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New organic crystals for pulse shape discrimination

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Efficient, readily-available, low-cost, high-energy neutron detectors can play a central role in detecting illicit nuclear weapons since neutrons are a strong indication for the presence of fissile material such as Plutonium and Highly-Enriched Uranium. The main challenge in detecting fast neutrons consists in the discrimination of the signal from the gamma radiation background. At present, the only well-investigated organic crystal scintillator for fast neutron detection, in a n/γ mixed field, is stilbene, which while offering good pulse shape discrimination, is not widely used because of its limited availability and high cost.

In this work we report the results of our studies made with a number of new organic crystals, which exhibit pulse shape discrimination for detection of fast neutrons. In particular 1,1,4,4-tetraphenyl-1,3-butadiene features a light yield higher than anthracene and a Figure of Merit (FOM) for the pulse shape discrimination better than stilbene. New crystals are good candidates for the low-cost solution growth method, thus representing promising organic scintillators for widespread deployment for high-energy neutron detection.

***Index Terms*—Neutron detectors, Scintillation detectors.**

I. Introduction

The ability to efficiently detect low-level high-energy neutrons in a strong gamma ray background is of major importance for nuclear nonproliferation and for the detection of illicit nuclear materials since fast neutrons are strongly suggestive of the presence of fissile material such as Plutonium and Highly-Enriched Uranium. Organic scintillators are employed to detect fast neutrons partly due to their high content of hydrogen that allows neutron detection via proton recoil [1]. For these detectors, the discrimination of the neutrons over gamma rays is possible with the use of the pulse shape discrimination (PSD), whereby the gamma ray and the neutron responses of the material are distinguished by way of the delayed temporal signal characteristics of neutrons [2]-[4].

At present only few liquid organic scintillators featuring the PSD property are available for neutron detection. Among solid compounds, single-crystal stilbene has been found to be the most effective material for n/γ discrimination [5]. Nevertheless, a widespread deployment of this crystal is limited since the Bridgeman growth technique utilized results in high cost and low availability. We are motivated to identify both lower cost crystal growth methods and to identify organic crystals alternative to stilbene with a final goal to establish a database of scintillation properties of organic crystals with potential for fast neutron detection.

Recent developments in commercial ultrafast waveform digitizers have opened the door to digital PSD [6]-[8], which represents a powerful tool for fast screening of new scintillator materials for neutron detection. In this work, we report first results on the scintillation and PSD studies made with several new organic crystals. For this research, we focus our attention on common aromatic compounds with low Z constituents and high content of hydrogen. Among the new crystals we have grown and studied are ammonium salicylate, salicylamide, triphenylbenzene, tetraphenylbutadiene, anthracene and diphenylanthracene, which exhibit good optical quality and have scintillation light yields (LY) comparable to stilbene. Since all investigated crystals were grown using solution-growth technique, which is generally the lowest cost option for producing large-size optical crystals [9], some of these materials may enable future widespread deployment of organic crystal-based high-energy neutron detectors.

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II. Equipment and Methods

In this study, we tested the scintillation and PSD properties of six different single crystals from four types of luminescent compounds:

- Derivative of benzene (one phenyl ring) compounds: ammonium salicylate and salicylamide;
- Poly-phenyl rings compounds: 1,3,5-triphenyl-benzene and 1,1,4,4-tetraphenyl-1,3-butadiene;
- Condensed poly-phenyl rings compound: anthracene;
- Compound with a combination of separated and condensed poly-phenyl rings: 9,10-diphenylanthracene.

All crystals were grown using slow evaporation techniques. Raw materials and solvents (methanol, ethanol and toluene) were purchased from Aldrich or Acros Organics. Some of the initial commercially produced compounds had visible traces of impurities shown by the yellow color in prepared solutions. In most cases, this coloring could be almost completely removed by multiple re-crystallization (as for 1,3,5-triphenyl-benzene). Crystals of 9,10-diphenylanthracene, however, remained slightly yellow indicating the need for more complex purification procedures that may be pursued in future work. Additional studies were made with commercial stilbene that was used as a scintillation and PSD comparison standard.

