Luminescent properties of a new in-based organic liquid scintillation system.

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Luminescent properties of a new In-based organic liquid scintillation system

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A novel liquid scintillator system using metal β-diketonate chemistry based on loadings of indium, a target of current interest in low energy solar neutrino detection, is developed. The optical absorption, fluorescence and scintillation properties for this new system are described. The scintillation light output as found from the irradiation by low energy gamma-rays is presented. Notable light yields are found.

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1. Introduction

The development of novel organic scintillator systems which can incorporate metals is of fundamental interest towards the creation of new luminescent materials. Metal $\beta$-diketonates [1] provide one important interface between the metal of interest and the organic medium. The recent first observation of electroluminescence from a functionalized oxadiazole-terbium(III) $\beta$-diketonate in a polymer and fluor mixture [2] illustrates the utility of these complexes as a bridge between organic and inorganic chemical environments.

The $\beta$-diketonate system described here, based on ideas first presented in [3], is of interest towards the development of a large scale scintillation detector for the study of low energy neutrinos from the Sun such as in the LENS (Low Energy Neutrino Spectroscopy) project [4]. The deficit of solar electron neutrinos [5–10] and the observation of the appearance of at least one other neutrino from a different family [11] confirms the "new physics" that must be explained. Evidence for disappearance of electron anti-neutrinos from nuclear reactors is now found [12].
The present work is focused on the optical aspects of the development of a novel scintillator system utilizing β-diketone chemistry that was investigated for use in the detection of low energy solar neutrinos from the Sun using indium. The first ideas on the nuclear aspects of an indium concept were proposed by Raghavan [13]. The needs of a low energy indium based solar neutrino detector prefer a scintillator having metal loadings in the 5-10 wt.% range, a total In amount of about 10 tons and a large light output (> 50 % of the light output of BC505 [14]) with long attenuation lengths (a benchmark of > 2.0 m at 430 nm). Several studies of In-loaded liquids have been published [15-17] but these scintillators were not suitable to the aforementioned needs of the LENS project.

The basic challenges are to achieve: high metal (In) loadings, chemical robustness (low reactivity with respect to other materials), high organic solubility, good scintillation light efficiency, optical clarity for long attenuation lengths, chemical stability and purity (very low levels of contamination from naturally occurring radio-isotopes). To the best of our knowledge, the scintillator described here is the first such...
heavily loaded $\beta$-diketonate organic liquid scintillator system. Work is also underway as regards the use of carboxylates by us and other members of the LENS project [18].

2. Scintillator composition

The In-$\beta$-diketonates are all produced by us as all forms commercially available that were investigated were, from the viewpoint of optical absorbance properties, too impure in the blue region.

Although the synthesis of the indium $\beta$-diketonate compound is in principle relatively straightforward, in order to meet the additional demands of optical transmission and high solvent solubility an investigation was made to achieve a useful scintillator material. The chemistry details about the complete synthesis and the subsequent purification steps are described in [19].

The scintillator system is based on the highly stable metal $\beta$-diketonate complexes of indium. The $\beta$-diketone molecule has a section R1-(C=O)-CH$_2$-(C=O)-R2 consisting of two ketones (C=O) that "sandwich" a methylene carbon atom; R1 and R2 are carbon-based side chains. The central methylene carbon looses a hydrogen (e.g. by ad-
dition of base) to form a delocalized negative charge, and the chelate subsequently strongly binds via the ketones to the positive metal ion forming a complex stabilized by resonance. The carbon side chains promote solubility in the organic scintillator base solvent. The compounds have high temperature stability (to approximately 200°C) and unusually high vapor pressures (few mbar, 150-200°C). This feature permits purification of the material by sublimation.

The organic nature of the chelate provides a system in which the metal can be manipulated into organic liquids. As summarized in [19], several side chain configurations and the solubilities of the resulting compounds in the various solvents were investigated. For the case where R1 and R2 are methyl groups (the β-diketone is then 2,4-pentanedione, Hacac), anisole (1-methoxybenzene, a "benzene-like" scintillator base solvent) has a high solubility for In(acac)3 such that an In-loading (by weight % indium) of up to 7.9% is possible [19]. The anisole (Aldrich, 99 %) is reagent grade and, where noted, further purified using a weak acidic Al2O3 column.

