SAND2015-1938C

# Photoluminescence via MOF Metal-Ligand Tunability

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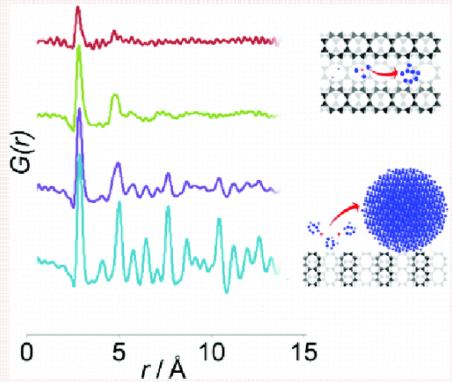
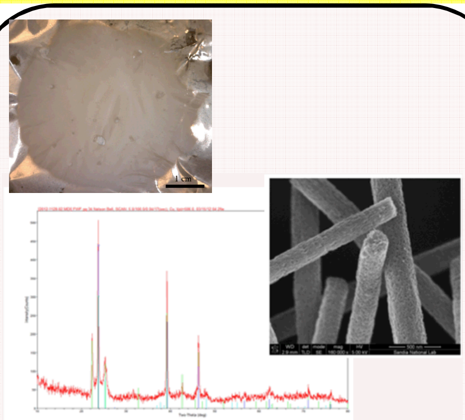
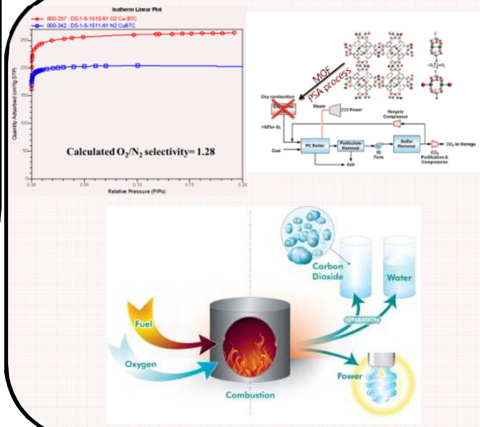
## Nanoparticle Occluded Zeolites: Catalysis and Separations



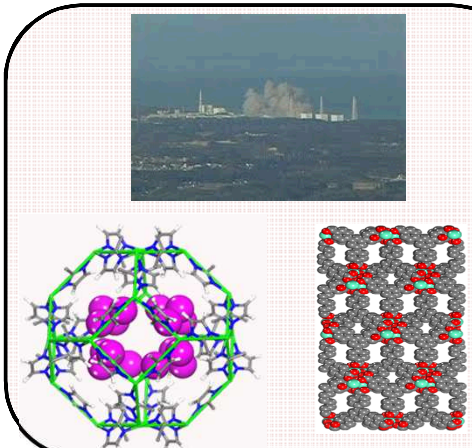

## High Temperature Membranes for Gas Separations: Nanoporous Nanofibers



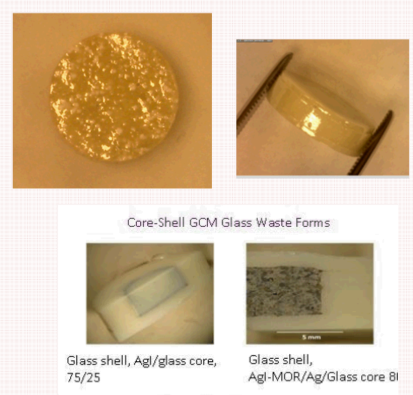
## MOFs for Gas Separations and Use in Oxyfuel Combustion



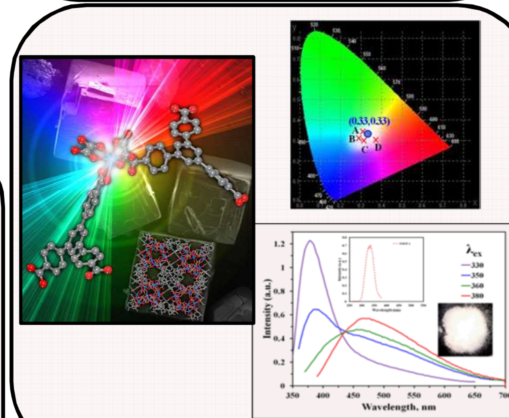

**Materials design, synthesis, characterization, and testing**



## Volatile Radionuclides Capture

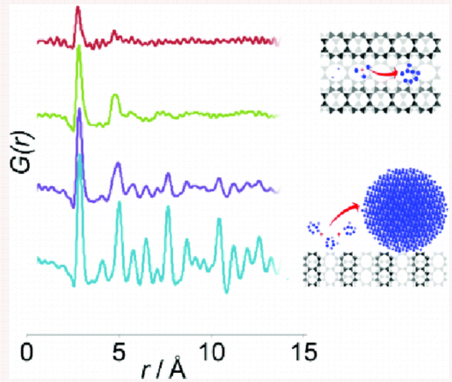



## Nuclear Waste Glass and Ceramics

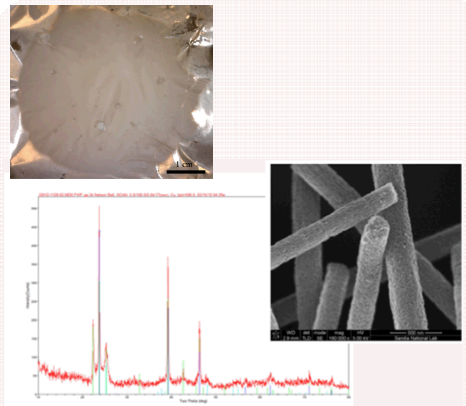



## Solid-State Lighting

## Nanoparticle Occluded Zeolites: Catalysis and Separations




## High Temperature Membranes for Gas Separations: Nanoporous Nanofibers

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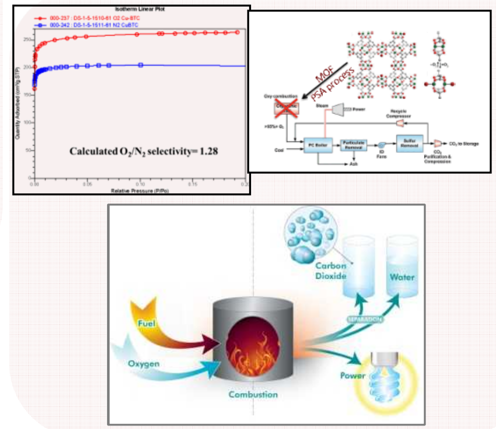


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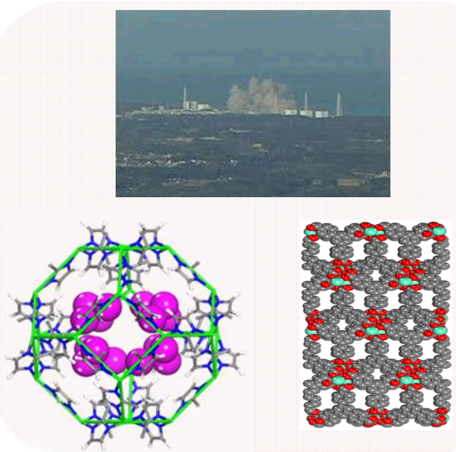
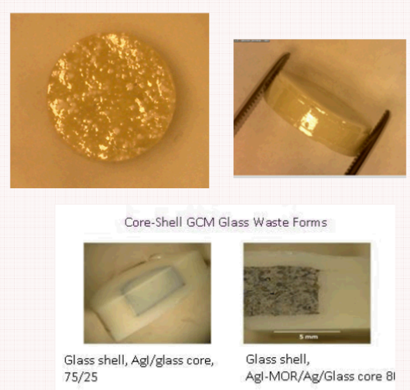


## Volatile Radionuclides Capture

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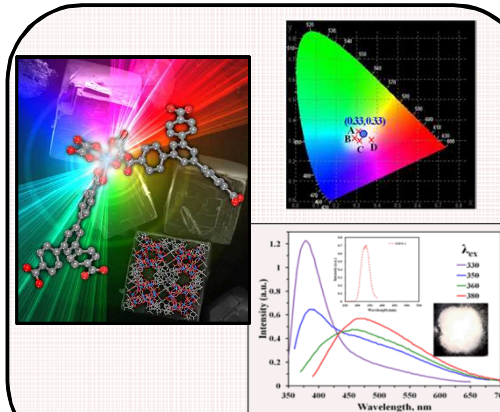



## Solid-State Lighting

# Solid State Lighting (SSL): Towards Single Component Phosphors

- The ability to generate white light from a single phosphor:
  - an alternative to existing approaches that achieve white light through color mixing
  - a promising approach for next-generation SSL materials

- Current white LEDs for SSL are based on blue InGaN LEDs that excite a yellow-emitting YAG:Ce phosphor (cool white light) made warmer by incorporating a red-emitting phosphor

- Warm white LEDs can also be achieved by utilizing near-UV InGaN LEDs to excite blends of red-, green-, and blue-emitting phosphors. Unfortunately, the additional down-conversion step (near-UV to blue) *significantly lowers the conversion efficiency of the device.*

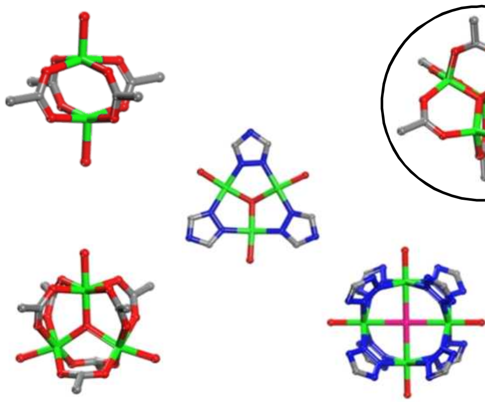
- In this context, MOFs are promising candidates for single component phosphors due to their highly tunability of both organic and inorganic component, pre- or post- synthesis

