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Neutron detection with single crystal organic scintillators

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ABSRACT

Detection of high-energy neutrons in the presence of gamma radiation background utilizes pulse-shape discrimination (PSD) phenomena in organics studied previously only with limited number of materials, mostly liquid scintillators and single crystal stilbene. The current paper presents the results obtained with broader varieties of luminescent organic single crystals. The studies involve experimental tools of crystal growth and material characterization in combination with the advanced computer modeling, with the final goal of better understanding the relevance between the nature of the organic materials and their PSD properties. Special consideration is given to the factors that may diminish or even completely obscure the PSD properties in scintillating crystals. Among such factors are molecular and crystallographic structures that determine exchange coupling and exciton mobility in organic materials and the impurity effect discussed on the examples of trans-stilbene, bibenzyl, 9,10-diphenylanthracene and diphenylacetylene.

Keywords: single crystal organic scintillator, solution crystal growth, neutron detection, pulse shape discrimination (PSD), stilbene, bibenzyl, diphenylacetylene, 9,10-diphenylanthracene.

1. INTRODUCTION

Detection of high-energy neutrons is based on the existence of the two-decay component fluorescence observed in some organic scintillator, in which, in addition to the main scintillation component decaying exponentially (prompt fluorescence), there is usually a slower emission that decays at the same peak energy, but longer decay times (delayed emission).[1] The two-decay fluorescence gives rise to the pulse shape discrimination (PSD) phenomena first demonstrated and developed using single crystals of anthracene, *trans*-stilbene, p-terphenyl and p-quaterphenyl,[2-5] among which *trans*-stilbene was found to have the best properties for discrimination of different types of radiation. Recent availability of high-speed waveform digitizers brought big advantages in the further development of the studies of neutron-gamma discrimination phenomena.[6-8] The majority of these studies, however, have been made with liquid organic scintillators or, for the rare exception with single crystal stilbene, which is still considered to be the best suitable material for neutron-gamma discrimination. The composition of the liquid scintillators typically includes several traditional compounds, such as toluene, xylene, p-terphenyl, PPO (2,5-diphenyloxazole), POPOP (1,4-bis(5-phenyl-2-oxazolyl) benzene), with only few additional molecules found to exhibit PSD in the complex liquid mixtures. This limited number of empirically identified compounds forms only a small fraction of known organic scintillators, the majority of which have never been grown as single crystals or have never been investigated for their PSD properties before. In our current work, we undertake a survey of the PSD properties of a broad variety of fluorescent organic materials in the isolated crystalline state. This study, which involves experimental tools of crystal growth and material characterization in combination with advanced computer modeling, aims to better understand the correlations between the nature of the organic materials and their PSD properties, to enable the directed selection of more efficient scintillators for application in modern detectors. Experimental tests made so far with more than 100 organic compounds already allowed for the identification of a number of efficient PSD materials.[9] Further studies on these and additional organic crystals revealed that precise evaluation of the discrimination properties and quantitative comparison of new materials can be done only if a number of factors that may diminish or even completely obscure the PSD properties in crystalline matter are taken into consideration. Among such factors are the molecular and crystallographic structures, which determine exchange coupling and triplet mobility in organic materials, and the impurity effects. In the present paper, these effects are illustrated using examples of *trans*-stilbene, bibenzyl, 9,10-diphenylanthracene (DPA) and diphenylacetylene.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

Selection of the organic compounds for investigation was made based on their fluorescence and scintillation properties either reported in literature[10,11] or expected from their structures, which contained aromatic groups and certain substitution groups. For better interaction with high-energy neutrons, only low-Z materials were considered. Single crystals were grown from solutions at room temperature using slow evaporation technique. Organic solvents used for solution preparation varied depending on the solubility of the crystallizing materials. Stilbene was found to have similar solubility measured at about 0.13 g/g of solvent, both in toluene and 1,2-dimethoxyethane (DME) solutions at 24°C. Diphenylacetylene could be grown from the same solvents saturated at much higher solubility of 1.6 g/g of toluene and 2g/g of DME. Much lower solubility was measured in saturated solutions of DPA in toluene and xylene (about 0.04g/g solvent). In many cases, the growth solutions were prepared without measurements of the solubility by placing excessive amounts of the solid powders in respective solvents. The solutions were allowed to stir for a few days to reach the saturation, then separated by filtration into separate covered vessels (typically 100-200 ml), overheated 10-15°C above the saturation temperature and then allowed to cool. A few millimeter size seeds obtained prior to the growth by spontaneous nucleation were added to the solutions above the room temperature through a hole left open in the cover of the glass for further slow evaporation. Solid powders and solvents for crystal growth were purchased from different vendors (Aldrich, Acros Organics, Alfa Aesar). Commercially produced melt-grown stilbene used for comparison was purchased from Amcrys-h company (Ukraine).

