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Bismuth-loaded plastic scintillators for gamma-ray spectroscopy

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Abstract – Polyvinylcarbazole polymer scintillators with high loading of a bismuth organometallic exhibit good light yields, and are found to be capable of gamma-ray spectroscopy. When activated by a standard fluor, diphenylanthracene, a bismuth-loaded polymer produces ~ 12000 photons/MeV, exhibits an emission maximum at 420 nm, a ~ 15 ns decay, and energy resolution of 9% at 662 keV is measured. The same bismuth-loaded polymer doped with an iridium complex fluor has an emission maximum of 500 nm, a decay time of 1.2 μ s, a light yield of ~ 30000 photons/MeV, and energy resolution better than 7% FWHM at 662 keV.

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Scintillator-based gamma-ray spectroscopy requires scintillator materials with high light yield, excellent light yield proportionality, prompt emission decay and high effective atomic number for high photoelectric cross-section. Plastic scintillators find many uses in radiation detection due to their low cost and ease of fabrication in large volumes. Plastic scintillators are generally used for gross counting, though some work using energy windowing has been shown useful to provide differentiation between gamma sources [1]. Unfortunately plastic scintillators also have low light yields, and more importantly, their low effective Z ($Z_{\text{eff}} \approx 4.5$) results in poor photopeak efficiency. Attempts to increase Z_{eff} by doping with heavy metals to induce a photopeak have been made in the past [2–4]. However, difficulties due to poor solubility of the high- Z component and quenching of luminescence were never resolved. More recently, thin films of polyvinylcarbazole (PVK) doped with an iridium complex (Ir-complex) fluor were found to offer improved scintillation light yields [5]. This is due to the same mechanism now widely employed in organic light-emitting diodes (OLEDs), wherein it has been found that Ir-complex fluors are capable of capturing and emitting both singlet and triplet excitons, due to spin-orbit coupling [6]. While work with thin films demonstrated that higher light yields are possible with Ir-complexes, large scintillator volumes are needed for practical counting rates. Furthermore, if a high- Z component can be introduced, without decreasing

the light yield, the capabilities of such a material could result in a practical gamma-ray spectroscopy scintillator for radioisotope identification applications.

In this report, we describe our work on forming plastic monoliths incorporating soluble organometallic bismuth compounds and Ir-complexes to produce high light yield scintillators capable of gamma spectroscopy with good energy resolution. Additionally, we provide rationalization for the superior performance of these materials over previous attempts to produce a photopeak in plastic scintillators. While phenyl derivatives of heavy metals such as tin, lead and bismuth have been added to plastic scintillators in the past, and in some cases resulted in the appearance of poorly resolved photopeaks with gamma-ray excitation, the materials were never considered useful because of the severe quenching of luminescence upon addition of organometallics. Although results were never fully rationalized in the literature, modern understanding of exciton migration and fluorescence phenomena suggests two mechanisms which may account for this decreased light yield. The HOMO-LUMO gaps for the phenyl metal derivatives (*e.g.* 4.1 eV for BiPh_3)¹ and the most commonly used plastic scintillator matrix, polyvinyl toluene (4.2 eV) [7], are of similar energy and exciton transfer between the two is likely facile (fig. 1(A)). If the organometallic species either: 1) introduces a fast exciton relaxation pathway, or, 2) have a fast intersystem crossing to the triplet exciton state (a non-emissive state for the organic fluors in these

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¹Estimated from UV-vis.

Table 1: Composition and summary of spectroscopy results of the samples used in this study.

Sample	Matrix	Fluor	BiPh ₃ Wt. %	β LY (Ph/MeV)	Relative gamma light yield, 662 keV	Resolution FWHM, 662 keV	Resolution, FWHM, 59.5 keV
1a	PVK	3% DPA	40%	11880	0.66	9%	39%
2a	PVK	3% FIrpic	40%	30641	0.78	6.8%	26%
2c	PVK	3% FIrpic	—	24191	0.73	9%*	30%
Eljen EJ208	PVT	Proprietary	—	17000	1.0	8%*	30%

*From fit to Compton edge.

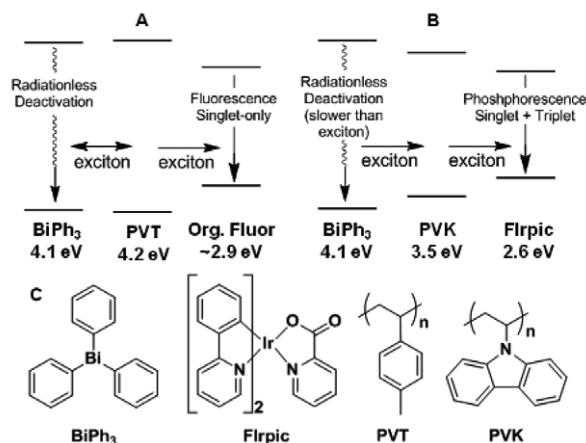


Fig. 1: (A) Energy levels of Triphenyl Bismuth (BiPh₃), Polyvinyltoluene (PVT) and a typical organic fluor, Diphenyl Anthracene (DPA). (B) Energy levels of BiPh₃, Polyvinylcarbazole (PVK) and an iridium complex fluor (FIrpic). (C) Chemical structures of the constituent materials used in the high-Z polymer scintillators described in this work.

systems), the light yield of the resulting scintillators will be significantly diminished.