# Metal-Organic Frameworks (MOFs )

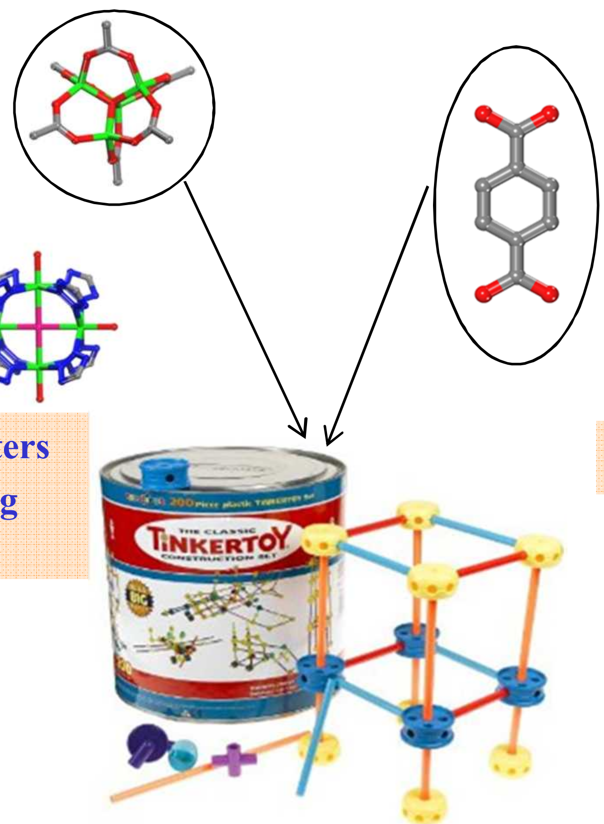
"Tunable" frameworks for gas selectivity / high capacity due to high surface areas

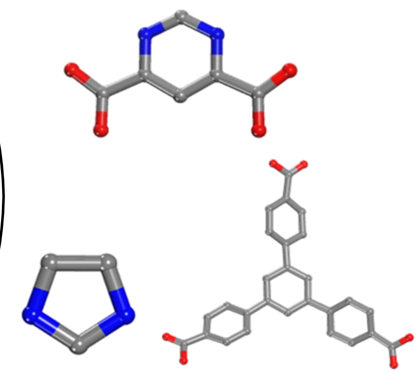
Novel Separations and Waste Forms Technologies via Structure – Property Determination using *Integrated Synthesis, Characterization and Modeling*

eg., Volatile gases/long-lived fission products pose *unique scientific issues* with regards to detection, storage, capture of volatile gases – including $^{129}I$, $^{85}Kr$, $^{14}C$ ($CO_2$), $^{3}H$



**Common metal clusters (molecular building blocks)**



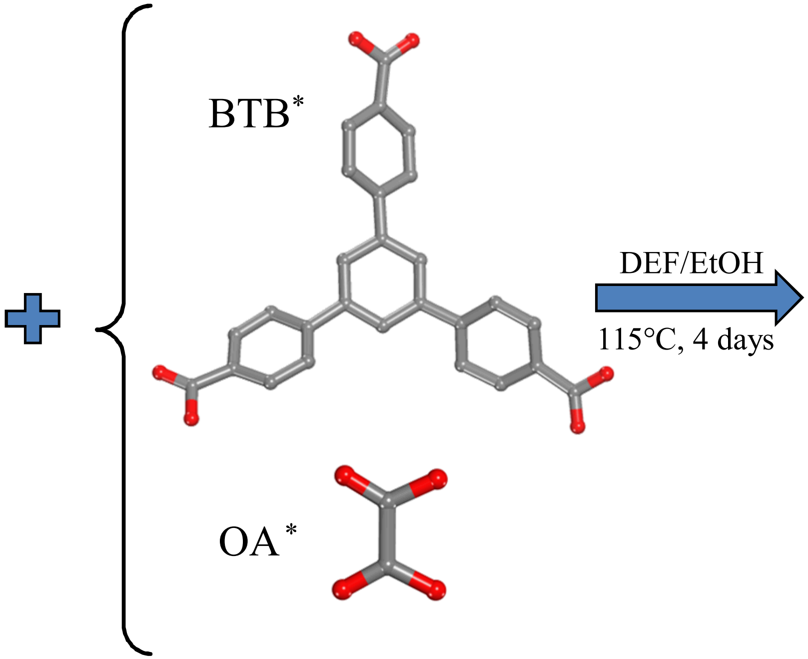



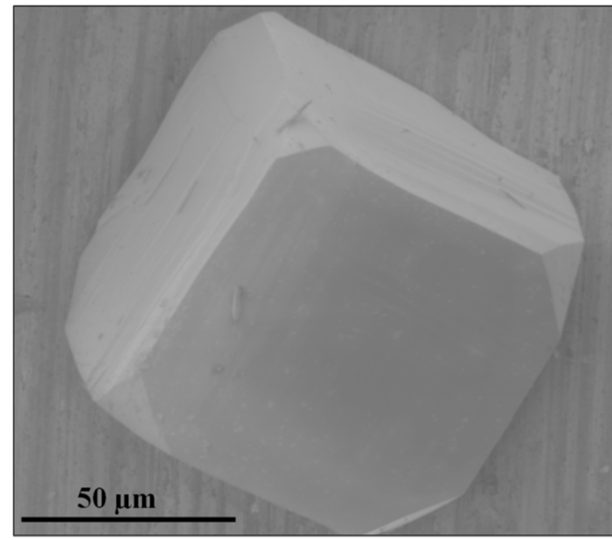
**Organic Linking Units**

# SMOF-1 (Sandia Metal-Organic Framework-1): A Novel In-BTB framework

$In(NO_3) \bullet H_2O$ + 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) + 1.5 oxalic acid (OA) + N,N'-diethylformamide(DEF) / EtOH mixture; 115° C, 4 days -> $In(BTB)_{2/3}(OA)(DEF)_{3/2}$

$In(NO_3)_3 \cdot H_2O$



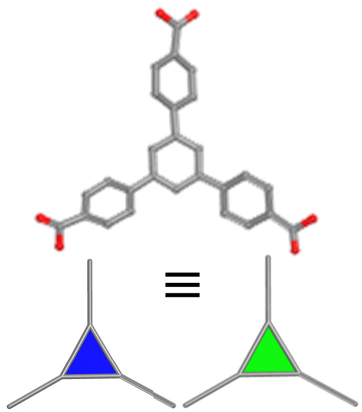




Cubic, 3-periodic
a= 33.975(3) Å, Ia-3
V= 39,217(10) $Å^3$

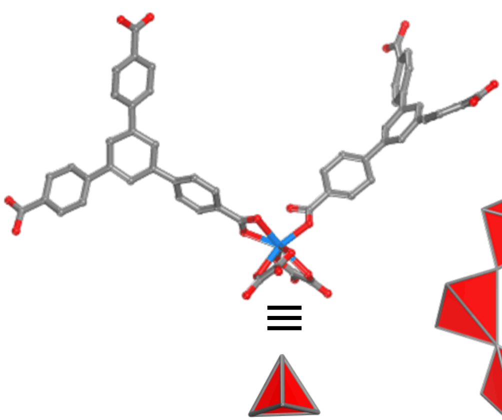
✓The first In-BTB reported net
✓The first oxalic acid-BTB system explored to date

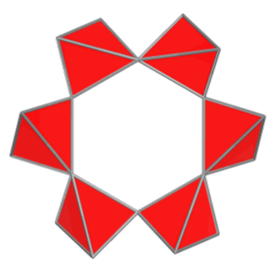
*J. Am. Chem. Soc.* **2012,** 134 (9), 3983.

# Structure Determined by Single Crystal X-ray Crystallography
# Topological evaluation: Unprecedented (3,3,4) Trinodal Net