For chemical analysis, samples of inclusion-free crystals were placed in 2.0 cc vials and dissolved in acetone:dichloromethane (1:1). 5 μL samples were analyzed 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°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°C to 250°C over 35.5 minutes. The mass selective detection was run in full-scan mode (30 to 550 m/z). Diphenylacetylene and stilbene were identified by MS=178 and 180 respectively and authenticated with a NIST library search.

Photoluminescence (PL) spectra were measured under the UV excitation using a commercial Fluoromax-2 spectrometer. The scintillation 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.

The pulse shape discrimination measurements were performed using a ^{252}Cf source shielded with two inches of lead to irradiate crystals coupled to a R6231-S Hamamastu 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 an organic crystal to discriminate between the neutrons and gamma rays emitted from the ^{252}Cf source was evaluated using the time-to-threshold method. In the offline analysis, the recorded waveforms were analyzed to determine the time required for the normalized pulse integral to reach 90-95% of the total integration over 300 nanoseconds. For quantitative performance comparisons of different crystals, the threshold was optimized for each scintillator within the gamma energy range of 400-600 keV to maximize the ratio of the distance (S) between the gamma and neutron peaks and the sum of the corresponding full widths at half maximum $(s_{gamma} + s_{neutron})$. Figure of merit calculated as FOM = $S/(s_{gamma} + s_{neutron})$ was used for quantitative comparison of different crystals.

Density Functional Theory (DFT) calculations at the PBE[12] 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 diphenylacetylene. 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[13]). The calculations were performed with VASP (Vienna *ab initio* simulation package)[14] using projector augmented wave (PAW) pseudopotentials to represent the ion-electron interactions[15].

3. RESULTS AND DISCUSSION

A specific feature of the crystals tested in the present work is that they were grown using solution growth techniques. The majority of organic crystals studied for scintillation properties previously[10] were grown by more traditional melt (Bridgman) techniques. Since the difference in temperature and presence of the additional compounds (solvents) could potentially result in the formation of compositional and structural polymorphs, preliminary test were made to confirm that materials produced by different growth methods were identical, and solution-grown single crystals could exhibit the PSD of the same magnitude as crystals grown from melt. Figure 1a shows one of the first stilbene crystals produced from toluene solution for these calibration tests.

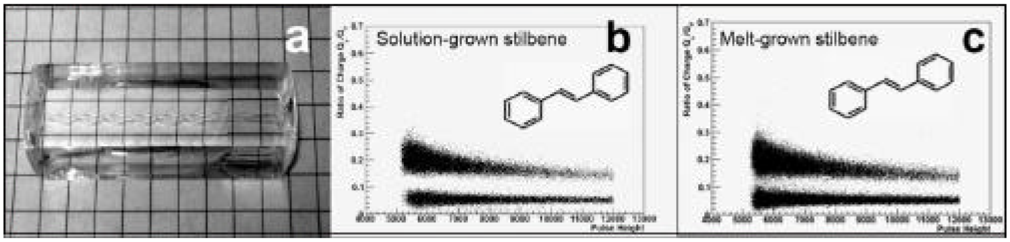


Fig. 1. (a) - *Trans*-stilbene single crystal grown from toluene solution by slow evaporation technique; grid squares are 6.5 mm on each side. (b) and (c) - PSD measured under the same conditions using a ^{252}Cf source for stilbene grown (b) from solution and (c) from melt.

X-ray crystallographic analysis made with this crystal showed structure identical to that reported for *trans*-stilbene crystals previously.[16] Measurements of the light yield (LY) produced the value of 24,000 Ph/MeV typical for efficient organic scintillators (~20,000 Ph/MeV in standard anthracene crystals). Comparison of the PSD made with the solution-grown crystal to that of the commercially produced stilbene of approximately same size and orientation also did not reveal any substantial difference, showing that the PSD properties of stilbene are not compromised by the variations of growth methods, and organic crystals with the excellent scintillation properties may be produced using solution crystal growth. Measurements made with other organic materials produced a broad spectrum of gamma-neutron discrimination patterns ranging from very weak PSD found in most of single-phenyl and condensed-phenyl ring materials (Figure 2 a and b) to excellent separation, even surpassing that of stilbene for some compounds (Figure 2 c). A number of materials did not exhibit any PSD at all (Figure 2 d).

