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# Novel Particle Detector Materials Based on Zinc-Stilbene Metal Organic Frameworks

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# Direct detection of fission-spectrum neutrons is inefficient using existing sensor materials

- Fission neutrons:
  - Sources: $^{235}U$, $^{241}Pu$
  - Spectra peak < 1 MeV (Maxwell dist.)

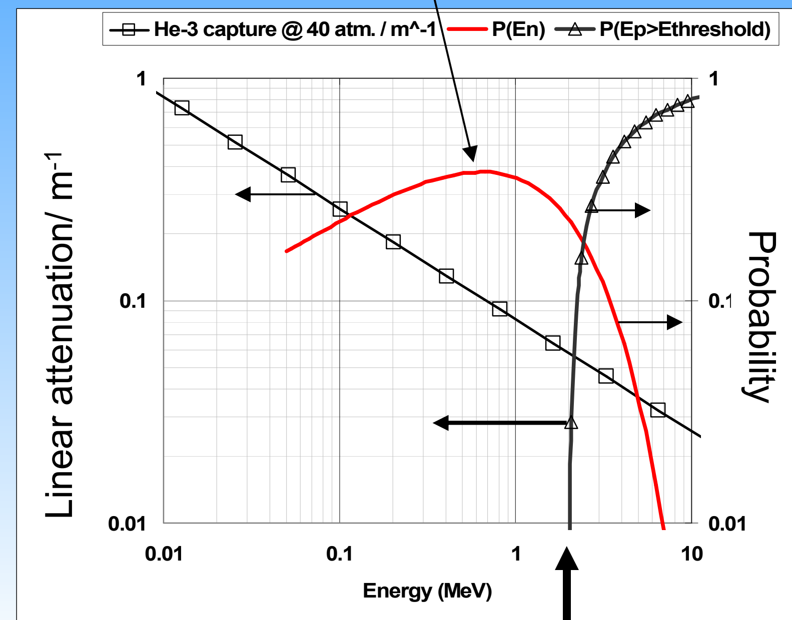
- Applications:
  - Detecting nuclear proliferation
  - Long term monitoring
  - Cargo screening
  - Neutron radiography

- Detection methods:

  <u>$^{3}$He capture **(*Moderator Required*)**</u>
  - Efficient only at $E_n$ < 0.01 MeV
  - Direct detection impractical (> 1m, 40 atm)
  - → Particle direction and energy are lost

  <u>Liquid organic scintillators **(*High Threshold*)**</u>
  - Low detection efficiency at $E_n$ < 10 MeV
  - Combustible
  - Toxic solvents

Fission neutron spectrum of $^{235}U$ stimulated by thermal n




Gamma discrimination threshold

*New scintillator materials are needed to enable practical detection of these particles*

# Scintillation light is partially quenched at high dE/dx

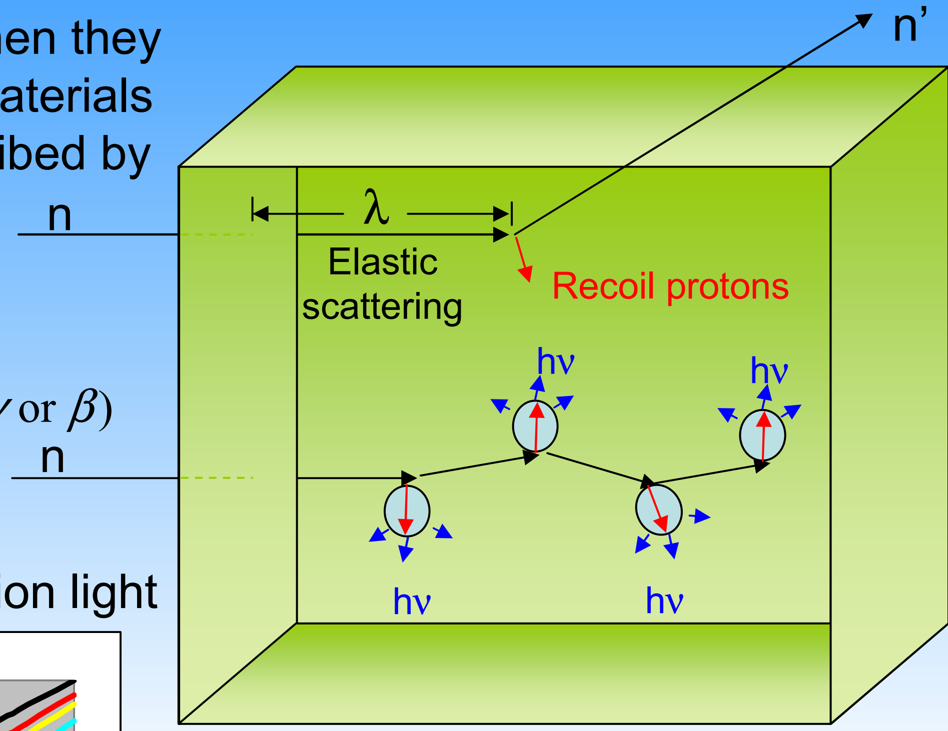
- Neutrons create ionizing protons when they elastically scatter in hydrogenous materials
- Light output from ion tracks is described by Birks' equation:

