

# Development of liquid scintillator containing 8-quinolinolate indium complex for a measurement of low energy solar neutrinos

**Yoshiyuki Fukuda and Kunihiko Watanabe**

Faculty of Education, Miyagi University of Education,  
149, Aobaku-aza-aoba, Sendai, Miyagi 980-0845, Japan

**Shigetaka Moriyama**

Kamioka Observatory, Institute for Cosmic Ray Research,  
University of Tokyo  
456, Higashi-Mozumi, Kamioka-cho, Hida, Gifu 506-1205, Japan

**Abstract.** An organic liquid scintillator containing indium complex was studied for a measurement of low energy solar neutrinos. The energy of the emitted electrons from those processes could be transferred to the molecular of complex via the organic solvent molecules, and the luminescence from the indium complex would be detected by the photo-multiplier. Here we report some results obtained by photo-luminescence and the  $\gamma$ 's induced energy spectra of tris (8-quinolinolate) indium ( $\text{InQ}_3$ ) complex. Benzonitrile was chosen as a solvent because of good solubility for the quinolinolate complexes ( 2 wt%) and of good light yield for the scintillation induced by  $\gamma$ 's irradiation. The photo-luminescence emission spectra of  $\text{InQ}_3$  of 30 M solution in benzonitrile was measured. The emission maxima for  $\text{InQ}_3$  is found at 559nm as excitation wavelength: 397nm. We prepared  $\text{InQ}_3$  (50mg ~ 200mg) of benzonitrile solutions (20 mL). Two secondary scintillators, 100 mg of 2,5-diphenyloxazole (PPO) and 10 mg of 1,4-bis[2-(5-phenyloxazolyl)]benzene (POPOP), are also dissolved in above solutions and they play a role of wavelength shifter from the UV region emitted by excited benzonitrile molecules to the visible region emitted by  $\text{InQ}_3$  complex. The energy spectra of electrons emitted by Compton scattering of incident  $\gamma$ 's using  $^{60}\text{Co}$  radio isotope was obtained. These results are the first observation of the  $\gamma$ 's energy spectra using luminescent metal complexes.

## keyword:

low energy solar neutrinos (低エネルギー太陽ニュートリノ)  
liquid scintillator (液体シンチレータ)  
8-quinolinolate complex (キノリノール錯体)

## 1. Introduction

Super-Kamiokande has discovered the evidence of atmospheric muon neutrino oscillation in 1998[1], and the K2K experiment has confirmed the oscillation at 99.995%C.L. using  $\nu_\mu$  beam produced by KEK 1 GeV Proton Synchrotron in 2005[2]. Therefore the neutrino physics lead to beyond the standard model of elementary particle physics.

Also Super-Kamiokande and Sudbery Neutrino Observatory experiment have established electron neutrino oscillation in their solar neutrino data [3, 4]. A long way problem so called Solar Neutrino Problem in past 30 years was almost solved by the LMA oscillation. Independently, KamLAND experiment confirmed the oscillation using reactor anti-neutrino in sense of  $\Delta m^2$  [5]. Even though Borexino reported the first results of  ${}^7\text{Be}$  solar neutrino flux [6], the oscillation mixing angel ( $\theta_{12}$ ) obtained by global fit using all solar neutrino data was not restricted as well as  $\theta_{23}$  observed in atmospheric neutrino data. For the future solar neutrino experiment, a precise  $\theta_{12}$  should be measured with 1% accuracy due to the observation for solar pp/ ${}^7\text{Be}$  neutrinos in order to obtain finite value of  $\theta_{13}$  in case of only upper limits obtained by T2K nor the reactor experiments.

## 2. Low energy solar neutrino experiment using ${}^{115}\text{In}$

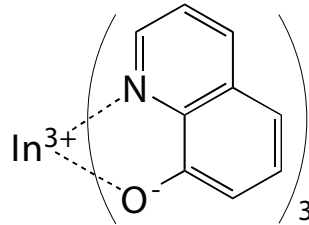
In 1976, R.Raghavan proposed new technique for the measurement of low energy pp/ ${}^7\text{Be}$  solar neutrinos [7] via following reaction;



