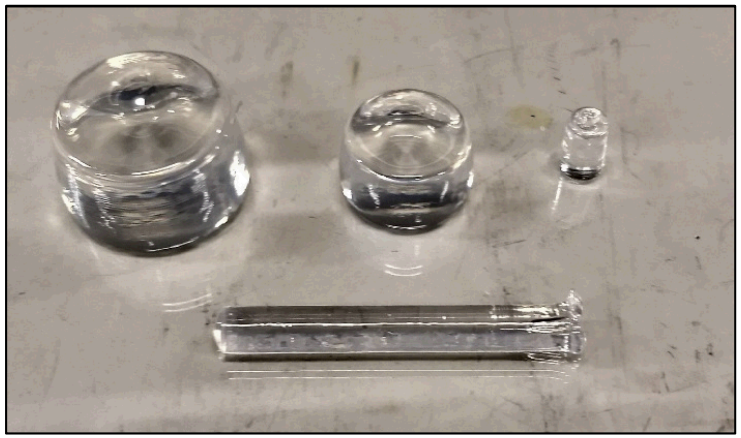
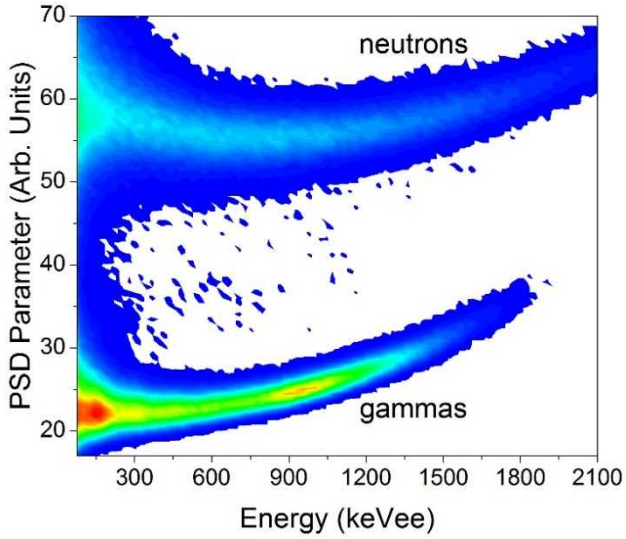
SAND2017-12307PE

Taking Advantage of Disorder: Small-Molecule Organic Glasses for Radiation Detection and Particle Discrimination





Joey Carlson

The University of Tennessee

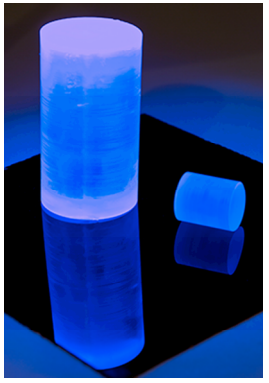
Radioluminescent Materials for Radiation Detection

- **Inorganic Crystals**
  -high light yield, cheap
  -Pulse shape discrimination (PSD) only at high energy, hygroscopic

- **Liquid Organic Scintillators**
  -large and cheap, resistant to radiative degradation
  -flammable, volatile, decomposition and triplet quenching (Oxygen)

- **Plastic Scintillators**
  -10 photons/keV light yield, cheap, large volume, strong
  -poor PSD, prone to hazing over time

- **Pure Organic crystals**
  -High light yield, best PSD
  -expensive, fragile, anisotropic (symmetry controlled properties)

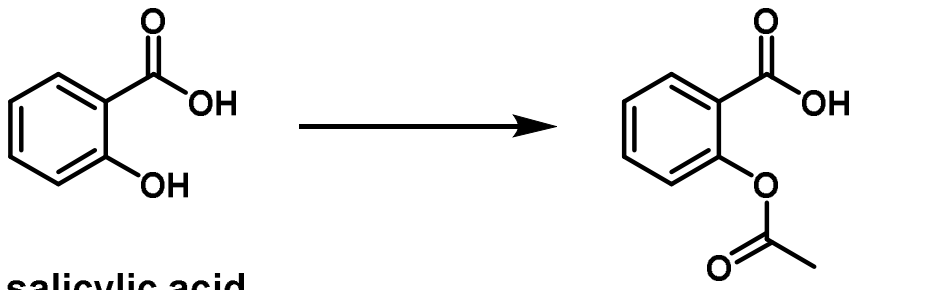


Stilbene Single Crystal

Image: Inradoptics.com

Knoll, G.F. *Radiation Detection and Measurement* **2010**, John Wiley & Sons, Fourth Edition

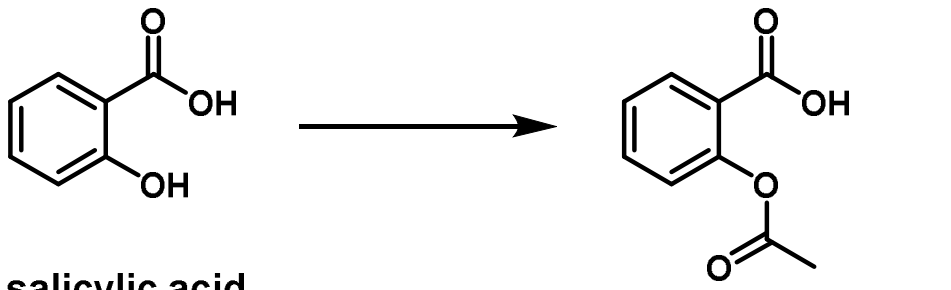
Synthetic Organic Chemistry as a Tool



salicylic acid

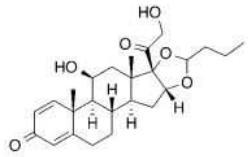
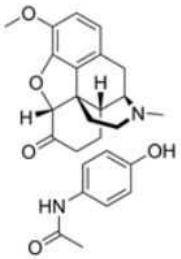
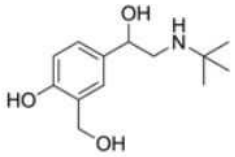
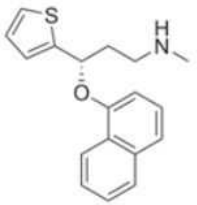
acetyl salicylic acid
"aspirin"

Top Drugs in 2013



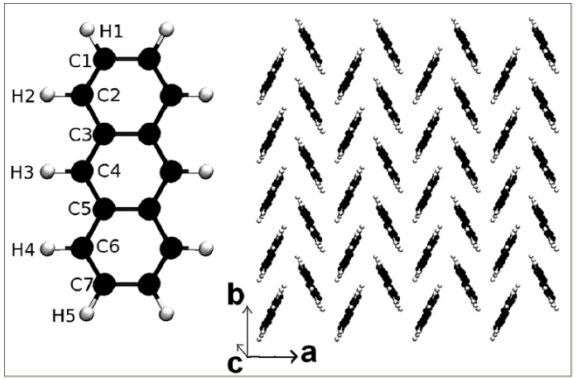
salicylic acid

acetyl salicylic acid
"aspirin"

1 Budesonide	2 Hydrocodone/APAP	3 Proair HFA	4 Cymbalta
(Budesonide)	(Hydrocodone & Acetaminophen)	(Salbutamol)	(Duloxetine)
			
ALM DER RES	Nervous System	Respiratory System	Nervous System
Approved 1997	Approved 1982	Approved 2004	Approved 2004

McGrath, N. A.; Brichacek, M.; Njardarson, J. T. *J. Chem. Ed.* **2010**, *87*, 1348.

