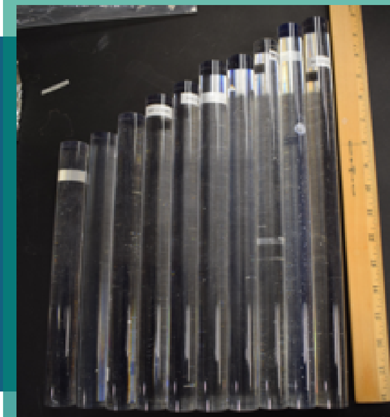
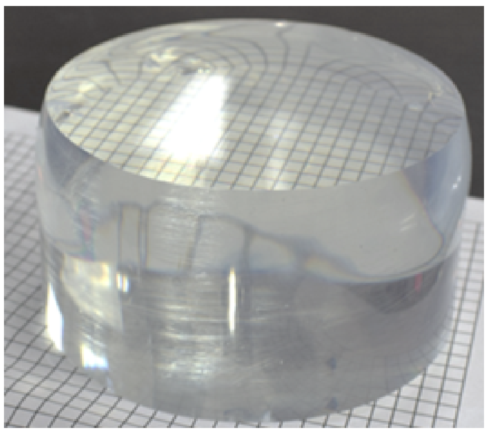
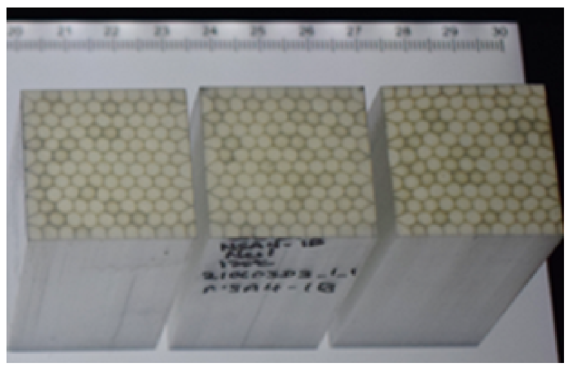
SAND2021-9064C

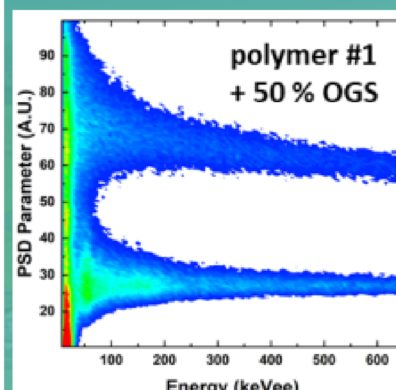
Sandia National Laboratories

Recent Developments in Organic Glass Scintillators









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Outline

Formulation R & D

- -Stabilizing amorphous state
- -Thermal neutron detection
- **-Polymer blends**

Manufacturing

- **-Scintillating “Nanoguide”**
  - Formulation choice
  - Kg-scale production
- -OGS pixelated arrays

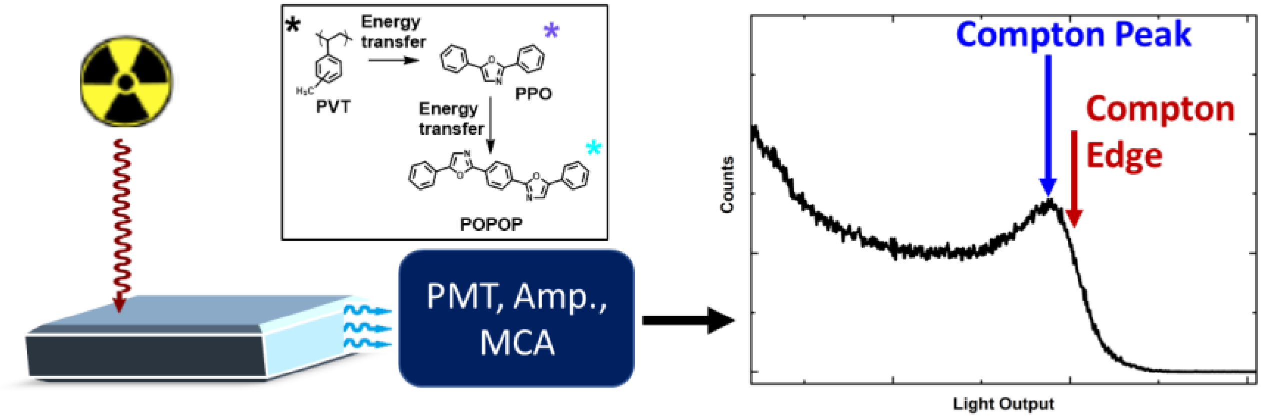
Characterization

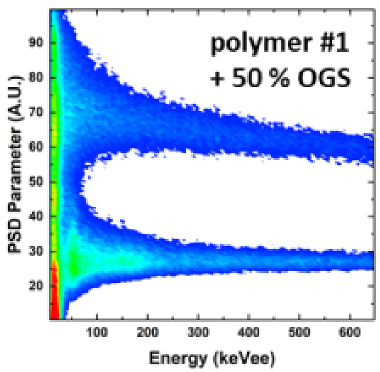
- -Scintillation
- -Neutron light yield
- -Optical transmission
- -Thermal aging studies

Introduction

Scintillator: A material that emits fluorescent pulses upon exposure to ionizing radiation

Gamma-ray scintillation process





Pulse shape discrimination: Time resolved measurements allow separation of scintillation events resulting from different excitation sources, e.g. gamma-ray vs. fast neutron.