The scintillation properties of the crystals were evaluated from the emission spectra acquired under alpha and beta excitation. A $^{90}Sr/^{90}Y$ source (average beta energy ~1 MeV), which provides an excitation in the crystals expected to be equivalent to that produced by gamma rays, was employed to obtain beta-radioluminescence spectra. To measure alpha-induced radioluminescence, the samples were irradiated with a gold-plated ^{210}Po source (alpha average energy of ~4.5 MeV). The emission spectra of the crystals were collected into a Princeton Instruments/Acton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera. The scintillation light yield obtained from the emission spectra was evaluated in comparison with two standard inorganic crystals: BGO and BaF_2.

The pulse shape discrimination measurements were performed using a ^{252}Cf source to irradiate crystals coupled to a H3378-50 Hamamastu photomultiplier tube (PMT), characterized by a very fast response (0.7 ns rise time) and equipped with a bialkali photocathode (peak wavelength at 420 nm). The collection of light was optimized by the use of silicone grease, for a better optical coupling between the crystal and PMT entrance window, and by wrapping the crystals with several layers of Teflon tape. The signals collected at the PMT anode were recorded using a high resolution waveform CompuScope 14200 digitizer with a sampling rate of 200MS/s, for offline analysis. The ability of an organic crystal to discriminate between the neutrons and gamma rays emitted from the ^{252}Cf source was evaluated with the charge comparison method based on the consideration that, for a defined amplitude value, the signal produced by a neutron has a larger slow component with respect to the signal produced by a gamma ray [6]-[8]. In the offline analysis, the recorded waveforms were numerically integrated over two different time intervals: Δt_S and Δt_F, corresponding to the slow and the fast component of the signal respectively. The value of the ratio of charge $R=Q_S/Q_F$ over these two time intervals indicated whether the considered event was due to a neutron (high R value) or a gamma ray (small R value).

III. Results and Discussion

Scintillation and PSD characterization was made with the crystals similar to those shown in the photographs of Fig.1.

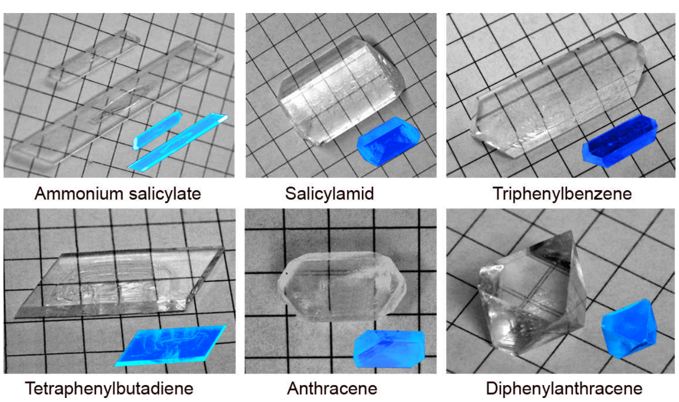


Fig.1. Solution-grown single crystals of organic scintillators. Pictures were taken under white- and UV-light (blue color) illumination. The size of the background square is 6.5 mm.

All results were obtained with samples freely exposed to air, because our studies made with stilbene indicated that, as long as crystals had a millimeter or larger size, neutron/gamma discrimination was not affected by the presence or absence of oxygen.

The beta-excited radioluminescence spectra for the crystals are presented in Fig.2. The wavelength of emission, for all the selected compounds, ranges between 350 nm and 470 nm and thus results well matched with the optical range of most PMTs. Spectra were corrected for the spectral response of the grating/CCD system, and so may be compared in an absolute sense.

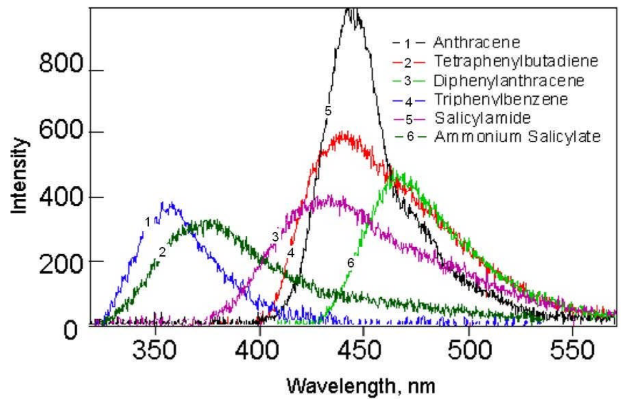
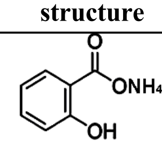
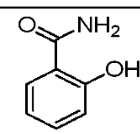
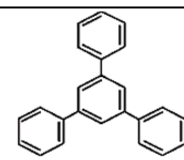
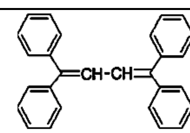
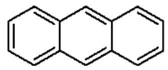
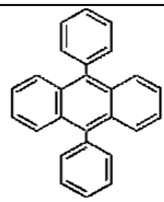
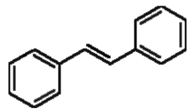


Fig.2. Beta-excited radioluminescence spectra acquired for all the solution-grown crystals tested for this study. Light yields may be compared in an absolute sense.