Strategy for Single Crystal Organic Scintillators



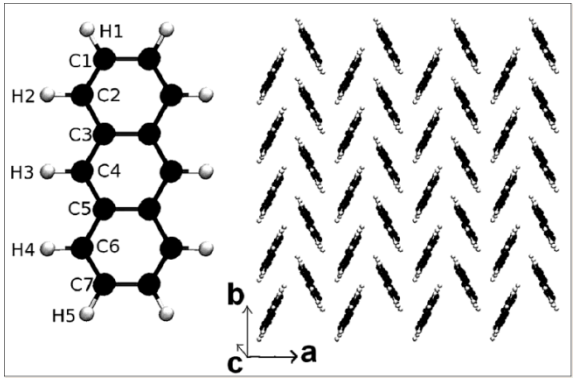
Problem:

Low-symmetry structures lead to several limitations in scintillator performance

- Fracture plane
- Anisotropic radioluminescence

Price, S.L. *Chem. Soc. Rev.* **2014**, *43*, 2098-2111.

Strategy for Single Crystal Organic Scintillators



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Impose molecular-level control to increase crystalline symmetry and improve scintillation properties

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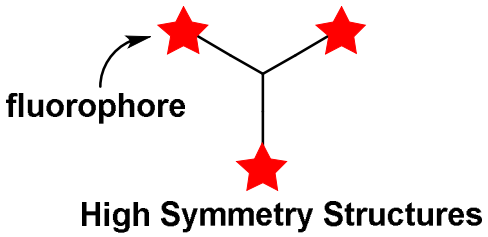

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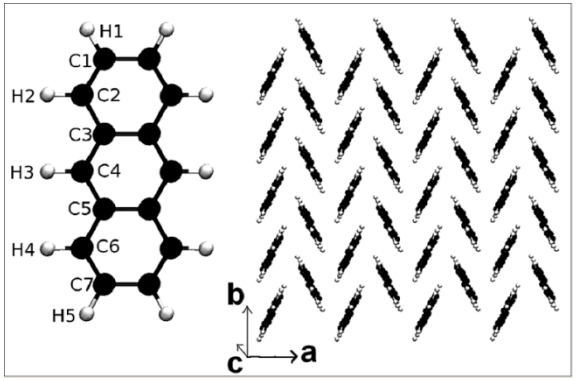

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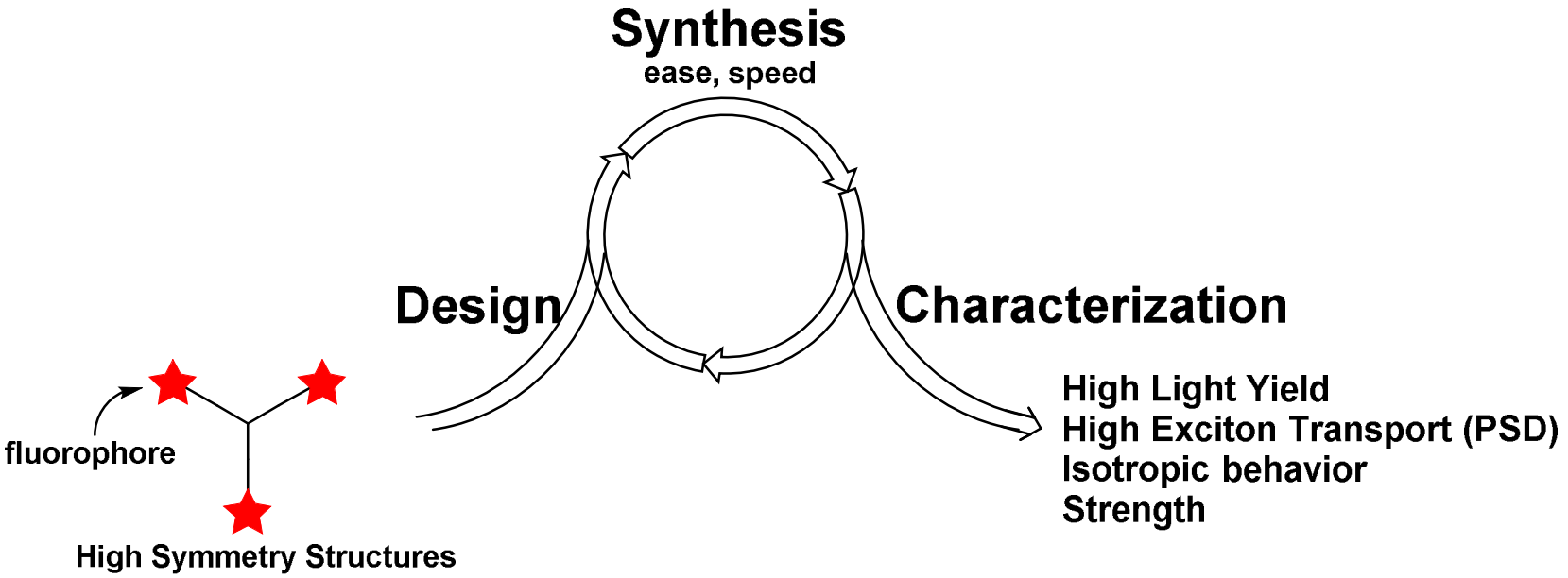
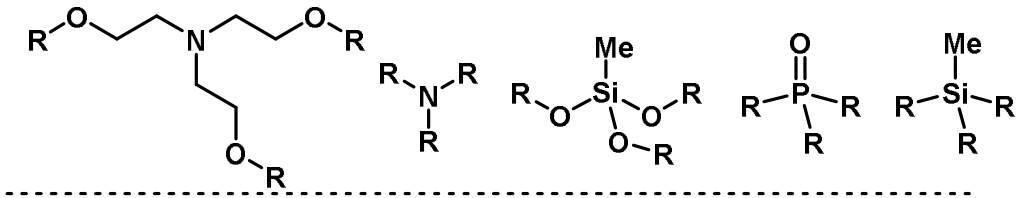


Price, S.L. *Chem. Soc. Rev.* **2014**, *43*, 2098-2111.

