Advanced Plastic Scintillators for Fast Neutron Discrimination

Project Number: SL11-PlasticScintND-PD2Jg

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1. INTRODUCTION

The present work addresses the need for solid-state, fast neutron discriminating scintillators that possess higher light yields and faster decay kinetics than existing organic scintillators. These respective attributes are of critical importance for improving the gamma-rejection capabilities and increasing the neutron discrimination performance under high-rate conditions. Two key applications that will benefit from these improvements include large-volume passive detection scenarios as well as active interrogation search for special nuclear materials. Molecular design principles were employed throughout this work, resulting in synthetically tailored materials that possess the targeted scintillation properties.

2. SUMMARY OF KEY FINDINGS

The present work reports progress in FY14 on ‘two-state’ triplet-harvesting scintillators, which for the first time enables direct control over the factors that enable neutron/gamma particle discrimination. This technology was granted a 2014 R&D100 award based on discoveries made during this project. Work during the first life-cycle (FY11-FY13) revealed several significant implications, for which further advances were made in FY14. A summary of these findings are provided below. Text in parentheses provide practical implications for each result.

- Demonstrated efficient fast neutron discrimination capabilities in a plastic scintillator with ~$1\cdot10^{-4}$ gamma-rejection at threshold of 400 keVee- (Mechanically robust, no toxicity/flammability concerns, convenient packaging).
- Materials are compatible with traditional pulse-shape discrimination (PSD) techniques- (Drop-in replacement for existing liquid scintillators).
- Devised a previously unreported spectral-based discrimination scheme (SSD) based upon the multi-wavelength emission properties of the ‘two-state’ scintillator- (Optical discrimination method relaxes timing/instrumental requirements vs. PSD).
- Introduction of new luminescence that boosts the scintillation light yield over traditional organic scintillators. Present materials show up to 20% higher light yields and neutron discrimination capabilities versus EJ-204 commercial plastic scintillator.
- Improved triplet-harvesting efficiency via electron- and hole-transport additives- (Reduced Ir^{3+} doping levels and longer optical path lengths).
- Tunable photophysical properties, including respective emission wavelengths and lifetimes from each luminescent dopant- (Properties can be rationally modified to suit the application of interest).
- Bi-exponential decay characteristics that are faster than traditional organic scintillator materials- (Improved scintillation performance at high count rates).

Activities in FY14 focused heavily on practical considerations related to reducing the doping requirements, obtaining longer optical path lengths, and optimizing the bulk polymerization conditions for reproducibility/scale-up.

3. RESULTS, DISCUSSION, AND CONCLUSIONS

A key breakthrough in FY14 was the implementation of electron- and hole-transporting additives to increase the efficiency of heavy-atom induced triplet harvesting. This strategy was initially proposed based on knowledge of the different energy-transfer processes that may occur in organic host-guest systems. In FY11-FY13, scintillator materials were developed based upon direct orbital overlap (Dexter energy transfer) of pi electrons on the host polymer and the metal-to-ligand charge-transfer (MLCT) electrons on the dopant complex. The efficiency of this interaction has been shown to obey an exponential distance dependence, which constrains this process to relatively short distances on the order of several nanometers. Consequently, initial triplet-harvesting scintillator compositions required relatively high doping concentrations on the order of 0.05-0.2% Ir^{3+} (w/w) to provide sufficient delayed luminosity for neutron/gamma particle discrimination. It was of interest to achieve similar performance at lower Ir^{3+} doping ratios due to the high cost of iridium and the increased potential for optical self-absorption in more highly doped samples.