The corresponding alpha and beta LYs are summarized in Table 1.

TABLE I
Alpha and Beta Radioluminescence Light Yields

Crystal	Molecular structure	α LY (γ/MeV)	β LY (γ/MeV)
Ammonium Salicylate		1150	11960
Salicylamide		4690	21540
Triphenyl-benzene		6270	7360
Tetraphenyl-butadiene		5070	22490

Anthracene		5750	19550
Diphenyl-anthracene		9130	12750
Stilbene		5747	19552
BGO		1800	9000
BaF_2		3600	12000

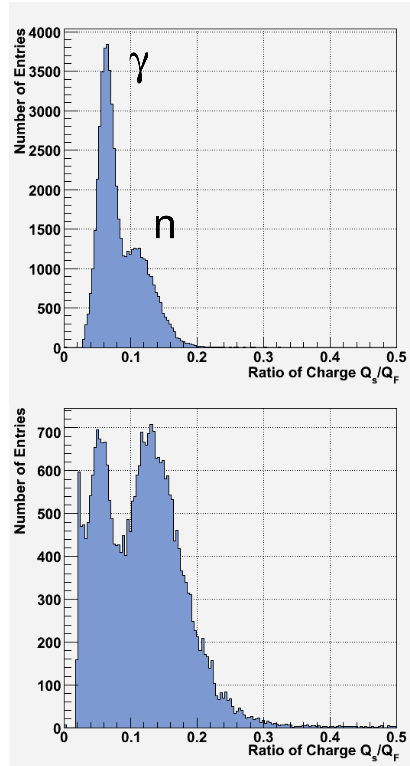


Fig.3. Neutron/Gamma separation profile for ammonium salicylate (top) and salicylamide (bottom).

The estimated value of the LY for the solution-grown anthracene crystal is in good agreement with the typically reported value for this material grown by more traditional melt techniques [10] of 20,000 Photons/MeV, indicating that, as expected, the growth method does not introduce any principal difference in the scintillation properties. Comparison of the results of Table 1 shows that some of the newly-grown crystals (salicylamide, 1,1,4,4-tetraphenyl-1,3-butadiene) exhibit LY even higher than that of the best known scintillation standards, such as stilbene and anthracene. Furthermore, in two additional crystals (1,3,5-triphenylbenzene and 9,10-diphenylanthracene), the presence of absorptive impurities can be responsible for the reduced LY that may be increased in further purification procedures.

The histograms for the ratio of charge R from the n/γ pulses generated by the ^{252}Cf source for the one phenyl rings compounds are presented in Fig.3. These pulse shape discrimination plots indicate that, for the cases of ammonium salicylate (Fig. 3 top) and salicylamide (Fig. 3 bottom), the PSD property is not predominant in the decay waveform.

In Fig. 4 we presented the histograms for the ratio of charge R for the two multiple phenyl rings crystals that have been grown and tested in this work. For these crystals the separation between the neutrons and gamma rays appears to be considerably enhanced leading to an effective discrimination between the two populations of events. In order to quantitatively evaluate the PSD performance of these two crystals, we estimated the Figure of Merit (FOM) defined as $M=S/(F_n+F_\gamma)$, where S is the separation between the centroids of the neutron and the gamma peaks and F_n and F_γ represent the full width at half maximum of the two peaks respectively, [4], [11], [12]. In order to evaluate the FOM in a specific energy range, the energy scale of the system was calibrated by means of the Compton edge of three γ ray emitting sources: ^{137}Cs, ^{22}Na and ^{60}Co. In the energy range between 700 to 800 keV we estimated M=1.6 for triphenylbenezene, M=2.3 for tetraphenylbutadiene and M=2.2 for a commercial stilbene crystal that was tested for comparison. It should be taken into account that the comparison was made between the first crystals grown without the use of any advanced purification or crystallization equipment and best commercially available stilbene produced by well-established crystal growth techniques. Higher FOM and LY values measured for tetraphenylbutadiene make it already a very promising material superior to stilbene for fast neutron detection. Further studies should be also conducted with triphenylbenzene which, having more modest FOM, is a remarkable material that can be easily grown to very large sizes by application the rapid growth solution technique [9]. Furthermore, our preliminary studies indicate that while the separation S between the centroids of the neutron and gamma peaks remains more-or-less constant for the same material, the width of the distributions are significantly dependent on the impurity content and the optical quality of the particular tested crystal suggesting the possibility to improve the FOM by further optimization of the crystal growth process.