The prompt electron has an energy with  $E_\nu - 118$  keV, here  $E_\nu$  is an energy of incident neutrinos. An excited state of  ${}^{115}\text{Sn}$  shown in Eq.(1) decays into the ground state with a lifetime of  $4.76\mu\text{s}$ , and emits two  $\gamma$ 's (116 keV and 497 keV). This signature is also able to use for a triple-coincidence to extract neutrino signal from huge backgrounds. However,  ${}^{115}\text{In}$  itself has natural  $\beta$  decay into the ground state of  ${}^{115}\text{Sn}$  with a lifetime of  $4.41 \times 10^{14}$  years and maximum  $\beta$  energy of 495keV. The radiative Bremsstrahlung could produce fake coincidence for the neutrino signal. In order to avoid this, a detector with both good vertex resolution (a few cm) and well energy resolution (10% @ 100keV) is necessary [8].

Many possible detectors using indium were designed in last few decade, however, no realistic detector has been made. In 1988, Suzuki and Fukuda developed the InP solid state detector ( $1\text{mm}^2 \times 10\mu\text{m}$ ) using the pn-junction and the detector observed the  $\gamma$ 's from the radioactive sources [9]. New detector using InP semi-conductor has been re-evaluated for last several years, and a realistic size of InP detector was established by using semi-insulating substrate[11].

For large volume detector, a liquid scintillator containing indium was developed by Suzuki *et al.*[10] and LENS project [12]. Recently LENS group presented the feasibility of realistic way for a proto-type detector (Mini-LENS) [13], which will use MVA indium complex in the Liner Arkyl Benzen (LAB) [14].



**Figure 1.** tris (8-quinolinolate) indium complex.

A tris (8-quinolinolate) aluminum complex is very famous as an organic electron luminescent (OEL) device, and the chemical characteristics were studied in 1970s. The metal coupled with the ligand could be exchanged by other metal such as Gallium and Indium. The optical property was also studied [15] and every complexes have almost same maximum wavelength ( $\sim 550\text{nm}$ ) for the luminescence. We used tris (8-quinolinolate) indium complex as shown in Fig.1 for not only solute of liquid scintillator but the fluorescent material in the scintillator system.

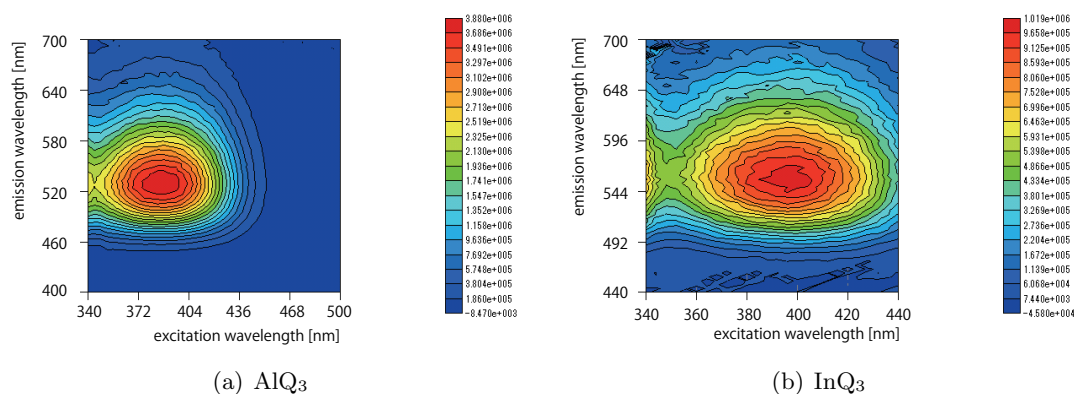
### 3. Synthesis of InQ<sub>3</sub> complex

A tris (8-quinolinolate) aluminum complex (molecular mass : C<sub>27</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>Al F.W.=459.44) is commercially produced as an organic electron luminescent device, however, a tris (8-quinolinolate) indium complex (molecular mass : C<sub>27</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>In F.W.=547.28) is not popular. Therefore, we have to synthesize using metal salt compound and quinolinolate ligand. A 2.1773g of 8-quinolinolate ligand and 1.1562g of ammonium acetate were added in 25mL of H<sub>2</sub>O, and then a 35mL of ethanol was also added. This solution was heating with 50 °C in order to dissolve them. In this solution, a 1.7744g of indium(III) nitrate trihydrate with 8mL of H<sub>2</sub>O was added. Immediately, the yellow powder was precipitated with primary complex, and it was agitated during 10 minutes. Then the precipitated material was filtrated and put into the vacuum desiccator. The primary yield was obtained by 2.8596g, and it corresponds to 100% efficiency. The obtained primary complex could include an impurity, so that we had sublimated it (0.3201g) under the vacuum ( $7.5 \times 10^{-4}$ Torr). The temperature was almost 350°C. After 2 times of sublimation, we obtained 0.2449g of a tris (8-quinolinolate) indium complex. The efficiency was achieved by 77%.

