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National Nuclear Security Administration
Defense Nuclear Nonproliferation

Office of Defense Nuclear Nonproliferation Research & Development

Detection, Emergency Response, Safeguards, Radiological Source Replacement, Arms Control and Enabling Capabilities Program Review

WMS 2014

Advanced Plastic Scintillators

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SAND #: ______

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Motivation and Technical Approach

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Project Goals:

- Prepare fast-neutron discriminating plastic scintillators via ‘two-state’ emission
- Impose control over luminosity, spectral, and timing characteristics (eliminate TTA dependency)

Technical Approach and Challenges:

- Triplet-harvesting via spin-orbit coupling of heavy atom dopant
  - ➢ Delayed luminosity controlled by doping level and molecular properties
- Efficiency of triplet harvesting mechanism / energy transfer
- Cross-absorption and singlet quenching effects

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Comparison to Existing Materials

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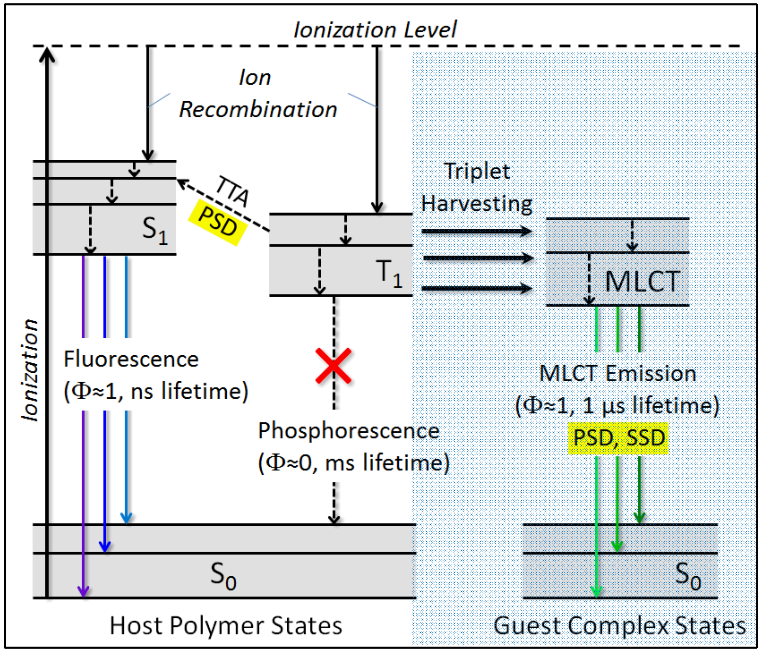

‘Single-State’
Scintillator

‘Two-State’ Scintillator

Property	Single-State Scint.	Two-State Scint.
Emission Type	Single	Dual
Kinetics	Power-law	Bi-Exponential
Tunable Pulse Shape?	Partial (prompt only)	Yes
Tunable Spectrum?	Partial (single emission)	Yes
Internal Q.E.	25% Maximum	>25%

Triplet harvesting mechanism:
Unimolecular, direct emission

Traditional Organic Scintillators:
Bimolecular, transport limited (dispersive)

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Case Study I: Ideal Energy Alignment

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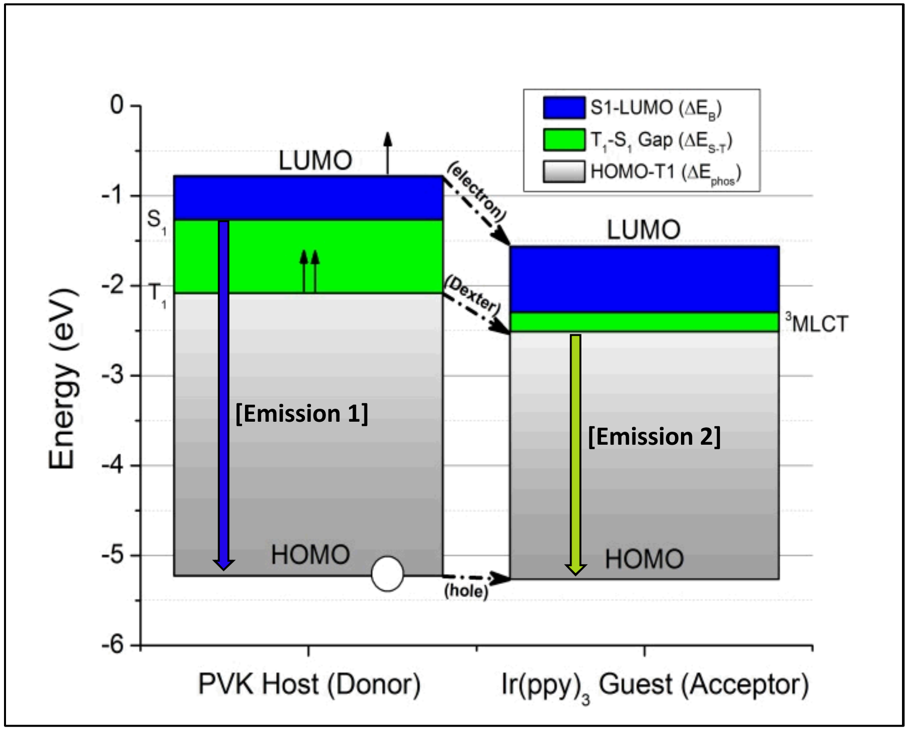

100% Internal Quantum Efficiency for Triplet Harvesting

Three Energy-Transfer Processes to Ir^{3+}:

1. Dexter Mechanism (T_1 states)
   - [↑ Maximize]
2. Direct Hole and Electron Transfer
   - [↑ Maximize]
3. Förster Mechanism (S_1 states)
   - [↓ Minimize]