The molecules of anisole in the scintillator are the "primary" mole-
cules excited in the initial excitations resulting from the neutrino-induced nuclear gamma-ray or electron emissions. Codoped fluors are adjusted to maximize the non-radiative energy transfer so as to achieve significant light output in the visible (blue) region. The In(acac)$_3$ itself can act as a "sink" (details in section 4) by absorbing UV light, consequently fluor selection and loading are crucial. The fluors investigated: PPO (2,5-diphenyloxazole, 221.24 g/mol), butyl-PBD (2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole, 354.42 g/mol), PBD (2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole, 298.32 g/mol), pTP (1,4-diphenyl-benzol, 230.29 g/mol) and PMP (1-phenyl-3-mesityl-2-pyrazoline, 264.37 g/mol) are reagent grade and used as received. The fluor BPO ((2-(4-Biphenyl)-5-phenyloxazole, 297.33 g/mol) was specially prepared by our Russian collaborators (see Acknowledgements). The secondary fluor, bis-MSB (1,4-bis(2-methylstyril)benzene, 310.42 g/mol) is a reagent grade wavelength shifter used in conjunction with a primary fluor.

The weight percentage of In, (wt.% In), is in all cases determined directly by weight and double checked as needed using atomic absorp-
tion spectroscopy (AAS) as described in [19].

3. Optical properties

For the measurements described below, 1 cm (3.5 ml) or 10 cm (30 ml) long quartz cells were used. Before each measurement the sample was first filtered with a 0.2 μm filter and then bubbled for at least 5 minutes with N₂ to remove oxygen.

3.1. Absorbance properties

Absorption spectra were obtained using a Cary 400 UV–Visible spectrophotometer from Varian. Instruments are operating at room temperature.

Particular interest lies in achieving long transmission lengths, especially at wavelengths longer than 400 nm, the region of best sensitivity of phototubes to the fluor emission. The two major absorbance contributions in this region are the In material (In(acac)₃) and the fluor.

The absorbance is dominated at low PPO-concentrations by the In(acac)₃ material. In Fig. 1 the wavelength dependence of the molar extinction coefficient is shown for the molecule in absence of fluors. The solvent is ethanol and the In(acac)₃-concentration for the measurement is 18 mg/l (M.W. 412.15 g/mol). The maximum of the
absorption peak is at 285 nm; only 18 nm to shorter wavelengths from the maximum of the PPO-absorption.

Absorbance measurements of scintillator components (In-material, fluors, primary scintillating solvent) were recorded in the wavelength region where highest transmission is most important. Some results are shown in Fig. 2. In this figure we plot the attenuation length $\Lambda$ of the different components of the scintillator mixture as determined from the experimental measurements. The quantity $\Lambda$ is equal to $0.4343 \cdot \frac{x}{A}$ where the absorbance change $A$ is defined as $\log_{10} \left( \frac{I_{in}}{I_{out}} \right)$ and $x$ is the path length in meters. The light loss mechanism applicable in the low absorbance region could still be due to scattering or absorption of any impurities, thus we use the term attenuation length.

Fig. 2 shows that the attenuation lengths of various components of a 5 wt.% In scintillator mixture are in the range of a few meters. The fluor concentrations that the scintillator is based on are determined in a set of measurements below (see section 3.3) and briefly discussed in section 4. At a PPO concentration of 200 g/l and an In-loading of 5 wt.% both ingredients contribute approximately the same amount
to the absorbance (see Fig. 2).

Fig. 2 also shows a plot of the attenuation length for the fluor component of the scintillator using BPO at a concentration of 100 g/l. The attenuation lengths of the BPO system are shorter at a given wavelength than those for the PPO system. The absorption spectrum of BPO is shifted to longer wavelengths compared to that for PPO. At these BPO concentrations, the absorbance in the region of interest is dominated by the fluor.

