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Functionalization of Polymers for Efficient Neutron and Gamma Detection

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U.S. Department of Homeland Security
DNDO
Domestic Nuclear Detection Office

Radiation Detector Objectives

- Cheap , large and structurally sound (preferably not liquid);
- Gamma sensitive
- Neutron sensitive
- Neutron – gamma discrimination
- Gamma energy resolution (photo peak)

Germany's mythical animal:

Die eierlegende Wollmilchsau

(All-in-one Breakfast Animal)

Our approach:

Plastic Scintillator

We have worked on:

-> neutron sensitive doping

-> pulse shape discrimination

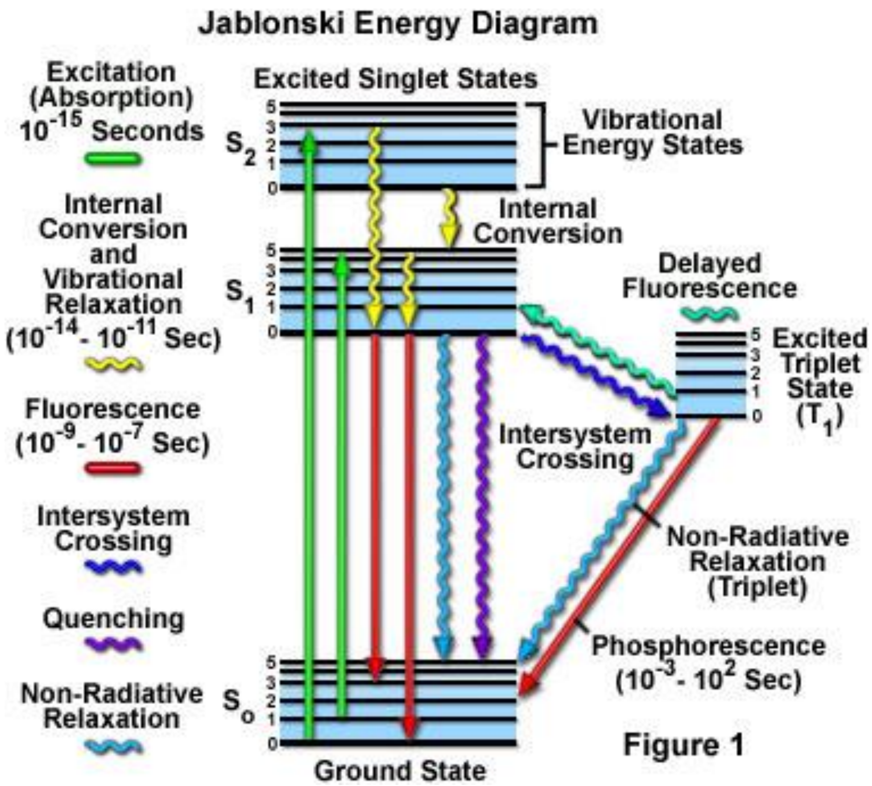
We are now starting on:

-> heavy element doping

-> spectral shape discrimination

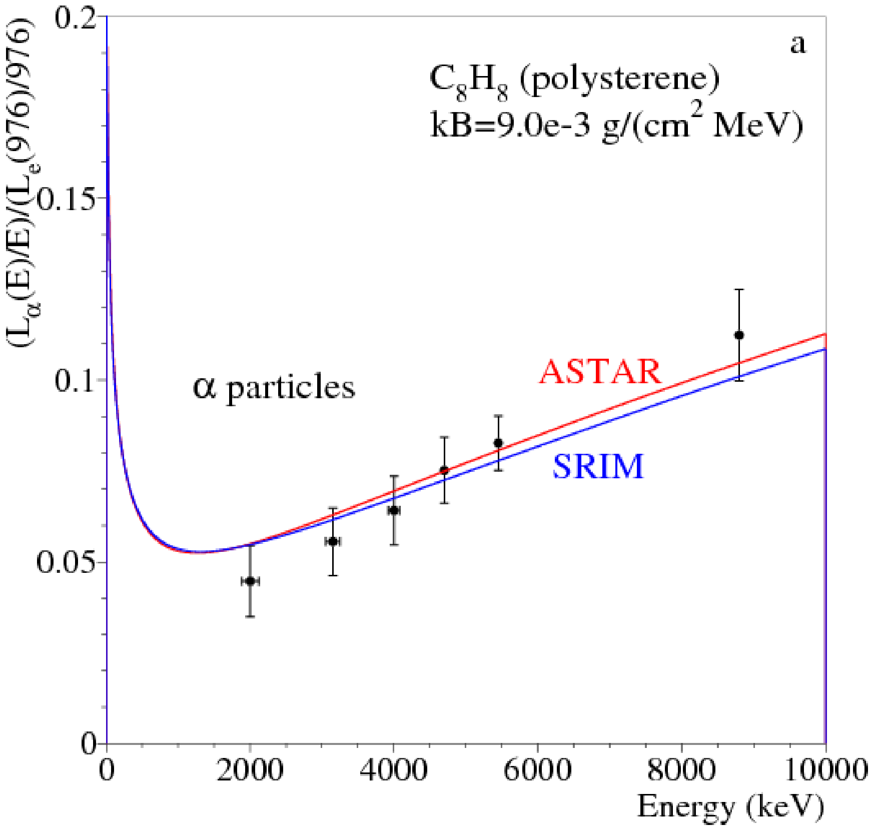
Energetics and Alpha Quenching

Energetics in Fluorescent Polymer



http://micro.magnet.fsu.edu/primer/techniques/fluorescence/fluorescenceintro.html

Polymer Response to Light Ions

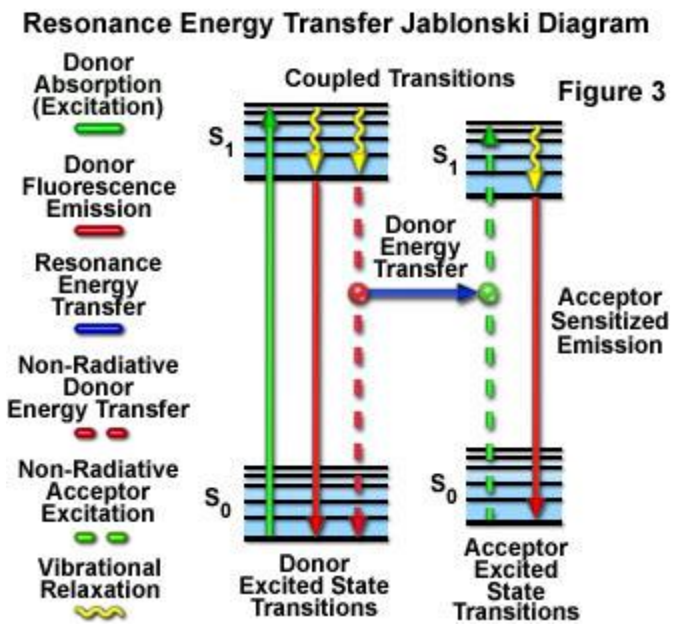


V. Tretyak, Astropart.Phys. 33 (2010) 40-53

Light ions deposit (LET) energy with higher density compared to electrons -> need for low density polymers.

