LLNL-JRNL-481354

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April 26, 2011

IEEE Transaction on Nuclear Science

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Abstract

Pulse shape discrimination (PSD) properties utilized for detection of high-energy neutrons were investigated using a model system of mixed diphenylacetylene-stilbene single crystals of different compositions. The results of the studies, which include experimental tools of crystal growth and characterization combined with computer simulation, showed that the presence of impurities with lower band gap energies is the major factor influencing PSD properties of organic materials. Depending on the concentration determined by the percolation threshold, an impurity may suppress or increase the rate of excited triplet state interaction leading, respectively, to a complete disappearance or enhancement of PSD. The results are applied to produce novel materials with controlled decay characteristics. Single crystals with a large fraction of delayed light and enhanced PSD have been grown for high energy neutron detection, while crystals with a very short decay were produced for use as ultra-fast scintillators for energetic neutron detection in time-of-flight experiments. The results were also applied to obtain liquid and plastic scintillators with improved PSD properties.

1. Introduction

The most widely used method for high-energy neutron detection in the presence of gamma radiation background utilizes the difference in the shapes of the scintillation pulses excited by neutrons (recoil protons) and γ-rays in organic scintillators. Pulse shape discrimination (PSD) phenomena discovered and demonstrated many decades ago [1] are based on the existence of two-decay component fluorescence, in which, in addition to the main component decaying exponentially (prompt fluorescence), there is usually a slower emission that decays at the same peak energy, but longer decay times (delayed emission). According to a commonly accepted mechanism [2,3], the fast component results from the direct radiative de-excitation of excited singlet states (S_1) , while the slow component originates from the collisional interaction of pairs of molecules (or excitons) in the lowest excited π-triplet states (T_1). The process is illustrated by Figure 1a. Since triplets are known to be mobile in some compounds, the energy migrates until two triplets collide and experience an Auger upconversion process: $T_1 + T_1 \rightarrow S_0 + S_1$. The lifetime of the delayed emission is determined by the lifetime of T_1 and the rate of T_1T_1 collisions. The short range of the energetic protons produced from neutron collisions yields a high concentration of triplets, compared to the longer range of the electrons from the gamma interactions, leading to the enhanced level of delayed emission with longer decay times in neutron-induced pulses in comparison to those produced by the gamma excitation (Figure 1 b).

From this general mechanism, a high concentration of hydrogen and the presence of aromatic rings are obvious conditions for neutron interaction and efficient fluorescence. However, its relevance to other specific properties of organic materials, such as physical state, molecular and crystallographic structure, or presence of impurities is practically unknown. The problem very much relates to a limited number of organic materials historically studied for their

PSD properties. The earliest work on scintillation decay [4] reported slow decay component measurements in anthracene, *trans*-stilbene, p-terphenyl, p-quaterphenyl, and diphenylacetylene single crystals. Later studies [5-7] limited to the same sets of crystals established the best ability to discriminate between different types of radiation in stilbene, but did not confirm detection of any delayed light or PSD properties in diphenylacetylene. No additional studies had been conducted to understand the differences. However, since no new names have been added

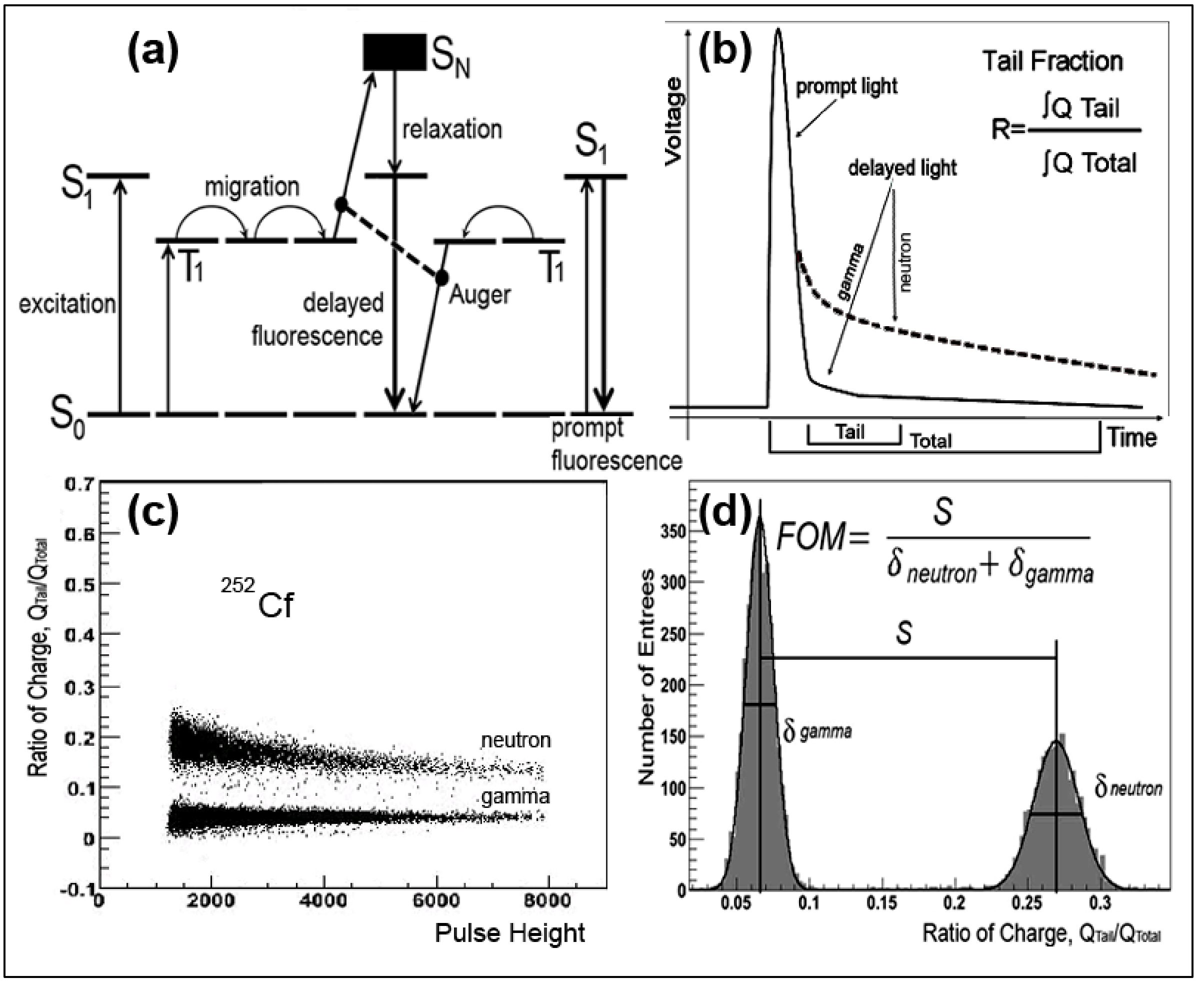

Figure 1. (a) - Basic physical processes leading to the delayed fluorescence characteristic of neutron excitation of organics with phenyl groups; (b) – average waveforms indicating different levels of delayed light in neutron and gamma scintillation pulses; (c) - typical PSD pattern of a stilbene crystal obtained by digitized separation of neutron and gamma pulses; (d) – PSD profiles of experimental data used for calculation of the PSD Figure of Merit (FOM).

for decades to the small list of the initially tested crystals, stilbene received a reputation of the best organic scintillator for fast neutron detection, while diphenylacetylene became a classical example cited in the literature as an aromatic crystal without PSD [1, 3, pp. 392 and 495, respectively].

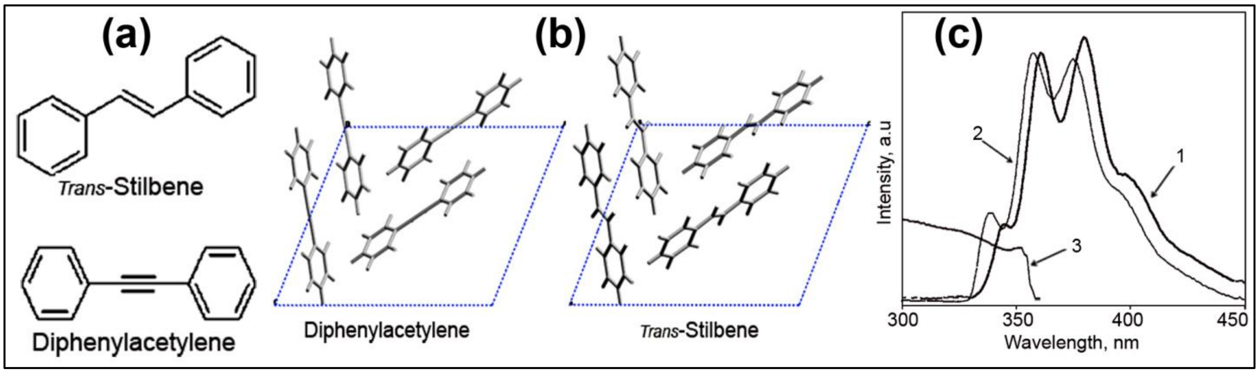

Figure 2. Comparison of stilbene and diphenylacetylene (DPAC) crystals: (a) – Molecular formulas. (b) – Crystal structures; lattice parameters for DPAC: a=15.488 Å, b=5.754 Å, c=12.766 Å, α=90°, β=113.36°, γ=90°; for stilbene: a=15.478 Å, b=5.66Å, c=12.287 Å, α=90°, β=112.03°, γ=90°; (Ref.8 and 9, respectively). (c) – Photoluminescence spectra of stilbene and DPAC emission (1 and 2, respectively); stilbene excitation spectrum (3) shows the overlap needed for the excitation transfer from DPAC to stilbene molecules.

