SAND2011-4926P

Structural Origins of Scintillation: Metal Organic Frameworks as a Nanolaboratory

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Basic Research Technical Review
July 2011

Structural Origins of Scintillation: Metal Organic Frameworks as a Nanolaboratory

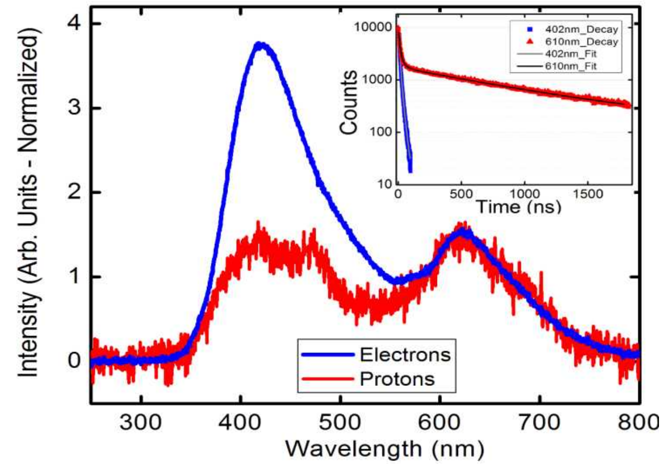
PI: F. Patrick Doty, Sandia National Labs

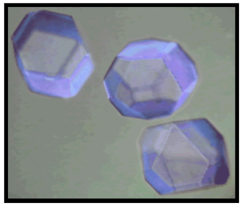
Award Number: 131554

Objective: Elucidate mechanisms of scintillation, through studies of metal organic framework materials (MOFs), and explore the potential of improved MOF-based sensor materials.

Relevance:

- •Determine applicability of MOFs to neutron detection
- •Demonstrate rational design to tailor scintillation
- •Develop Models for organic scintillator response





Approach: Synthesize a systematically designed range of materials and structures designed to probe physics of scintillation process. Materials characterization using steady-state and time-resolved photoluminescence, radioluminescence, and scintillation measurements. Use theoretical models to describe MOF electronic states and the influence of structure and chemistry on kinetics of scintillation.

Personnel Support: Staff Members, 3; Post-Docs, 2; Students, 2; Technologist, 1

Results this year:

- •Demonstrated correlation between structure and luminescence properties for interpenetrated/non-interpenetrated MOFs
- •Described luminescence modification via extrinsic infiltration, excimer, and exciplex formation
- •Discovered new MOF-based spectral neutron/gamma discrimination scheme based on heavy-metal induced triplet harvesting.

Funding:

Year 1: FY08-$250k, Year 2: FY09-$250k, Year 3: FY10-$250k

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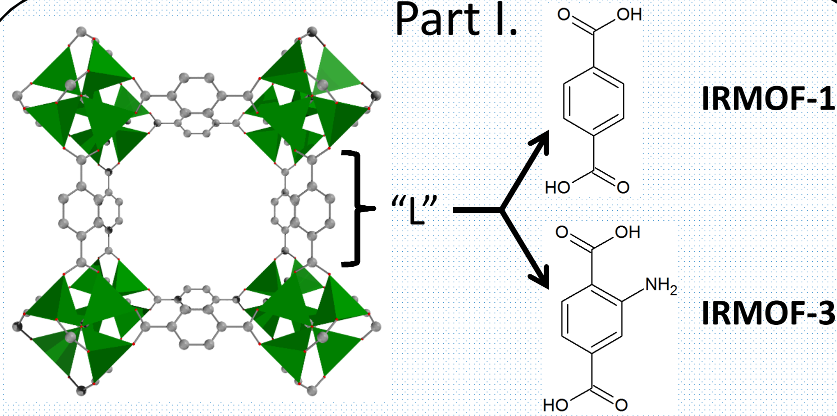
Program Objective

- Origins of luminescence and energy transfer in Metal-Organic Frameworks
  - Structure-property relationships for radiation detection and sensing applications.
    - Luminescence as a signal transduction mechanism
  - Systematic ‘design rules’ for MOF-based scintillators
    - Wavelength, intensity, timing characteristics
    - Distinctions from purely organic fluorophores
  - Intermolecular and charge-transfer interactions
    - Effects of framework structure
    - Control over the triplet state luminosity

Fundamental aspects of MOF luminescence have not been investigated

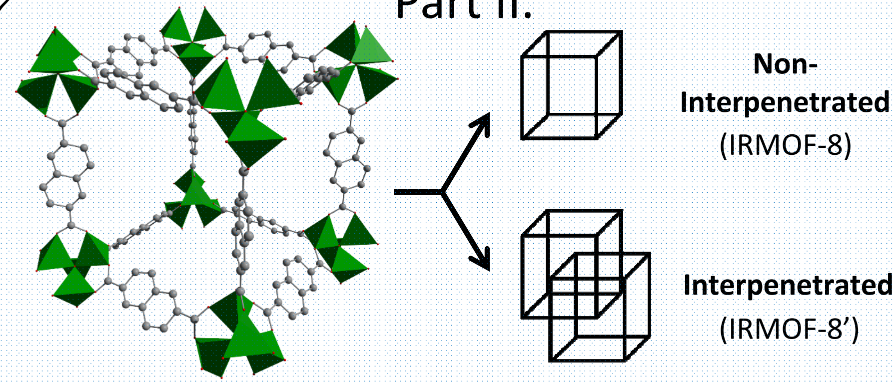
Areas of Study

Part I.



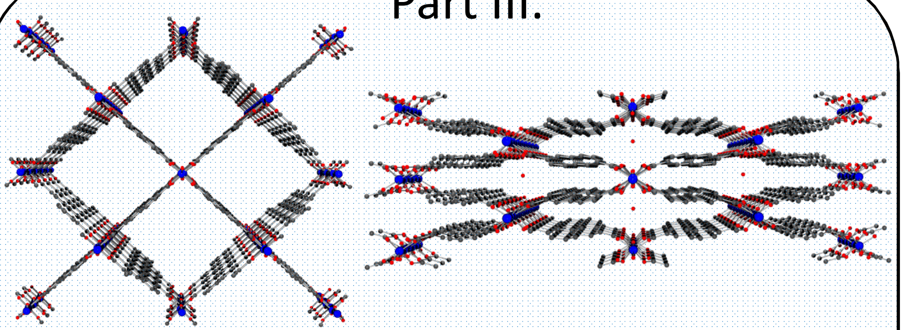
- Electronic effects upon optical/luminescence properties

Part II.



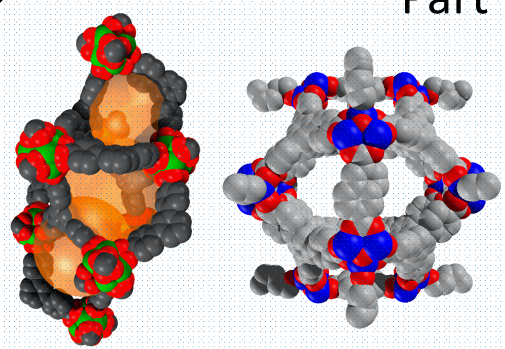
- Effects of framework interpenetration upon PL and radioluminescence spectra

Part III.



- Framework flexibility and intermolecular interactions
- Host/guest complexes and charge-transfer interactions

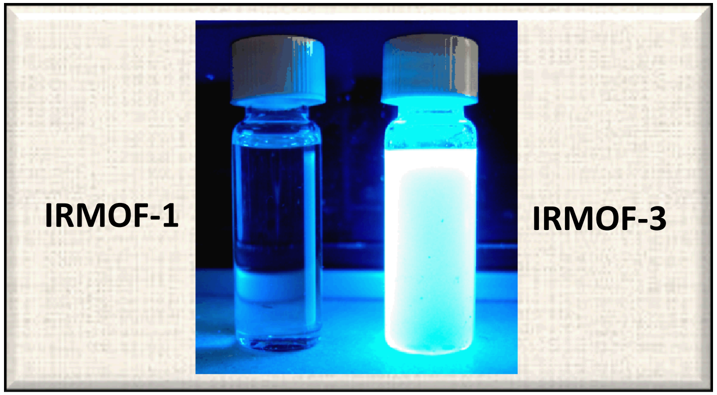
Part IV.

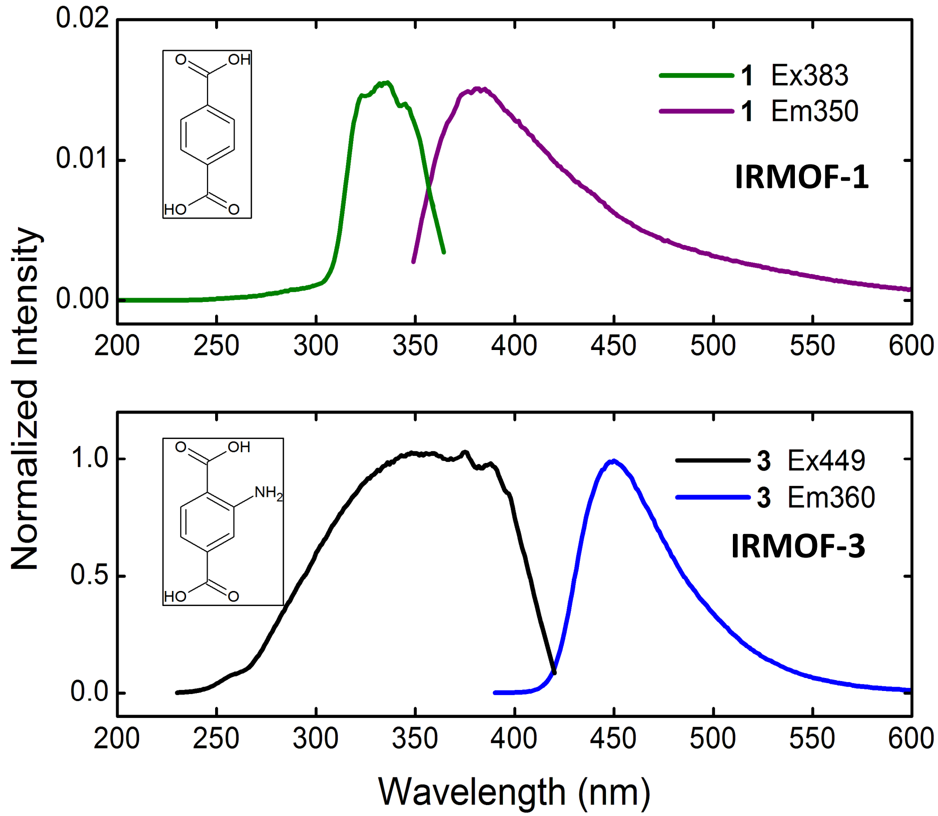


Triplet Harvesting

- Energy transfer via spin-orbit coupling
- Spectrally-resolved particle discrimination

Effects of Interpenetration: IRMOF-8’

