

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

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Abstract

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/ (tonne · 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 $-\text{OC}_3\text{H}_7$ or $-\text{OC}_2\text{H}_5$ 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.

Key words : Neutrino Mass (ニュートリノ質量)
Neutrinoless Double Beta Decay (ニュートリノを放出しない2重ベータ崩壊)
Zirconium (ジルコニウム)
Liquid Scintillator (液体シンチレータ)
Metal Complex (金属錯体)

1. Introduction

In 1998, Super-Kamiokande discovered atmospheric ν_μ oscillation in its zenith angle measurement [1]. This was the first evidence of a non-zero neutrino mass which indicates the existence of physics beyond the standard model. Recent leptogenesis models postulate the existence of heavy right-handed neutrinos, which

are also generally present in the See-Saw model, and strongly favor the existence of Majorana neutrinos. The observation of neutrinoless double beta decay would confirm the Majorana nature of the neutrino and would also provide more information about the neutrino mass scale and hierarchy. Therefore, it is important to try to detect a real signal from neutrinoless double beta decay ($0\nu\beta\beta$).

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The half-life of $0\nu\beta\beta$ is given by

$$[T_{12}^{0\nu}(0^+ \rightarrow 0^+)]^{-1} = G_{0\nu} M_{0\nu}^2 \frac{m_\nu^2}{m_e^2} \quad (1)$$

where $G_{0\nu}$ is the kinematic phase space factor, $M_{0\nu}$ is the matrix element including Fermi, Gamow-Teller and tensor contributions, m_e is the electron mass, and m_ν is the effective neutrino mass. According to Eq. 1, we have to be able to measure a half-life of the order of 10^{25} years assuming the neutrino mass to be 100 meV. On the other hand, the half-life can also be expressed experimentally as

$$T_{12}^{0\nu} \sim a \frac{MT}{\Delta E B} \quad (2)$$

where a is the abundance of the target isotope, M is the target mass, T is the measurement time, ΔE is the energy resolution, and B is the background rate. For next-generation $0\nu\beta\beta$ experiments, the target isotope mass should reach the order of 1000 kg and the background rate should stay around 0.1-1 counts/(tonne · year) with an energy resolution of 4% at 2.5 MeV. (Alternatively we could combine a relatively low target mass target with very high energy resolution.)

Many $0\nu\beta\beta$ experiments are now ongoing and more are planned as future experiments with several target isotopes. Table 1 shows a summary of future $0\nu\beta\beta$ experiments. According to Table 1, there is no experiment planning to use ^{96}Zr (Q-value = 3350 keV) as a target isotope. Here we report new liquid scintillator containing a zirconium complex that could be used in a future $0\nu\beta\beta$ experiment.

experiment	isotope [Q (keV)]	target mass (kg)	T_{12} (yr)	m_ν (keV)
GERDA	^{76}Ge [2040]	40	2×10^{26}	90
		1000	6×10^{27}	40
MAJORANA	^{76}Ge [2040]	60	2×10^{26}	300
		1000	6×10^{27}	40
EXO	^{136}Xe [2479]	200	6.4×10^{25}	220
		1000	8×10^{26}	63
KamLAND-Xen	^{136}Xe [2479]	400	4.5×10^{26}	80
CUORE	^{130}Te [2533]	200	6.5×10^{26}	50
Super-NEMO	^{82}Se [2995]	200	2×10^{26}	110
SNO+	^{150}Nd [3667]	56	4.5×10^{24}	300
		500	3×10^{25}	120
CANDLES	^{48}Ca [4271]	0.35	a few $\times 10^{24}$	500

Table 1. Next-generation experiments for $0\nu\beta\beta$. The Q-value is in kilo-electron volts, Mass is in kilograms, T_{12} is in years, and m_ν is in milli-electron volts. All values are quoted from Ref. [2] except CANDLES [3].

2. Liquid scintillator containing zirconium complex

To use ^{96}Zr for a $0\nu\beta\beta$ experiment, we have developed a liquid scintillator containing a zirconium complex. A liquid scintillator was used for neutrino experiments such as KamLAND and SNO, because of their large target masses. As described in the previous section, a next-generation $0\nu\beta\beta$ experiment should also have a target isotope mass of about a tonne and a good energy resolution in order to detect a neutrino mass below 100 meV. However, a large volume detector generally worsens both the energy resolution and the background rate. Therefore, we need to make a small detector filled with a liquid scintillator with a large target mass.