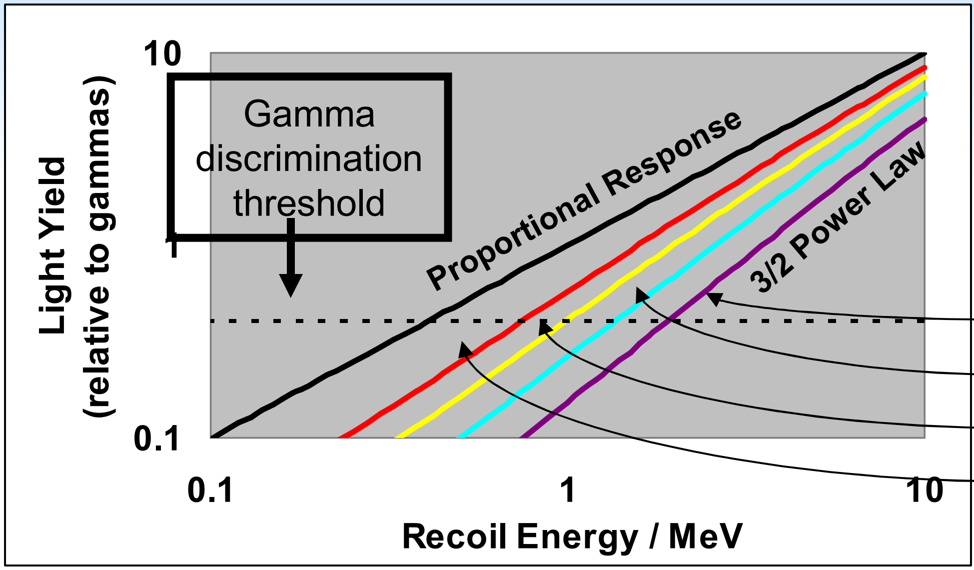
$$L(E) = S\int_0^E \frac{dE}{1 + kB(dE/dx)}$$

$$L(E) = SE \ \text{ in the limit of low } dE/dx \quad (\gamma \text{ or } \beta)$$

  – dE/dx ∝ density

➡ Predicts decreasing density will decrease quenching of scintillation light




**Commercial Scintillator EJ301:**
**Birks eq. fits observed *L(E)* ~ $E^{3/2}$**
**Density 0.88 g/cm³**

**Density 0.44 g/cm³**
**Density 0.22 g/cm³**
**Density 0.11 g/cm³**

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# dE/dx Scintillation Quenching

*A case of static fluorescence quenching*

Fluorescence quenching is modeled by:

$$[M*]+[Q]\longleftrightarrow[MQ*]$$

Where

$[M*]=$ Fluorescent state concentration

$[Q]=$ Quenching species

$[MQ*]=$ Nonradiative complex

$$K=\frac{[MQ*]}{[M*][Q]}\longrightarrow[MQ*]=K[Q][M*]$$

$$[M^*_{total}]=[M^*]+[MQ^*]$$

$$[M^*_{total}]=[M*]+K[Q][M*]$$

$$\boxed{\frac{[M^*_{total}]}{[M*]}=\frac{L_0}{L}=1+K[Q]}$$

Stern-Volmer equation

Along a particle track we assume:

$[M*]\propto$ Light yield / unit track length

$[M^*_{total}],[Q]\propto$ Energy / unit track length

$$[M*]\propto(dL/dx)$$

$$[Q]\propto(dE/dx)$$

$$[M^*_{total}]\propto(dE/dx)$$

*Substituting into Stern-Volmer*

$$S\frac{(dE/dx)}{(dL/dx)}=1+kB(dE/dx)$$

$$\boxed{\frac{dL}{dx}=S\frac{(dE/dx)}{1+kB(dE/dx)}}$$

Birks' equation

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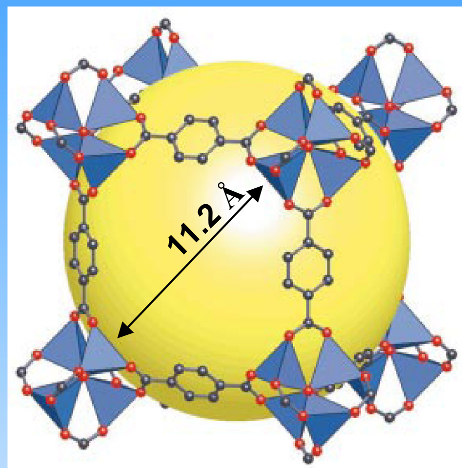
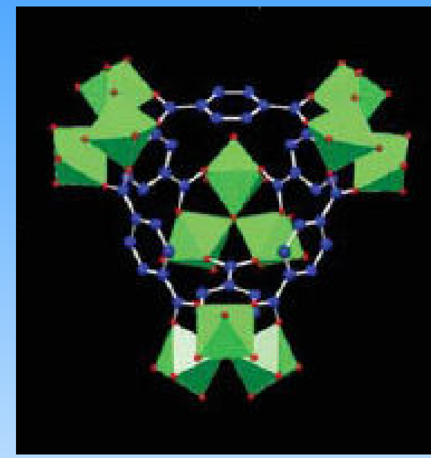
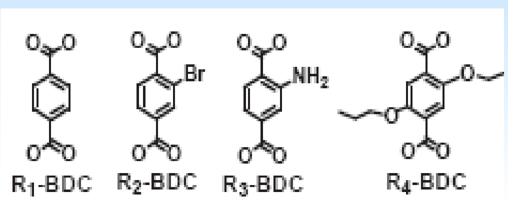
# Nanoporous coordination polymers provide an opportunity for tunable scintillator density