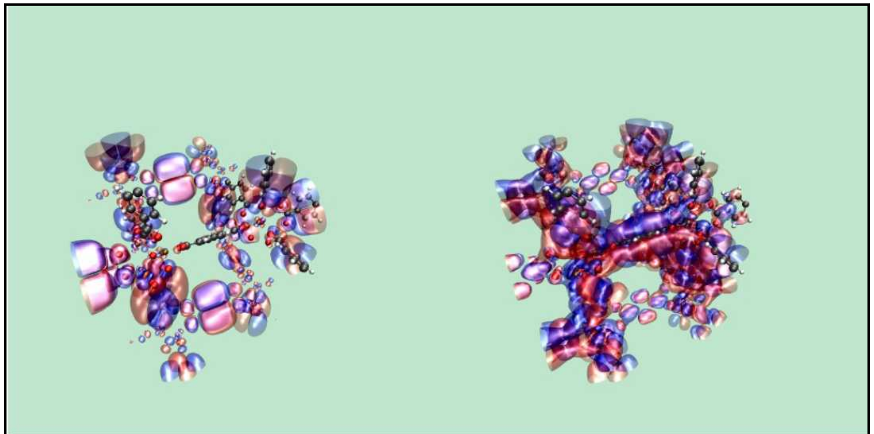




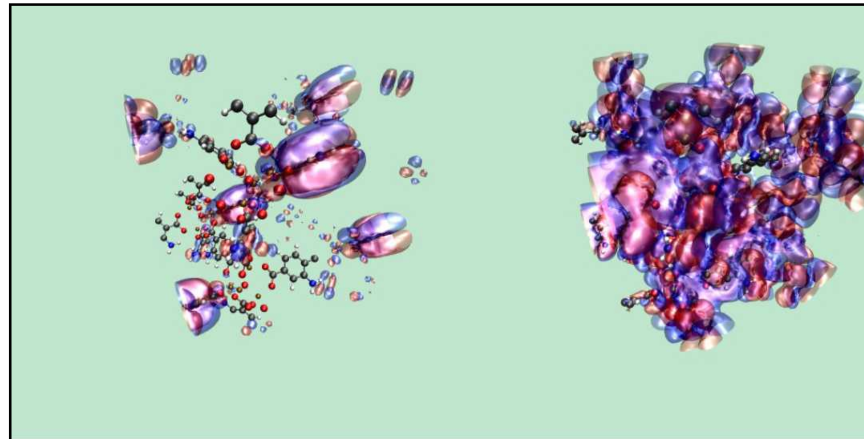
Chemical Functionalization:

- Intermolecular interactions and symmetry breaking
- Luminosity: >60 times brighter upon –NH_2 substitution
- Stokes shift: 47 nm (IRMOF-1), 95 nm (IRMOF-3)
- Additional differences?

DFT: HOMO and LUMO Wavefunctions



(a) IRMOF-1 wave function at VBM (b) IRMOF-1 wave function at CBM

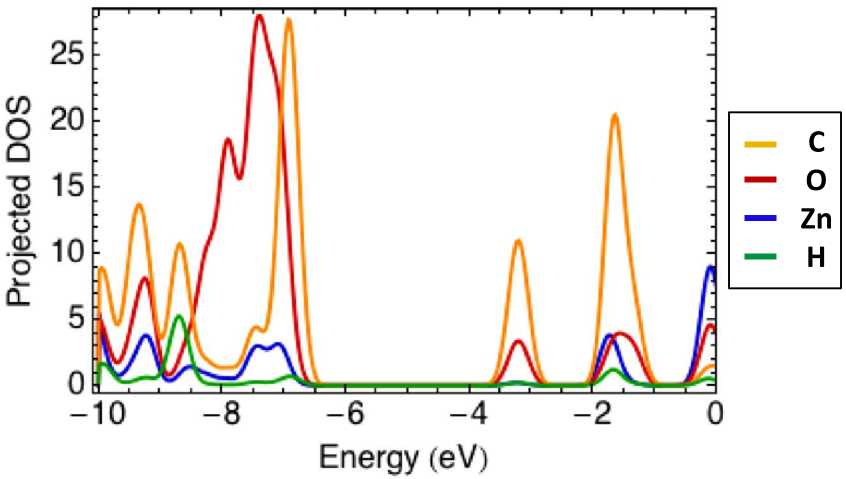


(c) IRMOF-3A wave function at VBM (d) IRMOF-3A wave function at CBM

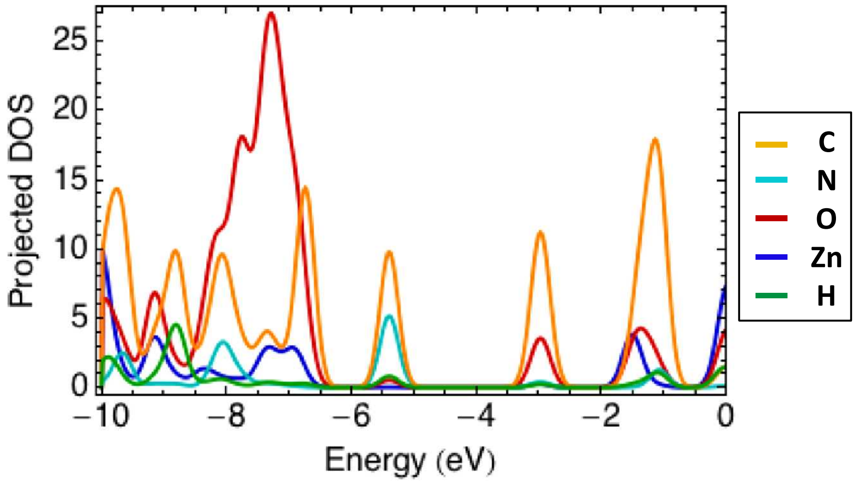
- HOMO's are localized on the discrete linker groups
- LUMO's of IRMOF-1 and IRMOF-3 are delocalized over neighboring linker groups but do not penetrate Zn_4O cores
- Indicates that wide-bandgap n-type semiconducting behavior is expected

Metal orbitals are not associated with HOMO or LUMO states:
Linker-Centered Properties

DFT Projected Density of States



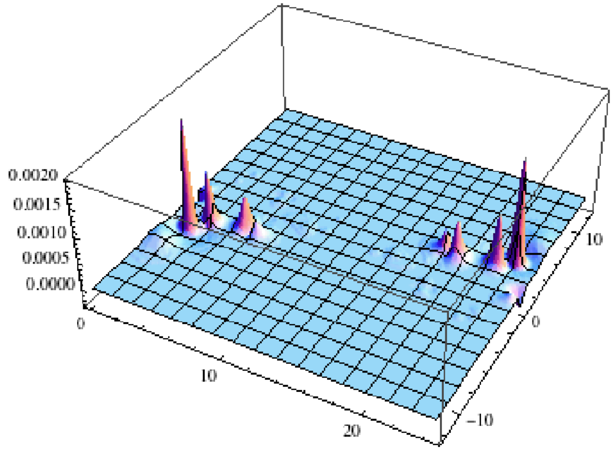
IRMOF-1
3.2 eV bandgap



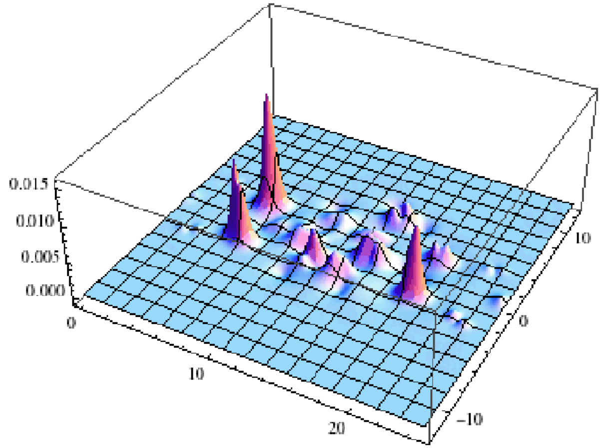
IRMOF-3
2.5 eV bandgap

- Non-participation of Zn states in VBM and CBM
- Zn_4O states are closer to VBM in IRMOF-1 vs. IRMOF-9/10
- Presence of amine in IRMOF-3 adds new states in IRMOF-1 bandgap

