Melt-Cast Organic Glasses as High-Efficiency Fast Neutron Scintillators

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Abstract:

In this work we report a new class of organic-based scintillators that combines several of the desirable attributes of existing crystalline, liquid, and plastic organic scintillators. The prepared materials may be isolated in single crystalline form or melt-cast to produce highly transparent glasses that have been shown to provide high light yields of up to 16,000 photons/MeVee, as evaluated against EJ-200 plastic scintillators and solution-grown *trans*-stilbene crystals. The prepared organic glasses exhibit neutron/gamma pulse-shape discrimination (PSD) and are compatible with wavelength shifters to reduce optical self-absorption effects that are intrinsic to pure materials such as crystalline organics. The combination of high scintillation efficiency, PSD capabilities, and facile scale-up via melt-casting distinguishes this new class of amorphous materials from existing alternatives.

Keywords:

Organic scintillator; pulse-shape discrimination; neutron; glass; plastic; crystal

Introduction:

An ongoing objective in the field of organic radiation detection materials is to achieve a balance between scintillation performance characteristics and cost. Organic molecular crystals possess superior light-yields and neutron/gamma pulse-shape discrimination (PSD) but possess anisotropic properties and are expensive to produce in large sizes. In contrast, liquid and plastic scintillators are readily scalable to large sizes, although both are characterized by reduced light yields and particle discrimination properties. For example, the brightest (non-PSD) plastic scintillators possess light yields of ~10,400 photons/MeVee, which is approximately 80% that of solution-grown *trans*-stilbene crystals. [1] The light yield of a commercially-available PSD-capable plastic scintillator (Eljen EJ-299-33A) is ~8600 photons/MeVee, while a peak light yield of 13,000 photons/MeVee has been reported for research-grade plastic scintillators. [2-4] For the above reasons, our efforts are focused on developing high-performance solid-state organic scintillators that provide stable performance and have reduced preparation costs.

We previously reported a series of high-symmetry organic crystals that are based upon molecules that possess local C_3 -symmetry. [5] In that work, it was shown that increased molecular and crystallographic symmetry led to significantly higher light yields and PSD relative to their respective low-symmetry parent chromophores. High-symmetry space groups are also associated with improved crystal growth properties and mechanical robustness due to the presence of a greater number of independent slip systems to dissipate stresses induced by thermal or mechanical stimuli. [6] A similar strategy was employed in this work for compounds based upon three fluorene chromophores arranged around a silicon central atom, as shown in Scheme 1. Initial photophysical characterization of these materials showed that they behave as efficient scintillators in their respective crystalline forms, although an unexpected finding was that they also form stable and highly transparent organic glasses following cooling of the melt (Figure 1). Photoluminescence, thermoanalytical analysis, and scintillation measurements were performed to assess these materials and benchmark their performance against well-known organic scintillators. The combined results indicate that stable organic glasses present a promising new route towards high light-yield and low-cost PSD scintillators.

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Experimental:

Compounds **1–3** were synthesized via lithiation of the corresponding 9-alkyl-2-bromofluorene using standard organic synthesis techniques. Purification was achieved via flash column chromatography and recrystallization from toluene. Glasses of **1–3** were prepared by melting the powders in a Teflon-lined mold (20mm x 20mm x 20mm) or by casting the liquid samples onto a glass slide and allowing to cool ($\varnothing$ 10mm x 5mm). The different samples were prepared to confirm that the light collection efficiency and corresponding light yields remained constant for these small sample sizes in the experimental configuration described below. No additional surface treatment was performed on the obtained glasses. Reference samples of EJ-200 plastic scintillator were purchased from Eljen Technologies in dimensions of (10mm x 10mm x 10mm) and ($\varnothing$ 25.4mm x 25.4mm). All EJ-200 surfaces were polished to optical quality using a diamond tipped lathe. The obtained pulse-height spectra for different sizes of glasses of **1–3** and EJ-200 revealed light yields that did not vary with the size and geometry of each sample studied. The *trans*-stilbene reference sample of dimensions (20mm x 20mm x 20mm) was prepared according to the technique described by Carman et al., comprising synthetic preparation from styrene, followed by crystal growth from anhydrous anisole. [7] The crystal faces were polished; the face perpendicular to the *c*- crystallographic axis was optically coupled to the PMT. The purity and light-yield of the prepared sample is consistent with the published results, which provided a light-yield more than twice that of a melt-grown *trans*-stilbene crystal obtained from ScintiTech, Inc. [7]