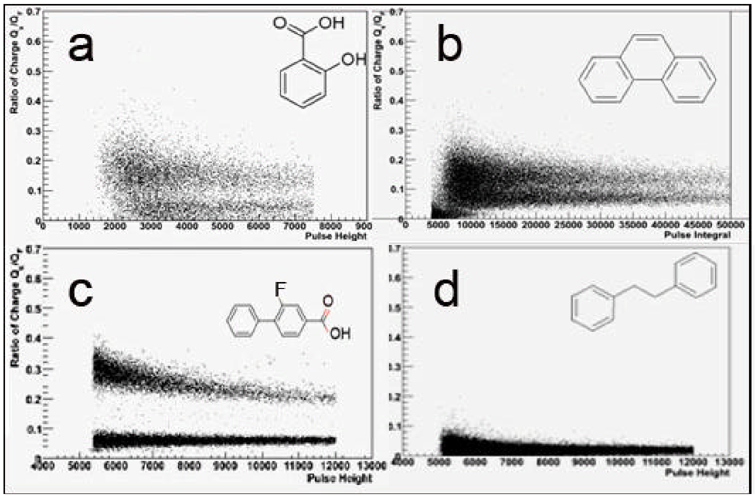


Figure 2. Examples of different PSD patterns measured in single crystals of different aromatic compounds: (a) – salicylic acid, (b) – phenathrene, (c) – 2-fluoro-4-biphenylcarboxylic acid, (d) – bibenzyl. ^{252}Cf source used in all measurements.

Precise comparison of the PSD properties of different crystals requires development and introduction of new quantitative parameters that may depend on the crystal quality, size, light yield, measurement conditions, etc. Even more efforts are needed to understand how these parameters depend on the molecular and crystallographic structure of the materials. According to a commonly accepted mechanism,[1,4,17] the slow component that determines the PSD phenomena originates from the collisional interaction of pairs of molecules (or excitons) in the lowest excited ***p***-triplet state T_1, while the fast component originates from the direct radiative de-excitation of excited singlets S_1. The process is illustrated by Figure 3. It begins with intersystem crossing (ISC), where the excited singlet state (S_1) nonradiatively relaxes to the excited triplet (T_1). 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 enhanced level of delayed emission for neutrons arises from the short range of the energetic protons produced from neutron collisions (thereby yielding a high concentration of triplets), compared to the longer range of the electrons from the gamma interactions. The resulting higher concentration of triplets from neutrons, compared to gamma interactions, leads to the functionality of PSD.

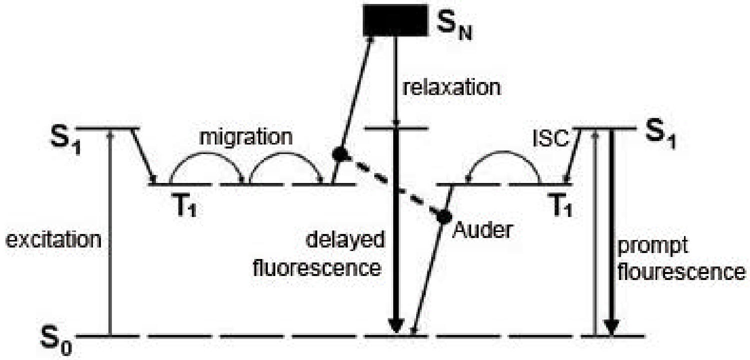
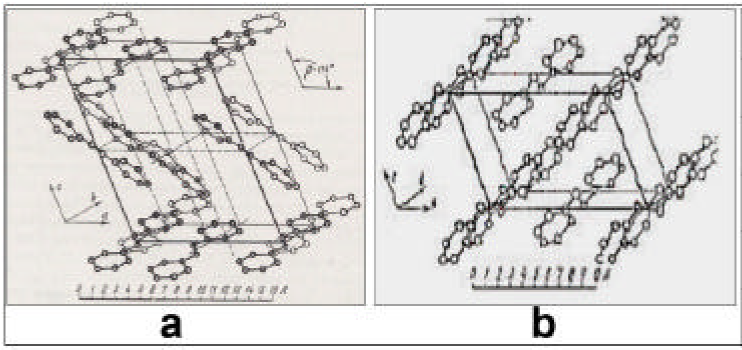


Figure 3. Basic physical processes leading to the delayed fluorescence characteristic of neutron excitation of organics with phenyl groups.