For the cases presented here, anisole is used as a solvent. A small absorbance at 430 nm is due to impurities in the anisole. It is possible to remove such impurities in the anisole by a column purification procedure using a weakly acidic Al₂O₃ column packing. The attenuation length of the unpurified anisole is roughly 8 m at 430 nm. After the column purification this increases to more than 11 m (for these measurements a 10 cm cuvette was used for better sensitivity) assuming that the attenuation length is infinite (namely the absorbance is zero) at the minimum (580 nm) of its absorbance spectrum. No significant effect on the light yield of the scintillator is observed using the column
procedure.

In summary, a combined attenuation length of approximately 1.5 m (0.7 m) at 430 nm using PPO (BPO) is achievable in a 5 wt.% In-anisole-fluor mixture; found by summation of the absorbances of the two ca. 3 m components. If the results are due to impurities then possible further improvements in the absorbance properties can be achieved for the In(acac)$_3$ (for example by a second sublimation step in the purification procedure) as well as for the PPO (Aldrich, 99%) or BPO (non-commercial synthesis) for which we use no special purification steps. If the absorption of the fluor at the long wavelengths is due to intrinsic spectroscopic properties then further purification steps will not help. A first measurement showed that excitation at wavelengths greater than 420 nm gave no fluorescence emission, indicating further purification investigations could be useful.

3.2. Fluorescence properties

The fluorescent properties of the In (5 wt.%)/anisole/PPO/bis-MSB scintillator system are described here as illustrated for the base case of PPO (200 g/l)/bis-MSB (500 mg/l) along with some other fluor combinations.
The fluorescence measurements below were made using a Varian Cary Eclipse fluorimeter, and, unless otherwise noted, the front face geometry was used. In this mode, the excitation light enters on the same side of the cuvette as that which is observed by the detector of the emitted light. This geometry ensures that the reabsorption of the emitted light in the scintillator is negligible because the light is absorbed and emitted in a very thin layer close to the wall of the cuvette.

The primary fluor (e.g. PPO) is the central ingredient for light emission in the visible region and, present in relatively large quantities, is either directly excited by the initial radiation, or excited by energy transfer from the solvent. The secondary fluor (e.g. bis-MSB), present in very small quantities, shifts the emission to longer wavelengths by non-radiative energy transfer. The solvent provides for a means to dissolve the In-material in large quantities and is itself a UV fluorescent aromatic. Because of the absorbance band of the In material, the key to significant light output is the "tuning" of the non-radiative transfer processes so as to maximize the solvent-to-primary fluor energy
transfer pathway over the solvent-to-In material or primary fluor-to-In material modes of the non-radiative energy transfer "triangle".

The absorption and the emission spectrum of anisole diluted in cyclohexane is shown in Fig.3. The emission maximum for anisole is 293 nm when excited at 271 nm, the absorption maximum. This UV emission is shifted to longer wavelengths by the primary fluor. However the In-material also absorbs in this region (see Fig.1). There is insignificant light emission from the In(acac)₃ molecule. A sample in a 1 cm cuvette containing 18 mg/l In(acac)₃ dissolved in ethanol was excited at its absorption peak maximum of 285 nm. Negligible light emission was found to occur in the wavelength region between this excitation value to 600 nm. Consequently it is preferable to avoid energy loss to the In-material.

To maximize the light output various fluorors all of which have a strong absorbance in the range of the emission peak of the anisole were tested. The solubility in anisole varies by orders of magnitude for the different fluorors (see Table 1). For the cases of PPO, butyl-PBD and BPO more than 100 grams dissolve per liter of the solvent without
any aggregation. These fluors, in higher concentrations, are suitable both for direct primary excitation light production and energy transfer from the anisole. For PBD, p-TP and PMP the solubility is much less and/or their light yields are more limited.

To shift the wavelength further to greater than 400 nm bis-MSB was used as a secondary fluor. In the base case, the PPO (absorption maximum 303 nm, emission maximum 360 nm) is well matched, e.g. [20],
to this fluor (absorption maximum 345 nm). The bis-MSB leads to a broad emission peak having a maximum at 425 nm in our scintillator system. The bis-MSB amounts are too small to contribute notably to direct, primary excitation light; it thus serves only in a non-radiative transfer role.