A curious discrepancy of these original results relates to the fact that stilbene and diphenylacetylene are very similar molecules, differing only by the double and triple bonds between the central carbon atoms (Figure 2 a). Moreover, according to the literature, they have identical crystallographic structures [10], with only small difference in the corresponding lattice parameters (Figure 2 b), and very close photoluminescence spectra (Figure 2 c). This similarity, however, was not reflected either in PSD properties or in the scintillation efficiency also controversially reported for diphenylacetylene largely superior or inferior to that of stilbene in the early works [11-13]. Consideration of these results indicated that the molecular and crystallographic structures might not be the only parameters determining PSD properties of the tested compounds. However, no other factors that could influence the PSD phenomena in organic materials have been reported after these initial studies. The absence of a proper understanding of the connection between PSD and the specific nature of organic compounds made it difficult to predict the possible presence or absence of PSD properties in large varieties of organic materials, largely limiting the choice of organic scintillators used for efficient neutron detection. So far this choice has included rarely used stilbene crystals and a few empirically found liquid scintillator mixtures. The typical excellent PSD performance of stilbene produced the widely excepted opinion that crystals are superior to liquids. Scintillating plastics were always found to exhibit discrimination much poorer than that in crystals or liquids [14] and became known as materials unsuitable for efficient fast neutron/gamma discrimination.

The modern availability of high-speed waveform digitizers [15-17], allowing for easy separation of neutron and gamma pulses (Figure 1 c), brought big advantages in conducting PSD studies. Combined with recent developments in solution growth techniques that enable production of large varieties of organic single crystals [18, 19], they now can be used for more advanced understanding of the processes leading to the scintillation phenomena in different organic materials. In our recent work, a broad survey of about 150 fluorescent organic crystals has been conducted with a dual goal of empirical identification of new efficient PSD materials [18] and better understanding the mechanisms of scintillation [20]. Single crystals which represent fluorescence of pure materials in their condensed state are convenient objects for studies of properties of individual compounds that then can be combined in more complex combinations. The initial results of the conducted studies showed that, in addition to the molecular and crystallographic structures, which determine exchange coupling and triplet mobility in organic materials, one of the most important factors influencing PSD is the effect of impurities. The detailed consideration of this effect made with stilbene-diphenylacetylene used as a model system explained the controversy in the properties observed with these compounds in the past. Applied to the recent survey, the results helped to understand variations of PSD properties measured in different types of organic crystals. In a broader sense, the results provided better understanding of energy migration and excited state interactions in organic crystals and opened new opportunities for design and engineering of scintillating crystals with controlled decay times and efficient PSD, as well as non-crystalline organic scintillators (liquid and plastics) with improved PSD properties.

2. Experimental and computational methods

Raw material of *trans*-stilbene (96%), diphenylacetylene (DPAC, 98%) and other solid powders used for crystal growth were purchased from different vendors (Aldrich, Alfa Aesar, Acros Organics and TCI America). Prior to growth, all compounds were purified by at least three-time re-crystallization from toluene (Aldrich, 99.8%) solutions. A simple evaporation technique similar to that described previously [19] was used to grow small single crystals (1-2 cm in size) for the initial tests. Mixed crystals were grown from solutions containing DPAC and stilbene in certain initial ratios. The chemical composition of the growth solutions and crystals was measured by gas chromatography-mass spectrometry (GC-MS) using a Hewlett Packard (HP) 6890 GC coupled to a HP5973 mass selective detector with the injection temperature set at 250^{o}C. Chromatographic separation was achieved using a DB-5MS column (30m x 0.25 mm id, 0.25 μm film thickness), with the GC oven ramped from 40^{o}C to 250^{o}C over 35.5 minutes. The mass selective detection was run in full-scan mode (30 to 550 m/z). DPAC and stilbene were identified by MS=178 and 180 respectively and authenticated with a NIST library search. They were quantified using pure stilbene and DPAC standards.

Photoluminescence (PL) spectra were measured under UV excitation using a commercial Fluoromax-2 spectrometer. The scintillation efficiency of crystals was evaluated using gamma and beta excitation. Gamma light yield (LY) was calculated from the position of the Compton edge in the ^{137}Cs spectra relative to the Compton edge of a pure stilbene crystal in the same energy range. Beta-induced light yield was evaluated from the emission spectra acquired under beta excitation using a ^{90}Sr/^{90}Y source, in comparison with two standard inorganic crystals: BGO and BaF_2.

Neutron detection properties of grown crystals were studied using the pulse shape discrimination (PSD) technique which allows for the separation of the scintillation pulses produced by neutron and gamma events *via* the relative increase in delayed light for neutron stimulations [9,10]. The measurements were performed using a ^{252}Cf source shielded with five cm of lead, which reduced the gamma rates to the same order as neutrons, to irradiate crystals coupled to an R6231-S Hamamatsu photomultiplier tube (PMT). 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 crystals to discriminate between the neutrons and gamma rays emitted from the ^{252}Cf source was evaluated using the Q_{Tail}/Q_{Total} PSD discriminant. The waveforms were numerically integrated over two time intervals: Δt_{Total} and a subinterval Δt_{Tail}, corresponding to the total charge and the delayed component of the signal respectively. The value of the ratio of charge $R=Q_{Tail}/Q_{Total}$ for the two time intervals indicate whether the considered event was produced by a neutron (high R value) or a gamma ray (small R value). The time gates used for PSD measurements were optimized to maximize Figures of Merit (FOM in Figure 1 d) for each material.

Density Functional Theory (DFT) calculations at the PBE [21] level of approximation to the exchange-correlation potential was used to obtain the relaxed geometry in the first triplet excited state (T_1) and in the ground state (S_0) of both stilbene and DPAC. The triplet excitation energy was taken as the total energy difference between the triplet and the ground states at their respective optimized geometries (known as the spin-unrestricted or Δ self-consistent field (ΔSCF) method [22]). The calculations were performed with VASP (Vienna *ab initio* simulation package) [23] using projector augmented wave (PAW) pseudopotentials to represent the ion-electron interactions [24].

3. Results and discussion

Examples of crystals used for the studies are presented in Figure 3 a. More detailed crystallographic analysis is required to confirm if stilbene and DPAC form truly mixed crystals with periodic incorporation of the different molecules in the crystallographic lattice. Frequent growth of nice, faceted crystals, with similar shapes and practically identical angles between the corresponding facets can be considered as an indication of relatively homogeneous structure and composition of the mixed crystals. More proof of this suggestion is provided by the results of the X-ray diffraction (XRD) analysis (Figure 3 b). Similar XRD patterns obtained for all crystals should result from the similarity of the crystallographic structures, while the noticeable shift of the same-indexes reflection lines should be produced by the gradual change of corresponding lattice parameters from those of pure DPAC to the parameters of regular stilbene crystals.

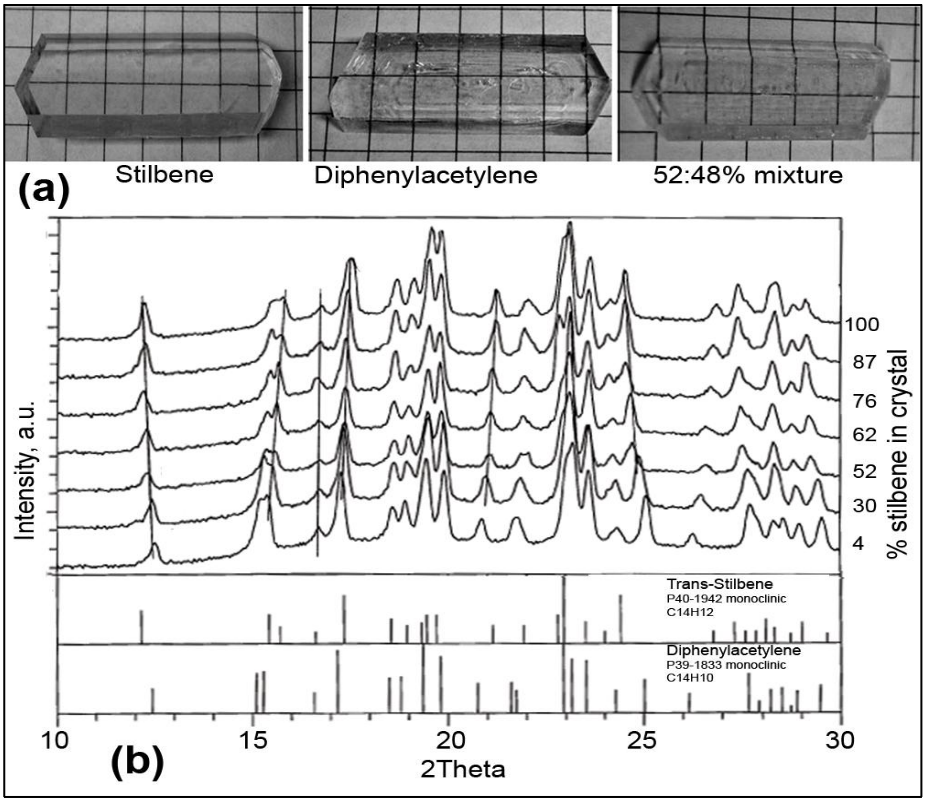

Figure 3. (a) - Examples of pure and mixed crystals grown for studies by solvent evaporation technique; the side of the background square is 6.5 mm. (b) - XRD patterns of DPAC-stilbene crystals showing a gradual shift of corresponding reflection lines with the change of stilbene concentration.

