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LDRD PROJECT TITLE: Low Afterglow Scintillators for High-Rate Radiation Detection

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ABSTRACT: The present work reports on the development of two types of metal-loaded plastic scintillators that seek to improve the decay kinetics and light-yield properties of existing materials used for high count-rate radiation detection. The strategy followed in this work involves the addition of an organometallic iridium or organometallic tin compound to reduce the extent of deleterious delayed luminescence following exposure to ionizing radiation. Key results include a seven times greater light yield compared to existing high-rate scintillators (i.e. BC-422Q plastic, stilbene-doped bizenzyl crystal), while achieving comparable or even faster decay characteristics than these benchmark materials.

INTRODUCTION: There is a pressing need for high-speed scintillating materials, as relevant to several diverse applications such as nuclear non-proliferation and inertial confinement fusion (ICF) studies. In the former, the NNSA seeks new technologies to enhance the detection of special nuclear materials (SNM) at border crossings and ports-of-entry. An invaluable technique to this end is active interrogation, wherein a radiation pulse induces fission events from difficult to detect SNM such as highly enriched uranium. Present detectors for this application are inadequate due to insufficient timing response characteristics and low light yields that limit the measurement fidelity under typical acquisition conditions.

A similar problem exists when attempting to measure the neutron spectrum in ICF studies at the National Ignition Facility (NIF), Z-machine, or Omega laser facility. These measurements can supply information on the source characteristics such as the fuel and linear areal densities. Unfortunately, significant background radiation is produced in these experiments, which precedes the neutron signals of interest and limits the ability to measure the neutron spectra. The response time of existing materials is too slow to resolve these events, which leads to overlapping signals and insufficient measurement resolution. This work will address the count-rate limitations of existing materials by applying an innovative optical filtering approach in conjunction with a new class of scintillators developed at Sandia.

Previous approaches to this problem all involve the addition of a triplet-quenching additive, whereby the term triplet refers to the spin multiplicity of the excited electronic state. For example, the benchmark high-rate plastic scintillator BC-422Q produced by Saint-Gobain employs between 0.5% and 2% (w/w) benzophenone to quench the excited triplet states that contribute to delayed luminescence and afterglow. Unfortunately, benzophenone non-specifically decreases the prompt and delayed scintillation components, which results in a light yield that is reduced by an order of magnitude relative to the benzophenone-free scintillator. A similar result is obtained for stilbene-doped bibenzyl crystals, whereby the stilbene dopant is able

to trap the triplet excitons prior to delayed fluorescence. A similarly low light yield is observed for this second benchmark material, which obviates the need for a higher luminosity alternative.

A third benchmark high-rate material that addresses the low light yield problem comprises oxygen-saturated liquid scintillator. Since oxygen is a paramagnetic material, it is able to efficiently and selectively interact with excited triplet states of organic molecules. As a result, oxygen-saturated liquid scintillators possess high light yields nearly equivalent to the oxygen-free liquids, while decreasing the probability for delayed fluorescence via triplet states. However, there are two significant problems with oxygen-saturated liquids: (1) the scintillation decay rate is still markedly slower than the other two reference materials discussed above, and (2) oxygen-saturated liquid scintillators pose a packaging problem for many applications and have been shown to be unstable over time.

Discussions with end-users of these detectors have revealed several desired properties for an improved detector material: (1) robust solid-state physical properties to enable flexible packaging arrangements and deployment conditions, (2) fastest possible scintillation response for the best possible timing resolution, and (3) highest possible light yield to increase the detection sensitivity for particular events of interest. The present work improves upon considerations (1) and (3), while achieving comparable performance for (2) relative to existing alternatives.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD: The experimental approach employed in this work was inspired by experimental observations from a prior scintillator development project funded by NNSA/NA-22. In that work, organometallic iridium complexes were added to a plastic scintillator composition to selectively convert non-luminescent triplet host (polymer) excited states to highly luminescent guest (iridium) states, as relevant to fast neutron discrimination. A unique characteristic of this approach is the ability to selectively modify the emission wavelength of the host (prompt) and guest (delayed) emission properties, which distinguishes these materials from traditional scintillators. In that application, the ratio of prompt to delayed luminescence was then used to differentiate fast neutrons from gamma rays.