Spin-polarized Triplet Charge Densities



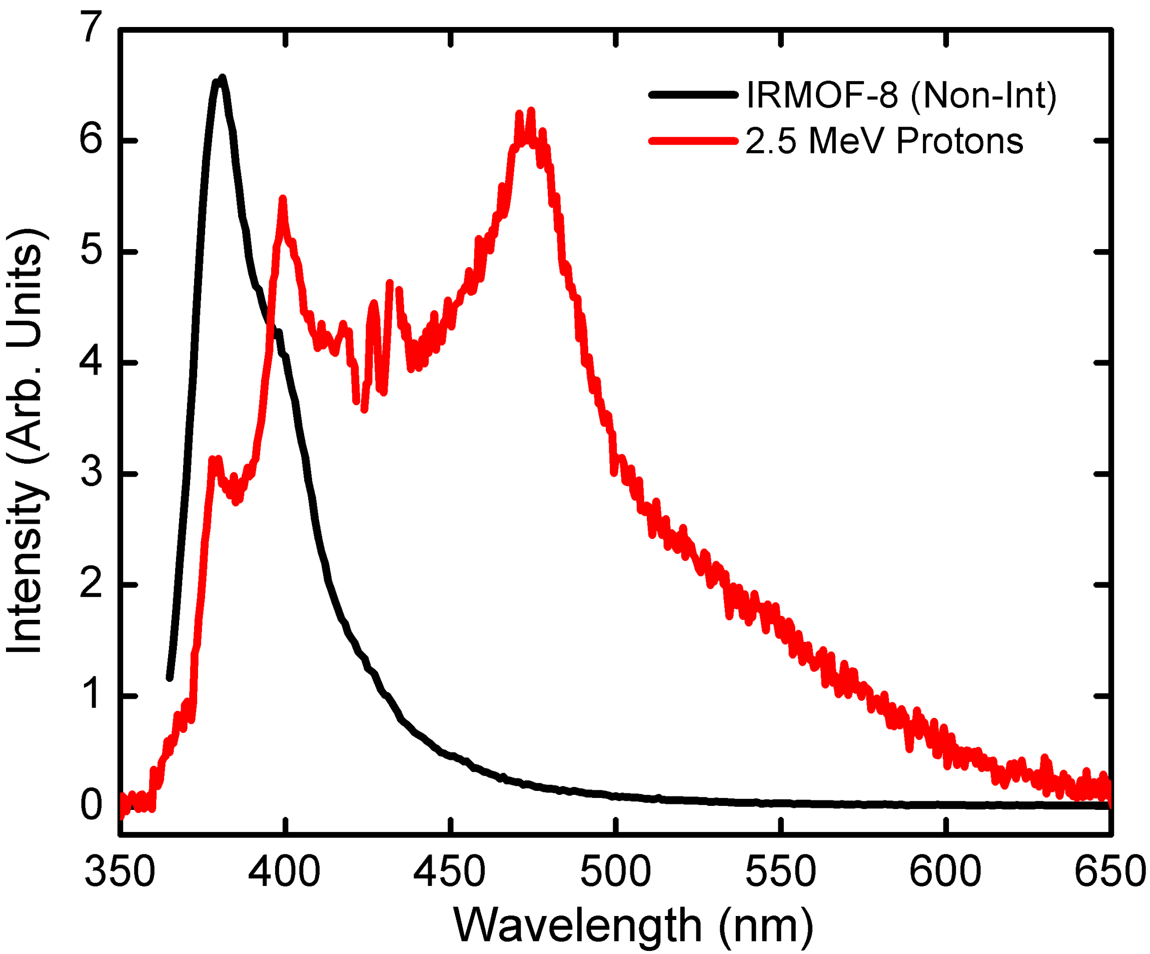
IRMOF-1

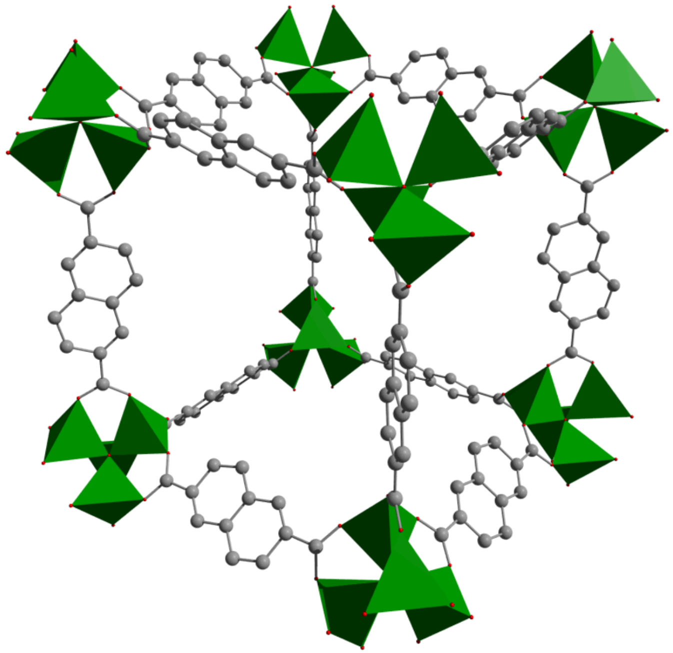


IRMOF-3

- Symmetry effects
- Relative magnitude of spin-up vs. spin-down densities
- Structural rearrangement in the excited triplet state
- Luminescence quantum yields and magnitude of Stokes’ shifts

Naphthalene-based Framework: IRMOF-8





Non-interpenetrated: Cubic Fm-3m

•Monomer vibronic progression still observed

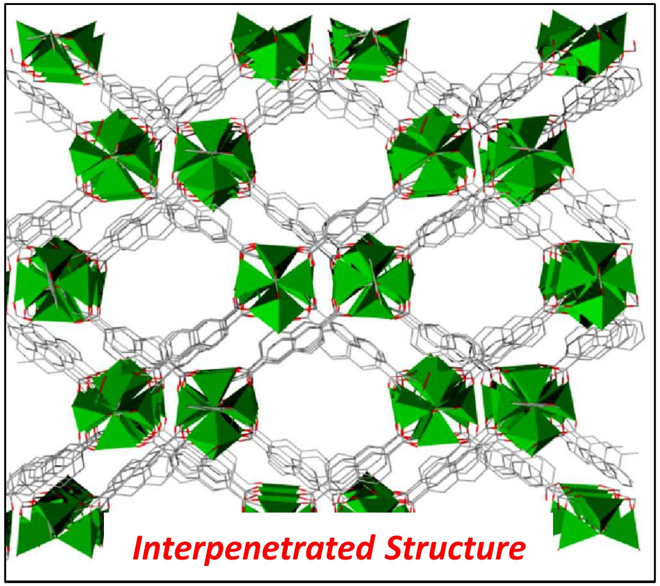
•Red-shifted IBIL peak at λ_{em}=476nm

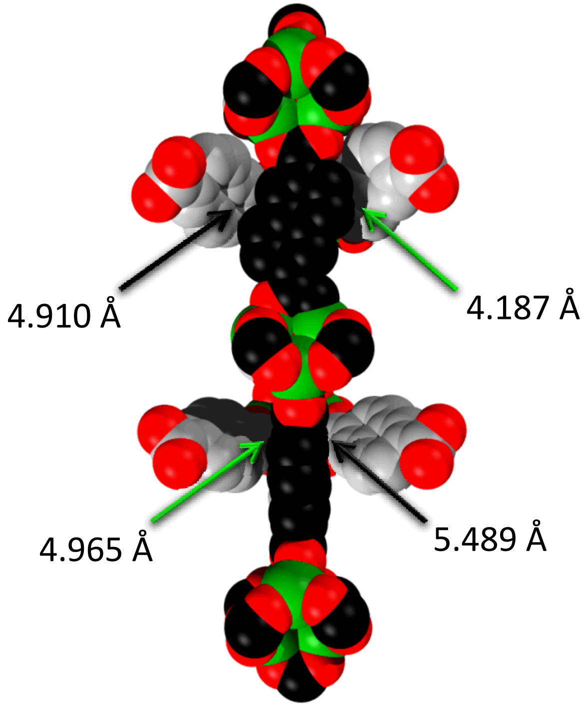
•***Lifetime***: Decay times of 4ns (96%) and 22ns (4%)

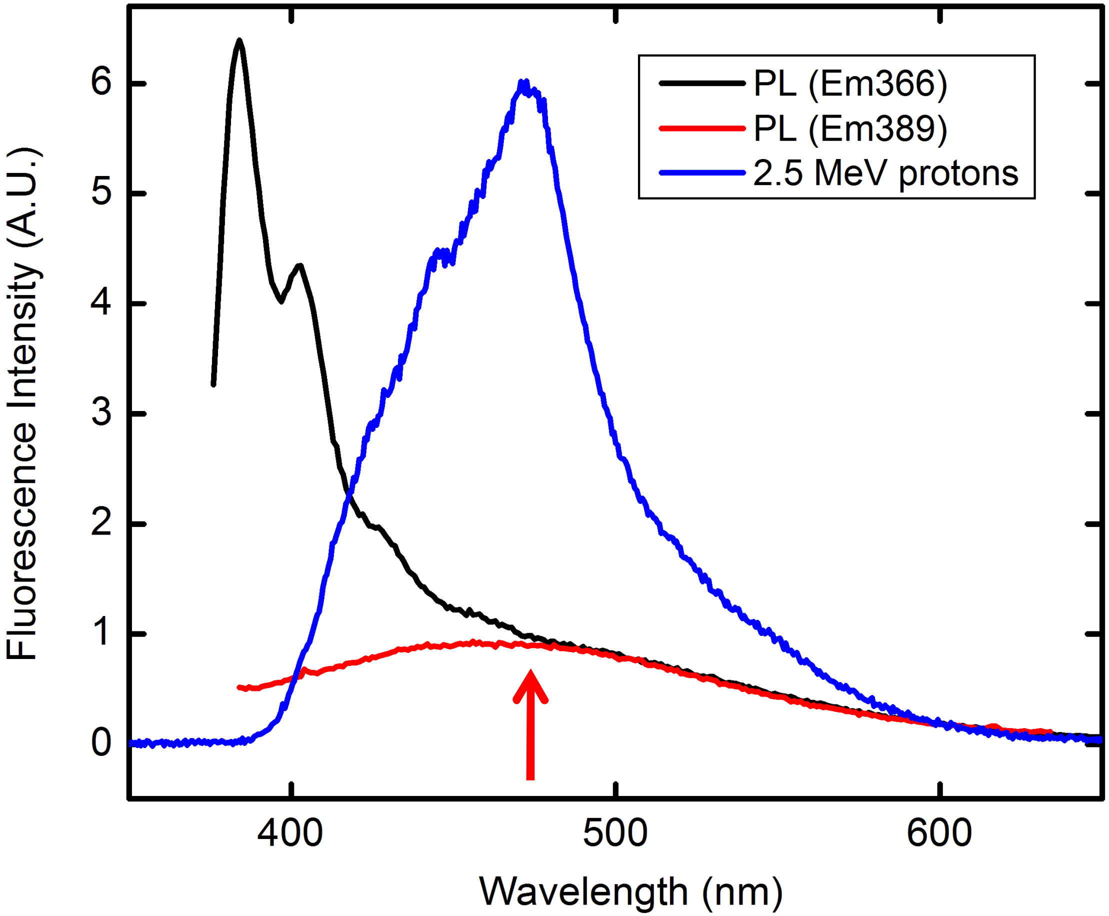
•***Intensity***: 65% anthracene (proton radioluminescence)

•***Structural changes upon Ionization?***
- 476 nm peak reminiscent of naphthalene excimer emission

Effects of Interpenetration: IRMOF-8’

