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Solution growth of a deuterated *trans*-stilbene crystal for fast neutron detection

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Abstract. The paper reports results on growth and characterization of the first deuterated analog of the *trans*-stilbene crystal. The high optical quality stilbene-d₁₂ single crystal was grown by application of the solution technique using specially synthesized raw material and an aromatic solvent (anisole). Optical, physical, and scintillation properties of the new material are compared to those of the regular *trans*-stilbene crystal. The new deuterated material is promising for use in fast neutron spectroscopy without the need for time-of-flight measurements.

Keywords: A2.Deuterated stilbene crystal; B3.Neutron detection; B3.Pulse shape discrimination, B1.Organic scintillator; B3.Neutron spectroscopy

1. Introduction

Recent developments showed that solution growth methods traditionally applied to inorganic crystals grown from aqueous solutions can be successfully used to obtain single crystals of organic materials. Growth of large optical-quality crystals of pure aromatic compounds from organic solvents have been reported in a number of publications [1-3]. Exploration of the new materials was made mainly for potential applications in radiation detection [4-6]. It has been known for decades that hydrogen-rich fluorescent crystals of aromatic compounds present the

best materials for high-energy (fast) neutron detection that utilizes the pulse shape discrimination (PSD) technique [7]. The method, which is widely described in the literature [8-11], allows for separation of scintillation pulses produced by neutrons from the pulses of the usually present gamma radiation background. The discrimination is based on different mechanisms of neutron and gamma interactions with organic media. Both gammas and neutrons can be detected by scintillators because they excite fluorescent molecules with production of scintillation pulses. However, while gamma-rays in organic scintillators interact mainly with atomic electrons via the Compton effect, heavier neutrons elastically scatter on hydrogen atomic nuclei with production of recoil protons. With hydrogen-based organic scintillators, PSD techniques can be used for efficient neutron counting, while accurate measurements of neutron energies traditionally involve more complicated time-of-flight methods [12]. Early [13] and more recent studies conducted with liquid scintillators [14-16] demonstrated that neutron spectroscopy can be performed without time-of-flight if hydrogen atoms (^1H) are replaced by deuterium (^2H). The unique features of the deuterated scintillators arise from enhancing the forward recoil peak that corresponds to a specific energy of the incident neutron spectrum. However, scintillators with improved PSD are still needed for many applications [16]. Deuterated liquid scintillators are commercially available and often used to study nuclear reactions. Among single organic crystals, growth and characterization was reported only for a relatively small (10 mm in diameter x 21 mm long) anthracene-d₁₀ crystal [17]. This paper presents information on the growth of a large deuterated single crystal of *trans*-stilbene (stilbene-d₁₂). In its hydrogenated version, *trans*-stilbene-h₁₂ (regular stilbene) has proven to have much superior PSD compared to both anthracene and commercial liquid scintillators [5]. The neutron spectroscopy properties of the stilbene-d₁₂ crystal have been studied recently in detail and will be reported in separate

publications [18, 19]. This paper describes the synthesis, growth, and characterization of the basic physical and scintillation properties of the new material.

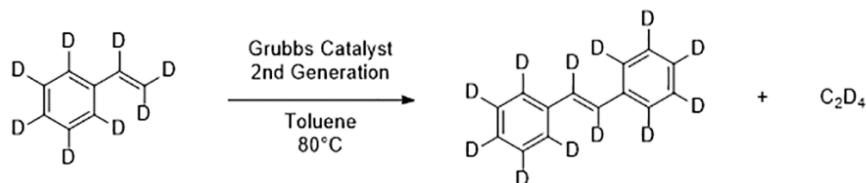
2. Materials and characterization methods

Octadeuterostyrene (styrene- d_8 , $C_6D_5CD=CD_2$) with a deuteration level ≥ 98 atom % 2D and “Grubbs’ CatalystTM 2nd Generation” were purchased from Sigma-Aldrich (now Millipore-Sigma). Anhydrous toluene and anisole were used as solvents in the synthesis and crystal growth, respectively. Confirmation of the molecular structure and isotopic enrichment were determined by NMR spectroscopy on samples dissolved in deuterated chloroform using a Bruker 600 MHz NMR spectrometer. Powder X-ray diffraction (XRD) measurements were conducted on a Bruker AXS D8 ADVANCE X-ray diffractometer equipped with a Ni-filtered $Cu K\alpha$ X-ray (8.0478 keV) source operated at 40 kV and 40 mA. Photoluminescence (PL) spectra were measured with UV excitation using a commercial Fluoromax-4 spectrometer. The scintillation light output (LO) and neutron/gamma discrimination properties of such crystals, as described in previous reports [2-5, 20], were evaluated from the position the Compton edge in the ^{137}Cs spectra and analysis of the PSD histograms, respectively.