Based on these results, we hypothesized that it might be possible to decrease the average scintillation decay time by selectively removing the delayed scintillation components by optical filtering. Such a capability is only possible with the iridium-doped plastic scintillators, also referred to as “Triplet-Harvesting Plastic Scintillators” (THPS).

During the course of this project, we devised an alternate approach towards the same end using organometallic tin compounds in place of iridium. The reasoning behind this choice stems from the intrinsic spin-orbital coupling of the organotin complex, which is capable of selectively thermalizing (deactivating) excited triplet states from the host polymer. A key potential benefit

of this approach over the iridium-doped materials is the non-luminescent nature of the triplet state on the organotin complex, which would not require any optical filtering.

Two key experimental measurements were targeted for this study to assess the relative scintillation performance of the developed materials. The first comprises measurement of the

scintillation decay properties via time-correlated single photon counting. This method determines with high dynamic range the average scintillation decay curve for a given scintillator. A ^{137}Cs gamma-ray source was selected to provide the monoenergetic source photons to excite the scintillator. The acquisition system was configured with an optically well-coupled photomultiplier tube as the scintillation start pulse and a second, weakly coupled PMT as the single-photon stop pulse. By histogramming the delay time between the PMT events, one is able to reconstruct the scintillation decay curve across many orders of magnitude. In this way, the minor decay components that lead to afterglow may be accurately assessed and compared. The second characterization method employed in this work comprises scintillation pulse-height spectra, which were obtained by integrating the charge produced by the individual scintillation pulses detected by the PMT. The relative scintillation light yield for each sample was assessed by comparing the position of the Compton edge in each pulse-height spectrum.

Several reference materials were selected as benchmark scintillators for comparison. The first material selected was a ‘standard’ plastic scintillator composition produced by Eljen Technologies, Inc., referred to as EJ-200. This plastic scintillator possesses a high light yield but possesses significant delayed luminosity/afterglow. As a result, this material was chosen as the light-yield reference standard. The second reference material used in this study is the well-known ‘BC-422Q’ high-rate plastic scintillator produced by Saint Gobain. This material possesses a low light yield on the order of 10% EJ-200 but exhibits much faster scintillation decay kinetics/reduced afterglow. The 1% (benzophenone) version of this product was selected due to its ubiquity for high-rate measurements and its balance between light yield and decay rate. The third reference material employed in this work was stilbene-doped bibenzyl, which is a molecular crystal grown from solution. This material possesses the lowest afterglow among known organic scintillators, although the primary decay time is longer than for BC-422Q. Stilbene-doped bibenzyl possesses a low fluorescence quantum yield ($\phi_F=0.1$) and a scintillation light yield that is comparable to BC-422Q (1%). Scintillation timing data from the literature were digitized due to the unavailability of this material. Table 1 provides the key advantages and disadvantages for these reference materials in comparison to the plastic scintillators developed in this work.

Table 1. Summary of scintillator key attributes.

<u>Scintillator Name</u>	<u>Advantages</u>	<u>Disadvantages</u>
Eljen EJ-200	Very high light yield, robust solid	Significant afterglow
Saint Gobaint BC-422Q (1%)	Low afterglow, robust solid	Low light yield
Stilbene-doped Bibenzyl	Lowest afterglow	Low light yield, low availability, fragile crystalline solid
Ir-doped Plastic (no filter)	High light yield, robust solid	Significant afterglow
Ir-doped Plastic (LP filter)	High light yield, low-moderate afterglow	Requires optical filter, low-moderate afterglow

Sn-loaded Plastic	Very high light yield, low afterglow, robust solid	Tin content may increase gamma-ray sensitivity
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RESULTS: Benchmark experiments were first performed for EJ-200 and BC-422Q (1%) reference materials to establish baseline values for the scintillation light yields and timing distributions. Stilbene-doped bibenzyl crystals were not commercially available and are prohibitively difficult to grow in the sizes required for these experiments. As a result, published literature data were cited for this referenced material.