Material examples

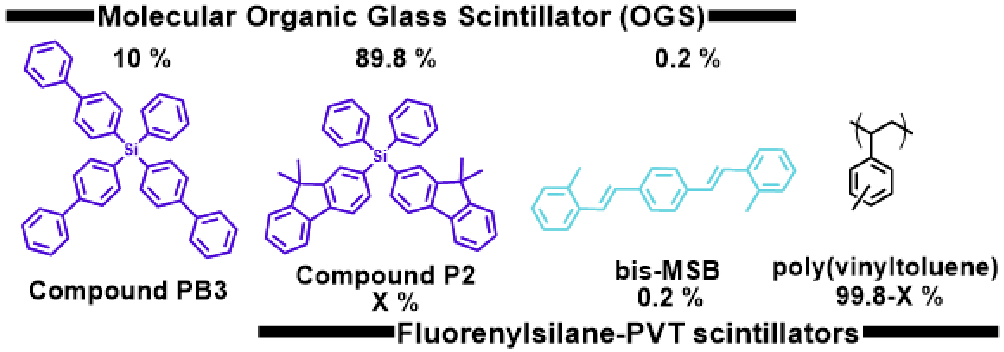
Inorganic: CsI (Tl) for gamma light yield and energy resolution, “CYLC” for PSD

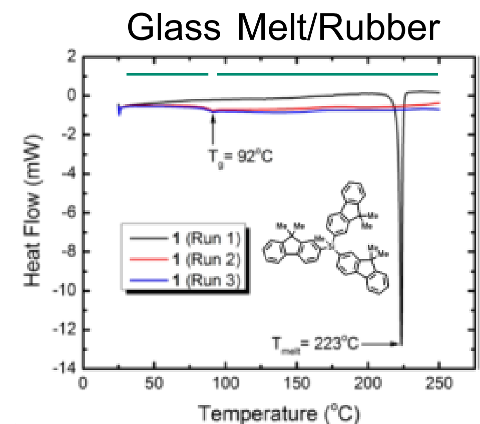
Gaseous: ^{3}He, BF_3 for neutron detection

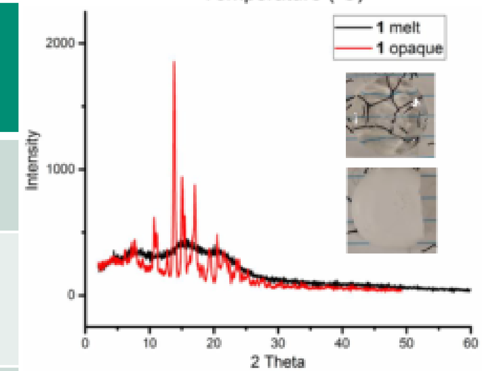
Hybrid: organic perovskites for gamma light yield and energy resolution

Organic: single crystals, liquids, polymeric blends, molecular organic glasses

Organic Scintillator Comparison

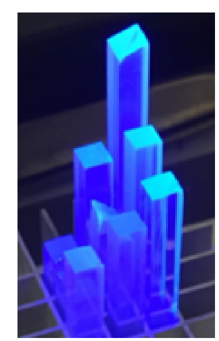






	trans-Stilbene	Organic Glass Scintillator (OGS)*	40 % FS- PVT	EJ-200 (commercial plastic scint.)
Type	Single crystal	Amorphous	Amorphous blend	Amorphous blend
Production	Single crystal growth	Melt-cast to shape	Melt-cast to shape	Melt-cast to shape
Gamma-ray Light Yield	15,700 photons/MeV	18,200 photons/MeV	14,300 photons/MeV	10,000 photons/MeV
PSD FoM	3.53	2.67	2.18	0.58

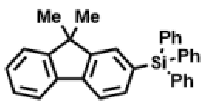
- While PSD quality of OGS is less than stilbene, gamma-ray light yield is improved, and melt-casting enables custom detector geometries
- Much of the scintillation performance of OGS is maintained after incorporation of 50+ wt. % vinylaromatic polymer



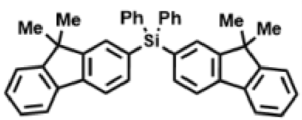
*OGS is now a commercial product offered by BlueShift Optics

Three Methods of Stabilizing the Amorphous State

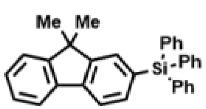
Formulation



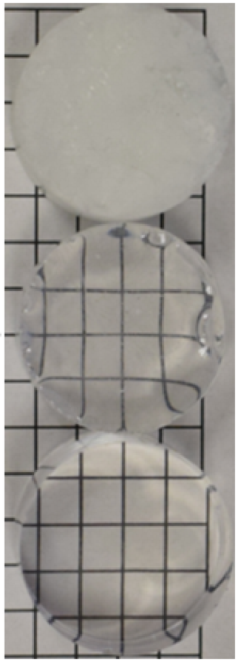
Compound P1

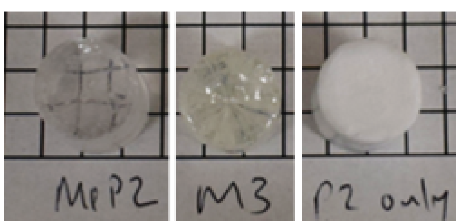


Compound P2



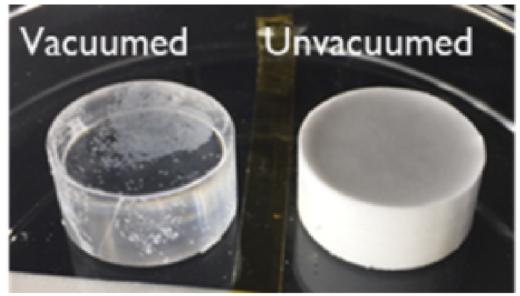
Compound P1
(50 % in PVT)

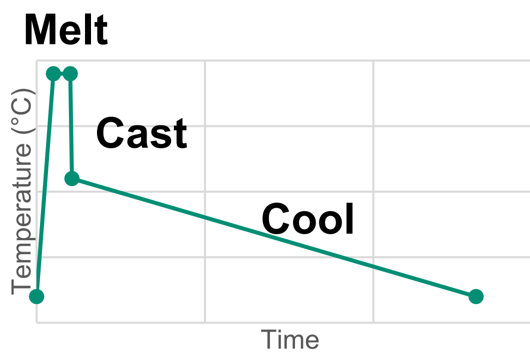




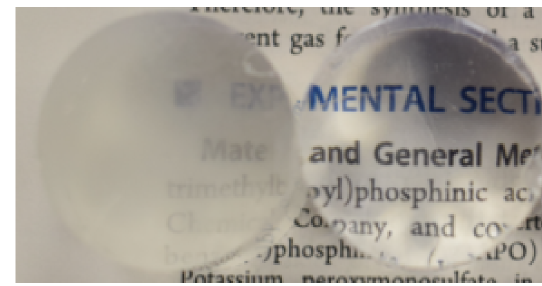
[Image after one week at 80°C]