3. Results and discussions

3.1. Synthesis and characterization of stilbene- d_{12} powder

A previous study showed that high-purity *trans*-stilbene can be obtained by styrene metathesis using Grubbs' catalyst [21]. By analogy, the synthesis of deuterated stilbene was conducted from commercially available deuterated styrene, according to the following reaction:



To synthesize the stilbene-d₁₂, styrene-d₈ and toluene were added in a 2:1 volume ratio to a round bottom flask. The solution was sparged for 15 minutes with dry nitrogen, then 0.0002 equivalents (relative to styrene) of Grubbs Catalyst™ 2nd Generation was added and a reflux condenser with a positive pressure nitrogen balloon was attached. The solution was refluxed for 16 hours, then cooled to -20°C to precipitate the solid, which was collected by vacuum filtration and washed with toluene. The resulting powder was recrystallized from toluene to obtain pure deuterated stilbene.

The spectra of the NMR analysis conducted to verify that deuterated stilbene had been synthesized are shown in Figure 1. The leftmost image shows the ¹H NMR spectra of natural abundance and deuterated stilbene. The presence of all four proton peaks in the ¹H spectrum of the deuterated material confirms the identity of the material as stilbene. The absence of splitting in the deuterated stilbene spectrum confirms the high degree of deuterium enrichment. There is a slight amount of splitting on peak “d,” indicating that the protons on the ethylene bridge are not fully deuterated. This is most likely due to incomplete deuteration of the ethylene used in

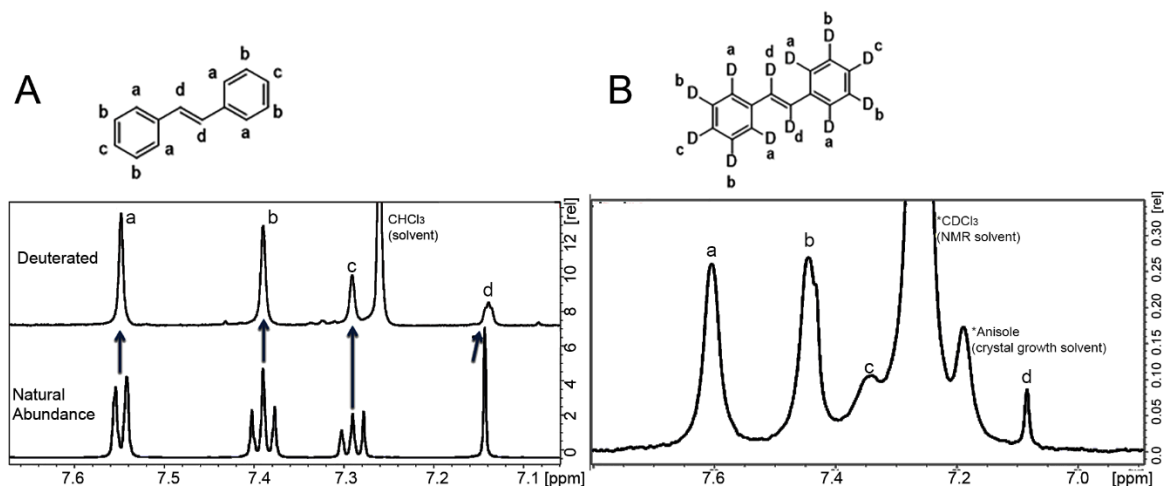


Figure 1. Results of NMR analysis of natural abundance stilbene and stilbene-d₁₂. Left: comparison of ¹H NMR spectra of natural abundance and deuterated stilbene. Right: ²H NMR spectrum of deuterated stilbene. Spectra were obtained from samples dissolved in deuterated chloroform.

styrene production process (benzene + ethylene → ethylbenzene → styrene). The rightmost image is the ²H spectrum of the deuterated stilbene. The presence of all 4 peaks indicates that there are deuterium atoms in all hydrogen positions in the deuterated stilbene. The overall high deuteration level of stilbene-d₁₂ also indicates that strong covalent bonds between carbon and deuterium are not severed during synthesis, so there should be no hydrogen–deuterium exchange expected upon dissolution in hydrogen-based solvents.