Fig. 4 shows the fluorescence emission of the In (5 wt.%)/anisole/PPO (200 g/l)/bis-MSB (500 mg/l) base case scintillator mixture following excitation at the 271 nm anisole absorption maximum. For this measurement a triangular cell was used in backface geometry (i.e. the excitation light enters the cell at 45 degrees to the hypotenuse and exits through the liquid out a side, with the emission 90 degrees to
the incident excitation beam). Therefore the fluorescence light propagates several mm through the scintillator mixture before detection.

This geometry was chosen to examine the effect of short range self-absorption by the bis-MSB. There is a cutoff at 400 nm due to self-absorption such that the peak appears shifted to the right from the usual bis-MSB emission peak (e.g. Fig. 6). In fact, 50% of the light is emitted above 440 nm.

There are three different possible approaches towards improving the light yield involving the transfer of energy from the solvent to the fluor. One is to increase the transfer rate from the solvent to the fluor by using higher fluor concentrations (examined in the next section), second is to optimize the light from a given fluor by choice of fluor, and the third is to try to decrease the competing transfer rate from the solvent to the In(acac)$_3$.

To optimize the light yield by choice of fluor, the performance of several fluor candidates was investigated experimentally. The results obtained, using the limited set of common candidates listed in Table 1, lead to PPO, butyl-PBD and BPO. They have high solubility in anisole
and thus can be used in higher amounts so as to emit more light. Furthermore, with similar In-concentrations (wt.% In) and comparable fluor amounts, they emit notably more light than PMP or p-TP. In Fig. 5 we show the emission spectra of 5 wt.% In-loaded scintillators using these three fluors at a common weight loading of 100 g/l each. The integrated emission spectrum (integrated as a function of wavenumber, using front face geometry) is 45 % higher for the butyl-PBD scintillator compared to the PPO system. Correspondingly, the integrated BPO spectrum is 70 % higher than the PPO one.

Finally, as seen in Fig. 5, the BPO system has an advantage in that it emits at longer wavelengths. Since PPO and butyl-PBD both emit around 365 nm, the emission still overlaps somewhat with the absorbance of In(acac)₃. Therefore, the bis-MSB wavelength shifter is more important for these fluors, than it is for the BPO case.

To reduce the transfer rate from the solvent to the In(acac)₃, the third variation, one would prefer a solvent, which emits at a longer wavelength than the ansiole. The intensity of the fluorescent emission of an In-loaded scintillator using PPO and bis-MSB as fluors increases
as the wavelength of the excitation light increases from the anisole absorption at 271 nm to longer wavelengths. Up to 305 nm, slightly beyond the absorption peak of the PPO (303 nm), the difference is small, but at 320 nm there is a significant increase in fluorescence light emission; this is shown in Fig. 6. Consequently, a solvent having an emission greater than 300 nm would be of interest.

Such solvent components exist in the form of the dimethoxybenzenes (dmb). They have a high solubility for In(acac)₃ and emit mainly above 300 nm. The isomer 1,4-dmb, a solid at room temperature, when dissolved in anisole at a wt. ratio of 20:1, has a fluorescent emission at 321 nm. Tests of the actual light yield however, made using the luminescent capability as described immediately below, surprisingly revealed no improvement in the light yield for In-loaded scintillators compared to the pure anisole based version of the scintillator. Perhaps the rate of energy transfer to the 1,4-dmb is too slow such that it does not overcome the rate of transfer to the In-molecule. Smaller light yields were observed as well using 1,4-dmb/anisole mixtures that were 1:1 by weight. The liquids 1,2-dmb (emission maximum 305 nm) and
1,3-dmb (emission maximum 299 nm), also gave lower yields. In summary, the anisole system gave us, so far, the best fluorescent results.

3.3. Luminescence under irradiation with a test source

The luminescence of the base In-scintillator system and variations were performed using a $^{137}$Cs-source (662 keV photons). The photons scatter off of electrons in the scintillator, ejecting energetic electrons. These lead to light production primarily through the direct excitation of the anisole and primary fluor components.

The experimental setup for the measurement is located in a dark room. A blue sensitive bi-alkali photocathode PMT (Photonis XP2262) looks at a 1 cm quartz cuvette containing the scintillator sample. The sample is irradiated by the radioactive source. The PMT is read out by a VME acquisition system with a charge sensitive ADC: the light signal is proportionally converted into a current pulse which is integrated to give the "PMT charge signal".