3.1. Delayed light and pulse shape discrimination

Measurements made with numerous stilbene crystals grown in our experiments always revealed excellent PSD similar to that shown in Figure 1 b and c. The situation was different for DPAC crystals which, depending on the batch of initial material, showed large variations of PSD from a good level to its complete absence. Combined chemical and PSD analysis made with many crystals showed that a good level of PSD was typical for pure DPAC crystals (Figures 4 a), in which no impurities were detected. A surprising result obtained in analysis of DPAC crystals without PSD was that all of them contained stilbene as an impurity in the amount of 1-2 %. More

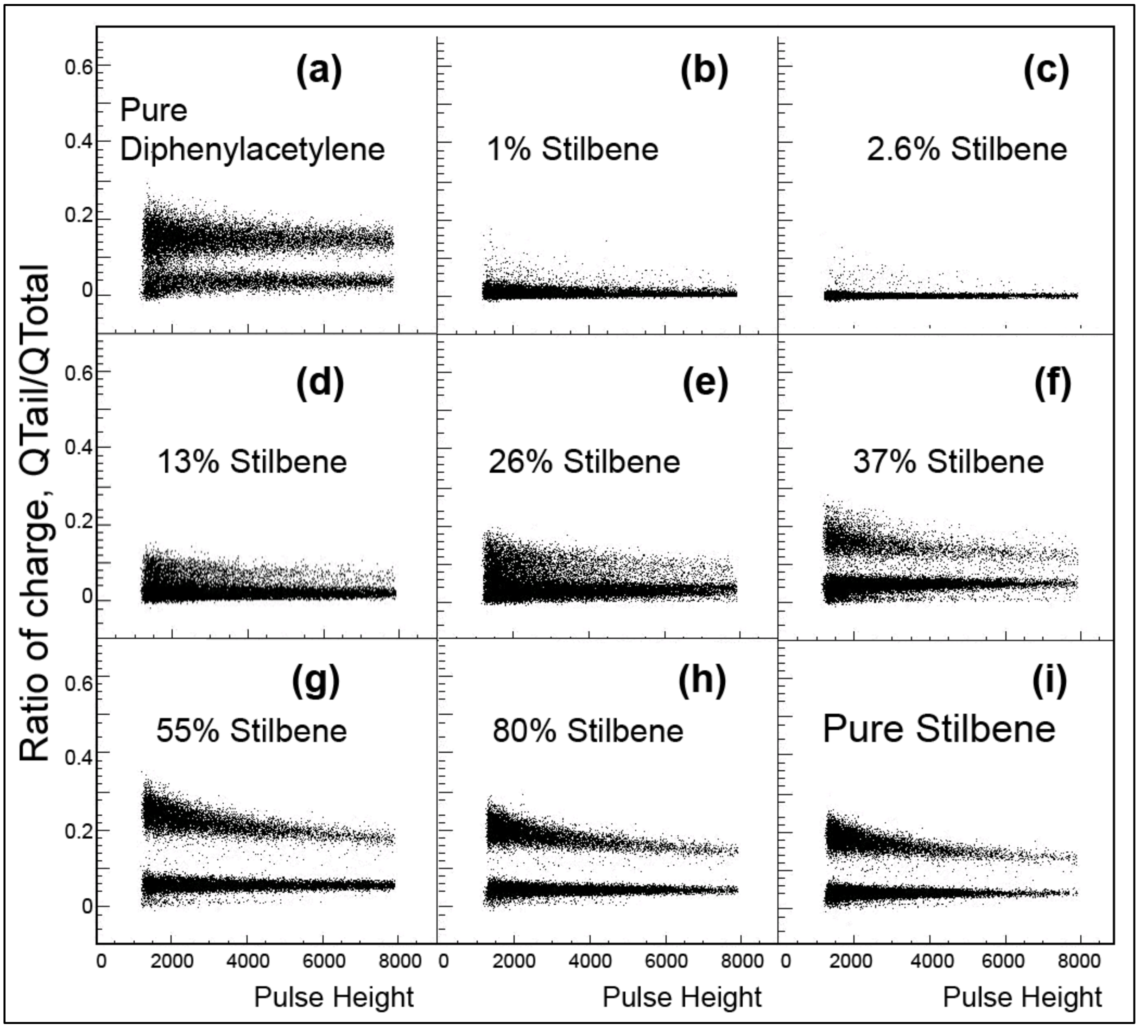

Figure 4. Experimental patterns showing variation of PSD in mixed DPAC-stilbene crystals: neutron/gamma discrimination properties of pure DPAC (a) vanish at low concentrations of stilbene (b, c); the delayed light re-appears at higher concentrations (d - f) with further increase to an excellent separation (g-h) similar to that of pure stilbene (i). ^{252}*Cf source used for the measurements.*

detailed experimental studies conducted with DPAC crystals intentionally doped with controlled stilbene additions confirmed the sharp quenching effect of the stilbene impurity on the PSD of DPAC in the range of stilbene concentrations of about 0.5-10%. As a result of the PSD loss the neutron and gamma peaks clearly separated in pure materials joined in one narrow pattern corresponding to a sharply decreased fraction of the delayed light and short decay times (Figure 4 b and c). Further analysis of the mixed crystals grown at higher stilbene concentrations showed re-appearance of the delayed light resulted first in a broadening of the single pattern (Figure 4 d-e) followed by its rapid return to neutron/gamma separation (Figure 4 f) and PSD similar or even exceeding that typical for the best stilbene crystals (Figure 4 g-i). For more detailed consideration of the physical processes giving rise to this non-linear dependence of the delayed light on chemical composition, the experimental results were compared in the same energy calibrated γ-equivalent energy ranges. Figure 5 shows only a few, most typical examples of the profiles used for the evaluation of the delayed light fraction in numerous crystals of different composition.

