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# ジルコニウム96を用いたニュートリノを放出しない2重ベータ崩壊事象の探索

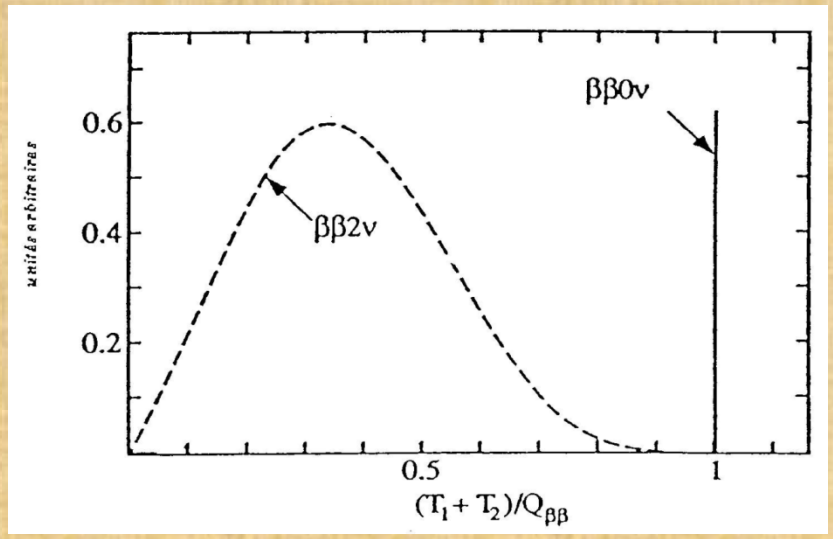
新学術領域「先端加速器LHCが切り拓くテラスケールの素粒子物理学」
研究会
2013年5月24日

宮城教育大学　教育学部
福田　善之

# Neutrinoless double beta decay

$\beta\beta$ emitters with $Q_{\beta\beta}$ >2 Mev

| Transition | $Q_{\beta\beta}$ (keV) | Abundance (%) ($^{232}Th = 100$) |
|---|---|---|
| $^{110}Pd \rightarrow ^{110}Cd$ | 2013 | 12 |
| $^{76}Ge \rightarrow ^{76}Se$ | 2040 | 8 |
| $^{124}Sn \rightarrow ^{124}Te$ | 2288 | 6 |
| $^{136}Xe \rightarrow ^{136}Ba$ | 2479 | 9 |
| $^{130}Te \rightarrow ^{130}Xe$ | 2533 | 34 |
| $^{116}Cd \rightarrow ^{116}Sn$ | 2802 | 7 |
| $^{82}Se \rightarrow ^{82}Kr$ | 2995 | 9 |
| $^{100}Mo \rightarrow ^{100}Ru$ | 3034 | 10 |
| $^{96}Zr \rightarrow ^{96}Mo$ | 3350 | 3 |
| $^{150}Nd \rightarrow ^{150}Sm$ | 3667 | 6 |
| $^{48}Ca \rightarrow ^{48}Ti$ | 4271 | 0.2 |



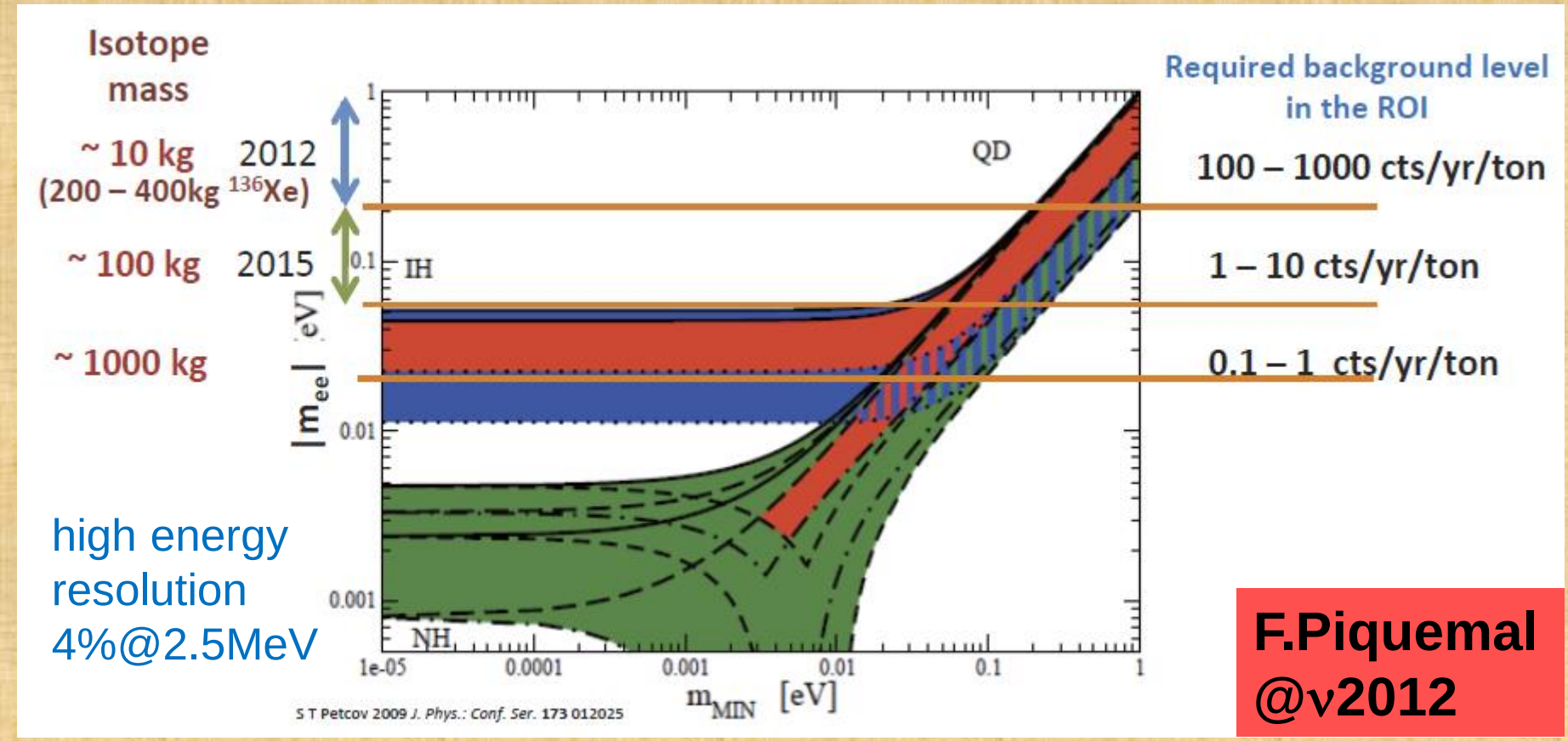

$$[T_{1/2}^{0\nu}(0^+ \rightarrow 0^+)]^{-1} = G_{0\nu}(E_0,Z)|M_{0\nu}|^2\langle m_\nu\rangle^2$$

$T_{1/2} \sim a(Mt/\Delta EB)$ a: abundance M: mass

t: meas.time $\Delta E$: energy res. B: BG rate

Requirement : Low BG, Large target mass, High energy resolution

# For future experiments

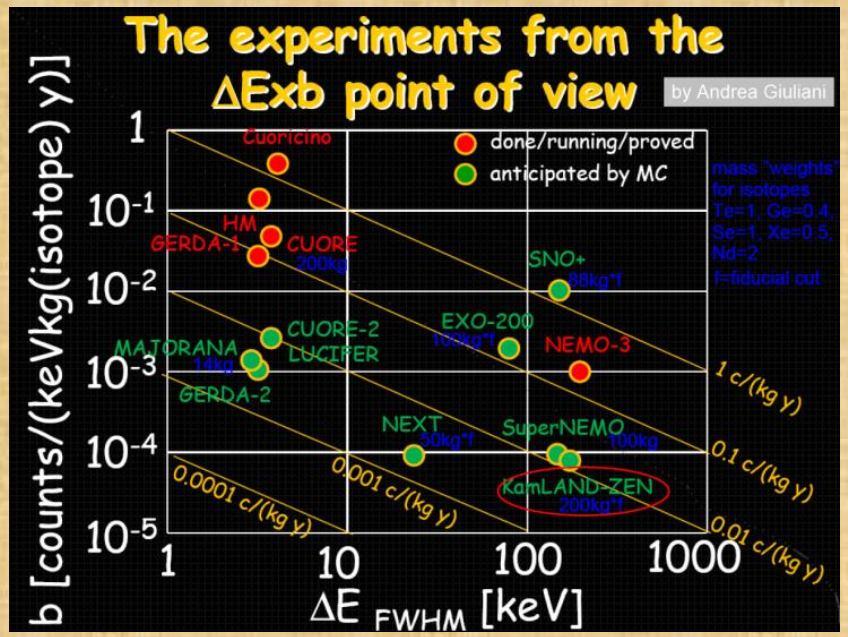



http://kds.kek.jp/getFile.py/access?contribId=37&sessionId=16&resId=2&materialId=slides&confId=9151

~tons of target will be needed for next generation detector

# Future experiments for Neutrinoless double beta decay

- Experimental requirement for BG rate and ΔE

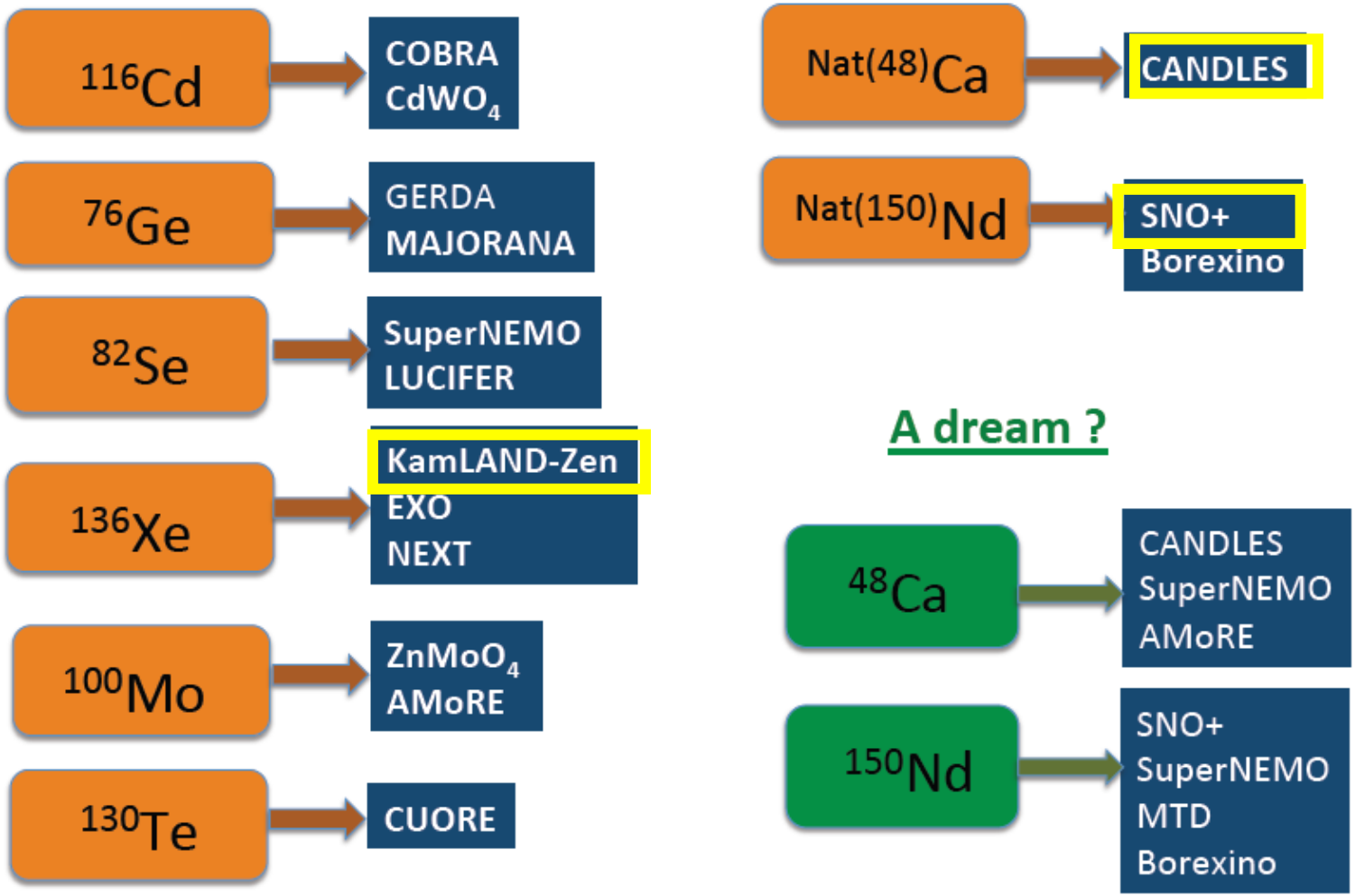



- To achive $m_\nu$ < 100meV
  - high energy resolution 4%@2.5MeV
  - low background rate 0.01count $kg^{-1}$ $y^{-1}$
  - ton scale of target