Steady-state spectra, quantum-yields, and time-resolved photoluminescence measurements were collected using a Horiba Jobin-Yvon Fluorolog FL3-21 fluorescence spectrometer equipped with an integrating sphere attachment. Data were collected on powder samples at 90° incidence for steady-state spectra and time-resolved measurements, and in the front-facing geometry for quantum-yield data. Differential scanning calorimetry data were collected using a Mettler Toledo DSC 822 instrument and processed using the STARe SW 12.10 software package. A heating rate of 10°C was used during data acquisition. Powder X-ray diffraction data were obtained using a PANalytical Empyrean instrument equipped with a 40 kV Cu K-alpha source and an XY-rotating sample stage. 33 keV X-ray spectra were obtained using the Barium $K_{\alpha 1}$ and $K_{\alpha 2}$ X-rays emitted from a ^{137}Cs source. The relative pulse heights in Table 1 were evaluated from the position of the 33 keV photopeak. No background corrections were required due to the high relative intensity ratios for these X-ray emissions and the high photoelectric cross sections of organic scintillators in this energy range. 662 keV gamma-ray scintillation pulse-height spectra were similarly obtained for bulk samples using a ^{137}Cs source. All samples were evaluated using an Electron Tubes 9124-QB bialkali photomultiplier tube biased at 1000 V. All samples were wrapped on five sides by reflective PTFE tape, coupled to the PMT face, and covered by an aluminum light shield. The ^{137}Cs and AmBe sources were placed directly on the aluminum shield, resulting in a source-to-scintillator distance of ~1mm. Pulses were digitized using a 600 MHz, 12-bit LeCroy HRO 66Zi oscilloscope and histogrammed using a 500ns integration time for scintillation pulse-height measurements. Neutron/gamma pulse-shape discrimination data were obtained using a similar experimental configuration but processed off-line using the charge-comparison method. [8] The charge-comparison PSD parameters were optimized for each sample, comprising the prompt/delayed cutoff time and total integration time.

Results and Discussion:

Photoluminescence Spectroscopy:

Photoluminescence measurements were performed on glasses of compounds **1–3**. Steady-state excitation and emission spectra for **1** are provided in Figure 2, illustrating properties that are dependent upon the preparation method. Data in the top plot was obtained on a glass prepared via sublimation, whereas the data in the bottom figure was obtained for a melt-cast glass. The emission spectra reveal a

38nm blue-shift in the peak emission wavelength for sublimed versus melt-cast samples of **1**. The presence of fine structure in both spectra suggests that the shift is not due excimer or exciplex formation but instead associated with the activation of different phonon modes on the discrete fluorene chromophores. The spectral shift is imposed by differences in molecular packing and this assignment is further supported by the presence of common vibronic transitions and comparable fluorescence lifetimes ($\tau_1=0.8$ ns [56%], $\tau_2=2$ ns [44%]) observed for both forms. Respective fluorescence quantum yields of 0.39 and 0.47 were obtained for equivalently pure samples of **1**-sublimed and **1**-melt, which is somewhat surprising considering the large spectral overlap for **1**-sublimed. However, all glass samples described below were prepared via melting due to the improved scalability of this method.

Wavelength Shifters:

A fundamental limitation that contributes to the limited light yields of plastic and liquid scintillators is a low fluorescence quantum yield for the host matrix, which ranges from 0.12 for polystyrene/polyvinyltoluene to 0.17 for toluene. Equations 1 and 2 indicate the significance of this limitation, as the efficiency (E) of fluorescence resonant energy transfer (FRET) is associated with the fluorescence quantum yield of the donor (Q_D). Other variables in these equations include the donor-acceptor distance (r), dipole orientation factor (κ^2), Avogadro's number (N_A), refractive index of the medium (n), and spectral overlap integral (J).

$$E = \frac{1}{1+(r/R_0)^6} \quad (1)$$

$$R_0^6 = \frac{9(\ln 10)}{128\pi^5 N_A} \frac{\kappa^2 Q_D}{n^4} J \quad (2)$$

High fluorescence quantum yields and efficient FRET energy transfer are therefore pre-requisites for high-efficiency organic scintillator mixtures since the final step of energy conversion always proceeds through the fluorescent excited state. It is worth noting that a similar FRET constraint is not required for single-component scintillators such as organic crystals since there is no donor or acceptor. However, crystalline scintillators intrinsically suffer from a different type of performance degradation due to self-absorption of the overlapping excitation and emission spectra. This limitation is also particularly evident in the sublimed glass of **1**.