In the first series of experiments, the baseline scintillation light yield was referenced to the ^{137}Cs pulse-height spectrum for EJ-200. This reference material is known to possess a scintillation efficiency of 10,000 photons/MeV electron equivalent, which translates to a relative light yield 64% that of anthracene primary light-yield standard. Photoluminescence measurements revealed a maximum emission wavelength of 425 nm, which ideally overlaps with the spectral sensitivity curve of a standard bialkali photomultiplier tube (PMT) used for optical photon detection. This property is associated with maximum detection efficiency for emitted photons. The maximum of the Compton scattering feature in the pulse-height spectrum was selected as the reference point for each scintillator's light yield. In the case of EJ-200, the light yield was 26 nV·sec (Figure 1), the units of which correspond to charge generated by the PMT. The charge was determined by integrating the digitized scintillation pulses over a time interval of 100 ns. The pulse-height spectrum for BC-422Q (1%) was similarly collected and found to provide a light yield of 2.8 nV·sec, which corresponds to a scintillation efficiency of 1,100 photons/MeV or 7% that of anthracene. The order-of-magnitude reduction in light yield relative to EJ-200 is consistent with the quenching mechanism for benzophenone, which non-specifically reduces both the prompt and delayed scintillation intensities. A similar light yield was reported for stilbene-doped bibenzyl, although the mechanism differs for these materials. In stilbene-doped bibenzyl, the low light yield is instead associated with the intrinsically low fluorescence quantum yield of bibenzyl.

Pulse-height spectra were collected for the two types of metal-loaded plastic scintillators, as shown in Figure 1. The traces labeled DNDO #119 and NRM-7.29.3 correspond to organotin-loaded plastic scintillators at tin loading ratios of 7% w/w and 16.5% w/w, whereas the Ir^{3+} doped sample traces correspond to 300 ppm Ir^{3+} w/w. For these samples, relative light yields of 0.44-0.94 EJ-200 were obtained, corresponding to 4,400-9,400 photons/MeV electron equivalent. The tin-loaded samples differ in the particular tin compound used, where DNDO #119 is based on $\text{Bu}_3\text{Sn}(\text{methacrylate})$ and NRM-7.29.3 is based on Me_4Sn . These results show that the light yield may be modified on the basis of the identity of the tin additive as well as the tin loading ratio. These observations are further supported by the scintillation timing distribution experiments, as discussed below. Another notable observations relating to the organotin-loaded plastics is the appearance of a photoelectric absorption peak, which corresponds to the full energy of the incident ^{137}Cs gamma ray (662 keV). This increased X-ray and gamma-ray

sensitivity distinguishes these samples from other organic scintillators. Pulse-height spectra for the iridium-doped plastic scintillators were collected with and without a long-pass optical filter

to assess the effect of selective wavelength-dependent emission. From the data in Figure 1, it is apparent that there is 50% reduction in the detected light yield for the optically filtered emission. This effect is qualitatively expected due to the removal of a significant amount of luminescence by the filter.

Scintillation timing distributions were collected for the reference materials as well as the metal-loaded scintillators prepared in this work. A representative set of these data are shown in Figure 2. From these data, it is apparent that sample PLF191 (300 ppm Ir^{3+}) exhibits the slowest scintillation decay kinetics. Although not shown in this plot, the reference scintillator EJ-200 possesses very similar decay behavior to PLF191 on this time-scale (100ns). The addition of a 450nm short-pass optical filter between PLF191 and the PMT photodetector results, as expected, in a significant decrease in the total afterglow rate. This is evident in Fig. 2 as a reduced amount of persistent luminescence over time. However, the filtered decay kinetics for PLF191 remains slower than the benchmark BC-422Q (1%) material. The other reference material, stilbene-doped bibenzyl, exhibits the most complete decay characteristics, for which the light intensity has decreased by four orders of magnitude after 80 ns. However, inspection of the prompt luminescence decay component for this scintillator reveals that the prompt decay lifetime is longer than both BC-422Q (1%) and DNDO #119 (7% Sn w/w). Bibenzyl may thus be characterized to possess the lowest overall afterglow but only an intermediate decay rate for the prompt emission component. Interesting decay kinetics were observed for DNDO #119, which comprises a 7% tin-loaded plastic scintillator composition. Inspection of the decay curve for DNDO #119 reveals a prompt decay that is faster than stilbene-doped bibenzyl but slower than BC-422Q (1%) and an afterglow that is less than BC-422Q (1%) and more than stilbene-doped bibenzyl. This is a noteworthy result, particularly when combined with the 7-fold greater light yield (Fig. 1) than either of these reference high-rate scintillators.