Based on this general model, the PSD properties of materials should depend on the electronic structure, mutual position (configuration) and distances that determine the exchange coupling between organic molecules in a crystallographic lattice. Comparison of the sets of compounds found on the opposite sides of the broad PSD properties spectrum (excellent PSD and complete absence of PSD) may present a special interest for consideration of how the discrimination properties of different compounds relate to their chemical and crystallographic structures. Among a number of such sets found in the studies, one of the most striking is represented by the pair of stilbene and bibenzyl. The pair is remarkable because all measurements made with stilbene resulted in good PSD, while numerous crystals of bibenzyl always revealed complete lack of PSD (Figure 2 d). No impurities were detected in any of the crystals, so that the explanation of the difference should most likely be related to the nature of the compounds themselves.

Stilbene and bibenzyl have very similar molecular structures (Figures 1 and 2 d), differing only by the double (stilbene) or single (bibenzyl) C-C bond between the two central carbon atoms. Both crystals belong to the same monoclinic space group ($P2_1/a$). However, as shown in Figure 4, a distinctive difference in the packing arrangements leads to very different configuration of the molecules that may result in considerably different rates of triplet migration and recombination. Preliminary estimations made using fragmented spin difference (FSD) calculations based on the configuration interaction with single excitations (CIS) method[18] for both compounds showed that the exchange coupling of neighboring pairs of stilbene molecules has larger values than in bibenzyl (for neighbor separations and orientations found in the respective crystals; see table in Figure 4). As a result, the triplet migration in bibenzyl may be too slow to allow for an appreciable amount of triplet-triplet collisions and delayed luminescence to occur before non-radiative de-excitation of the triplets. However, since the calculated exchange couplings show strong directional anisotropy and are not,zero in every direction, even for bibenzyl, additional study is required to determine unequivocly if delayed fluorescence in bibenzyl is really absent or if the sensitivity of the measurement is not sufficient for its detection. More extensive studies of the transfer integrals and the possible effects of directional energy transfer in organic crystals will be the subject of further investigation to help answer this question, in conjunction with further experiments.



Molecule	Configuration	Exchange Coupling (meV)	PSD
stilbene		0.77	Good
stilbene		2.11	Good
stilbene		0.40	Good
bibenzyl		0.30	Bad
bibenzyl		0.06	Bad

Figure 4. Crystal structures of (a) stilbene and (b) bibenzyl (Ref. 16 and 19, respectively) with the table showing calculated values of the coupling exchange for different configuration of molecules in crystals

The low exchange coupling and consequently slow triplet migration rates are intrinsic properties expected to influence delayed fluorescence and PSD in organic materials. Another well-known factor influencing the PSD is the effect of impurities. It has been known from the early works[4] that the slow scintillation component is not observed in liquid scintillators containing dissolved oxygen. Our results show that a similar effect can be also observed in scintillation crystals containing certain kind of impurities, as happens, for example with the diphenylacetylene crystals. The earliest works on the scintillation decay measurements[20] reported some evidence of the slow decay component in diphenylacetylene observed in the same experiments with anthracene and stilbene. Later studies, however, did not confirm the observation, and as a result, diphenylacetylene became a material listed in the classical literature as an exceptional organic crystal unsuitable for the PSD.[1,17]