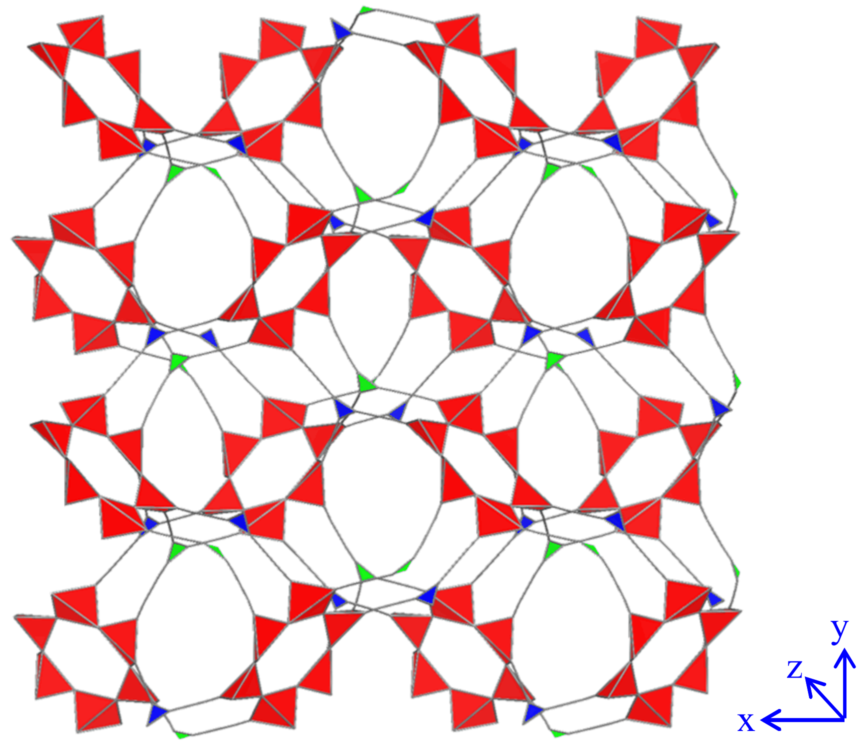



Two topologically distinct 3-connected nodes



4-connected node

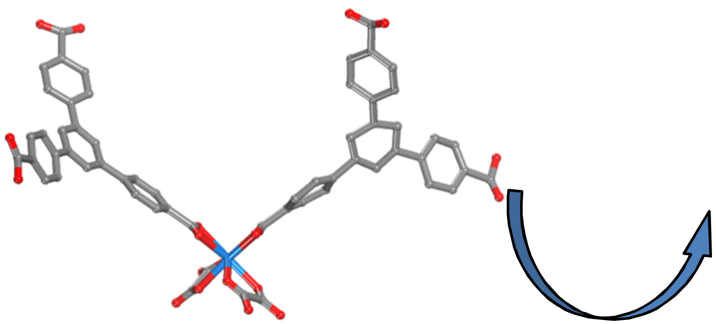


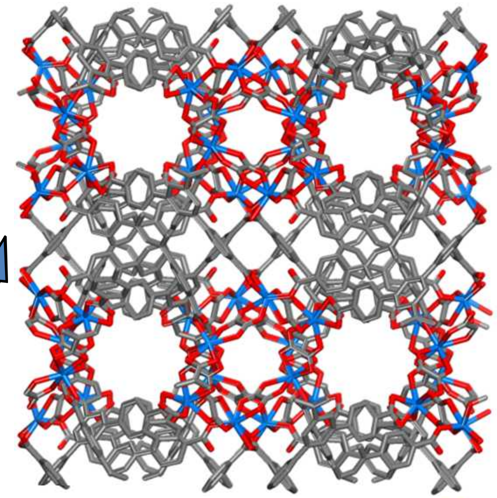

Coordination sequences:
V1 : 3 9 22 36 58 88 114 151 196 234
V2: 3 9 22 39 54 79 119 151 186 240
V3: 4 10 21 39 60 85 117 154 195 242

The short Schläfli (point) symbol: $\{6^3.8^3\}3\{6^3\}2$

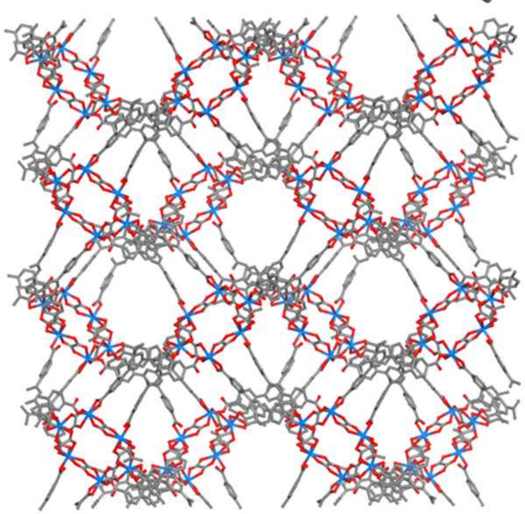
# SMOF-1 (Sandia Metal-Organic Framework-1): A Novel In-BTB framework

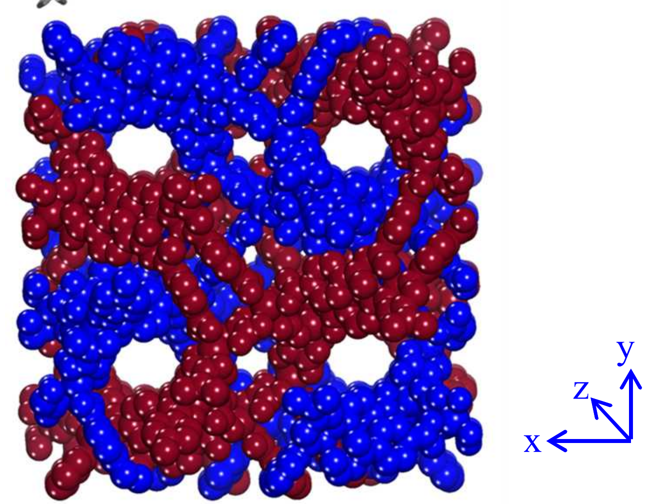
$In(BTB)_{2/3}(OA)(DEF)_{3/2}$





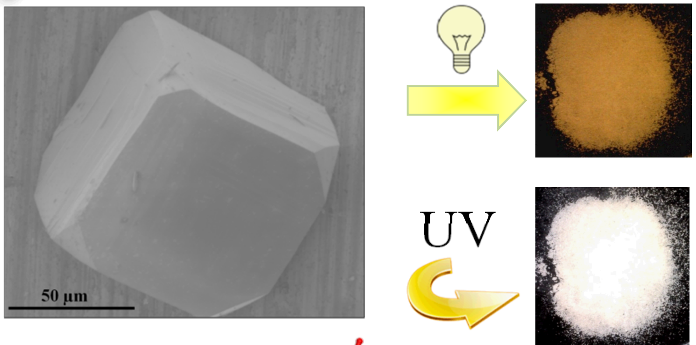
Potential open channels in all directions, accessible through passages of ~4.3Å