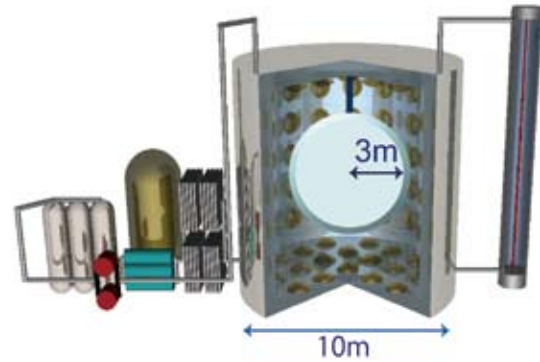


Figure 1. Detector design for Zirconium Complex in Organic liquid Scintillator for double beta decay (ZICOS) experiment.

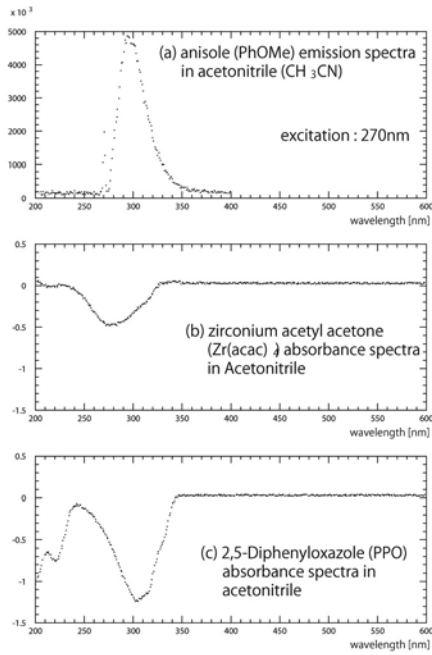


Figure 2. The emission spectrum of (a) anisole, (b) the absorbance spectrum of $Zr(acac)_4$, and (c) the absorbance spectrum of PPO.

In order to realize this configuration, it is important that the solubility of the complex should be high enough. Assuming 100 tonne of liquid scintillator, we need a spherical detector with a 3 m radius as shown in Fig.1. This must be located in a cylindrical tank, filled with pure water, which has 5 m radius and 10 m height. The photomultiplier must be mounted on both the spherical detector and the tank wall, respectively. Outer pure water detector should be used for the veto detector against the external backgrounds. This detector will be placed in an underground location, such as the Kamioka Observatory.

Assuming 20% solubility of the complex in the liquid scintillator, the amount of zirconium required is of the order of 3 tonne. However, the natural abundance of ^{96}Zr is 3%, so we must enrich ^{96}Zr up to 10%. For the first step, we searched for a zirconium complex having high solubility in the chosen solvent. Indium acetylacetonate ($In(acac)_3$) has good solubility (over 10 wt.%) in anisole, as reported in Ref. [4]. Instead of indium, zirconium could also be used in the form of zirconium (IV) acetylacetonate ($Zr(acac)_4$). However, in Ref. [4], it is also reported that the absorption

peak of $In(acac)_3$ overlaps with the emission peak of anisole. A quenching will occur so that the scintillation light should decrease in proportion to the concentration of the complex. In the case of zirconium, we also observed similar overlap, as shown in the left side of Fig. 2, and observed similar quenching, as shown in Fig. 3. 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 other substituent groups in the β -diketone complex.