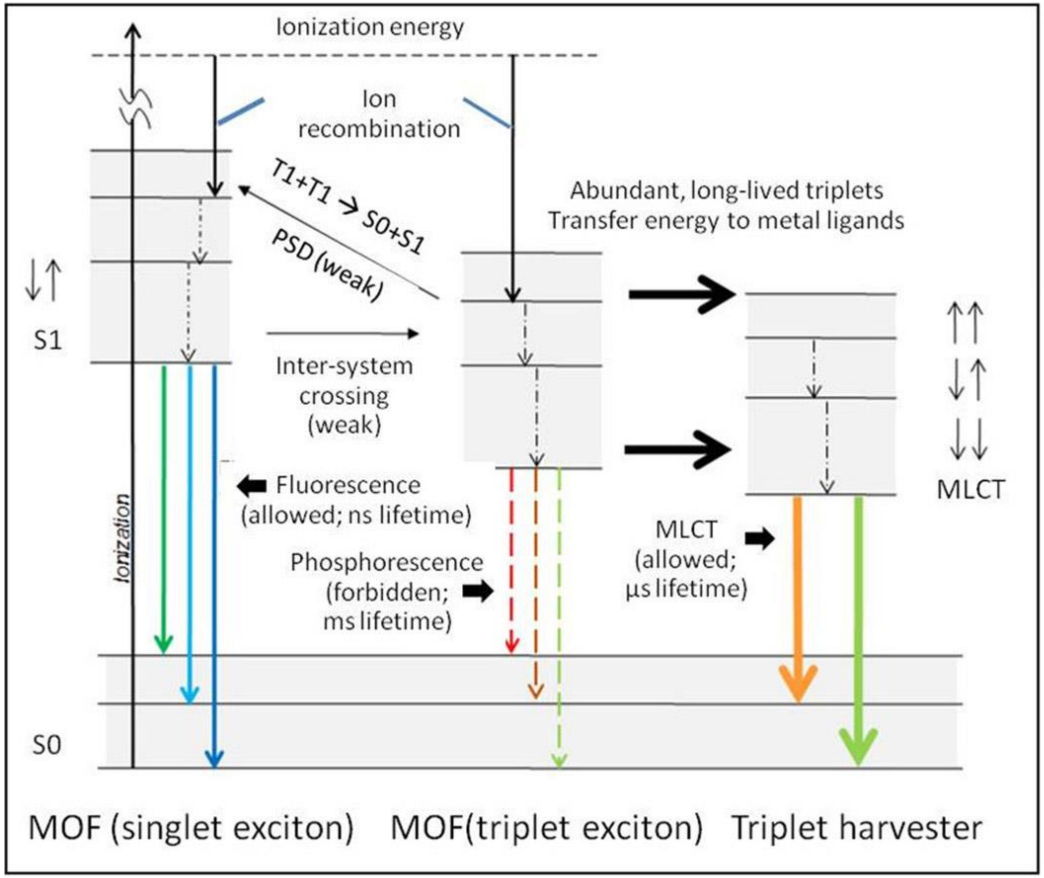
Energetics for Improvement

Foerster Resonant Energy Transfer to the Fluorescent Dopant



$$P(E_t) = 1/(1+(r/R_0)^6)$$

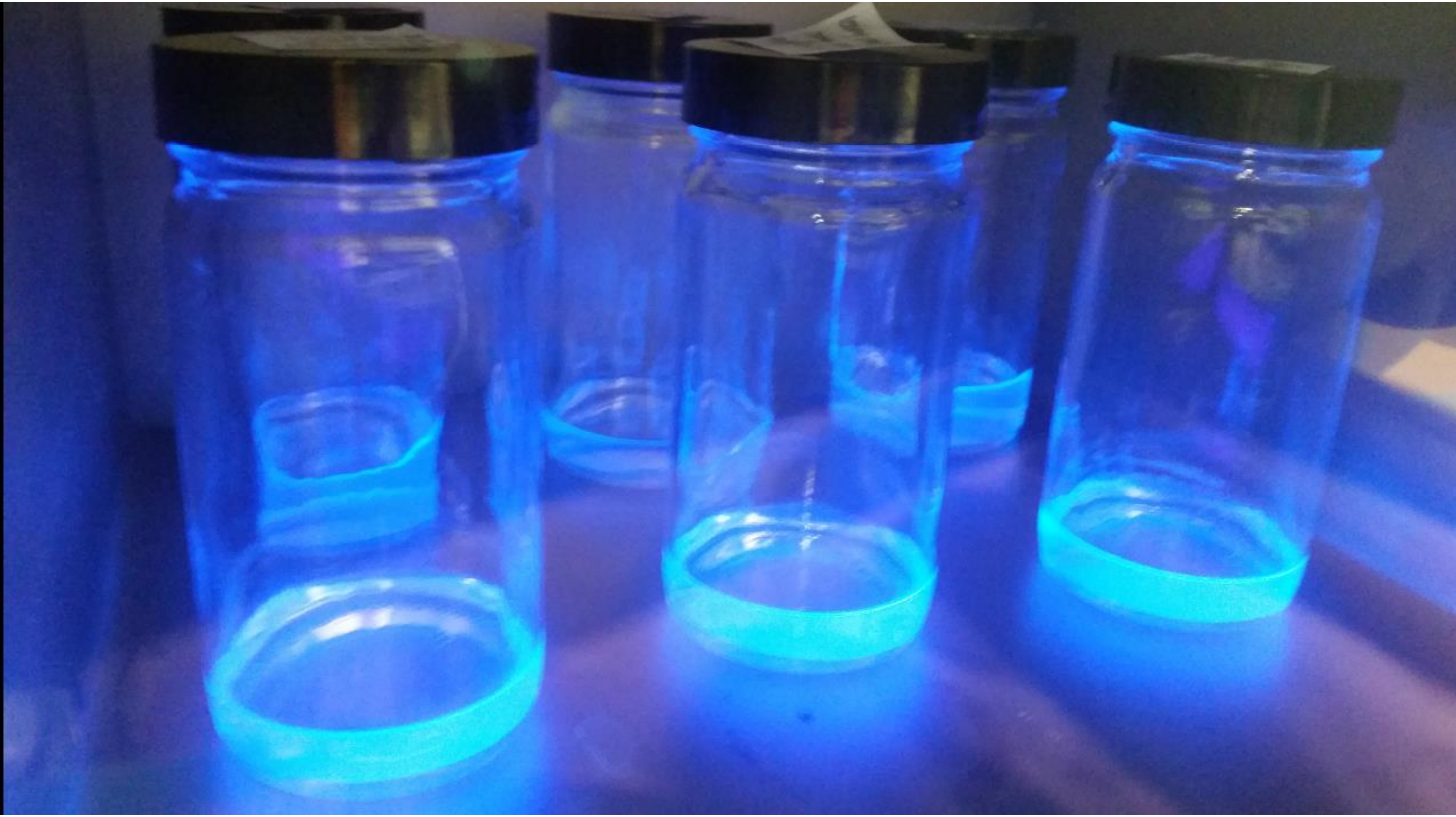
Triplet Harvesting



Mark Allendorf, F. Patrick Doty and Patrick L. Feng

Sandia National Laboratories, Livermore, CA

Technical Approaches



Technical Approaches

a) Boron containing organic molecules with high solubility in plastic matrices;

b) Fluorescent dopants with high solubility in plastic matrices and pulse shape discrimination;

c) Combination of boron content and fluorescent ligands in one molecule to achieve both functions with lower additive concentration;

d) Versions of the above with reactive ligands that allow co-polymerization to improve FRET and enhance mechanical stability at high additive concentrations;

e) Triplet harvesting and spectral shape discrimination;

f) Heavy element doping to achieve photo peak formation in gamma spectra.

Neutron sensitivity - why Boron?

-> Replacement of 3-He gas detectors in the currently used portal monitor systems;

-> Need for similar neutron sensitivity and gamma background insensitivity;

-> Similar cross section for thermal neutrons in 10-B:

sigma (thermal; 3-He) = 5400 barn (natural abundance 0.0137%)

sigma (thermal; 10-B) = 4200 barn (natural abundance 19.9%)

sigma (thermal; 6-Li) = 900 barn (natural abundance 7.59%);

-> Lithium is also tricky in organic chemistry;

-> Price: 10-B is easily available and not export controlled, per Mol factor 100 less then 3-He

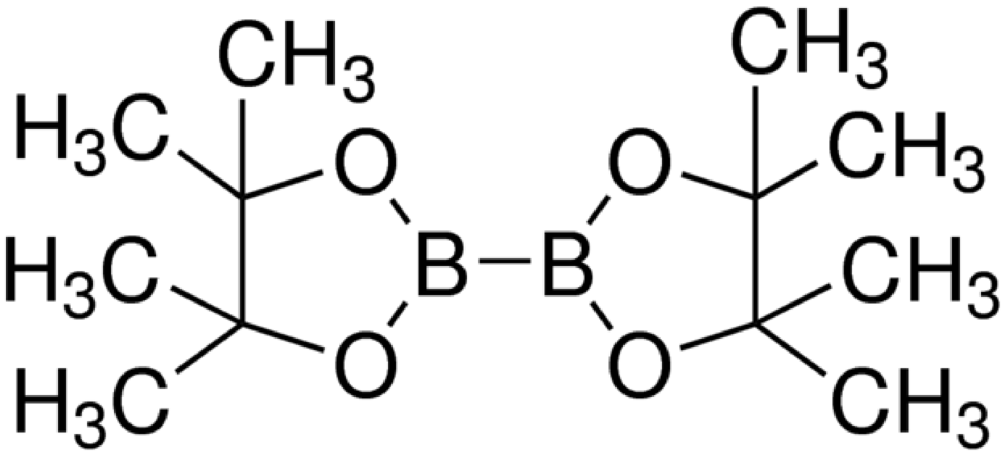
Disadvantage:

-> Need for separate neutron – gamma discrimination scheme

-> Alpha quenching leads to low energy signal response

$$^{10}B + {}^{1}n_{th} \implies {}^{7}Li\ (1.0\ MeV) + \alpha\ (1.8\ MeV)$$
$$Q = 2.792\ MeV \quad 7\%$$

$$^{10}B + {}^{1}n_{th} \implies {}^{7}Li^{*}\ (0.83\ MeV) + \alpha\ (1.47\ MeV)$$
$$Q = 2.310\ MeV \quad 93\%$$
$$\hookrightarrow {}^{7}Li^{*} \implies {}^{7}Li + \gamma\ (0.48\ MeV)$$



B2Pin2

Bis(pinacolato)diboron is a boron containing two pinacolato ligands. With the formula $[(CH_3)_4C_2O_2B]_2$, it is a colourless solid that is soluble in organic solvents. It is a commercially available reagent for making pinacol boronic esters for organic synthesis.

~ 8% B by weight; ~ $1/g

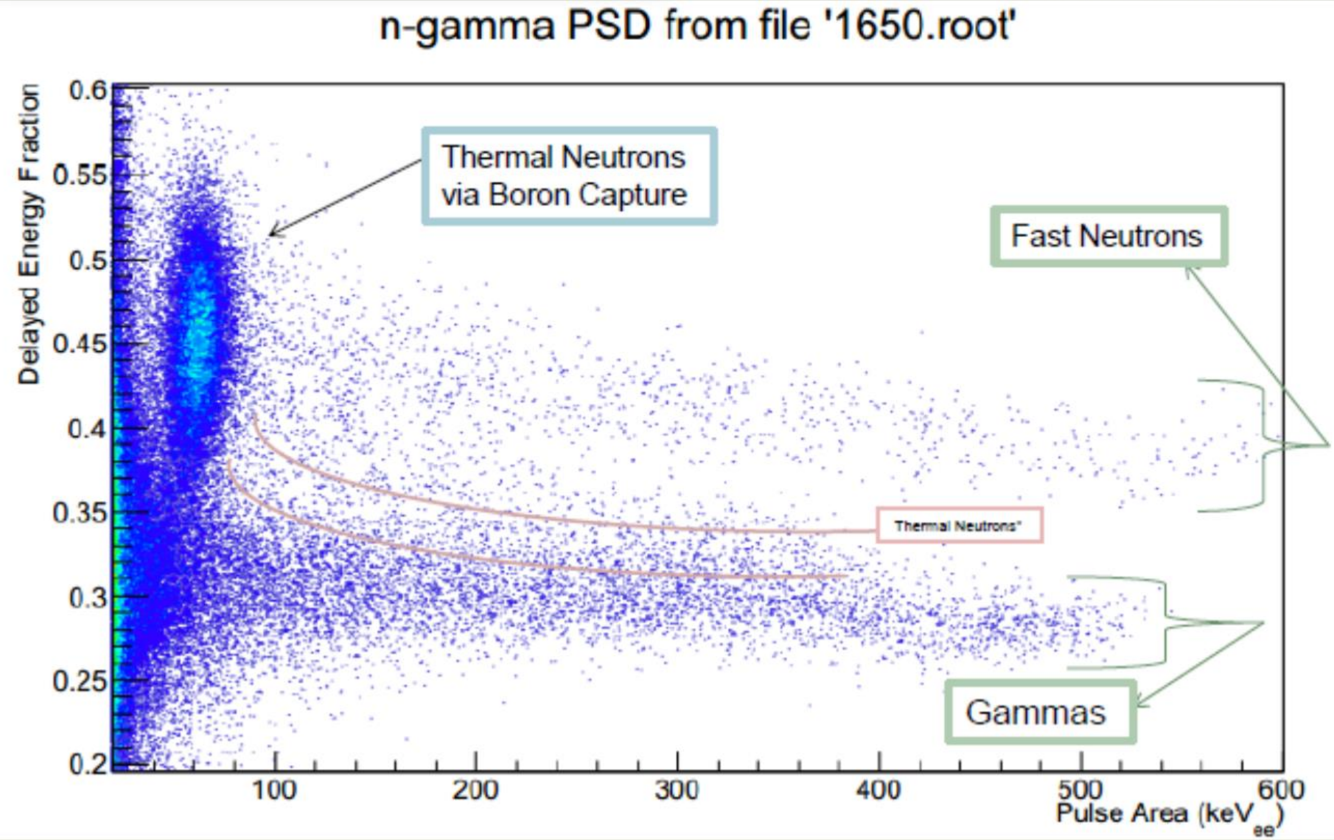
A. Mahl et al., NIM A 816 (2016) 96

$$^{10}B + {}^{1}n_{th} \implies {}^{7}Li\ (1.0\,MeV) + \alpha\ (1.8\,MeV)$$
$$Q = 2.792\,MeV \quad 7\%$$

$$^{10}B + {}^{1}n_{th} \implies {}^{7}Li^{*}\ (0.83\,MeV) + \alpha\ (1.47\,MeV)$$
$$Q = 2.310\,MeV \quad 93\%$$
$$\hookrightarrow {}^{7}Li^{*} \implies {}^{7}Li + \gamma\ (0.48\,MeV)$$