This obtained complex was analyzed by two methods. One is the elemental analysis (EA) and the other is the high resolution mass spectrometry (HRMS). The elements of InQ<sub>3</sub> complex consists of C :59.26, H:3.32, and N:7.68. Found elements by EA are C:59.233, H:3.534, and N:7.652, respectively. They are completely consistent with the elemental structure. Also the HRMS (ESI) with the m/z calcd for C<sub>27</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>NaIn [M+Na<sup>+</sup>] expected total mass 570.0283. The found mass is 570.0279. Therefore, the impurity of synthesized InQ<sub>3</sub> complex should achieved above 99%.

### 4. Photo luminescence of InQ<sub>3</sub> complex and quantum yield

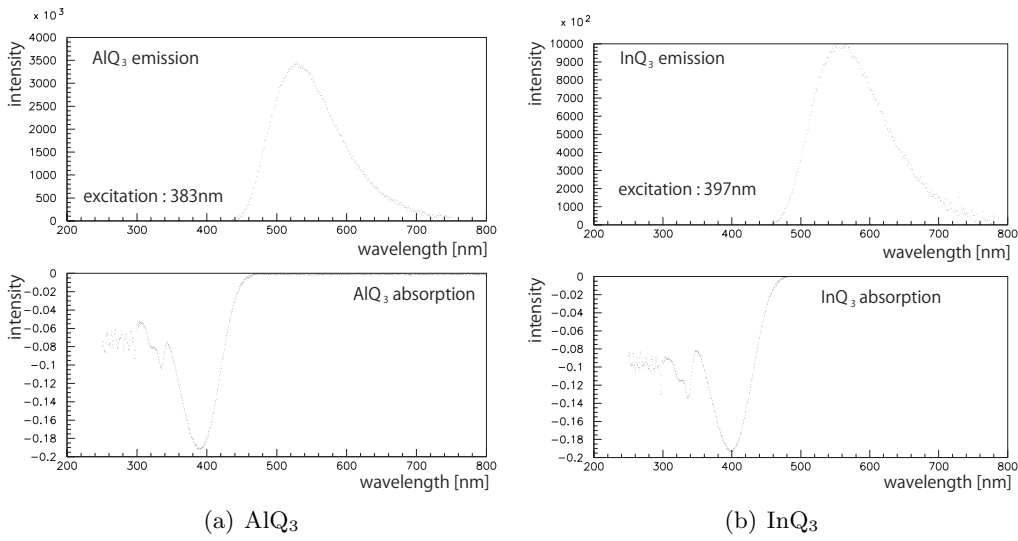
We have searched for an organic solvent which should have high solubility of InQ<sub>3</sub> complex. Some typical aromatic solvent such as toluene or xylene, which were generally used for the base of liquid scintillator, could not dissolve InQ<sub>3</sub> nor AlQ<sub>3</sub> complexes so much. These are not a polar molecular. We have found benzonitrile (C<sub>6</sub>H<sub>5</sub>CN: PhCN) and benzyl alcohol (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH: PhCH<sub>2</sub>OH) have an order of a few % dissolution for AlQ<sub>3</sub> and InQ<sub>3</sub> complexes. The maximum photo luminescent wavelength are 291nm and 270nm in UV region, respectively. For the current development, we have chosen PhCN as solvent because of larger photo yield. The PhCN has a flash point of 75 °C, and the attenuation length is 66cm for the InQ<sub>3</sub> 0.5wt% concentration.



**Figure 2.** 2-dimensional plot of fluorescence of (a) AlQ<sub>3</sub> and (b) InQ<sub>3</sub> complex dissolved in PhCN are shown. Horizontal and vertical axis shows the wavelength of excitation and emission light.