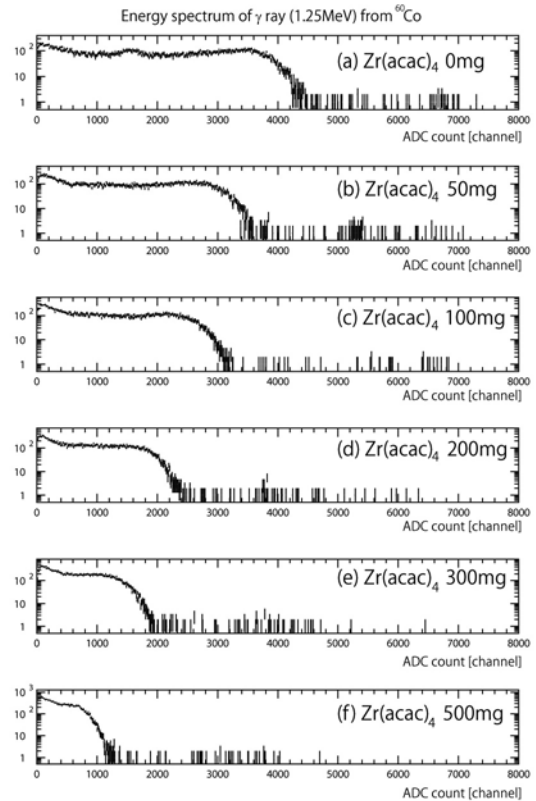


Figure 3. Measured spectrum of photons from ^{60}Co using a liquid scintillator cocktail with some different concentrations of $Zr(acac)_4$. Scintillation light yield decreased in proportion to the concentration of (a) 0mg to (f) 500mg.

3. Zirconium complex with substituent groups

There are substituent groups that can be used to shorten the absorption wavelength. We chose a β -keto ester complex with $-OC_3H_7$ (isopropyl acetoacetate) and $-OC_2H_5$ (ethyl acetoacetate), instead of the β -diketone (acetylacetonate) complex. Actually, we measured the absorbance spectra for each ligands

solved in the hexane and acetonitrile, those are typical solution of the optical measurement. We also used toluene as typical aromatic solvent for the absorbance measurement. Figure 4 shows the absorbance spectra for each ligands.

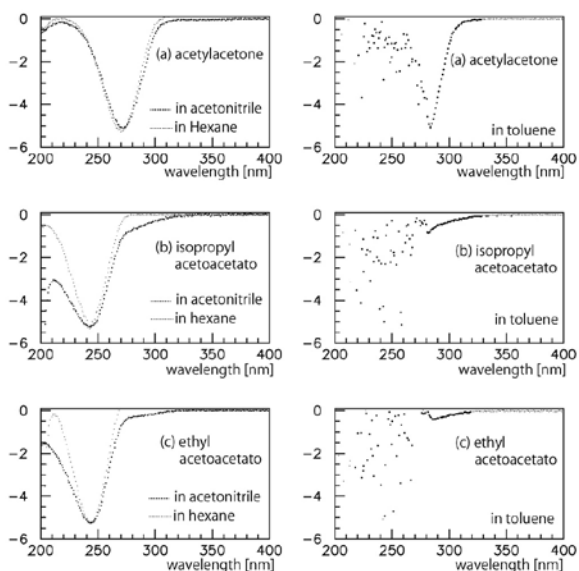


Figure 4. Absorbance spectra for (a) an acetylacetonate, (b) an isopropyl acetoacetate and (c) an ethyl acetoacetate. The left side panel shows them in hexane (light dots) and in acetonitrile (deep dots), and the right side panel in toluene.

As mentioned above, the peak of an absorbance of β -keto ester ligands were found around 245nm in any solution. Even though a toluene has the absorption below 250nm due to an aromatic solvent, we have never seen the absorption around 270nm for β -keto ester ligands.

We and Prof. Takahiro Gunji (Tokyo University of Science) synthesized the zirconium β -keto ester complex shown in Fig. 5. The molecular masses of a tetrakis (isopropyl acetoacetate) zirconium complex ($\text{Zr}(\text{CH}_3\text{CCOCHCOOCH}(\text{CH}_3)_2)_4$; $\text{Zr}(\text{iprac})_4$) and a tetrakis (ethyl acetoacetate) zirconium complex ($\text{Zr}(\text{CH}_3\text{CCOCHCOOCH}_2\text{CH}_3)_4$; $\text{Zr}(\text{etac})_4$) 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 right-hand figures of Fig. 2. The absorption peaks of $\text{Zr}(\text{iprac})_4$ and $\text{Zr}(\text{etac})_4$ were shifted to a shorter wavelength (~ 240 nm) than that of $\text{Zr}(\text{acac})_4$ (\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.

4. Light yield of liquid scintillator

To transfer the energy in the solvent to the photomultiplier, we dissolved 2,5-diphenyloxazole (PPO), which has an absorption peak at 310 nm and an emission peak at 368 nm, as a secondary scintillator. The addition of 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP), which has an absorption peak at 364 nm and an emission peak at 427 nm, improves the quantum efficiency of the energy transfer to the photomultiplier. We used 100 mg PPO and 10 mg POPOP in 20 ml of anisole as the typical scintillator cocktail.