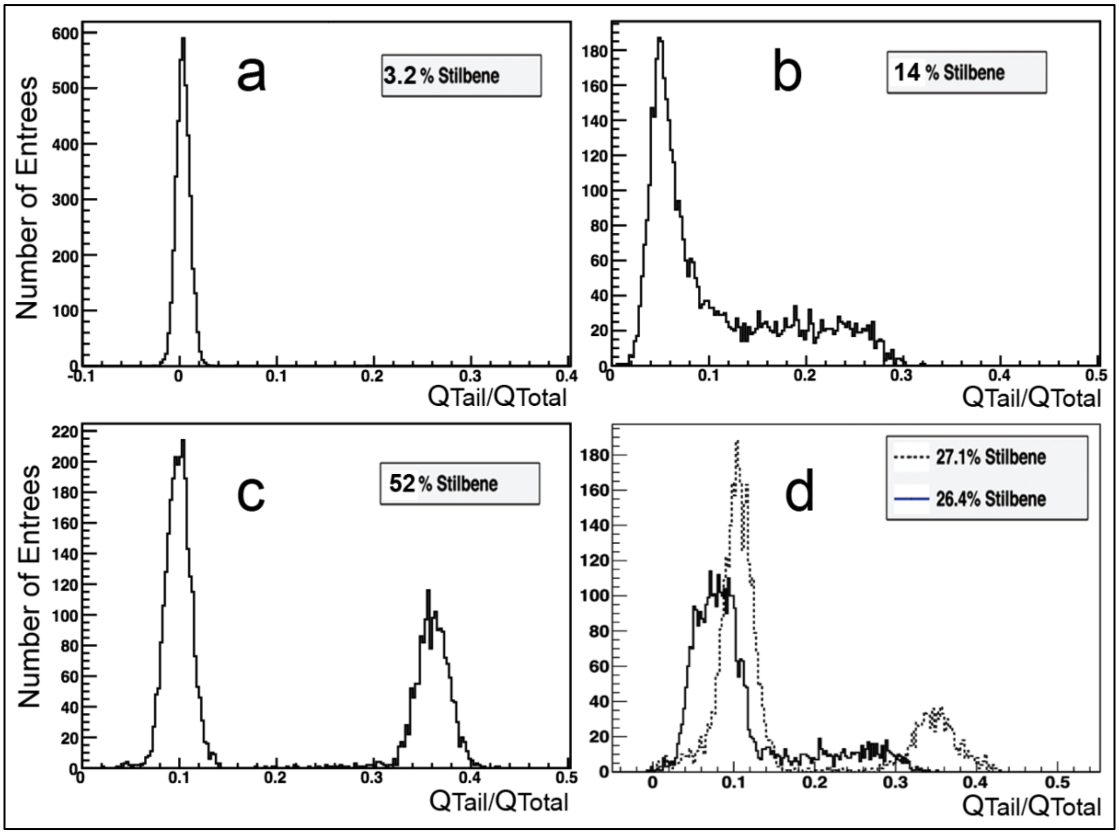

Figure 5. Examples of typical PSD patterns used for evaluation of the delayed light fractions in DPAC-Stilbene crystals of different composition: (a) – prompt scintillation with short decay and no delayed light; (b) – a pattern containing both prompt and delayed components without clear separation; (c) – PSD pattern with clearly defined separation between two components; (d) – nearly identical samples in chemical analysis which give very different PSD patterns; evidence of inhomogeneity

Delayed light from triplet excitation annihilations is generally present for both gamma and neutron stimulations in materials with good PSD. We have investigated the dependence of delayed light fraction as a function of the stilbene/DPAC mix for gamma (^{137}Cs) and mixed fields (^{252}Cf). The slow component of a crystal stimulation response, Q_{Tail}, is taken as the integral of the PMT baseline subtracted waveform from 65ns to 1750ns. The total output, Q_{Total}, is the integral from -75ns to 1750ns, where the peak sample sets the 0 time (Fig. 1 B). The delayed light fraction is then measured as Q_{Tail}/Q_{Total}. The timing values were selected to produce approximately the best neutron-gamma PSD separation as measured by the Figure Of Merit (Fig. 1 D) for high stilbene concentrations.

The dependence of delayed light fraction for ^{137}Cs gamma stimulations as a function of the percent stilbene is show in Fig. 6. The stilbene fraction (or 1-DPAC fraction) based on chemical analysis is shown on the horizontal axis. The vertical axis displays the mean of the Q_{Tail}/Q_{Total} distribution for a large number, generally 40k, of waveform acquisitions. Most of the crystals were too small for accurate energy calibration via measurement of the Compton edge, but as visually evident in the gamma bands of Fig. 4 the average amount of delayed light is largely energy independent. For each crystal, the data were split into five or six un-calibrated energy bins of roughly equal statistics, and the vertical error bars indicate the Standard Deviation, Sqrt((1/N)*(Sum(x_i-x_mean)^2)), of the delayed light fraction for these bins. Several of the crystals for this study showed clearly anomalous PSD patterns for ^{137}Cs and ^{252}Cf exposure most likely indicative of inhomogeniety and/or possibly impurities. Representative anomalous Q_{Tail}/Q_{Total} distributions are shown in Fig. 5 B and D as solid lines, however no data from these crystals were included in this analysis.

The data clearly show a sudden onset of delayed light at approximately 20% stilbene as well as a maximum delayed light fraction soon after the sudden increase. We include a fit based on the function for infinite cluster probability from percolation theory combined with dropping effective triplet concentration, as discussed in more detail in the next section. The functional form is $y = a\frac{(x-x_c)^b}{x}$ for $x>x_c$ and 0 otherwise. The best-fit parameters from a χ^2 minimization are a = 0.0833 x_c= 0.187 and b = 0.386. The percolation threshold, x_c is in the range of FCC site (0.198) and BCC bond (0.1803) percolation while the critical exponent, b, is relatively close to the value of 0.41 expected for 3-deminsional percolation []. We note that pure percolation theory does not include the $1/x$ factor, which accounts for the enhancement due to concentrating the energy solely on the stilbene subsystem in the mixture.

Although harder to interpret, we have studied the neutron/gamma delayed light separation, S in Fig. 1 D, as a function of stilbene fraction for the mixed field from ^{252}Cf as well. Figure 7 shows the separation between the mean delayed light fraction, $Q_{\mathrm{Tail}}/Q_{\mathrm{Total}}$, for neutrons and gammas as measured using the nearly the same method as for ^{137}Cs stimulations. The major difference is that we do not know for certain on an even by event basis if the waveform was generated by a neutron or a gamma, particularly for the 0.2 to 20 % stilbene region which exhibits little to no PSD. We therefore fit the low $Q_{\mathrm{Tail}}/Q_{\mathrm{Total}}$ region of the distribution with a Gaussian to estimate the gamma contribution. The mean of the fitted Gaussian is taken as a measure of the gamma delayed light. This Gaussian is then subtracted from the total $Q_{\mathrm{Tail}}/Q_{\mathrm{Total}}$ distribution, and the mean of the remaining distribution is taken as a measure of the neutron delayed light. The vertical error bars are again the Standard Deviation derived from splitting the data for each crystal into equal statistics uncalibrated energy bins. A fit to the percolation based form of $y = a\frac{(x-x_c)^b}{x}$ for $x>x_c$ and 0 otherwise is also included. The best-fit parameters from a χ^2 minimization are a = 0.235 x_c= 0.184 and b = 0.672.

We have calculated the gamma/neutron separation in terms of the Figure of Merit for crystals that had a good ^{137}Cs Compton edge and exhibited good PSD. These FOM values for 500-550 keV gamma equivalent (near the ^{137}Cs Compton edge) as measured from double Gaussian fits of the Q_{Tail}/Q_{Total} distributions are included in Figure 7. The vertical error bars are based on propagation of errors for the fit value errors through the FOM formula. We see that even though the mean Q_{Tail}/Q_{Total} separation for pure DPAC is similar to crystals with high stilbene concentration the FOM is significantly lower. This is consistent with DPAC having lower light yield. Also seen, is a slow drop in FOM with increasing stilbene concentrations beyond 50%.

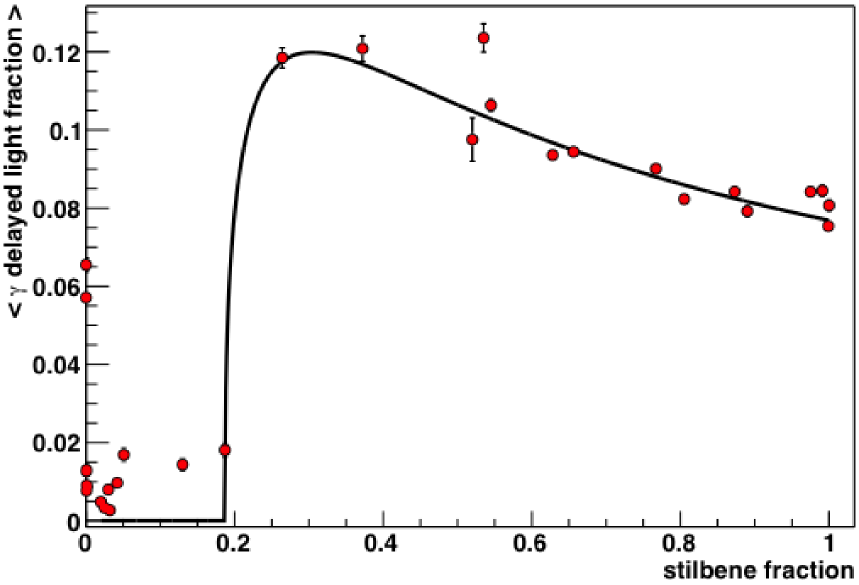

Figure 6. The average amount of delayed light in mixed stilbene-DPAc crystals from ^{137}Cs gamma stimulations as a function of stilbene fraction. The solid curve shows a percolation theory fit described in the text.