We used HORIBA FluoroMax-4 spectrofluorometer for scanning the photo luminescence. Figure 2 shows the 2-dimensional plot of the wavelength between an excitation and an emission light for (a) AlQ<sub>3</sub> and (b) InQ<sub>3</sub> complex dissolved in PhCN, respectively. The concentration of both complexes was  $3 \times 10^{-5}$  mol/L. The emission light yield is also shown in the color on the contour.

Figure 3 shows photo luminescence and absorption of AlQ<sub>3</sub> and InQ<sub>3</sub> complex in PhCN solution. Maximum emission wavelength of AlQ<sub>3</sub> and InQ<sub>3</sub> complex are found at 529.9nm (excitation wavelength : 383nm) and 559.3nm (excitation wavelength : 397nm), respectively. The absorbance of AlQ<sub>3</sub> and InQ<sub>3</sub> complex also measured by HITACHI U-3000 spectrophotometer. The maximum absorption wavelength were located at 389.6nm for AlQ<sub>3</sub> and 394.7nm for InQ<sub>3</sub> complex, respectively.



**Figure 3.** Photo luminescence and absorbance of (a) AlQ<sub>3</sub> and (b) InQ<sub>3</sub> complex dissolved in PhCN are shown. The maximum emission wavelength of AlQ<sub>3</sub> and InQ<sub>3</sub> were found at 529.9nm and 559.3nm with the excitation wavelength at 383nm and 397nm, respectively. Also the maximum absorption wavelength were located at 389.6nm and 394.7nm, respectively.

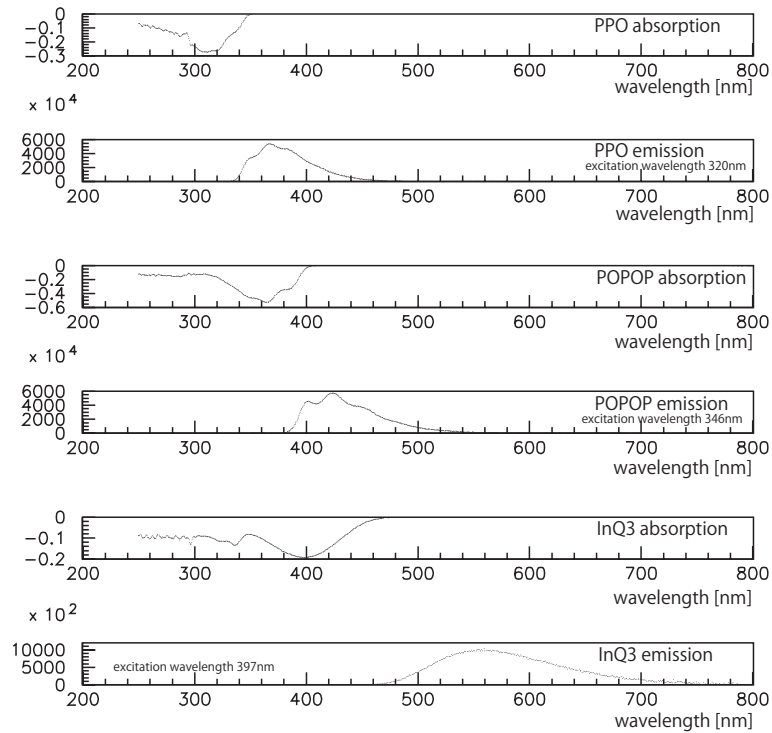
The quantum yield of tris (8-quinolinolate) complex was obtained by the standard material. Quinine ((6-Methoxyquinolin-4-yl) [(2S,4S,5R)-5-vinyl-1-aza-bicyclo[2.2.2]oct-2-yl]- (R)-methanol) was used for the reference material which has known quantum yield 0.55 and relative light yield to the maximum at 100% as a function of the wave number are shown in Ref.[16]. The emission spectra in Fig.3 was not corrected by the quantum efficiency of the photo multiplier which is used in FluoroMax-4. Using relative light yield for measured fluorescence of Quinine, we have corrected the emission spectra, and have obtained the area of each spectrum. The quantum yield was defined by following formula;

$$\Phi_c = \Phi_r \times \frac{S_c}{S_r} \times \frac{A_r}{A_c} \quad (2)$$

Here,  $\Phi_r / \Phi_c$ ,  $S_r / S_c$ , and  $A_r / A_c$  is the quantum yield, area of spectrum, and the maximum absorbance of Quinine and tris (8-quinolinolate) complex, respectively.  $\Phi_r$  is referred as 0.55 in [16]. The obtained quantum yield were 0.17 and 0.05 for AlQ<sub>3</sub> and InQ<sub>3</sub> complex, respectively. These values are quite consistent with the published value as shown in Ref.[17].