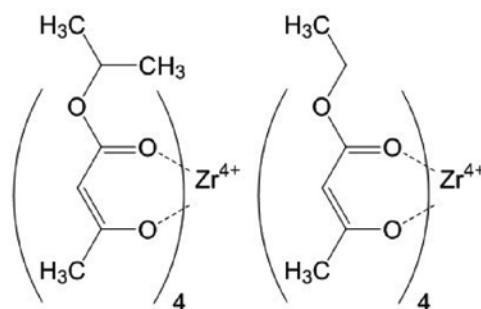


Figure 5. A tetrakis(isopropyl acetoacetate) zirconium complex (left) and a tetrakis(ethyl acetoacetate) zirconium complex (right).

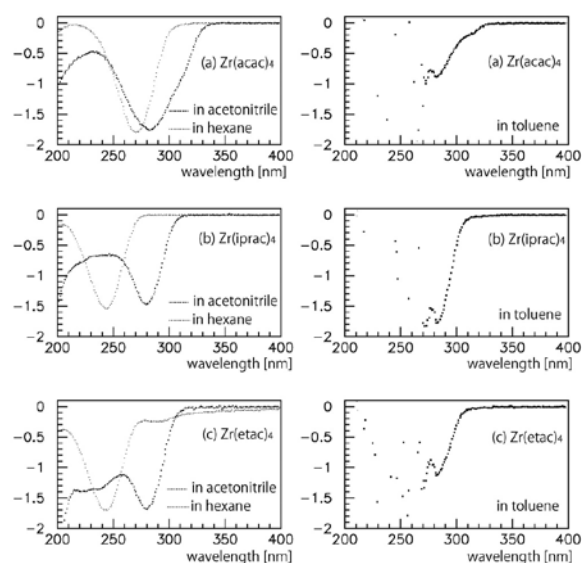


Figure 6. Absorbance spectra for (a) a tetrakis(acetylacetonate) zirconium, (b) a tetrakis(isopropyl acetoacetate) zirconium and (c) a tetrakis (ethyl acetoacetate) zirconium. The left side panel shows them in hexane (light dots) and in acetonitrile (deep dots), and the right side panel in toluene.

We attempted to resolve $Zr(iprac)_4$ and $Zr(etac)_4$ in the scintillator cocktail with concentrations of 1 wt.% and 5 wt.%. However, as Figure 7 shows, we observed the same quenching as for $Zr(acac)_4$ even though the absorption peak should be at a shorter wavelength.

The above shifted absorbance spectra were measured by using hexane as a solvent. The absorbance spectra in anisole and in hexane could be different. Unfortunately, we could not use anisole for measuring the absorbance spectrum due to the large absorption found below 250 nm. In fact, the absorption peak of β -keto ester zirconium complex in acetonitrile was quite different from that in hexane as shown in Fig.6. The absorption peaks of $Zr(iprac)_4$ and $Zr(etac)_4$ did not move, and their spectra were almost same as that of $Zr(acac)_4$. Also we found small absorption tail in toluene even though they were not seen in case of ligand. This means that the absorption tail (or peak) of $Zr(iprac)_4$ and $Zr(etac)_4$ still might exist in anisole.

To solve this problem, we have to investigate the chemical component in those solutions using a Gas Chromatography.

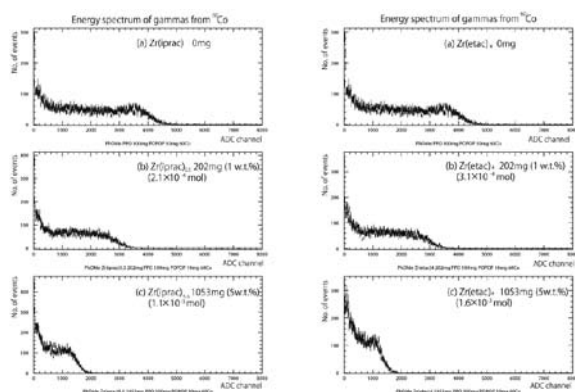


Figure 7. Measured spectrum of gamma-ray from ^{60}Co using a liquid scintillator cocktail with $Zr(iprac)_4$ (left side panel) and $Zr(etac)_4$ (right side panel) with (a) no complex, (b) 1 wt.%, and (c) 5 wt.% concentrations.