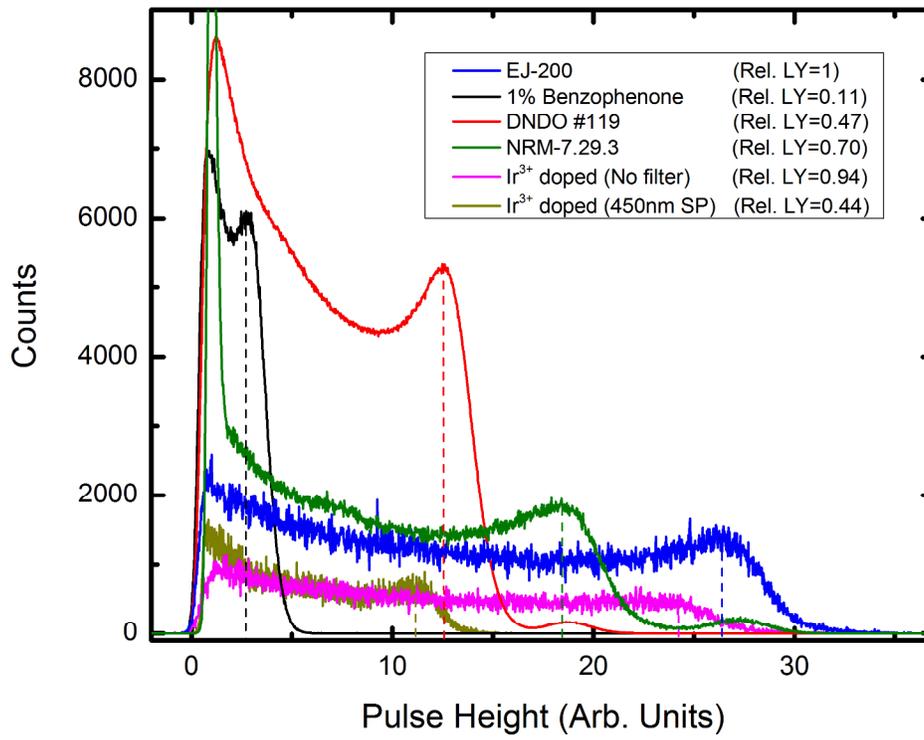


Figure 1. ¹³⁷Cs scintillation pulse-height spectra.

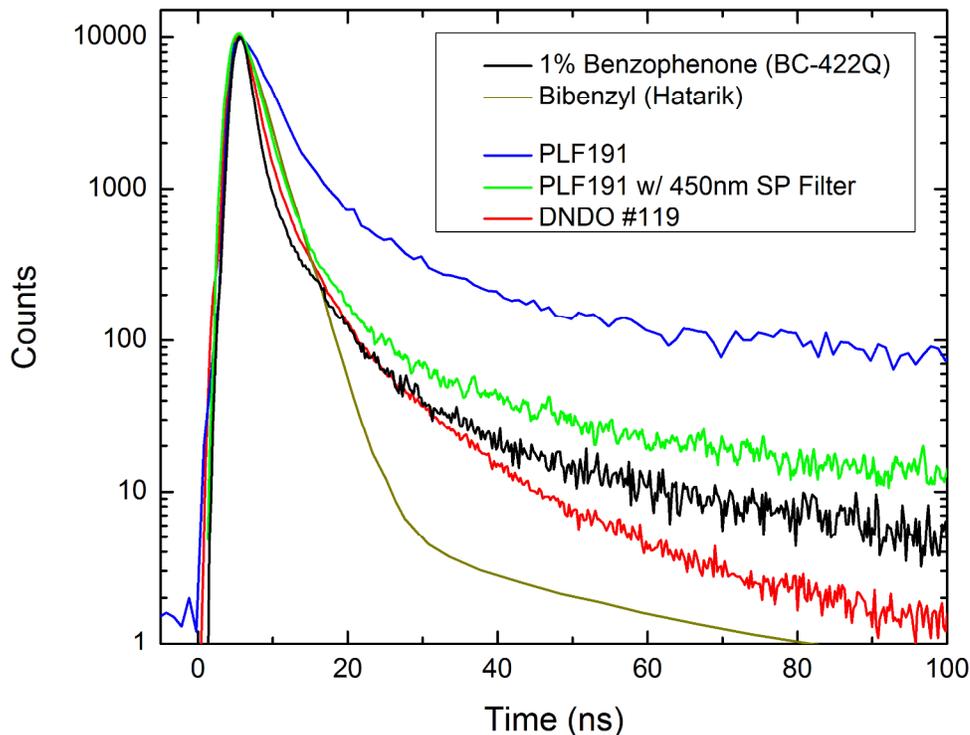


Figure 2. ^{137}Cs scintillation timing distributions. The stilbene-doped bibenzyl data were digitized from Ref. [1].