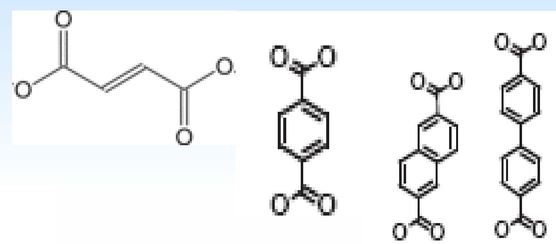


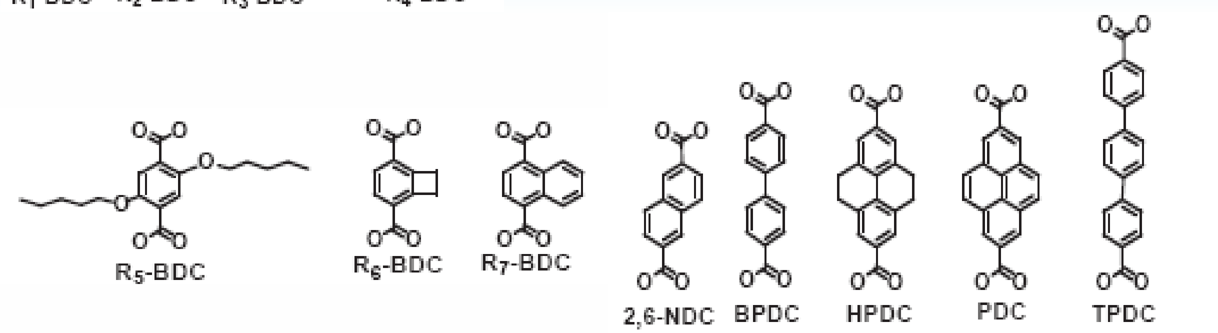

**IRMOF-1:** Rigid, open framework with tunable pore size, chemistry (Yaghi et al., *Science* 2002)



**Cr and Fe MIL:** 6000 $m^2/g$ surface area *(Férey et al., Science 2005)*



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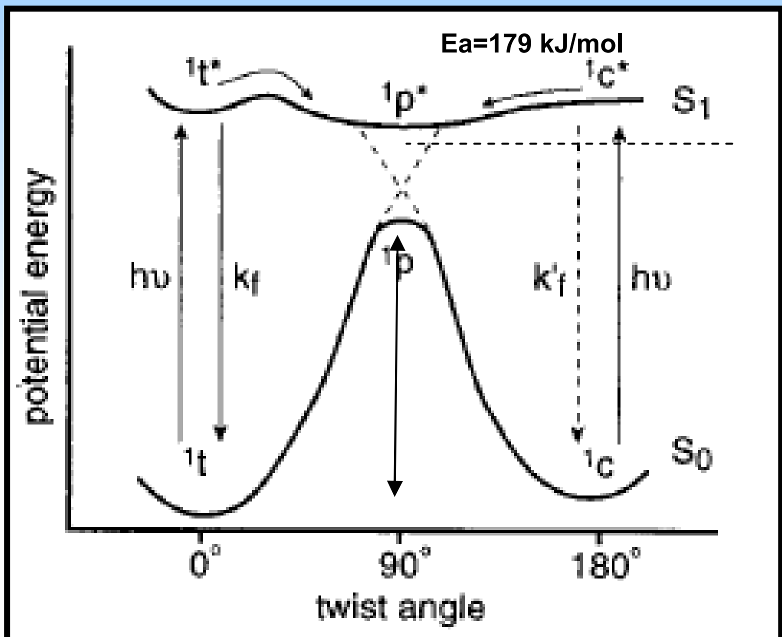
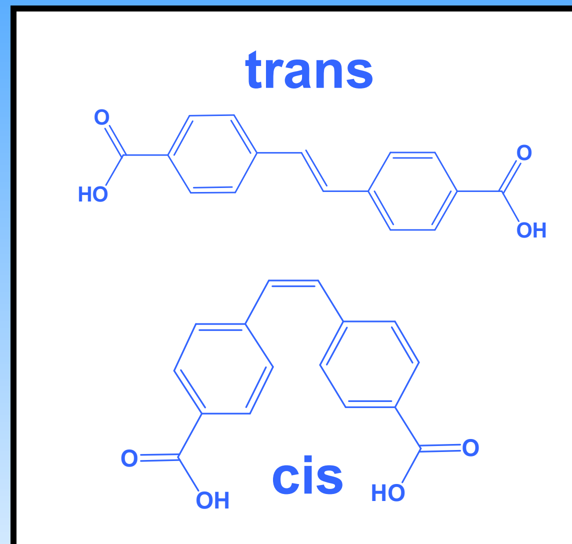
# Fluorescent MOFs: entry point for creating scintillators based on coordination polymers