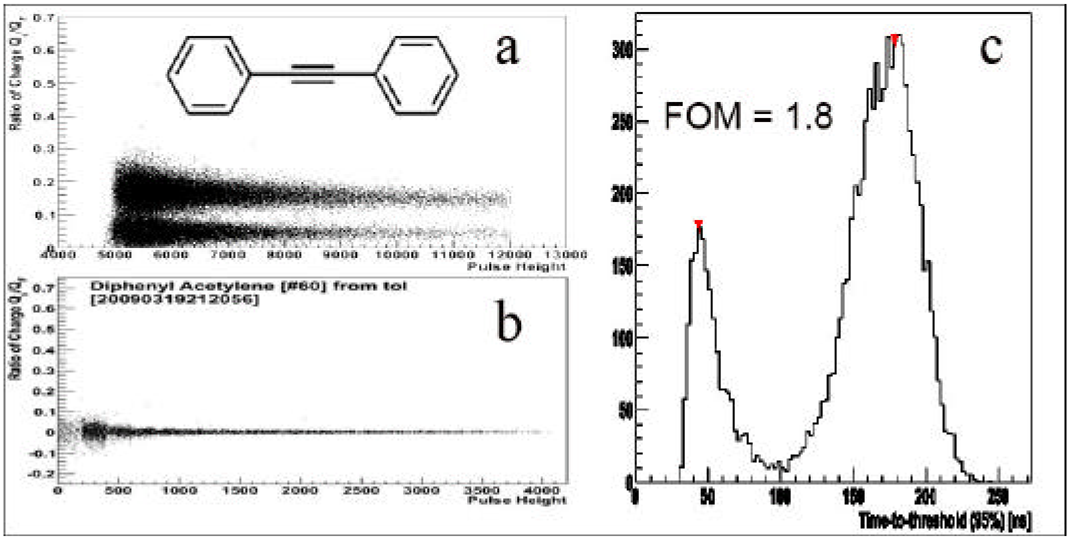


Figure 5. (a) and (b) - PSD patterns measured in two diphenylacetylene single crystals grown from different batches of raw material; (c) – separation profile of the PSD used from data (a) for the FOM calculation. ^{252}Cf source used in all measurements.

The results of the measurements obtained in our experiments with diphenylacetylene are illustrated by Figure 5, where PSD measurements from two crystals grown from different raw materials are shown. Both crystals were tested under the same conditions using a ^{252}Cf source. However, while the first one shows a clearly distinguished PSD, exhibiting a FOM of 1.8 (the highest value obtained in stilbene under similar conditions is 3.8), the second crystal does not reveal any evidence of the neutron/gamma discrimination properties. Measurements made with additional crystals grown from the same raw materials showed complete correlation between the batch of the commercial powder used and the presence (group a) or absence (group b) of PSD. Transparent, colorless crystals grown from both batches had similar appearance with the same angles measured between the corresponding facets (Figure 6 a and b). Crystals had practically identical absorption and PL spectra (Figure 6 c), very similar to the spectra of single crystal stilbene. The only difference was revealed by chemical analysis. All crystals from the group a (PSD) did not have any detectable impurities, while the crystals from the group b (no PSD) showed the presence of stilbene in the amounts of about 2 %. It should be also noted that, similarly to the previously reported results,[21] much higher light yield (22,000 Ph/MeV) was observed in stilbene-containing diphenylacetylene in comparison to pure diphenylacetylene crystals (2500 Ph/MeV).

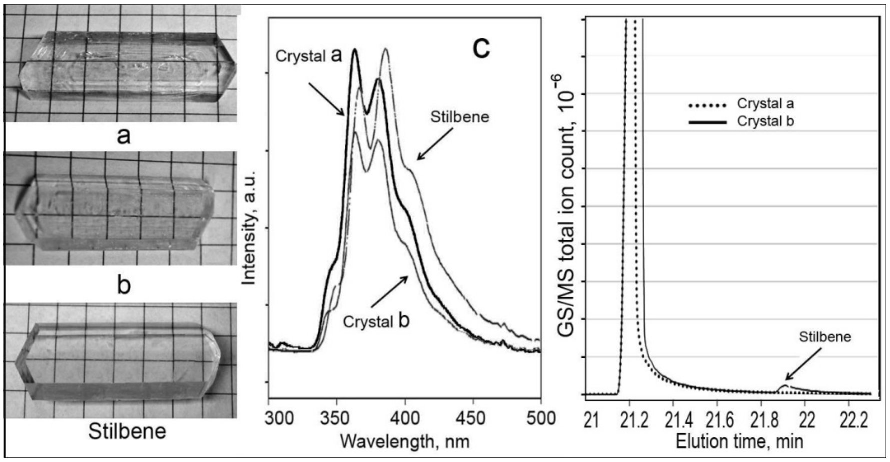


Figure 6. (a) and (b) – pictures of diphenylacetylene crystals used to obtain respective PSD patterns shown in Figure 5; photograph of a fully faceted stilbene crystal is given for comparison; side of background square is 6.5 mm; (c) – photoluminescence spectra of diphenylacetylene and stilbene crystals; (d) – GS-mass spectroscopy patterns obtained from the diphenylacetylene crystals.