Corrected melting point ranges of the deuterated and regular stilbene were measured as 123.8°C – 125.9°C and 124.0°C – 126.1°C, respectively. The 0.2°C difference in the melting point ranges possibly arises from the slightly different size of the deuteron relative to the proton, reducing the van der Waals interactions between molecules in the crystal. The results of optical and XRD analysis are shown in Figure 2. The nearly identical PL spectra and the coincidence of the

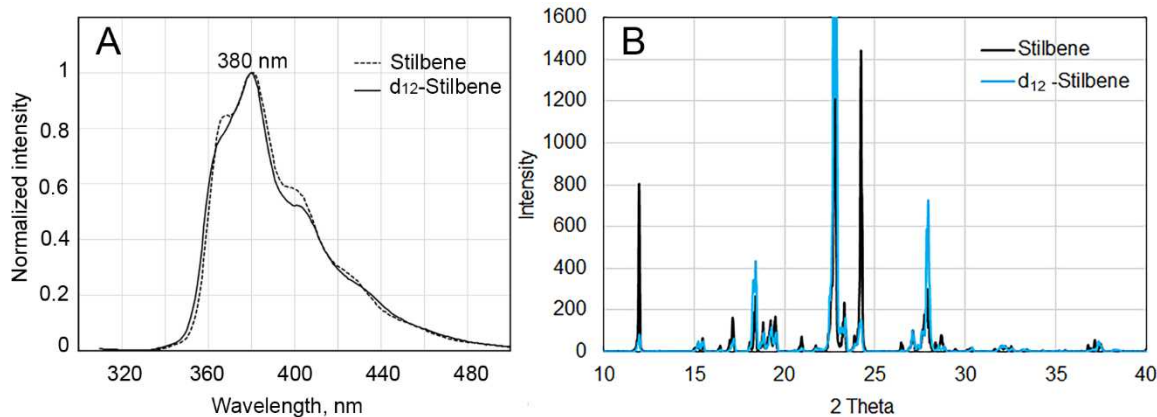


Figure 2. Results of (A) – PL and (B) – XRD analysis made with the synthesized d_{12} -stilbene powder. Comparison to corresponding spectra of regular stilbene indicates similar molecular and crystallographic structures.

diffraction peaks present additional confirmation that the deuterated powder had molecular and crystallographic structures similar to those of regular hydrogen-based stilbene.

3.2. Crystal growth

Similarly to stilbene, stilbene- d_{12} grows from toluene and anisole solutions in the shape of needles or thin rods. A collection of such rods was grown using a simple evaporation technique from anhydrous solvent. The least defective crystal with nice faceting, as described previously [2], was selected as a seed that was glued in the center hole of an aluminum platform designed to restrict growth of $\{111\}$ stilbene facets and sharp $[010]$ edges (Figure 3). The general design of a solution growth crystallizer used previously for the rapid growth of water-soluble KDP- DKDP (KH_2PO_4 and KD_2PO_4) crystals [22] and later adjusted to production of crystals from organic

solvents has been described previously [2]. Anhydrous anisole, found to be the most efficient solvent for stilbene crystal growth, was used to prepare an initial solution with the saturation temperature of $\sim 50^{\circ}\text{C}$. The filtered solution was transferred to the 0.5 L crystallizer, overheated for 12 hours at $\sim 65^{\circ}\text{C}$, and then cooled to the seed-loading temperature of 57°C . The seed-