20%PPO 0.1%POPOP 11.75%B2Pin2

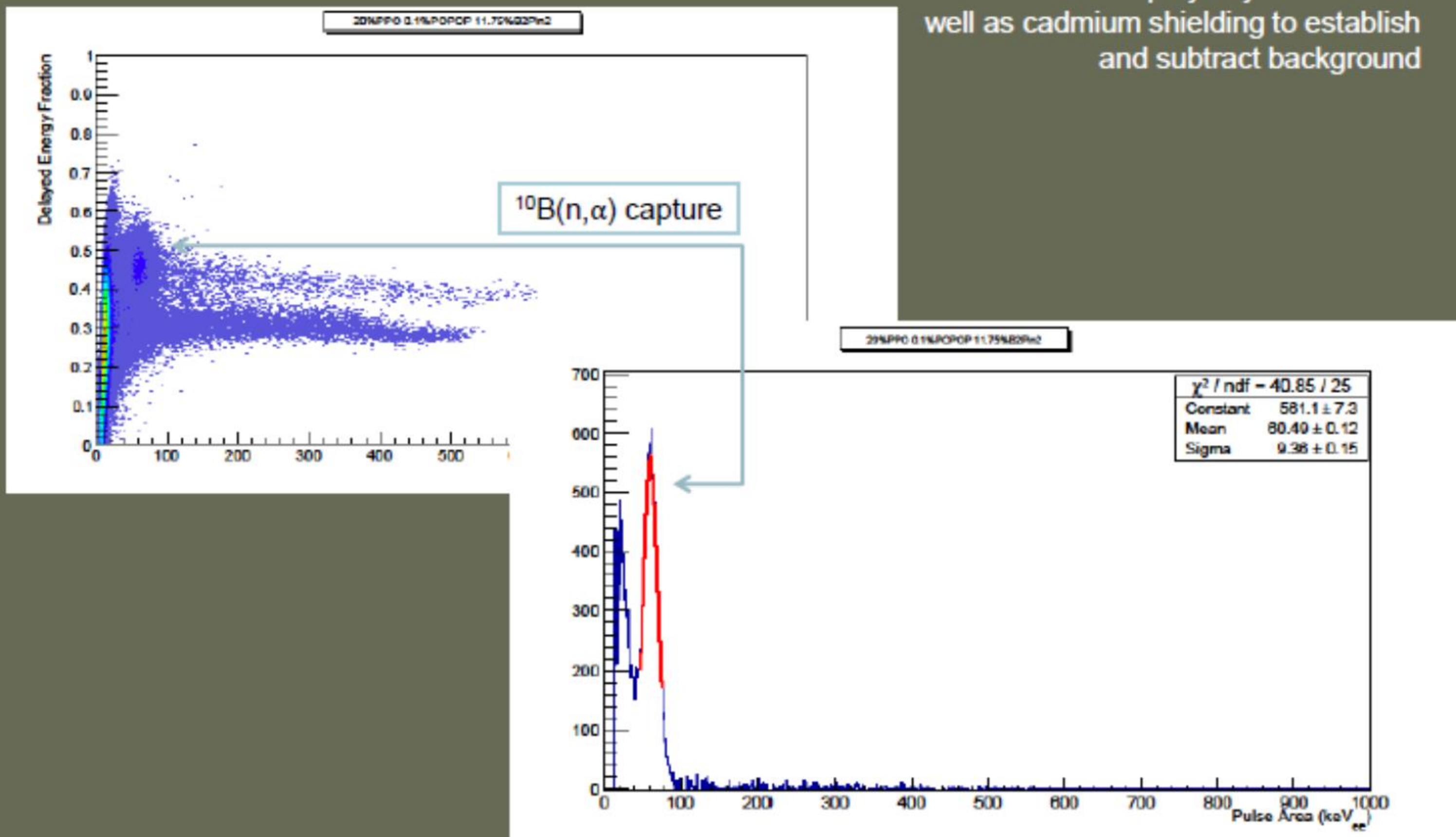
Small thermal neutron line arises from second decay channel due to excited lithium nucleus. Only discernible with good PSD



- Capture Peak @ 60.5 keVee

20%PPO 0.1%POPOP 11.75%B2Pin2

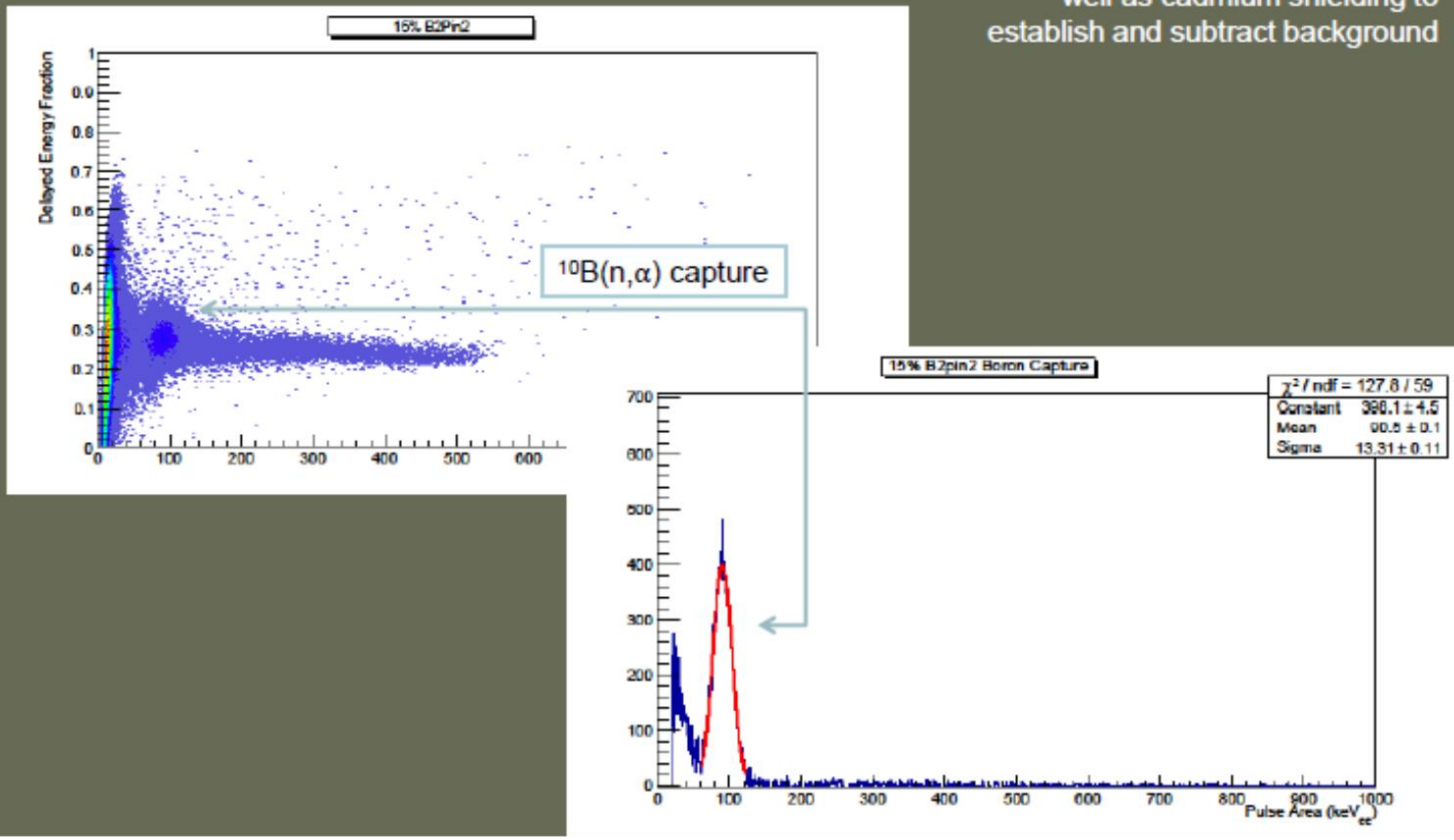
Sample exposed to thermalized neutron flux in a polyethylene cave as well as cadmium shielding to establish and subtract background



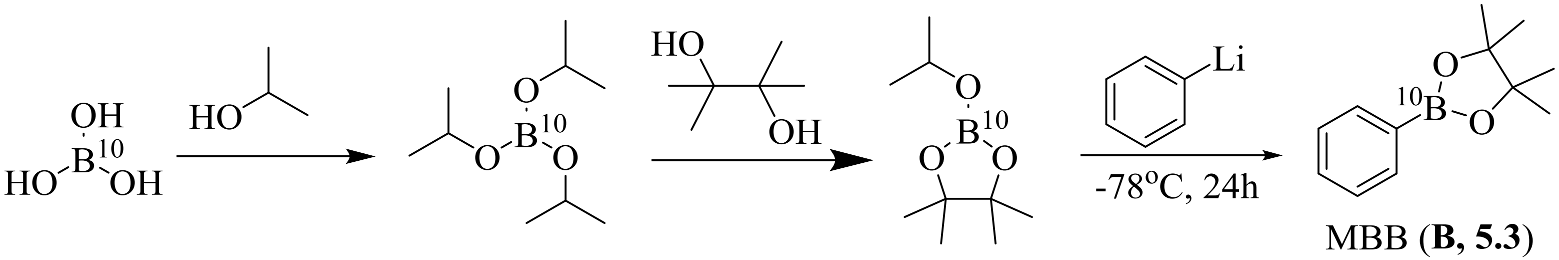
Capture Peak @ 90.5 keVee

1%PPO 0.1%POPOP 15%B2Pin2

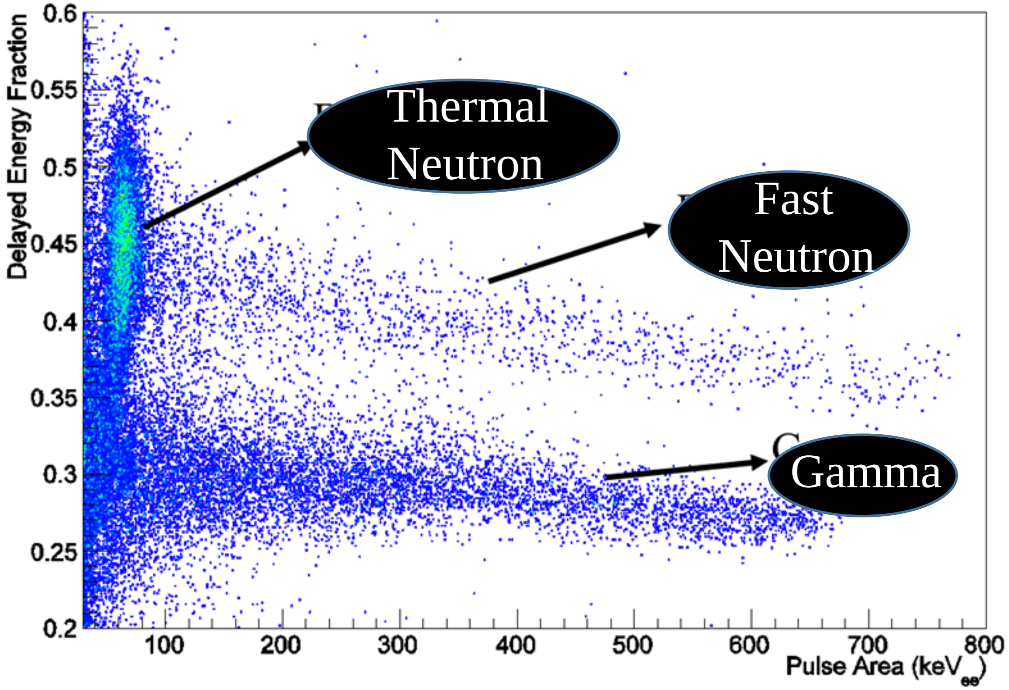
Sample exposed to thermalized neutron flux in a polyethylene cave as well as cadmium shielding to establish and subtract background