Efforts Towards Improved *Crystalline* Scintillator



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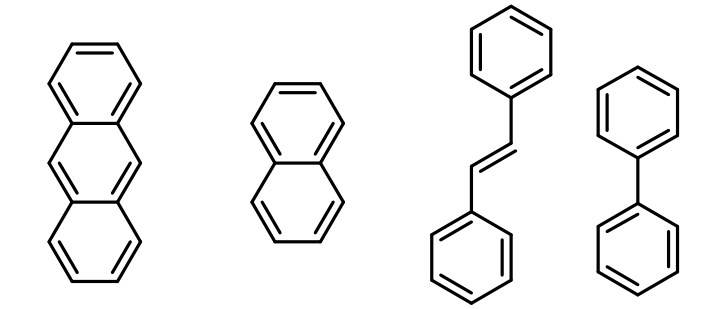
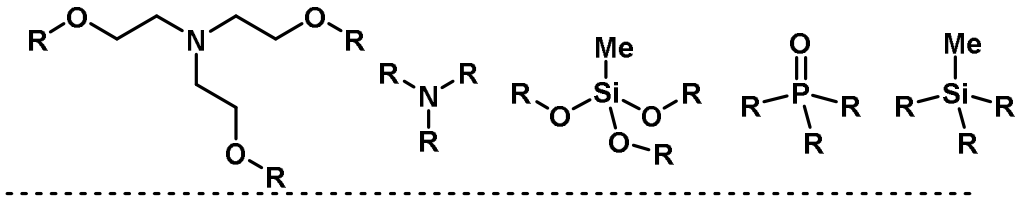


anthracene napthalene stilbene biphenyl

Efforts Towards Improved *Crystalline* Scintillator



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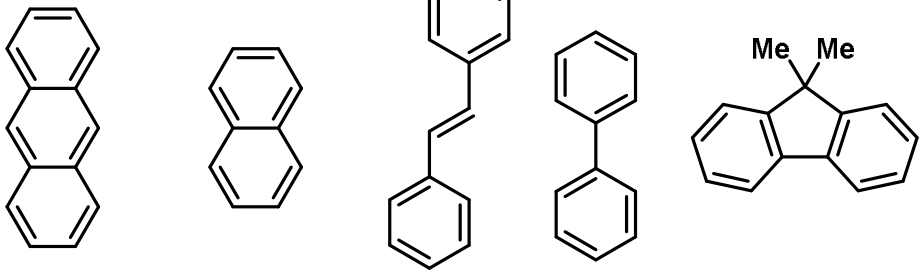
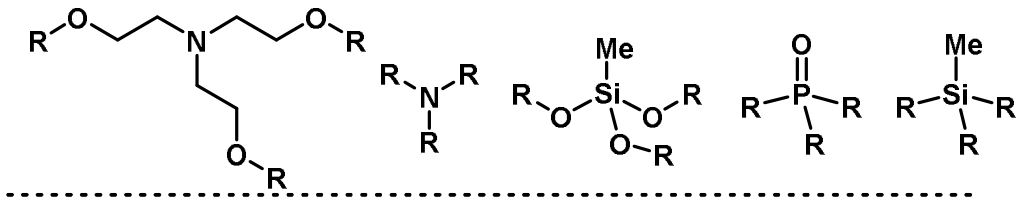


anthracene napthalene stilbene biphenyl fluorene

Efforts Towards Improved *Crystalline* Scintillator



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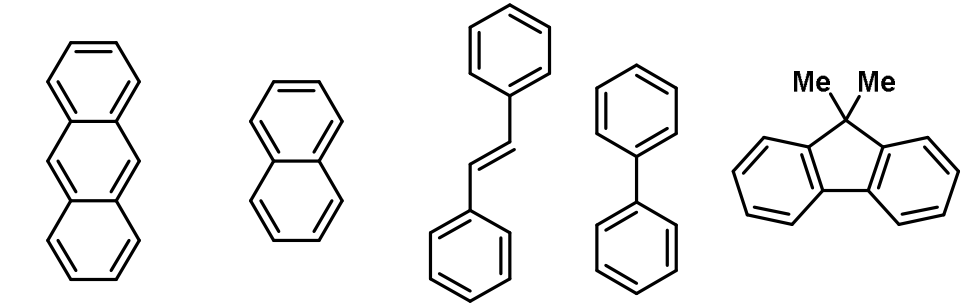

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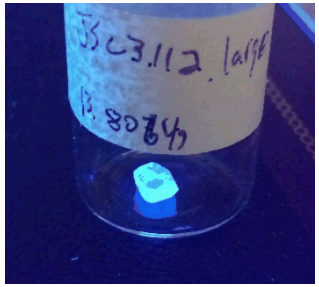
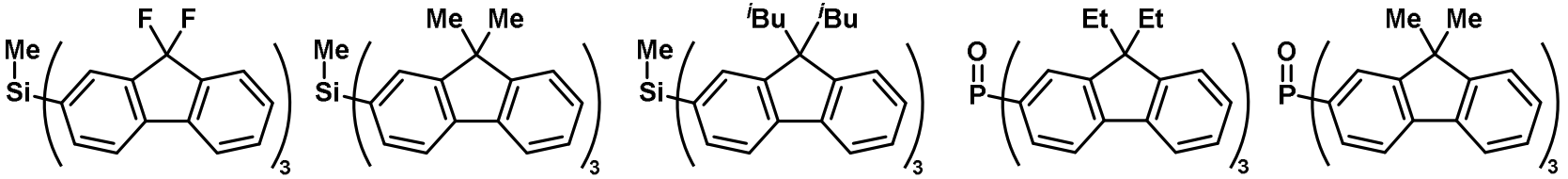
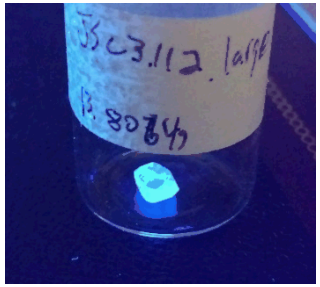


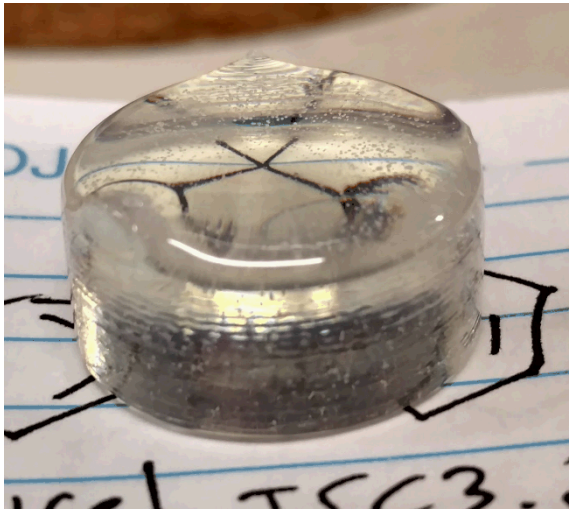


P_1 (Triclinic) $P2_1$ (monoclinic) $P2_12_12_1$ (orthorhombic) Pc (monoclinic) R-3 (trigonal)

Discovery of the Glassy State



heat



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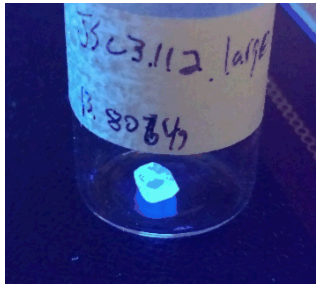