Liq. Scintillator is easy to scale up target volume

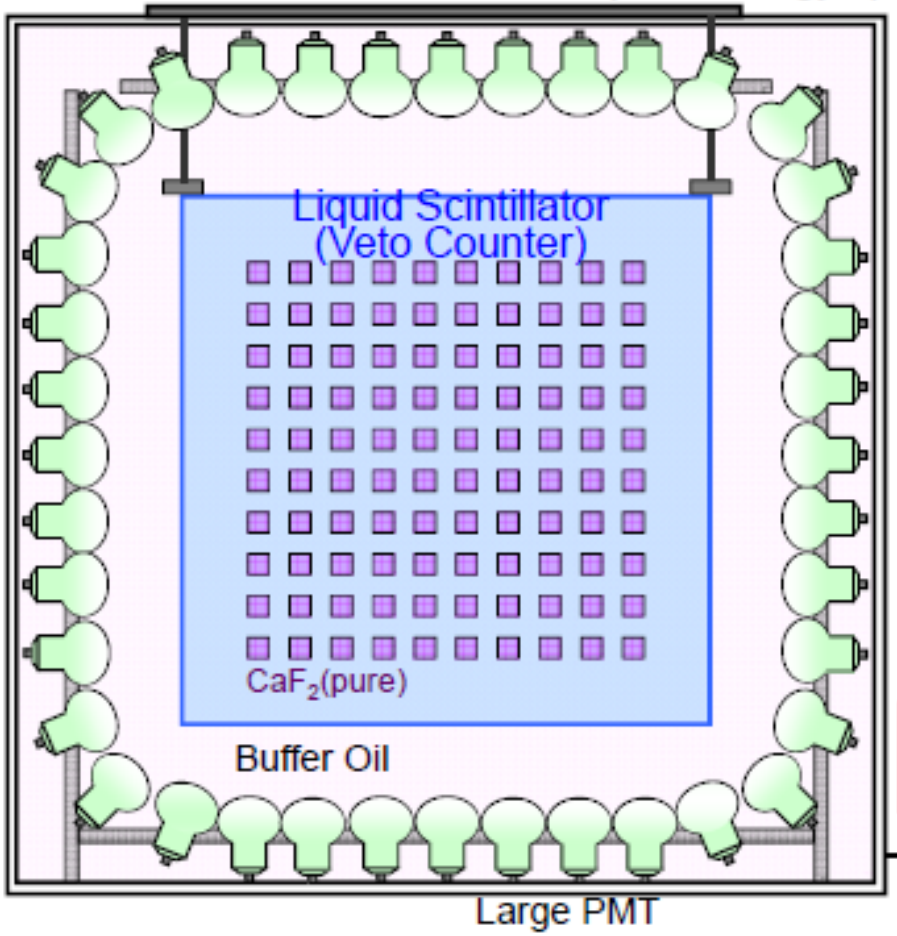
# Studied isotopes

Piquemal@ν2012



# Design Concepts of CANDLES

**CANDLES**
CAlcium fluoride for studies of Neutrino and Dark matrters
by Low Energy Spectrometer




- $CaF_2$(pure) scintillator
  - Long attenuation length (>10m@350nm)
  - Double beta decay source
    $^{48}Ca$ ($Q_{bb}$=4.27MeV)
- Liquid scintillator
  - 4 π Active Shield
- Large photomultiplier tube
  - Signals from both scintillators are detected simultaneously

⇩

- Active Shielding Technique

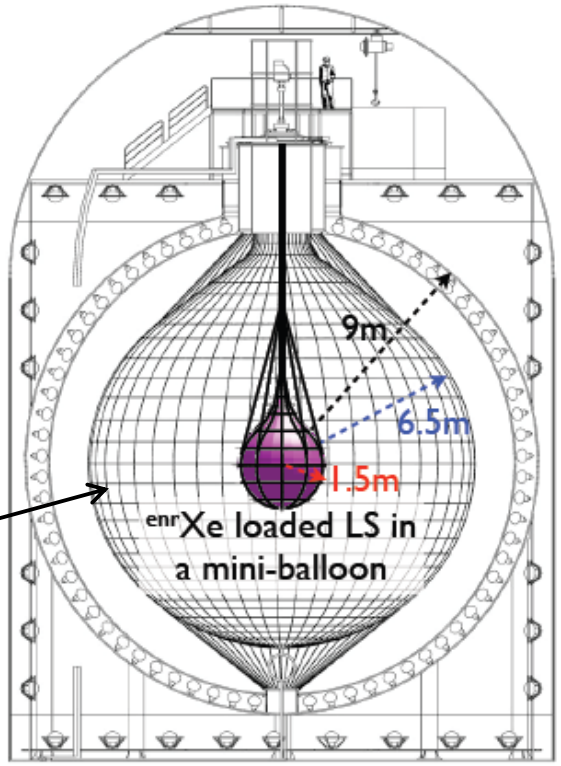
Different time constants
$CaF_2$(pure) : ~1μsec
Liquid scintillator : a few 10 nsec

UMEHARA Saori, 16th Nov. 2011, DBD11

# KamLAND-Zen

K.Inoue@ν2012

Zero Neutrino
double beta decay search




**Pseudo-cumene 20%**
**+**
**Dodecane 80%**
**+**
**PPO 0.15wt%**

idea to load Xe into LS is from Raju PRL72,1411(1994)

~320kg 90% enriched $^{136}$Xe installed so far
total 600+ kg in the mine
production reaches 700kg in this year

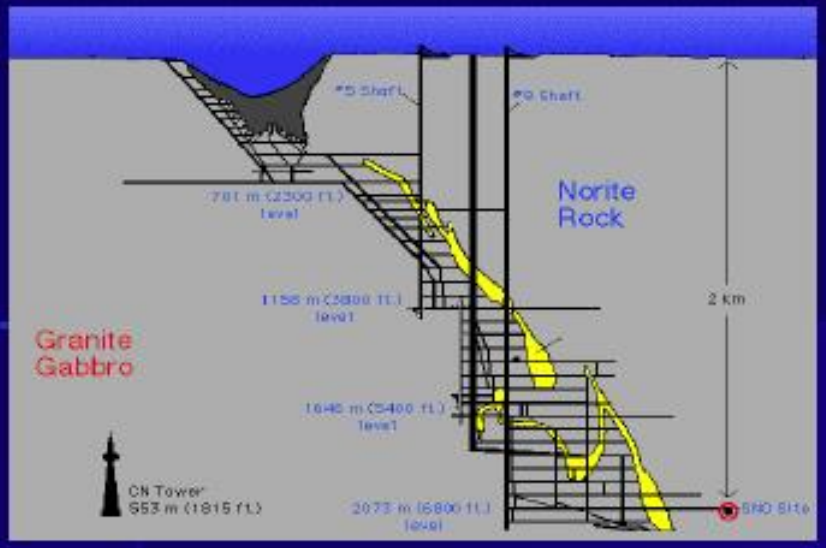
Good features of us

- running detector
  → relatively low cost and quick start
- huge and clean (1200m$^3$, U: 3.5x10$^{-18}$ g/g, Th: 5.2x10$^{-17}$)
  → negligible external gamma
  (Xe and mini-balloon need to be clean)
- Xe-LS can be purified, mini-balloon replaceable if necessary, with relatively low cost
  → highly scalable (up to several tons of Xe)
- No escape or invisible energy from β, γ
  → BG identification relatively easy
- anti-neutrino observation continues
  → geo-neutrino w/o japanese reactors

Disadvantages toward an ultimate sensitivity

× relatively poor energy resolution
tolerable thanks to slow 2ν2β and low BG

× no β/γ discrimination so far
× delicate balloon film
× limited LS composition (for density matching)




SNO+

~~1000 tonnes $D_2O$~~ → **780 tonnes liquid Scintillator (LAB)**

12 m diameter Acrylic Vessel

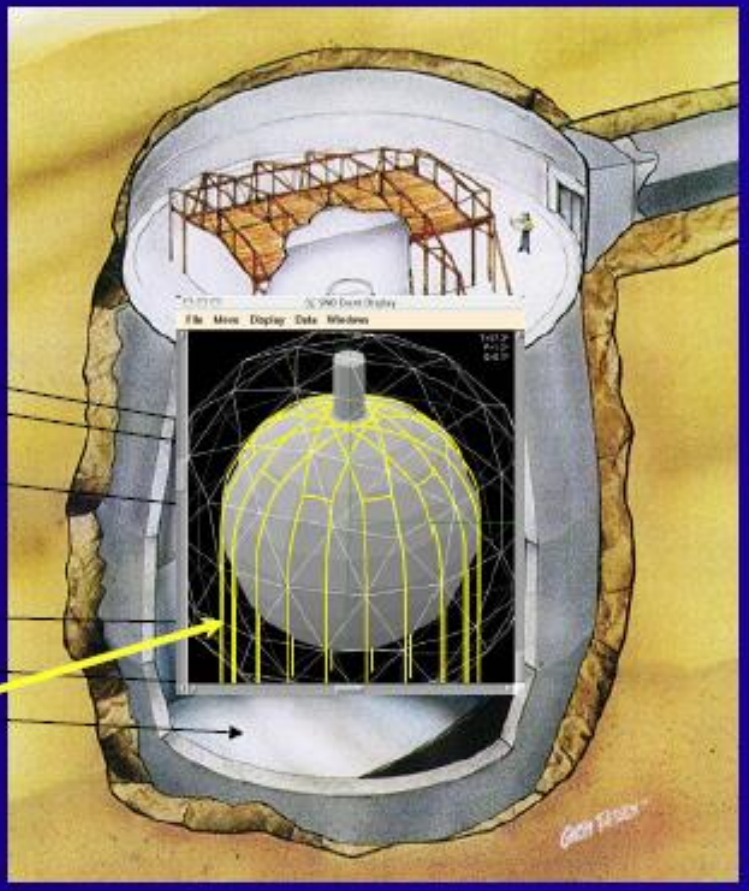
18 m diameter support structure; 9500 PMTs

(~60% photocathode coverage)

1700 tonnes inner shielding $H_2O$
5300 tonnes outer shielding $H_2O$
Urylon liner radon seal