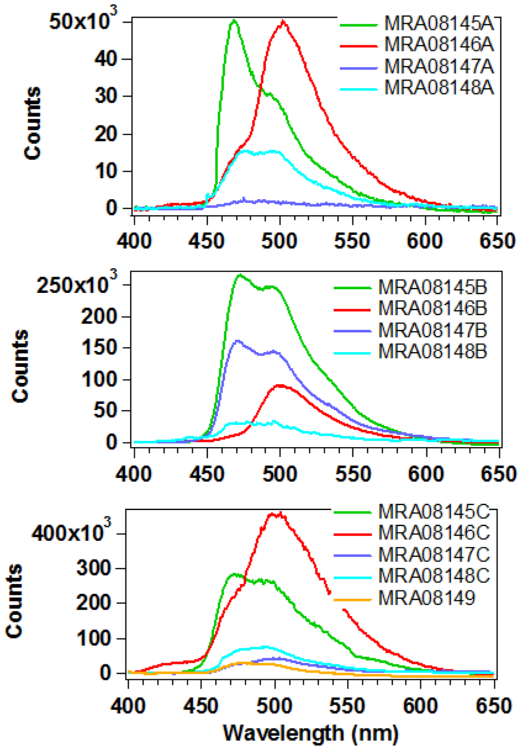


Figure 1. Cathodoluminescence emission spectra for MRA-08-145(A-C) through MRA-08-148(A-C). Compositions with an "A" suffix correspond to 0% Ph_3PO additive, whereas "B" and "C" suffixes correspond to 5% and 10% Ph_3PO (w/w).

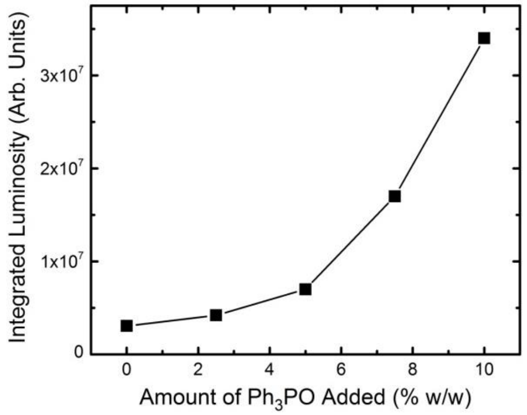


Figure 2. Plot of the integrated cathodoluminescence intensity for MRA-08-146(A-E) as a function of added Ph_3PO electron-transporting material. The contents of each sample were otherwise identical.

Direct recombination of electrons and holes was considered in FY14 to increase the efficiency of triplet harvesting, thereby lowering the iridium doping requirements. In this process, mobile electrons and holes may contribute to additional triplet guest luminescence based on the Coulombic forces contributing to exciton formation. In a simplified interpretation, increased mobility of electrons and holes within the scintillator will lead to a higher probability for radiative recombination at emissive Ir^{3+} sites. An initial test of this hypothesis was performed using a polyvinylcarbazole (PVK) scintillator doped with 0.2% Ir^{3+} that was previously shown to exhibit PSD. A PVK-based material was selected for this initial test due to the intrinsic hole-transporting nature of this material. By contrast, polystyrene and polyvinyltoluene do not efficiently transport electrons or holes. Cathodoluminescence (CL) emission spectra, scintillation pulse-height spectra, and scintillation timing measurements were collected for the as-synthesized triplet-harvesting scintillator material and an analogous sample to which 2.5-10% (w/w) of triphenylphosphine oxide (Ph_3PO) electron-transporting material was added. The initial CL results were quite convincing in showing that the balanced hole and electron transport in the Ph_3PO-containing samples led to significant improvements in the luminosity of the material (Fig. 1). For example, the addition of 10% Ph_3PO led to an eleven-fold increase in the integrated CL emission intensity of MRA-08-146A vs. MRA-08-146C. Similar results were observed in the scintillation timing measurements, for which the increased light yield could be directly attributed to delayed Ir^{3+} emission. A plot of the integrated CL luminosity as a function of Ph_3PO additive is provided for samples