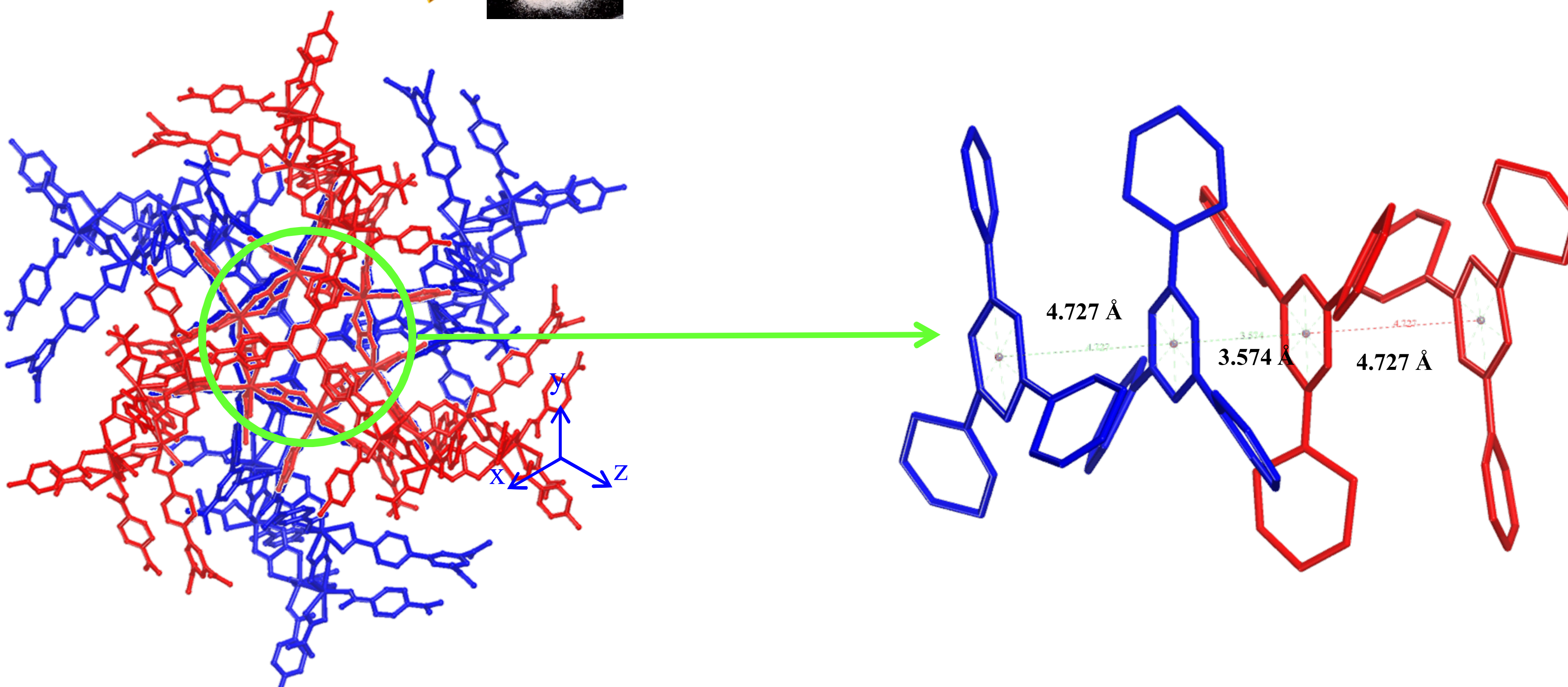



Corrugation ⟺ Interpenetration

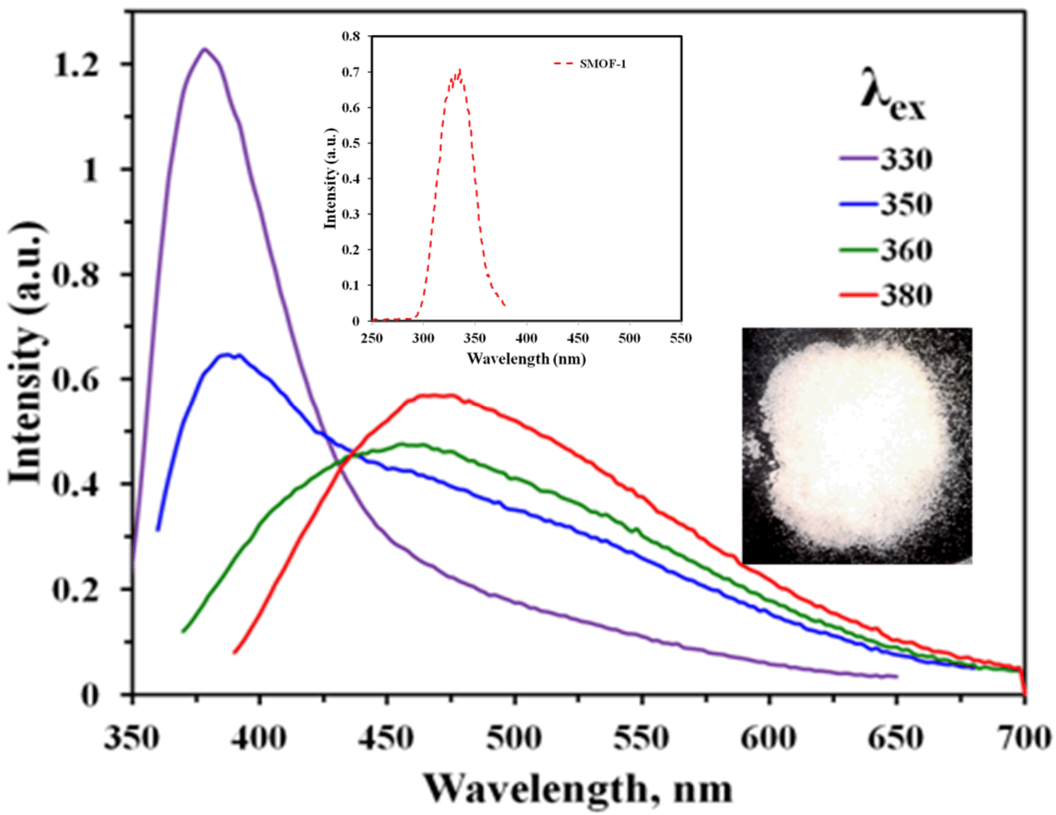
# SMOF-1: White Light Emitter Due to Framework Corrugation and Interpenetration




Unique arrangement of BTB linkers in SMOF-1 results in a cascade of π---π* aromatic interactions



# Direct white-light broadband emission : Combination of π---π* aromatic interactions & Ligand to Metal charge transfer (LMCT)




Excitation and emission spectra in SMOF-1

Color properties in SMOF-1

| $\lambda_{ex}$ | CRI* | CCT* (K) | x | y |
|---|---|---|---|---|
| 330 | 77.4 | 34463 | 0.209 | 0.193 |
| 350 | 84.5 | 22413 | 0.241 | 0.268 |
| 360 | 85.1 | 33290 | 0.234 | 0.275 |
| 380 | 81.1 | 21642 | 0.235 | 0.387 |

✓CRI values fall within intended ranges (81-85)

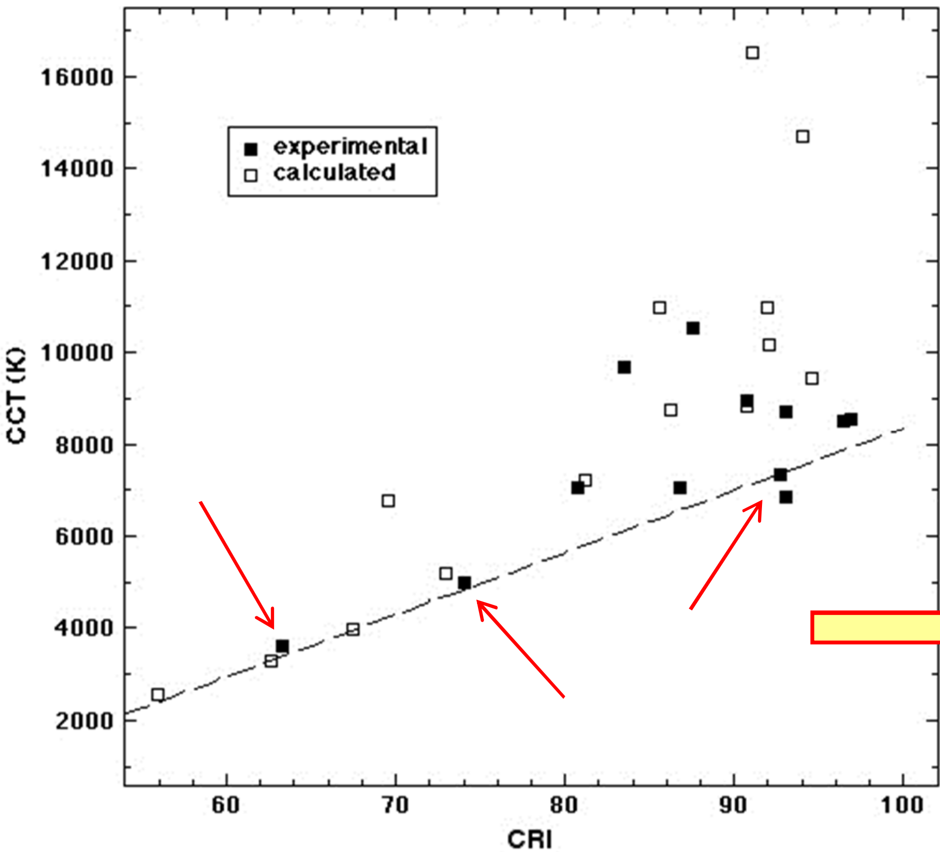
- High CCT (21642-33290 K)

*CRI (Color Rendering Index) ~ 90
*CCT (Correlated Color Temperature) ~ 3200

Department of Energy; Solid-State Lighting
http://www1.eere.energy.gov/buildings/ssl/

# Optimized Simulated Spectra Guides Successful In-framework Eu Co-doping

Calculated and experimental CCTs and CRIs for 2.5, 5, and 10% Eu-doped SMOF-1



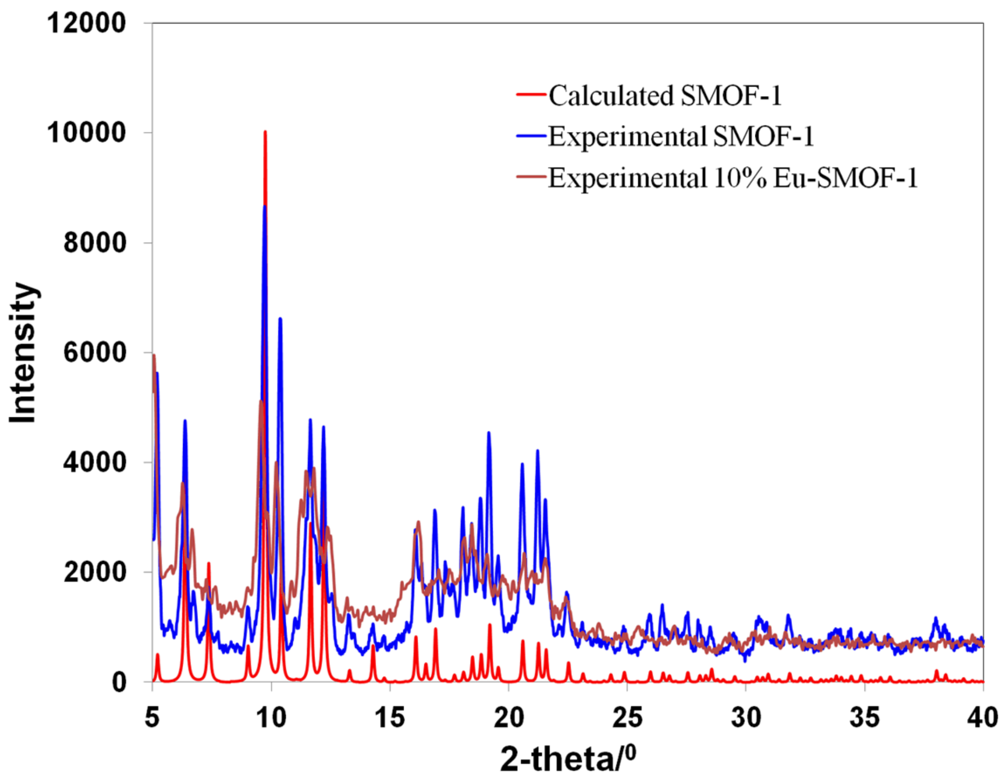

- *Simulated spectra* were generated by summing an SMOF-1 and $Eu^{3+}$ spectra, at excitation wavelengths of 350, 360, and 380 nm, respectively.