DISCUSSION AND ANTICIPATED IMPACT: The most compelling result of this study was the preparation of scintillators that emit 7 times more light than BC-422Q (1%) and stilbene-doped bibenzyl, while retaining similar scintillation decay kinetics to these reference materials. The implications of this finding are significant towards the applications stated above, namely high-rate radiation detection where pulse pile-up leads to a reduction in the fidelity of collected scintillation data. Pulse pile-up is simply defined as the observance of overlapping pulses that are not able to decay fully within the time-scale of recurring radiation events.

Active interrogation is one important application in which this problem is observed. Active interrogation is the use of an intense neutron or gamma-ray source to induce fission in special nuclear materials such as highly enriched uranium (HEU). This is of particular importance due to the low spontaneous fission rate of HEU and easily shielded characteristics of this illicit material. Existing scintillator materials used for active interrogation include inorganic scintillators for delayed gamma rays and organic scintillators for fast neutrons. In both cases, there is a need for high detection efficiency and timing resolution. These properties are intrinsic to the material of interest, as well as correlated with the size and geometric arrangement of the detector material. For this reason, the observation of increased gamma-ray sensitivity for the tin-loaded plastic scintillators produced in this work has positive implications for the detection of prompt and delayed gamma rays following an induced fission event from active interrogation.

However, the increased gamma-ray sensitivity in the tin-loaded plastics serves to increase the gamma-ray background signal when performing prompt or delayed neutron experiments. For this reason, one must carefully balance the experimental needs with the scintillator composition to achieve the best balance of physical and emission properties. A potential topic of future research is the systematic evaluation of the effects of spin-orbital coupling upon the scintillation decay kinetics. The present work has investigated an extreme and intermediate case, corresponding to organometallic additives that possess enormous spin-orbital coupling constants (Ir^{3+}) and additives that possess a moderate extent of spin-orbital coupling (Sn^{4+}). Additional studies would focus on additives with smaller atomic numbers than tin to decrease the photoelectric absorption cross section, as relevant to decreased gamma-ray backgrounds in high-rate neutron detection experiments.

Another application that could benefit from the low afterglow and high luminosity characteristics of the developed scintillators is in neutron diagnostics in inertial confinement fusion (ICF) studies. These experiments are concerned with elucidating the neutron yield and temperature (energy) for induced fission events in a particular target material. There are several avenues to this end, including excitation via the Z-machine at Sandia, NIF at LLNL, and the Omega Laser Facility at the University of Rochester. Figure 3 provides a representative illustration of the type of data obtained at the Z-machine using BC-422Q (1%) plastic scintillator as the detector material. Several features are highlighted on this plot, corresponding to the different radiation signatures obtained via neutron time-of-flight. In this case, the largest feature at ~ 3050 ns corresponds to the background Bremsstrahlung radiation that is inherent to the Z-machine. The scintillator afterglow is evident by the finite duration of the decay back to baseline, which requires approximately 150 ns. Interestingly, the secondary DT neutron peak appears around this time as a small feature in the spectrum. This is a particular instance where a higher luminosity and lower afterglow scintillator would benefit this application, where the higher luminosity would increase the signal-to-noise and the lower afterglow would further reduce the amount of overlap from the Bremsstrahlung background and the neutron peak of interest. A similar benefit would be observed for the very important down-scattered DD neutron feature, which is barely resolved in the present spectrum due to low signal-to-noise and overlap with the tail of the DD neutron peak.

Based on the above attributes, the materials developed in the present work are well positioned to transition into a full development project. One particularly relevant opportunity comprises the 2015 DNDO-TARD call for proposals, which sought detector materials for the detection of neutrons or gammas from photon and/or neutron induced fission. Of particular relevance was the requirement of low cost, non-liquid, non-gaseous, and non-hazardous detector materials that are temperature insensitive and mechanically robust. All of these attributes are characteristic to the metal-loaded plastic scintillators reported in this study.