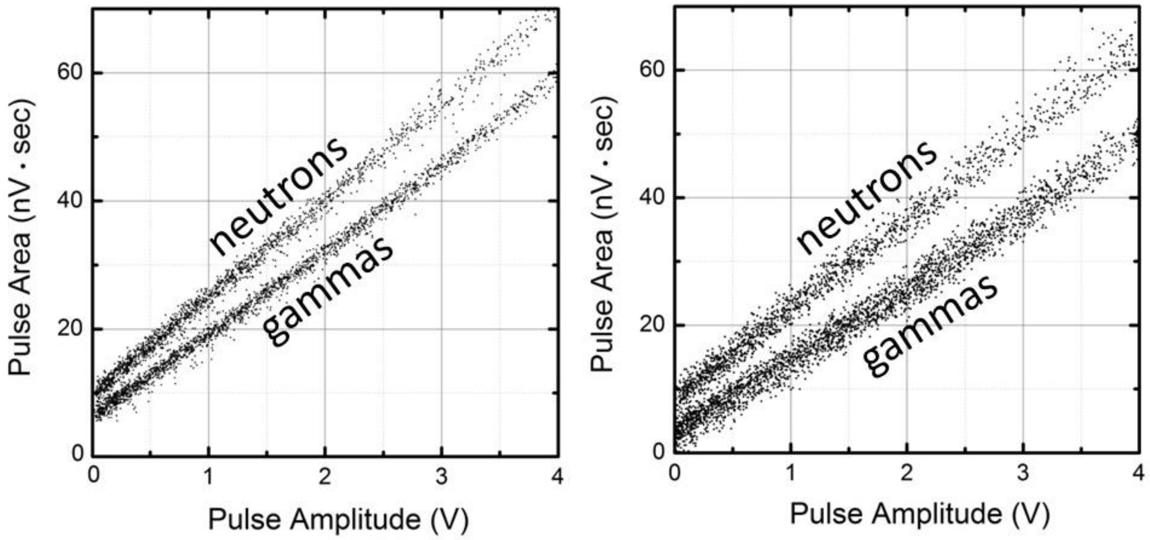
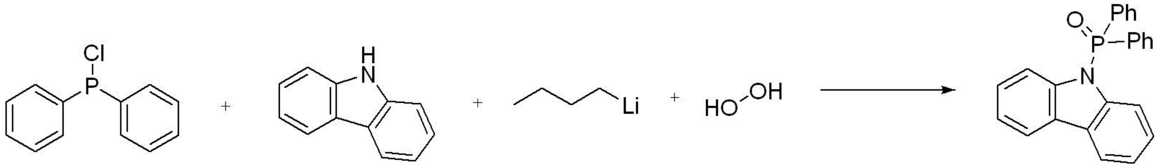


Figure 3. **Pulse-shape discrimination histograms for an unshielded AmBe source at a discrimination threshold of 400 keVee for EJ-301 reference liquid scintillator (left) and an equivalent 10 mL volume of a triplet-harvesting plastic scintillator (right).**



Scheme 1. **Generalized synthesis of a bipolar electron- and hole-transport additive based on diphenylphosphine oxide and carbazole, respectively.**

MRA-08-146(A-E) in Fig. 2. Other electron-transport and bipolar electron/hole transport materials were also investigated, comprising amine-, phosphine oxide-, oxadiazole-, and carbazole functional groups. In particular, a bi-functional compound based on carbazole and diphenylphosphine oxide subunits was found to improve the transport properties of polystyrene-based compositions due to the presence of both electron- and hole-transport moieties (Scheme 1).

Corresponding PSD measurements were collected on the above samples to determine if particle discrimination capabilities are retained following the addition of transport compounds. It was initially hoped that the greater delayed luminosity at a given Ir^{3+} concentration could also be used to significantly increase the overall scintillator luminosity beyond the 10,000-11,000 photons/MeV obtained for PSD compositions produced in FY13. However, experiments in FY14 have generally shown that PSD eventually degrades as the singlet:triplet luminosity ratio decreases. As a result, the best performing scintillator composition produced to date yields 12,400 photons/MeVee and $\sim 1 \cdot 10^4$ gamma-rejection at a discrimination threshold of 400 keVee. Consequently, the improved triplet-harvesting efficiency mediated by electron- and hole-transport additives finds greatest utility towards decreasing the Ir^{3+} doping requirements for lowest cost and longest optical attenuation length. While this 12,400 photons/MeVee light yield is approximately one third greater than the PSD plastic reported in: Zaitseva et al, Nucl. Instr. Meth. A, 2012, 88-93, the measured PSD-FOM values at a given energy threshold were found to be comparable. A PSD histogram for the above referenced triplet-harvesting plastic scintillator is provided in Fig. 3 (right) versus EJ-301 liquid scintillator (Fig. 3, left). The above properties were previously predicted using the Photon Arrival Quantile Statistics (PAQS) model described in the FY11-FY13 final report. This model ultimately determines the optimum pulse shape for PSD based