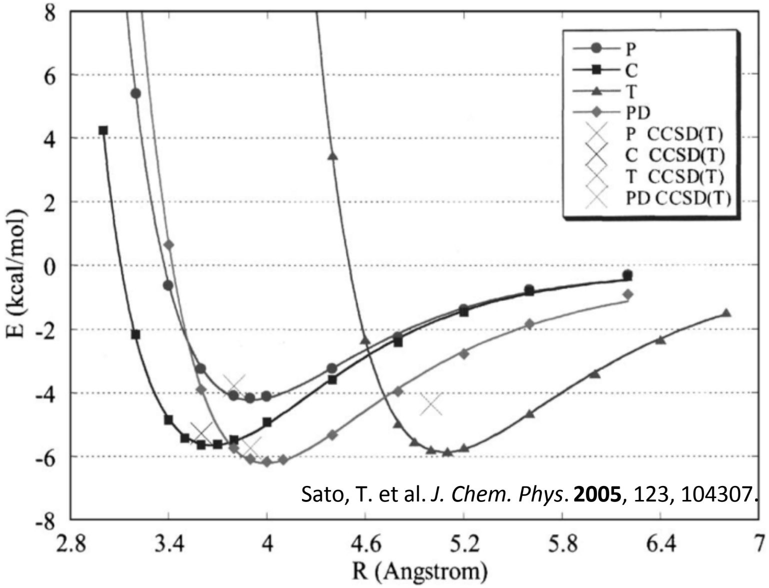


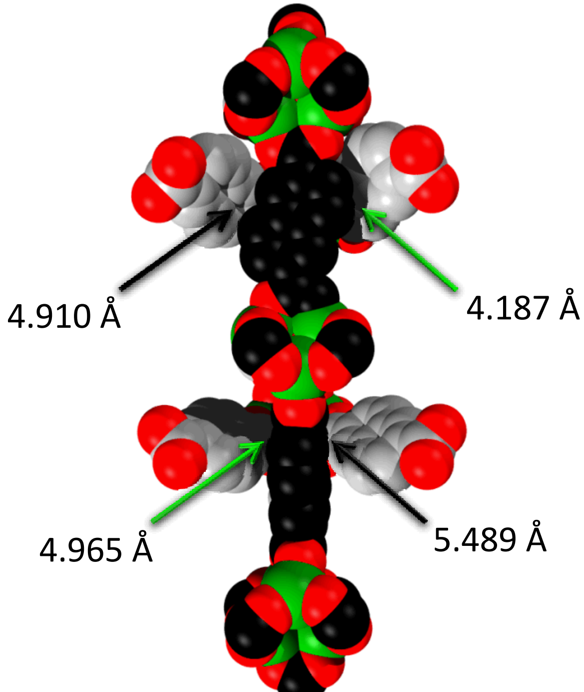


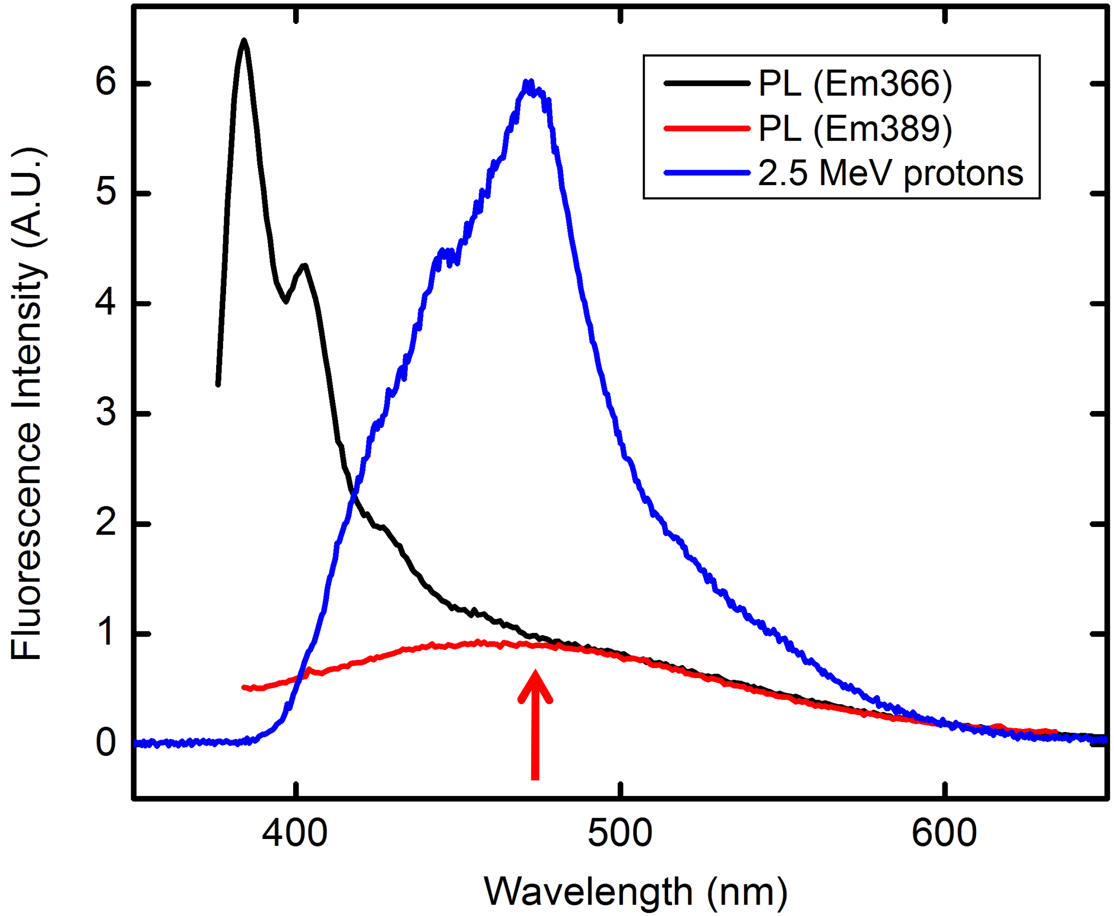


- Reminiscent of naphthalene excimer
  - Broad maximum at 475nm
  - Similar relative peak intensities
- Wavelength dependent emission in IRMOF-8’
  - Rigidified structure imposes ground-state interactions

Effects of Interpenetration: IRMOF-8’







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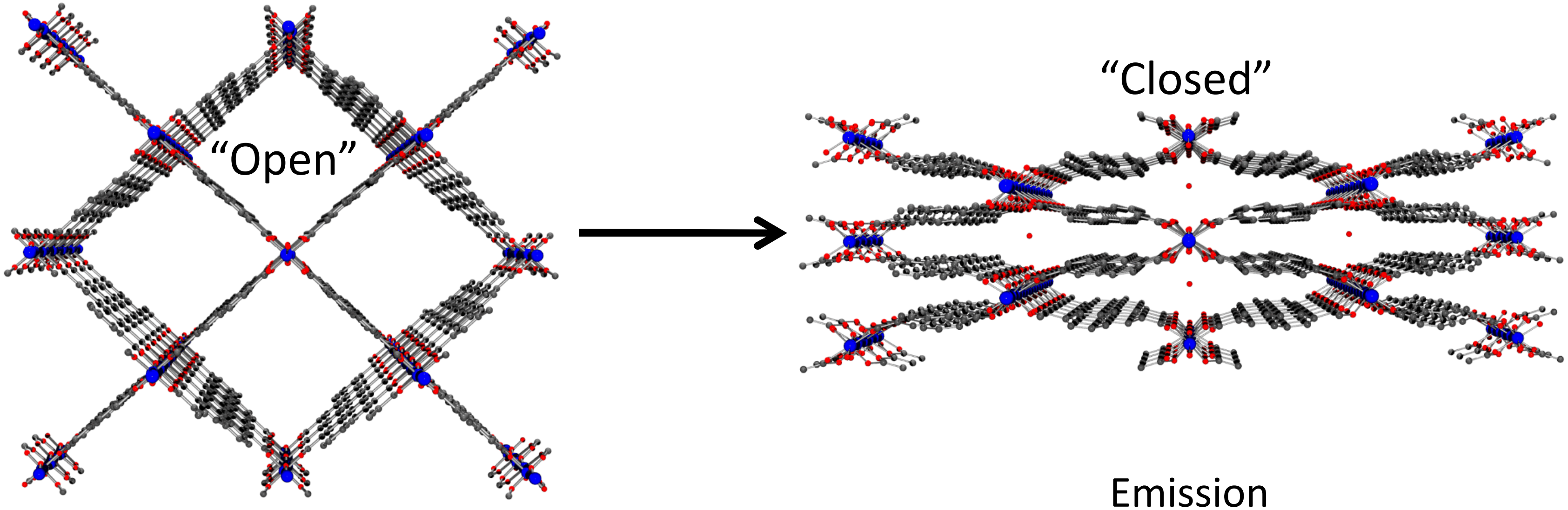
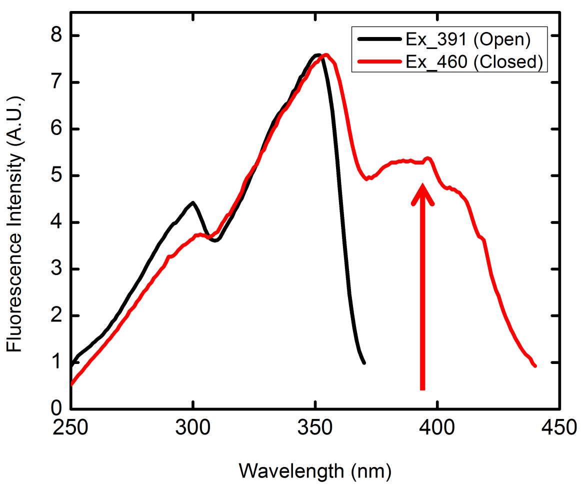
  - Rigidified structure imposes ground-state interactions

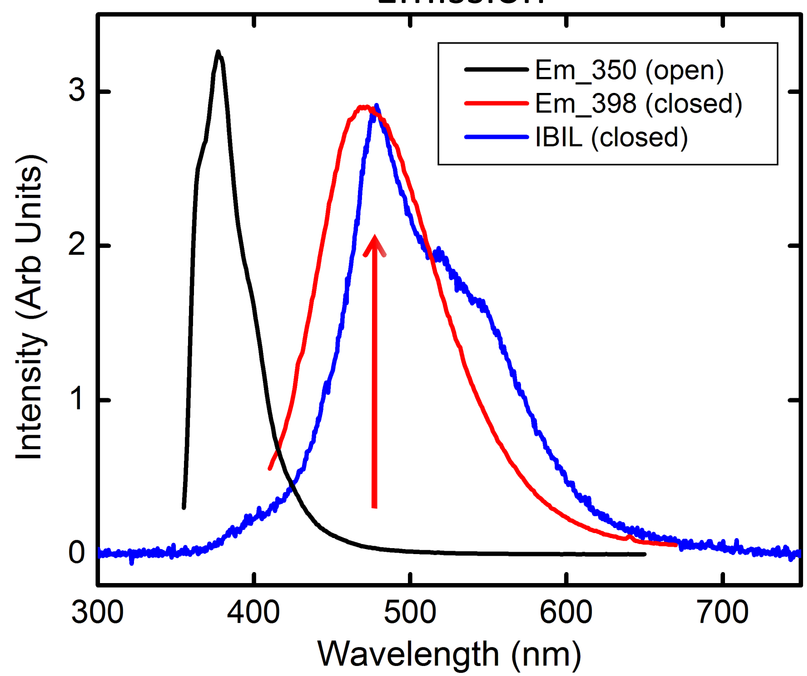
Intermolecular Dimer Interactions: Flexible (Al) MOF