Proper materials choice can circumvent both of these problems. Use of a polymer matrix with an excited state energy level lower than that of the organometallic dopant should allow energy transfer to the matrix from the dopant to be competitive with relaxation and intersystem crossing pathways and prevent energy transfer in the other direction (fig. 1(B)). Since one outcome of the high-loading of bismuth organometallics may be to increase the proportion of triplet excitons in the system, it is even more desirable that a spin-orbit coupling fluor be used to enhance the light yield. Although it is beyond the scope of this study to show to what extent mechanisms 1) and 2) are operating in these materials, we show conclusively that following the outlined materials selection strategy results in plastic scintillators with photopeaks and high light yields.

For this study we have chosen polyvinylcarbazole (PVK) as the polymer matrix (bandgap 3.5 eV) [7], triphenylbismuth (BiPh₃) as the high-Z dopant, and two different fluors, a standard organic fluor, diphenylanthracene (DPA), and an Ir-complex, FIrpic (bandgap 2.6 eV) [8]

as the spin-orbit coupling fluor. Additional comparisons are made with a commercial PVT scintillator from Eljen Technologies. The materials choices were based on: 1) the energy levels of the materials (shown in figs. 1(A) and (B)), 2) the high-Z/volume ratio that the Bi complex can attain in this matrix, combined with its low toxicity and low cost, and 3) the high fluorescence efficiency of FIrpic from both singlet and triplet states. We made two series of polymer scintillators. Samples 1a–c are PVK-based parts with 3% by weight DPA and 40%, 25% and 0% by weight of BiPh₃ respectively. In samples 2a–c FIrpic is used as fluor, also 3% by weight. Structures are shown in fig. 1(C). A summary of selected sample compositions and important measured values can be found in table 1.

All samples except the Eljen standard were synthesized by bulk polymerization of 9-vinyl carbazole initiated by a peroxide. The monomer, peroxide initiator, BiPh₃ and fluor were placed in a polymerization vessel under nitrogen atmosphere and heated overnight. The temperature was maintained between the melting point of 9-vinyl carbazole (65 °C) and the decomposition temperature of BiPh₃ (100 °C). The maximum loading of BiPh₃ in the PVK-based samples was 40% by weight, resulting in $Z_{\text{eff}} = 26$, above which the Bi compound is not soluble. These compositions gave transparent samples which were light yellow when they contained FIrpic and colorless with DPA. Longer heating times gave darker yellow or brown samples, presumably from the decomposition of BiPh₃. Samples were right cylinders 18 mm in diameter and 2 mm in height after being shaped and polished, except the Eljen standard which was 10 mm by 5 mm.

Decay lifetimes were acquired using a flashlamp-pumped Nd:YAG laser at 266 nm with 20 ns FWHM pulses. Luminescence was collected with a monochromator coupled to an R928 Hamamatsu PMT and read out by an oscilloscope. The decay times measured for the DPA and the FIrpic fluors were 14 ns and 1.25 μ s, respectively. Radioluminescence spectra were acquired using a ⁹⁰Sr/⁹⁰Y source (average beta energy \sim 1 MeV), and were collected with a Princeton Instruments/Acton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera and corrected for spectral sensitivity. All FIrpic-containing samples were found to have higher beta light yields (β LY) than the Eljen standard, using silicon CCD readout. Figure 2(A) shows that the radioluminescence for the PVK/DPA/BiPh₃ system decreases

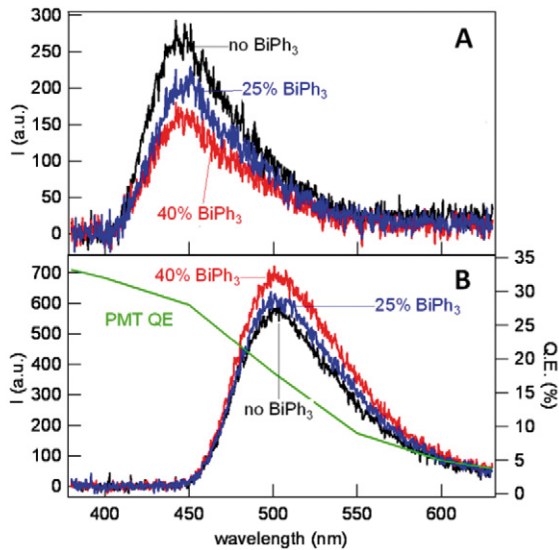


Fig. 2: (Colour on-line) (A) Beta radioluminescence spectra acquired with samples 1a–c. (B) Beta radioluminescence spectra acquired with samples 2a–c and the spectral response quantum efficiency curve for a super-bialkali photomultiplier tube. All spectra may be compared in an absolute way. Note that the standard blue-emitting organic fluors such as DPA are a much better spectral match to the PMT response.