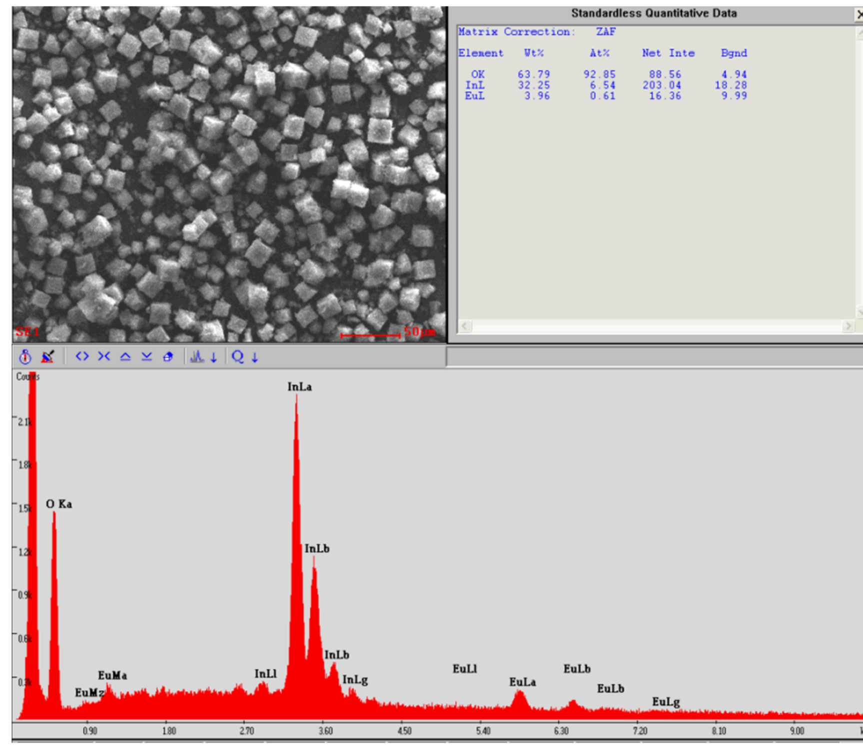
- Then, the amplitudes of each spectra were varied to find the optimal color properties.

- The best values of CRI and CCT fall *along* or *below* the dashed line in the plot

By increasing the $Eu^{3+}$ concentration to 10%, the CRI and CCT shift closer to the set target of CRI~90 and CCT~3200K

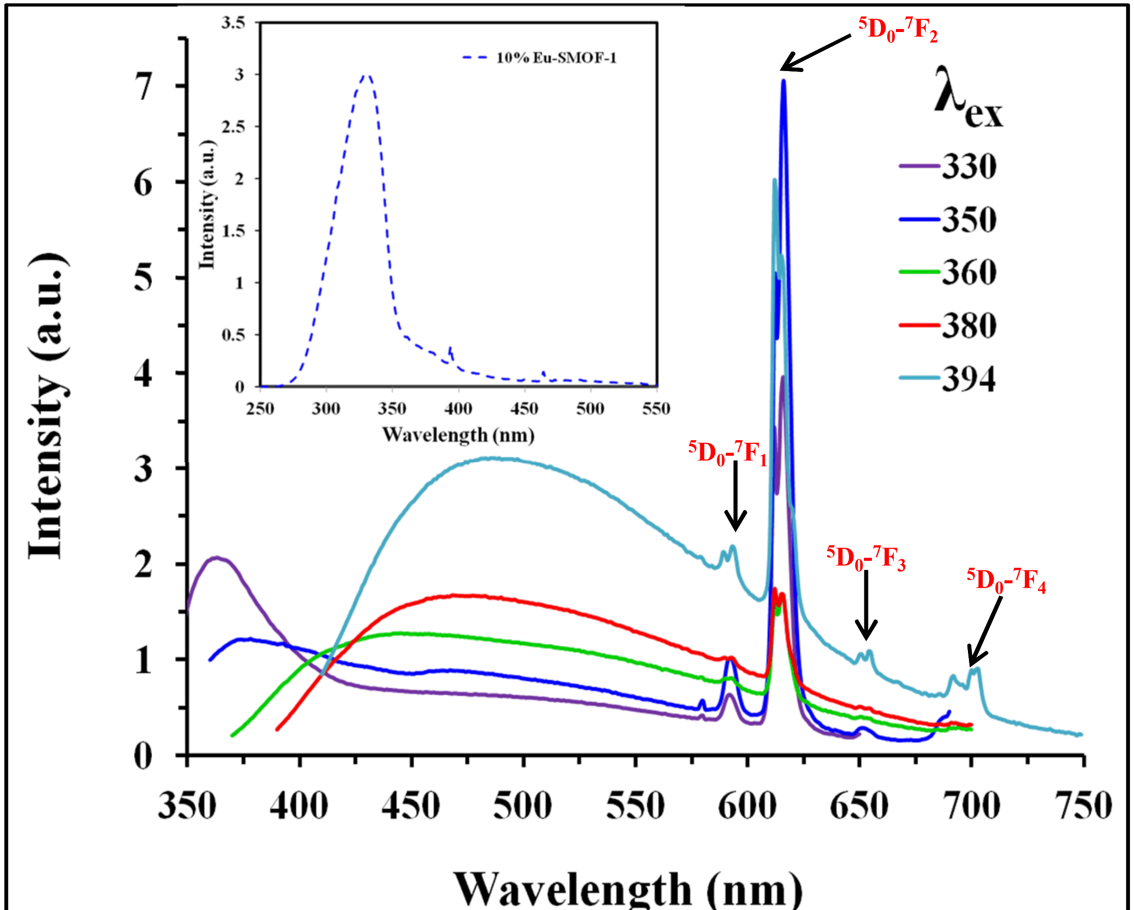
# Successful In-framework Eu Co-Doping at 2.5, 5, and 10%




Unit cell refinement of the 10% Eu-doped SMOF-1 sample reveals *enlarged unit cell parameters* a=34.57(6) Å, compared to a=33.975(3) Å.

# Enhanced System Tunability: Improved color Properties within Framework 10% Eu Co-doping




Color properties in 10% Eu-doped SMOF-1

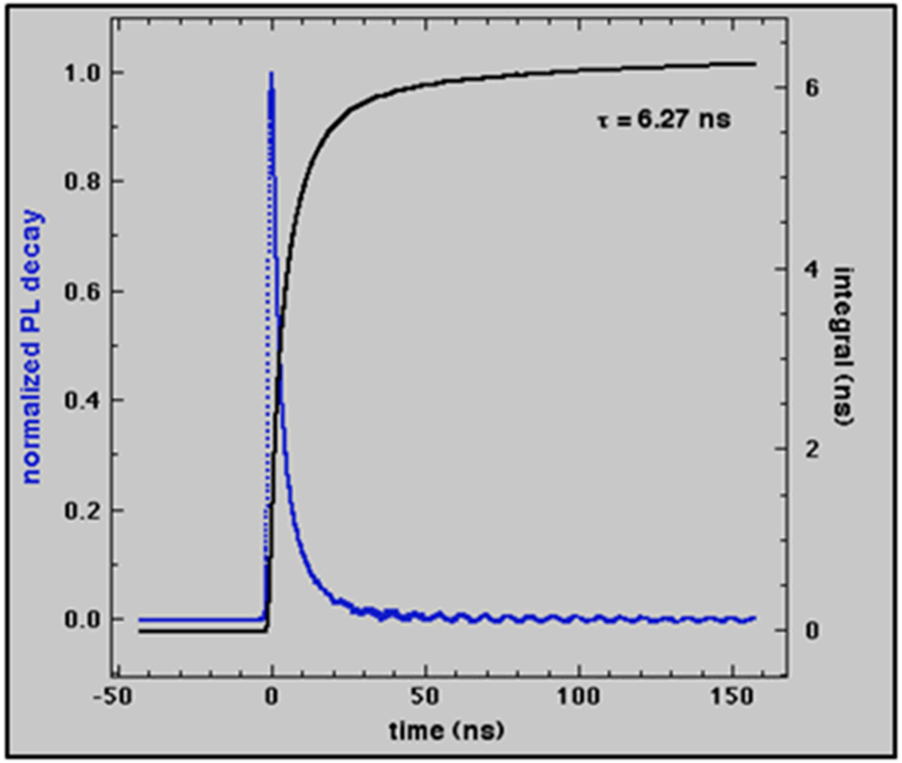
| $\lambda_{ex}$ | CRI | CCT (K) | x | y |
|---|---|---|---|---|
| 350 | 63 | 3606 | 0.369 | 0.301 |
| 360 | 81 | 7068 | 0.309 | 0.298 |
| 380 | 93 | 8695 | 0.285 | 0.309 |
| 394 | 93 | 6839 | 0.304 | 0.343 |

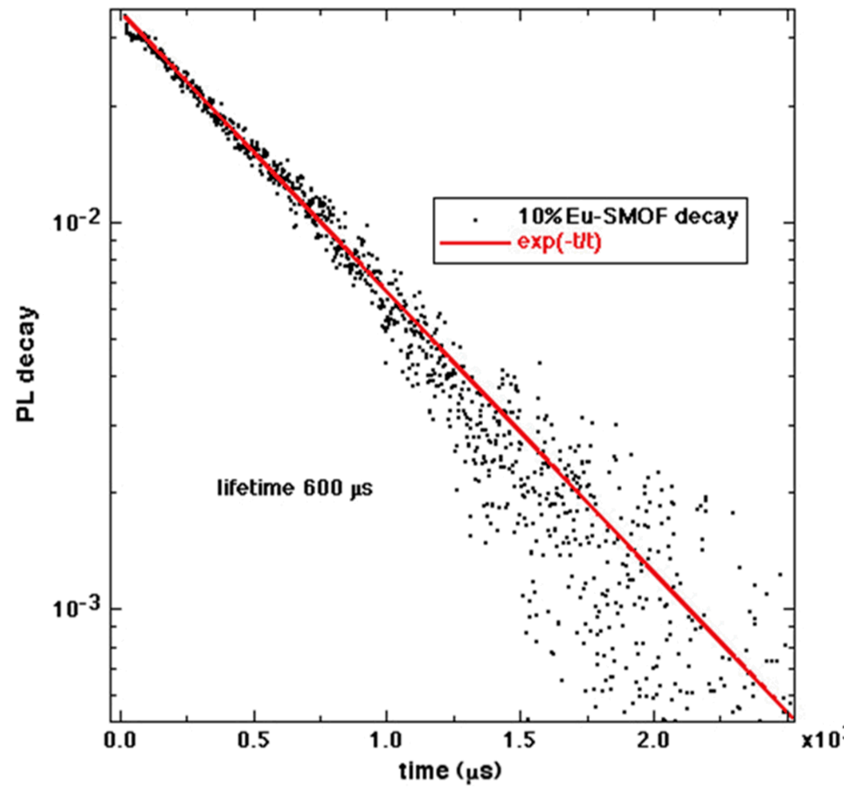
✓CCT values are significantly improved

Absolute QY ~ 4.3% at 330 nm

Narrowband emission peaks observed from the $Eu^{3+}$ component, attributed to the parity forbidden $^5D$-$^7F$ transitions, and electric dipole transitions