Excitation

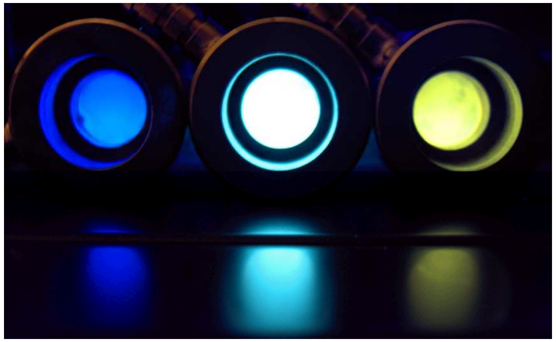


Emission



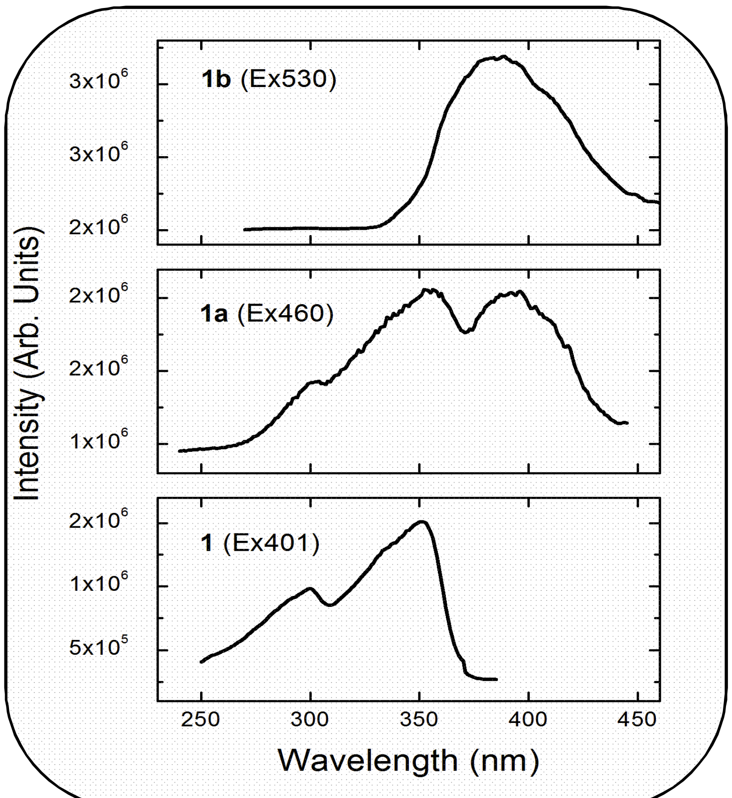
•New excitation at 398 nm: Ground-state dimer interactions

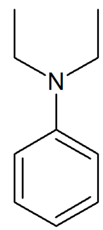
Host-Guest Interactions: Donor-Acceptor Complexes

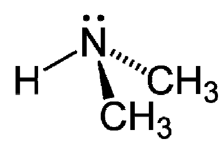


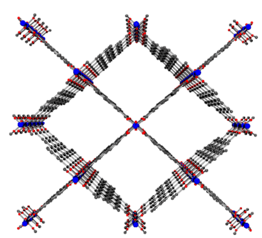
- Guest-dependent charge-transfer (CT) emission
- Exciplex vs. ground-state complex formation
- Intense CT fluorescence

Excitation

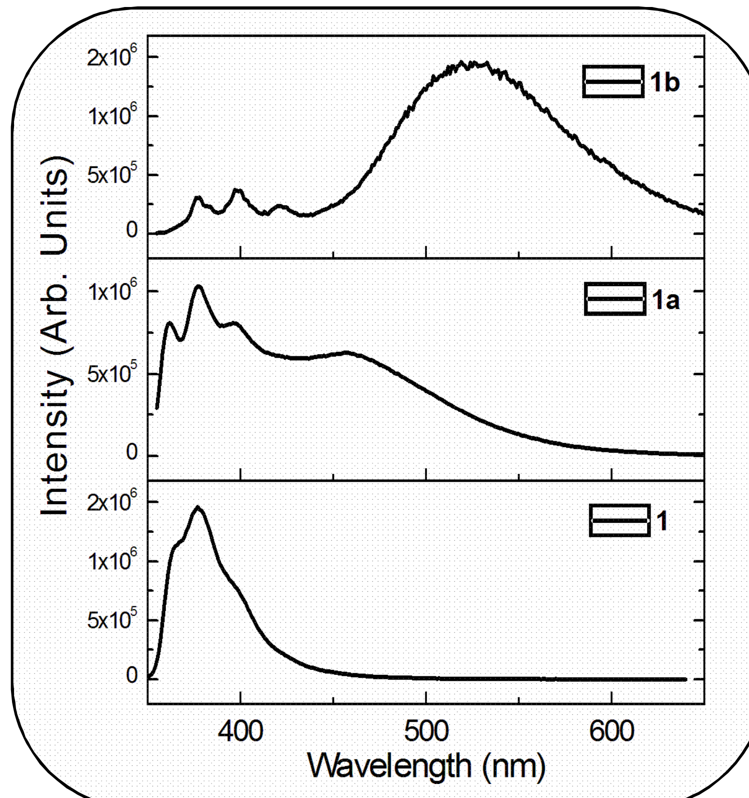




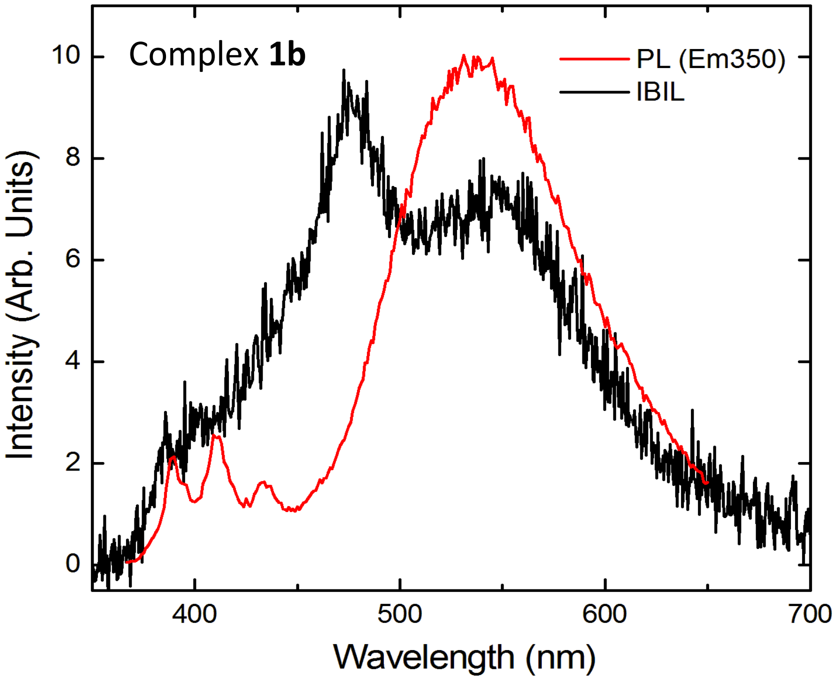


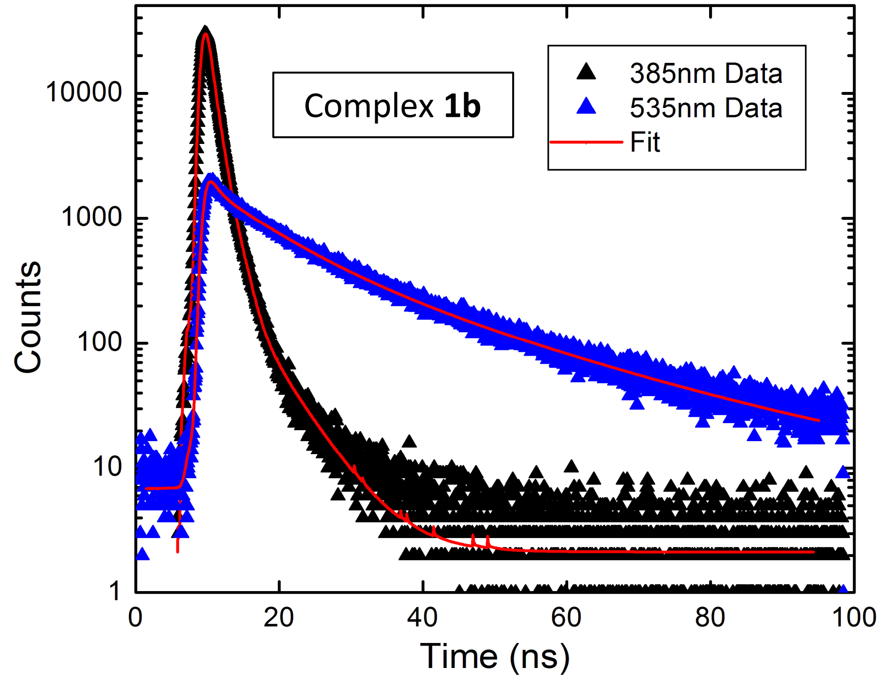


Emission



Luminescence Properties

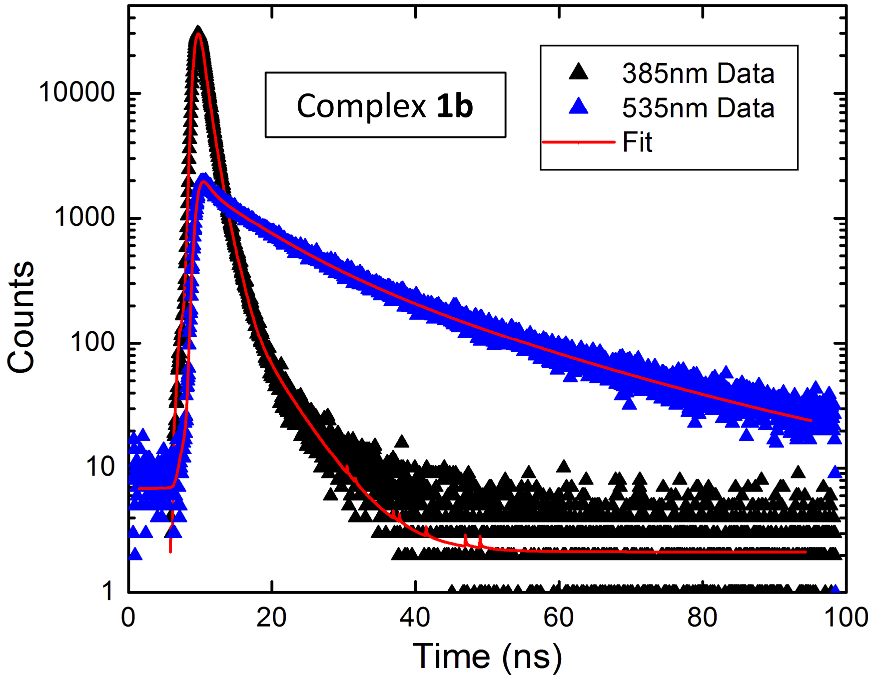


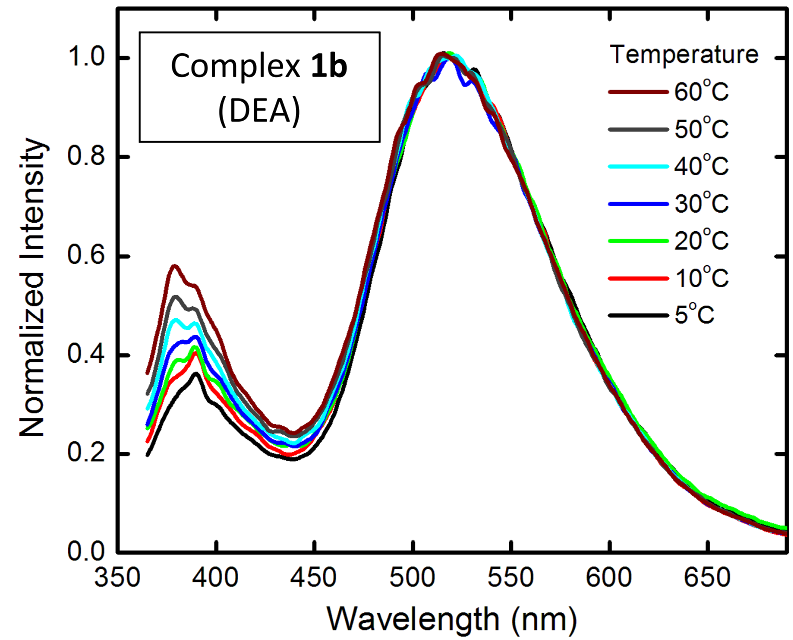


Compound	Monomer λ_{em} (nm)	CT λ_{em} (nm)	I_p (eV)	Lifetime (monomer), (ns)	Lifetime (CT), (ns)	ΔH_f (kJ/mol)
1	385	-	-	6 (100%)	-	-
1a (DMA)	385	**460**	**8.14**	1 (64%), 5 (36%)	6 (11%), 19 (89%)	+4.6
1b (DEA)	385	**535**	**6.99**	1 (68%), 5 (32%)	8 (24%), 34 (76%)	-9.2