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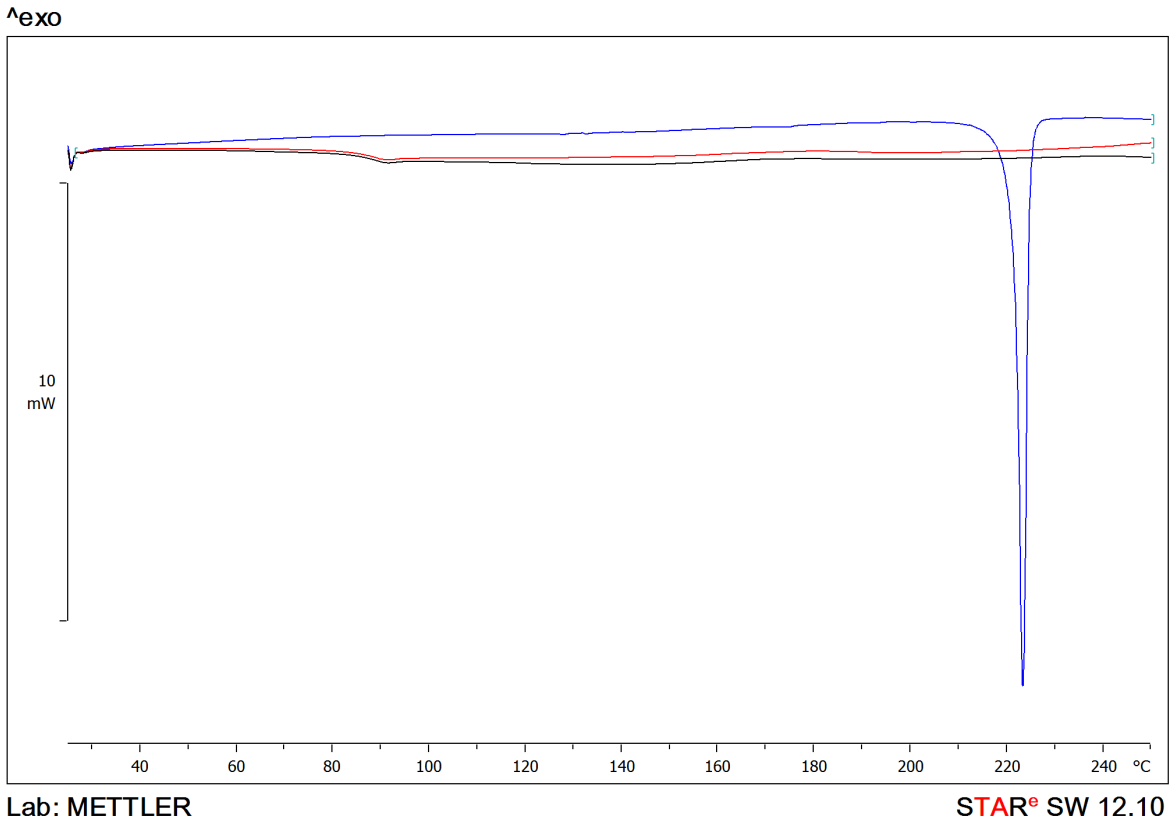
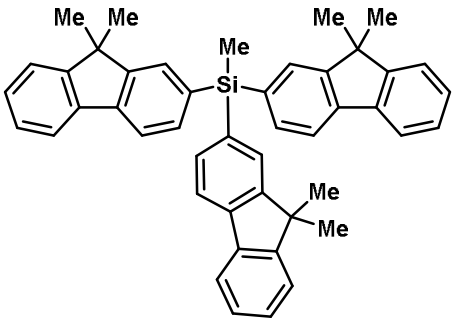
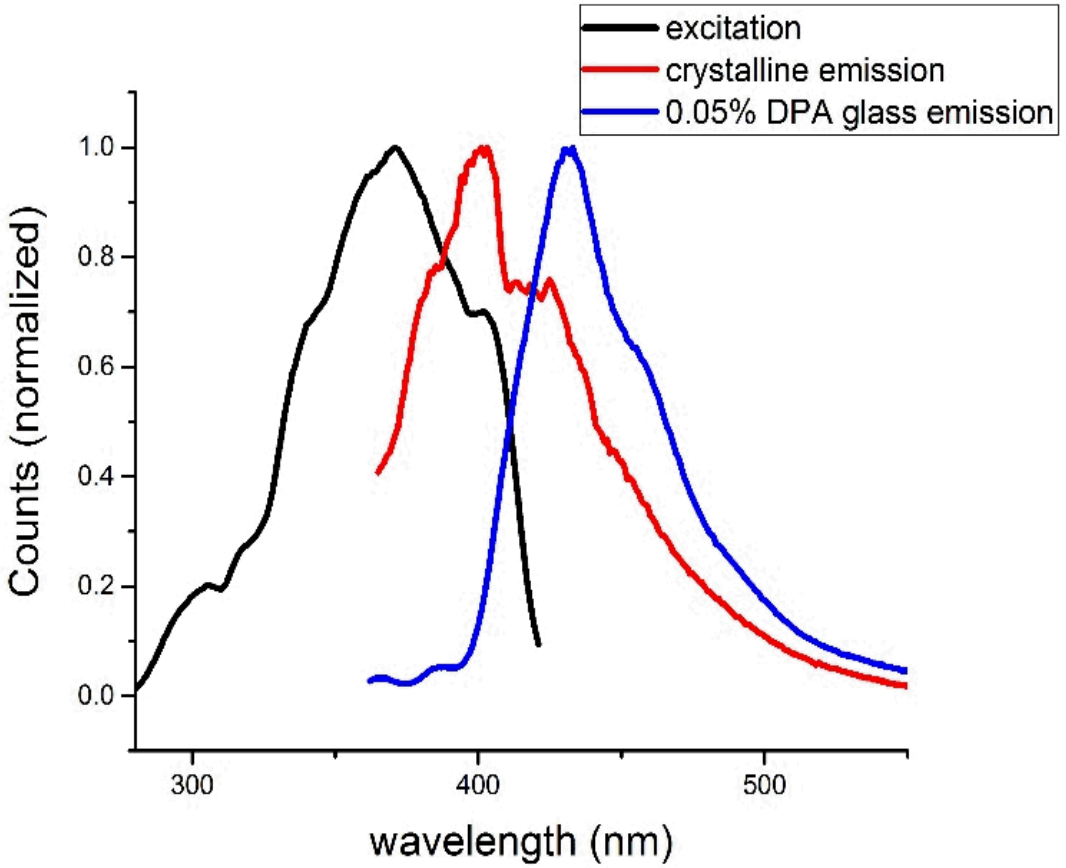