## 5. Performance of liquid scintillator containing InQ<sub>3</sub> complex

The  $\gamma$ 's from sources of <sup>137</sup>Cs (662keV) and <sup>60</sup>Co (1.17MeV and 1.33MeV) could interact with electrons in liquid scintillator, and emit an electron via photo-electric effect or Compton scattering. Light nuclei such as Hydrogen and Carbon has larger cross section of Compton scattering than that of photo-electric effect. The energy of emitted electron could be deposited by the electron-magnetic interaction with other electrons during going through the material. Those electrons received the energy would be transited to the excited state, and after proper time, the electron would be back lower energy state with the photon emission such as scintillation.

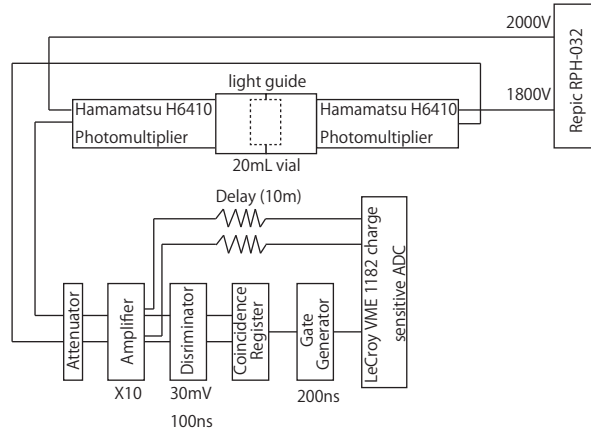


**Figure 4.** Absorption and emission of PPO, POPOP and InQ<sub>3</sub> in PhCN.

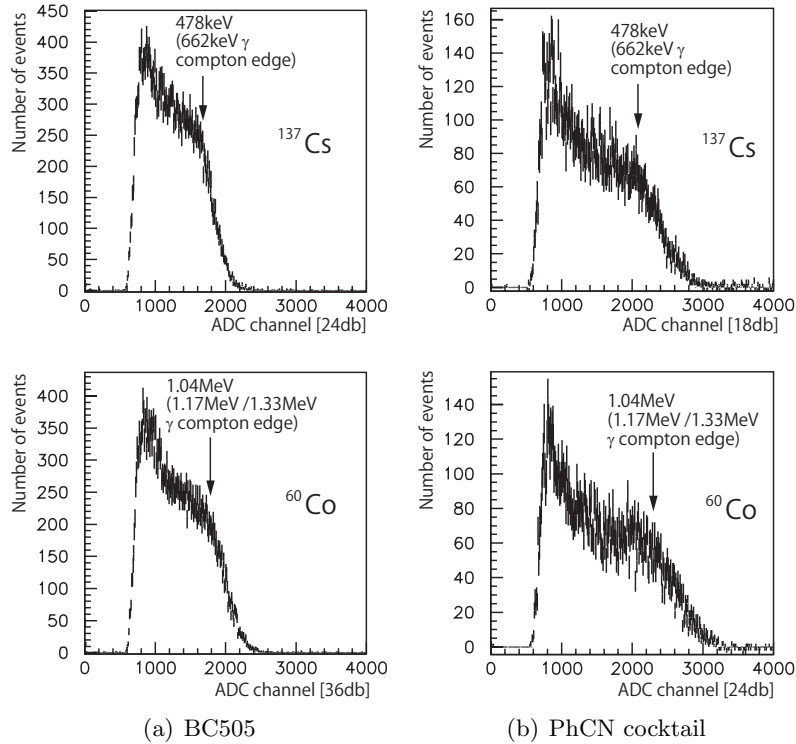
PhCN has larger scintillation light yield than PhCH<sub>2</sub>OH, however, the wavelength of luminescence did not match the absorption of InQ<sub>3</sub> as shown in Fig.4. In order to transfer the energy to the photomultiplier, we dissolved 2,5-Diphenyloxazole(PPO), which has absorption maximum at 309.7nm and fluorescence maximum at 368.0nm, as a secondary scintillator in PhCN. In addition, 1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP) or 1,4-Bis(2-methylstyryl)benzene (Bis-MSB) would help the energy transfer due to more overlap with the absorption of InQ<sub>3</sub> complex. Figure 4 shows photon absorption and emission of PPO, POPOP and InQ<sub>3</sub> complex, respectively.

