4$ were shifted to a shorter wavelength ($\sim$ 240 nm) than that of Zr(acac)$_4$ ($\sim$ 270 nm) in hexane, which means there is no overlap between the absorption peak of the β-keto ester complex and the emission peak of anisole. We attempted to resolve Zr(iprac)$_4$ and Zr(etac)$_4$ in the scintillator cocktail (PPO 10mg and POPOP 10mg in 20mL anisole) with concentrations of 1 wt.% and 5 wt.%. However, as the middle and right side figure of Fig. 1 show, we observed the same quenching as for Zr(acac)$_4$ even though the absorption peak should be at a shorter wavelength.

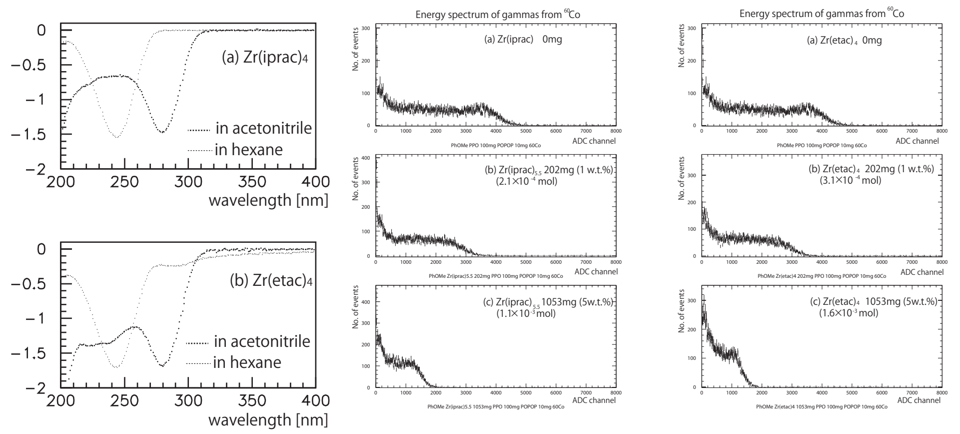

Figure 1: Left side figure shows absorbance spectra for (a) a tetrakis(isopropyl acetoacetate) zirconium and (b) a tetrakis (ethyl acetoacetate) zirconium. The middle and the right side figure shows the measured spectrum of photons from ^{60}Co using a liquid scintillator cocktail with Zr(iprac)$_4$ and Zr(etac)$_4$ for (a) no complex, (b) 1 wt.%, and (c) 5 wt.% concentrations.

The above shifted absorbance spectra were measured by using hexane as a solvent. The absorbance spectra in anisole and in hexane could be different. In fact, the absorption peak of β-keto ester zirconium complex in acetonitrile was quite different from that in hexane as shown in the left side figure of Fig.1. The absorption peaks of Zr(iprac)$_4$ and Zr(etac)$_4$ did not move, and their spectra were almost same as that of Zr(acac)$_4$. This means that the absorption tail (or peak) of Zr(iprac)$_4$ and Zr(etac)$_4$ still exist in anisole. However, this problem could be resolved by using a pure anisole.

2. Tetrakis (diethyl malonate) zirconium

We are trying to synthesize another zirconium complex: tetrakis (diethyl malonate) zirconium now. The absorbance of a diethyl malonate was obtained as shown in the left side figure of Fig,2, and we found the absorption peak existed around 210 nm, which was much shorter than that of Zr β-keto ester complex. Therefore, we could expect no quenching occurs in case of a tetrakis (diethyl malonate) zirconium.

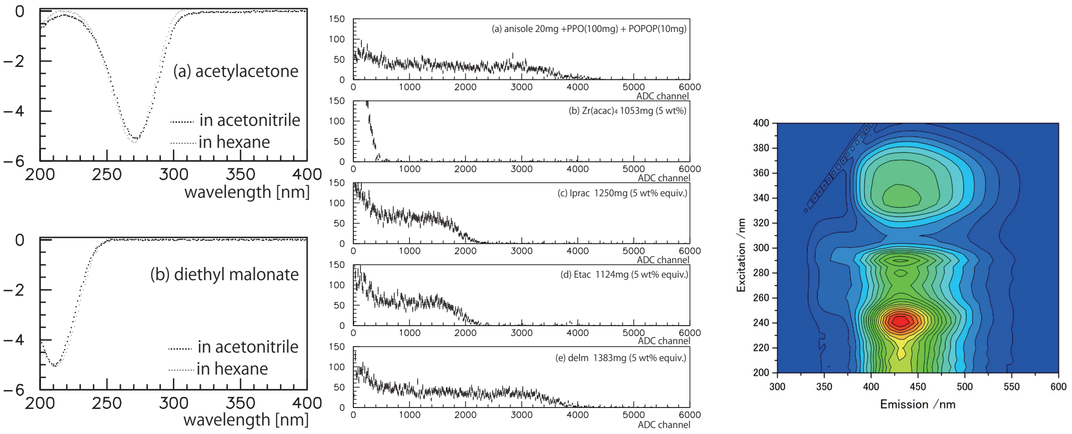

Figure 2: Left side figure shows absorbance spectra for (a) an acetylacetone and (b) a diethyl malonate. Middle side figures show the measured spectra of photons from ^{60}Co in case of several ligands. Right side figure shows a two-dimensional plot between the excitation and the emission light for a $Zr(ODZ)_4$ complex.

The middle figure of Fig.2 shows the scintillation light yield for $Zr(acac)_4$, an isopropyl acetoacetate, an ethyl acetoacetate, and a diethyl malonate in case of 5 wt.% concentration. According to this results, the light yield of the liquid scintillator solved β-keto ester ligand decreased 45%. On the other hands, the light yield of the liquid scintillator with a diethyl malonate was almost same as that of an original liquid scintillator.

3. Zirconium complex with photo luminescence

We choose ODZ (2-(2-Hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole; $C_{14}H_{10}N_2O_2$) [2] as a luminescent ligand, and synthesized the $Zr(ODZ)_4$ complex (MW=1040.18). The right side figure of Fig. 2 shows a two-dimensional plot of the wavelengths between the excitation and the emission light for the $Zr(ODZ)_4$ complex dissolved in acetonitrile. There are three peaks for the emission light (425nm) at 240 nm, 290 nm, and 340 nm for an excitation wavelength. The solubility of the $Zr(ODZ)_4$ was about 5 wt.% in benzonitrile. we obtained a quantum yield of $\sim$10% at 340nm for the emission. Using the differences of emission efficiency observed in the right side figure of Fig. 2, the quantum yield of the first emission around 240 nm was estimated to be about 30%.

References

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