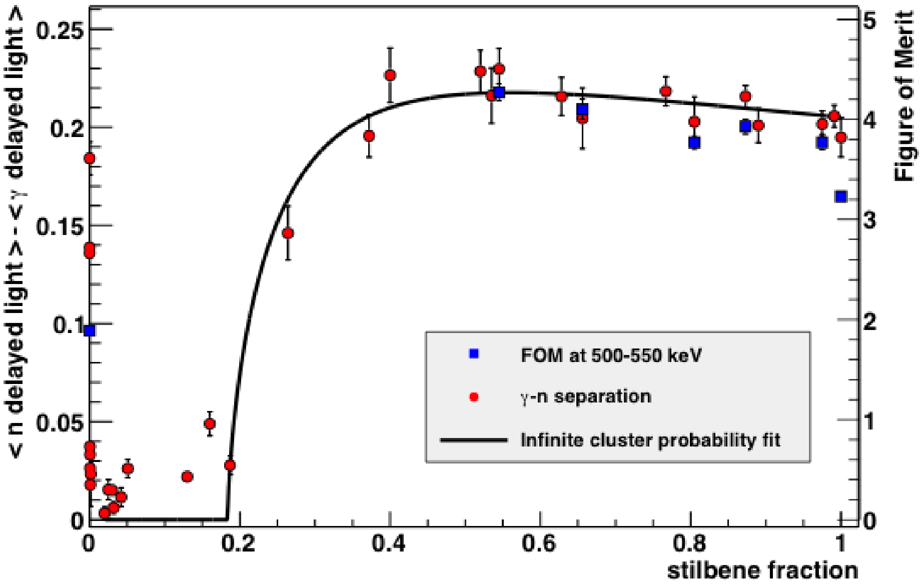

Figure 7. The red dots are average delayed light neutron/gamma separation as a function of stilbene fraction (left axis). The blue squares are neutron/gamma separation Figure of Merit near the ^{137}Cs Compton edge *as a function of stilbene fraction (right axis). The solid curve shows a percolation theory fit described in the text.*

Although unexpected because of stilbene acting as a quenching impurity, the initial effect of PSD disappearance in DPAC crystals can be easily understood based on the well-known phenomena of energy transfer studied previously in various mixtures of organic scintillators [2]. The high efficiency of energy transfer in organic crystal solutions is due to the rapid non-radiative migration of the excitation energy between neighboring molecules of the host lattice and impurities (exchange coupling). In the mixed crystals, the impurity molecules with lower energies of the excited states may act as traps for both singlet and triplet excitations of the host, thus quenching the host emission efficiency and reducing decay times. Calculations of the triplet excitation energies made in the current work using the ΔSCF method find that stilbene, which has a slightly longer wavelength of emission (Figure 2 c), also has a smaller T_1 triplet excitation energy (2.4 eV) than DPAC (2.7 eV). As a result, stilbene molecules act as traps that prevent the

DPAC triplet energy migration and annihilation needed for the formation of delayed light in DPAC crystals containing stilbene in small concentrations, corresponding to “no PSD” regions in Figures 4 and 7.

More unexpected broadening of the experimental patterns at higher stilbene concentrations followed by a sharp rise of the PSD (Figure 4 d-f) at a certain threshold concentration (~ 20% in Figure 7) requires some additional consideration. Lower band gap stilbene molecules still should work as traps for DPAC triplets. However, the re-appearance of the delayed light must correspond to a restored exciton mobility resulted from the increased concentration of stilbene. The phenomenon can find an explanation by consideration of the threshold concentration to go from trapped excitations to migration of excitations as a percolation problem. From the basic principles of the percolation theory [25], it can be suggested that in pure DPAC, even if stilbene is present at very low concentration below 0.5%, the average distance between traps is much larger than the excitation density, and so the host molecules still can transfer excitation needed for triplet recombination and formation of the delayed light (PSD in the initial DPAC crystals in Figure 4 a). At slightly higher stilbene concentrations (before the percolation threshold) traps capture all triplet excitations leading to a quenched recombination and absence of PSD (Figure 4 b and c). When the concentration of stilbene in the mixed crystal becomes large enough, high trap density leads to a dramatically increased probability of stilbene network formation. Now traps act as an excitation transport medium resulting in a sudden rise of PSD. At the initial stages of this network formation (percolation threshold) stilbene chains providing paths for the triplet migration are highly sensitive to concentration uniformity which may result in non-uniform scintillation pulses with varying fractions of the delayed light and absence of clear separation between gamma and neutron peaks in the PSD patterns (Figure 4 d and e) for crystals with inhomogeneities larger than the average cluster size but too small to be easily seen in chemical analysis. And finally, when stilbene network reaches infinite dimensions required for the efficient triplet migration and interaction, the scintillation pulses become more uniform, resulting in clear peak separation and PSD essentially that of pure stilbene. It is, however, interesting to note that the general dependence of the delayed light fraction on the stilbene concentration shown in Figure 7 goes through the maximum just above the percolation threshold. The phenomenon is most likely due to a maximum in the effective triplet density and decreased self-absorption of stilbene present at this concentration in more diluted state in the mixed crystals.

3.3. Scintillation light yield

The scintillation gamma- and beta-induced LY measured in the mixed DPAC-stilbene crystals of different composition is presented in Figure 8. In both cases, the LY of a pure stilbene crystal grown from the same material as in the mixtures was taken as a reference point of a unit (corresponding to about 2000 Ph/MeV). Question: don’t you mean 20,000?? The large scatter of the experimental results most likely is determined by the difference in size (meaning different levels of self-absorption)

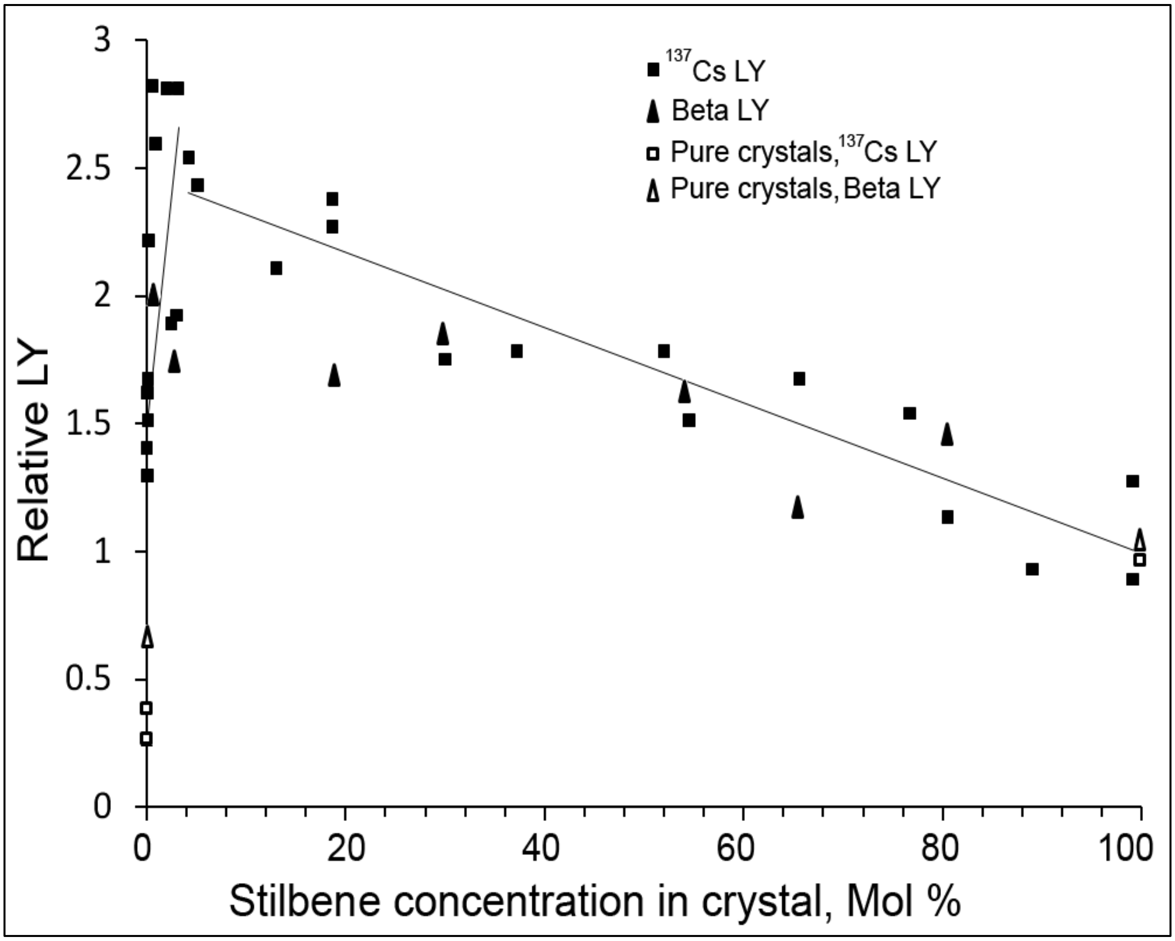

Figure 8. Relative scintillation light yield (LY) measured in mixed DPAC-stilbene crystals using gamma (^{137}Cs) and beta (^{90}Sr/90^{Y}) excitation sources. LY of a pure stilbene crystal grown from the same material as used in the mixed crystals was taken as a unit.

and insufficient optical quality of crystals grown by the evaporation technique. However, measurements obtained in several independent sets of experiments show a similar dependence, in which a relatively modest LY in pure DPAC crystals sharply increases almost by an order of magnitude at very small additions of stilbene, and then gradually decreases with the changing composition to the LY of pure stilbene. The lack of direct correlation between the dependences of the PSD and the scintillation LY shown, respectively, in Figures 7 and 8 is not surprising taking into account that the delayed light formed by the triplet annihilation contributes only a small fraction to the total scintillation LY produced mostly by the emission of the excited singlet states. It is well-known [2] that in a binary host-impurity system, the exciting radiation is absorbed almost exclusively by the host, being then efficiently transferred to the impurity molecules with the lower energy band gaps. From this point of view, the increased level of LY in the mixed crystals, in comparison to pure DPAC, must be produced by stilbene molecules efficiently excited through the energy transfer from the excited singlet states of less efficient DPAC. The mechanism is supported by the measurement of the photoluminescence spectra, which always correspond to those of stilbene in all mixed crystals. The stilbene spectra exhibited a slight blue-shift in the region corresponding to the highest LY, reflecting, most likely, the transformation of the molecules from their state in pure stilbene crystals to the state of single fluorescing molecules in the DPAC crystal lattice. By analogy with liquid scintillators, stilbene acts as a solute producing the most efficient scintillation because of decreased self-absorption in the diluted state. Due to energy-dependent photon statistics, the higher LY efficiency of stilbene molecules can be also reflected in the enhanced PSD produced by the stilbene network in the mixed crystals.