Simplest (Ideal) Case:

1. Two Components:
   a. Polymer matrix with appropriate donor energy levels
   b. Iridium complex acceptor

Issue: Not all polymers possess the required donor energy levels

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Case Study II: Quenched Emission

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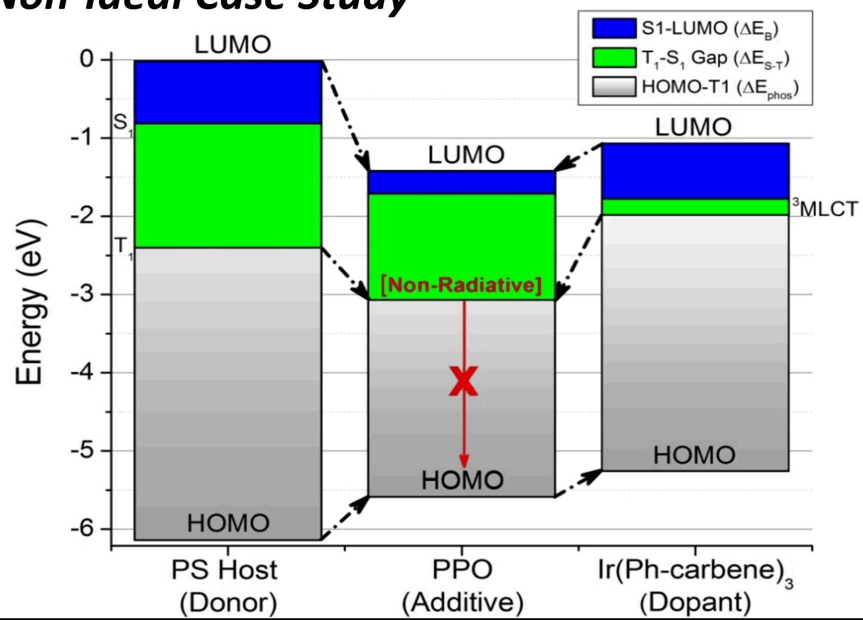
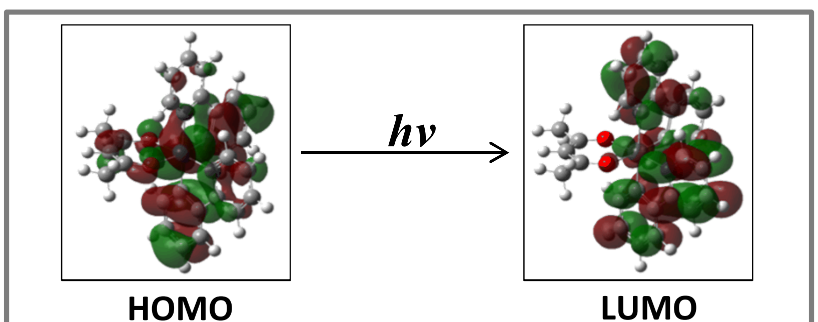
Non-Ideal Case Study



2% Quantum Efficiency (Quenched)



Goal:

- Employ polystyrene host matrix
  - Low-cost
  - Mechanically stable

Challenges:

- Energetic mismatch with Ir-dopant:
  - Deep HOMO
  - High LUMO
  - Lower energy T_1 state

Strategy:

- Select appropriate additive
- Tune energy levels of Ir-complex based on targeted chemical modification
  - ↑ LUMO via electron-withdrawing groups
  - ↓ HOMO via electron-donating groups

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Case Study III: Energy-Transfer Additive

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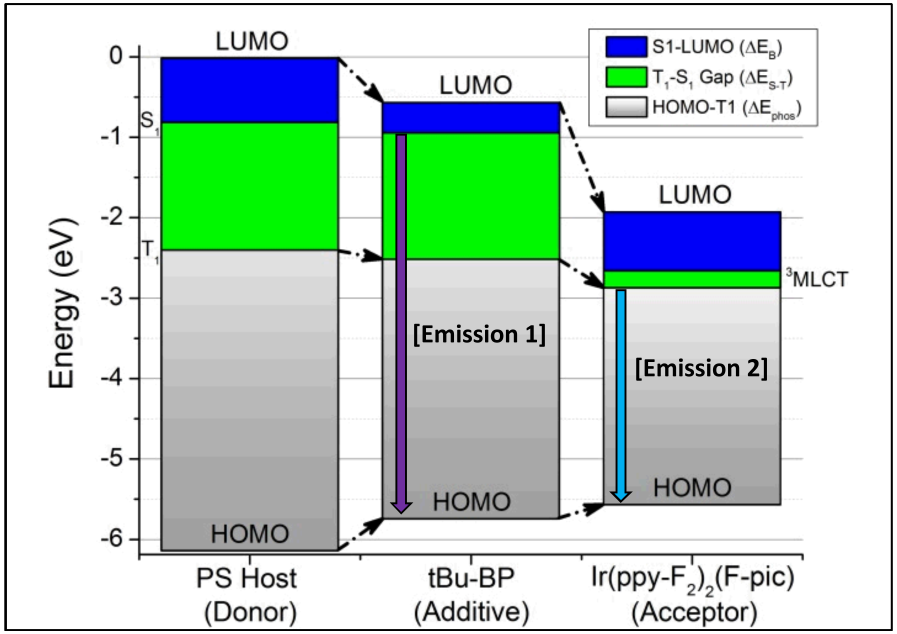
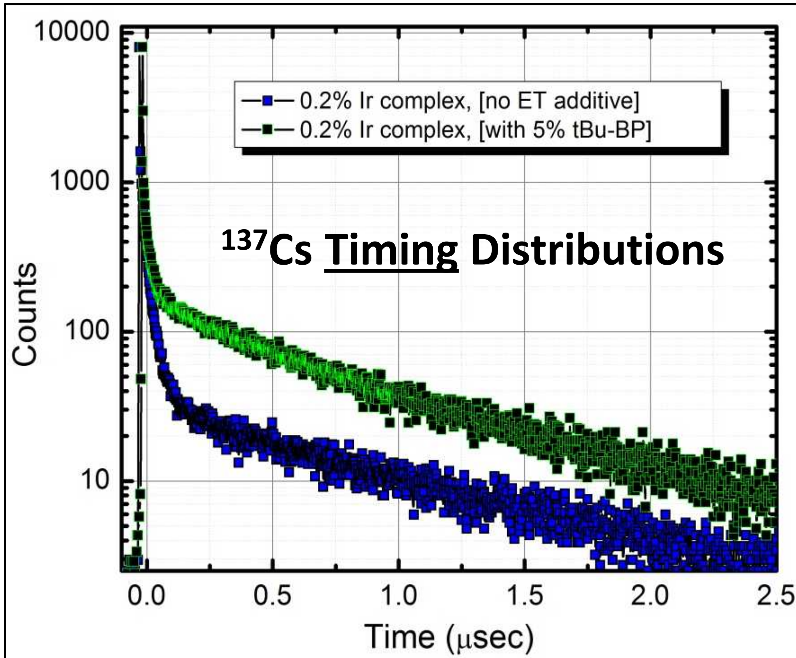