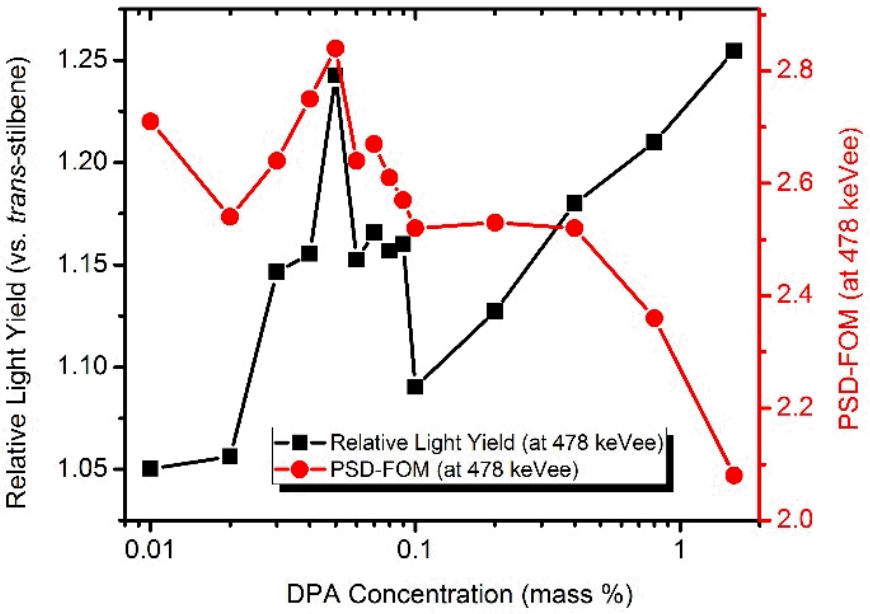
New type of isotropic scintillator!

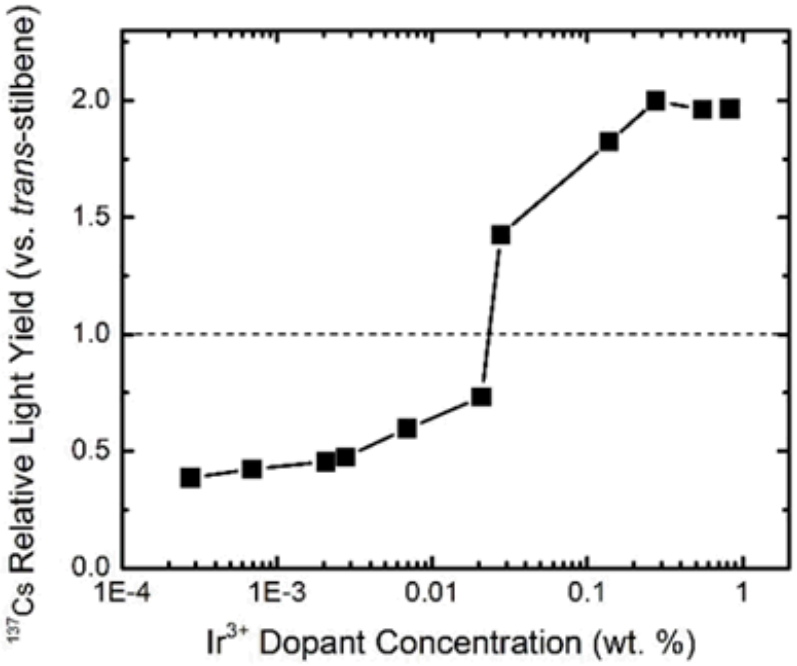
Efforts Towards Improved *Amorphous* Scintillator