5. Dissolution of complex

The gas chromatography (GC) is one of best tool to prove the chemical component. We have analyzed the data obtained by $Zr(iprac)_4$ solved in (1) hexane, (2) acetonitrile, and (3) anisole. There

was no peak for $Zr(iprac)_4$ complex in all data due to out of range. In hexane, we found the peak of hexane around 1.8 minutes, and no other peak was found. In acetonitrile, on the other hands, we found the peak of an acetonitrile around 1.6 minutes, and also the broad peak of an isopropyl acetoacetate around 5.2 minutes, which was directly observed by the measurement of an isopropyl acetoacetate. Also small fraction of peaks were seen around 16 to 20 minutes, however, we did not identify them. These results showed us that $Zr(iprac)_4$ was stable in hexane, however it was dissolved into ligands in acetonitrile due to an exchange reaction of ligand. This is the reason why the absorption peak of $Zr(iprac)_4$ was not shifted in acetonitrile.

Same things might be found in case of $Zr(etac)_4$, however, we did not explain the quenching observed in anisole as shown in Fig.7. We analyzed data obtained by $Zr(iprac)_4$ solved in anisole, and found same broad peak of an isopropyl acetoacetate around 5.2 minutes with the peak of anisole around 4 minutes. This means that $Zr(iprac)_4$ was also dissolved into the ligand, and the absorption peak of $Zr(iprac)_4$ might not shifted in the anisole. This is the reason why the same quenching as $Zr(acac)_4$ was occurred.

We used a reagent anisole (97 %) for the solution. A reagent anisole includes water and it could hydrolyzed the ester. Therefore we use anhydrous anisole for the GC measurement. As a results, there was no peak except an anisole. Therefore, we have to use anhydrous anisole or have to distillate usual anisole.

6. Tetrakis (diethyl malonate) zirconium

We and Prof. Takahiro Gunji tried to synthesize another zirconium complex: tetrakis (diethyl malonate) zirconium as shown in Fig.8. The molecular masses of a tetrakis(diethyl malonate) zirconium ($Zr(CH_3CH_2OCOCHCOOCH_2CH_3)_4$) is 727.84.

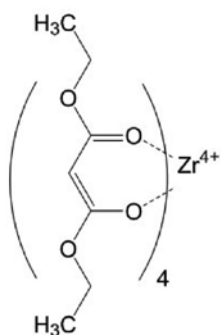


Figure 8. Tetrakis (diethyl malonate) zirconium

The absorbance of a diethyl malonate ligand was obtained as shown in Fig.9, and we found the absorption peak existed around 210 nm, which was much shorter than that of Zr β -keto ester complex, in both hexane and acetonitrile. No absorption tail was found in toluene. Therefore, we could expect no quenching occurs in case of a tetrakis (diethyl malonate) zirconium.

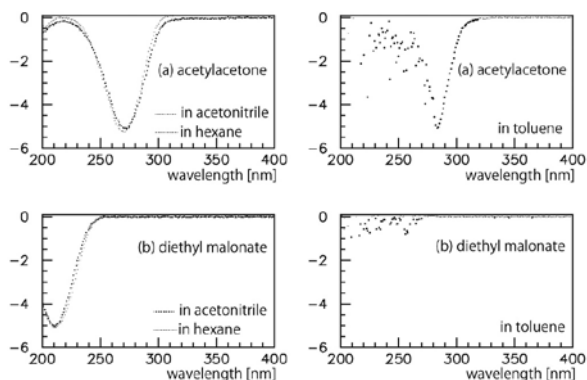


Figure 9. Absorbance spectra for (a) an acetylacetonone and (b) a diethyl malonate. The left side panel shows them in hexane (light dots) and in acetonitrile (deep dots), and the right side panel in toluene.

Since we have not obtained the complete tetrakis (diethyl malonate) zirconium yet, we measured the scintillation light yield using those ligand. At this time, we adjusted amount of ligand as the molecular number which is calculated by $Zr(acac)_4$ solved in anisole. For instance, 1 wt.% corresponds to 202mg of $Zr(acac)_4$ in anisole. We calculated the number of molecular in case of 1 wt.% and 5 wt.%, and the amount of an isopropyl acetoacetate, an ethyl acetoacetate, and a diethyl malonate were obtained by number of molecular

times 4, respectively. Figure 10 shows the scintillation light yield for $Zr(acac)_4$, an isopropyl acetoacetate, an ethyl acetoacetate, and a diethyl malonate in case of 1 wt.% and 5 wt.%. According to this results, the light yield of a liquid scintillator solved β -keto ester ligand decreased 77% and 45%, even though those numbers were much better than that of $Zr(acac)_4$. On the other hands, the light yield of a liquid scintillator with diethyl malonate was almost same as that of an original liquid scintillator. This means that the absorption peak of diethyl malonate (210nm) did not affect for the energy transfer of lights (the emission of anisole and the absorption of PPO). Therefore, we concluded the zirconium complex with a diethyl malonate should be a best material for a loading zirconium in liquid scintillator, and we will construct the detector for the neutrinoless double beta decay experiment using this scheme.