Improved Energy-Level Alignment:

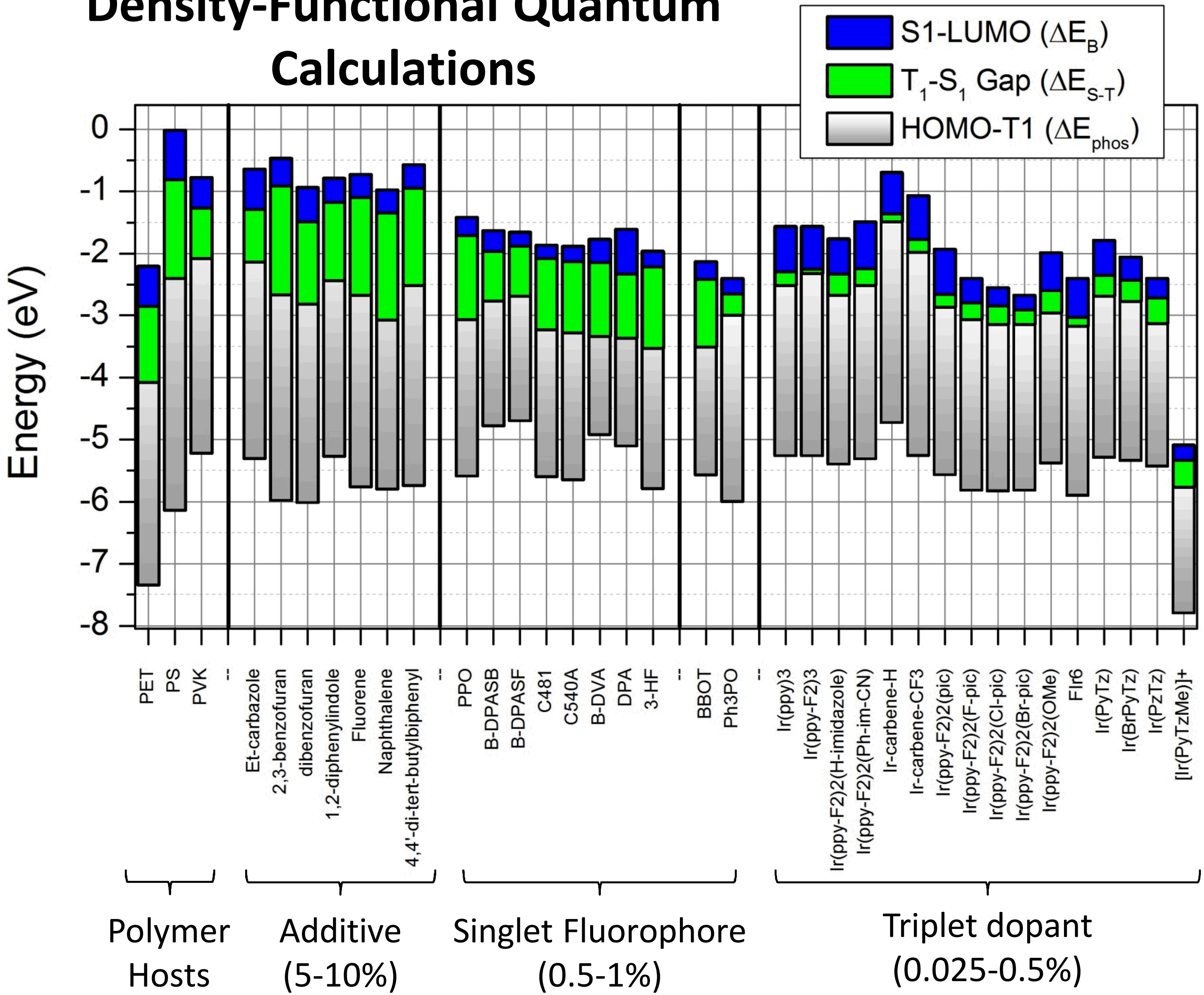
1. Additive to facilitate transport:
   - Intermediate HOMO and LUMO levels
   - Intermediate T_1 level