as the BiPh₃ loading increases. In contrast, fig. 2(B) shows that the β LY for the PVK/FIrpc/BiPh₃ system, light yield increases slightly with addition of BiPh₃. This may be attributable to an increased triplet population with addition of BiPh₃. An increased triplet population would decrease the light yield from DPA as it emits only from the singlet state, while the Ir-complex fluor emits efficiently from singlet and triplet states and would not be subject to the the same decrease in light yield.

Gamma-ray spectra were acquired using a Hamamatsu R6231-100 superbialkali PMT. Plastic scintillators were centered on the entrance window, optically coupled to the PMT with optical grease and wrapped with several layers of Teflon tape. The PMT signals were shaped with a Tennelec TC 244 spectroscopy amplifier (8 μ s shaping time for FIrpc activated samples and 1 μ s for DPA activated samples) then recorded with an Amptek MCA8000-A multi-channel analyzer. The spectra were fit with a spectrum simulator to evaluate the Compton edge and photopeak positions (to estimate the scintillation light yield), its energy resolution, assessed by a Gaussian full width at half maximum (FWHM), as well as the escape peak, due to the Bi $K\alpha$ X-rays. The spectrum simulator utilized is a simple one-dimensional treatment based on the average geometric chord length of the scintillator optic, and incorporates the effects of photoelectric absorption, Compton scattering, Compton scattering followed by photoelectric absorption, double Compton scattering, and double Compton scattering followed by photoelectric absorption. Gamma light yields are determined by direct

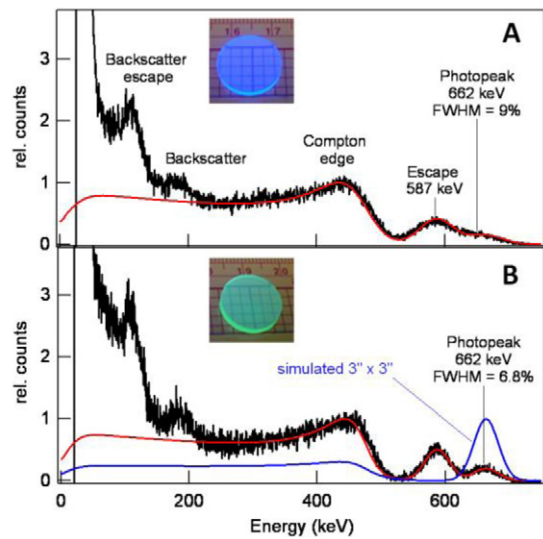


Fig. 3: (Colour on-line) (A) Cs-137 pulse height spectrum acquired with sample 1a exhibits several spectral features, including the photopeak, an escape peak (due to the Bi-209 $K\alpha$ X-rays 74.8 and 77.1 keV), the Compton edge, a backscatter peak and the backscatter escape peak. A fit reveals energy resolution at 662 keV of 9% is overlaid (red trace). The inset photo shows the sample used, illuminated by a UV lamp. (B) Cs-137 pulse height spectrum acquired with sample 2a, and a fit that indicates energy resolution at 662 keV of 6.8% (red trace). An additional simulated spectrum is shown, of a 3" \times 3" PVK/FIrpc/BiPh₃ sample with equivalent performance to the \sim 1 cm³ sample studied here. With a larger-size sample, the escape peak is not observed, and gamma spectroscopy with resolution similar to NaI(Tl) would be obtained.

comparison of the Compton edge with that of an Eljen EJ208 sample. Figure 3(A) shows the pulse-height spectra acquired using the 662 keV gamma from ¹³⁷Cs for the DPA-activated sample 1a, with resolution measured at 9%. Figure 3(B) shows the FIrpc-activated sample 2a, producing resolution of 6.8% at 662 keV. In these samples two peaks are present, a full energy peak and an escape peak corresponding to the loss of a 77 keV X-ray generated when an electron falls in to the vacancy in the core Bi shell created by the photo electron. This escape peak is greater in area than the full energy peak due to the moderate Z_{eff} of the samples and their small volume. We have modeled the gamma spectra of scintillators of different sizes but the same composition as sample 2a. This simulation, shown in fig. 3(B), reveals that a cylindrical sample with diameter and height of 3" \times 3" should give only the full energy peak, and offer gamma spectroscopy performance similar to NaI(Tl). The peak-to-total ratio for the simulated spectrum for a 3" \times 3" Bi-loaded plastic scintillator is 0.3. This compares well with the peak-to-total ratio for NaI(Tl) of 0.5 for the same size, and would thus constitute a useful counting rate for gamma-ray spectroscopy.