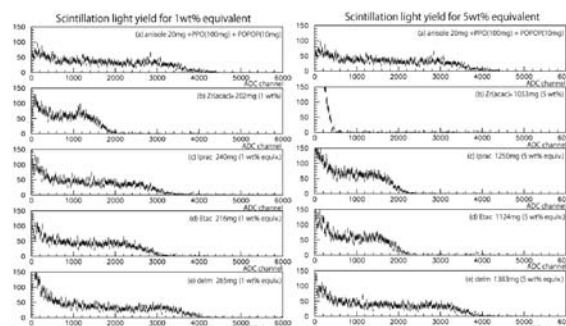


Figure 10. Measured spectrum of photons from ^{60}Co using a liquid scintillator cocktail with $Zr(acac)_4$, isopropyl acetoacetate, ethyl acetoacetate, and diethyl malonate with 1 wt.% (left), and 5 wt.% (right) concentrations.

7. Zirconium complex with photo luminescence

Another possibility for the use of a zirconium complex is to utilize photo luminescence. We synthesized a tetrakis (8-quinolinolate) zirconium (ZrQ_4 , $C_{36}H_{24}N_4O_4Zr$, M.W.=667.84) complex, and found its solubility to be 2 wt.% in benzonitrile. The photo luminescence spectrum of ZrQ_4 in benzonitrile was measured, and the maximum emission peak was found to be around 548 nm (excitation wavelength : 387nm). The absorbance spectrum of a ZrQ_4 also measured by the spectrometer. The maximum absorption

wavelength were located at 383.3nm.

We made a liquid scintillator cocktail using ZrQ_4 (50 mg) in benzonitrile solutions (20 ml) with both PPO (100 mg) and POPOP (10 mg), and measured the spectrum of induced gamma rays. However, the light yield was small due to low quantum yield (0.08).

To improve the quantum yield, we introduced a dimethoxytriazine substituent [5] into the quinolinolate ligand (Fig.11 left), and synthesized an indium complex instead of a zirconium complex (Tris [5-(4,6-dimethoxy-1,3,5-triazine-2-yl)-8-quinolinolate] indium $In(Q-T)_3$ M.W. = 964.62.). We obtained a better quantum yield (0.26) and the shorter emission peak wavelength (503 nm) in comparison with the original 8-quinolinolate indium complex (quantum yield: 0.10; emission peak wavelength: 559 nm; excitation wavelength : 397nm). However, the quantum yield was still low.

To get a much larger quantum yield and shorter emission wavelength, we chose an ODZ (2-(2-Hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole; $C_{14}H_{10}N_2O_2$) ligand [6], and synthesized the $Zr(ODZ)_4$ complex (MW=1040.18) shown in the right side of Fig. 11. The photo luminescence of the $Zr(ODZ)_4$ complex was measured by Horiba FluoroMax-4 spectrometer. The left side of Figure 12 shows a two-dimensional plot of the wavelengths between the excitation and the emission light for the $Zr(ODZ)_4$ complex dissolved in acetonitrile. The concentration was 3×10^{-5} mol/l. There are two or three peaks in the emission light (425nm) at 240 nm, 290 nm, and 340 nm for an excitation wavelength.

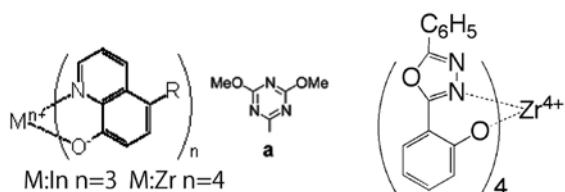


Figure 11. An 8-quinolinolate complex with dimethoxytriazine substituent group (left) and zirconium ODZ complex (right).