2. Iridium dopant:
   - Modulate levels through chemical substitution

Higher Efficiency Triplet Harvesting:

1. Additives decrease Ir^{3+} doping requirements:
   - Increased optical attenuation lengths
   - Reduced cost

Density-Functional Quantum Calculations



Pulse-Shape/Emission Engineering

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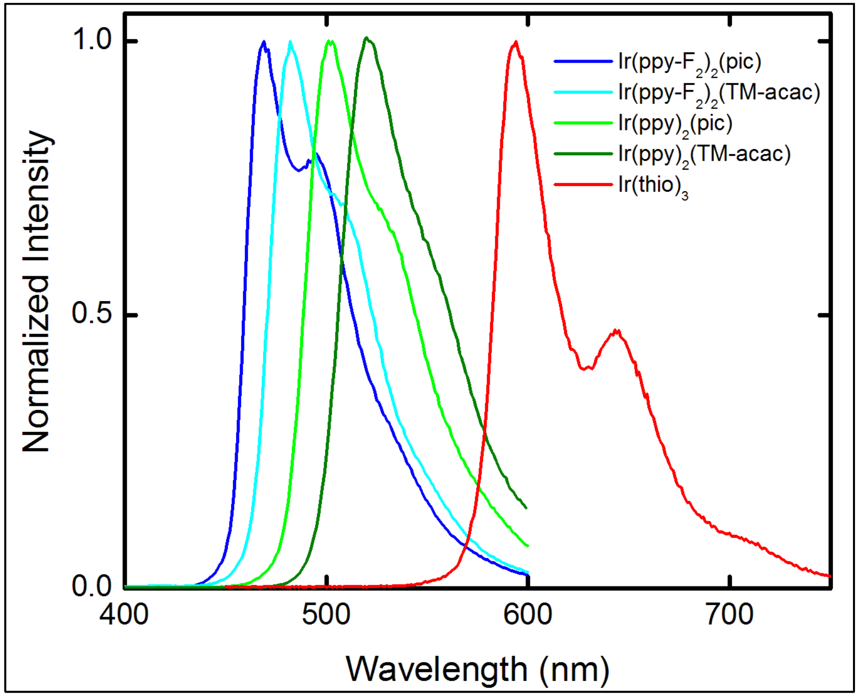
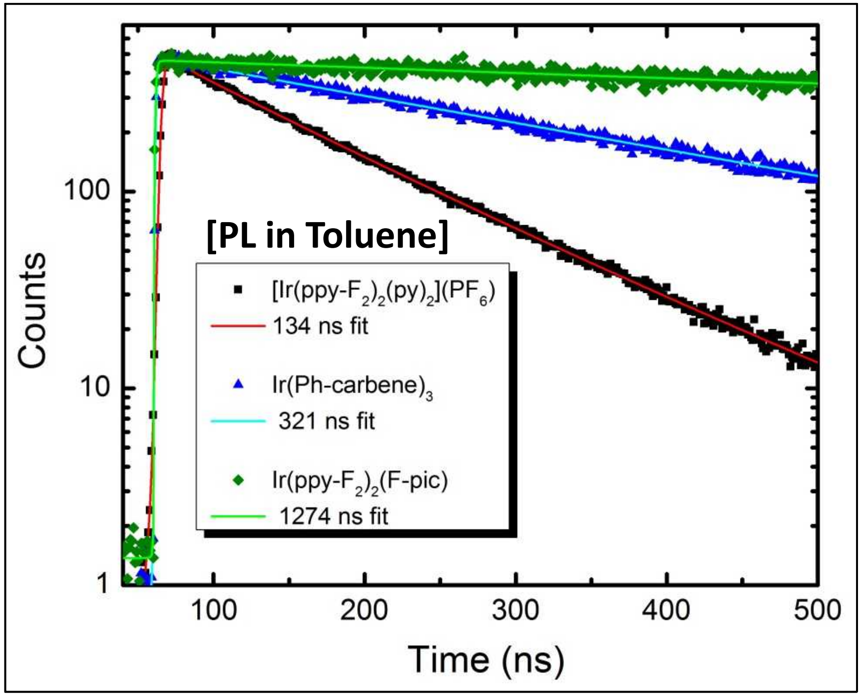
Emission Wavelength Tuning



Emission Lifetime Tuning



Emission Structure-Property Relationships:

- Blue-shift emission by electron-withdrawing groups
- Red-shift emission by electron-donating groups, and/or pi-conjugation

Lifetime Structure-Property Relationships:

- Modify emission lifetime by controlling degree of metal-ligand charge-transfer in triplet state
- HOMO/LUMO wavefunctions

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Conc. Dependence of Scintillation Properties