## Stilbene: a fluorescent linker for MOF synthesis

**Potential energy surface**




A. Simeonov, *Science*, 2000




<u>Stilbene linker offers</u>:

- Potential for low density frameworks
- Constrained linker conformation

→ High fluorescence quantum efficiency

- Zn-based compounds: transparent

→ Low self adsorption

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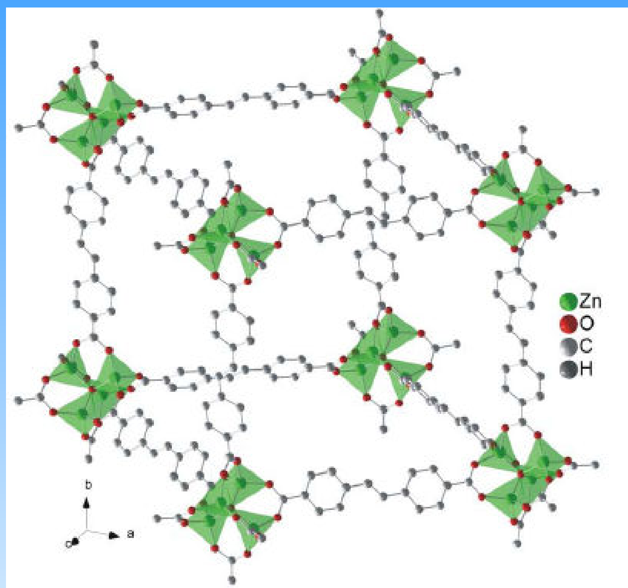
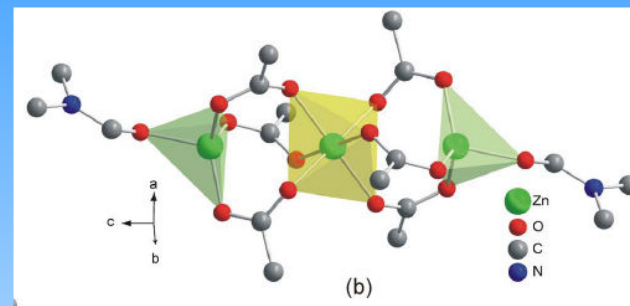
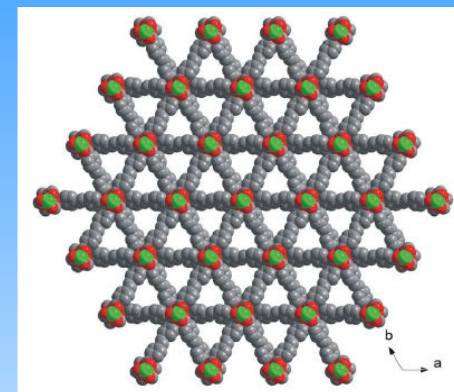
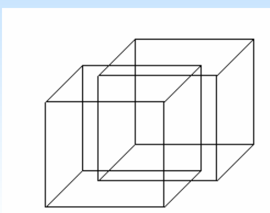
# New stilbene MOFs: multiple structures result from the same starting materials under different synthetic conditions



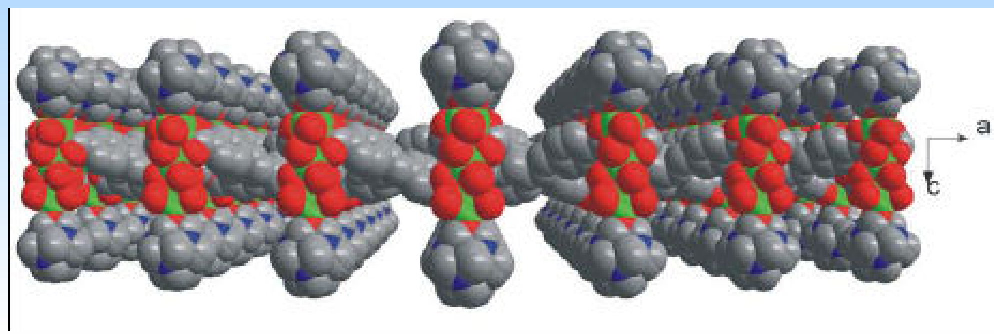




Formula unit: $ZnL_3(DMF)_2$
L = 4,4'-stilbenedicarboxylic acid



Formula unit: $Zn_4OL_3$




<u>"3D" cubic structure</u>

- DEF, 105 °C/ 16 hours
- Interpenetrated, IRMOF-type structure
- Open porosity
- Surface area = 580 $m^2/g$

<u>"2D" hexagonal structure</u>

- DMF, 70 °C/16 hrs; 85 °C/ 4 hrs
- Dense material

Bauer et al., *J. Amer. Chem. Soc.*, in press, 2007.