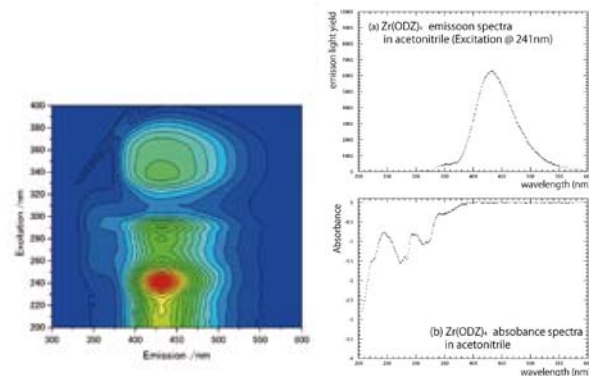


Figure 12. A two-dimensional plot of the wavelengths between the excitation and the emission light for a $Zr(ODZ)_4$ complex dissolved in acetonitrile in left side and (a) the photo emission and (b) the absorbance spectrum of $Zr(ODZ)_4$ in right side panel.

The photo emission and the absorbance spectrum of $Zr(ODZ)_4$ in acetonitrile was measured as shown in the right panel of Fig.12. The maximum emission peak was found around 430 nm and the wavelength is very sensitive to the photomultiplier. This is consistent with the photo luminescence measurement. On the other hands, the absorption peaks were found around 270nm and 320nm. These peaks are not exactly same as the results from the photo luminescence measurement.

The solubility of the $Zr(ODZ)_4$ was about 5 wt.% in benzonitrile. We prepared the scintillator cocktail using a combination of 100 mg $Zr(ODZ)_4$, 100 mg PPO, and 10 mg POPOP. It can be seen from Figure 13 that the $Zr(ODZ)_4$ did not work as the secondary scintillator because it has a shorter absorption wavelength than the emission peak of the benzonitrile (270 nm). However, it could help the energy transfer due to the photo luminescence. In fact, the second emission peak around 340 nm was used for the emission of the $Zr(ODZ)_4$ complex, and we obtained a quantum yield of 10% for this emission. Using the differences of emission efficiency observed in Fig. 12, the quantum yield of the first emission around 240 nm was estimated to be 30%. This is almost the same yield as that provided by the 8-quinolinolate with dimethoxytriazine substituent. However, the emission peak of the $Zr(ODZ)_4$ (425 nm) is much better than that of the 8-quinolinolate with a dimethoxytriazine

substituent (~ 500 nm) for the photomultiplier. Therefore, the light yield almost doubled due to the improved quantum efficiency of the photomultiplier.

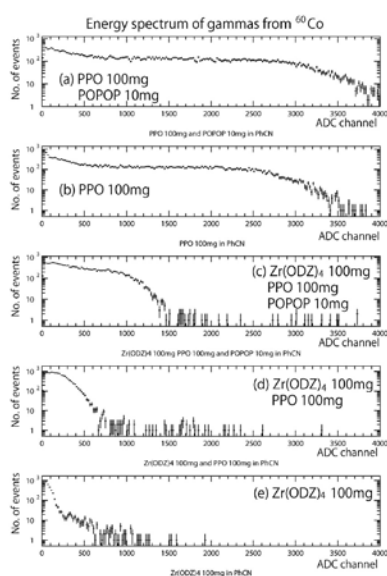


Figure 13. Measured gamma-ray spectra from ^{60}Co of (a) PPO 100mg and POPOP 10mg (b) PPO 100mg, (c) $\text{Zr}(\text{ODZ})_4$ 100mg, PPO 100mg, and POPOP 10mg, (d) $\text{Zr}(\text{ODZ})_4$ 100mg and PPO 100mg, and (e) $\text{Zr}(\text{ODZ})_4$ 100mg in right panel.

8. Conclusion

We have synthesized a isopropyl acetylacetate zirconium and an ethyl acetylacetate zirconium, and succeeded to shorten the absorption peak around 240nm, if we use anhydrous anisole. However, the absorption spectra spread and slightly overlapped with the emission of anisole. Therefore we would better to use a diethyl malonate zirconium instead of β -keto ester complex due to shorter absorption peak (210nm) which should not affect to the emission of anisole. We concluded that the zirconium complex with a diethyl malonate should be a best material for a loading zirconium in liquid scintillator, and we will construct the ZICOS detector for the neutrinoless double beta decay experiment using this scheme.

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