The light yield is found by recording the characteristic Compton spectrum (number of events vs. PMT charge signal) and determining, for a given deposited energy (indicated by characteristic features in the spectrum, e.g. the Compton edge), the corresponding
PMT signal. The light yield is then compared to a BC-505 standard. In order to check the stability of BC505 we regularly use additional standards (5 g/l BPO and 1.5 g/l PPO in pseudocumene (1,2,4-trimethylbenzene)). The light yield of the PC/BPO standard was measured to be between 8-10 % higher than BC-505; the yield of the PC/PPO standard was approximately 5 % lower than BC-505 (BC505 is defined to be fixed at 100% light yield). Standards are cross-checked with colleagues at the Laboratori Nazionali del Gran Sasso, Italy.

The system using PPO as the fluor was investigated in most detail and comprises the base case scintillator mixture. At a concentration by weight of 6 g/l PPO in anisole, the saturation value for the light yield is reached at (77 ± 2) % light yield compared to the BC-505 standard, errors sufficiently estimated from repeated measurements. With the addition of In(acac)$_3$ to a concentration of 1 wt.% In the light yield drops to about 25 %, then increases with increasing PPO-concentration.

Higher PPO-concentrations increase the overall energy transfer rate
to the PPO component and therefore the light yield. Additionally, there are more directly excited primary fluor molecules. For a loading of In at 1 wt.%, scintillator light yields of more than 50 % could be reached by adding primary fluors to levels of 50 g/l PPO and secondary fluors to 500 mg/l bis-MSB or more. For the base case of a 5 wt.% In-loaded scintillator the light yield is 35 % at 200 g/l PPO and 500 mg/l bis-MSB. This number can be compared to an artificial benchmark termed the "aromatic limit" defined as the ratio of solvent in the actual In-scintillator versus that in an unloaded scintillator times the light yield of the unloaded scintillator. Here that number is 63 % of the BC-505 light yield, indicating that the In-material still acts as a sink to otherwise potentially useful light output.

Table 2 summarizes the main results for PPO and fluor variations. A wide range of useful light yields is found. At a weight concentration of 100 g/l of primary fluor and 200 mg/l bis-MSB approximately 10 % more light using butyl-PBD instead of PPO (at 5 wt.% In) results. Using BPO at the same weight concentration a light yield of 51 % BC-505 is measured without any additional secondary wavelength-
shifter; a result which is more than a factor two higher than the value obtained using PPO at the same weight concentration. With bis-MSB in addition to BPO, only a small increase in the light yield is observed. For this case, measurements with the fluorimeter however show that the emission is shifted to longer wavelengths. This could still be advantageous if one goes to longer pathlengths, since the emission is in a more transparent region of the spectrum. Thus we are continuing to study the BPO system in greater detail.

One can convert the unit of the In-concentration given in weight % into grams per 100 ml by multiplying the number in the table by the density. The density of one scintillator, (BPO + bis-MSB), entry two in Table 2, was measured to be 1.044 kg/l; this illustrates the typical density.

For completeness in Table 3 and Table 4, the main results of the light yield measurements with fluors having lower solubility in anisole and/or lower light yields are listed.
4. Discussion and energy transfer features

In this system, in a simple qualitative view, the useful light is mainly due to excitation of the primary fluor acceptor (A) molecules either directly, \( A \rightarrow A^* \) for terminology, or indirectly by energy transfer from the solvent (anisole) donor molecules (D), \( D^* \rightarrow A^* \). The solvent quantity is essentially fixed at the amount needed to dissolve the In material; and, itself, contributes negligibly to useful direct light in the visible region. Moreover, the secondary fluor (bis-MSB), due to its small quantity, also contributes negligibly to direct light; it serves to shift essentially all the primary fluor emission by energy transfer. The non-radiative transfer processes are described by Förster [21] and Dexter [22]. We have additionally engaged in modeling such systems and refer to those works [23] for further details or definitions.