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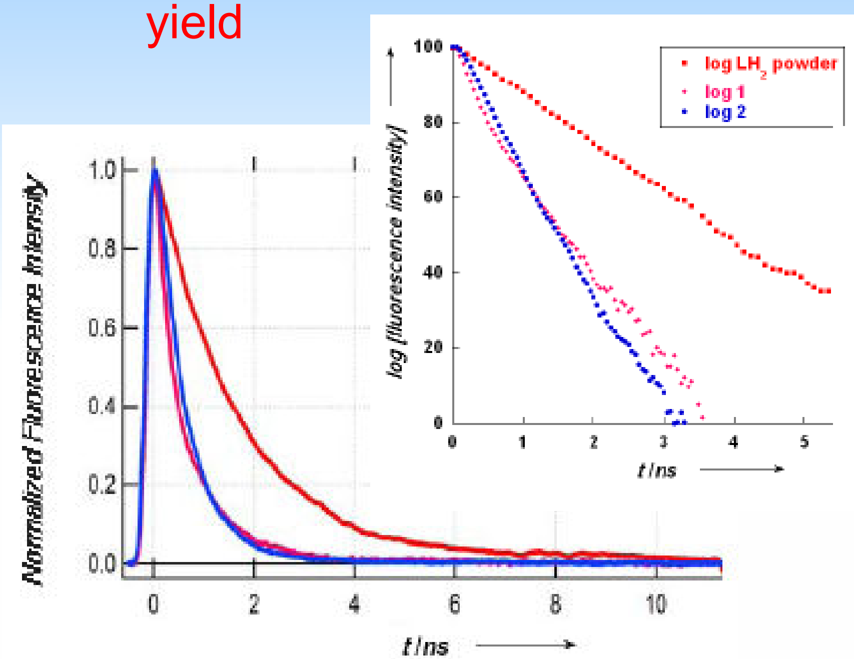
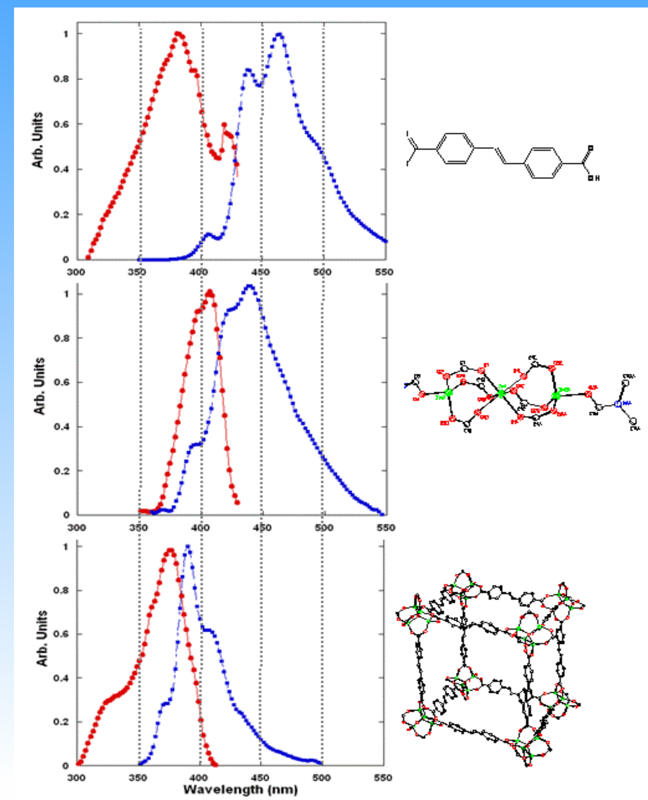
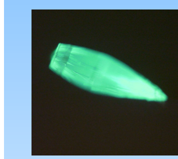
# Constrained orientation of stilbene group in MOF increases fluorescence light yield

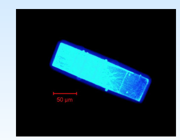
- **Increased fluorescence lifetimes**
  - Stilbene in solution: $\tau_1 < 100$ ps
  - $LH_2$: $\tau_1 = 0.73$ ns, $\tau_2 = 2.49$ ns
  - 2D MOF: $\tau_1 = 0.2$ ns, $\tau_2 = 0.95$ ns
  - 3D MOF: $\tau = 0.50$ ns
  - ☞ Implies higher quantum yields
  - ☞ Potential for high scintillation light yield