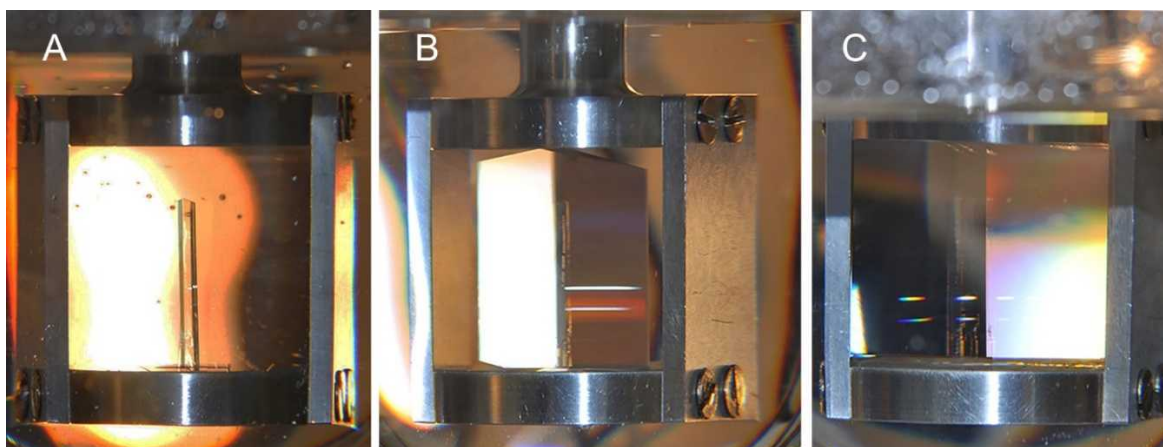


Figure 3. Photos taken during growth of stilbene- d_{12} crystal: A – initial seed glued into a hole located in the center of the round aluminum platform; B – a growing faceted crystal at the moment of attachment to the upper restricting bar; C – close to the end, when the growing crystal fills space between the horizontal and vertical bars. The distances between the bars are 35 mm (vertical) and 30 mm (horizontal).

holding platform preliminarily preheated to the same temperature (57°C) in a separate tank, was introduced into the briefly opened solution that was immediately sealed after loading. The crystallizer with the platform reversibly rotating at 20 rpm was slowly cooled to a temperature $\sim 0.3^{\circ}\text{C} - 0.5^{\circ}\text{C}$ above the assumed saturation point which then was verified by careful observation of the first signs of growth using 0.1°C temperature reduction increments. After the precise saturation temperature of the solution was established as $49.2 \pm 0.05^{\circ}\text{C}$, the platform rotation rate was increased to 50 rpm, and the seed was allowed to slowly regenerate at a constant temperature of 49.1°C .

Figure 3 shows photographs of the growing stilbene-d₁₂ crystal found to have a shape and morphology identical to those of the regular stilbene crystals. Knowledge of the angles between the facets made it possible to apply simple methods for the crystal mass (M) calculations based on the sizes measured during growth and the density of 1.24 g/cm³ derived from the mass difference of hydrogen and deuterium atoms. Preliminary measurements also showed practically identical solubility of both types of stilbene in anisole, allowing for daily calculations of the supersaturation as:

$$\sigma = \left(\frac{PC_0 - M}{C_{0t}(P - M)} - 1 \right) 100\%, \quad (1)$$

where P and C_0 are the weight and the equilibrium concentration of the initial growth solution, respectively, C_{0t} is the equilibrium concentration of the growth solution at the temperature of measurement, t . A very moderate growth rate of about 2 mm/day in the horizontal direction was



Figure 4. The final stilbene-d₁₂ crystal grown in the shape of a hexagon. The initial seed is still seen through the optically transparent material that does not show any visible defects. The crystal mass is 38 g with a height of 35 mm.

controlled by gradual increase of the supersaturation from ~0.3% in the beginning of growth to ~6% by 25°C when the run was ended. The final crystal grown in the shape of a symmetrical hexagon is shown in Figure 4. Observations during the growth did not reveal formation of any visible defects in the crystal or precipitation of spontaneous crystals from solution. It should be also noted here that the relatively small weight and dimensions of the final crystal were determined by the limited amount of the initial high cost materials rather than by any limitations in the solution technique used. Since no difference was observed in the growth properties of deuterated and regular crystals, stilbene-d₁₂ can be easily grown to much larger scale, i.e. dimensions >10 cm as currently achievable for production of normal *trans*-stilbene crystals [5]. It should also be noted here that, similarly to regular stilbene, stilbene-d₁₂ is stable in air and non-hygroscopic, which provides many practical advantages in comparison to hazardous and environmentally unfriendly liquid scintillators commonly used for neutron detection.