Moving to 10-B enriched materials – Mono-borylated Benzene from 10-B boric acid



MBB (**B, 5.3**)

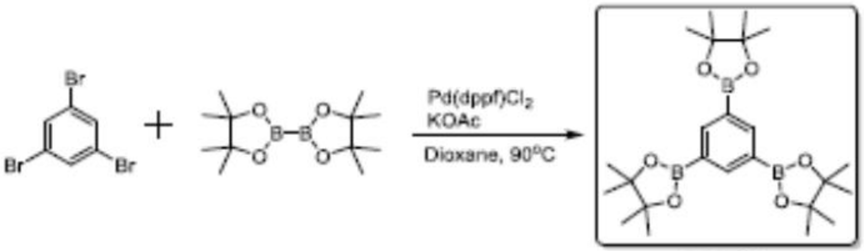


- MBB is NOT stable at ambient conditions
- It results in a cloudy plastic scintillator
- However, efficient at capturing thermal neutron
- 20 wt% PPO, 1 wt% MBB

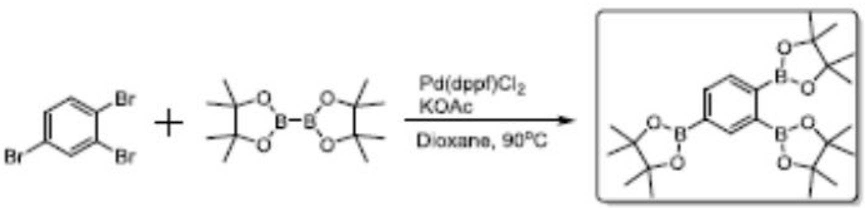
A. Mahl et al., in preparation

Boron containing benzene derivatives for thermal neutron detection-Synthesis

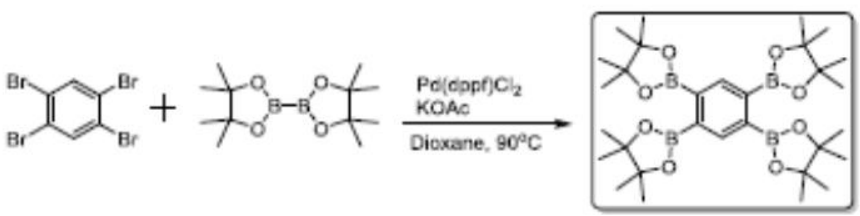
Aim: Synthesize boron-rich benzene derivatives



B, 7.11



B, 7.1



B, 7.43

Product	Traditional yield (24hr)	Microwave (40min)
B, 7.11	69	61
B, 7.1	97	83
B, 7.43	36	41

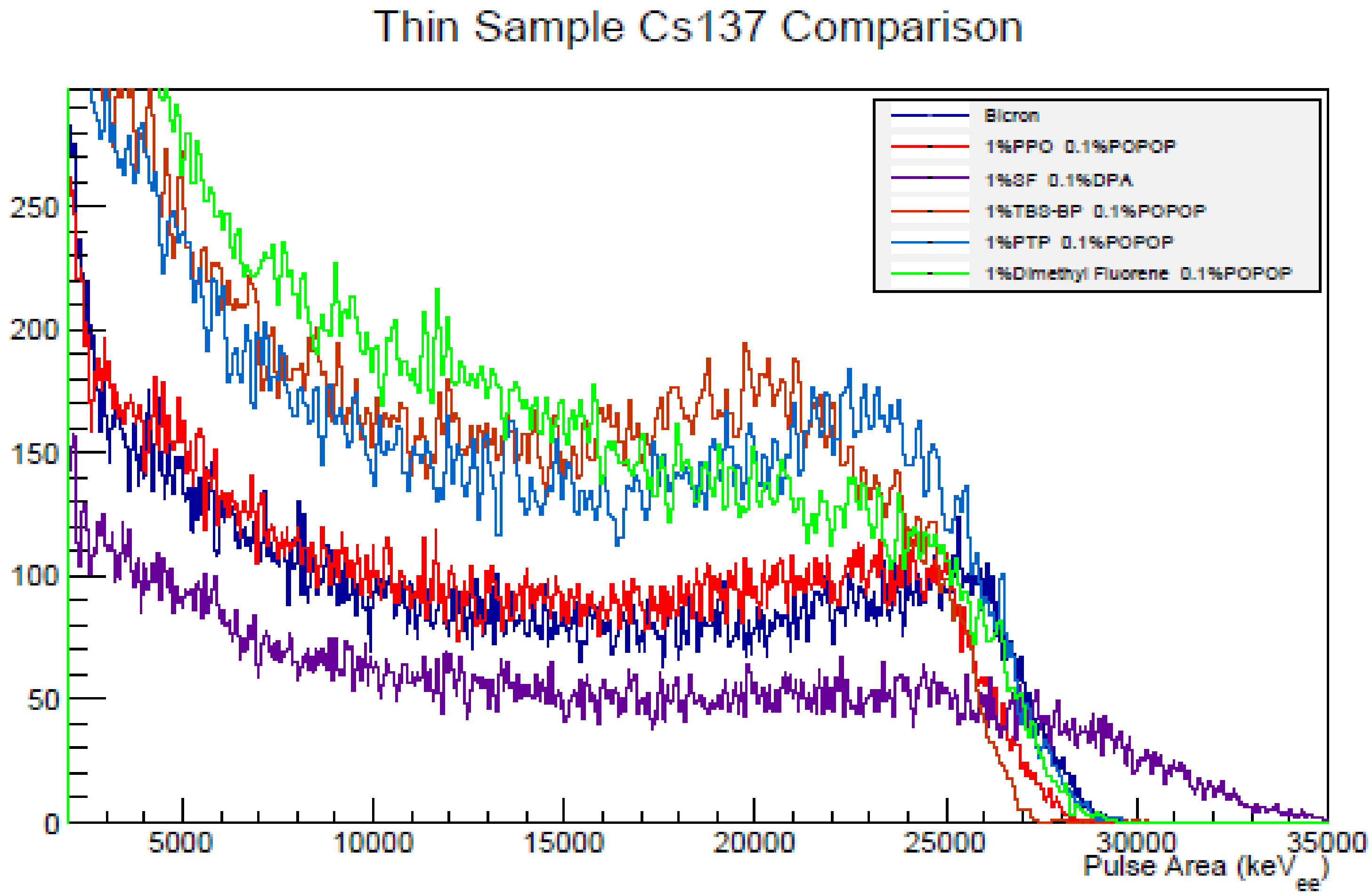
Manuscript ~~in revision~~

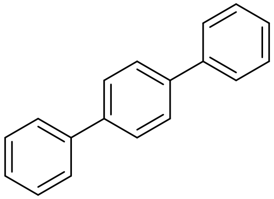
1,2,4,5-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (TBB),
1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (135TrBB)
and 1,2,4-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene 124TrBB)

H. Yemam et al.,
Scientific Reports 5 (2015) 13401

Problem: Softening of Samples when overdoping with PPO for PSD remains.

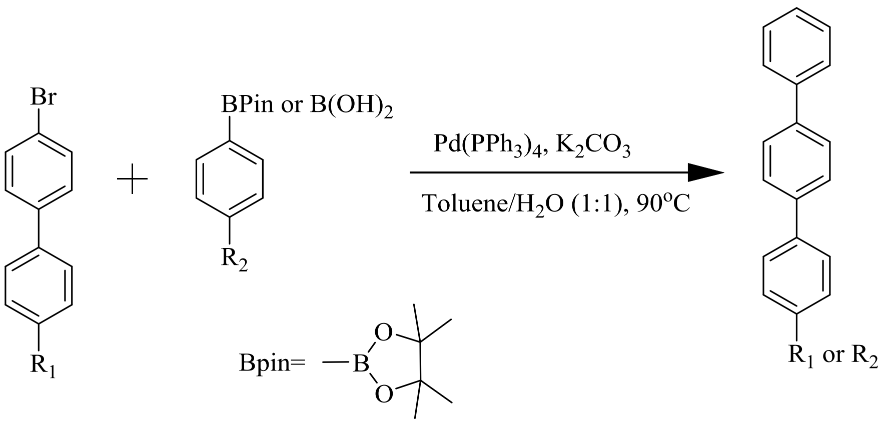
However, there are plenty of other fluorescent dopants with comparable light output.





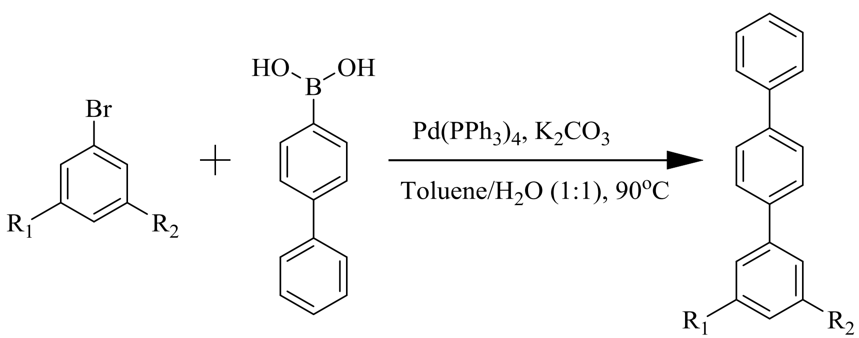
p-terphenyl

- 93% PLQY
- Short excited lifetime (~2ns)
- Commonly used by commercial scintillators to achieve high light output
- However, low solubility in PVT (~2.5%)



R_1 =-H, R_2=-tBu
R_1=-H, R_2=-nBu
R_1=-(2-ethylhexyl), R_2=-H
R_1=-heptyl, R_2=-H