**hold down rope net**

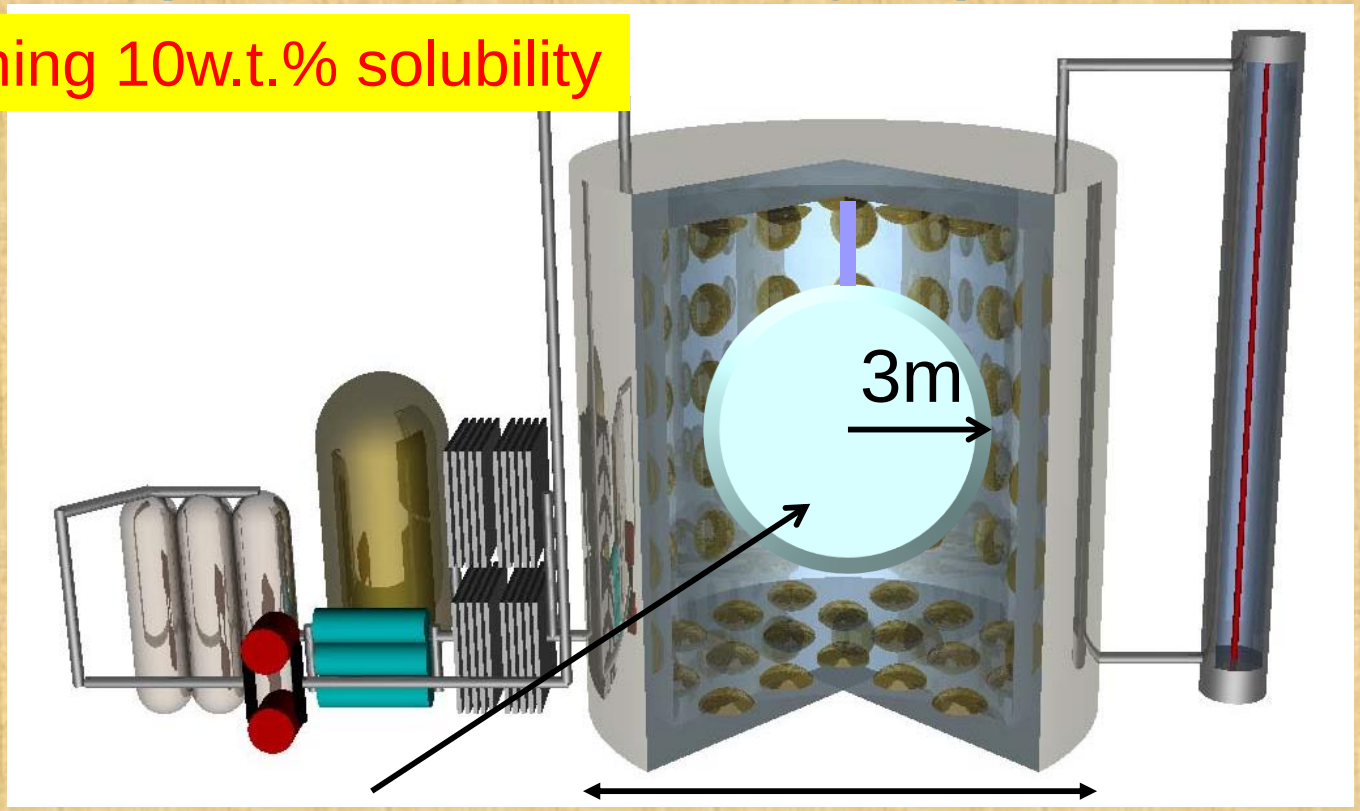
depth: 2092 m (~6010 m.w.e.) ~70 muons/day



# Detector design for ZICOS experiment

- **Zirconium Complex in Organic liquid Scintillator (ZICOS) for double beta decay experiment**

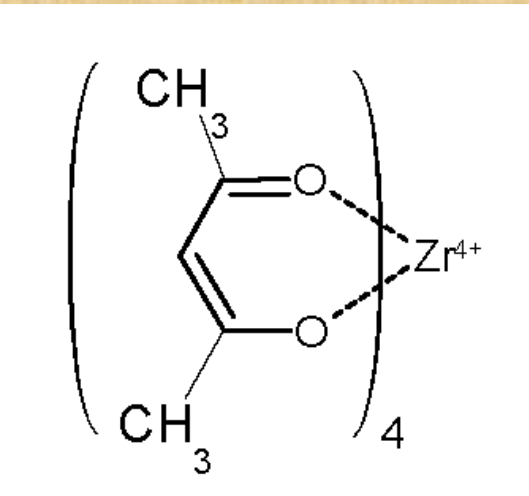
Assuming 10w.t.% solubility




Zirconium loaded 100ton LS

# Zirconium β-diketon complex

- Zirconium(IV) acetylacetonate ($Zr(acac)_4$)

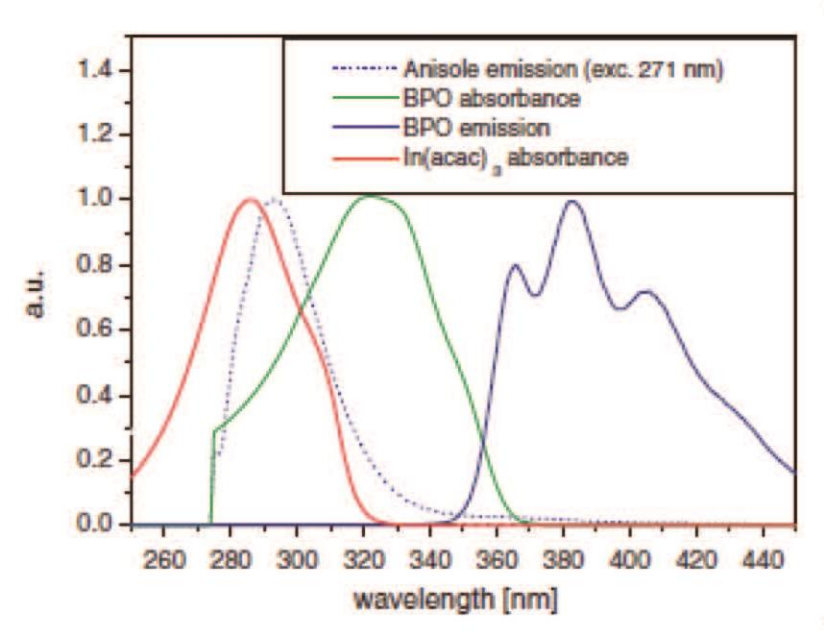



Molecular weight : 487.66

- Advantage
  - good solubility (over 10w.t.%) in Anisole (PhOMe)
  - Stable and cheep
  - Commercial product
- Disadvantage
  - Low scintillation light yield

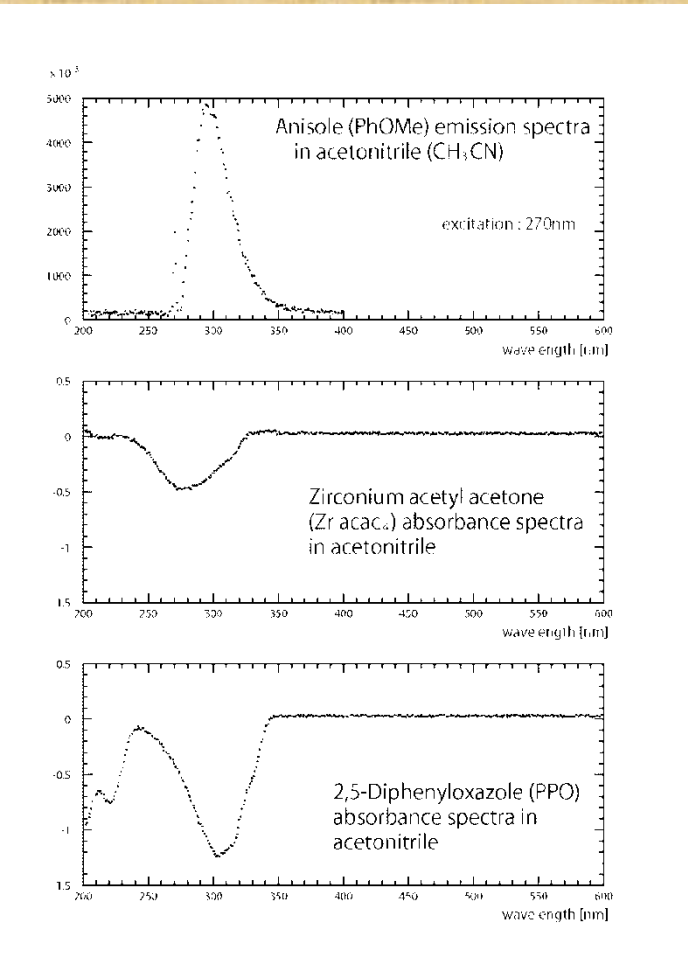
# What's problem

- Absorption spectra of $In(acac)_3$ (indium acetyl acetone) was overlapped with the emission spectra from Anisole（Chem. Phys. Lett., 435(2007), 252)




Same overlap between the emission and the absorption could be occurred even if different metal (Zr) was used.

# Observed absorption spectra of $Zr(acac)_4$



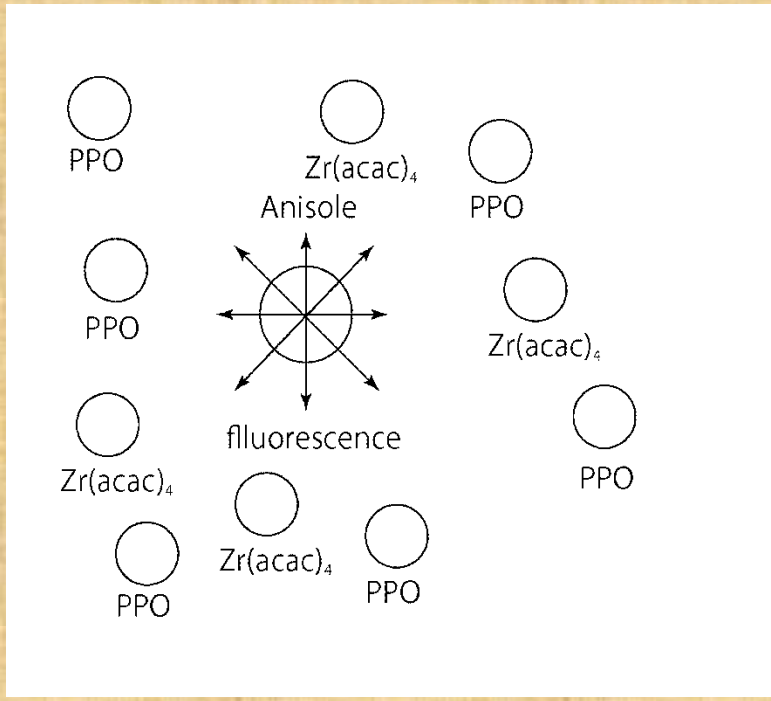

- Emission peak of anisole was observed around 295nm.
- Absorption peak of $Zr(acac)_4$ was observed around 270nm.