3.3. Scintillation properties

Trans-stilbene crystal has been known as one of the most efficient organic scintillators with high light output (LO), excellent PSD, and emission wavelengths well-matched to typical PMTs and photo-diodes [5]. To evaluate the scintillation performance of the deuterated analogue, a crystal of precisely the same shape and dimensions was cut from a larger, high optical quality solution-grown crystal of regular stilbene (Figure 5). Measurements made with the ¹³⁷Cs gamma-ray source showed equal LO for both crystals within the detection uncertainty (~5%). A ²⁵²Cf

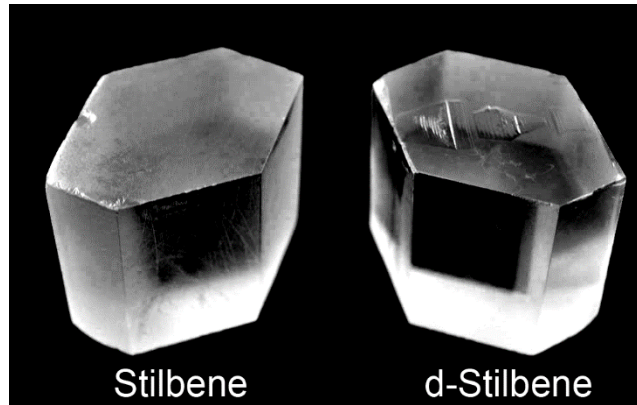


Figure 5. A photo of the regular and deuterated stilbene crystals of the same shape and dimensions used for the quantitative evaluation of the scintillation properties of stilbene-d₁₂.

source, an isotope that emits both neutrons and gammas, was used for the PSD evaluation by the charge integration method [10] described in detail in our previous publications [5, 20]. In this method, each scintillation pulse was numerically integrated to obtain the ratio of charge $R=Q_{Tail}/Q_{Total}$ of the respective total (Q_{Total}) and the delayed component (Q_{Tail}) of the signal. Pulses were separated based on the value of R determined by the different proportion of the delayed component known to be higher for the neutron-induced pulses (high R value) in comparison to those produced by gamma rays (small R value). The experimental PSD plots obtained with both crystals are presented in Figure 6 A and B. While excellent PSD is typical for all stilbene crystals, the deuterated analogue exhibits noticeably better discrimination as noted by the PSD figure of merit (FOM). This is shown in Figure 6 C for the electron-equivalent energy range of 460-500 keV_{ee} down to energies of 50 keV_{ee}. The difference in PSD relates most likely to the difference in the masses of deuterons and protons produced in deuterated and hydrogenated materials by the neutron excitation. The heavier, therefore slower moving, deuterons lead to a higher excitation density that may be favorable to the excited triplet state interactions required to produce delayed

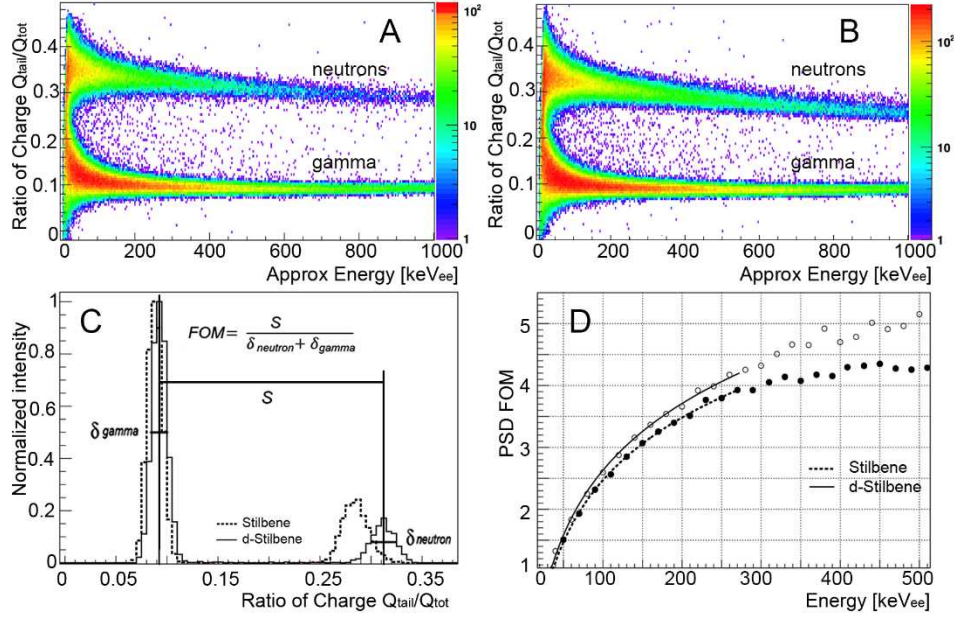


Figure 6. Scintillation properties of d₁₂-stilbene in comparison to regular stilbene: A – experimental neutron/gamma scatter plot obtained with d₁₂-stilbene; B – similar plot measured with a precisely same shape and size regular stilbene crystal; C – comparison of the PSD distributions calculated for both types of crystals in the electron-equivalent energy range of 460-500 keV_{ee}; schematic illustrates the method for calculation of the FOM; D - PSD FOMs vs energy showing better discrimination properties of d₁₂-stilbene in all energy ranges.