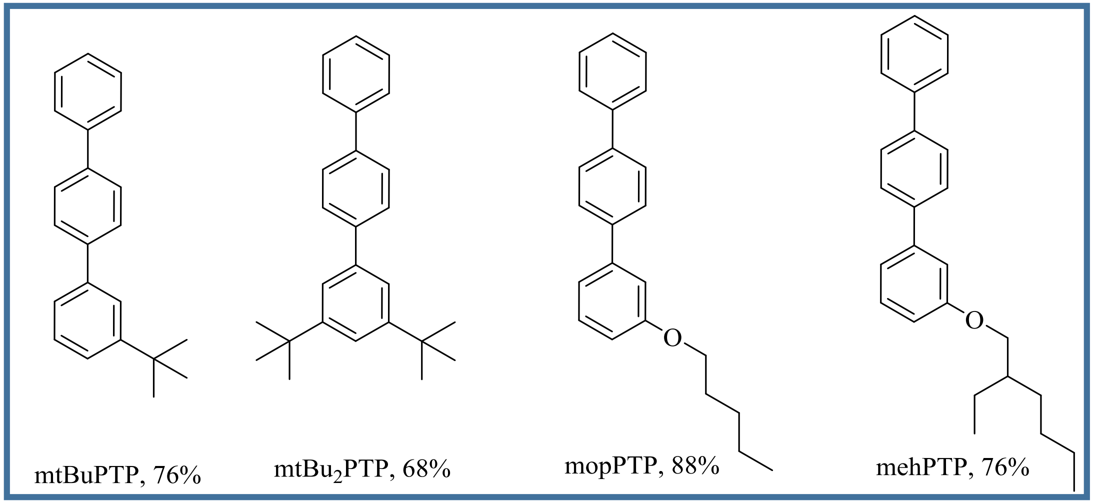
para-alkylated PTP

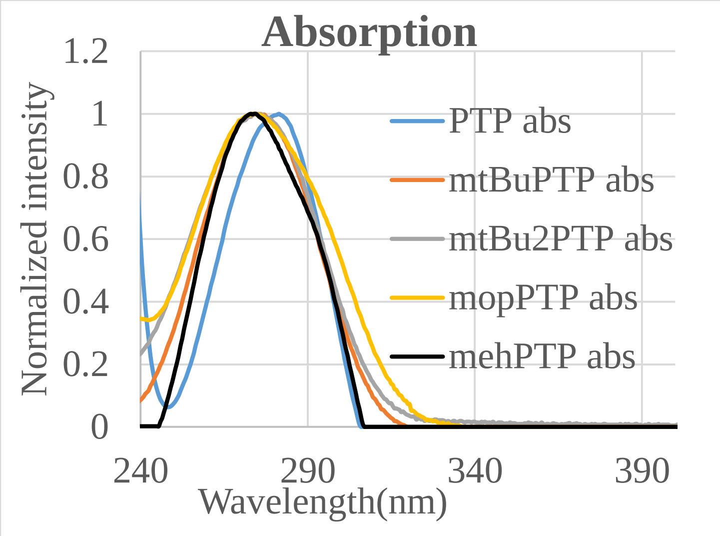


R_1 =-H, R_2= -tBu
R_1=-tBu, R_2=-tBu
R_1=-H, R_2=-OPentyl
R_1=-H, R_2=-(2-ethylhexyl)

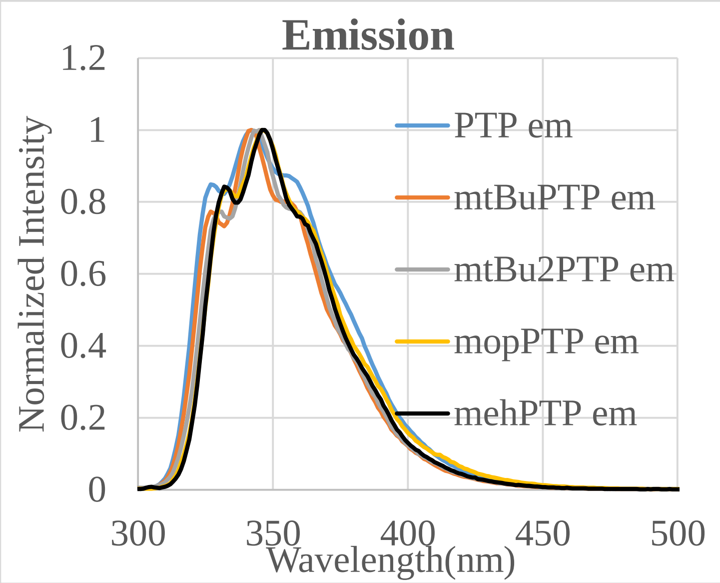
meta-alkylated PTP

Yemam, Henok, et al. *C-EAJ*, 2017 (in print).



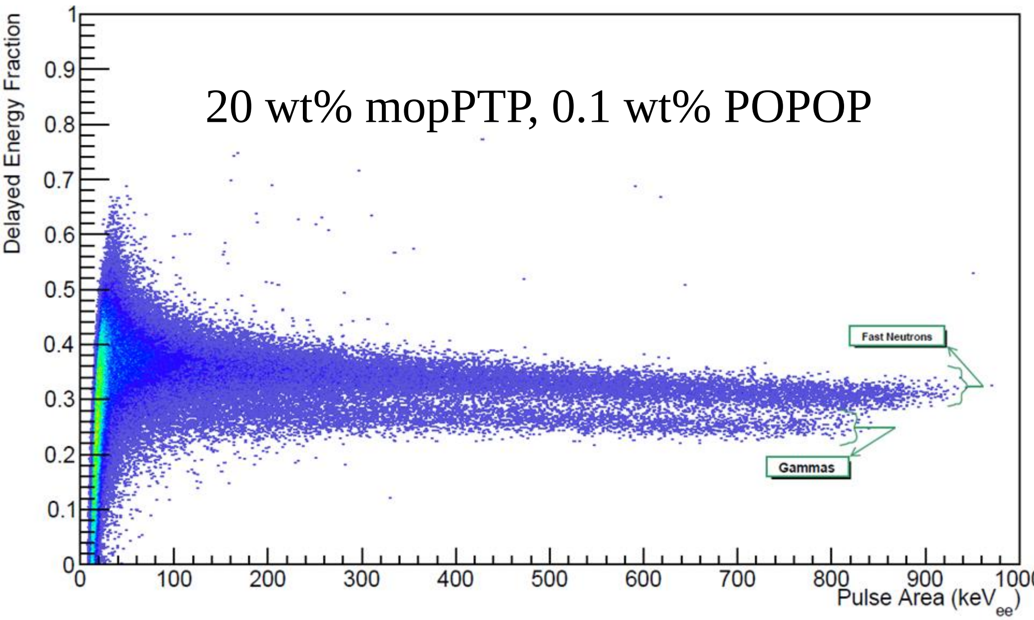


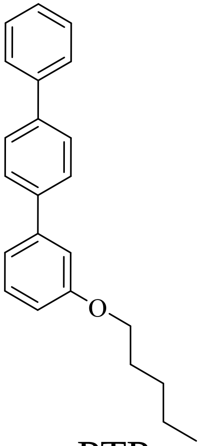
Primary dopants	Tm (ºC)	LC-phase (ºC)	UV-max (nm)	PL-max (nm)	PLQY (%)
PTP	213	N/A	281	341	93
mtBuPTP	94	N/A	274	342	90
$mtBu_2PTP$	136	N/A	275	345	97
mopPTP	64	57-62	275	346	95
mehPTP	11	N/A	274	346	100



- m-PTP's: similar optical property as PTP
- Much lower melting point than PTP
- Increased solubility in PVT (> 20 wt%)

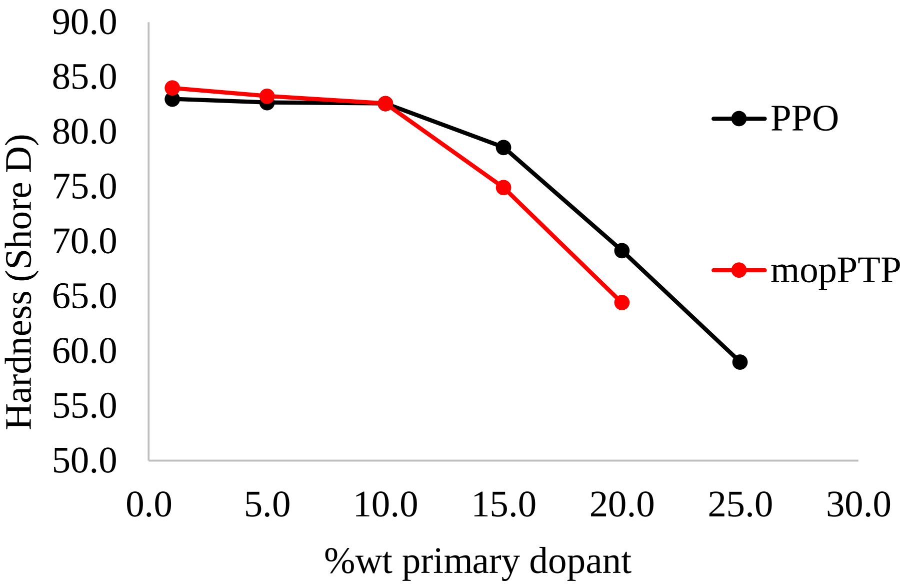
Yemam, Henok, et al. *C-EAJ*, 2017 (in print).





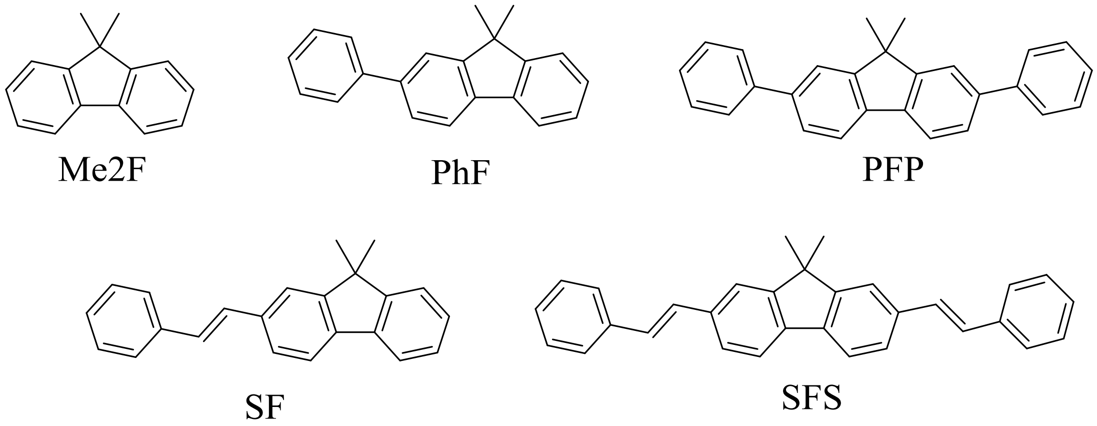
mopPTP

Primary Dopants	5.0 wt% FOM	10.0 wt% FOM	15.0 wt% FOM	20.0 wt% FOM
PTP	-	-	-	-
mtBuPTP	0.79	0.81	0.72	-
$mtBu_2PTP$	0.57	0.79	0.81	-
mopPTP	0.64	0.71	0.77	0.87
PPO	0.65	1.10	1.21	1.61