The liquid scintillator was put into 20mL quartz vials. Two 2-inch photomultiplier (Hamamatsu H6410) are connected to the vial through acrylic light guide. The signal was attenuated because of wide dynamic range for observed scintillation light yield. The coincidence method using two signals from those photomultiplier was used for avoiding backgrounds. The setup for data acquisition is shown in Fig.5.

Figure 6 shows the energy spectrum of electrons emitted by induced  $\gamma$ 's for both standard scintillator BC505 and PhCN with PPO 100mg and POPOP 10mg (PhCN cocktail scintillator). Clear Compton edges of  $\gamma$ 's was observed for each sources. While two  $\gamma$ 's are emitted simultaneously from <sup>60</sup>Co source, those gamma-rays do not have same direction. Therefore,



**Figure 5.** Data acquisition for scintillation lights through the photomultiplier.



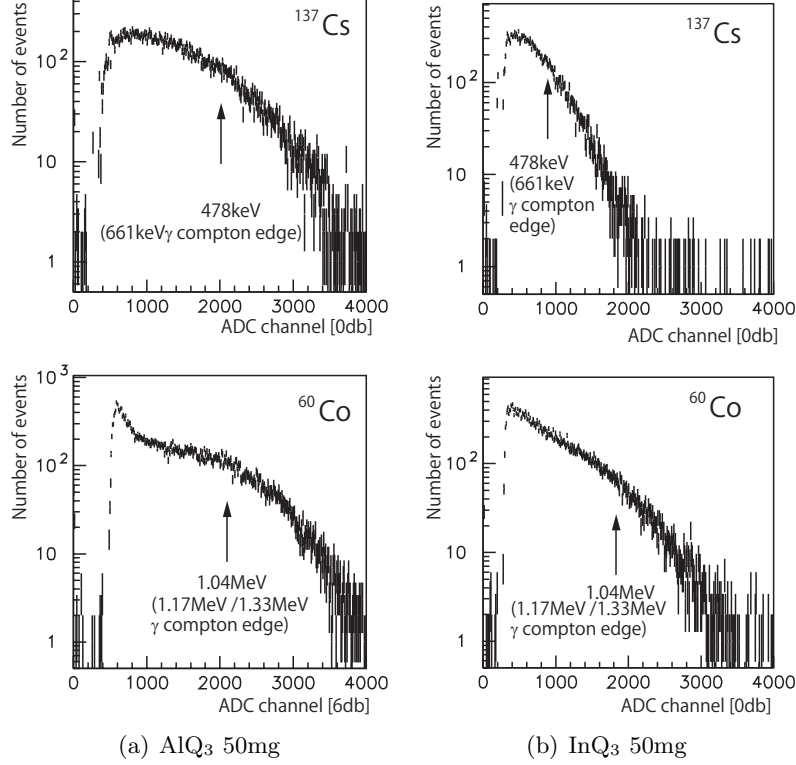
**Figure 6.** Photon spectrum of electrons emitted by  $\gamma$ 's interaction using  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  sources for both standard liquid scintillator BC505 and PhCN cocktail scintillator.

one of two  $\gamma$ 's could be entered into the liquid scintillator. Since those energy should be too close to distinguish each  $\gamma$ 's due to poor energy resolution, we observed as single  $\gamma$ 's with averaged energies.

The PhCN cocktail scintillator had 63% of light yield relative to that of BC505. Here, the wavelength of emitted lights for both scintillators are almost same ( $\sim 420\text{nm}$ ). The quantum efficiency of Hamamatsu H6410 photomultiplier is 25% at this wavelength.