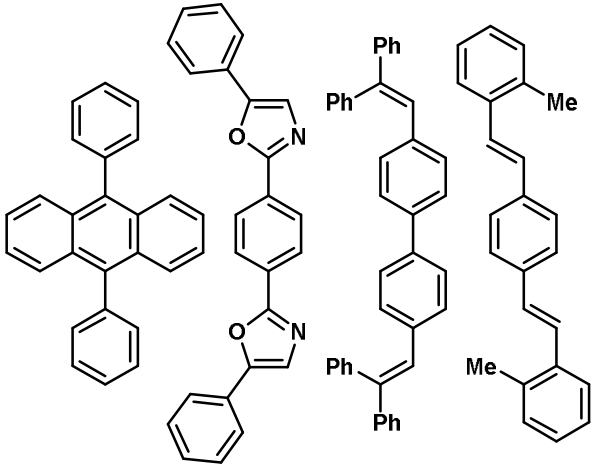




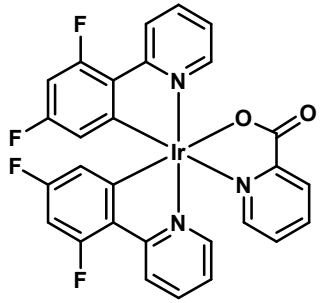
Performance Increase with Dopants





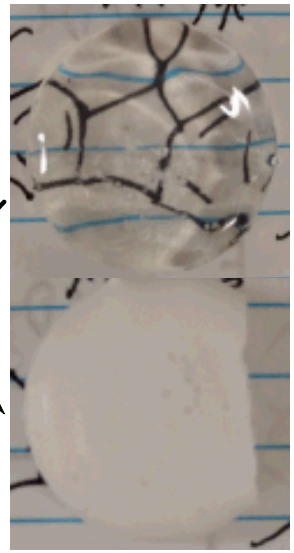


DPA POPOP DPVBi MSB



FIrpic

Instability of the Glassy State



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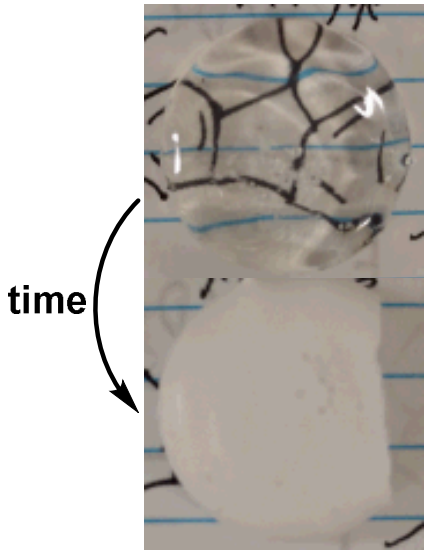
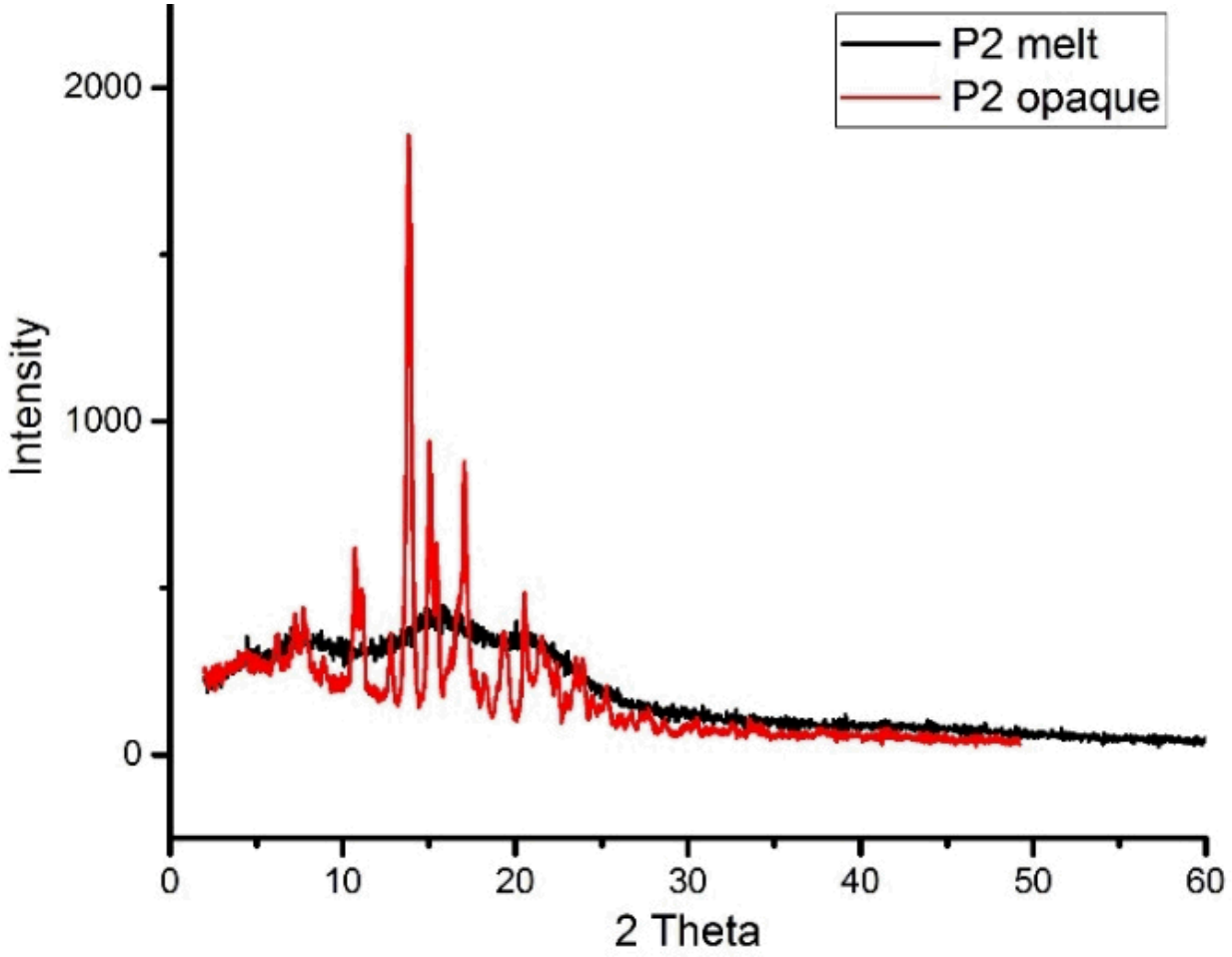
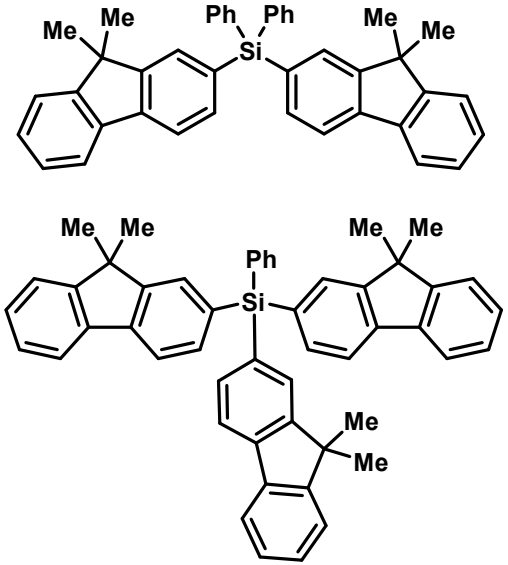




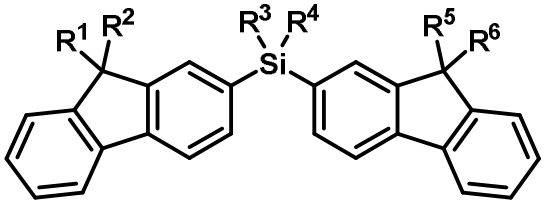
Enhanced Stability via Co-melting

via Co-melting



4 : **5** (w/w)a	Tg (°C)[b]	Transparency at 80 °C[c]
100 : 0	72.6	< 24 hours
90 : 10	75.2	Indefinite
70 : 30	80.2	Indefinite
50 : 50	81.0	Indefinite
30 : 70	89.4	Indefinite
10 : 90	95.1	< 72 hours
0 : 100	98.9	< 24 hours

via molecular design



[a]200 mg samples. [b]T_g value at the onset of the transition. [c]Evaluated by observation using a jeweler's loop.

Optimization on 2 gram Scale

Sample[a]	Dopant (w/w)	Lifetime[c] (ns)	QY[d] (Φ)	Light Yield[e]	PSD[f]
Stilbene[b]	–	2.41	1.00	1.00	3.15
EJ-301	–	2.00 (89%) 16.21 (11%)	0.81	0.63	2.57
G5	0.05% MSB	1.45	1.50	1.10	3.73
G6	0.07% MSB	1.53	1.61	1.14	3.56
G7[g]	1% FIrpic	1.01 μs	0.40	2.00	N/A

[a]Glass samples composed of 9:1 mixture of **4**:**5** [b]Single Crystal of similar size [c]Fluorescence lifetime measured at emission maximum [d]Relative to stilbene, measured at the absorption maximum [e]Cs-137 relative light yield (478 keVee) [f]PSD-FOM at 478 keVee) [g]200 mg sample.

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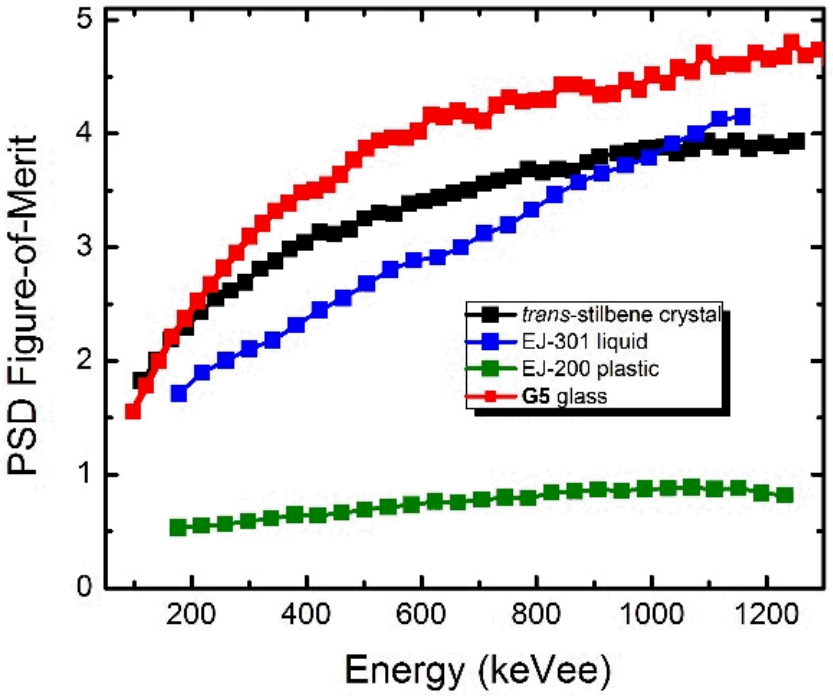