Casting Process





Coatings



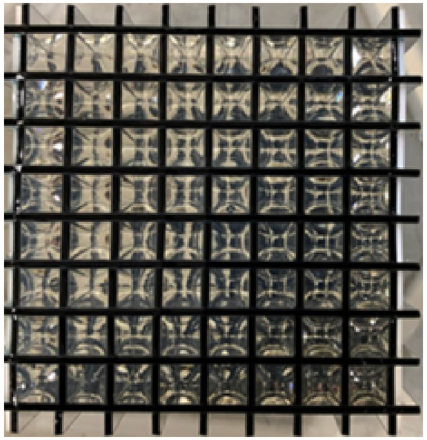
Uncoated, 1.5 months at 60°C

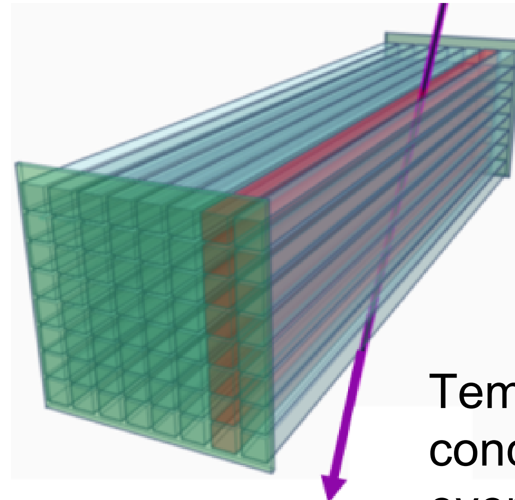
PVA coating, 1.5 months at 60°C

(We've also demonstrate vapor-deposited Parylene-C and epoxy coatings as surface-stabilizing)

Each strategy can independently improve amorphous stability by orders of magnitude

Melt-Casting Enables Form-Factor Flexibility and New Applications



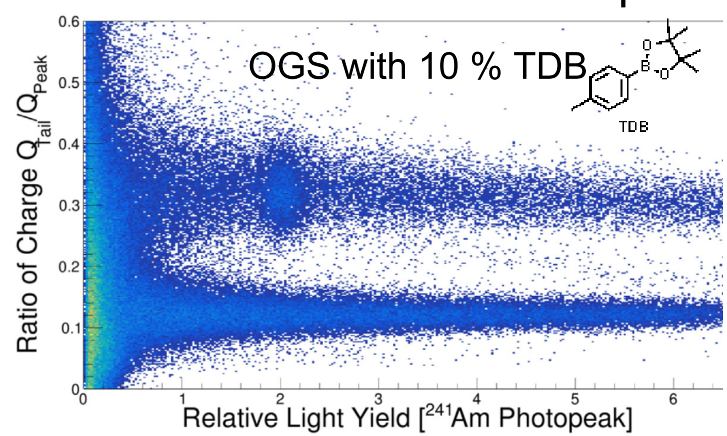


Pixelated array of 64 5x5x50 mm OGS elements prepared by melt-casting

Temporal response of concerted scintillation events reveals particle trajectory[1] (single-volume scatter camera)

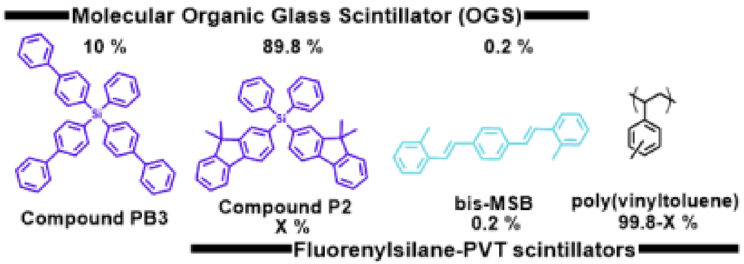
“3-D printing” of OGS feasible with glue gun (shown) or injection molding

Boron thermal neutron capture[2]

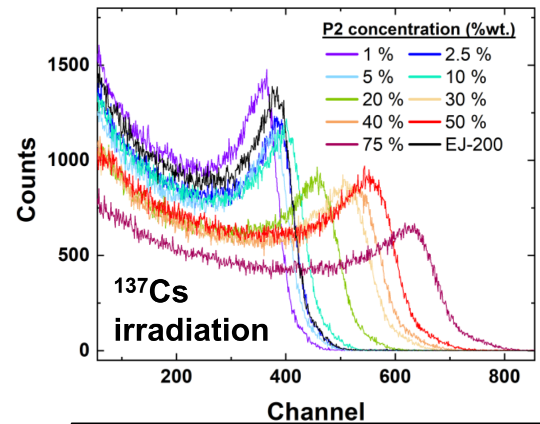


[1]A. Galindo-Tellez *et al* JINST 16 (2021) P04013
[2]L.Q. Nguyen, G. Gabella, B.L. Goldblum *et al* Nuclear Inst. and Methods in Physics Research, A 988 (2021) 164898

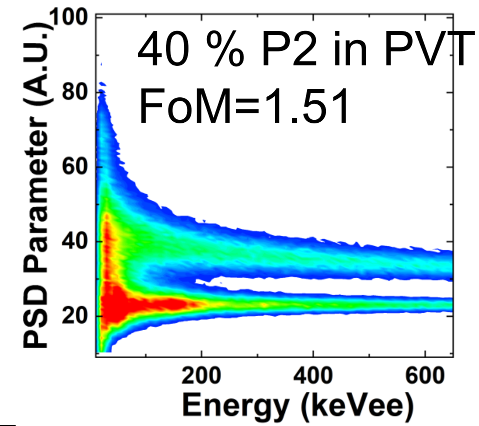
Fluorenylsilane-Polymer Blends: Initial Studies



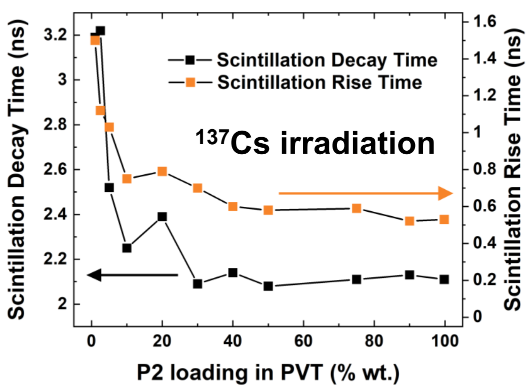
P2 and PVT/PS are miscible



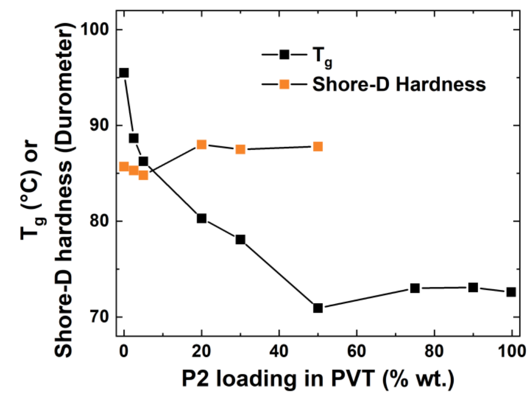
Gamma-ray light yield linear with [P2] in 1" samples