4. Applications of results

The DPAC-stilbene system is a rare representative of a small group of compounds which can form mixed crystals because of the close similarity of their molecular and crystal structures. From this point of view, detailed consideration of such a unique system may seem to be a relatively useless excise. However, our experience shows that the use of the results obtained with this model system can be helpful for better understanding of the experimental problems identified in current or earlier works. As shown by a few examples described below, they also can be useful for application leading to the development and engineering of new materials.

4.1. Explanation of the previous results

The results correct a previously accepted opinion [1, 2, 9] that DPAC has a negligible delayed component of the scintillation emission and therefore is unsuitable for PSD. Pure DPAC has PSD (Figure 5 a), in this respect not being very different from stilbene or other hydrocarbon compounds of similar structure. The actual scintillation efficiency discussed in conflicting reports previously [2, 13-15] must be inferior to that of stilbene, because all pure diphenylacetylene crystals, defined by chemical analysis or presence of PSD, showed a LY (gamma, beta, and PL) lower than in any stilbene crystal.

4.2. Interpretation of PSD in newly tested materials

Studies made with the DPAC-stilbene system enabled better understanding and interpretation of the results obtained in the PSD survey of new organic crystals. As reported previously [18, 20] a number of new materials with PSD close or even superior to stilbene were identified in the survey and selected for further development. However, the overall results obtained in the initial studies were difficult to interpret prior to this work. The problem was that the majority of the measured PSD patterns, the most typical examples of which are shown in Figure 9, were difficult to interpret because of the lack of a visible correlation between the PSD and molecular or crystallographic structures of the tested materials. Now it can be understood that a complete

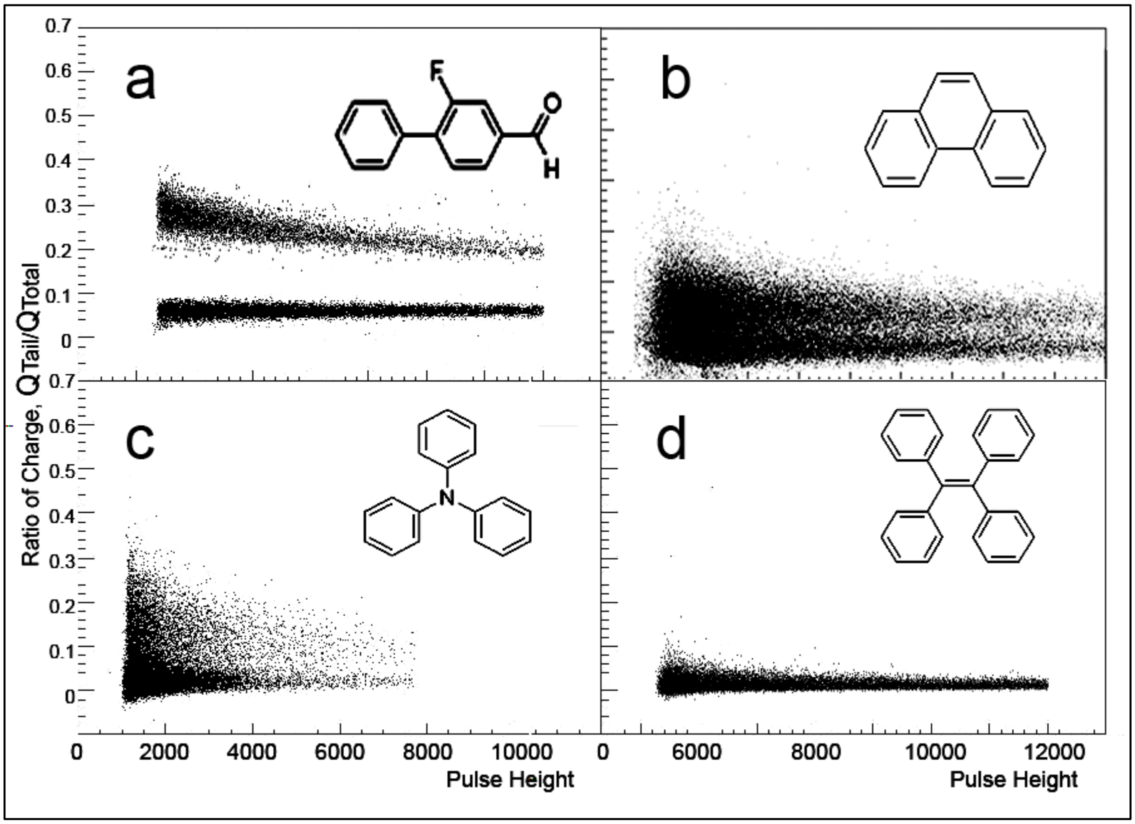

Figure 9. Examples of typical PSD patterns measured in large varieties of new organic crystals grown for the survey of neutron/gamma discrimination properties: (a)-good PSD with clear separation of the prompt and delayed components; (b and c)-bad PSD containing large fraction of the delayed light not separated from the prompt component; (d)-no PSD, with low fraction of delayed light. ^{252}*Cf source used in all measurements.*

absence of PSD or "bad PSD" do not necessary reflect actual discrimination as well scintillation efficiency properties, but can be largely affected by the presence of impurities. It should be noted here that 95-98% purity is very typical for commercially produced organic materials. Further purification of such materials can be especially difficult in the case of close similarity of the host and impurity molecules. The controversy about the delayed light in DPAC crystals was very much determined by the fact that stilbene is used as the initial starting material for the DPAC synthesis [26]. Commonly introduced in DPAC during synthesis, stilbene is very difficult to remove by re-crystallization because of its preferential incorporation into crystals. Figure 10 shows the deterioration of the initially good PSD produced as a result of the intentional addition of lower-band-gap impurities in some other organic crystals. As shown by the example of the bibenzyl (BB)-stilbene combination (Figure 10 a), small addition of a certain impurity may cause a complete suppression of the delayed

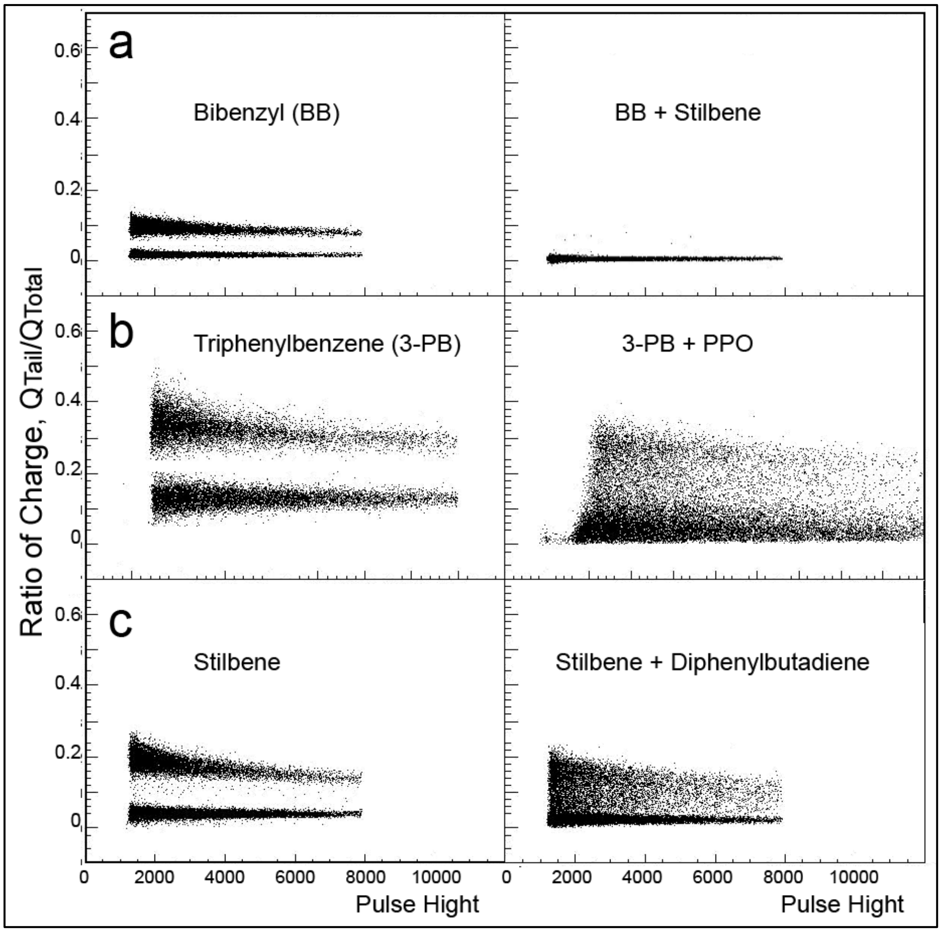

Figure 10. Deterioration of PSD under the effect of impurities in scintillation crystals. Right column patterns correspond to pure crystals. Left column are respective patterns obtained from crystals of the same compounds grown with intentionally added lower energy band gap impurities. ^{252}Cf source used in all measurements.