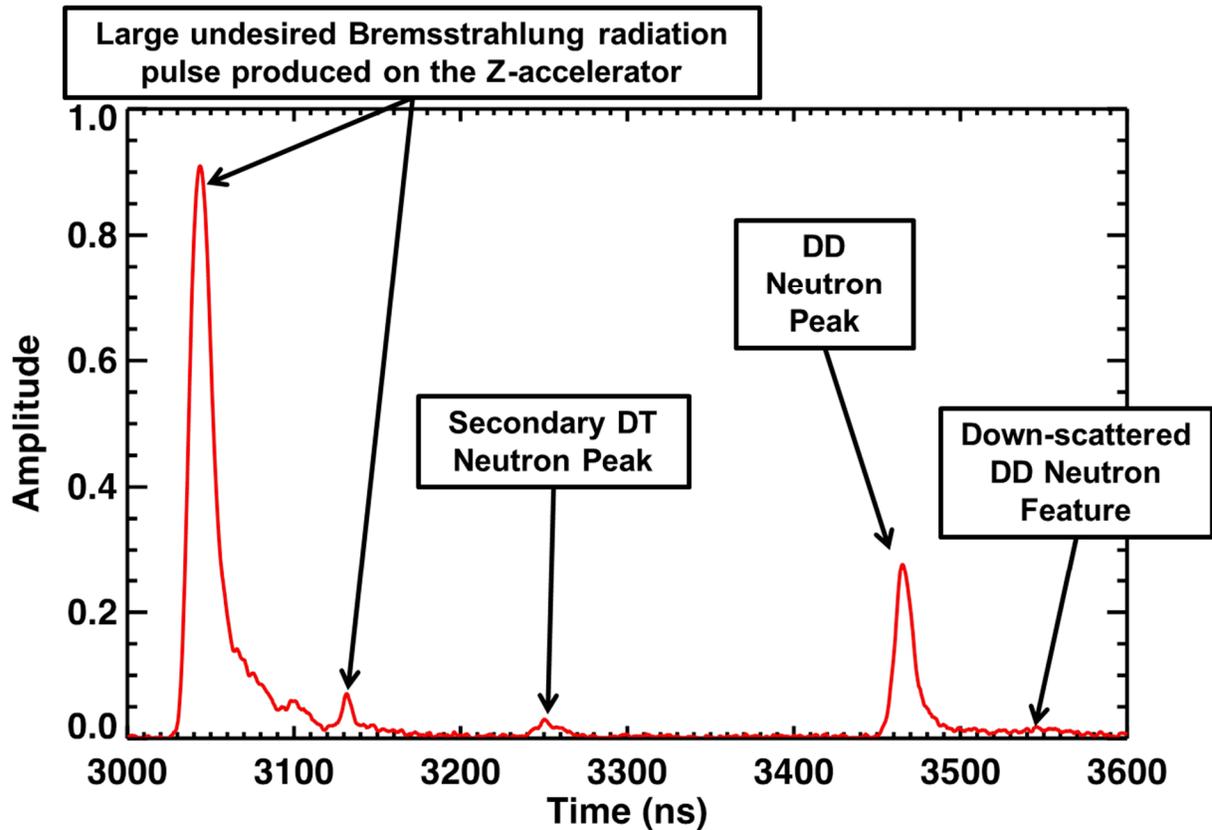


Figure 3. Detector intensity versus time plot for a neutron time-of-flight experiment on the Z-machine using BCF-422Q (1%) plastic scintillator as the detection material.

CONCLUSION: Recent progress in high-rate radiation detection experiments in active interrogation and inertial confinement fusion studies have obviated the need for improved detector materials. Of particular importance are higher scintillation light yields for improved signal-to-noise of weak radiation signatures and faster scintillation decay rates for improved timing resolution in time-of-flight measurements. The present work has shown that the addition of carefully designed organometallic additives to plastic scintillator matrices may improve both of these properties relative to scintillators presently used in these applications.

REFERENCES:

[1] Hatarik, R.; Bernstein, L.A.; Caggiano, J.A.; Carman, M.L.; Schneider, D.H.G. *Rev. Sci. Instrum.* **2012**, *83*, 10D911.