Additional measurements made with a number of diphenylacetylene crystals and raw materials showed broad variation of the stilbene concentration from 0.5 to 10%, confirming previously reported observations[10] that stilbene is a very common impurity for diphenylacetylene, probably introduced in it in the process of the synthesis. Both molecules have very similar sizes and shapes and form almost identical crystal structures (Figure 7), leading to the formation of mixed crystals. Under these conditions, it is not surprising that common methods of purification may be not effective, in some cases leading even to the enrichment of stilbene, as occurs during re-crystallization, in which stilbene preferentially incorporates in the crystallizing fraction of diphenylacetylene.

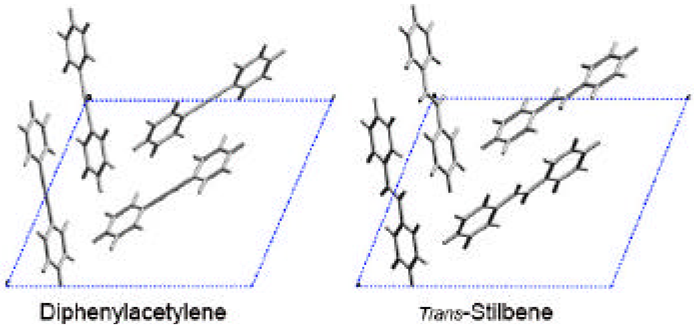


Figure 7. Crystal structures of diphenylacetylene and *trans*-stilbene (Ref.22 and 16, respectively). Lattice parameters for diphenylacetylene: a=15.488 Å, b=5.754 Å, c=12.766 Å, α=90°, β=113.36°, γ=90°; for stilbene: a=12.287 Å, b=5.66

Å, c=15.478 Å, α=90°, β=112.03°, γ=90°.

More surprising is the fact that the complete quenching of the PSD in diphenylacetylene occurs under the effect of such impurity as stilbene, which by itself is known as one of the best materials for the PSD application. It can be assumed that the effect most likely relates to quenching of the energy transfer process of the triplet migration[23]. An additional explanation comes from the consideration of the excited states energies of the two molecules.

The first triplet excited state of stilbene could be calculated using the ΔSCF method, which was shown in ref. 24 to be comparable in accuracy to Time-Dependent DFT (TDDFT) and to other high-level *ab initio* quantum chemical methods for estimating excitation energies. Calculations of the triplet excitation energies for stilbene and diphenylacetylene made in the current work using the ΔSCF method find that stilbene is predicted to have a smaller T_1 triplet excitation energy (2.4 eV) than diphenylacetylene (2.7 eV). This suggests that when stilbene is present as an impurity in diphenylacetylene crystals, stilbene molecules may act as an excitation trap and quench the PSD, as observed.

In the T_1 state of stilbene, the central C-C bond was found to rotate fairly easily (in the gas phase), with the potential energy surface for rotation being essentially flat, while the ground S_0 state exhibits a significant barrier to double bond rotation. However, in the crystal environment, because of steric interactions, it is likely that stilbene will remain planar even in the T_1 state. In the case of diphenylacetylene, the roles of the S_0 and T_1 state are reversed. In the S_0 state, the phenyl rings are almost free to rotate with a barrier height at 90 degrees of only 40 meV (~ $2kT_R$ at room temperature) and a minimum at 0 degrees (planar molecule). In the T_1 state, the central triple bond gets converted to a double bond upon excitation while the sigma bonds between the phenyl rings and the central carbons acquire some π character, shortening and stiffening those bonds. The potential energy surface (PES) of the phenyl-phenyl rotation in diphenylacetylene is presented in Figure 8 where the minima in the S_0 and T_1 states line up for planar molecules in both states, corresponding to the most likely geometries in the crystal.