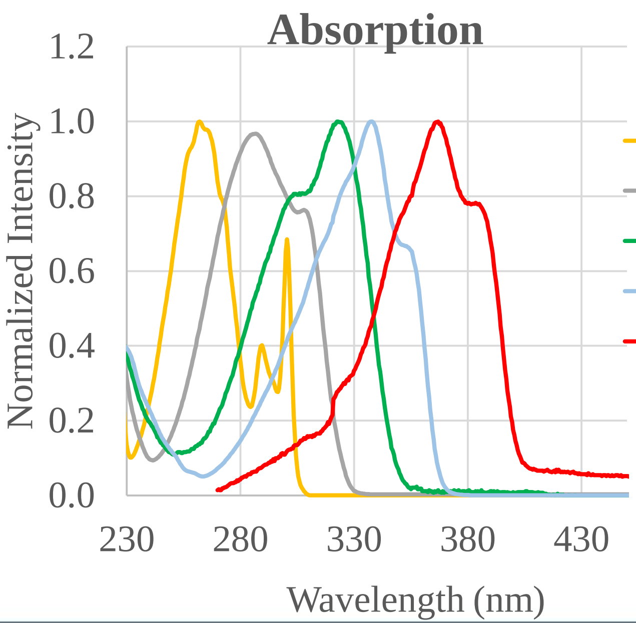


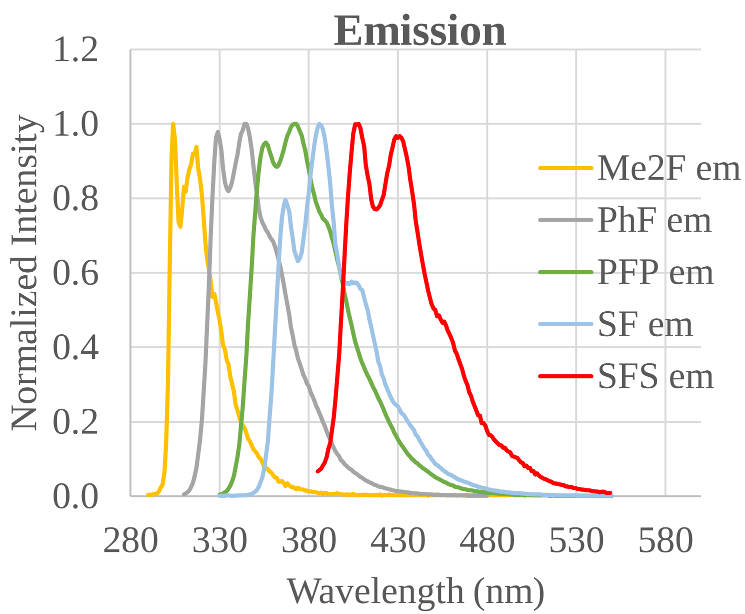
Yemam, Henok, et al. *C-EAJ*, 2017 (under review).

Fluorene Derivatives



Primary dopants	Tm (°C)	UV-max (nm)	PL-max (nm)	PLQY (%)
PPO	72	304	367	100
Me_2F	96	264	304, 317	45
PhF	86	289	330, 346	64
PFP	175	342	390	89
SF	113	338	387	72
SFS	125	371	411, 436	100





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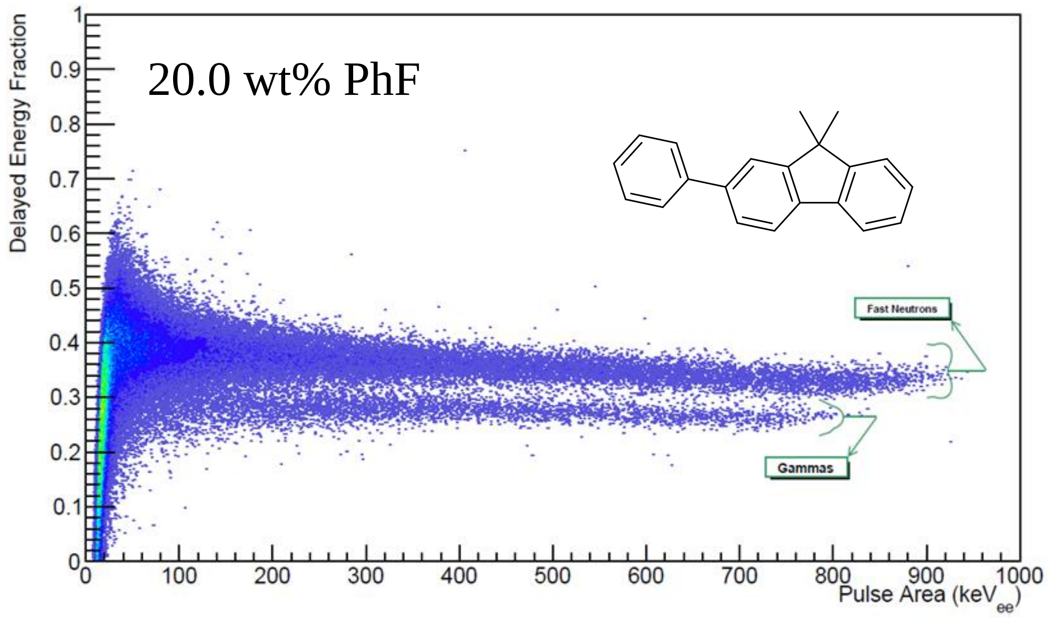
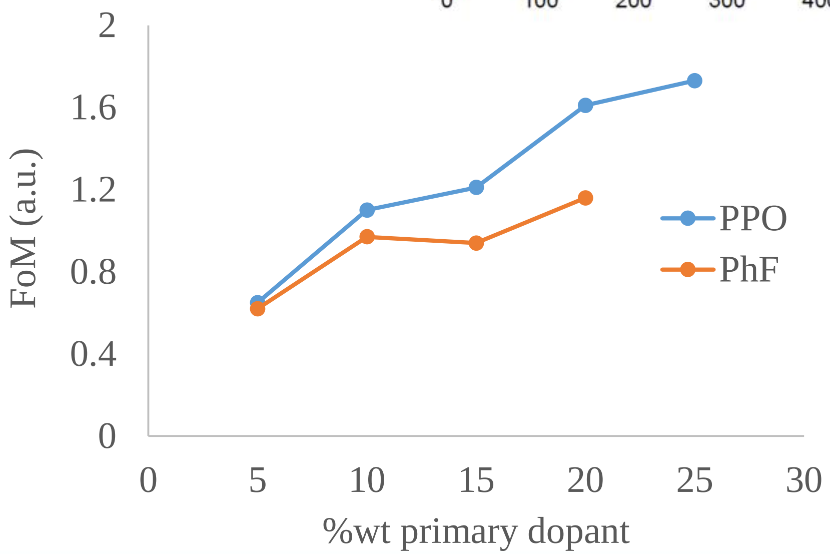
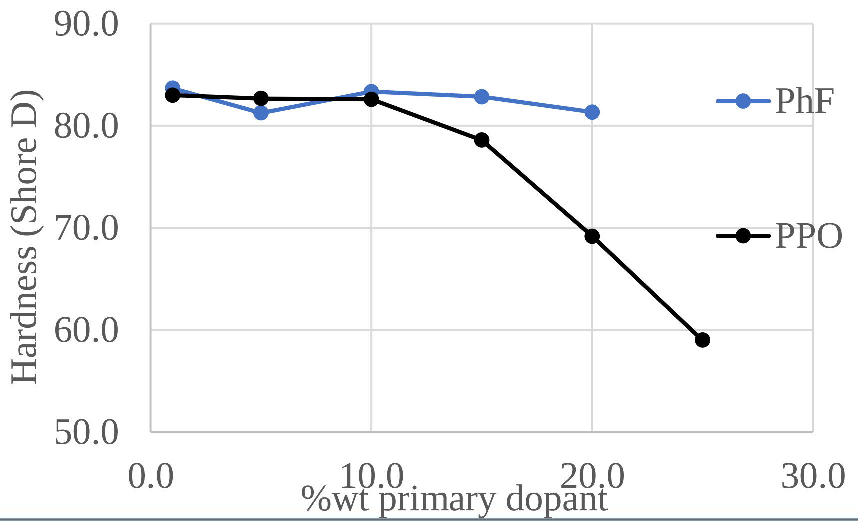
Yemam, Henok, et al. *C-EAJ*, 2017 (under review).

2-phenyl-9,9-dimethylfluorene (PhF)

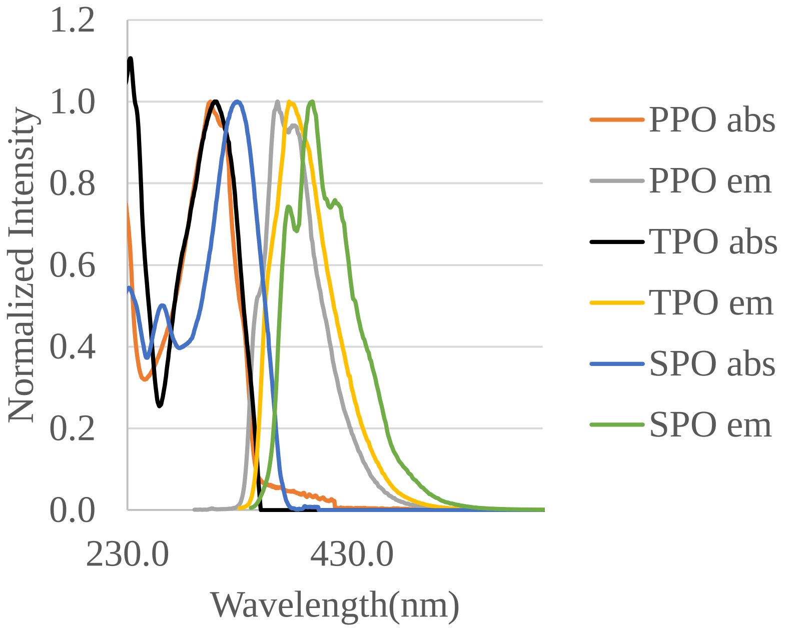


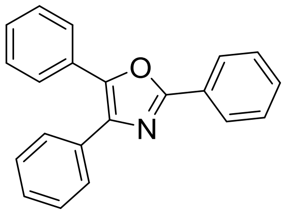




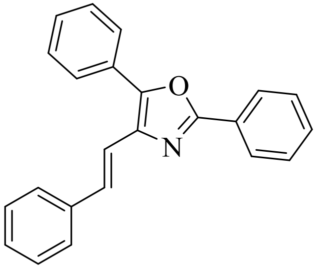
PPO Derivatives

Dopant	Tm (ºC)	Td (ºC)	UV-Vis (nm)	PL max (nm)	PLQY (%)
PPO	72	132	304	364	100
TPO	115	169	308, 309	375	67
SPO	114	196	328	395	-
VPO	139	-	-	-	-