Scintillation light from anisole (PhOMe) might be absorbed by $Zr(acac)_4$

# Simple expectation for quenching

- Assuming to same cross section for light

$$\text{Light yield} = L_0 \times \frac{\sigma_1 N_{ppo}}{\sigma_1 N_{ppo} + \sigma_2 N_{Zr}}$$

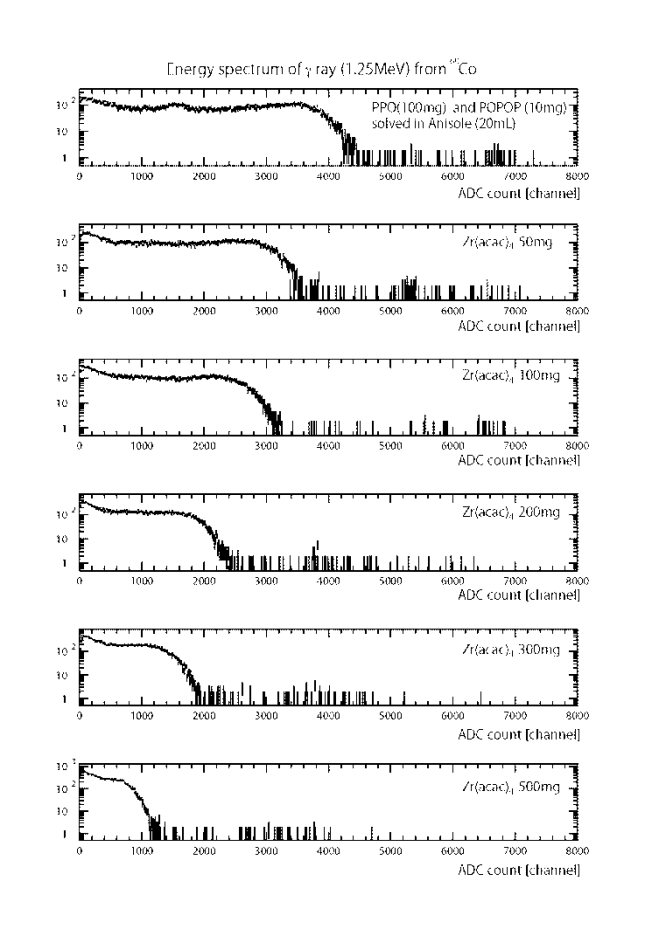



$L_0$ : Light yield of anisole + PPO + POPOP

$N_{ppo}$ , $N_{Zr}$ : Number of molecular for PPO and $Zr(acac)_4$

$\sigma_1, \sigma_2$ : cross section of absorbance for PPO and $Zr(acac)_4$

# Scintillation Light yield ($^{60}$Co) with respect to concentration of $Zr(acac)_4$

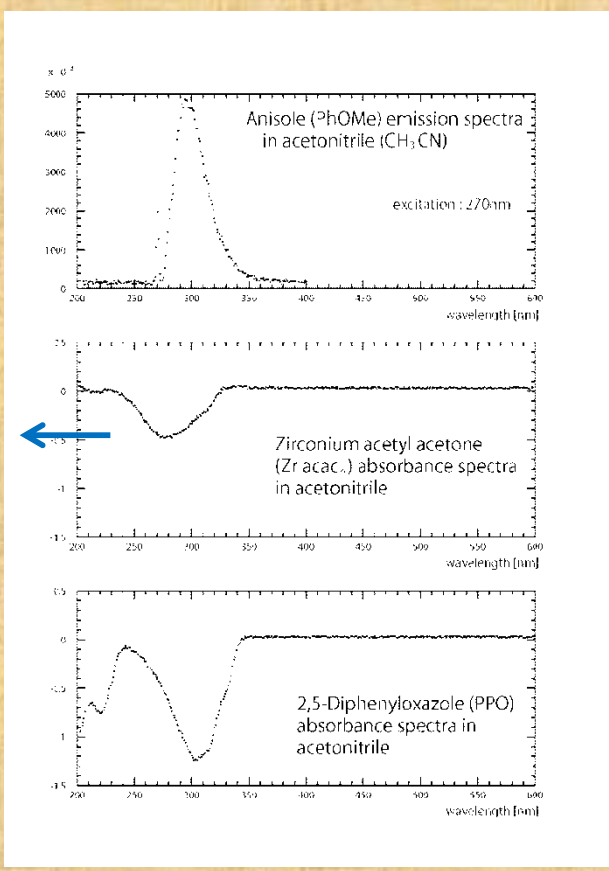



| concentration of $Zr(acac)_4$ | Observed channel | Expected channel |
|---|---|---|
| 0 mg | 3850 | 3850 |
| 50mg ($1.03X10^{-4}$) | 3175 | 3138 |
| 100mg ($2.05X10^{-4}$) | 2800 | 2651 |
| 200mg ($4.10X10^{-4}$) | 2000 | 2018 |
| 300mg ($6.15X10^{-4}$) | 1600 | 1613 |
| 500mg ($1.03X10^{-3}$) | 900 | 1178 |

PPO 100mg : $4.52X10^{-4}$ mol

# Improvement of scintillation light yield

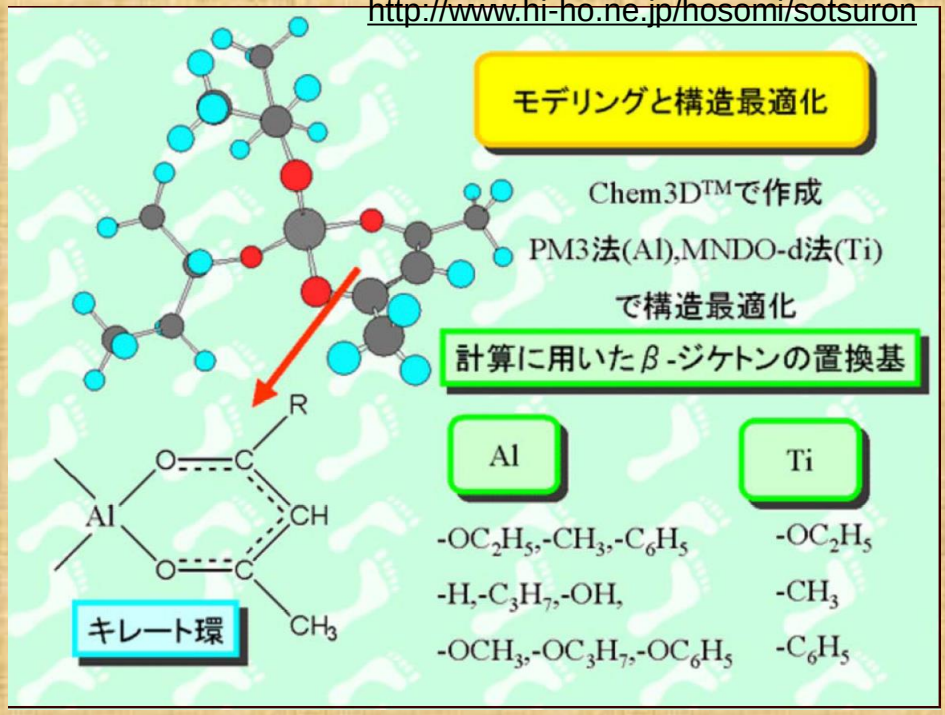
- Move absorption peak to shorter wavelength




- How to do it?

substituent groups

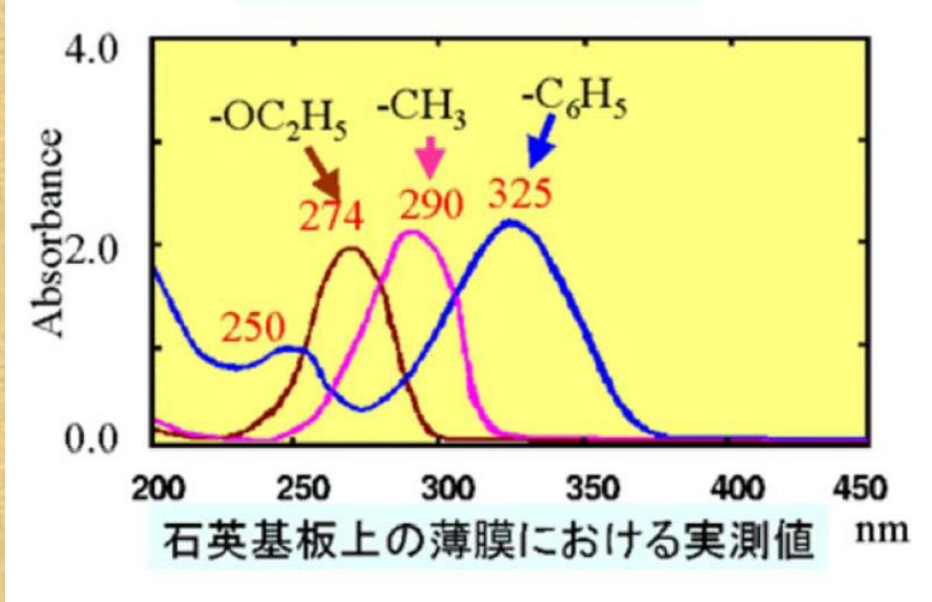
http://www.hi-ho.ne.jp/hosomi/sotsuron



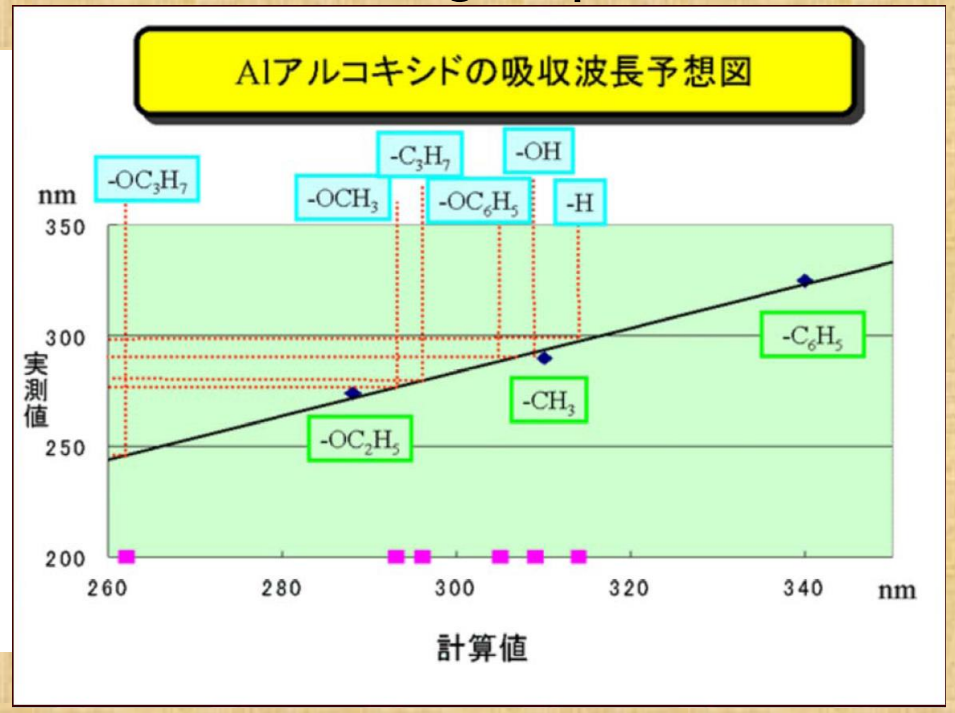

Courtesy of Prof. Yoshiyuki Kowada (Hyogo University of Education)