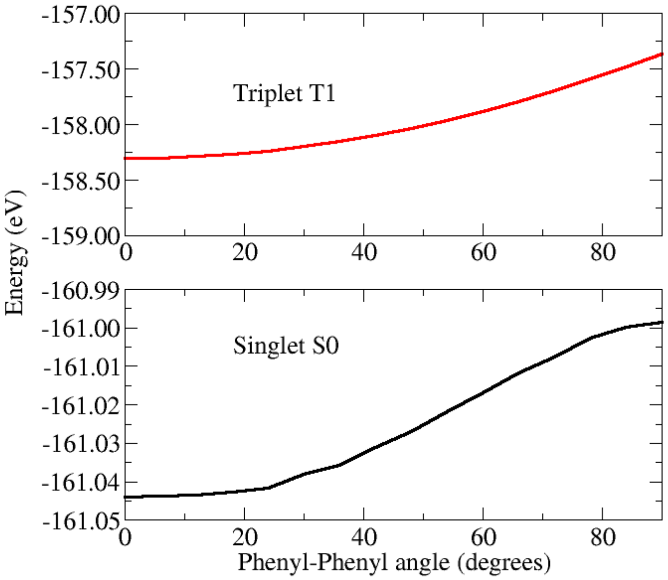


Figure 8. The PES for phenyl-phenyl rotation in diphenylacetylene. (Top) The T_1 state. (Bottom) The S_0 state. The triplet excitation energy is taken as the difference in total energy at the minima (0 degrees in diphenylacetylene).

The discussion above implies that impurities with a higher triplet excitation energy should not affect the PSD properties of the host material. A proof of such assumption is provided by the fact that stilbene crystals grown with similar concentrations of diphenylacetylene impurities (1-10%) did not show any change in the PSD properties compared to pure stilbene crystals.

The case of diphenylacetylene just discussed illustrated the effect of impurities that act as excitation traps in quenching PSD. Another type of impurity has also been observed, which does not quench PSD, but instead degrades the effect by reducing the light yield. An example of this effect is illustrated by the case of 9,10-diphenylanthracene (DPA).

Although DPA was found to be one of the most promising neutron detection materials,[9] much effort was required for purification of its raw material that, purchased from different vendors, always had yellow-brown color. Different intensity of this color indicated variations in the concentration of certain unknown impurities that could be removed by multiple recrystallization or sublimation procedures resulting in a purified product with a very pale-yellow color that may be characteristic of DPA itself. Figure 9 shows crystals grown on subsequent steps of such purification procedures. As seen from the numbers given next to the images, purification of the raw material resulted in the increased light yield of the crystals raising it in the final purified samples to the level of the best known organic scintillators. Measurements of the PSD also revealed the effect of impurities in all crystals. In this case, however, this effect resulted only in a gradual decrease of the gamma/neutron separation that never disappeared even in the most impure crystals (Figure 10 a and b).

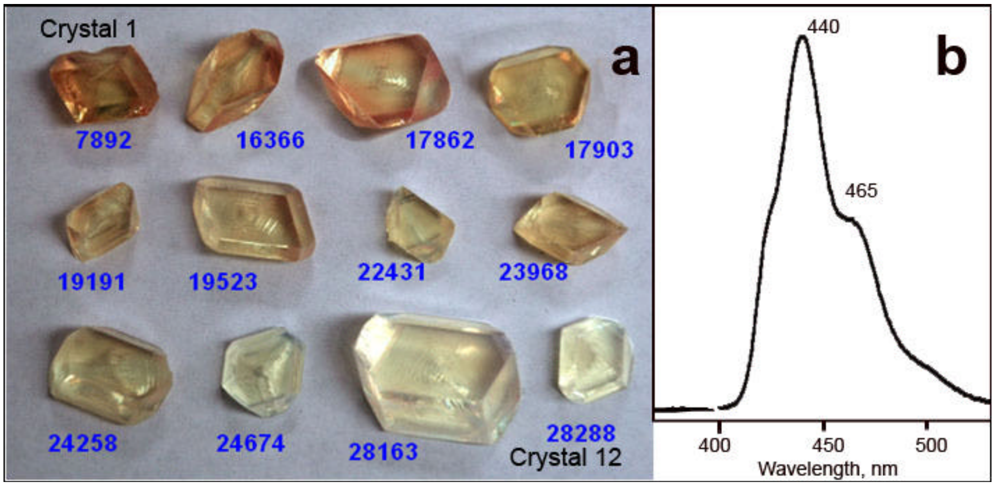


Figure 9. (a) - Crystals of diphenylanthracene grown from solutions of different purity. The first Crystal 1 was grown from initial powder without any purification. The last Crystal 12 was grown from 12-times recrystallized and additionally sublimed powder. Blue numbers show light yield in Ph/MeV.(b) - typical luminescence spectrum of diphenylanthracene crystals; UV excitation, 307 nm.