light and PSD not only in DPAC- stilbene, but in other mixed crystals (Figure 9 d). It should be noted here that, similar to the dependence shown in Figure 8, the complete suppression of the PSD in BB crystals containing small quantities of stilbene is also accompanied with a noticeable increase in its scintillation LY. In other cases, the fraction of the delayed light can be still high, not producing, however any clear separation between gamma and neutron events (Figure 9 b, c and Figure 10 b). And finally, an interesting result of these experiments is that always good stilbene, which probably does not get "PSD killing" impurities during its synthesis, can be also spoiled by the addition of a small amount of closely-structured diphenylbutadiene (Figure 10 c).

4.3. New single crystal scintillators with enhanced PSD performance

Identification and production of new scintillating materials that can be used for efficient neutron/gamma discrimination is an obvious and the most important goal of the conducted studies. As shown in Figure 4, both DPAC and stilbene have PSD suitable for use in neutron detectors. However, according to the main result obtained in the studies (Figure 4 g, h, k), the mixed crystals containing stilbene in concentrations above 50% may become more efficient materials with a performance better than that of pure crystals. An optimal composition of the mixed crystals is yet to be identified because, in addition to the scintillation properties, the selection should take into account the ability to grow single crystals to large sizes required for working detection devices. Growth of the large crystals that unavoidably will increase self-absorption in pure stilbene, may bring additional benefits of improved PSD in the mixed crystals with some intermediate stilbene concentration corresponding to the highest LY and maximum PSD. It should be noted, however, that scaling-up growth of these crystals by application of the solution growth technique is not a trivial task, because prior to this work the technique was used only for production of large crystals from aqueous solutions. Figure 10 shows pictures of unique, fully faceted DPAC-stilbene crystals grown, for the first time, from a pure organic solvent (anisole) using the rapid growth technique developed previously for growth of large KDP crystals from water solutions [27, 28]. These encouraging results indicate that larger and better quality single crystals can be grown with further development of the solution growth technique now applied to pure organic systems. It is also obvious that selection of such systems should not be necessarily limited to

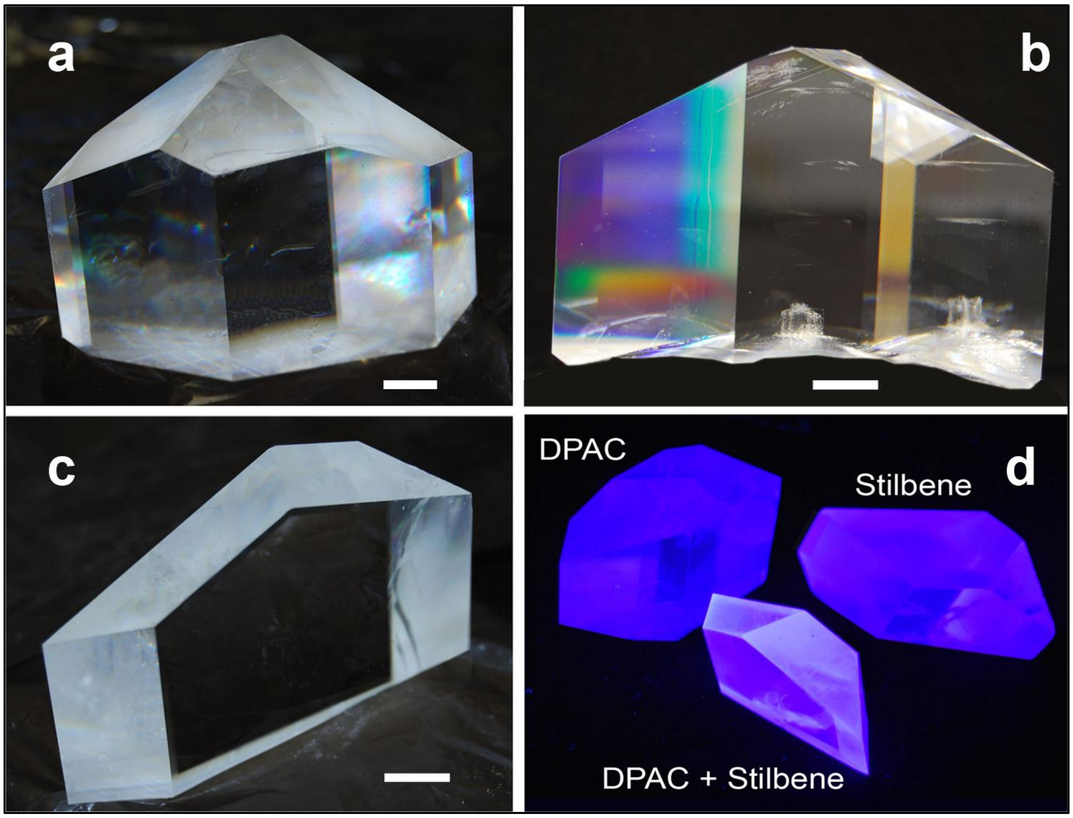

Figure 11. Single crystals of (a) - diphenylacetylene (DPAC), (b) - stilbene and (c) - mixed DPAC-stilbene (~50:50) grown from organic solvents by temperature reduction method; white bars correspond to approximately 1 cm in length. (d) – Photoluminescence image showing the higher brightness of the mixed crystal under the same UV illumination.

the DPAC-stilbene combination. It can be extended to other organic compounds that, grown from solution or melt, are known to form mixed crystals. Examples of such combination can include aromatic compounds with similar molecules, such as naphthalene and anthracene, biphenyl and p-terphenyl, p-terphenyl and p-quaterphenyl, etc., differing by the number of phenyl rings and, therefore, by the band gap energy. These similar compounds are known to form practically identical crystallographic structures [10], in which previously known effects of the scintillation efficiency changes can be combined with the variations of PSD that can be used for the engineering of new neutron detection materials.

4.4. Fast scintillators

Although the focus of this research is to understand the processes leading to the delayed light utilized for neutron/gamma pulse shape discrimination, the understanding of the PSD mechanisms in mixed crystals has allowed us to produce very fast scintillators with nearly no delayed light. The use of fast scintillators with very low afterglow is important for ion and neutron spectrometry at high intensity pulsed laser facilities which require separation of temporally close signals, particularly in cases when the delayed signals are significantly smaller than the earlier produced signals. One such high profile application includes a neutron diagnostic instrument designed to measure neutrons produced from deuterium-tritium target implosions in the National Ignition Facility (NIF), the world largest laser built at Lawrence Livermore National Laboratory [29]. The quantity of interest in the NIF experiments is the ratio of 14 MeV produced in the fusion reaction $D + T \rightarrow 4He + n$ and the 10-12 MeV neutrons scattered in the high-density compressed target. Neutrons with different energies can be separated by the time-of-flight method which uses different velocities of neutrons traversing down a flight path. The problem in determining the ratio is that for a 20m flight path 14MeV and 12 MeV neutrons are separated by just 30 ns and the expected intensity of the 10-12 MeV neutrons produced as a result of scatter is a thousand times lower than that of the 14 MeV neutrons. This condition produces a need for fast organic scintillators with a minimized fraction of the delayed light not exceeding 10^{-3}. A possible solution of the problem is the use of liquid scintillators containing dissolved molecular oxygen known for its ability to suppress the delayed light via the efficient quenching of the excited triplet states responsible for the slow scintillation component [30]. The disadvantage of this method is that, even if the desired short decays are reached in the liquid scintillators, the presence of molecular oxygen leads to the simultaneous suppression of not only the delayed, but also the prompt component of fluorescence resulting in the total decrease of the scintillation efficiency