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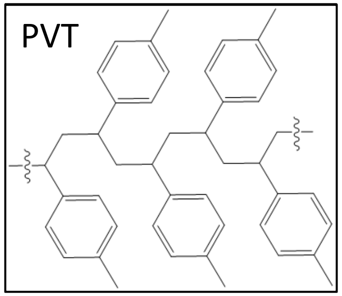
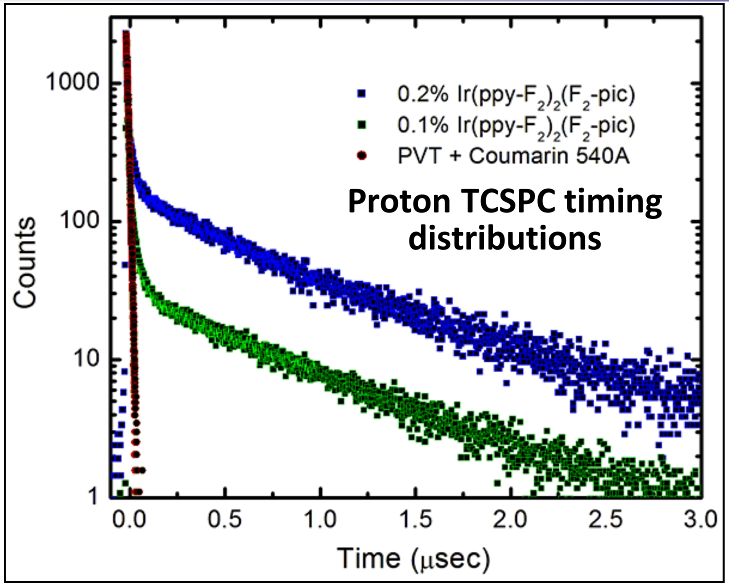
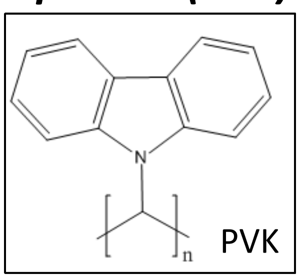
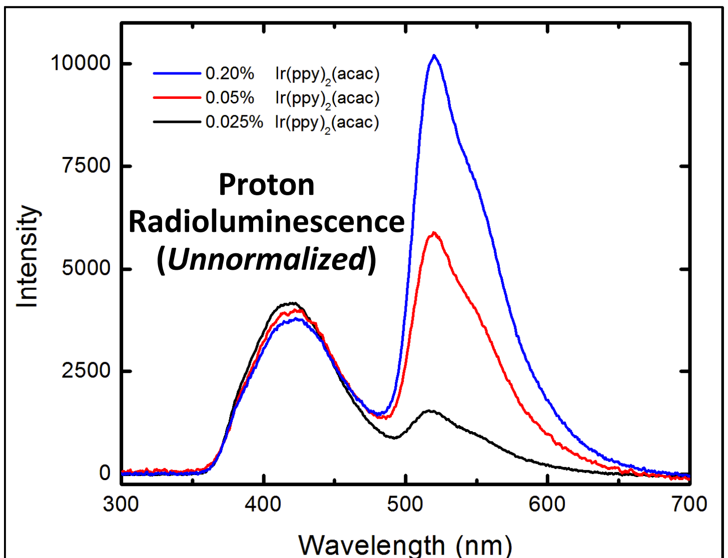
Timing (PSD)





Spectral (SSD)



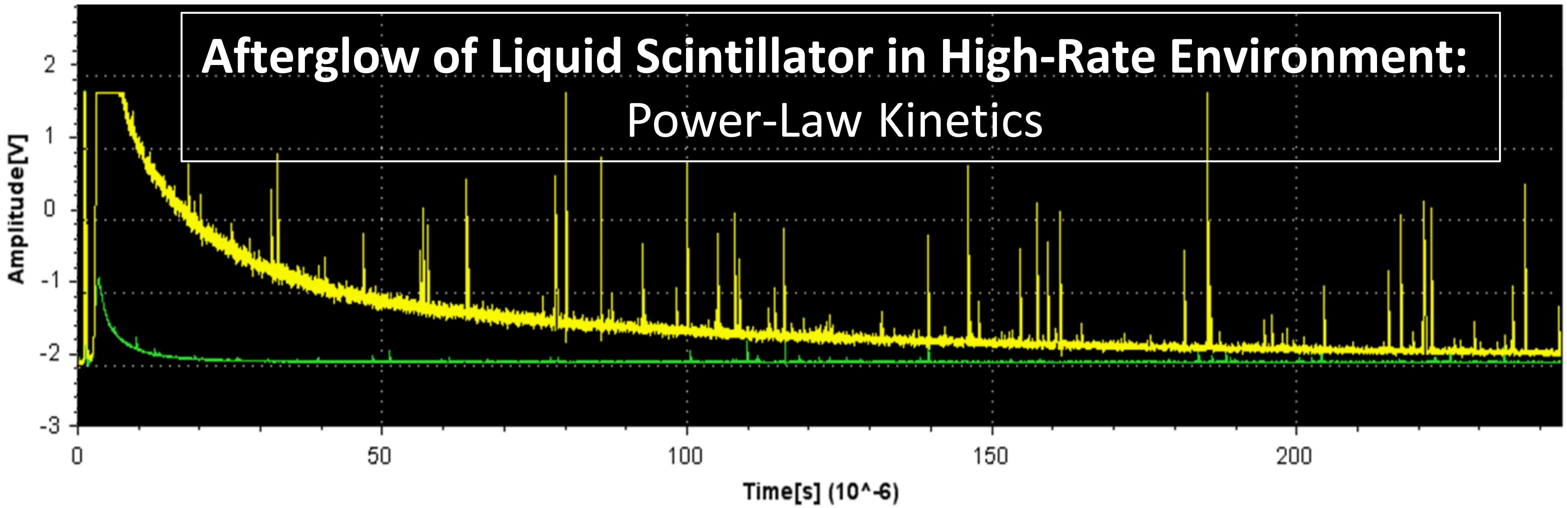


- Delayed luminosity tuned via:
  - Doping level
  - Chemical properties of Ir^{3+} complexes
- TD-DFT to predict host and guest properties
- Additive effect of triplet luminescence at modest doping levels
- Low Ir^{3+} concentrations required:
  (0.1% ≈ 300 ppm Ir^{3+})