The key feature is that light emission arises from two main pathways: direct and indirect excitation of A molecules. The In ("quencher" Q) concentration \( q \) enters the situation by opening up an energy quenching pathway, \( D^* \rightarrow Q^* \). What we do is close that possibility by adjustment of the concentration \( c \) of the acceptor A molecules.
In Fig. 7 the experimental light yield as a percent of the BC505 light yield is plotted versus the acceptor concentrations \( c \) (here in grams per liter anisole) based on measurements where the \( Q \) (In) concentration \( q \) is kept the same. As seen in the figure, for a fixed \( q \) there is a rapid increase in light output from zero followed by a tendency towards leveling off. For the larger fluor concentrations self-quenching is seen to occur; but despite this, the light still increases with the increasing fluor concentration because the more dominant effect of the \( \text{In(acac)}_3 \) quenching is still being overcome. A simple model, for discussion purposes, gives an idea of the main features.

In a codoped system where energy transfer is favorable and correspondingly the mole fraction of \( A \) is low (diminishing direct \( A^\ast \) contributions) the processes \( D^\ast \rightarrow A^\ast \) (rate constant \( k \)) and \( D^\ast \rightarrow Q^\ast \) (rate constant \( k' \)) tend to dominate, even over spontaneous \( D^\ast \) emission, \( \lambda_D \). Assuming just the \( D^\ast \) contribution as the main contribution for any direct light output, the ratio \( r \):

\[
r = \frac{kc}{(\lambda_D + kc + k'q)} \tag{1}
\]

can be used to examine the allocation of \( D^\ast \) energy flow. Then the
curve is approximately described for this experimental region by the following equation:

\[ I = I_0 \cdot \left( \frac{1}{1 + K \cdot \frac{q}{c}} \right) \]  (2)

where \( I_0 \) is the \( D^* \rightarrow A^* \) light output at a given \( q \) in the limit of large \( c \) and \( K \) is the ratio of energy transfer rates \( (k' / k) \). The use of rates is similar to the spirit of the Stern-Volmer equation and equation (2) applies where \( k, k' \) dominate over \( \lambda_D \); the mole fraction \( x_A \) is small; and the non-radiative rate is proportional to \( c \) (thus averaged over the radial distribution, as e.g. \( n(r) \) in [23] and the, short, time scale of the transfer). Limiting behavior outside this regime and more refined discussions need to be based on a full set of model equations, under investigation. Moreover, the quantity \( I_0 \) depends on the value for \( q \) because the mole fraction of donors drops with increasing \( q \) such that the primary ionization leads to less "good" \( D^* \) molecules and more "bad" \( Q^* \) molecules.

At a low acceptor concentration in the light curves, the ratio \( (q/c) \) is high and the quenching pathway is flooded leading to no light output. This is the point \((0,0)\) in Fig. 7. For an "infinite" \( c \), on the other
hand, there is no effective quenching by the indium material at all so the light from $D^* \rightarrow A^*$ in this case rises to the maximum $I_0$. As this limit is approached in practice, though, the mole fraction $x_A$ becomes large such that the main light emission arises from direct $A^*$ excitation; this is also in a regime which is outside the simplifying approximations made for our purposes here.

For the case of PPO in Fig. 7 in the region of lower acceptor concentrations, $I_0$ is approximately 20 % BC505 light yield. There is a point where $I$ is one-half $I_0$ (c approximately 20 g/l). At this point $K \cdot \frac{q}{c} = 1$ such that the rates of the quenching and the acceptor pathways are equally at play. To the left of this point in Fig. 7 the quenching path begins to dominate and the light yield drops. In that the typical ranges for the PPO critical acceptor concentrations ($c_0$, in e.g. [23]) above which the $D^* \rightarrow A^*$ mode usually dominates are in the fractional to few grams per liter range in the absence of quenching, well to the left in Fig. 7, increased values of c above $c_0$ seen here are indicative of the need to overcome the quenching rate. Although the light yields below about 10 % are below the sensitivity of our appa-
ratus, for \( c = 0 \) the light yield is zero as verified in our fluorimeter measurements. Thus at small \( c \) the light yield rapidly drops to zero.

Finally, in the upper curve of Fig. 7 one can see that the bis-MSB leads to higher light yields. This is attributable to the ability of bis-MSB to shift light (here from PPO) to longer wavelengths where the scintillator sample is more transparent and outside the self-absorbance of PPO.