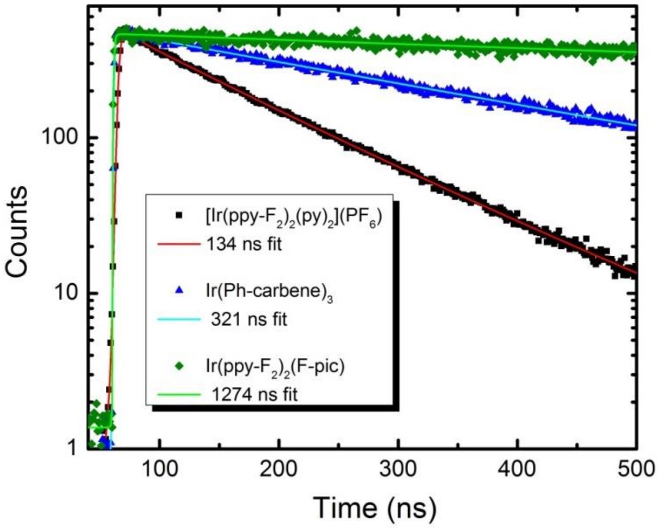


Figure 4. Photoluminescence decay curves for three organometallic complexes in cyclohexane solvent.

upon simulations of the detected photon distributions in the wavelength and time domains using order statistics. PAQS predicted that the PSD figure-of-merit would degrade most quickly for large relative numbers of photons emitted from long-lifetime states, i.e. longer than 1μs. With this consideration in mind, we turned our attention to synthesizing shorter-lifetime organo-metallic additives to replace the 800 ns-1.3 μs complexes used in preceding work. According to PAQS, the use of shorter lifetime dopants would enable greater resistance to PSD degradation at higher delayed luminosity levels.

Density-functional theory quantum calculations were thus employed to initially screen candidate iridium compounds that might be expected to have short emission lifetimes. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) wavefunctions for each compound was calculated to assess the degree of metal-to-ligand charge-transfer (MLCT) character, which correlates with the degree of spin-orbital mixing between Ir^{3+} and organic coordinating groups. It was hypothesized that weaker MLCT interactions would lead to properties closer to that of the free organic ligand, i.e. shorter emission lifetimes. Based on this assumption, we identified several candidate compounds based on the strength of their MLCT interactions. Two compounds that were synthesized include $Ir(Ph\text{-}carbene)_3$ and $[Ir(ppy\text{-}F_2)_2(py)_2][PF_6]$. Initial photophysical characterization of these complexes was performed for dilute solutions in cyclohexane. The photoluminescence decay data for these compounds are provided in Fig. 4, shown in comparison to the benchmark material $Ir(ppy\text{-}F_2)_2(F\text{-}pic)$. The results indicate that the above approach was successful in shortening the emission lifetime from approximately 1274 ns in $Ir(ppy\text{-}F_2)_2(F\text{-}pic)$ to 134 ns in $[Ir(ppy\text{-}F_2)_2(py)_2][PF_6]$.

Progress was made in FY14 towards improving the count-rate performance of existing organic scintillators. Existing materials are characterized by non-exponential delayed emission owing to the dispersive nature of triplet-triplet annihilation (TTA), as shown by the non-exponential tail for the EJ-301 liquid scintillator (red trace) in Fig. 5. In contrast, the molecularly-derived delayed emission for a triplet-harvesting scintillator (PLF #234) is intrinsically exponential in nature, as shown for the black trace in Fig. 5. Consequently, the luminescence for PLF #234 decays at a faster rate than EJ-301. Future work is required to further explore this property in the context of high count-rate applications such as active interrogation.

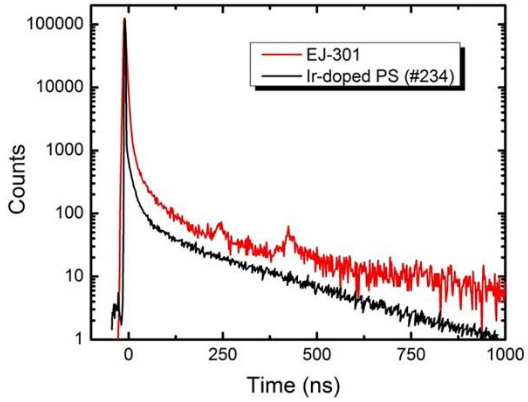


Figure 5. Scintillation timing distributions describing the average pulse shape for EJ-301 liquid scintillator and PLF #234 doped plastic scintillator. The excitation source was ^{137}Cs gamma rays.