Cs-137 pulse height spectra of the PVK/FIrpc/BiPh₃, 2a, and the PVK/FIrpc, 2c, samples are shown in fig. 4.

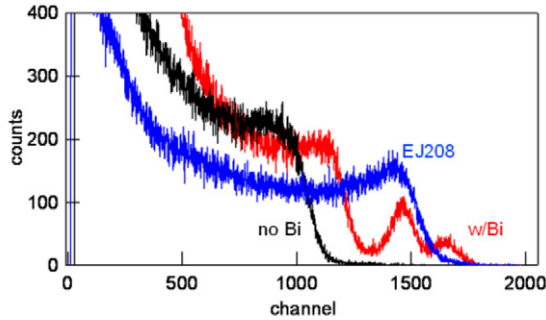


Fig. 4: (Colour on-line) Cs-137 pulse height spectrum acquired with samples 2a (red trace), sample 2c (black trace) and the commercial EJ208 sample, which is activated with a standard blue-emitting organic fluor (blue trace). The pulse heights reveal that the relative light yields with superbialkali PMT readout are EJ208 > PVK/FIrpc/BiPh₃ > PVK/FIrpc. Thus, even though the PVK/FIrpc samples produce a higher absolute light yield, as measured by beta radioluminescence, the effective light yields with PMT readout are slightly lower than the commercial plastic scintillator.

Although the normalized integrated β radioluminescence light yields, measured with a silicon photodetector, of these samples are in the 30,000 Ph/MeV range, their pulse heights with bialkali PMT readout are slightly less than that of the EJ208 sample. As in the β light yield measurements, sample 2a is brighter than 2c in the gamma pulse height spectra (Compton edge shifted to higher channel number). It may be that, as mentioned earlier, BiPh₃ increases the proportion of triplet excitons in the system, which are longer lived and more likely to reach a fluor molecule before relaxing. To verify this hypothesis detailed time-resolved transient absorption/luminescence spectroscopy studies will be required. Table 1 and fig. 4 show that the blue spectra from the EJ208 and the DPA-activated samples provide a higher effective light yield with PMT readout, compared to the green emission from the Ir-complex. Finally, in fig. 5, we measured the gamma spectra of the PVK/FIrpc/BiPh₃ and the PVK/FIrpc samples, 2a and 2c, with an Am-241 source, with gamma energy of 59.5 keV. The intensity of the photopeak is about 25 \times stronger for the BiPh₃-containing sample, and the resolution is slightly better, at 26%.

Polyvinylcarbazole-based plastic scintillators loaded with up to 40% triphenyl bismuth and activated with either standard singlet fluors or spin-orbit coupling fluors, may be formed with excellent mechanical integrity and high transparency. The light yields obtained with the iridium complex spin-orbit coupling fluor (FIrpc) is about 3 \times that of the standard fluor, and the energy resolution with this sample is superior, as well. Energy resolution measured for the FIrpc-activated sample at 59.5 and 662 keV are 26% and 6.8%, respectively. These initial

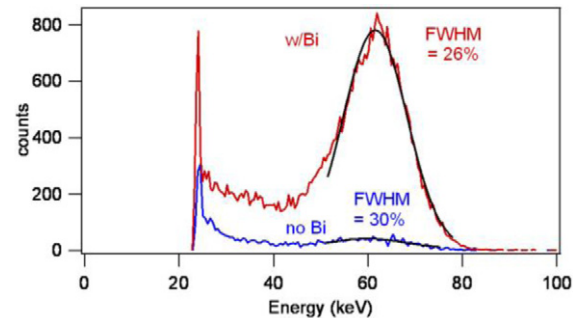


Fig. 5: (Colour on-line) Pulse height spectra acquired with an Am-241 source of sample 2a (red trace) and of sample 2c (blue trace) reveal resolution at 59.5 keV of 26% and 30%, respectively. The higher effective Z of sample 2a produces a $\sim 25\times$ stronger photopeak at this energy.

results acquired with small samples are very promising, and scaleup to larger volumes is in progress. Large polymer scintillators offering equivalent performance to those reported here would have a wide range of uses, potentially replacing single crystals for some applications, and expanding the capabilities of plastic scintillators in applications where they are currently employed.

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