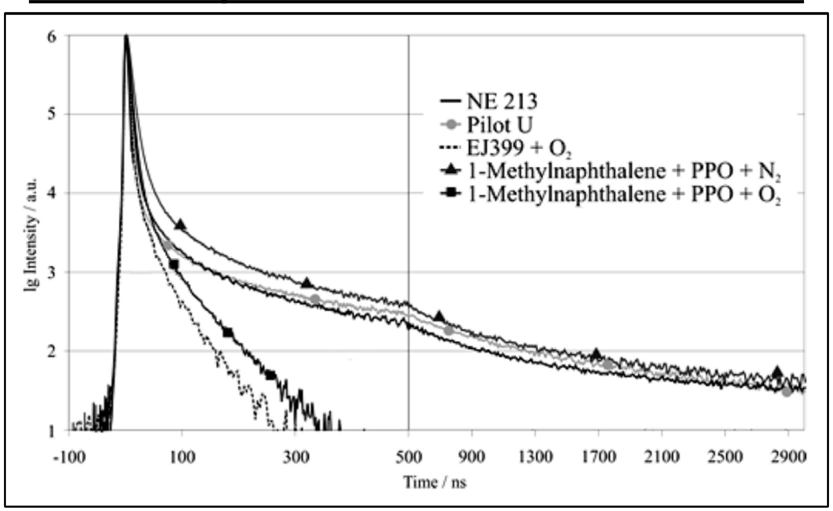
Two-state scintillator affords direct control over pulse shapes <u>and</u> spectra

Comparison of Decay Kinetics

Afterglow of Liquid Scintillator in High-Rate Environment:
Power-Law Kinetics

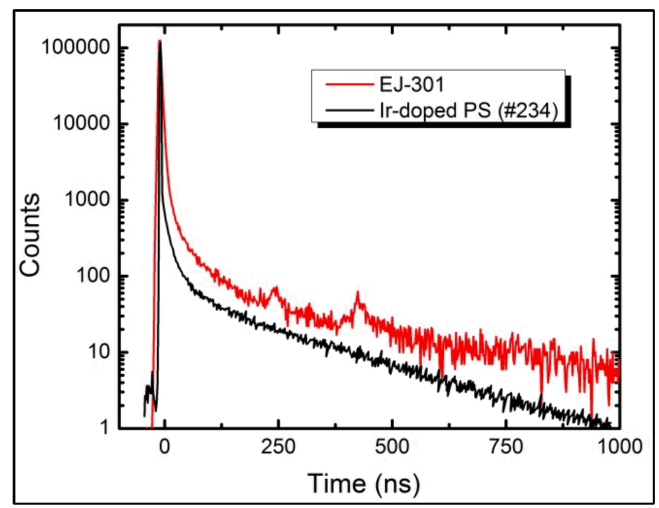


Pulse Shapes of Traditional Scintillators



T. Szczesniak et al. *IEEE Trans. Nucl. Sci*. **2010**, 57, 3846.

Exponential Decay of Two-State Scint.