# Framework Tunability is Reflected in the PL Lifetime



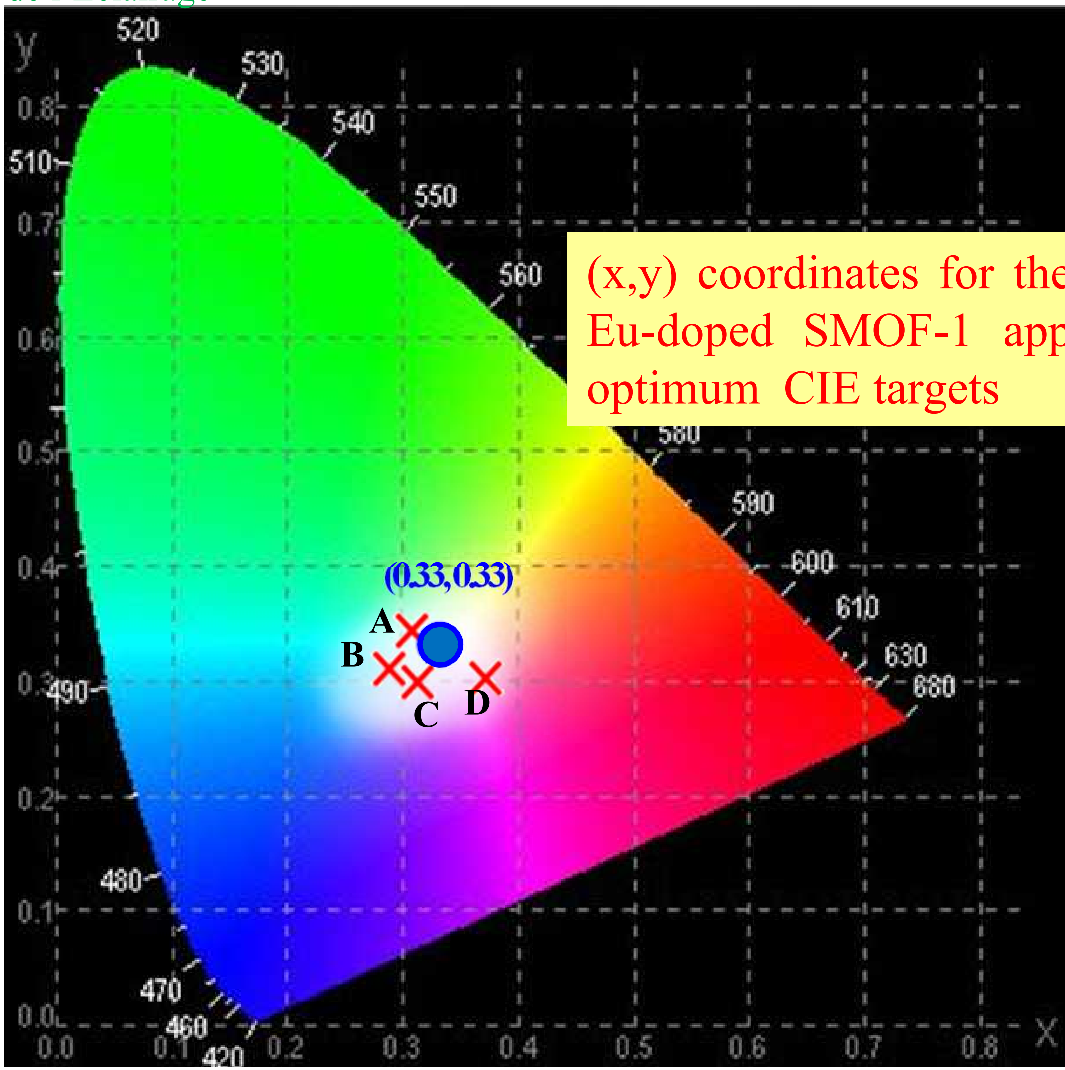




SMOF-1 harmonic average lifetime **6.27 ns**

10% doped Eu-SMOF-1 harmonic average lifetime **600 µs**
**(long lifetime: low oscillator strength of 4f-4f transitions of $Eu^{3+}$)**

# CIE* Optimum White-Light Chromaticity Coordinates Set at (0.33, 0.33)

*CIE: Commission Internationale de l'Eclairage




(x,y) coordinates for the 10% Eu-doped SMOF-1 approach optimum CIE targets

Metal–Organic Frameworks
DOI: 10.1002/anie.201203719
2012, 51, 8431

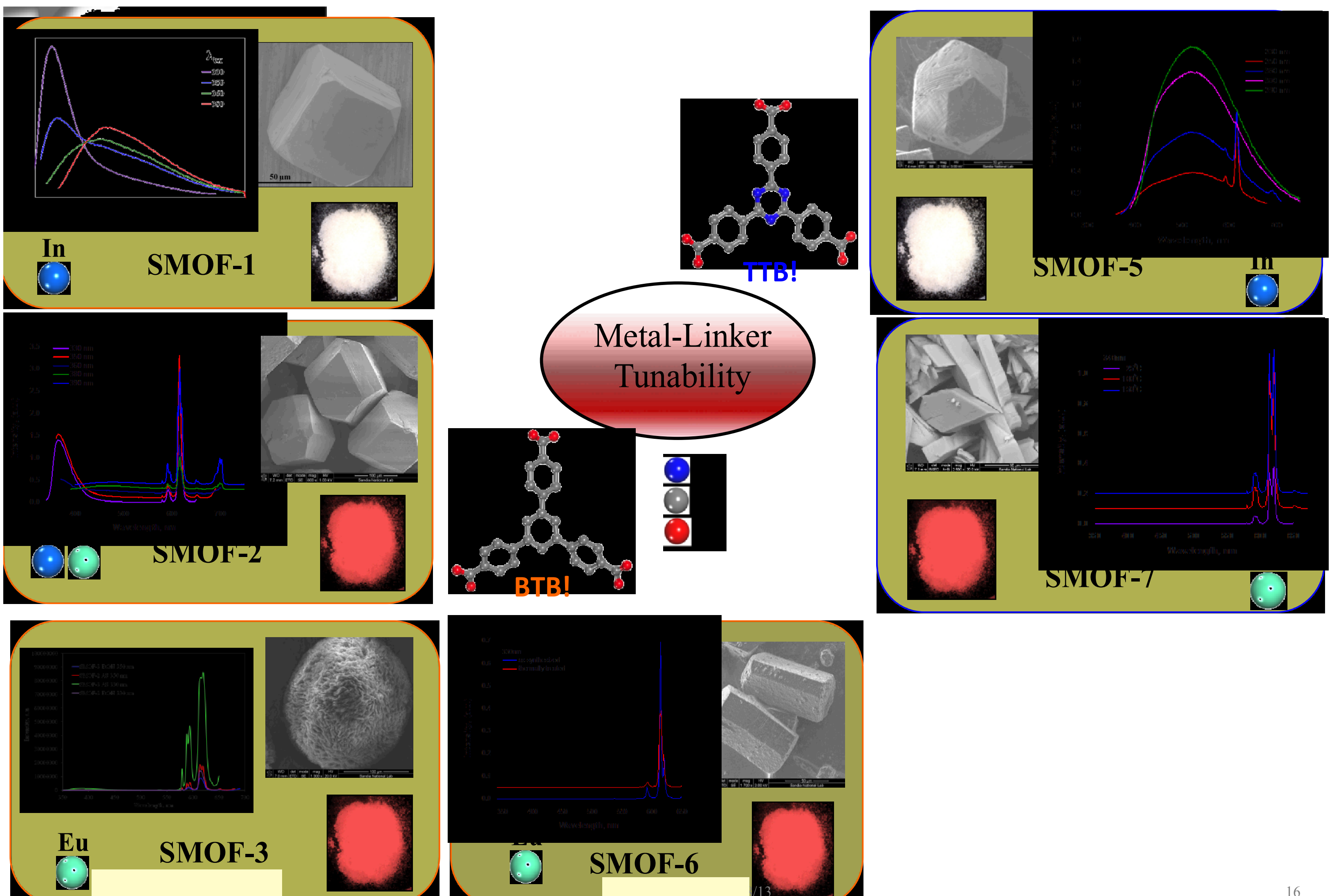
**Doping Light Emitters into Metal–Organic Frameworks****

*Paolo Falcaro and Shuhei Furukawa**

doping · light emission · metal–organic frameworks · molecular devices · porous coordination polymers

A-D: (x, y) chromaticity coordinates for $\lambda_{ex}$= 394, 380, 360, 350 nm.