For the above reasons, compounds **1–3** were evaluated as a new type of solid-state and transparent host matrix for wavelength shifting dyes. The fluorescence quantum yields for **1–3** are between 0.39–0.57, which is between 2–5 times that of liquid and plastic scintillator matrices. These higher quantum yields provide the possibility for enhanced FRET and scintillation light yields. The wavelength shifter 9,10-diphenylanthracene (DPA) was selected for this study due to good spectral overlap and strong molar absorptivity in the donor emission range. DPA concentrations in the range of 0.01–0.05% w/w were evaluated for solubility and fluorescence/scintillation enhancement. The results for wavelength-shifted organic glass materials are summarized in Table 1, revealing fluorescence quantum yields as high as 0.89 and 662 keV gamma-ray light yields of up to 123% *trans*-stilbene. The absence of any aggregation-induced spectral shifts for 0.01–0.05% DPA in glasses of **1–3** indicates that the wavelength shifter is soluble at these concentrations. This observation is consistent with the lack of any detectable phase separation or particle-induced light scattering in the samples. Figure 3 provides the PL spectra for DPA-containing compounds **1** and **3**. The spectra reveal a decrease in the extent of fluorescence self-absorption following the incorporation of wavelength shifter. Very little self-overlap is evident in the excitation and emission spectra for 0.05% DPA in compound **3** (Figure 3, bottom), as required for consistent scintillator performance in larger detector volumes. The highest scintillation light-yield and best PSD performance was indeed obtained for this sample.

Differential Scanning Calorimetry:

Differential scanning calorimetry (DSC) data were collected for compounds **1–3** to understand the crystallization, melting, and glass-formation properties of these materials. A representative dataset is provided in Figure 4 for compound **1**. The scans indicate that the crystalline as-synthesized powder undergoes a melting transition in the first run, as evident by the well-defined endotherm at 223°C. Subsequent runs were performed using the same experimental protocol after cooling the sample back to room temperature. Conversion to an amorphous material is indicated by the absence of a melting transition in the runs 2 and 3 and the concomitant appearance of a glass-transition at 92°C. This T_g value is comparable to polystyrene and higher than polyvinyltoluene, both of which are used in commercial plastic scintillators. Qualitatively similar behavior was observed for compounds **2** and **3**, as summarized in Table 2. The glass formation properties of compounds **2** and **3** were found to depend upon the cooling rate, whereby partial crystallization was observed upon slow cooling at 1°C/min. Crystallization was fully suppressed at faster cooling rates of >10°C/min, as confirmed using powder X-ray diffraction analysis. In contrast, compound **1** resisted crystallization even at slow cooling rates of less than 1°C/min.

Scintillation Pulse-Height Spectra:

Scintillation pulse-height spectra (PHS) were collected using ^{137}Cs gamma-rays for glass samples of compounds **1–3** using the measurement configuration described in the experimental section above. These measurements were performed to evaluate the light yields relative to EJ-200 plastic and *trans*-stilbene crystal reference materials. A comparison of the 662 keV gamma-ray pulse-height spectra is provided in Figure 5, with the results summarized in Table 1. The light yields for small $\sim 2\text{ mm}^3$ crystals of compounds **1–3** were first evaluated using the 33 keV X-rays emitted from ^{137}Cs . The observed photoelectric absorption peak for each sample was found to be greater than for the two reference materials, which provided a promising indication of the potential for these compounds. Corresponding spectra obtained for bulk melt-cast glasses of these materials revealed somewhat lower light yields, although the larger size of these samples ($\sim 8\text{ cm}^3$) also permitted measurement of 662 keV gamma-rays. The lower light yields for the glass samples is associated with differences in the intermolecular distances and angles associated with conversion into the amorphous state. This finding is consistent with previously reported results on scintillating chromophores arranged in different packing environments. [5] The 662 keV spectra for pure glasses of **1** and **2** indicate a broadening of the Compton edge (not shown), which indicates poorer energy resolution due to self-absorption (Figure 2). Subsequent light-yield measurements performed on glasses containing DPA wavelength shifter at 0.01–0.05% w/w reveal improvements in the light-yield and energy resolution. It is obvious from Figure 5 that the DPA-containing glass of **3** exhibits a different pulse shape than the two reference materials. The higher occurrence of events in the lower energy region of the spectrum suggests incomplete FRET energy transfer due to the overlapping Compton edge from the undoped sample in this region ($\sim 19\text{ nVs}$). Alternate explanations for this behavior include light scattering and/or incomplete light collection, although the highly transparent appearance and relatively small size of these samples minimize these effects. This was confirmed in scintillation pulse-height spectra, where consistent light yields were obtained for small samples ($0.5\text{--}8\text{ cm}^3$) of reference and DPA-containing glass materials of various shapes and sizes. Additional studies on the effect of wavelength shifter identity/concentration are required to fully understand and optimize the light-yield properties of these materials.