Decreasing linker interactions





**Single crystal fluorescence and excitation spectra**

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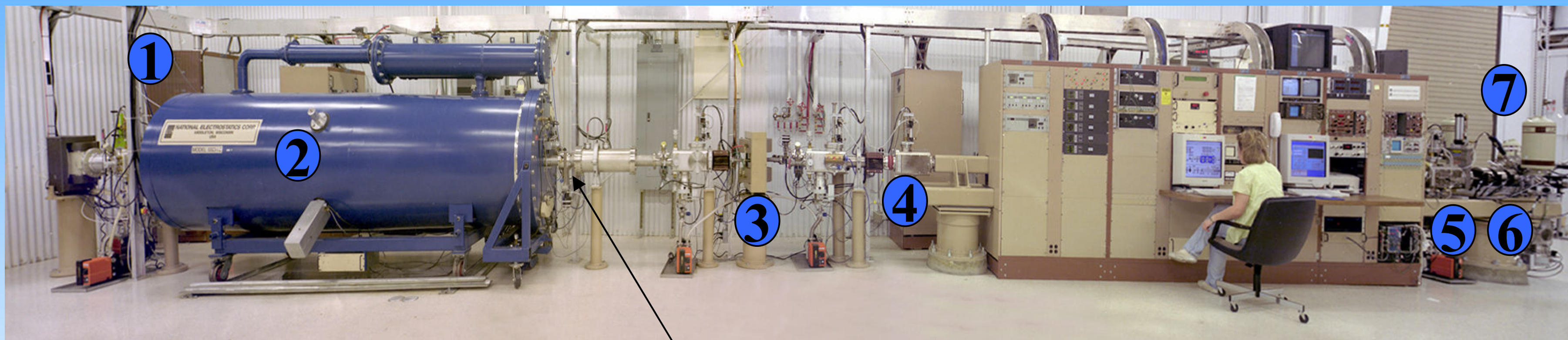
# The interaction of MOF compounds with charged particles can be probed using a nuclear microprobe

*An accelerator produces charged particles that can be focused and scanned across the sample with high spatial resolution*




**1 Ion Source ($H^+$ or $O^{3+}$)**
**2 Terminal 1.5 million volts**
**3 Bending magnet**
**4 Object slits (1 - 850 µm)**
**5 Image slits**
**6 Magnetic Lens**
**7 Sample Chamber**

Ion beam at this point:
$H^+$ accelerated to 3 MeV
or $O^{3+}$ accelerated to 6 MeV

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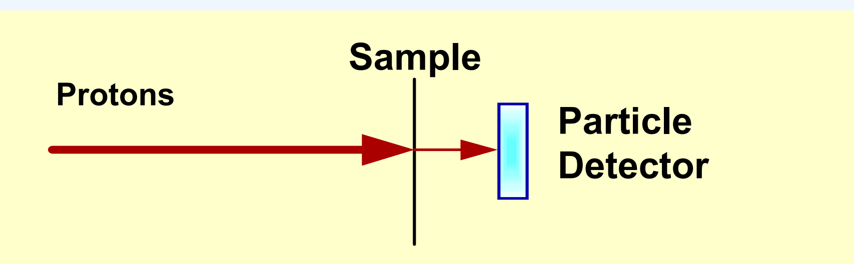
# Microprobe diagnostic tools enable quantitative measurement of light output by MOFs

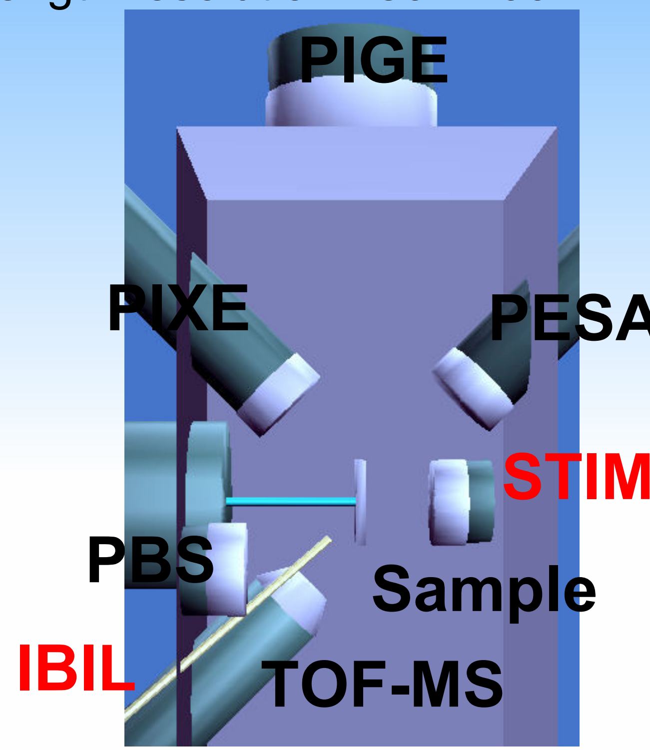
**Scanning Transmission Ion Microscopy (STIM)**

- Energy loss through sample
- Dependent on mass
- Minimal dependence on composition
- Forms images of the sample
- Max. spatial resolution = 0.5 µm
- Use to measure crystal size, thickness




**Ion Beam Induced Luminescence (IBIL)**

- Allows the differentiation of minerals or organics with similar elemental composition
- 1 nm wavelength resolution 180-1100 nm