- CT luminescence correlated with ionization potential of donor species

Luminescence Properties





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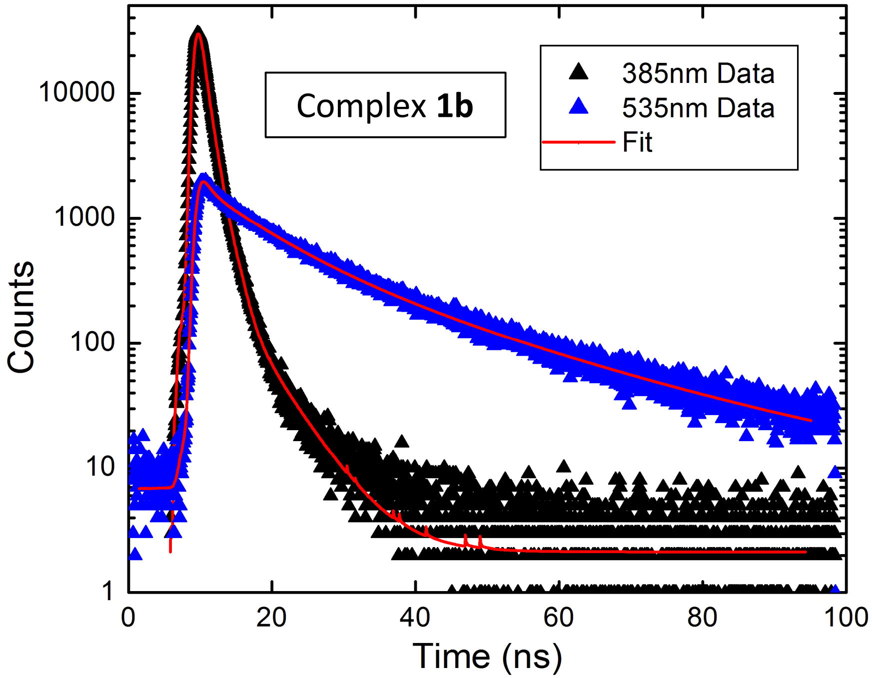
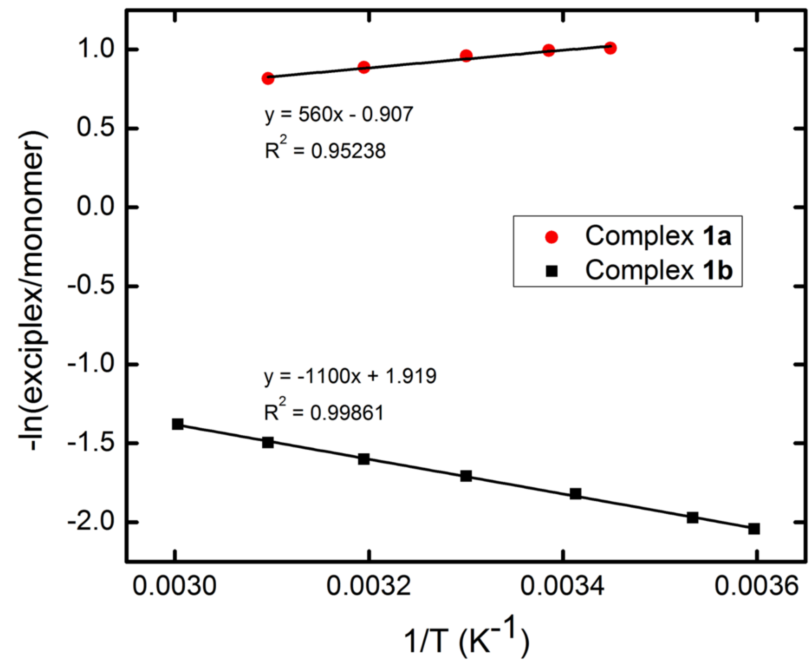
1b (DEA)	385	535	6.99	**1 (78%),** 5 (22%)	8 (24%), **34 (76%)**	-9.2

- CT lifetime associated with strength of host-guest interactions
- Compare to (H_2NDC + DEA) exciplex: 4ns lifetime

Luminescence Properties





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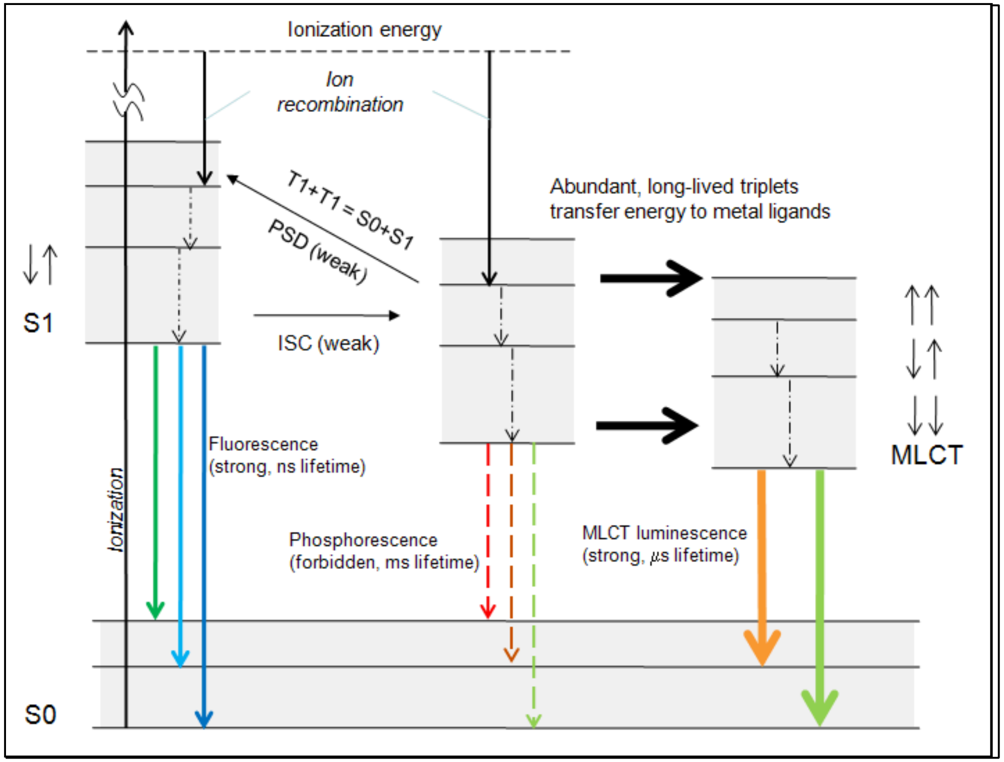
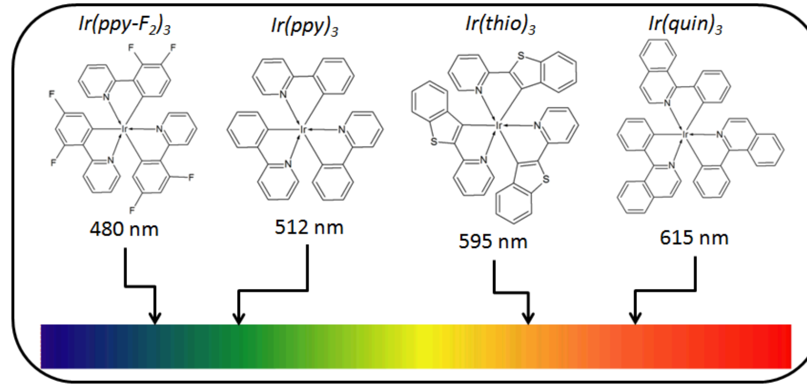
- Enthalpy of CT complex formation calculated from variable-temp. data
- Exothermic ΔH_f for **1b** associated with preferential adsorption into pores

Increasing Delayed Luminosity: Triplet Harvesting



•Intense $T_1 \rightarrow S_0$ via mixing of spin and orbital angular momenta

•Mediated by strong spin-orbit coupling of cyclometalated iridium guest complexes



Factors to be considered:

•Host-Guest energy level alignment

•Guest concentration

•Steric and orientation effects

•Strength of spin-orbit coupling
- •Lifetime
- •Quantum yield

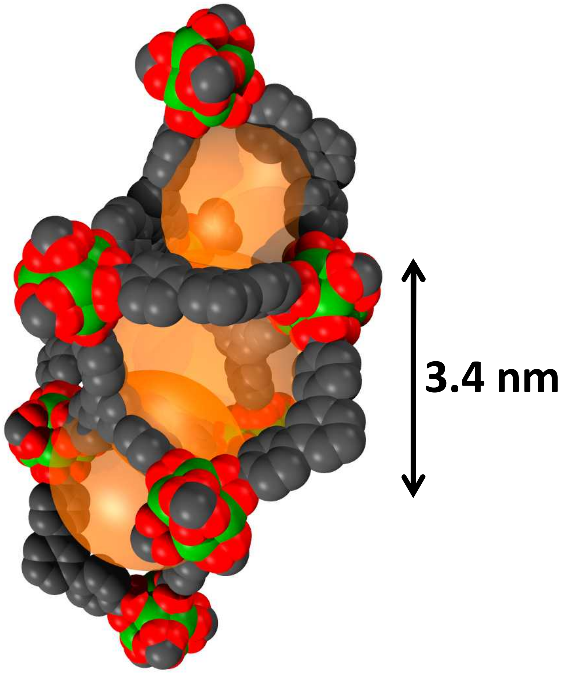
Increased intensity of delayed luminescence

Doty, F. P. et al. *SAND Report 2010-6724*, 2010.