# Platform of related frameworks with tunable color properties via systematic variations of metal-linker

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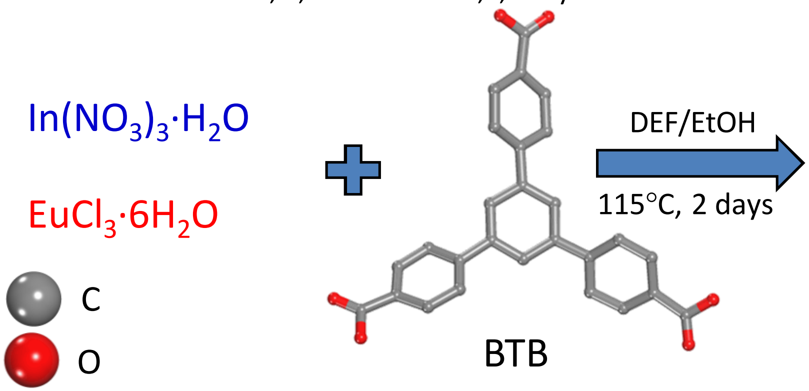
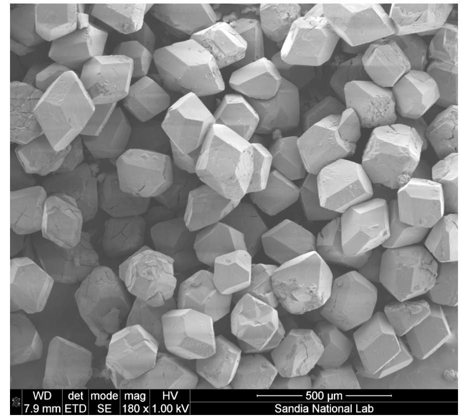
# Advanced Materials SMOF-2:
# Mixed In-Eu BTB Red Emitter Framework

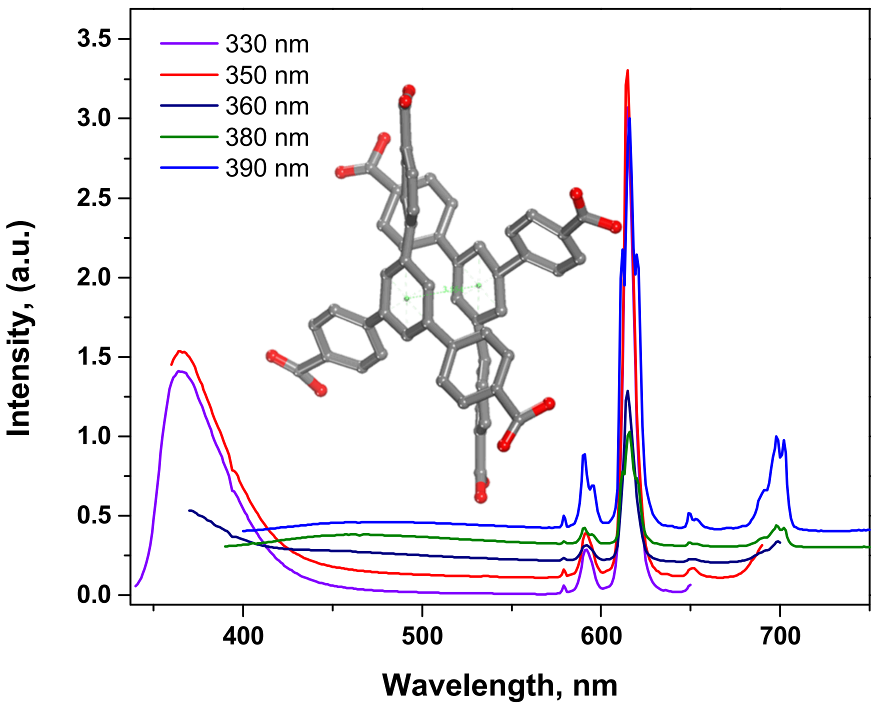
4,4',4'' -benzene-1,3,5-triyl-tri-benzoic acid



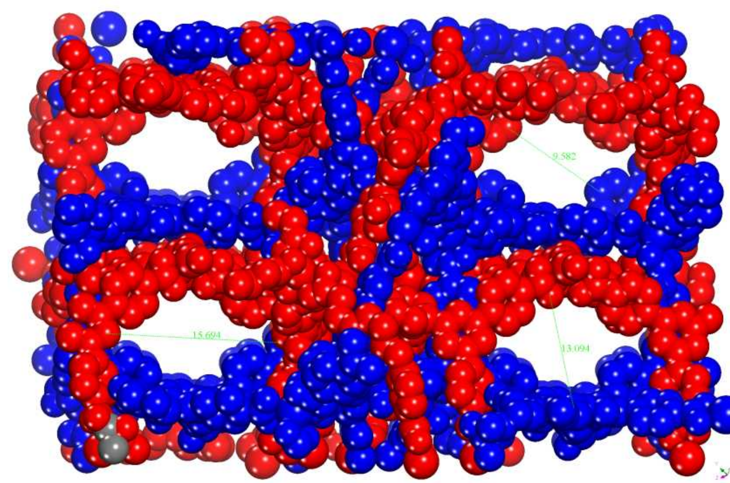




Single-crystal X-ray diffraction

Hexagonal, 3D framework
Space group: R-3
a= b= 43.671 Å
c = 41.867 Å
α= β= 90°
γ= 120°
Volume= 69149.5 $Å^3$




Absolute QY increases to ~ 11.2 %



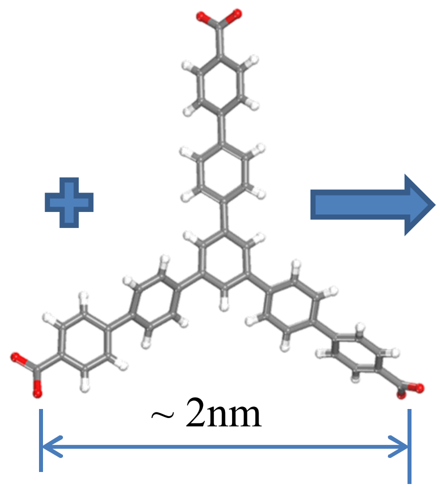
Sava, D.F. et.al, Chem. Mater. 2014, *26* (9), 2943–2951

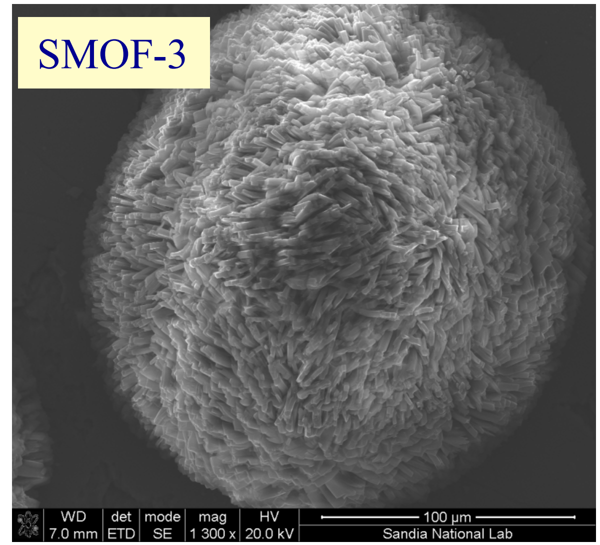
# Advanced Materials: SMOF-3
# Novel MOF red light emitters