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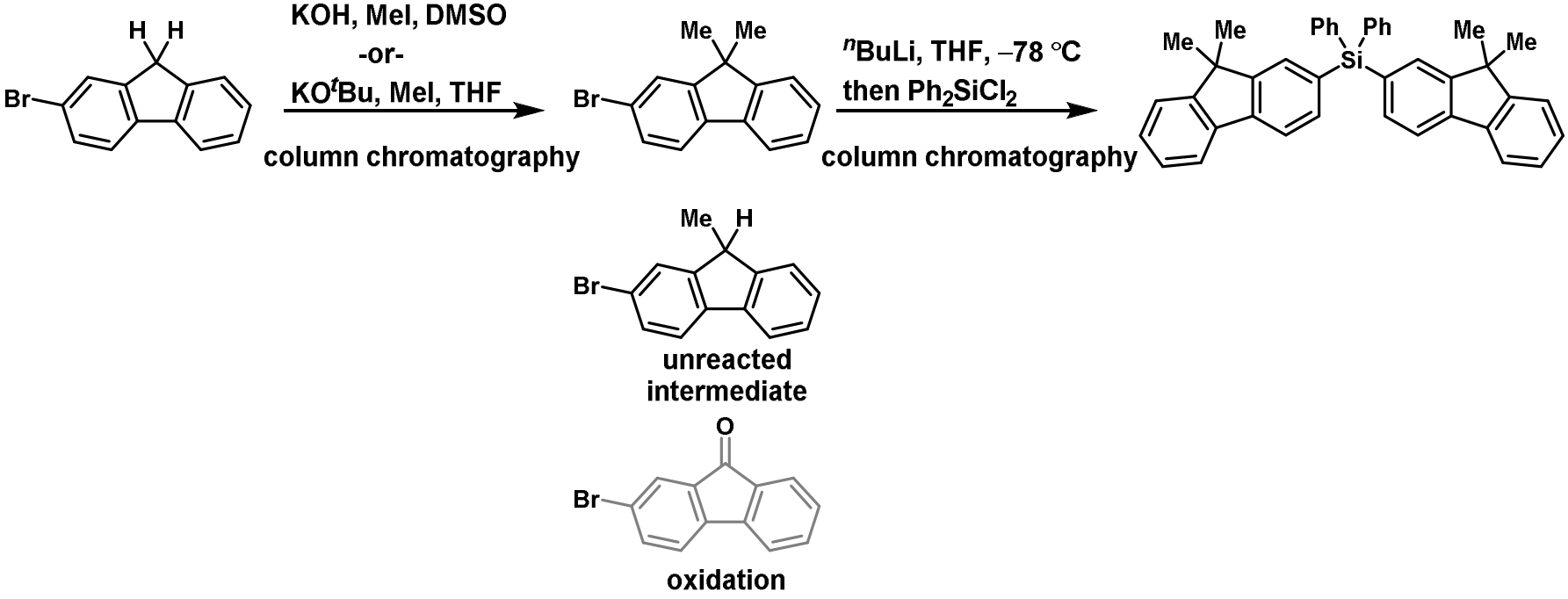
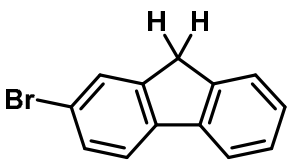
Synthesis

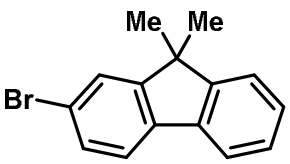

H H
Br
KOH, MeI, DMSO
-or-
KO^{t}Bu, MeI, THF
column chromatography
Me Me
Br
^{n}BuLi, THF, –78 °C
then Ph_2SiCl_2
column chromatography
Me Me
Ph Ph
Si
Me Me
Me H
Br
unreacted
intermediate
O
Br
oxidation

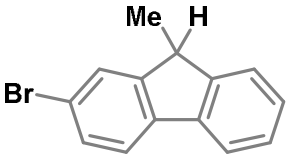
Synthesis



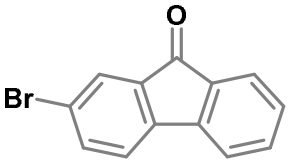
KOH, MeI, DMSO
-or-
KO^{t}Bu, MeI, THF

treat with KO^{t}Bu
then plug SiO_2
(repeat as needed)