5. Summary and Conclusion

In this paper the optical properties of a new In-loaded liquid scintillator are described. This is the first such scintillator of its kind, to our knowledge. Such a scintillator system is of fundamental interest in luminescence and to research in low energy solar neutrino detection – in part due to its stability. The most desirable features for such a scintillator are long attenuation lengths (meters) in the region around 430 nm and light yields of around 50% compared to BC-505 at as high a loading of In consistent with these guides (preferably 5–10 wt.% In). The actual absorption length for a 5 wt.% In loading in anisole is in the range 3.5–7.2 m (430–480 nm). The main limits on the overall
attenuation length in the final mixture (fluors plus In material) arise due to the further addition of the codoped fluors at the required high concentrations (from 430–480 nm: 1.5–3 m following PPO addition, calculated by summation). These numbers could possibly be improved in the future. For example, the contribution of the fluor depends on its purity level and concentration, which has to be optimized.

The base case scintillator, In (5 wt.%)/anisole/PPO (200 g/l)/bis MSB (500 mg/l), has a light yield of 35 % of BC505. In a base case variation, light yields above 50% compared to BC-505 using BPO as fluor at a concentration of 100 g/l are achieved (from 430–480 nm: 0.7–2 m following BPO addition, calculated by summation). Further studies on the (less readily available) BPO systems are ongoing.

In order to best measure the light yields over long path lengths and to study the actual attenuation lengths it is planned to use the multimeter scintillator module capability of the LENS Low-Level Background Facility at Gran Sasso [24].

In conclusion a notable luminescent light yield using In β-diketonate doped organic liquid scintillator systems – even at reasonably high
loadings of In has been achieved. These results are expected to generally be of interest to other suitable metal \( \beta \)-diketonates as well. Metal doped organic scintillating systems should be of interest to the development of new types of luminescent materials.

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Fig. 1: Absorption spectrum, in units of the molar extinction coefficient, of specially prepared In(acac)₃ dissolved in ethanol (18 mg/l; 43.8 μmol/l) showing a maximum at 285 nm.

Fig. 2: Wavelength dependence of the attenuation length for components of the main scintillator versions: PPO (200 g/l, 0.90 M) or BPO (100 g/l, 0.34 M) measured in 1 cm cells; and, 5 wt.% indium loading (0.44 M) measured in a 10 cm cell. The contribution of the anisole solvent is negligible.

Fig. 3: Absorption (molar extinction coefficient, left scale) and emission (relative light intensity, right scale) spectra of anisole diluted in cyclohexane (16 mg/l, 0.15 mmol/l). The absorption maximum is at 271 nm, the emission maximum at 293 nm (271 nm excitation).

Fig. 4: Emission spectrum of the base case 5 wt.% (0.44 M) In-loaded scintillator with PPO (200 g/l PPO, 0.9 M) and bis-MSB (500 mg/l, 1.6 mmol/l) excited at 271 nm in a triangular cell (backface geometry).

Fig. 5: Emission spectra of 4.5 wt.% (0.40 M) In-loaded scintillators excited at 271 nm in front face geometry. Data shown for equal weight primary fluor loadings (or 0.34 M BPO, 0.28 M butyl-PBD, 0.45 M
PPO) in the absence of the secondary fluor bis-MSB.

Fig.6: Emission spectra of the base case 5 wt.% In-loaded scintillator (200 g/l PPO, 500 mg/l bis-MSB) excited at 271 nm and 320 nm. These measurements were made in front face geometry, which together with Fig.4, shows the effects of the strong self-absorbance to the left of 400 nm.

Fig.7: Light yield for a 4.1 wt.% In liquid scintillator as a function of PPO weight concentration up to 200 g/l, no bis-MSB (bottom axis) and for a similar 5.0 wt.% In scintillator with PPO fixed at 200 g/l and increasing bis-MSB concentration (top axis). The estimated relative errors are ±5 %, except the first point which, at instrument threshold of about 10 %, has an absolute error of ±2 % BC505 light yield. For the case of no PPO, on the lower curve, the light yield is zero, as verified using the fluorimeter measurements.
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Figure 7.
Table 1

*Solubility of fluor*ors, investigated here, in anisole.