Calculated FOM for two extreme examples of Crystal 1 and Crystal 12 in Figure 9 a, showed its large increase from 2.1to 3.8 (equal to the FOM obtained with the best stilbene single crystals). The analysis (Figure 10 c and d) revealed that this large difference in the FOM values of the two crystals was determined mainly by the change of the full widths at half maximums s_{gamma} *and* $s_{neutron}$ rather than by the separation *S* between the gamma and neutron peaks that remained constant within the accuracy of the measurements. Since the widths of the peaks depend on the quantity of the light influencing the photon statistics, this result may indicate that the deterioration of the PSD with the increasing content of impurity in DPA crystals is most likely determined by the increasing light absorption in impure crystals and may not relate to more sophisticated factors affecting delayed fluorescence in the cases of bibenzyl and diphenylacetylene. To check this assumption, an energy calibration was made for each crystal using a ^{137}Cs source. A factor of three more light was collected from crystal 12 as compared to crystal 1. If one assumes that the width of the PSD peaks is dominated by the photon statistics in the delayed light component, then expected increase in the figure of merit would be 1.7 which is very close to the observed factor of 1.8. Unfortunately such assumption has not been yet confirmed by experimental or calculation data, because no impurities were found in any DPA crystals. The absence of the detectable impurities may relate to the limits of the GC MS method or to the specific properties of impurities that can have identical chemical composition with DPA (conformational isomers).

The identification of these impurities, as well as other factors influencing the PSD, is the subject of further studies being currently conducted with a broader number of organic scintillators.

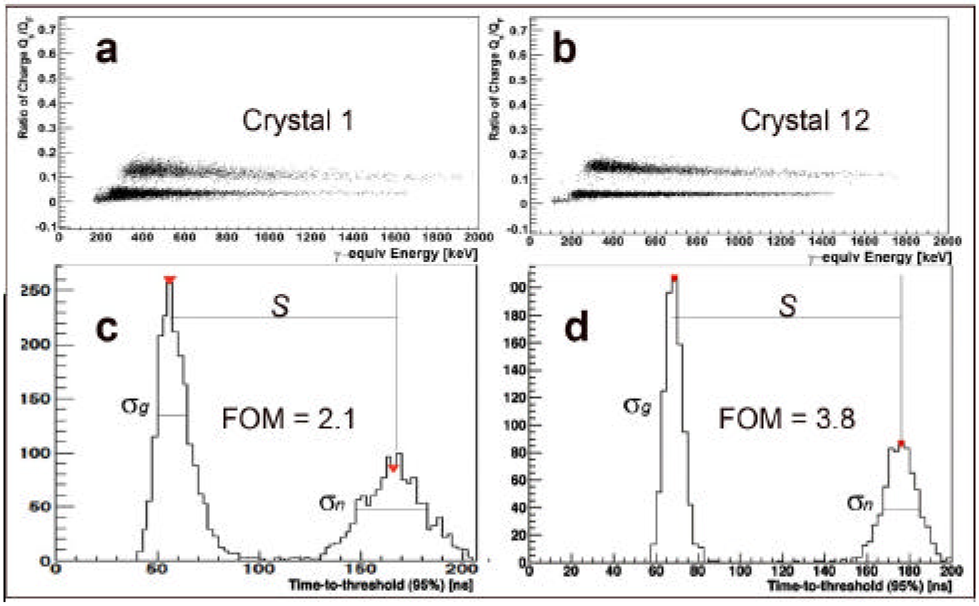


Figure 10. Comparison of PSD in two DPA crystals of different purity shown in Figure 9a as Crystal 1 and Crystal 12: (a) and (b) – PSD patterns at gamma-equivalent energies calibrated using ^{137}Cs. (c) and (d) – corresponding time-to-threshold profiles used for calculation of FOM.

4. CONCLUSION

Broad varieties of luminescent organic single crystals have been grown from solution for pulse shape discrimination (PSD) studies. Measurements made with single crystals of stilbene, used as a PSD standard, showed that neutron-gamma discrimination properties do not depend on the methods of crystal growth, and solution-grown organic crystals can have as high PSD performance as crystals grown by more traditional melt techniques. The results of the measurements obtained with other materials revealed a broad variation in the PSD properties of different crystals, from the levels of PSD exceeding that of stilbene to its complete absence. First analysis made by combination of experimental and computational methods showed that the absence of PSD in certain crystallographic structures may result from too slow triplet migration insufficient for an appreciable amount of triplet-triplet collisions, or from a specific relation between the triplet excitation energies, when an impurity with a smaller triplet energy may act as an excitation trap quenching the PSD in the host crystal. Other effects of impurities include light absorption that, at increasing concentrations, gradually decreases the light yield and the PSD dominated by the photon statistics in the delayed light component.

5. ACKNOWLEGEMENTS

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