# Absorbance peak for several substituent groups

- Measured absorbance peaks for several substituent groups

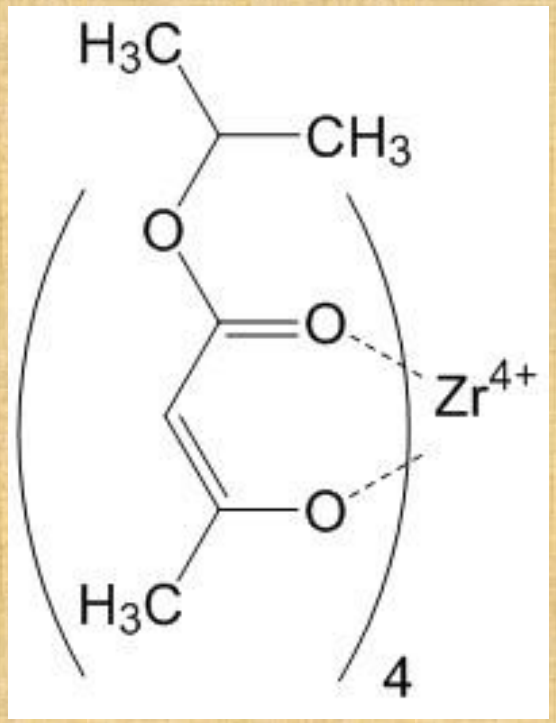



- Expected absorbance peak for several substituent groups

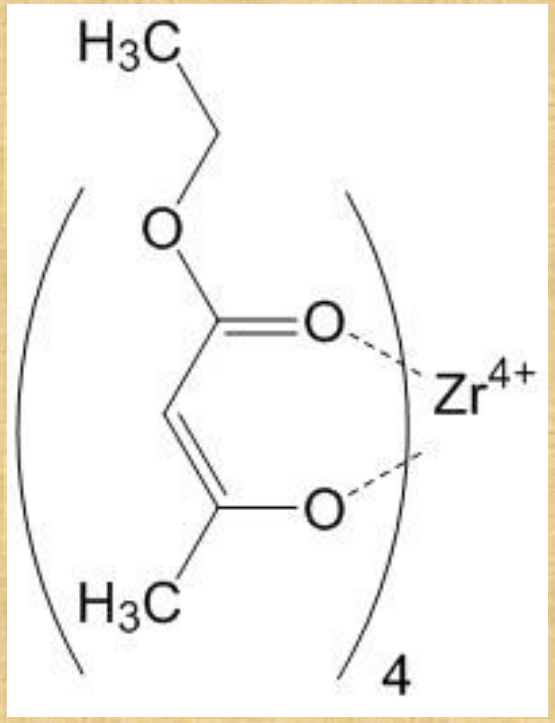


# Zr β-diketon complex introducing substituent groups (β-keto ester complex)

**Zr(CH3COCHCOOCH(CH3))$_4$ = Zr(iprac)$_4$**
**mw : 711.92**



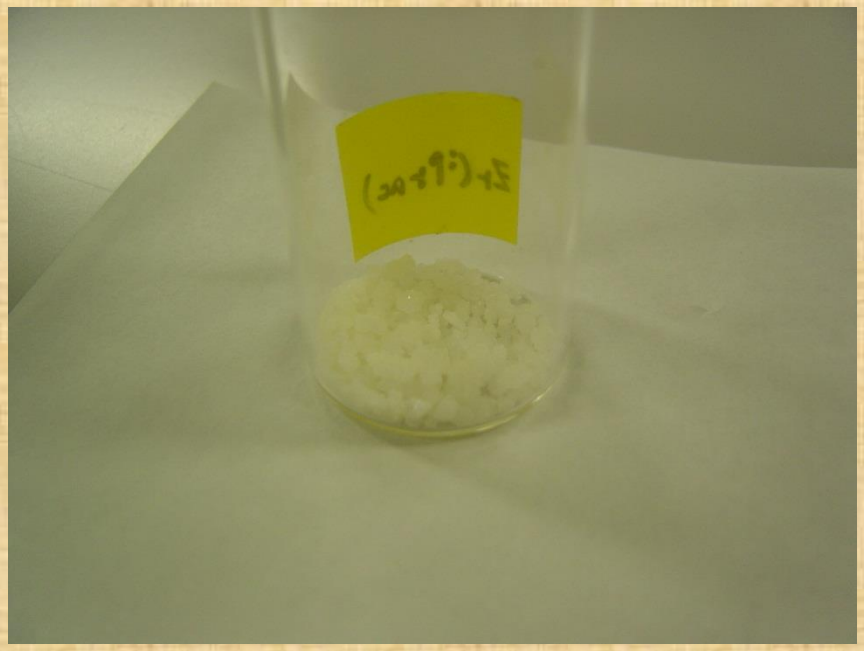

**Zr(CH3CCOCHCOOCH3)$_4$ = Zr(etac)$_4$**
**mw : 665.81**



# Zr β-keto ester complex

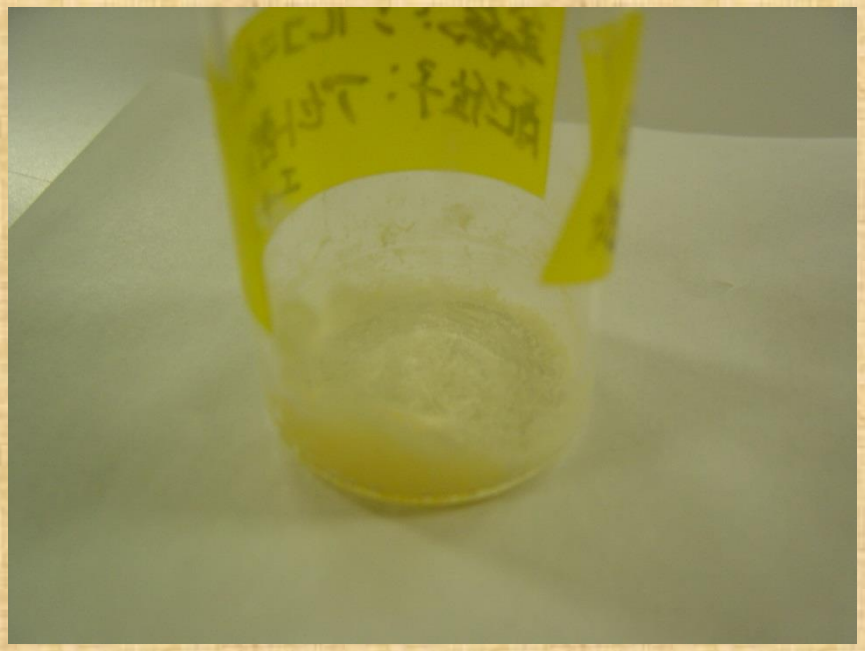
**$Zr(iprac)_4+(iprac)_{1.5}$**

**state: powder**



**$Zr(etac)_4$**

**state : dry solid**

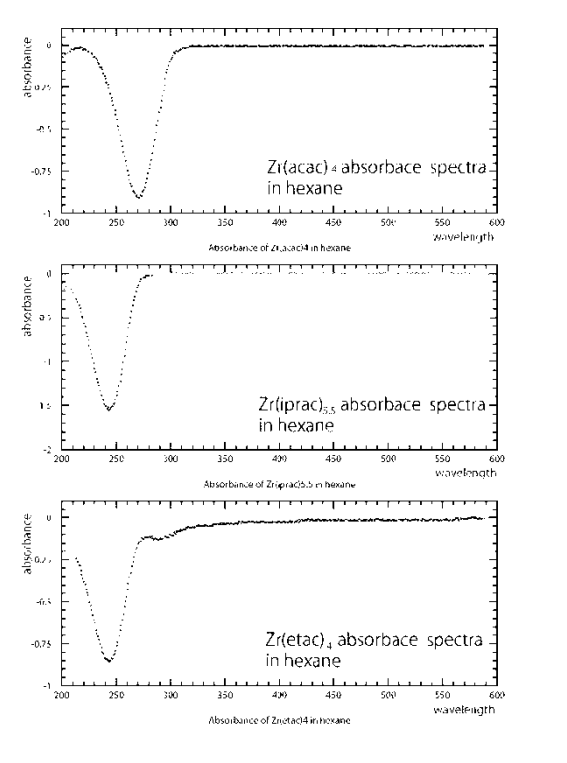


Synthesized by Prof. Takahiro Gunji (Tokyo University of Science)

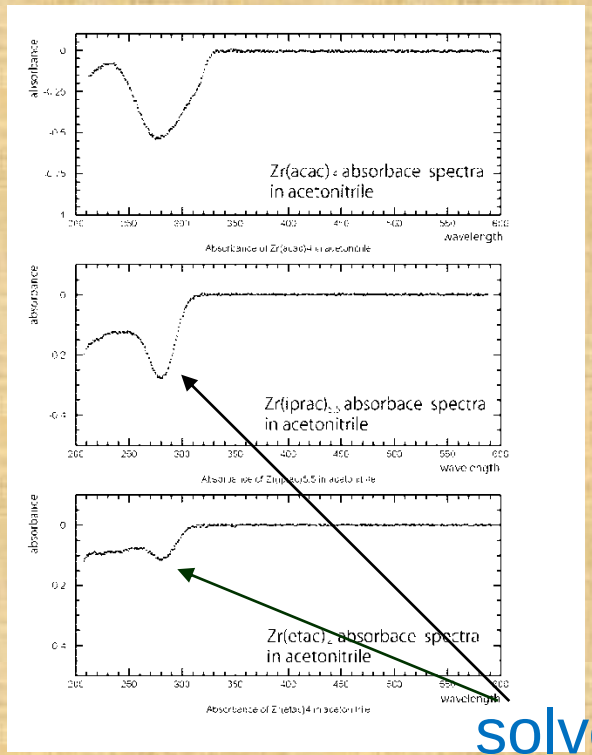
Solubility > 10 w.t.% for anisole

# Absorbance spectra (Solvent effect)

**Solution : Hexane**




**Solution : acetonitrile**

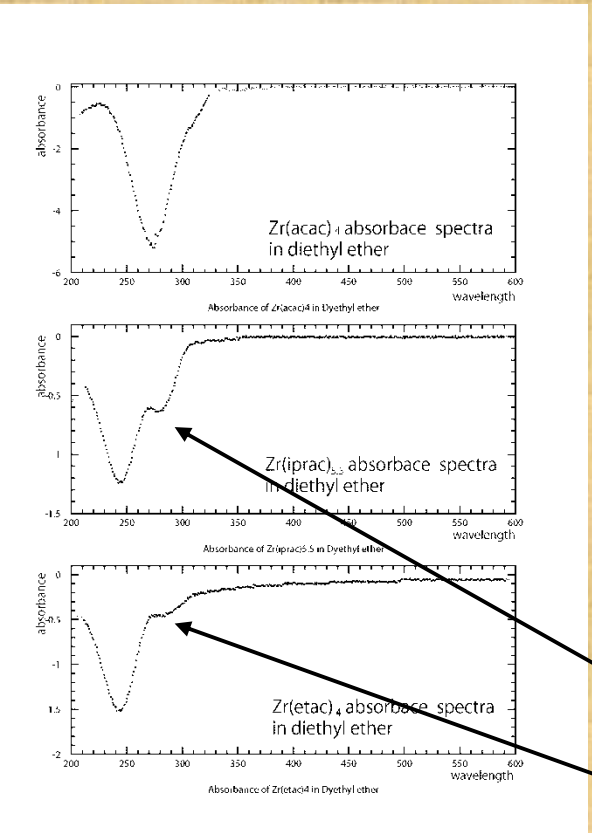



solvent effect

Absorption peak moves to shorter wavelength, however it depends on the polarity of solvent.