Scintillation Light Yield Comparison

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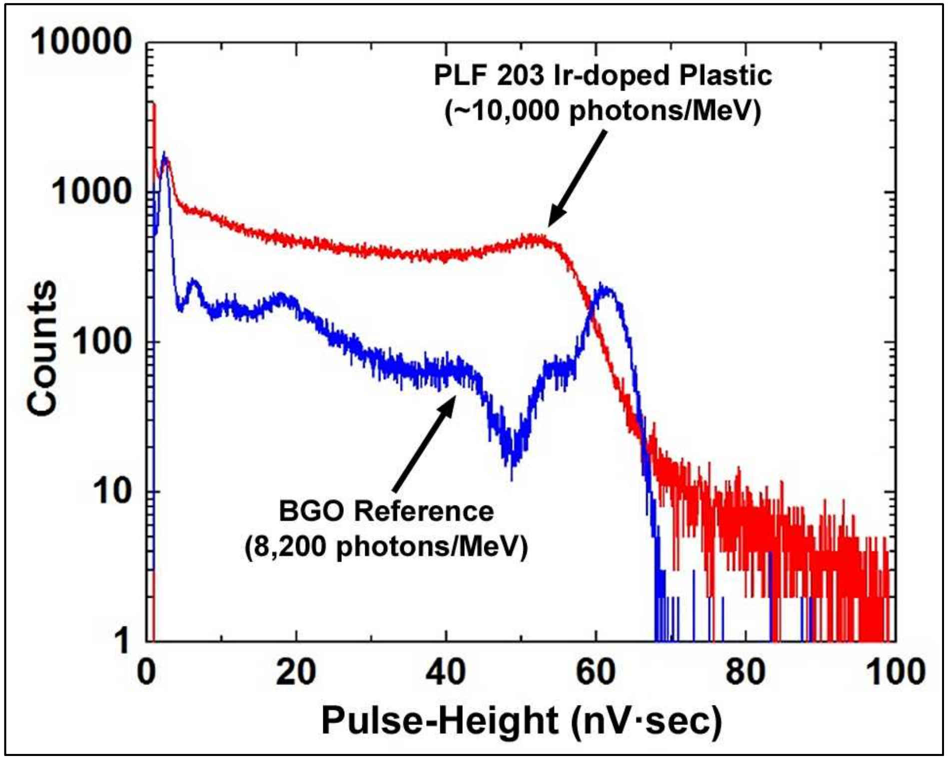
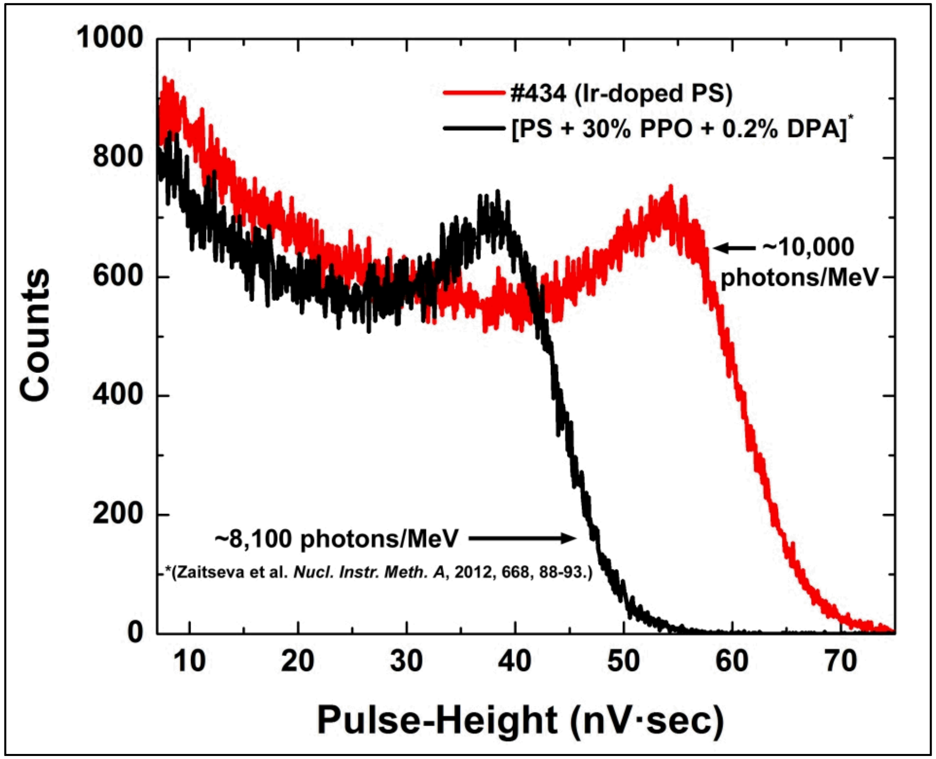
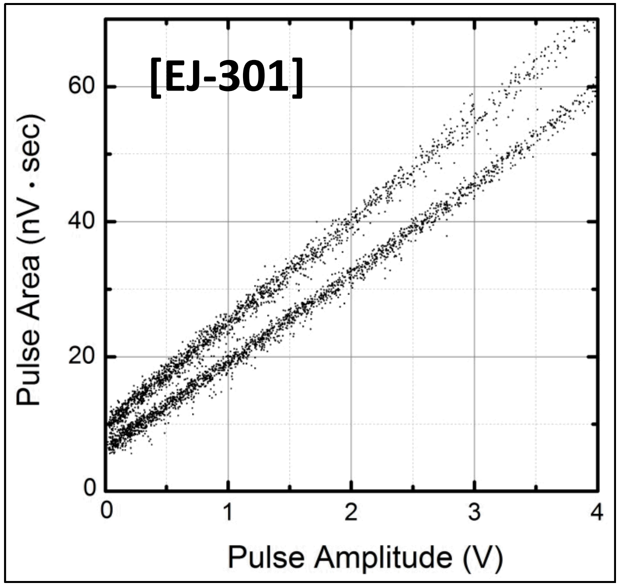
^{137}Cs Light Yield Comparison to BGO

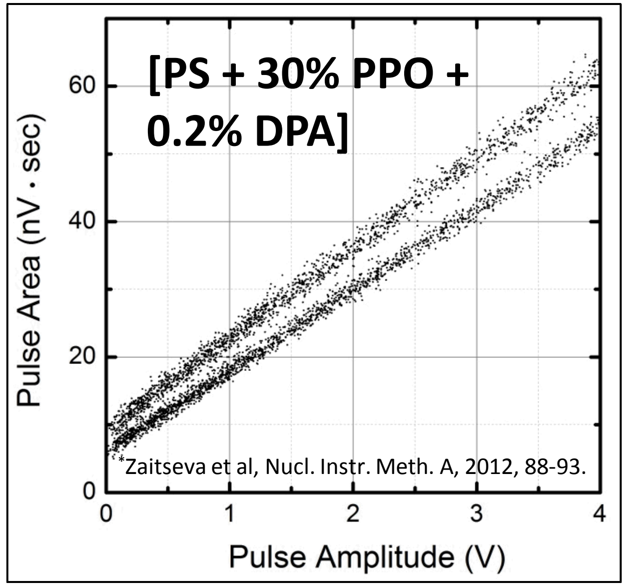


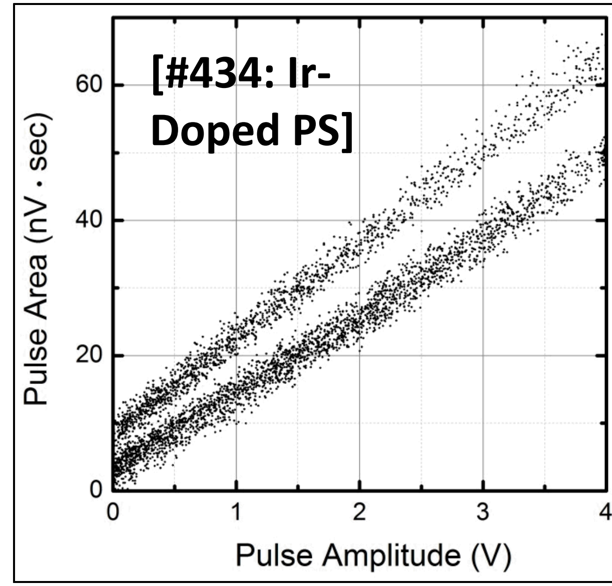
^{137}Cs Light Yield Comparison to PSD Plastic (30% PPO)