We measured the energy spectrum of induced  $\gamma$ 's from sources for 50mg of  $\text{AlQ}_3$  and  $\text{InQ}_3$  dissolved in PhCN cocktail scintillator as shown in Fig.7. The scintillation light yield of  $\text{InQ}_3$

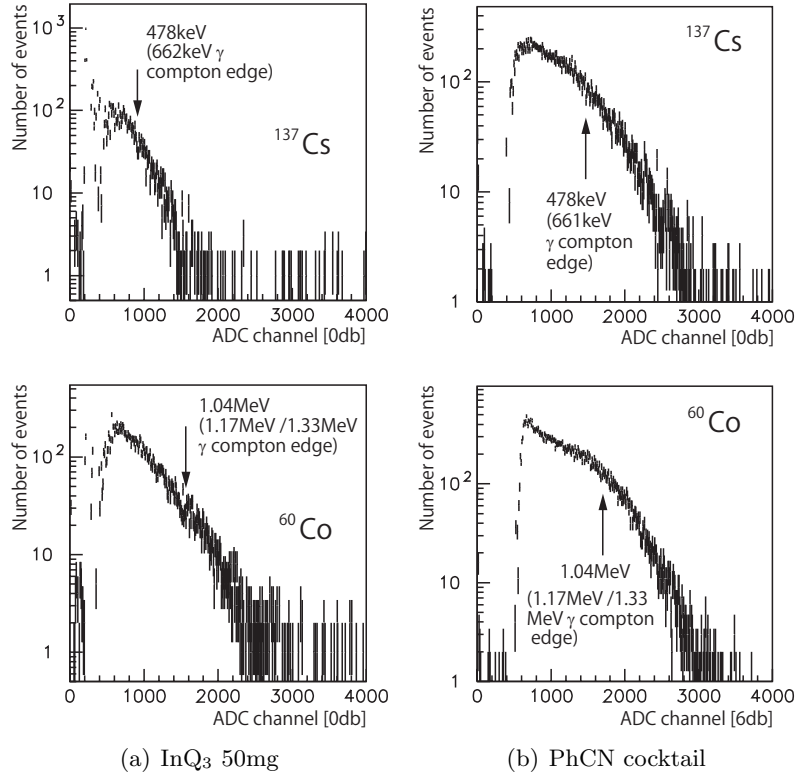
looks smaller than that of  $\text{AlQ}_3$ . This should be caused by the difference of quantum yield of those complexes.



**Figure 7.** Observed energy spectrum of (a)  $\text{AlQ}_3$  50mg (b)  $\text{InQ}_3$  50mg dissolved in PhCN cocktail scintillator for  $\gamma$ 's from  $^{136}\text{Cs}$  and  $^{60}\text{Co}$ .

The quantum yield of  $\gamma$ 's irradiation could be evaluated by difference of scintillation photon yield between the PhCN cocktail scintillator and PhCN cocktail scintillator containing the complex. Because of different wavelength of the scintillation light, we have to correct the light yield with the quantum efficiency of H6410 photomultiplier. The emission wavelength of  $\text{AlQ}_3$  and  $\text{InQ}_3$  complex in PhCN is 530nm and 560nm, respectively. The quantum efficiency is 12.6% and 9.3%, respectively. The quantum yield of  $\text{AlQ}_3$  and  $\text{InQ}_3$  dissolved in PhCN cocktail scintillator, therefore, are obtained by 24.7% and 15.6%, respectively. These values are larger than that obtained by the photo luminescence as described in Section 3.

According to the Fig.4, the photon emission from POPOP has slightly longer tail than the absorption distribution of  $\text{InQ}_3$  complex. This means that the residual photon could be contaminated in the emission spectrum of  $\text{InQ}_3$  complex. In order to evaluate the amount of POPOP residual light, we measured the emission of scintillation light from  $\text{InQ}_3$  dissolved in PhCN cocktail scintillator via the sharp cut filter (FujiFuilm : SC-48). This film has transparency of 92% above 530nm and quickly decrease the efficiency below 530nm (50% at 482nm and 10% at 470nm). The observed energy spectrum of  $\text{InQ}_3$  complex dissolved in PhCN cocktail scintillator was shown in Fig.8 (a). The photon light yield was lost about 34%. On the other hands, 23% of the light yield of PhCN cocktail scintillator still remained via SC-48 filter as shown in Fig.8 (b). Therefore the difference of quantum yield between the photo luminescence and the  $\gamma$ 's irradiation could be explained by the residual light from POPOP, and the amount of those lights was assumed to be  $\leq 10\%$  of original PhCN cocktail scintillation yield, at maximum.



**Figure 8.** Observed spectrum of  $\gamma$ 's via SC-48 filter. (a) The light yield was lost about 34% in case of PhCN cocktail scintillator containing  $\text{InQ}_3$  complex. On the other hands, (b) 23% of the light yield of PhCN cocktail scintillator still remained via SC-48 filter.