# Absorbance in liquid scintillator

**Solution : Diethyl Ether**

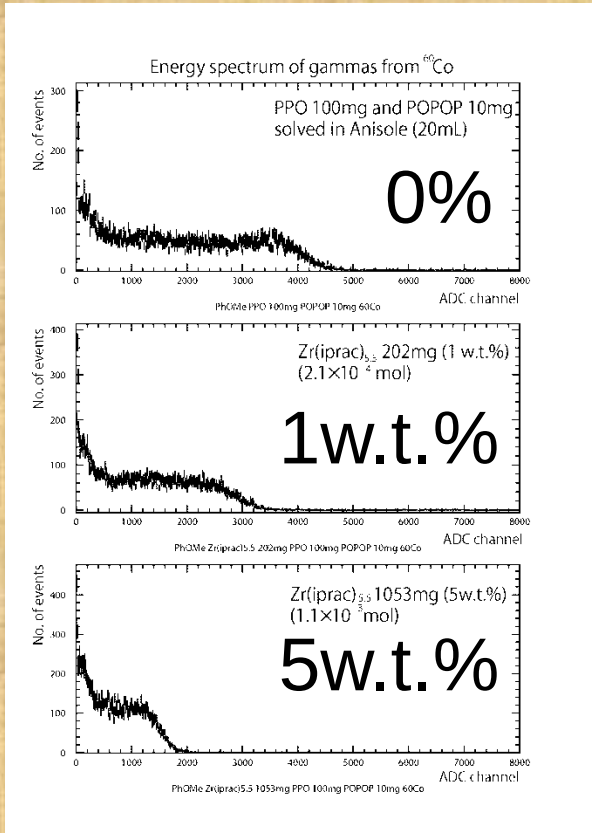



- Solvent effect could depend on the polarity (dielectric const.)
  - Acetonitrile : 37.5
  - Hexane : 1.89
  - Anisole : 4.3
- Need solution which has same polarity as anisole
  - Diethyl ether : 4.33

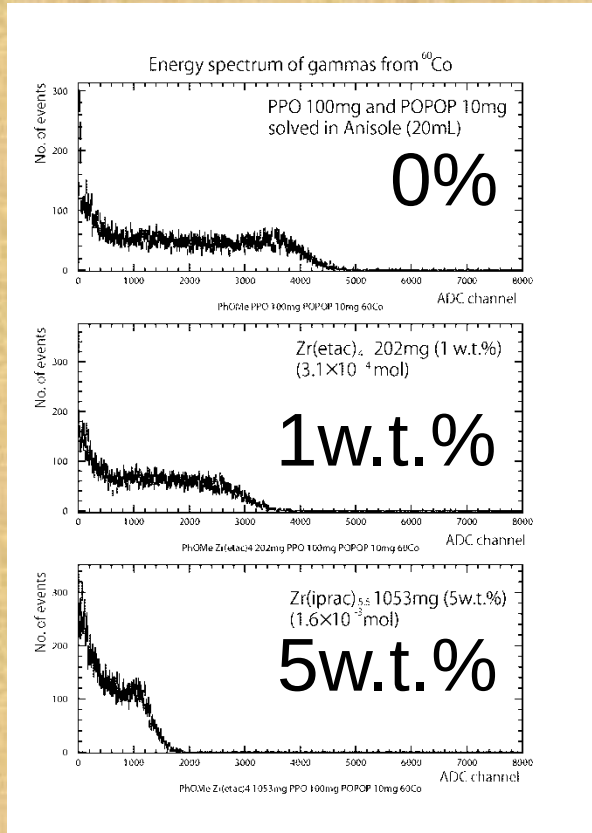
Still solvent effect remains around 270nm

# Light yield of Zr β-keto ester scintillator

## $Zr(iprac)_{5.5}$ in anisole




## $Zr(etac)_4$ in anisole




Same quenching as $Zr(acac)_4$ was observed

# Requirement of scintillator solvent

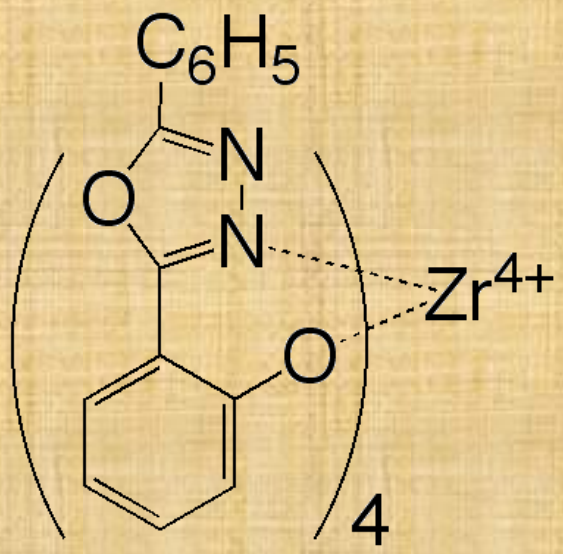
- Low polarity (low dielectric constant)
  - No absorption ~270nm
- Aromatic compounds
  - luminescence >270nm
- Keep high solubility > ~10%
- Keep luminescence from solvent

Possible solvent:
Toluene / Xylene

| Solvent | mp | bp | $D_4^{20}$ | $n_D^{20}$ | ε | $R_D$ | μ |
|---|---|---|---|---|---|---|---|
| Acetic acid | 17 | 118 | 1.049 | 1.3716 | 6.15 | 12.9 | 1.68 |
| Acetone | -95 | 56 | 0.788 | 1.3587 | 20.7 | 16.2 | 2.85 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Anisole | -3 | 154 | 0.994 | 1.517 | 4.33 | 33 | 1.38 |
| Benzene | 5 | 80 | 0.879 | 1.5011 | 2.27 | 26.2 | 0 |
| Bromobenzene | -31 | 156 | 1.495 | 1.558 | 5.17 | 33.7 | 1.55 |
| Carbon disulfide | -112 | 46 | 1.274 | 1.6295 | 2.6 | 21.3 | 0 |
| Carbon tetrachloride | -23 | 77 | 1.594 | 1.4601 | 2.24 | 25.8 | 0 |
| Chlorobenzene | -46 | 132 | 1.106 | 1.5248 | 5.62 | 31.2 | 1.54 |
| Chloroform | -64 | 61 | 1.489 | 1.4458 | 4.81 | 21 | 1.15 |
| Cyclohexane | 6 | 81 | 0.778 | 1.4262 | 2.02 | 27.7 | 0 |
| Dibutyl ether | -98 | 142 | 0.769 | 1.3992 | 3.1 | 40.8 | 1.18 |
| *o* -Dichlorobenzene | -17 | 181 | 1.306 | 1.5514 | 9.93 | 35.9 | 2.27 |
| 1,2-Dichloroethane | -36 | 84 | 1.253 | 1.4448 | 10.36 | 21 | 1.86 |
| Dichloromethane | -95 | 40 | 1.326 | 1.4241 | 8.93 | 16 | 1.55 |
| Diethylamine | -50 | 56 | 0.707 | 1.3864 | 3.6 | 24.3 | 0.92 |
| Diethyl ether | -117 | 35 | 0.713 | 1.3524 | 4.33 | 22.1 | 1.3 |
| 1,2-Dimethoxyethane | -68 | 85 | 0.863 | 1.3796 | 7.2 | 24.1 | 1.71 |
| *N,N* -Dimethylacetamide | -20 | 166 | 0.937 | 1.4384 | 37.8 | 24.2 | 3.72 |
| *N,N* -Dimethylformamide | -60 | 152 | 0.945 | 1.4305 | 36.7 | 19.9 | 3.86 |
| Dimethyl sulfoxide | 19 | 189 | 1.096 | 1.4783 | 46.7 | 20.1 | 3.9 |
| 1,4-Dioxane | 12 | 101 | 1.034 | 1.4224 | 2.25 | 21.6 | 0.45 |
| Ethanol | -114 | 78 | 0.789 | 1.3614 | 24.5 | 12.8 | 1.69 |
| Ethyl acetate | -84 | 77 | 0.901 | 1.3724 | 6.02 | 22.3 | 1.88 |
| Ethyl benzoate | -35 | 213 | 1.05 | 1.5052 | 6.02 | 42.5 | 2 |
| Formamide | 3 | 211 | 1.133 | 1.4475 | 111 | 10.6 | 3.37 |
| Hexamethylphosphoramide | 7 | 235 | 1.027 | 1.4588 | 30 | 47.7 | 5.54 |
| Isopropyl alcohol | -90 | 82 | 0.786 | 1.3772 | 17.9 | 17.5 | 1.66 |
| Methanol | -98 | 65 | 0.791 | 1.3284 | 32.7 | 8.2 | 1.7 |
| 2-Methyl-2-propanol | 26 | 82 | 0.786 | 1.3877 | 10.9 | 22.2 | 1.66 |
| Nitrobenzene | 6 | 211 | 1.204 | 1.5562 | 34.82 | 32.7 | 4.02 |
| Nitromethane | -28 | 101 | 1.137 | 1.3817 | 35.87 | 12.5 | 3.54 |
| Pyridine | -42 | 115 | 0.983 | 1.5102 | 12.4 | 24.1 | 2.37 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Toluene | -95 | 111 | 0.867 | 1.4969 | 2.38 | 31.1 | 0.43 |
| Trichloroethylene | -86 | 87 | 1.465 | 1.4767 | 3.4 | 25.5 | 0.81 |
| Triethylamine | -115 | 90 | 0.726 | 1.401 | 2.42 | 33.1 | 0.87 |
| Trifluoroacetic acid | -15 | 72 | 1.489 | 1.285 | 8.55 | 13.7 | 2.26 |
| 2,2,2-Trifluoroethanol | -44 | 77 | 1.384 | 1.291 | 8.55 | 12.4 | 2.52 |
| Water | 0 | 100 | 0.998 | 1.333 | 80.1 | 3.7 | 1.82 |
| *p* -Xylene | -25 | 144 | 0.88 | 1.5054 | 2.57 | 35.8 | 0.62 |