Neutron/gamma PSD



Gamma scintillation faster with increasing [P2]



Stable T_g and Durometer hardness with [P2]

Advantages of Blending FS with Polymer

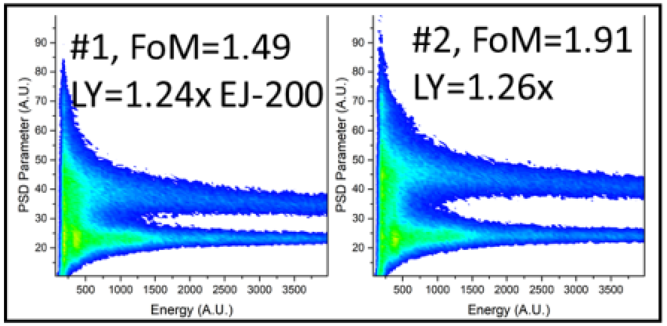
- Mechanically more robust than pure OGS
- Excellent stability against recrystallization
- Relatively low cost, easily scalable

Disadvantages

- Scintillation performance diluted relative to OGS
- More challenging to fabricate defect-free detectors

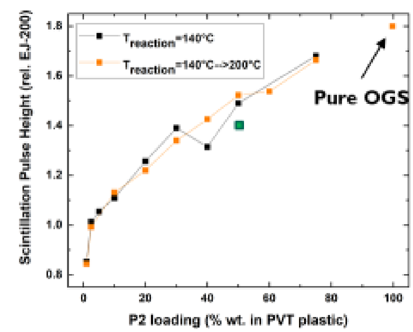
Optimizing Pulse Shape Discrimination in OGS-Polymer Blends

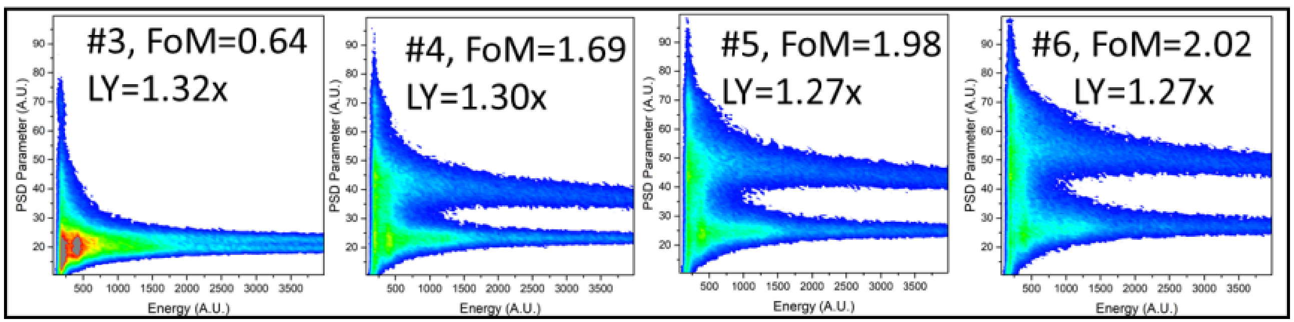
Formulation: 50 % P2, 0.2 % bis-MSB in PVTMI matrix (stock solution)

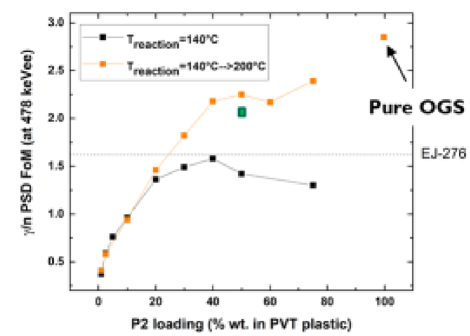


Reaction Parameters

Entry	Days at 140°C	Days at 200°C	% conv. (NMR)
1	0	1	nm
2	0	2	99.6
3	1	0	95.4
4	1	1	nm
5	1	2	nm
6	1	4	99.8



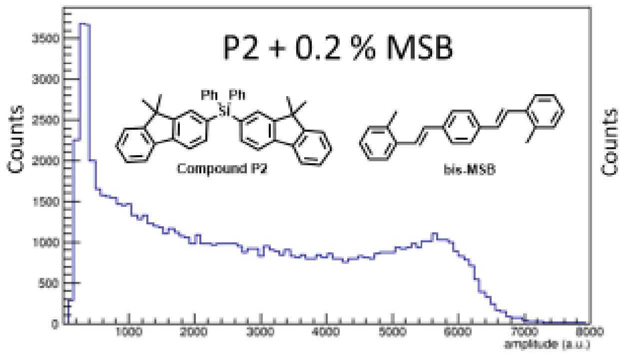


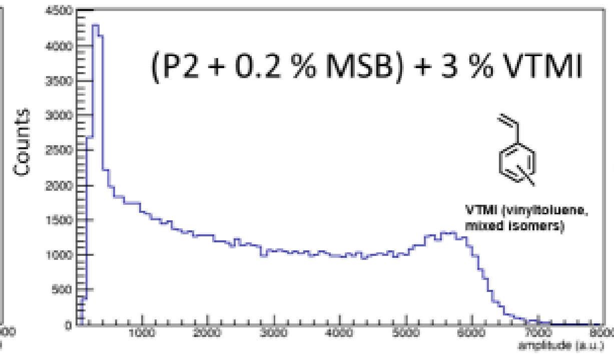


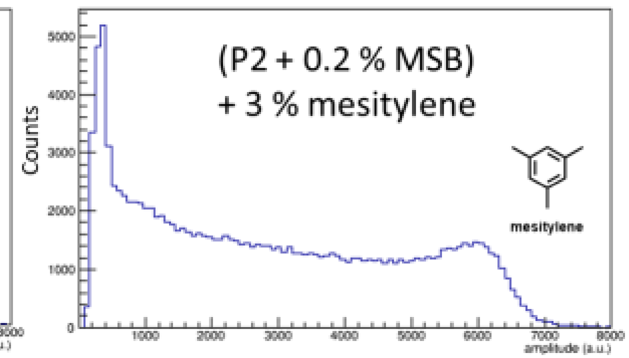
- PSD improved beginning at 20 % P2 in PVT/PS without detriment to light yield
- PMMA incorporation also allows improvement to PSD at 140°C reaction temp.
  - Green points are 25/25/50 PMMA:PVT:OGS, polymerized with 80-140°C ramp
  - Possibilities for lower index, scintillating PSD materials and improved mechanical resilien