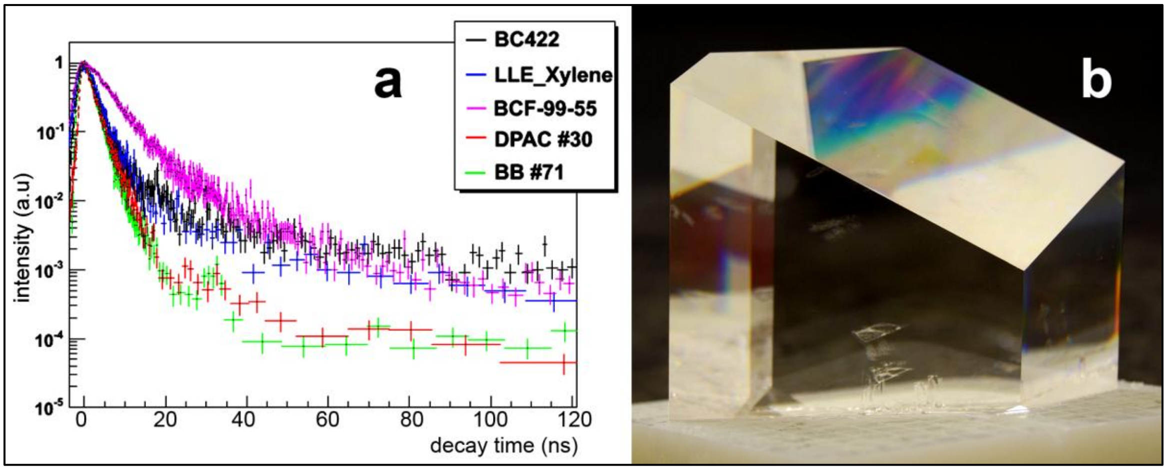

Figure 12. (a) - Scintillation decay curves of different organic scintillators tested for a potential use in NIF time-of-flight experiments: BC422 and BCF-99-55 are commercially available plastic scintillators from Saint Gobain, and LLE_Xylene is a commercial liquid scintillator quenched by oxygen; DPAC#30 and BB#71 are single crystal of diphenylacetyle and bibenzyl, respectively, both containing 1 % stilbene added to suppress slow component of scintillation. (b) - Bibenzyl-stilbene single crystal grown as a fast scintillator for NIF application;

essential for the high-resolution neutron spectrometry. Absence of PSD in the mixed DPAC-stilbene crystals (Figure 4 b and c) is also caused by the suppression of the delayed light therefore leading to a sharp decrease of the scintillation decay times. Comparative tests made with a number of commercially available scintillators showed that single crystals without PSD can have faster scintillation decays than oxygen-quenched liquid scintillators (Figure 12 a). Another attractiveness of the single crystals demonstrated in the DPAC-stilbene studies is that the addition of impurities used to suppress the delayed light does not produce any quenching effect on the prompt component of fluorescence, but on the contrary, leads to the enhancement of the scintillation LY. Since both suppression of the delayed light and increase in the scintillation efficiency can be obtained at very small additions of quenching impurities, different combination of host-impurity systems can be produced depending on the requirements to decay times, brightness, wavelengths of emission, etc. For the case of the NIF application, the combination of BB and stilbene was chosen (Figure 12 b) for further development because of the higher LY and better growth properties of BB in comparison with DPAC.

4.4. Non-crystalline organic scintillators

Consideration of PSD in non-crystalline organic scintillators is outside the scope of this paper and will be a subject of a separate report. It is, however, worth mentioning here that the understanding of the mechanisms of excited state migration and interaction obtained from the studies with mixed single crystals can be useful in application to organic liquid and plastic scintillators. A few experiments conducted in this work with complex liquid mixtures showed that more directional selection of the composition may help to improve the PSD properties of

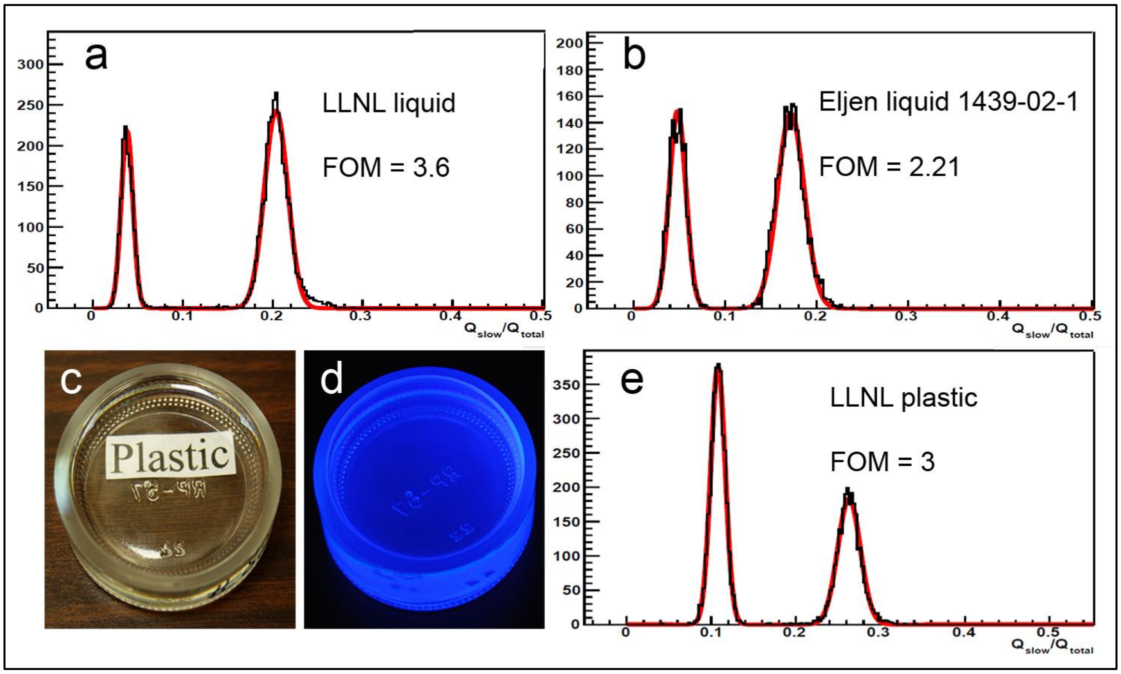

Figure 13. PSD measured in liquid and plastic scintillators with improved neutron/gamma discrimination properties: (a and b)-PSD profiles showing higher FOM in LLNL examples compared to a regular commercial liquid scintillators of approximately same volume; (c and d) - white and UV light - photographs of a 2" diameter and 1" thickness scintillating plastic with (e) – corresponding FOM showing PSD approaching the level of typical liquid and single crystal organic scintillators. All FOMs calculated in close gamma-equivalent energy ranges of 600-800 keV.

liquid scintillators (Figure 13 a and b). And probably the most interesting outcome of the studies is the creation of the first scintillating plastics with properties completely adequate for the detection of high-energy neutrons (Figure 13 c-e). Preliminary characterization of these novel materials still shows PSD inferior to the PSD in single crystals (FOM = 3 in comparison to ≥4 for close energy range in Figure 4 k). However, the fact that plastics can have PSD of the level known previously only for the best liquid and single crystal scintillators brings new opportunities in more comprehensive research of scintillation phenomena in organic materials of different physical states. Further development of these studies will be beneficial for production of new, more available and efficient materials for the specific needs of neutron detection

5. Conclusion

Pulse shape discrimination (PSD) properties utilized for detection of high-energy neutrons were studied with a number of new organic materials produced by solution growth. The major effort of the research using a model system of mixed diphenylacetylene-stilbene single crystals of different compositions was concentrated on the physical phenomena of excited state migration and annihilation leading to the formation of delayed light and PSD in organic materials. The results of the studies showed that, in addition to the molecular and crystallographic structures, presence of impurities with lower band gap energies is the major factor influencing PSD properties of organic materials. Due to the trapping effects, very small concentrations of such an impurity in a host crystal can substantially decrease the rate of triplet excited state migration leading to a sharp decrease of the decay times and complete disappearance of PSD. At a higher concentration of impurity PSD can reappear at a level exceeding that of PSD typical for both pure host and impurity. The concentration of the PSD re-appearance is determined by the percolation threshold resulting from the formation of the impurity molecules network that enables return of triplet energy migration. The results were applied to the explanation of PSD properties measured in different organic scintillators in previous works and in the recent survey of new materials. Understanding of the energy migration processes in complex systems resulted in growth of new organic scintillators with controlled decay characteristics. Crystals with a large fraction of delayed light can be used for high energy neutron detection via improved PSD, while crystals with very short decay may be of interest for further development as ultra-fast scintillators for energetic neutron detection in neutron time-of-flight experiments. The preliminary results obtained with non-crystalline organic materials show that application of the results obtained with single crystals can be beneficial for production of liquid and plastic scintillators with improved PSD properties.

Acknowledgement

We would like to thank Dr. Cheng Saw for providing X-ray analysis. The work was performed under the auspices of the U.S. DOE by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Financial support provided by the U.S. Department of Energy Office of Nonproliferation Research and Development (NA-22) and Department of Homeland Security (DNDO).

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