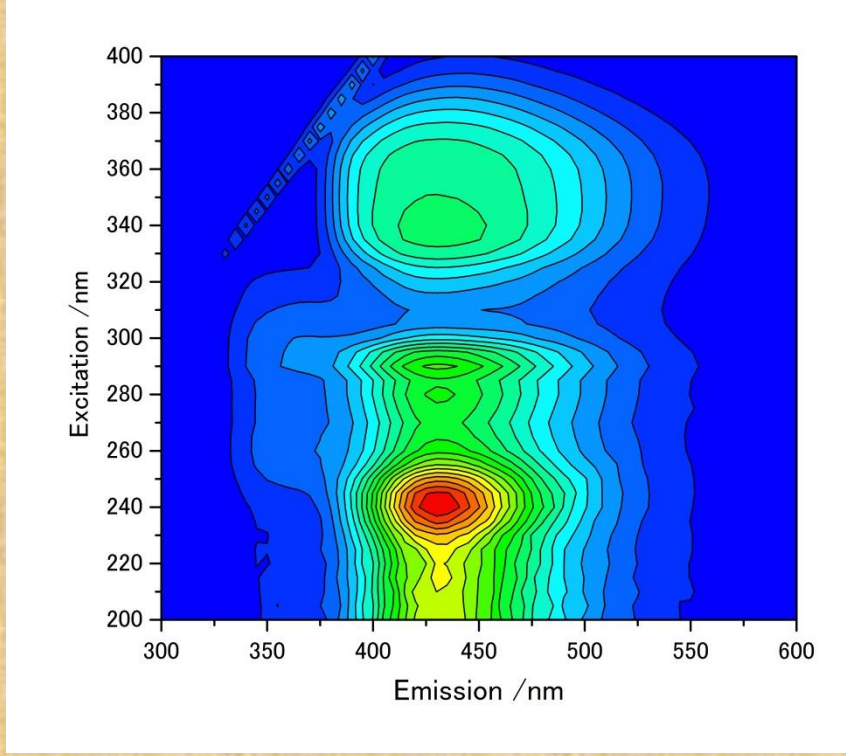
# Zirconium complex with luminescence

- Zr-ODZ complex



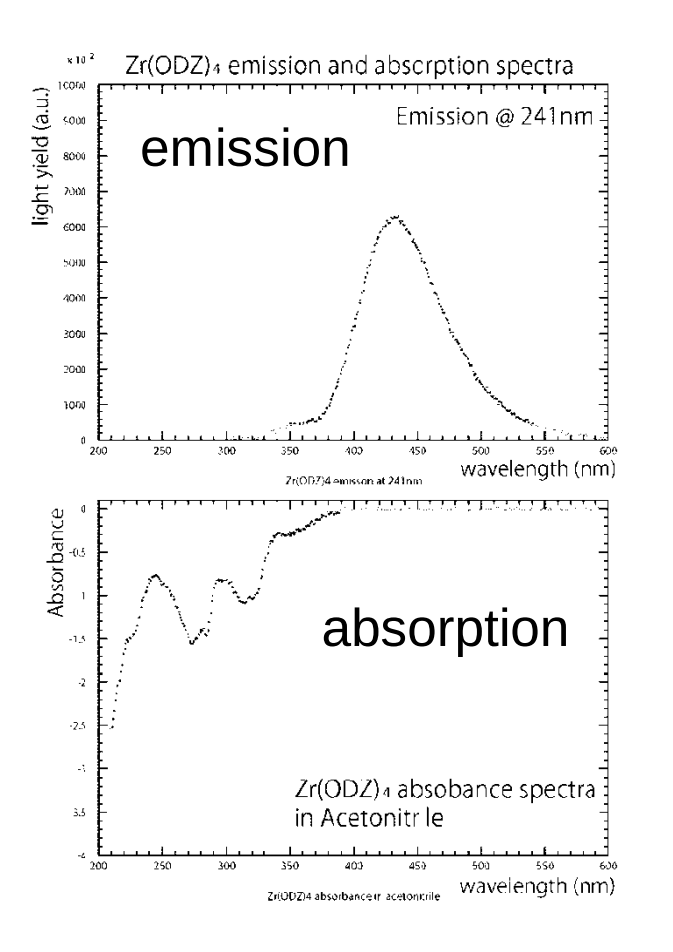

m.w. = 1040.18

- Photo luminescence




- **Solvent : Acetonitrile**
- **Concentration : $3.0 \times 10^{-5}$ mol/L**

# Emission and absorption spectrum of $Zr(ODZ)_4$




- Emission wavelength : 430nm

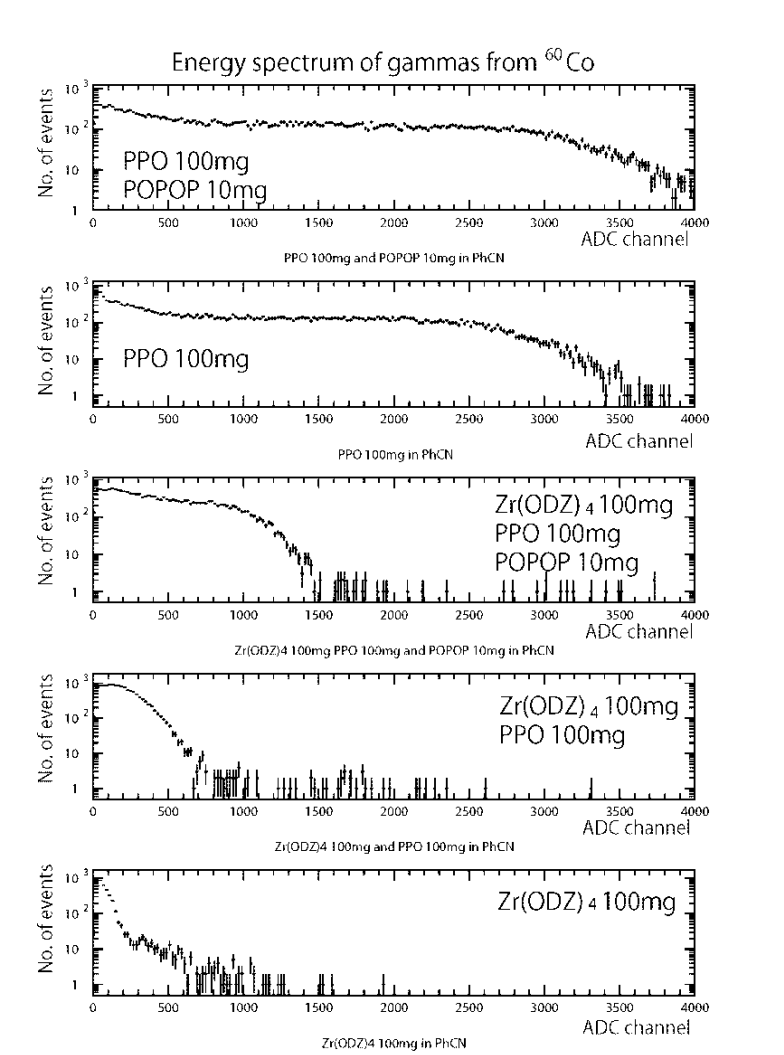
  ↓

  PMT sensitive
- Absorption wavelength: 270nm and 320nm

  ↓

  different from excitation W.L.
- Solvent : PhCN (Benzonitrile)
- Solubility : ~5w.t.%

# Response for γ-irradiation




- Most of emission light from PhCN was not used for the emission of $Zr(ODZ)_4$.
- third excitation of ~340nm from PPO was used for the emission of $Zr(ODZ)_4$.
- Estimated Quantum yield was obtained ~30% at first excitation of ~240nm.

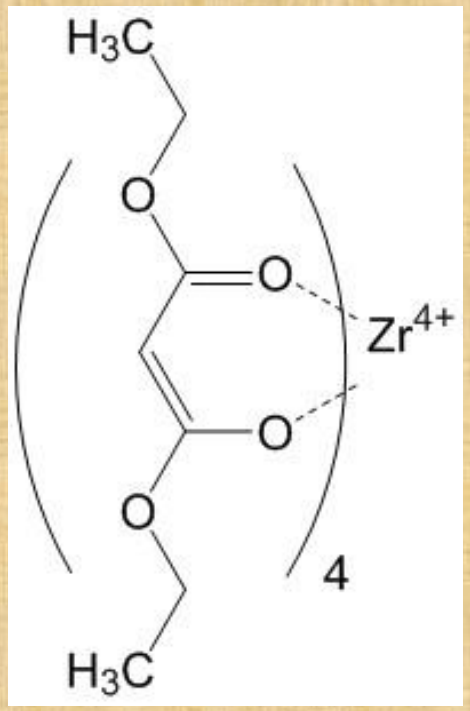
Need another solvent which has shorter emission wavelength than PhCN.

# Summary

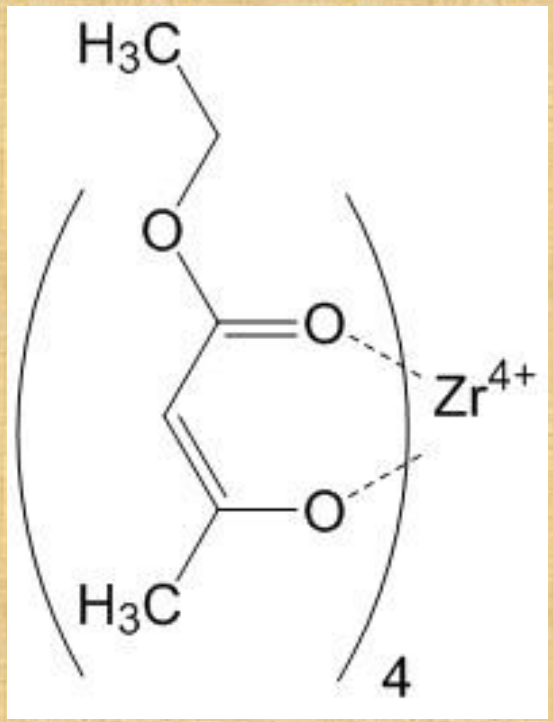
- High solubility of Zirconium β-keto ester in Anisole (>~10w.t.%) was achieved.
- Confirmed absorption peak moves to shorter wavelength (275nm → 245nm) by introducing ester substituent groups.
- Observed scintillation light yield decreased in proportion to the concentration of Zr β-keto ester complex due to solvent effect → Need low polarity solvent
- To avoid solvent effect, we will synthesize new complex tetrakis (diethyl malonato) zirconium.

# Tetrakis (diethyl malonato) Zr compex

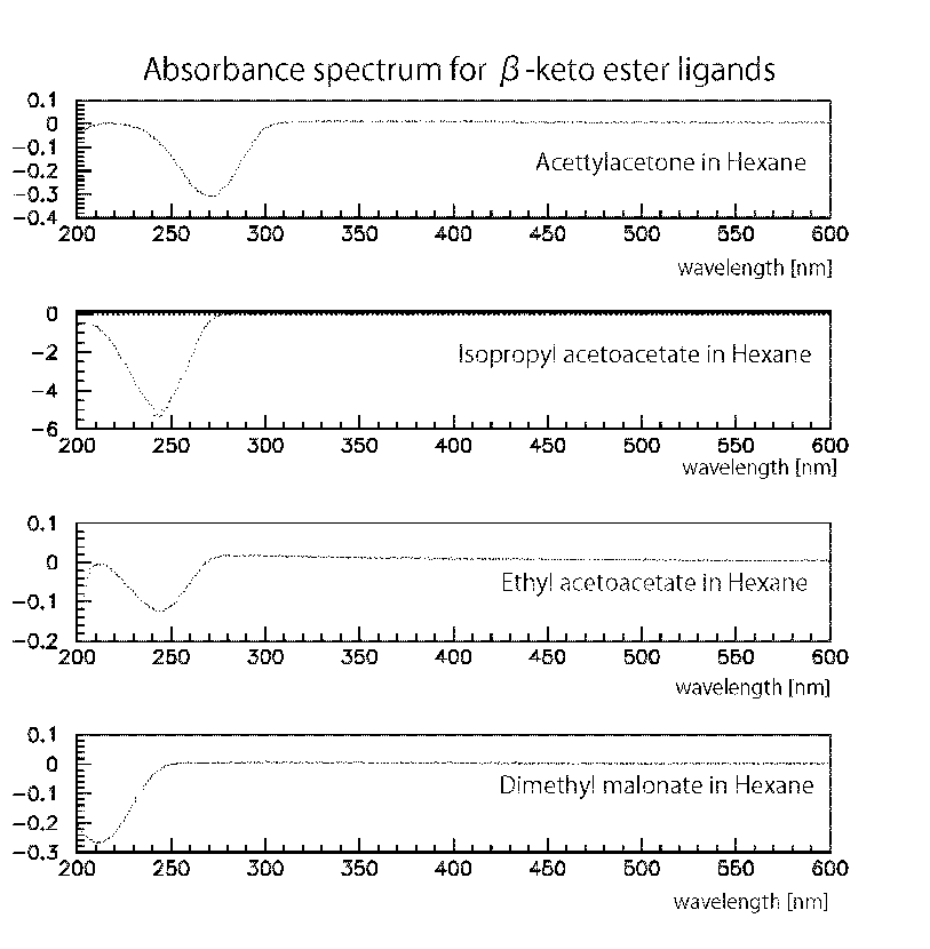
**$Zr(CH_3CH_2OCOCHCOOCH_2CH_3)_4$ = $Zr(dem)_4$**
**mw : 727.84**