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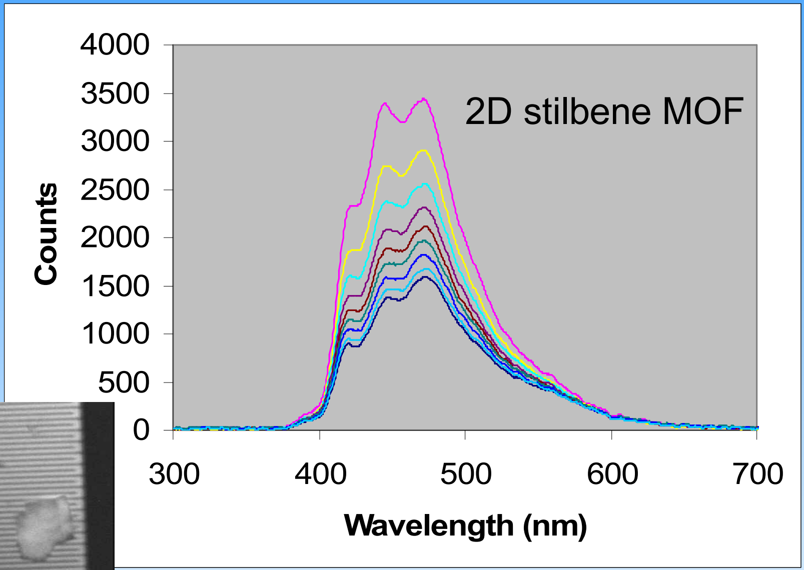
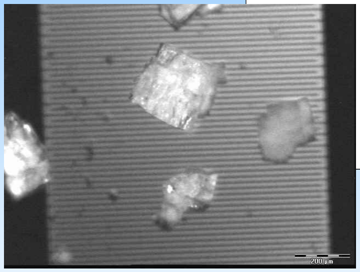
# IBIL spectra demonstrate that stilbene MOFs emit light when they interact with protons

- Samples mounted on gold foils, Mylar, or TEM grids
- SEM obtained before and after to verify integrity of crystals
- Beam energy: 3 MeV
- Beam dose rate: ~5 Mrad/s
- Data obtained for
  - Anthracene (standard)
  - 2d MOF
  - 3d MOF
- Note: IRMOF-1 exhibits no IBIL



**First reported demonstration of MOF radiation sensitivity: Proton-induced fluorescence.**

| SAMPLE | Mass (mg) | Dose rate J/kg/s | Cts/J peak ch | % Anthracene |
|---|---|---|---|---|
| Anthracene | 0.4 | 1.20E+04 | 1.13E+09 | 100% |
| 2D MOF | 0.38 | 9.33E+03 | 2.49E+08 | 22% |
| 3D MOF 1 | 0.22 | 1.00E+04 | 9.62E+07 | 9% |
| 3D MOF 2 | 0.49 | 9.33E+03 | 6.62E+07 | 6% |
| Stilbene | | | | 50% |
| BC422Q (commercial organic scintillator) | | | | 11% |

Comparable to commercial scintillators

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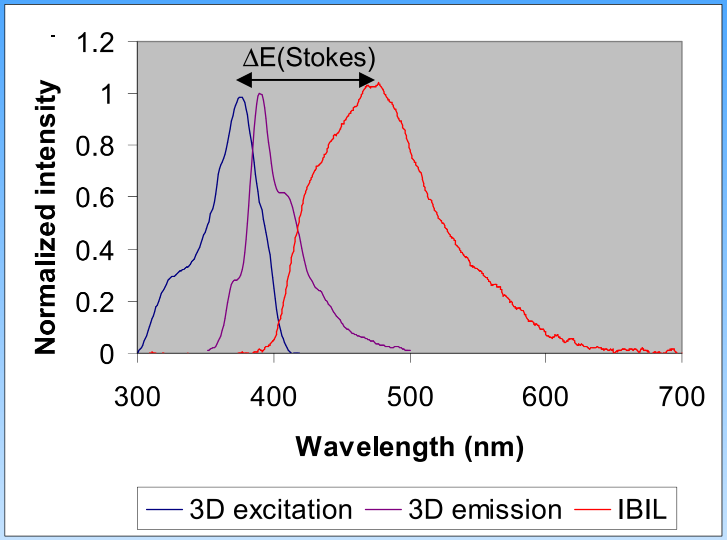
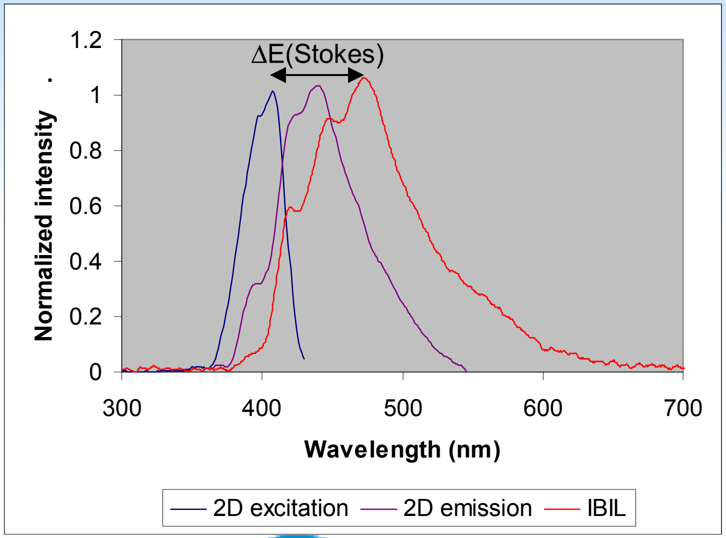
# Self absorption of luminescence should be minimal in stilbene MOFs