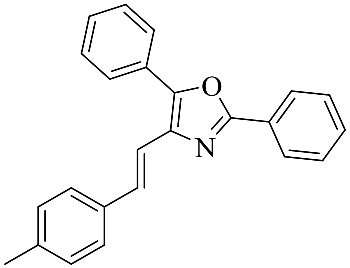




TPO



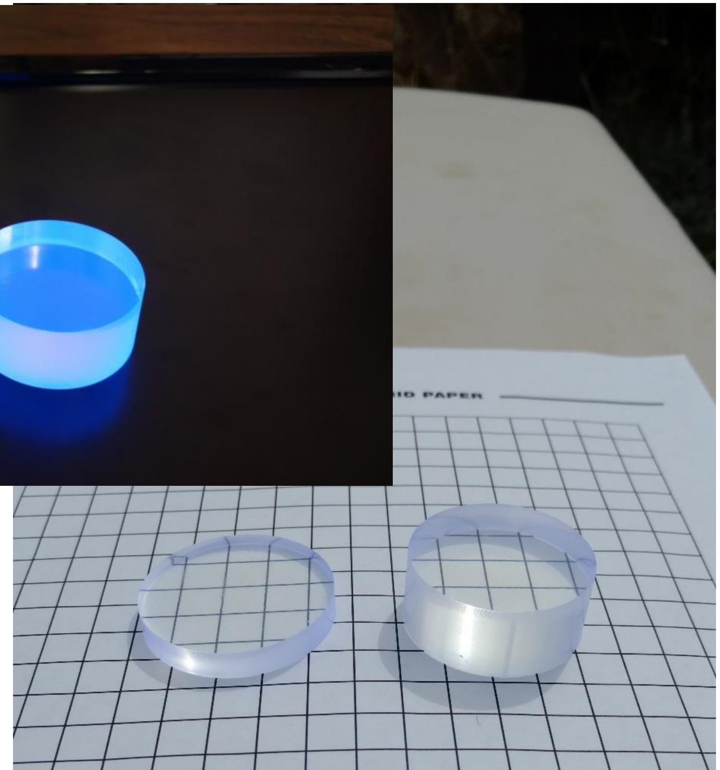
SPO



VPO

Yemam, Henok, et al. *Unpublished.* 2017

PPO Overdoping For PSD



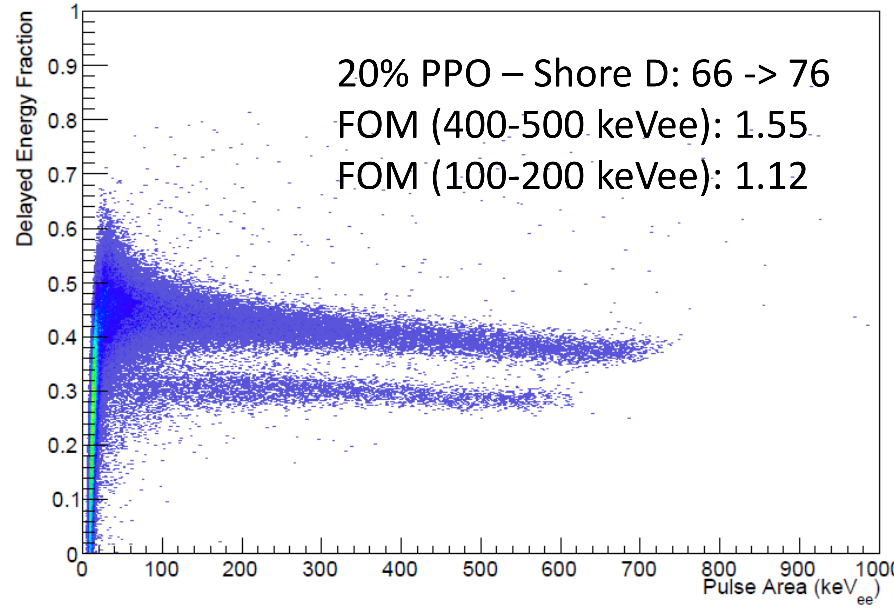
Machined samples containing 25 and 30% PPO by weight

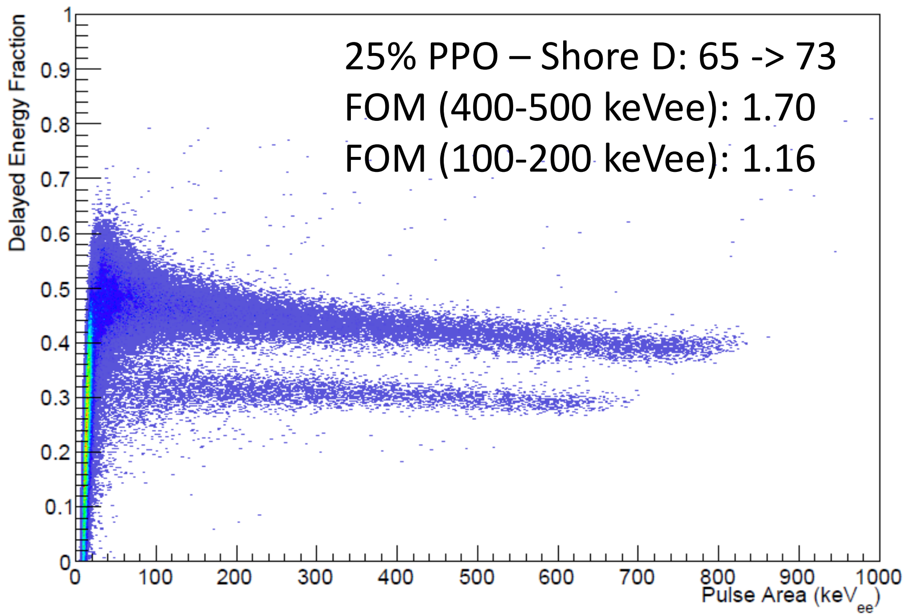
Commercial product EJ299 is claimed to be softer and harder to machine and polish. It also has a light yield app. 12% lower than regular plastic scintillator.

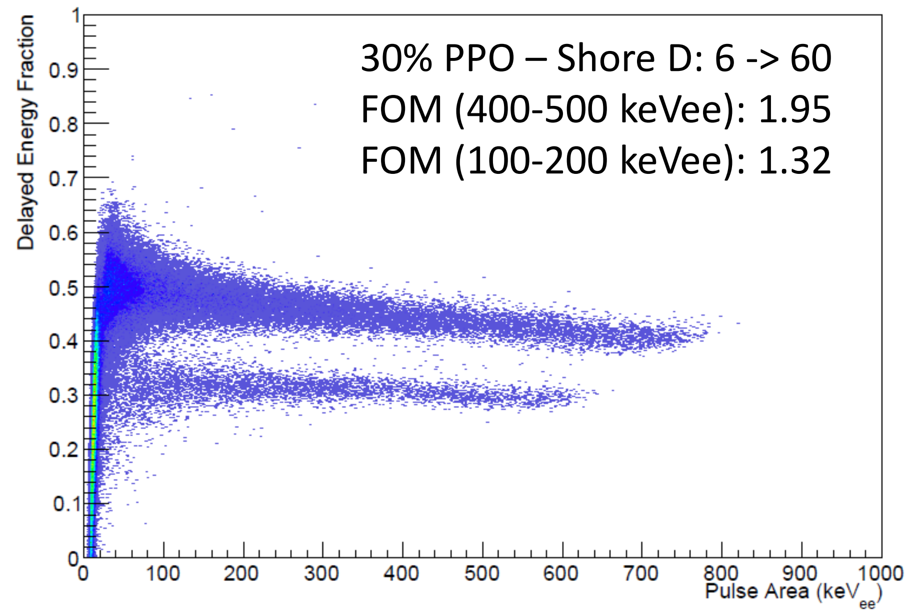
We developed a method to regain hardness (allowing machining) in formulations containing up to 30% PPO so far.

PPO overdoped and hardened plastic scintillator samples:
While untreated material can only be handsanded and gently polished, all treated samples can be machined on lathe, belt sander and machine polished.

Light Yield compared to BC-408:
Increase on average from 86% -> 92%;
some samples 100% of BC-408
Best 30% PPO Shore D: 73 (BC-408: 84)





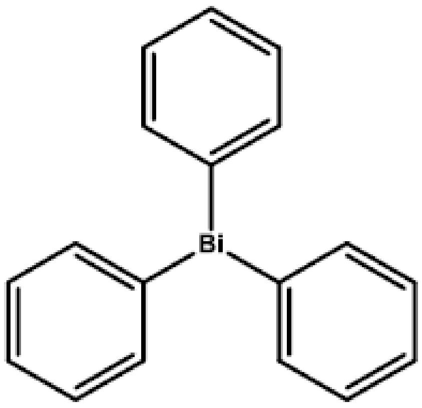


Conclusion and Outlook

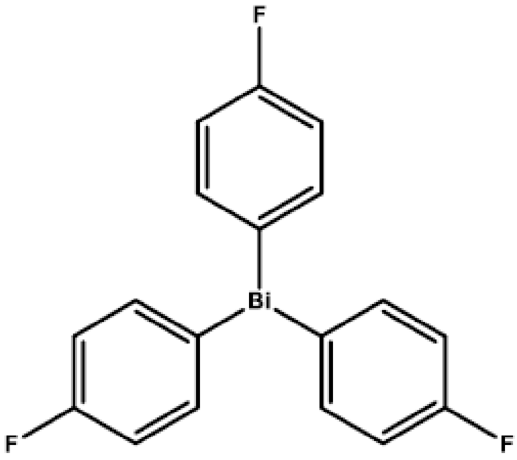
- Tested commercially available, inexpensive boron containing dopant for plastic scintillator;
- Developed synthesis route for enriched boron containing dopants and tested performance;
- Synthesized and tested several new fluorescent dopants (variants of p-terphenyl, fluorene and PPO) exhibiting PSD with increased solubility and mechanical strength;
- Developed new hardening method for PPO overdoped samples which preserves light yield and PSD.