Fig. 5 shows the PSD plot for anthracene and diphenylanthracene. These crystals, whose structures are composed of multiple phenyl rings in a condensed chain, show effective PSD properties. It is interesting that the separation between neutrons and gamma rays for anthracene is smaller than the separation measured for diphenylanthracene, which has an identical molecular structure with two more separated phenyl rings connected to the one in the center of the condensed phenyl chain. The difference, however, can be more influenced by the crystallographic structure, planned to be considered in relation to PSD properties of organic materials in our further studies.

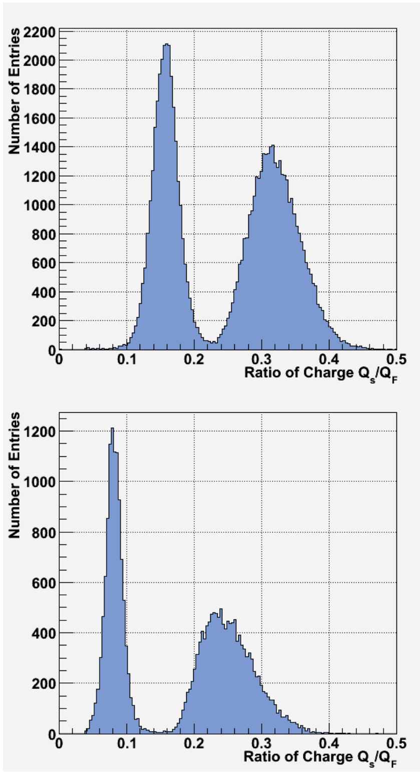


Fig.4. Neutron/Gamma separation profile for triphenylbenzene (top) and tetraphenylbutadiene (bottom).

IV. Conclusion

In this study we performed a survey of the scintillation and pulse shape discrimination properties of several organic crystals alternative to stilbene for fast neutron detection in the presence of a strong gamma ray background. All tested crystals exhibited good luminescence properties, with emission in a wavelength range well matched with standard PMT photocathodes and light yield close to that of anthracene and stilbene known currently as the most efficient single-crystal organic scintillators. The results of the studies showed a certain degree of PSD in all tested crystals, with the highest efficiency of n/γ discrimination found in poly-phenyl compounds. In particular, tetraphenylbutdadiene provided a better FOM for pulse shape discrimination than the best commercially produced stilbene crystals. Single-benzene derivatives and condensed phenyl ring compounds, whereas exhibiting high light yields, showed poorer discrimination between neutrons and gamma rays. These first results indicating the relevance of PSD to the molecular structure of organic compounds should be confirmed with larger number of materials considered in connection with their crystallographic structure.

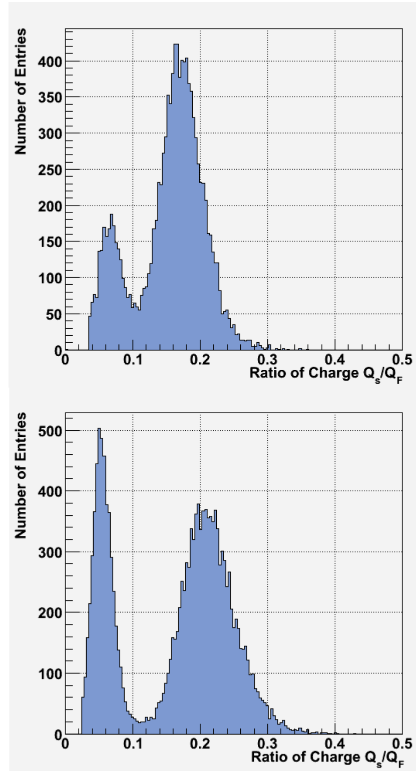


Fig.5. Neutron/Gamma separation profile for anthracene (top) and diphenylanthracene (bottom).

Acknowledgements

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