Residual Vinylaromatic Monomer Quenches PSD

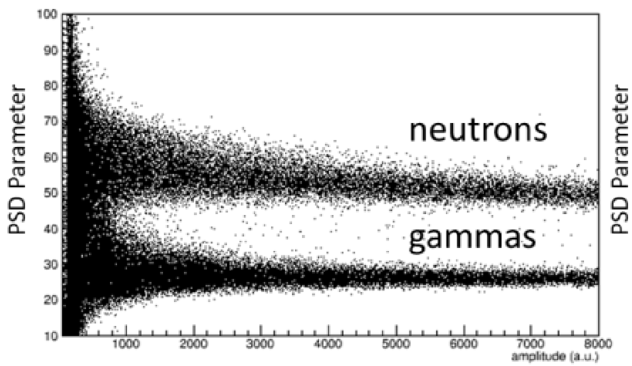
^{137}Cs gamma-only scintillation

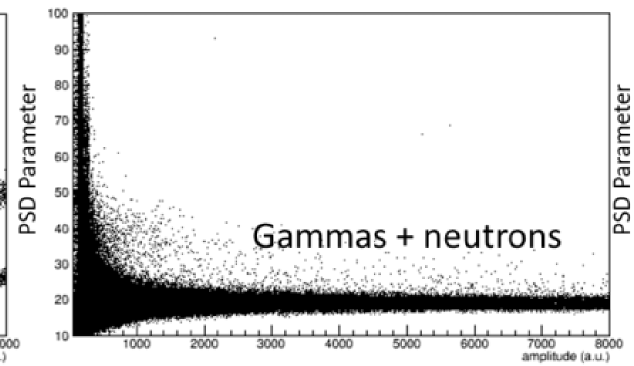


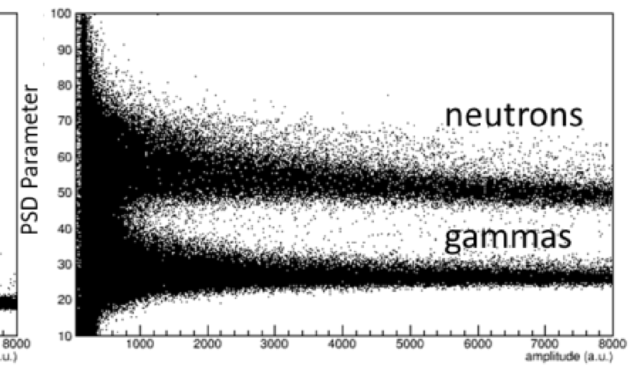




n/γ Pulse Shape Discrimination







- PSD returns upon heating VTMI sample (residual monomer polymerizes)
- Molecular modeling effort underway to better understand the excited state interactions responsib

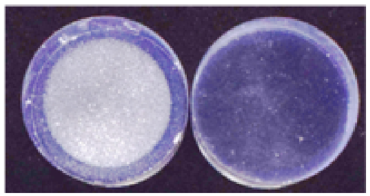
Reference on styrene quenching benzophenone/phenanthrene phosphorescence: A. S. Vinogradova and A. N. Faidysh Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika (1974), 17(4), 149-51.

Aging Studies of OGS-loaded and Other PSD Plastics

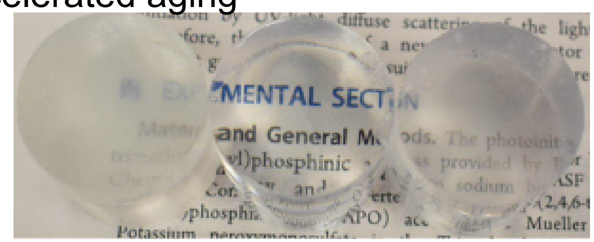
OGS plastics are compatible with fog-resistant compounds developed in CWMD project

50 % OGS in PVT | Left + 1 % HPA

40°C, 100 % R.H., 3 months (cooled to 22°C)



PVA coating prevents P2 recrystallization and light yield degradation during accelerated aging

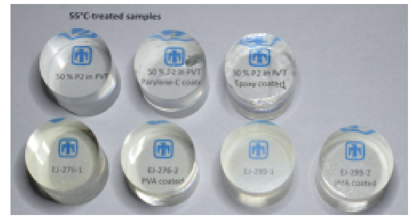


AA AB AC

% P2	Sample	Aging Condition	^{137}Cs Light Yield, relative to EJ-200, 1.5 mo (as-synthesized)	PSD FoM, 1.5 mo
50	AA	60°C, air, 1.5 mo	1.00 (1.34)	1.21
50	AB (PVA)	60°C, air, 1.5 mo	1.34 (1.32)	1.41
50	AC	22°C, air, 1.5 mo	1.28 (1.29)	1.3

Comparison to Commercial PSD Plastics

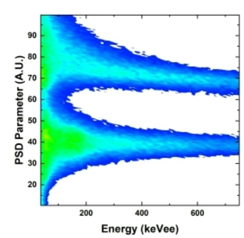
Pre-Aging



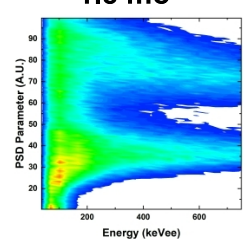
5 months in 55°C air

Sample	Coating	^{137}Cs Light Yield (init., 1.5 mo. aged)	PSD FOM (t_o, 1.5 mo. aged)
50 % P2 in PVT	None	1.40, 1.19	1.19, 1.11
"	Parylene-C	1.36, 1.19	2.08, 1.86
"	Epoxy	1.12, 0.99	1.43, 1.19
EJ-276	None	0.97, 0.36	1.96, 1.10
"	Poly(vinylalcohol)	0.99, 0.66	1.93, 1.47
EJ-299	None	0.86, 0.34	1.72, 0.95
"	Poly(vinylalcohol)	0.90, 0.60	1.70, 1.30
EJ-200	none	1.00	0.58