Pulse-Shape Discrimination:

Pulse-shape discrimination (PSD) measurements were conducted on the prepared organic glasses using an unshielded AmBe neutron/gamma source. Prior work has shown that PSD may be easily disrupted by the presence of small amounts of impurities, disorder, or defects in the material. [7, 9] For example,

Carman et al. has shown that the presence of 0.5% 2-phenylindene impurity in *trans*-stilbene led to a 42% reduction in the neutron/gamma separation efficiency. [7] Similarly, the disordered/amorphous structure of plastic scintillators typically precludes PSD unless very high dye concentrations or triplet-harvesting compounds are added. [1, 3, 4] These prior findings cast initial doubt as to whether the synthesized organic glasses would be capable of PSD. However, the results shown in Figures 6 and 7 show that these materials are indeed capable of efficient neutron/gamma particle discrimination. The pulse-shape discrimination figure-of-merit (PSD-FOM) was calculated to quantify the neutron/gamma separation efficiency at a given energy threshold. The PSD-FOM is defined by the separation between neutron and gamma events divided by the sum of the FWHM values for the respective histogram distributions shown in Figure 7. A PSD-FOM of 2.0 was obtained in the energy range of 400–500 keV for a melt-cast glass of 3+0.05% DPA, which compares to a corresponding PSD-FOM value of 2.35 for a solution-grown *trans*-stilbene reference crystal. In both cases, the charge comparison method was employed using integration time intervals that were optimized for each material. The best PSD-FOM was obtained for 3+0.05% DPA using a prompt/delayed cutoff of 40 ns after the pulse leading edge and a total integration time of 300 ns. Optimization of these parameters for the *trans*-stilbene reference sample led to a prompt/delayed cutoff of 30 ns and a total integration time of 400 ns.

Conclusion:

A new family of neutron/gamma discriminating scintillator has been developed that comprises stable organic glasses that may be melt-cast into transparent monoliths. These materials have been shown to provide light yields greater than solution-grown *trans*-stilbene crystals and efficient PSD capabilities when combined with 0.01–0.05% w/w of a wavelength-shifting fluorophore. Photoluminescence measurements reveal fluorescence quantum yields that are between 2–5 times greater than conventional plastic or liquid scintillator matrices, which accounts for the superior light yield of these glasses. The unique combination of high scintillation light-yields, efficient neutron/gamma PSD, and straightforward scale-up via melt-casting distinguishes the developed organic glasses from existing scintillators. Ongoing work has also shown that this strategy is effective for the preparation of organic glasses based upon different types of organic chromophores, which provides a flexible platform for the continued development of this new class of materials.

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Figure 1. Photograph of organic glasses of compound **1**. The sample shown in the main figure was drop-cast from the liquid, whereas the cube shown in the inset was melted and cooled in a silicone mold.

Scheme 1: General procedure for the synthesis of compounds **1–3**.

1 Table 1. Summary of photoluminescence quantum yields and gamma-ray scintillation light-yield data.

<u>Compound</u>	<u>PL Quantum Yield</u>	<u>662 keV Relative L.Y.</u>	<u>33 keV Relative L.Y.</u>
<i>Trans</i> -stilbene – Crystal	0.62	1.00	1.00
EJ-200 – Plastic	0.55 (PVT=0.12)	0.78	0.89
1 – Crystal	0.46	*	1.26
2 – Crystal	0.53	*	1.21
3 – Crystal	0.78	*	1.44
1 – Glass	0.39	1.02	0.97
2 – Glass	0.57	0.74	0.83
3 – Glass	0.48	0.59	0.68
(1 + 0.02% DPA) – Glass	0.89	1.03	0.93
(2 + 0.02% DPA) – Glass	0.66	1.11	1.11
(3 + 0.05% DPA) – Glass	0.67	1.23	1.18

*Not observed due to small crystal size.

Figure 2. Excitation and emission PL spectra for sublimed glass (top) and melt-cast glass (bottom) of compound **1**.

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2

3 Figure 3. Excitation and emission PL spectra for compound **1**-0.02% DPA (top), and **3**-0.05% DPA

4 (bottom), illustrating differing amounts of spectral self-overlap.

5

6

Figure 4. Differential scanning calorimetry data for compound **1**.

Table 2. Glass transition (T_g) and melting temperatures (T_{melt}) for compounds **1–3**, as derived from DSC data.

Compound Number	T_g (°C)	T_{melt} (°C)
1	92	223
2	63	175
3	55	184

Figure 5. ^{137}Cs scintillation pulse-height spectra obtained for *trans*-stilbene and EJ-200 reference samples and two melt-cast glasses of compound **3**. The dotted lines serve as guides to the eye for the respective Compton maxima.

Figure 6. Neutron/gamma pulse-shape discrimination scatter plot for a melt-cast glass of **3**+0.05% DPA in the energy range of 400-500 keV. The upper distribution corresponds to fast neutron events and the lower distribution gamma-ray events.

Figure 7. Neutron/gamma pulse-shape discrimination histograms obtained for a melt-cast glass of $3+0.05\%$ DPA (top) and a *trans*-stilbene single crystal (bottom) in the energy range of 400–500 keVee. The green and red traces correspond to Gaussian fits to the data for fast neutrons and gamma-rays, respectively.

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