The Future:

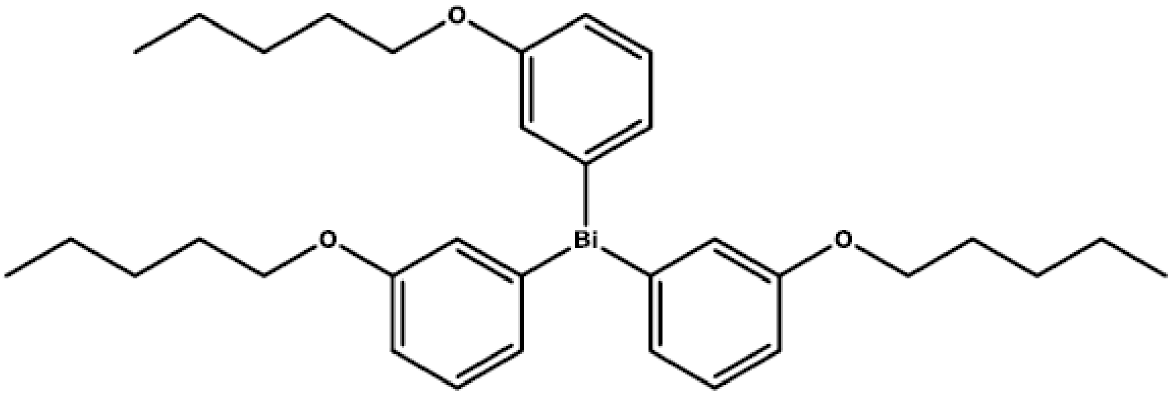
- Co-polymerization and cage concentration of fluorescent dopants;
- Photopolymerization;
- Bismuth containing dopants to enhance photo effect response;
- Triplet harvesting to achieve spectral shape discrimination (SSD).



triphenylbismuthane
Molecular Weight: 440.30



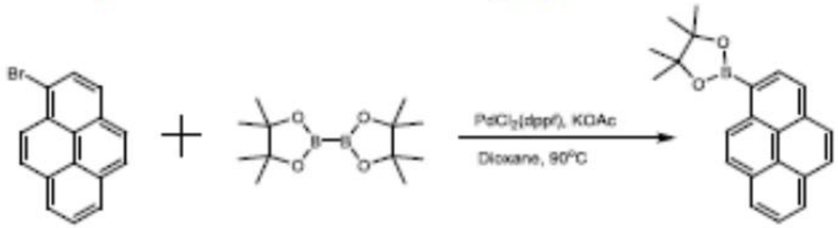
tris(4-fluorophenyl)bismuthane
Molecular Weight: 494.27



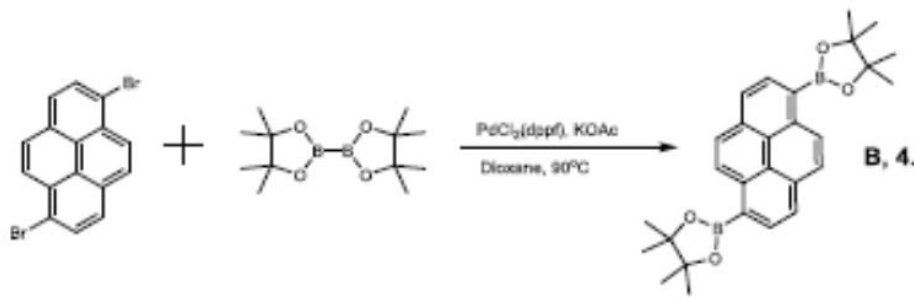
tris(3-(pentyloxy)phenyl)bismuthane
Molecular Weight: 698.70

Boron containing pyrene derivatives for thermal neutron detection-Synthesis

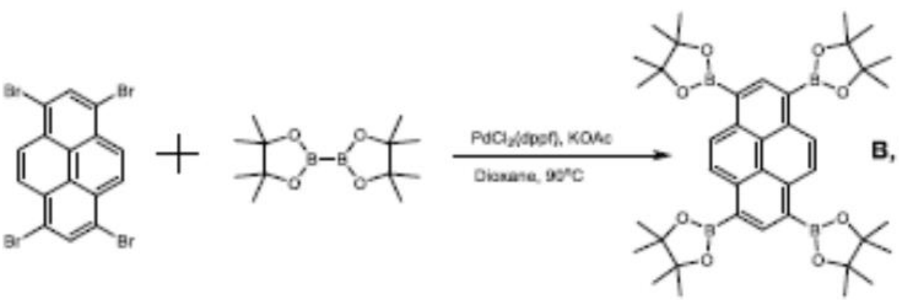
Aim: Synthesize boron containing pyrene derivatives



B, 3.29



B, 4.76



B, 6.12

	Trad yield (24hr)	Microwave (40min)
B, 3.29	75	68
B, 4.76	79	63
B, 6.12	87	85

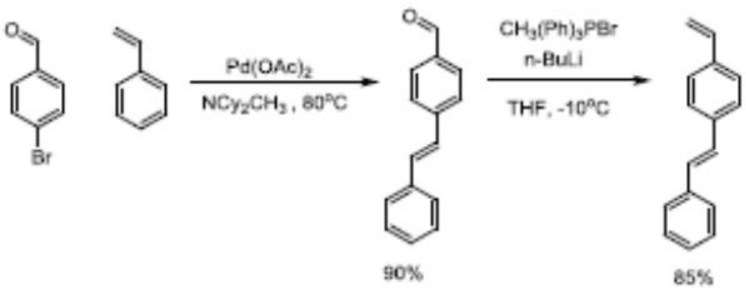
Borylated Pyrenes

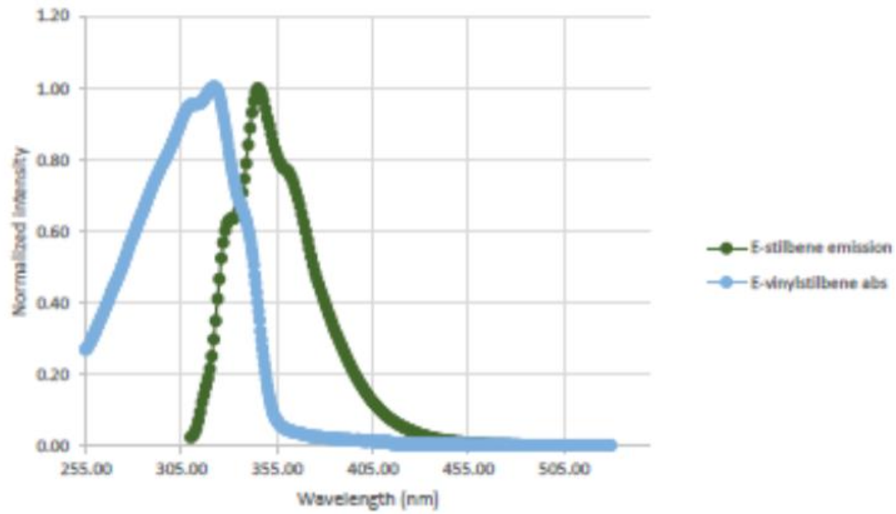
d) Versions of the above with reactive ligands that allow co-polymerization to improve FRET and enhance mechanical stability at high additive concentrations

Vinylfluorecent dopants-Synthesis and scale up challenges

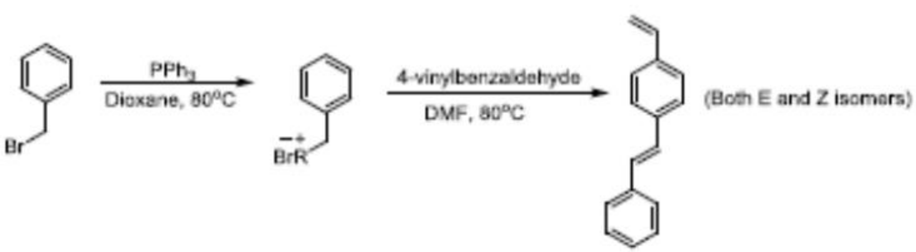
a. Vinylstilbene

i. Route-1





ii. Route-2



** Route-1 results in more trans (or E) isomer than route-2. This is important because only the E-isomer is fluorescent.

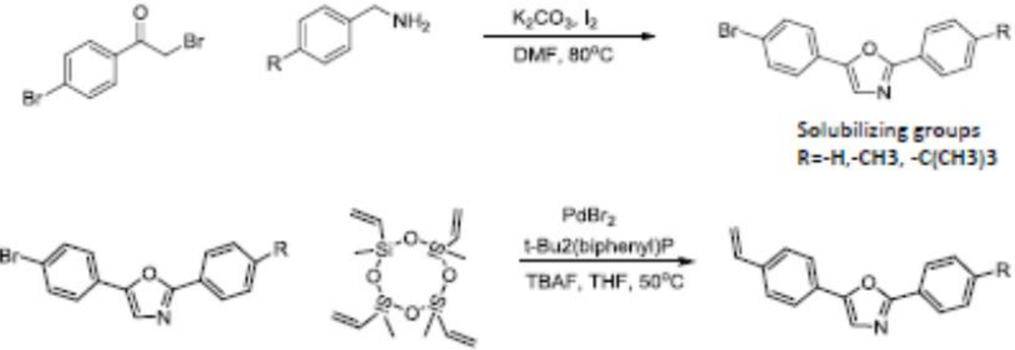
** Scaling-up these reactions is challenging!

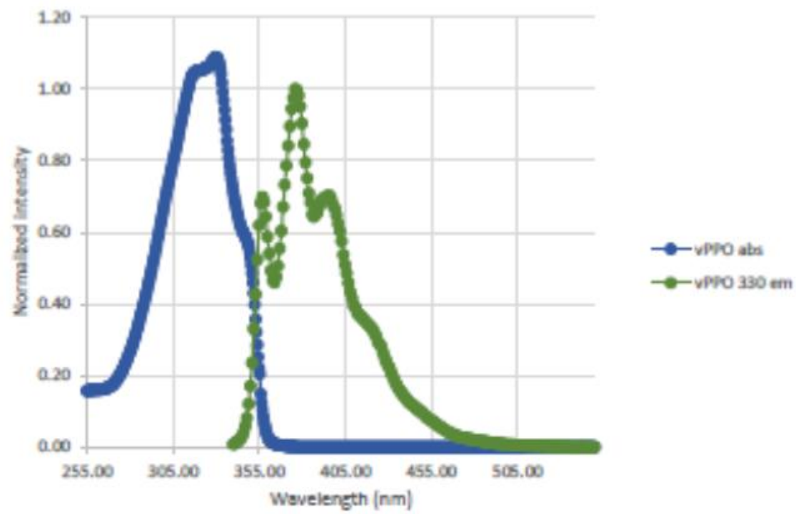
d) Versions of the above with reactive ligands that allow co-polymerization to improve FRET and enhance mechanical stability at high additive concentrations

Vinylfluorecent dopants-Synthesis and scale up challenges

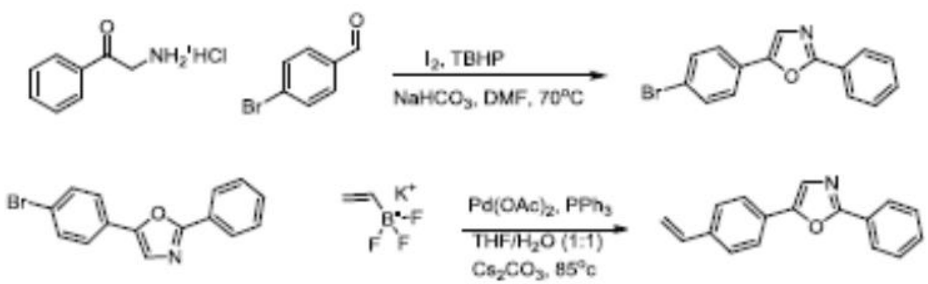
b. VinylPPO

i. Route-1





ii. Route-2



** Route-1 is better since we can put solubilizing groups on it.

** Scaling-up is challenging due to the difficulty of purifying precursors.

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