PSD Results







[EJ-301]

- 12,000 photons/MeV
- λ_{max} = 425 nm
- **PSD-FOM (AmBe, >400 keVee) = 2.1**

*[PSD-FOM @ 480 keV = 3.21]

[PS + 30% PPO + 0.2% DPA]

- 8,100 photons/MeV
- λ_{max} = 440 nm
- **PSD-FOM (AmBe, >400 keVee) = 1.6**

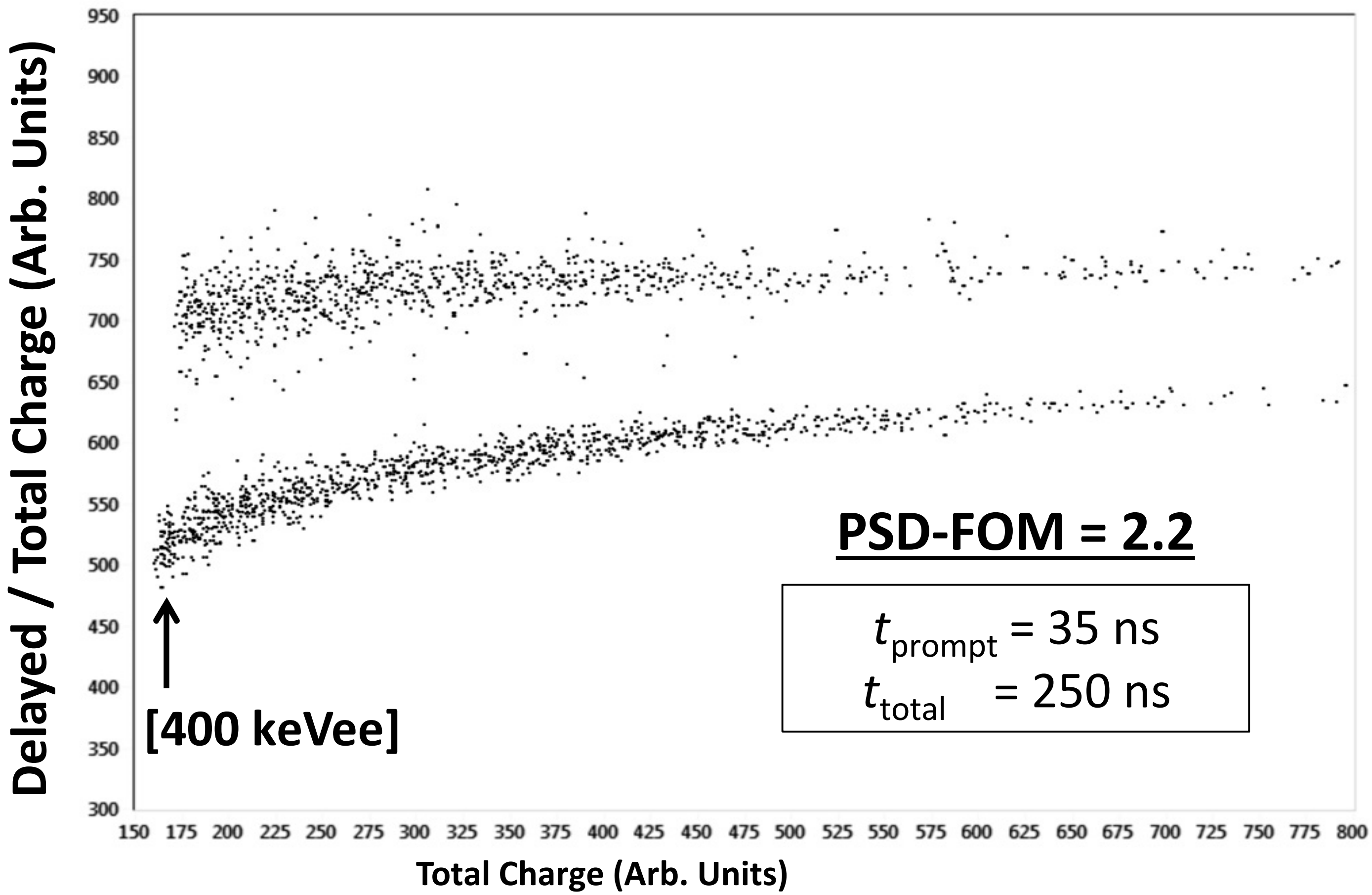
*[PSD-FOM @ 480 keV = 3.31]

[#434: Ir-Doped PS]

- 10,000 photons/MeV
- λ_{max} = 475 nm
- **PSD-FOM (AmBe, >400 keVee) = 1.7**

PSD Results II

Charge-Comparison PSD



PSD-FOM = 2.2

t_{prompt} = 35 ns
t_{total} = 250 ns

Sumary and Conclusions

Summary of Work to Date:

- Exerted synthetic control over the pulse shapes and spectra in the first "two-state scintillators"
- Utilized triplet-harvesting mechanism for scintillation light generation
  - Improved the triplet-harvesting efficiency by balancing donor/acceptor energy levels
- Characterized efficient n/γ particle discrimination via timing (PSD) and spectral (SSD) methods

Ongoing Goals and Challenges:

- High LUMO for Polystyrene: Other polymer hosts?
  - Aromatic polycarbonates via extrusion
- Limited number of commercially available singlet fluorophores (λ_{em}=450-500 nm) that exhibit efficient FRET w/ existing matrices
  - Reduced overall scintillation light yield

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