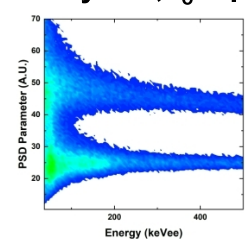
EJ-276, t_o



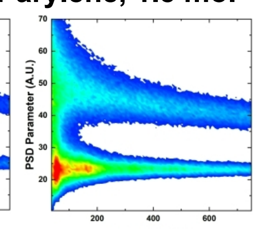
EJ-276, 1.5 mo



50 % P2, Parylene, t_o



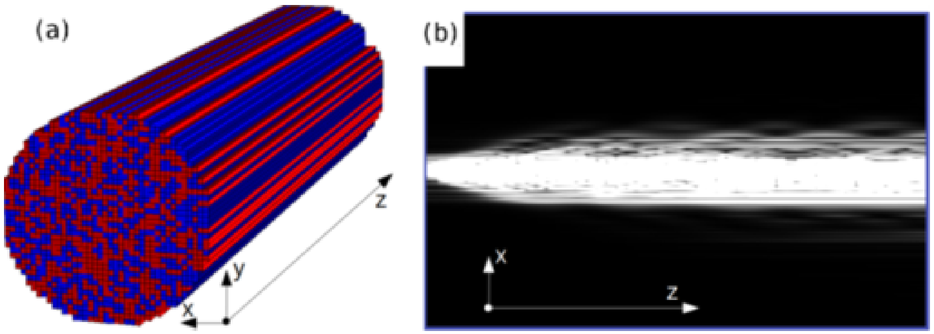
50 % P2, Parylene, 1.5 mo.

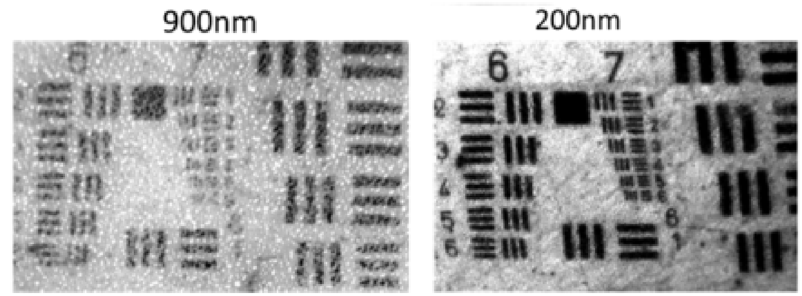


Scintillating "Nanoguide" For Advanced Neutron Imaging

Goal: Develop nanostructured, scintillating optical fiber for advanced radiography and source localization

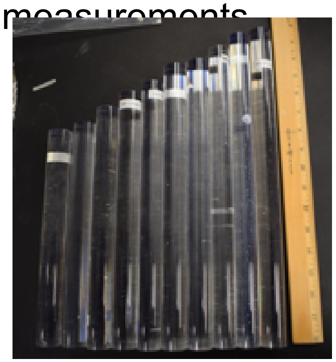
Transverse Anderson Localization[1]





- Random distribution of discrete, disparate RI fibers at 100 nm scale leads to light confinement effect
- This effect is hypothesized to lead to improved radiographic imaging resolution and light yield
- Ideal element size appears to be 1-2*λ

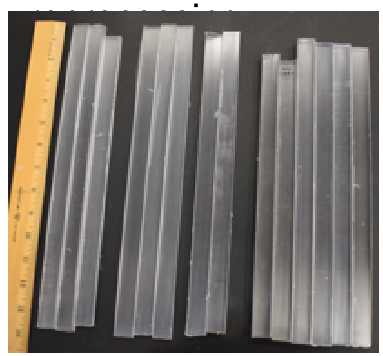
SNL: raw material synthesis, radiation measurements



1" x 12-16" rods, as-cast

Melt-draw into thin fibers, thermally reprocessed in channel mold

Incom: drawing and thermal reprocessing



Thin mini-channels of SNL materials drawn at Incom

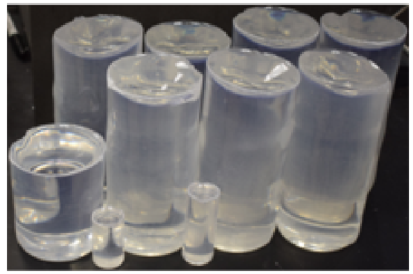
% P2 in PS	Qualitative Draw Difficulty
5	Easy
10	Easy
20	Easy
40	Easy-Moderate
50	Difficult, high MFI
75	Not possible without modification

[1]Mafi, A. Transverse Anderson localization of light: a tutorial review, arXiv:1505.01109v2 [physics.optics]

P2-in-PS “Nanoguide” Scale-Up

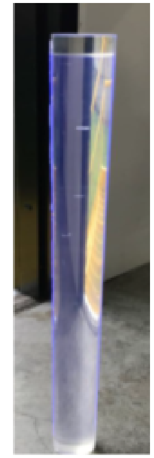
~5 L of prepolymer resin

Polymerize



4.5 kg of 2.5” diameter cylinders, 30

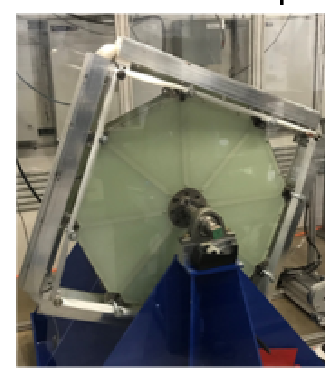
Fuse



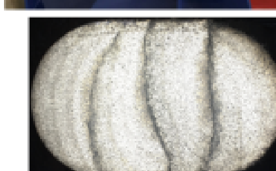
Fused P2-PS monolith

Load

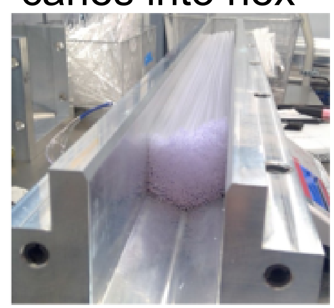
Co-draw with PMMA, collect fiber on square



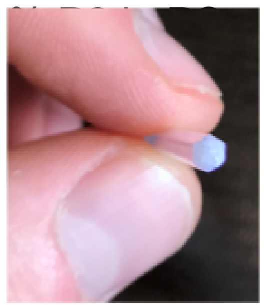
Fuse into circle preform, 1st cane draw



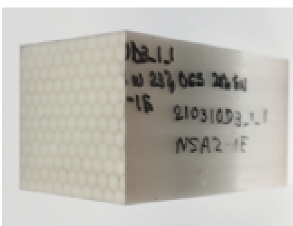
Pack circle canes into hex



Fuse, draw hex.