light [9]. Although only the basic characterization presented here demonstrates the excellent scintillator performance of stilbene-d₁₂, the expected advantages of this high performance solid-state deuterated scintillator for applications such as fast neutron spectrometry are outlined in [16]. More complete experimental studies for this and other applications with this same crystal will be reported elsewhere [18, 19]. As an example, in Figure 7 we display a PSD-gated light output spectrum for incident 14.1 MeV neutrons from a DT generator. As expected, a distinct peak corresponding to the incident 14.1 MeV neutrons is observed, demonstrating the potential of stilbene-d₁₂ for fast neutron energy spectroscopy without need for time of flight [16].

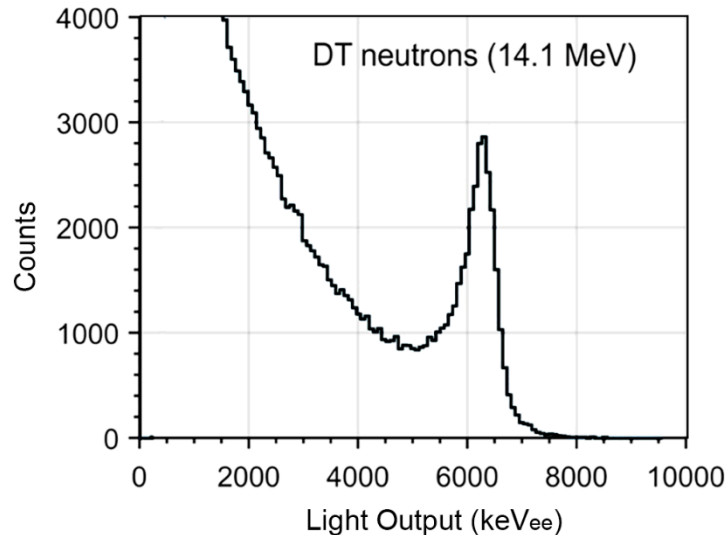


Fig. 7. Light output spectrum for 14.1 MeV neutrons incident on the stilbene-d₁₂ crystal [19].

Conclusion

The first deuterated analog of *trans*-stilbene was grown as a single crystal as a potential material for application in fast neutron detection and spectroscopy. The main motivation of the work was based on a known fact that replacement of hydrogen atoms (¹H) by deuterium (²H) atoms produces a change in the scintillator response to fast neutron interactions, allowing for identifying specific incident neutron energies without the use of complicated, usually lower-efficiency time-of-flight (TOF) methods. The initial stilbene-d₁₂ powder was synthesized and tested by NMR, XRD, and photoluminescence techniques to confirm similar molecular and crystallographic properties of deuterated and regular stilbene. The solution growth technique was applied to produce a single crystal of high optical quality with a linear size of ~35 mm. First studies of the scintillation properties showed that at approximately equal light output, stilbene-

d₁₂ has noticeably better PSD properties that, in combination with neutron energy recognition, makes it an excellent solid-state detector for high-energy neutron spectroscopy.

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References

1. G. Hull, N. Zaitseva, N. Cherepy, J. Newby, W Stoeffl, S. Payne, New organic crystals for pulse shape discrimination, *IEEE Trans. Nucl. Sci.*, 56 (2009) 899.
2. N. Zaitseva, L. Carman, A. Glenn, J. Newby, M. Faust, S. Hamel, N. Cherepy, and S. Payne, Application of solution techniques to rapid growth of organic crystals, *J. Cryst. Growth*, 314 (2011) 163.
3. L. Carman, N. Zaitseva, H.P. Martinez, B. Rupert, I. Pawelczak, A. Glenn, H. Mulcahy, R. Leif, K. Lewis, S. Payne, The effect of material purity on the optical and scintillation properties of solution-grown *trans*-stilbene crystals, *J. Cryst. Growth*, 368 (2013) 56.
4. N. Zaitseva, L. Carman, A. Glenn, R. Hatarik, S. Hamel, M. Faust, B. Schabes, N. Cherepy, S. Payne, Pulse shape discrimination in impure and mixed single-crystal organic scintillators, *IEEE Trans. Nucl. Sci.*, 58 (2011) 3411.