- $\Delta E(Stokes) = E_{max}(excitation) - \Delta E_{max}(emis)$
- Fluorescence Stokes shifts:
  - 2D MOF: 1215 $cm^{-1}$
  - 3D MOF: 815 $cm^{-1}$
  - Linker$(H)_2$: 4088 $cm^{-1}$
- IBIL Stokes shifts:
  - 2D MOF: 3415 $cm^{-1}$
  - 3D MOF: 5618 $cm^{-1}$
  - →IBIL emission is well separated from absorption
  - →Long detector path lengths should be feasible
- Broad emission on the long-wavelength side may be an indication of radiation damage along the ion track

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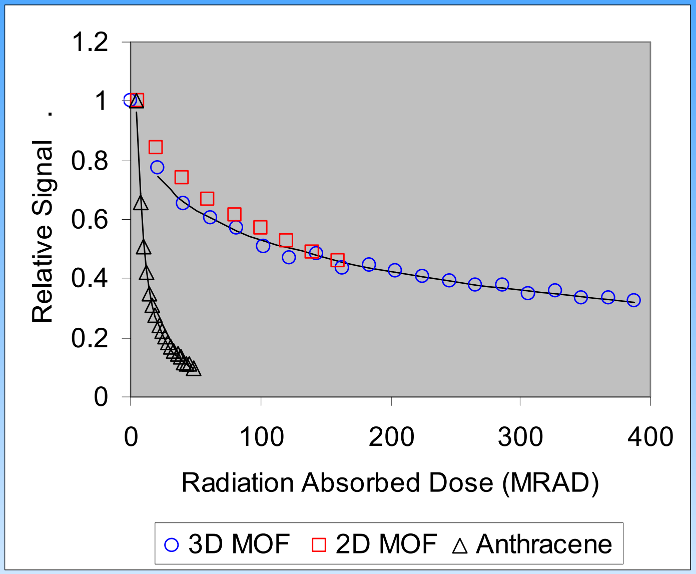
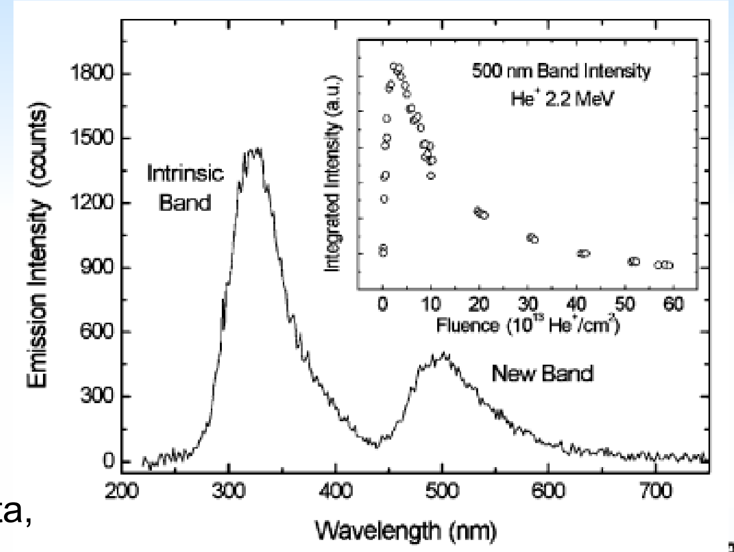
# Stilbene MOFs are much more resistant to radiation damage than the anthracene standard

- Anthracene: **loses > 90% of initial luminescence after 50 Mrad dose**
- 2D and 3D stilbene MOFs lose only ~ 68% **after 400 Mrad dose**

| | |
|---|---|
| 1 rad = | amount of energy absorbed/ mass |
| | = 100 ergs/g |

  - This dose is >> expected lifetime dose
  - Low density of 3D MOF should favor higher damage threshold:
    - Anthracene: 1.28 g/cm$^3$
    - Stilbene: 0.97 g/cm$^3$
    - 2D MOF: 1.52 g/cm$^3$
    - 3D MOF:0.50 g/cm$^3$
  - Clearly, factors beyond density must be accounted for
- Fluorescent polymers exposed to H$^+$ IBIL exhibit new emission
  - Attributed to radical formation leading to polymer crosslinking




IBIL spectrum of polyvinyltoluene, (A. Quaranta, *Nucl. Inst. Meth. Phys. Res. B*, 2005)

# Summary and conclusions

- Fluorescent metal organic frameworks constructed from stilbene dicarboxylates are luminescent when exposed to high-energy $H^+$
- Very high radiation tolerance is exhibited
- Damage caused by the beam made lead to new emission bands
  - Time-dependent IBIL may resolve this
- Low density (0.5 g/mol) 3D stilbene MOF is expected to a more proportional response to particle energy
  - IBIL measurements as a function of beam energy in the 0.1 – 5 MeV energy range needed to verify this theory
- MOFs are a novel and potentially promising solution to the problem of detecting fission neutrons

## Acknowledgements

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