<table>
<thead>
<tr>
<th>fluor</th>
<th>solubility [g/l]$	extsuperscript{1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPO</td>
<td>150 – 200</td>
</tr>
<tr>
<td>butyl-PBD</td>
<td>&gt; 200</td>
</tr>
<tr>
<td>PPO</td>
<td>&gt; 500</td>
</tr>
<tr>
<td>PBD</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>PMP</td>
<td>&gt; 200</td>
</tr>
<tr>
<td>pTP</td>
<td>6 – 12</td>
</tr>
</tbody>
</table>

$\textsuperscript{1}$Grams added to one liter of anisole.
Table 2

*Light yield measurements - high concentration fluors.*

<table>
<thead>
<tr>
<th>fluor</th>
<th>wt. conc. [g/l]</th>
<th>In-conc. [wt.%]</th>
<th>bis-MSB</th>
<th>light yield$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPO</td>
<td>100</td>
<td>4.7</td>
<td>-</td>
<td>51 %</td>
</tr>
<tr>
<td>BPO</td>
<td>100</td>
<td>4.6</td>
<td>200 mg/l</td>
<td>52 %</td>
</tr>
<tr>
<td>Butyl-PBD</td>
<td>100</td>
<td>4.6</td>
<td>-</td>
<td>20 %</td>
</tr>
<tr>
<td>Butyl-PBD</td>
<td>100</td>
<td>4.4</td>
<td>200 mg/l</td>
<td>29 %</td>
</tr>
<tr>
<td>PPO</td>
<td>100</td>
<td>5.0</td>
<td>-</td>
<td>19 %</td>
</tr>
<tr>
<td>PPO</td>
<td>100</td>
<td>4.8</td>
<td>200 mg/l</td>
<td>26 %</td>
</tr>
<tr>
<td>PPO</td>
<td>200</td>
<td>4.8</td>
<td>500 mg/l</td>
<td>35 %</td>
</tr>
</tbody>
</table>

$^1$Light yield versus BC505 using a $^{137}$Cs source, relative errors ±5%.
Table 3
*Light yield measurements – medium solubility PBD compared to PPO.*

<table>
<thead>
<tr>
<th>fluor</th>
<th>wt. conc. [g/l]</th>
<th>In-conc. [wt.%]²</th>
<th>bis-MSB</th>
<th>light yield³</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>30</td>
<td>1</td>
<td>–</td>
<td>37 %</td>
</tr>
<tr>
<td>PPO</td>
<td>30</td>
<td>1</td>
<td>500 mg/l</td>
<td>47 %</td>
</tr>
<tr>
<td>PBD</td>
<td>30</td>
<td>1</td>
<td>–</td>
<td>43 %</td>
</tr>
<tr>
<td>PBD</td>
<td>30</td>
<td>1</td>
<td>500 mg/l</td>
<td>53 %</td>
</tr>
<tr>
<td>PBD</td>
<td>30</td>
<td>4.8</td>
<td></td>
<td>13 %</td>
</tr>
</tbody>
</table>

¹PBD used at maximum loading of 30 g/l.

²Useful weight ranges of 1% at these fluor concentrations.

³Light yield versus BC505 using a $^{137}$Cs source, relative errors ±5%.
Table 4

Light yield measurements – low solubility or low light yield fluors compared to PPO.

<table>
<thead>
<tr>
<th>Fluor</th>
<th>Conc. [g/l]</th>
<th>In-conc. [wt.%]</th>
<th>Bis-MSB</th>
<th>Light yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>6</td>
<td>1</td>
<td>–</td>
<td>19%</td>
</tr>
<tr>
<td>PMP</td>
<td>6</td>
<td>1</td>
<td>–</td>
<td>9%</td>
</tr>
<tr>
<td>PPO</td>
<td>6</td>
<td>0.2</td>
<td>–</td>
<td>44%</td>
</tr>
<tr>
<td>pTP</td>
<td>6</td>
<td>0.2</td>
<td>–</td>
<td>24%</td>
</tr>
</tbody>
</table>

1pTP near limit of solubility.

2Values of In selected to illustrate useful weight ranges.

3Light yield versus BC505 using a $^{137}$Cs source, relative errors ±5%.