5. N. Zaitseva, A. Glenn, L. Carman, H. P. Martinez, R. Hatarik, H. Klapper, S. Payne, Scintillation properties of solution-grown trans-stilbene single crystals, *Nucl. Instrum. Meth. A*, 789 (2015) 8.
6. B. Fraboni, A. Fraleoni-Morgera, and N. Zaitseva, Ionizing radiation detectors based on solution-grown organic single crystals, *Adv. Funct. Mater.*, 26 (2016) 2276.
7. F.D. Brooks, "A scintillator counter with neutron and gamma-ray discrimination", *Nucl. Instrum. Methods*, 4 (1959) 151.
8. L.M. Bollinger and G.E. Thomas, Measurement of the time dependence of scintillation intensity by a delayed coincidence method, *Rev. Sci. Instrum.*, 32 (1961) 1044.
9. J.B. Birks, *The Theory and Practice of Scintillation Counting*, Pergamon Press, London, 1964.
10. C.L. Morris, J.E. Bolger, G.W. Hoffmann, C.F. Moore, L.E. Smith, H.A. Thiessen, A digital technique for neutron-gamma pulse shape discrimination, *Nucl. Instrum. Methods*, 137 (1976) 397.
11. F.D. Brooks, "Development of organic scintillators", *Nucl. Instrum. Methods*, 162 (1979) 477.
12. F.W.K. Firk, Neutron time-of-flight spectrometers, *Nucl. Instrum. Methods*, 162 (1979) 539.
13. J.B. Czirr, A comparison of scintillator solvents for pulse shape discrimination, *Nucl. Instrum. Methods* 88 (1970) 321.
14. V. Bildstein, P.E. Garrett, J. Wong, D. Bandyopadhyay, J. Bangay, L. Bianco, B. Hadinia, K.G. Leach, C. Sumithrarachchi, S.F. Ashley, B.P. Crider, M.T. McEllistrem, E.E. Peters, F.M. Prados-Estévez, S.W. Yates, J.R. Vanhoy, Comparison of deuterated and normal liquid scintillators for fast-neutron detection, *Nucl. Instrum. Meth. A*, 729 (2013) 188.
15. F.D. Becchetti, R.S. Raymond, R.O. Torres-Isea, A. DiFulvio, S.D. Clarke, S.A. Pozzi, M. Febbraro, Deuterated-xylene (xylene-d10; EJ301D): A new, improved deuterated liquid scintillator for neutron energy measurements without time-of-flight, *Nucl. Instrum. Meth. A*, 820 (2016) 112.

16. F.D. Becchetti, R.S. Raymond, R.O. Torres-Isea, A. Di Fulvio, S.D. Clarke, S.A. Pozzi, M. Febbraro, Recent developments in deuterated scintillators for neutron measurements at low-energy accelerators, *Nucl. Instrum. Meth. A*, 874 (2017) 72.
17. F.D. Brooks, W.A. Cilliers, B.R.S. Simpson, F.D. Smit, M.S. Allie, DTL. Jones, W.R. McMurray, J.V. Pilcher, Deuterated anthracene spectrometer for 5–30 MeV neutrons, *Nucl. Instrum. Meth. A*, 270 (1988) 149.
18. F.D. Becchetti, R.O. Isea-Torres, A. Di Fulvio, S.A. Pozzi, J. Nattress and I. Jovanovic, M. Febbraro, N. Zaitseva and L. Carman, Deuterated Stilbene (d12-stilbene): A New, Improved Fast Neutron Detector, Submitted for publication in *Nucl. Instrum. Meth. A*.
19. A. Di Fulvio, et al., Proceedings of SORMA XVII Conference 2018 (Ann Arbor, MI); Submitted for publication.
20. N.P. Zaitseva, A.M. Glenn, A.N. Mabe, M.L. Carman, C.R. Hurlbut, J.W. Inman, S.A. Payne, Recent developments in plastic scintillators with pulse shape discrimination, *Nucl. Instrum. Meth. A*, 889 (2018) 97.
21. Chatterjee, A.K., R.H. Grubbs, Synthesis of trisubstituted alkenes via olefin cross-metathesis, *Org. Lett.*, 1 (1999) 1751.
22. N. Zaitseva, L. Carman, Rapid growth of KDP and DKDP crystals, *Prog. Cryst. Growth Ch.*, 43 (2001) 1.