Fuse hex. elements



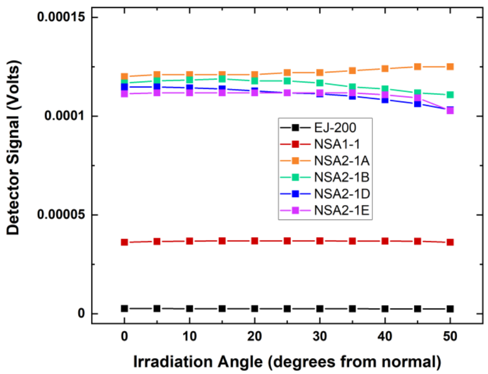
1”x1”x2” Nanoguide

Scintillating Composition	Sample ID	Draw Temperature (1-5 scale)	Process Outcome/yield
18 % wt. P2 in PS	NSA1	5	Successful, one 1x1x2”block
24 % wt. P2 in PS	NSA2	4	Successful, seven 1x1x2” blocks
24 % wt. P2 in PVT	NSA3	4	Failed at second draw step. Broken fibers, Nanoguide structure not maintained
30 % wt. P2 in PS	NSA4	3	Successful, three 1x1x2” blocks

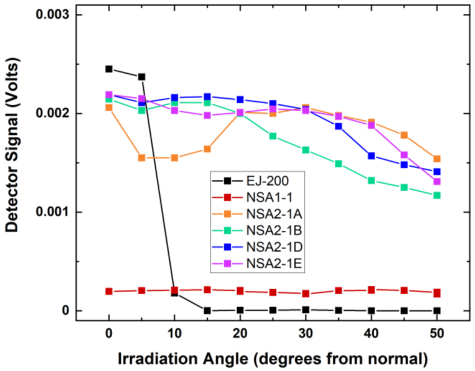
FS-PS "Nanoguide" Characterization

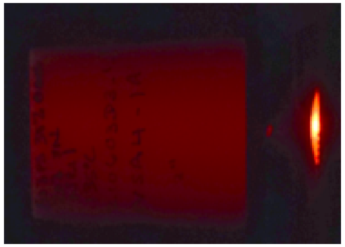
Optical Transmission with Laser Irradiation

355 nm (4π emission)



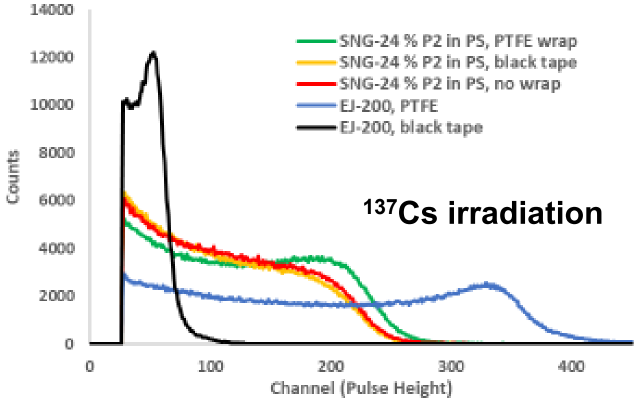
632 nm (light transport)



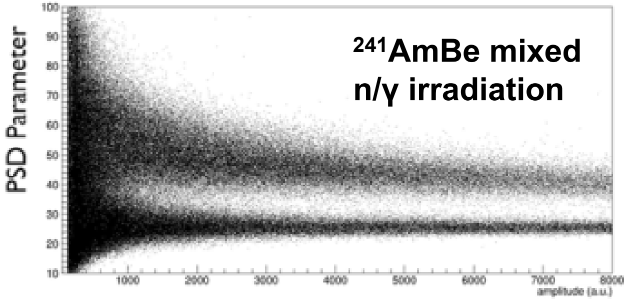


Light confining effect minimizes optical losses

Scintillation Measurements

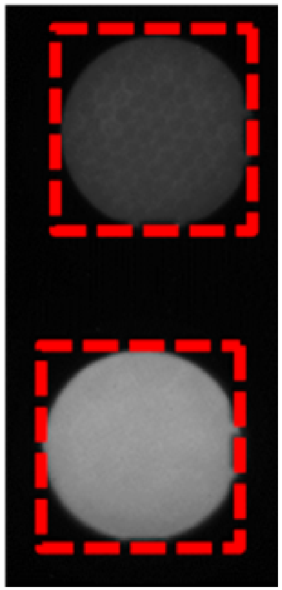


With PTFE reflector: Gamma-ray light yield ~60 % of EJ-200
Without PTFE: minimal change for SNG due to light confinement



PSD observed, as anticipated for 24 % FS-PS formulation

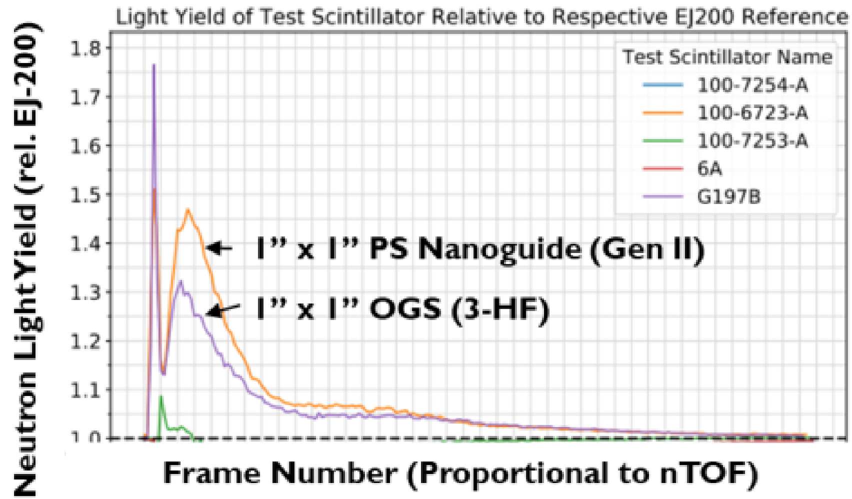
Neutron Light Yield of Scintillating "Nanoguide" at LANL



Reference scintillator (EJ-200)