## 6. Conclusion

An organic liquid scintillator containing  $\text{InQ}_3$  complex was developed using the photo luminescence of complex. The  $\text{InQ}_3$  complex dissolved in PhCN has maximum photo luminescence at 560nm and the attenuation length was about 66cm at 0.5wt% dissolution. The PhCN cocktail scintillator containing  $\text{InQ}_3$  has actually luminescence for  $\gamma$ 's irradiation. The quantum yield were 5% and 15% for the photo luminescence and  $\gamma$ 's irradiation, respectively. The difference could be explained by the residual light from the fluorescence of POPOP. The developed liquid scintillator containing  $\text{InQ}_3$  complex was successfully worked to detect  $\gamma$ 's. However, for the actual solar neutrino detector, it is still necessary more light yield to get better energy resolution, and more solubility to order of 5wt%. In order to achieve former point, we will produce new  $\text{InQ}_3$  complex with the substitution group, tris (5-aryl-8quinolinolate) metal complex. The  $\text{AlQ}_3$  complex with **1a** substitution group improved the quantum yield to be 0.533, and the maximum emission wavelength was shifted to 490nm [18]. Later means that better quantum efficiency of the photomultiplier will help to get more scintillation light yield.

The another metal such as zirconium (Zr) instead of aluminum or indium could be formed by 8-quinolinolate complex. We have already succeed to synthesize  $\text{ZrQ}_4$  complex, recognized same solubility for PhCN as  $\text{InQ}_3$ , and measured the photo luminescence. The  $^{96}\text{Zr}$  is one of the target nuclei for the neutrino-less double beta decay ( $0\nu\beta\beta$ ) with higher Q-value. Recently SNO+ group has decided to use zirconium instead of neodymium (Nd). Therefore, new technique to dissolved zirconium in liquid scintillator will be very important for realizing ton-scale  $0\nu\beta\beta$  decay experiments.



## Acknowledgments

This work was supported by KAKENHI Grant-in-Aid Scientific Research (C) 22540303 of Japanese Society for the Promotion of Science. We would like to thank Prof. Muramatsu for a measurement of fluorescence using HORIBA FluoroMax-4 spectrofluorometer, and Prof. Ikeyama for a measurement of absorbance using HITACHI U-3000 spectrophotometer.

## References

- [1] Y. Fukuda *et.al*, Phys. Rev. Lett. **81** (1998) 1562.
- [2] K2K collaboration, Phys. Rev. Lett. **94** (2005) 081802.
- [3] S. Fukuda *et.al*, Phys.Rev.Lett. **86** (2001) 5651.
- [4] SNO Collaboration Phys.Rev.Lett. **87** (2001) 071301.
- [5] KamLAND collaboration, Phys.Rev.Lett. **90** (2003) 021802.
- [6] Borexino Collaboration, Phys. Lett. B 658 (2008) 101.
- [7] R.S. Raghavan Phys. Rev. Lett. **37** (1976) 259.
- [8] R.S. Raghavan hep-ex/0106054.
- [9] Y. Suzuki, Y. Fukuda, Y. Nagashima, and H. Kan Nucl. Instr. and Meth. A275 (1989) 142.
- [10] Y. Suzuki, K. Inoue, Y. Nagashima and S. Hashimoto Nucl. Instr. and Meth. A293 (1990) 615.
- [11] Y. Fukuda *et. al*, Nulc. Instr. and Meth.A (2010), doi:10.1016/j.nima.2010.03.036
- [12] R.S. Raghavan Phys. Rev. Lett. **78** (1997) 3618.
- [13] D. Motta *et. al*, Nucl. Instr. and Meth. A547 (2005) 368.
- [14] R.S, Raghavan talked at Neutrino2010 conference.
- [15] V.A. Montes, R. Pohl, J. Shinar, P. Anzenbacher Jr. A European Journal **12** (2006) 4523
- [16] E. Lippert, W. Nagele, L. Seibold-Blankenstein, U. Staiger and W. Voss Physikalische Chemie, Stuttgart (1959)
- [17] J. Wang, K.D. Oyler and S. Bernhard Inorg. Chem. **46** (2007) 5700.
- [18] R. Pohl, V.A. Montes, J. Shinar and P. Anzenbacher Jr. J. Org. Chem. **69** (2004) 1723.