**$Zr(CH_3CCOCHCOOCH_3)_4$ = $Zr(etac)_4$**
**mw : 665.81**



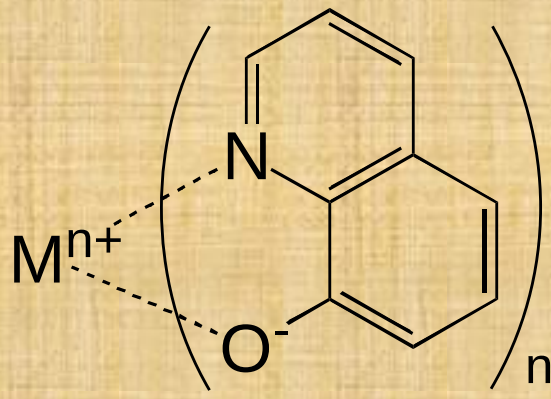
# Absorbance spectrum for β-keto ester ligands



# BACKUP

# Tetrakis 8-quinolinolate Zr complex loaded scintillator

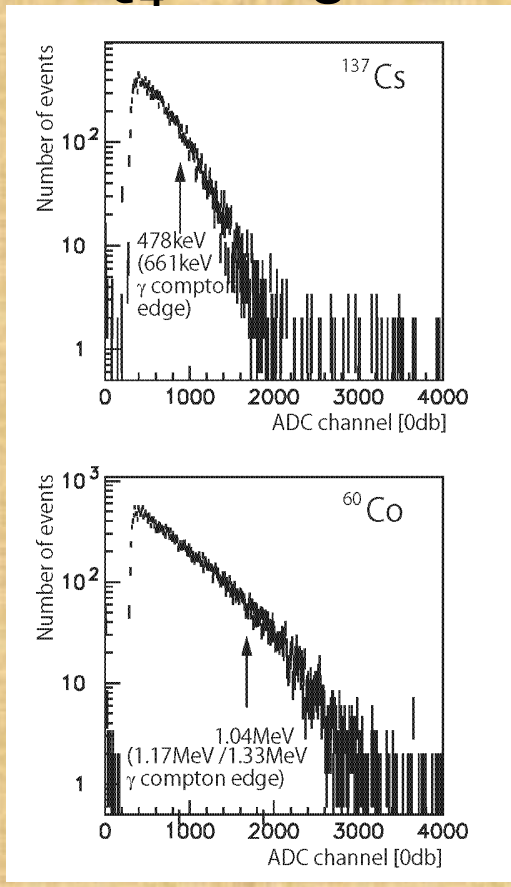
- Tetrakis (8-quinolinolate) Zirconium complex ($ZrQ_4$)




M = In, n = 3; M = Zr, n = 4

$ZrQ_4$ m.w. = 689.07

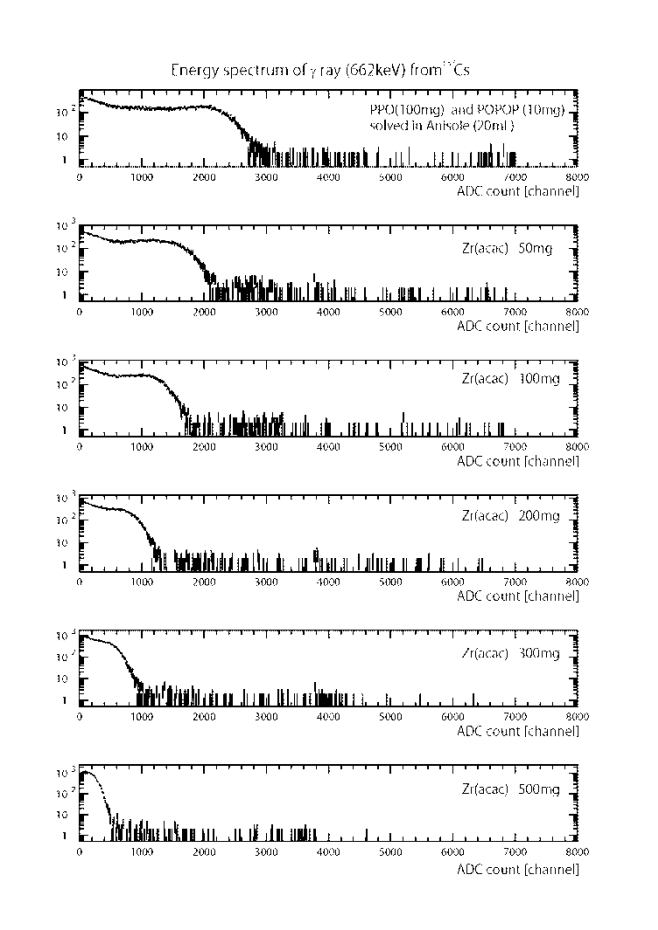
**$ZrQ_4$ 50mg in PhCN-POPOP**




Quantum Yield=1.1% obtained by optical method

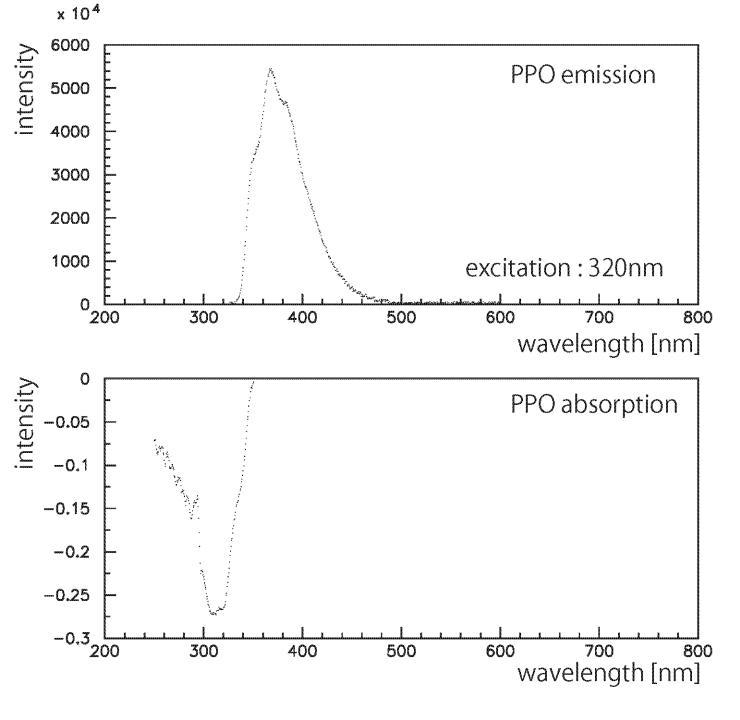
Light Yield to BC505: =7.3%

# Scintillation light yield ($^{137}Cs$) with respect to concentration of $Zr(acac)_4$



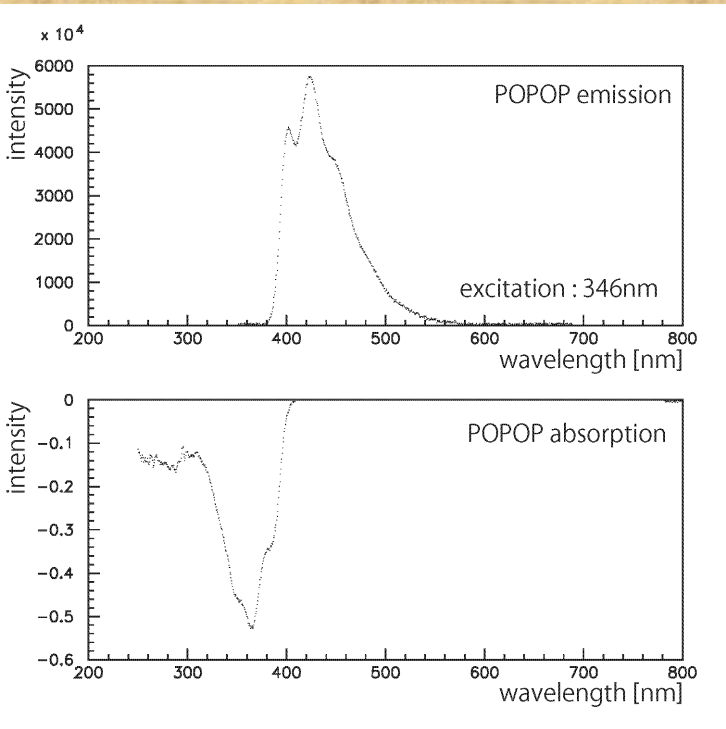

| concentration of $Zr(acac)_4$ | Observed channel | Expected channel |
|---|---|---|
| 0 mg | 2450 | 2450 |
| 50mg | 1800 | 1997 |
| 100mg | 1400 | 1687 |
| 200mg | 950 | 1284 |
| 300mg | 650 | 1038 |
| 500mg | 300 | 750 |

# Photo Luminescence and absorption of PPO



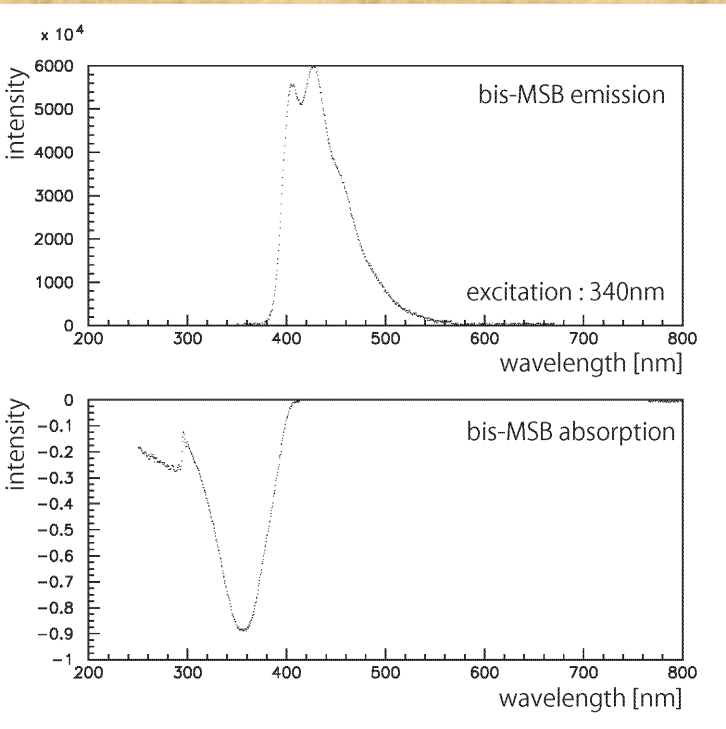

- Photo luminescence
  - Fluorescence device: HORIBA FluoroMax-4
  - Absorbance device : HITACHI U-3000
  - Solvent : Benzonitrile (PhCN)
  - Concentration : $1.0 \times 10^{-5}$ mol/L
  - 2,5-Diphenyloxazole
  - Molecular mass : 221.26
  - Max. emission wavelength : 368.0nm
  - Max. absorption wavelength : 309.7nm

# Photo Luminescence and absorption of POPOP




- Photo luminescence
  - Fluorescence device: HORIBA FluoroMax-4
  - Absorbance device : HITACHI U-3000
  - Solvent : Benzonitrile (PhCN)
  - Concentration : $1.0 \times 10^{-5}$ mol/L
  - 1,4-Bis(5-phenyloxazol-2-yl)benzene
  - Molecular mass : 364.40
  - Max. emission wavelength : 423.6nm
  - Max. absorption wavelength : 364.1nm

# Photo Luminescence and absorption of bis-MSB




- Photo luminescence
  - Fluorescence device: HORIBA FluoroMax-4
  - Absorbance device : HITACHI U-3000
  - Solvent : Benzonitrile (PhCN)
  - Concentration : $1.0 \times 10^{-5}$ mol/L
  - 1,4-Bis(2-methylstyryl)benzene
  - Molecular mass : 310.44
  - Max. emission wavelength : 426.6nm
  - Max. absorption wavelength : 355.3nm