Test scintillator

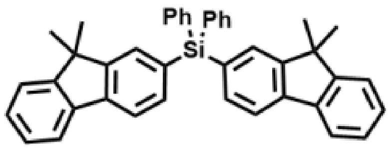
Neutron images acquired with variable neutron energy



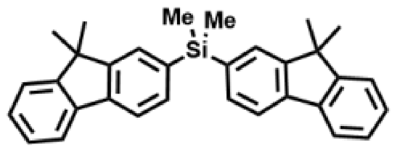
Light yield of equal areas calculated for test vs. reference scintillator across the available neutron spectrum

- Nanoguide material using commercial scintillating PS has enhanced neutron light yield across the full spectrum relative to non-light guiding EJ -200 (FS-PS Nanoguide to be evaluated next)
- 3-HF OGS sample features green-emitting wavelength shifter that is better matched to CCD sensitivity

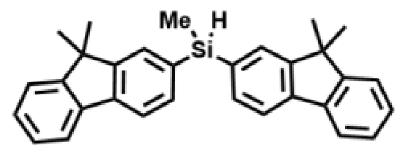
Alternative Fluorophores for FS-polymer blends



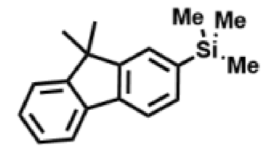
Compound P2



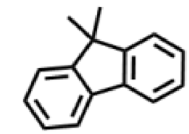
Compound M2



Compound MH2



Compound M1



9,9-DMF

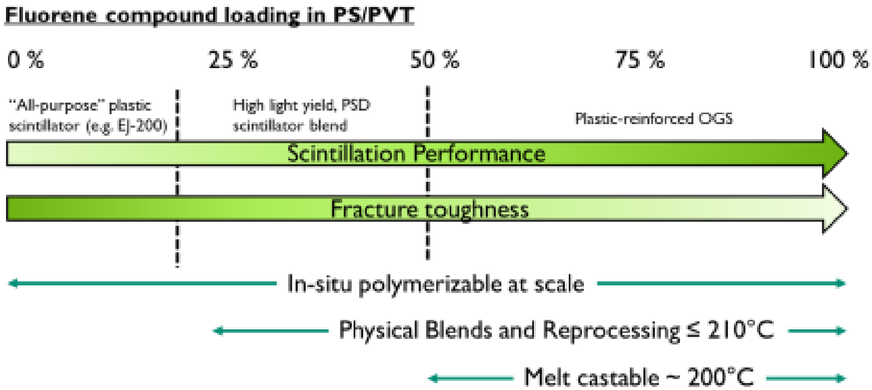
Composition (1" cylinder)	Gamma-ray scintillation light yield (rel. EJ-200)	Gamma/Neutron PSD FoM
40 % wt. P2 in PVT	1.43	2.18
35 % wt. M2 in PVT	1.45	1.84
35 % wt. MH2 in PVT	1.48	2.14
35 % wt. M1 in PVT*	1.48	1.66
20 % wt. 9,9-DMF in PVT	1.30	1.57
35 % wt. M1 in PMMA	0.98	1.28

*contains 0.1 % divinylbenzene crosslinker for mechanical reinforcement

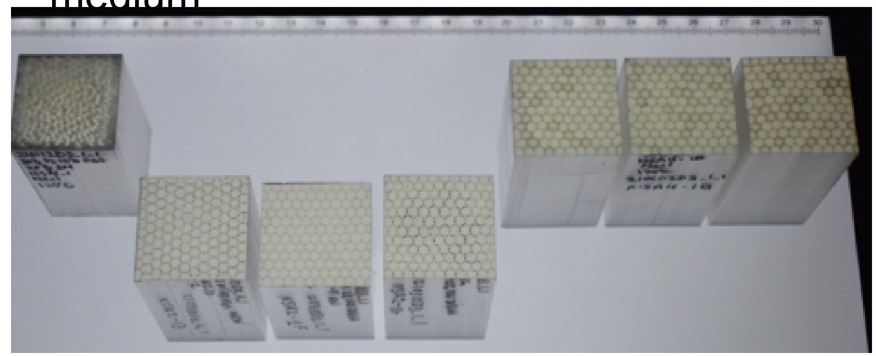
- Dimethylfluorene unit is responsible for outstanding gamma-ray light yield and PSD
- Plasticization effect of M1 and 9,9-DMF compounds limits usable loadings
- PSD FoM in this series may be a function of fluorene packing density
- 9,9-DMF and "M" series compounds are more easily synthesized and purified than

Summary

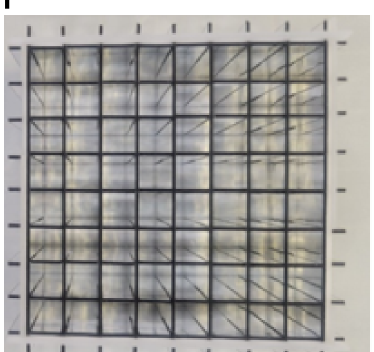
FS-polymer blends balance high performance of OGS with improved practicality

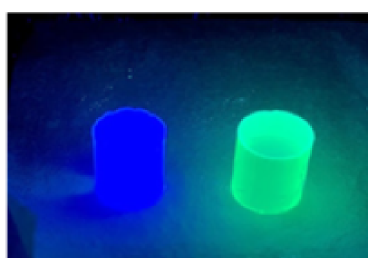


Scintillating Nanoguide 30-40 % wt P2 in PS successfully scaled to 5 kg batches and under investigation as neutron imaging medium

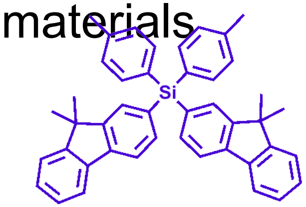


Solution processing method for OGS enables new detector geometries and applications



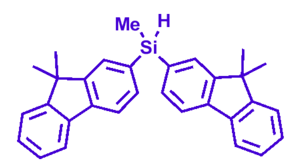


New fluorene-based scintillator materials



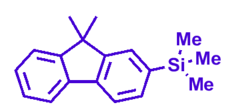
Compound MeP2

Stable glass without additives



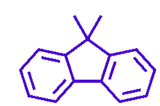
Compound MH2

Easier synthesized version of P2



Compound M1

Primary fluorophore of fluorene-based scintillating PMMA



9,9-dimethyl-9H-fluorene

Commercially-available fluorene souce