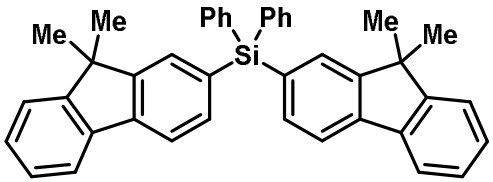
unreacted
intermediate



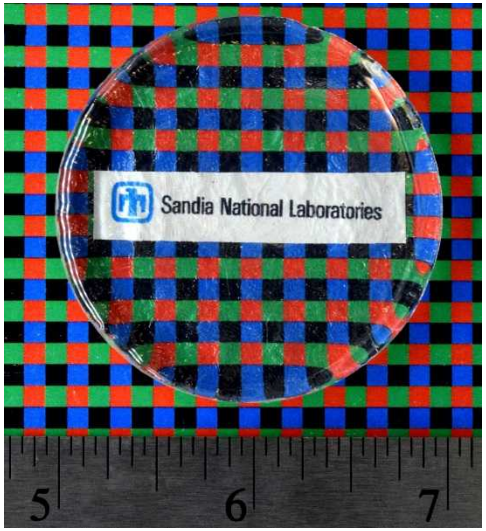
oxidation

^{n}BuLi, THF, –78 °C
then Ph_2SiCl_2

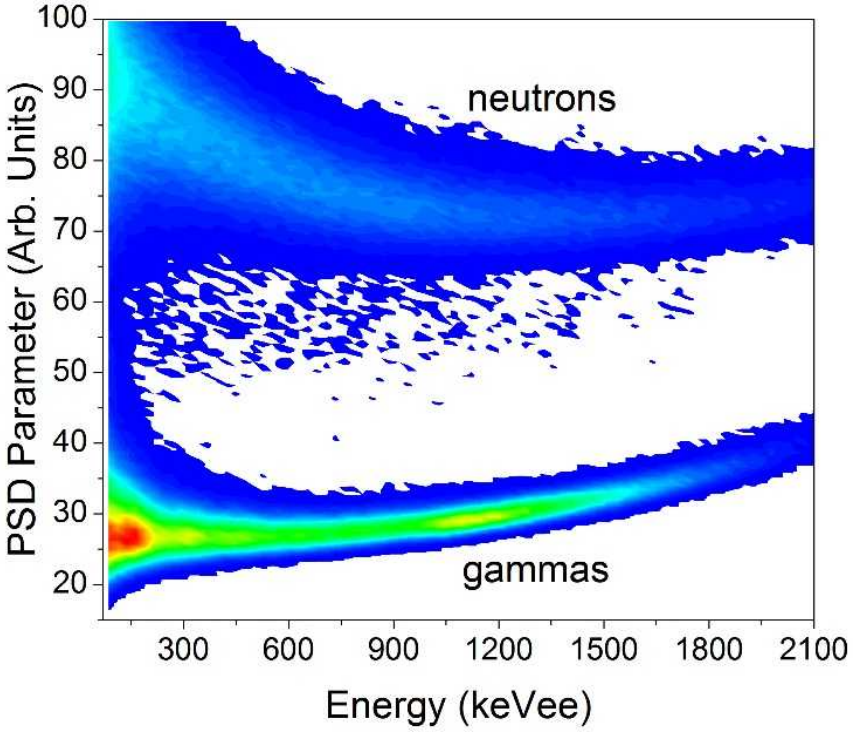
recrystallization
(twice)

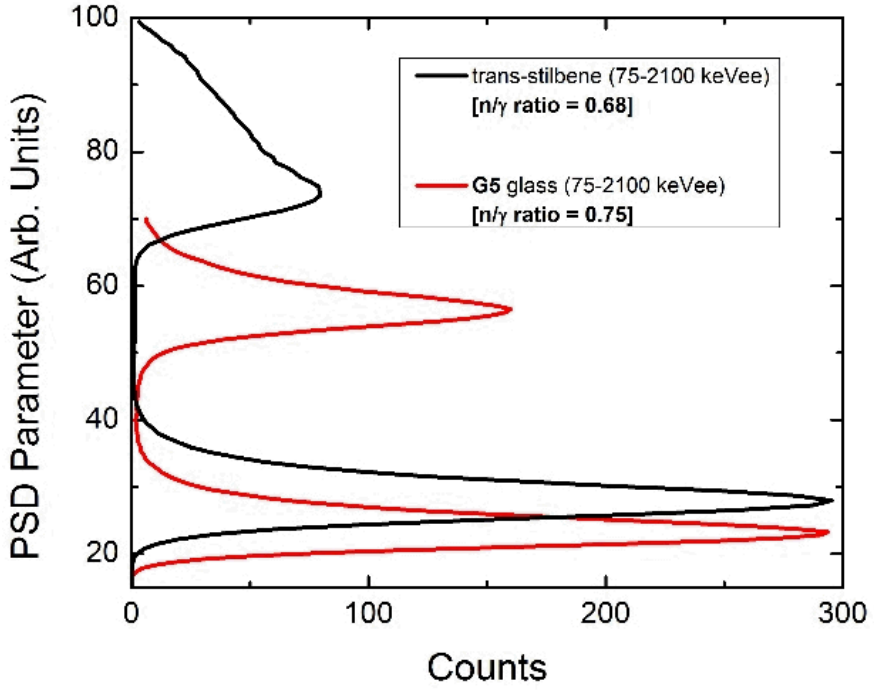


150 grams, 85% yield

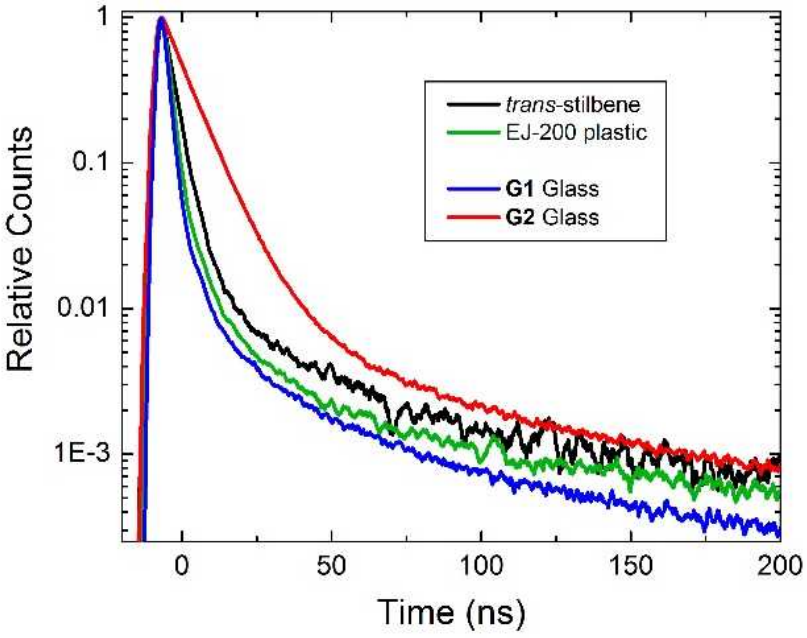


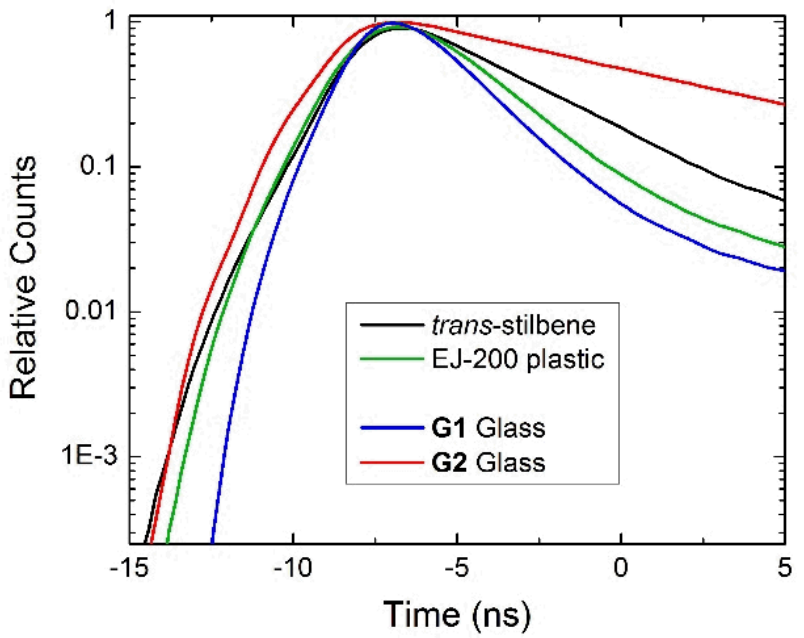
Ratio of Observed Neutron and Gamma Events





Scintillation Timing





Future Work

- Synthesis of new compounds to improve glassy state and scintillation
- Understanding mechanical properties and fabrication techniques
- Further development of additives for stability, spectroscopy, fast timing
- Scale Up! Hand off material to end-users for validation and research

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