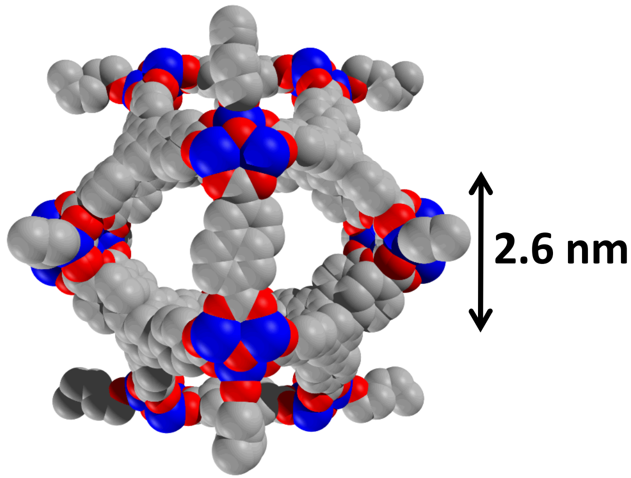
Triplet Harvesting in Large-Pore MOFs

Sandia National Laboratories

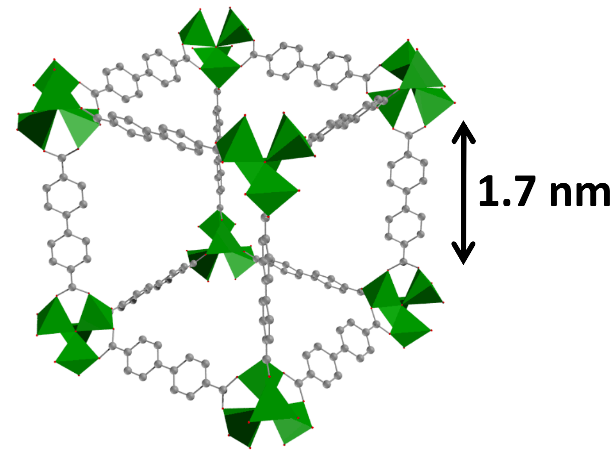
MOF-177



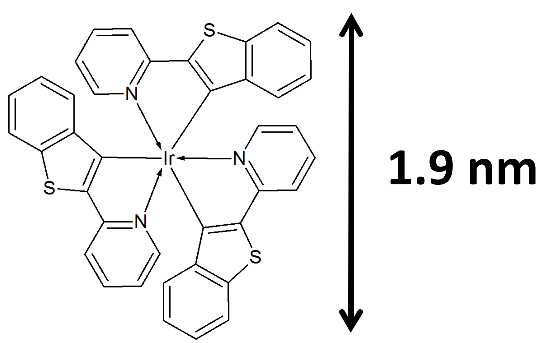
DUT-6



IRMOF-10

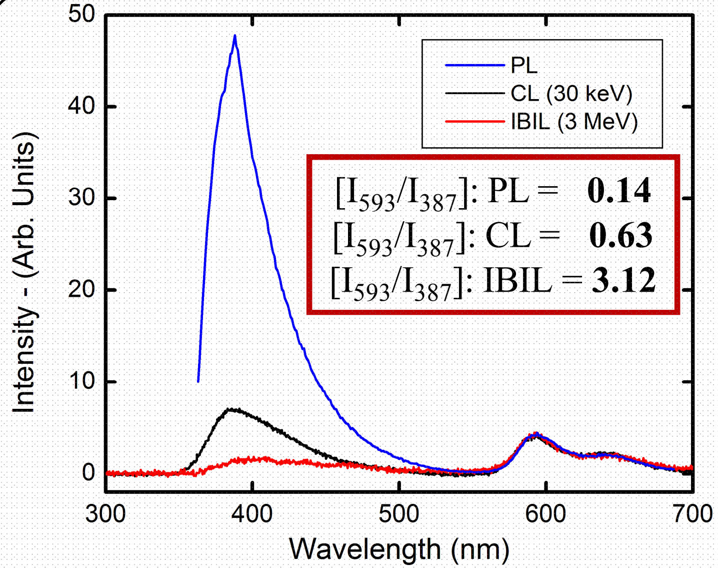


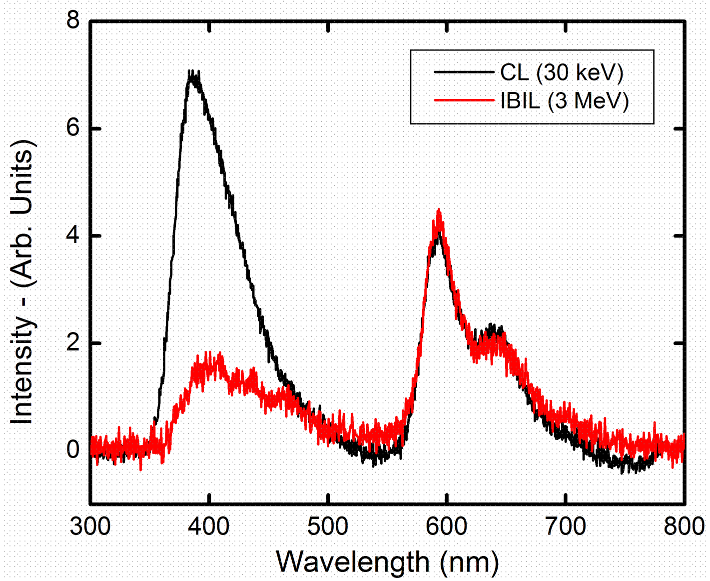
$Ir(thio)_3$

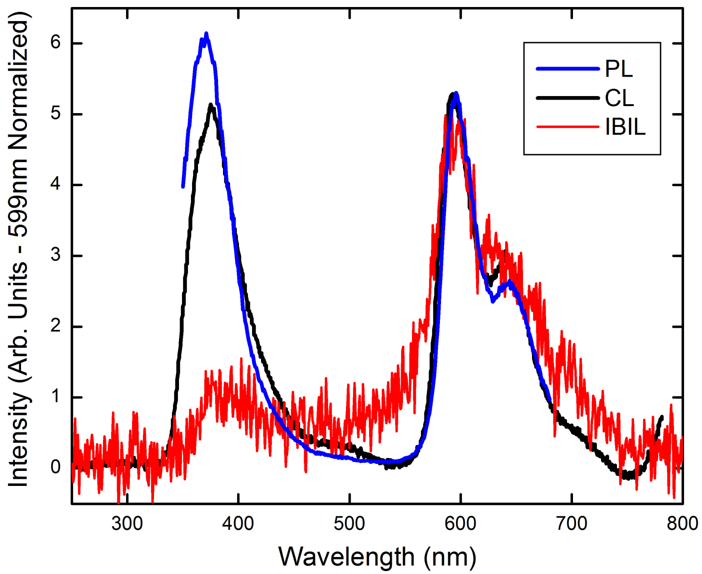


- Matching of guest molecule to host cavity
  - Short-range Dexter exchange mechanism
- Hexagonal vs. cubic pore environments
- MOF-177: Zn_4O, benzenetribenzoate
- DUT-6: Zn_4O, benzenetribenzoate
- IRMOF-10: Zn_4O, biphenyldicarboxylate

Energy Transfer and Spectral-Shape Discrimination







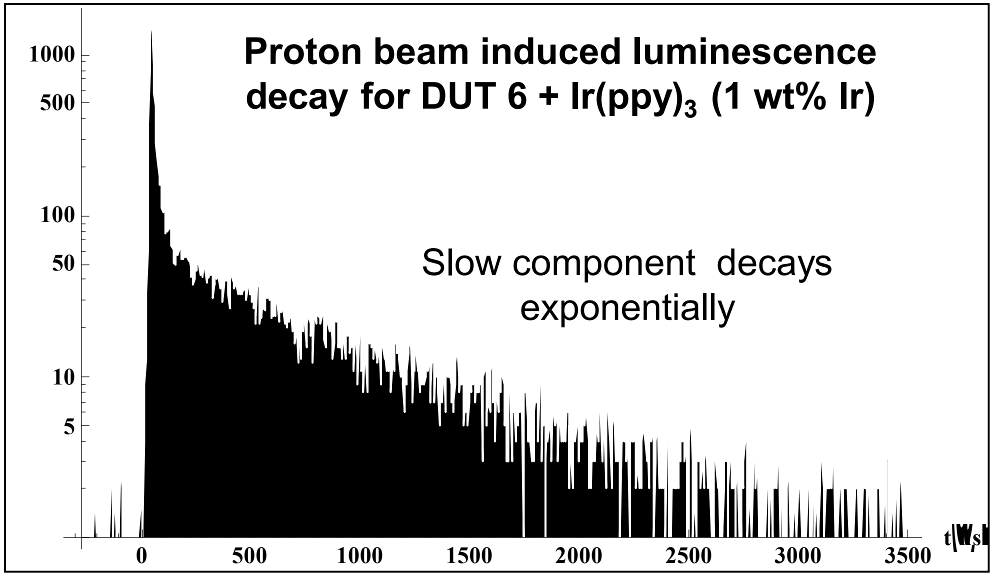
$[I_{599}/I_{387}]$: PL = **0.86**
$[I_{599}/I_{387}]$: CL = **1.03**
$[I_{599}/I_{387}]$: IBIL = **4.29**

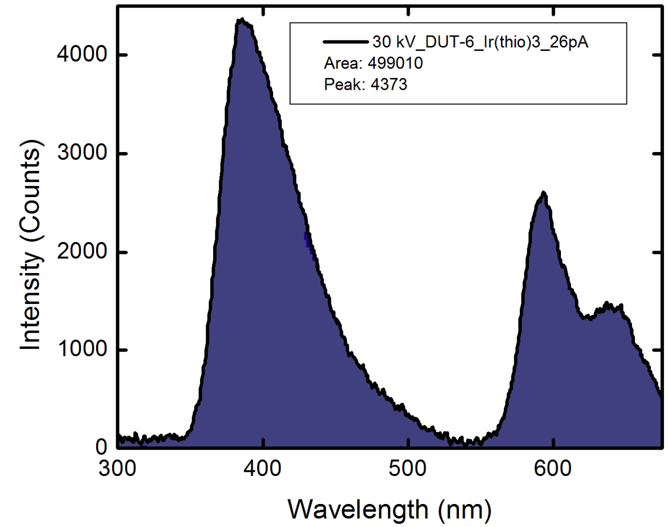
- Higher Iridium doping ratio is possible in MOF-177
  - -Larger pore size

- Comparison of relative singlet:triplet intensities indicates more efficient triplet transport in DUT-6
  - Dexter exchange mechanism

Particle-dependent Spectral Response

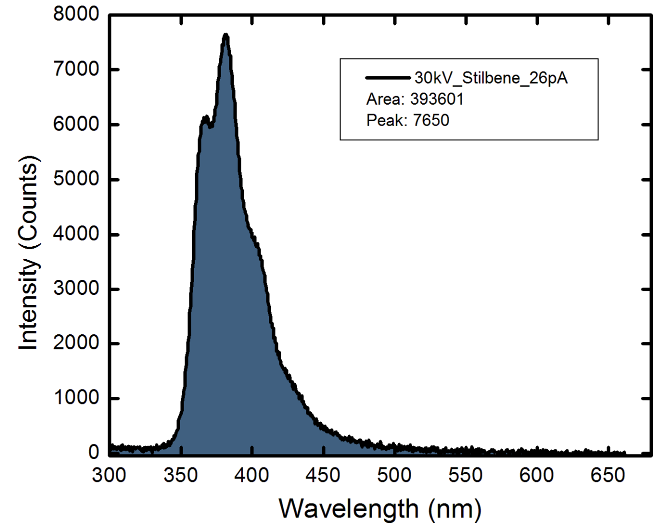
Radioluminescence Intensity and Decay



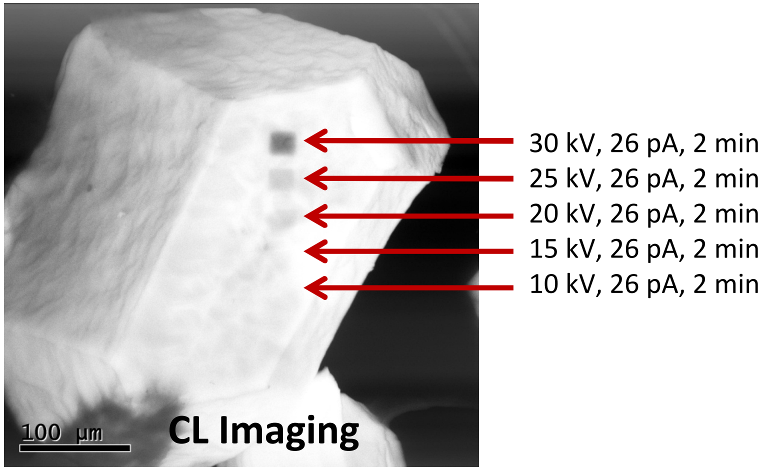


Delayed exponential decay characteristic of ^{3}MLCT emission

Integrated CL intensity for infiltrated DUT-6 is >125% *trans*-stilbene

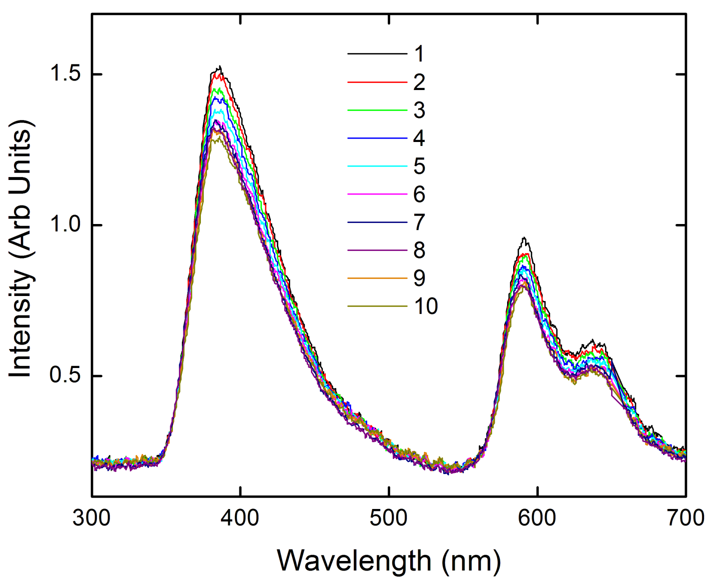


Radiation Damage Measurements

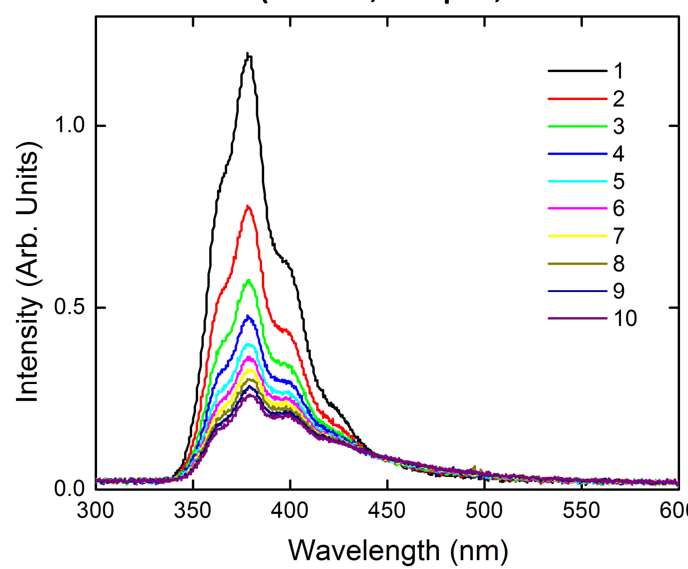


- MOF and stilbene spectra show uniform decrease with dose
- Similar decay rate for MOF host and Iridium guest luminescence

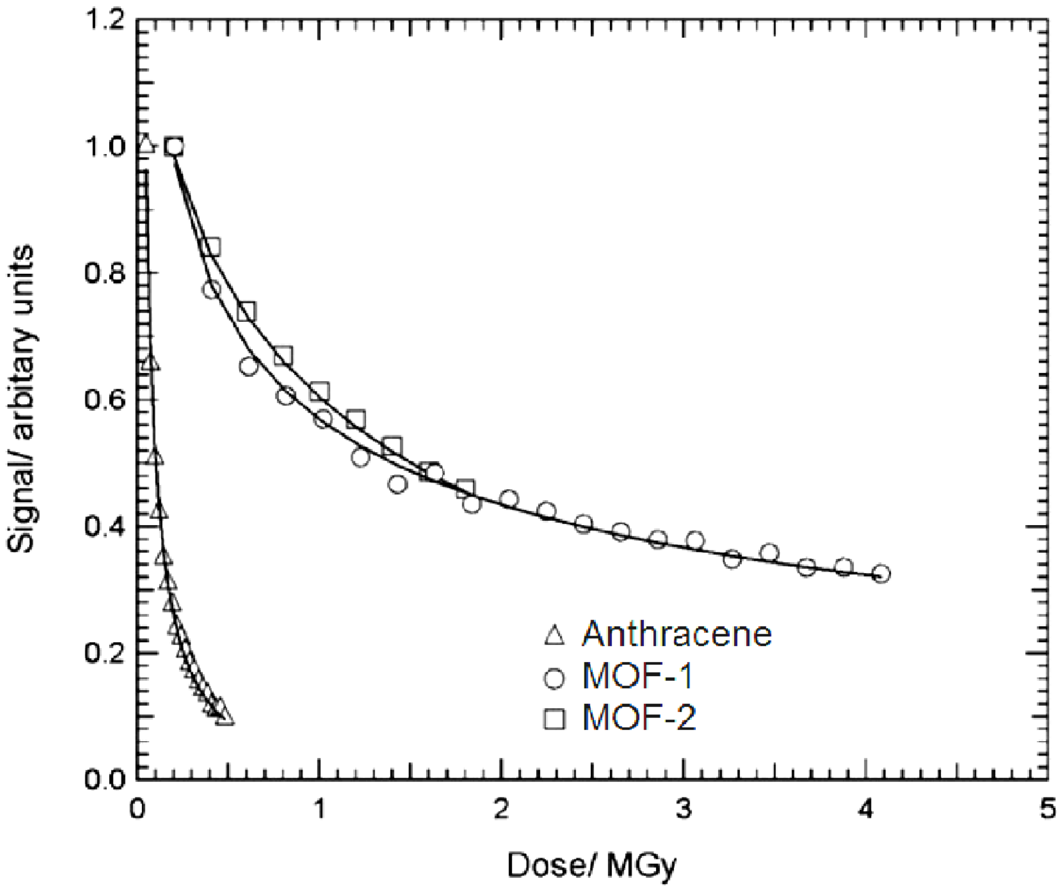
DUT-6: (15 kv, 26pA, 2min intervals)



trans-stilbene: (15 kv, 26pA, 2min intervals)



Radiation Damage: Proton Radioluminescence



$$I = \exp\left(-D/D_0\right)^{\beta}$$

Anthracene:
D_0 = 2.044 x 10^{-5} MGy
β = 0.187

MOF (λ_1):
D_0 = 2.303 MGy
β = 0.396

MOF (λ_2):
D_0 = 1.871 MGy
β = 0.434

Enhanced Radiation Hardness via Rigidified MOF structure

Accomplishments

- Publications
  - "Assessing the Purity of Metal-Organic Frameworks Using Photoluminescence: MOF-5, ZnO Quantum Dots, and Framework Decomposition," *J. Am. Chem. Soc*. **2010**, 132, 15487.
  - "Designing Metal-Organic Frameworks for Radiation Detection," *Nucl. Instr. Meth. A* **2011**, doi: 10.1016/j.nima.2011.01.102.
  - "Luminescent Metal-Organic Frameworks: A Nanolaboratory for Probing Energy Transfer via Interchromophore Interactions," *ECS Trans*. **2010**, 28, 137.
  - "Metal-Organic Frameworks for the Spectral Discrimination of Neutrons," In Preparation.
- Patents
  - Doped Luminescent Materials and Particle Discrimination Using Same. International Patent 20110108738, May 12, 2011.
- Presentations
  - "Investigation of metal-organic frameworks (MOFs) as hosts for luminescent molecules," X-Ray, Gamma-Ray, and Particle Technologies; Penetrating Radiation Systems and Applications XI, SPIE Conference, San Diego, Aug. 2 – 6, 2010.
  - "MOF-based Scintillators," X-Ray, Gamma-Ray, and Particle Technologies; Penetrating Radiation Systems and Applications XI, SPIE Conference, San Diego, Aug. 2 – 6, 2010.
  - "Effects of crystal structure and linker on MOF luminescent properties," American Chemical Society meeting, Boston, MA, Aug. 15 – 20, 2010.
  - "Scintillating Metal-organic-framework Materials for Radiation Detection: First Principles Calculations Towards Rational Design," MRS Fall 2010, Boston, MA, Nov. 29 – Dec. 3, 2010.
  - "Structure and Luminescence in Metal Organic Frameworks ," MRS Fall 2010, symposium EE Solid-State Chemistry of Inorganic Materials VIII, Boston, MA, Nov. 29 – Dec. 3, 2010.

Coordination/Collaboration and Transition

- Collaborative Efforts
  - NA-22 “MOF-based Scintillators”
- Undergraduate Students
  - Stefan Nikodemski (Colorado School of Mines – B.S. Physics, Spring 2010)
- Graduate Students
  - Janelle Branson (New Mexico Tech – Ph.D. Materials Science, expected Fall 2011)
- Postdoctoral Appointees
  - Alex Greaney (MIT)
  - Kirsty Leong (SNL)
  - Scott Meek (SNL)
  - John Perry IV (SNL)