Another platform for tuning light emissions

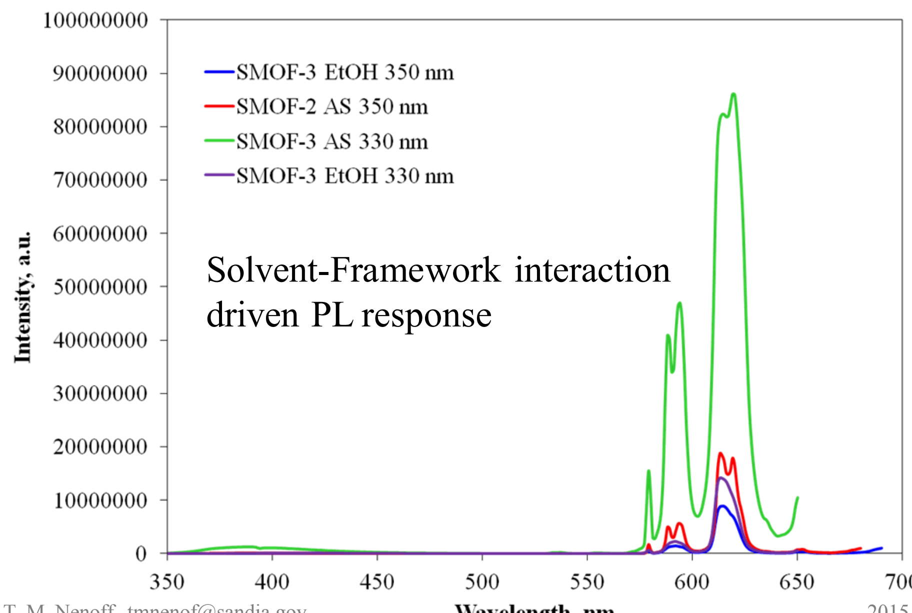
Sava, D.F. et.al, 2012, in prep

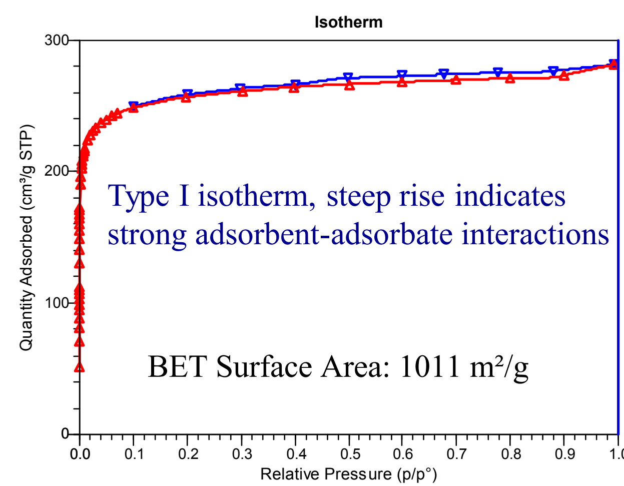
$EuCl_3 \cdot 6H_2O$ +



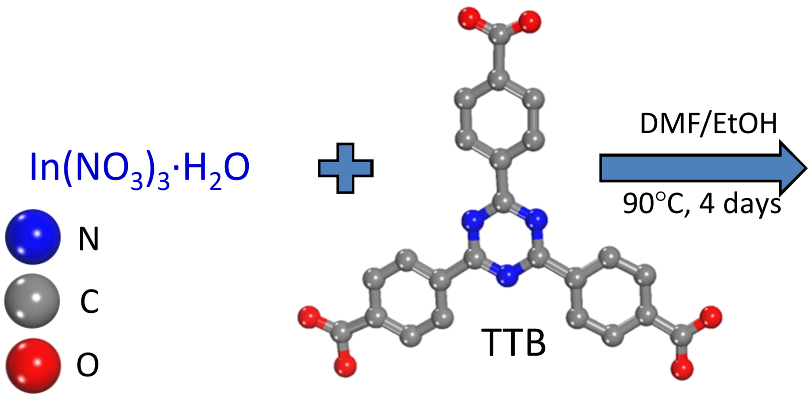

Absolute QY increases to = 21 %

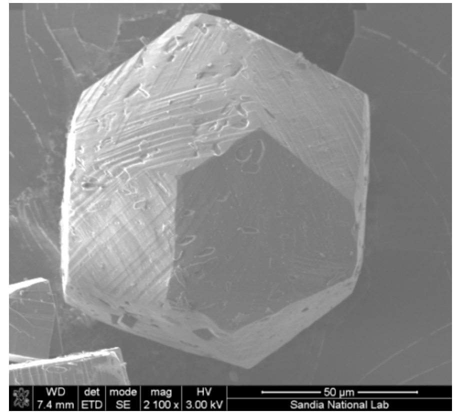


# SMOF-5: a SMOF-1 TTB-based analogue with improved color properties without dopants

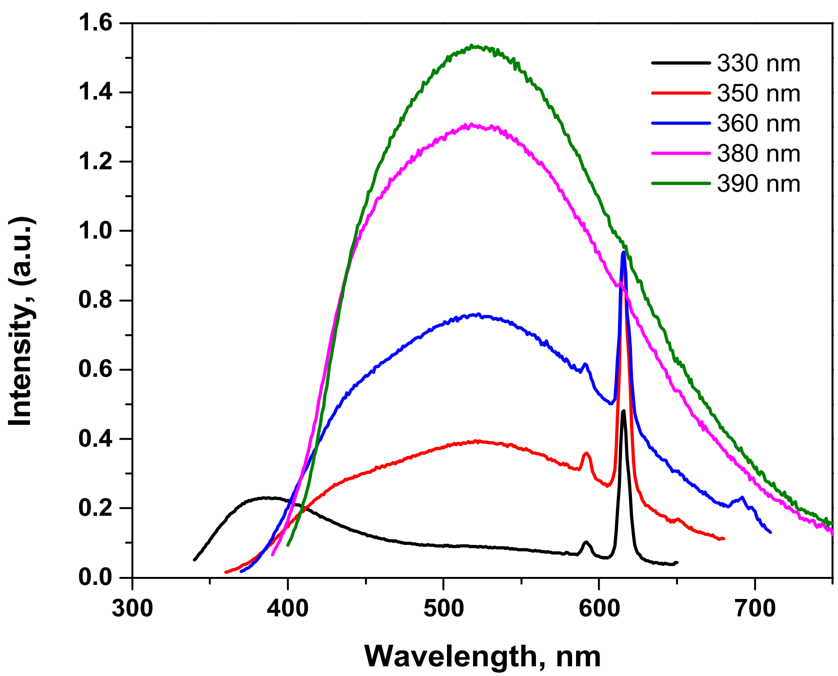
4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid




Single-crystal X-ray diffraction

Orthorhombic, 3D framework
Space group: IBCA
a= 32.092 Å
b= c= 34.184Å
α= β= γ= 90°
V= 37501$Å^3$

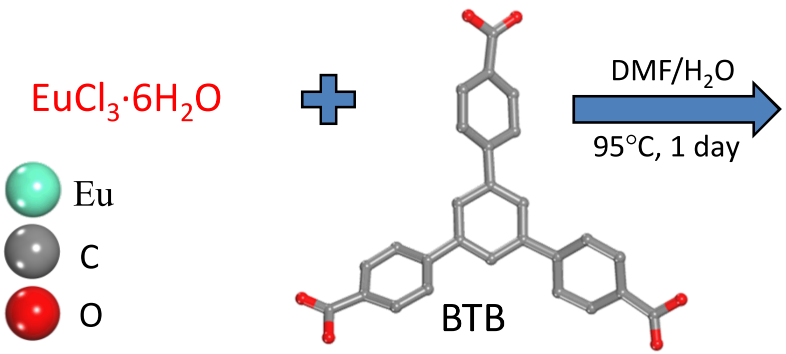


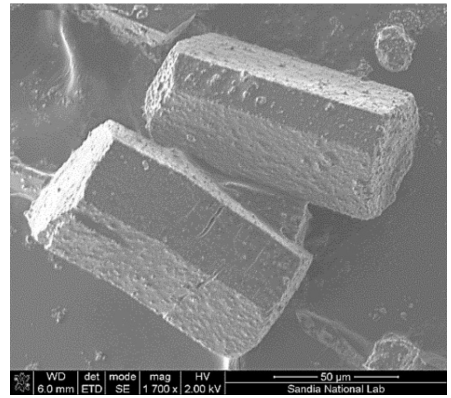

| Excitation wavelength (nm) | CRI | CCT (K) | x | y |
|---|---|---|---|---|
| 330 | 74 | 6236 | 0.323 | 0.281 |
| 350 | 96 | 5422 | 0.335 | 0.36 |
| 360 | 88 | 6100 | 0.317 | 0.364 |
| 380 | 82 | 6415 | 0.309 | 0.368 |
| 390 | 81 | 6140 | 0.315 | 0.381 |

✓CCT and CRI color properties fall within intended ranges without any additional doping

# SMOF-6: Eu-BTB red emitter

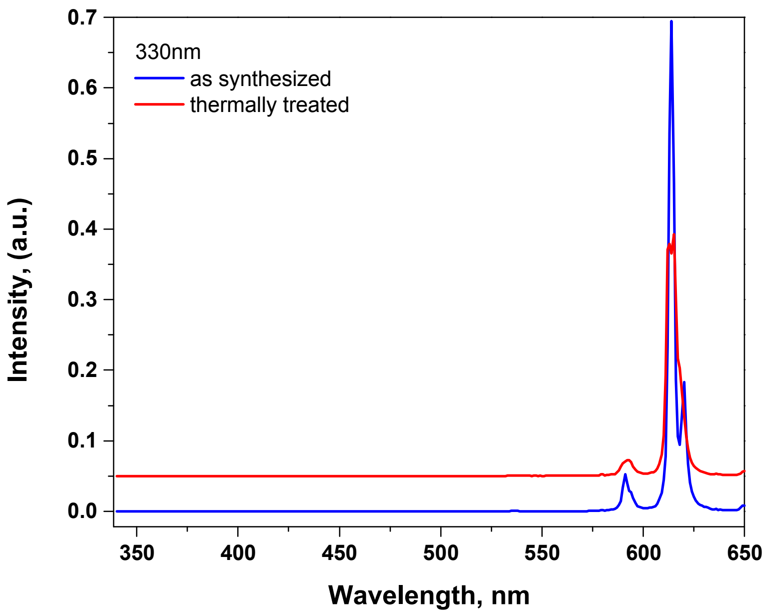
4,4',4'' -benzene-1,3,5-triyl-tri-benzoic acid

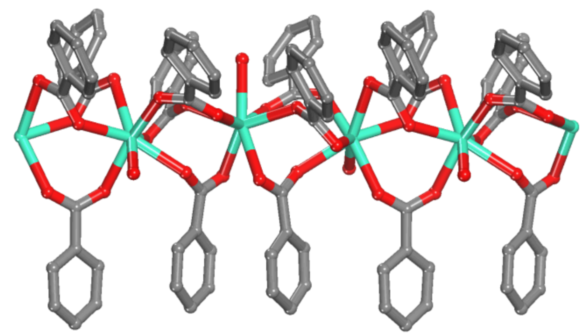



Single-crystal X-ray diffraction

Hexagonal, 3D framework
Space group: R32
a= b= 28.6264 Å
c= 12.2435Å
α= β= 90° γ=120°
V= 8689Å$^3$



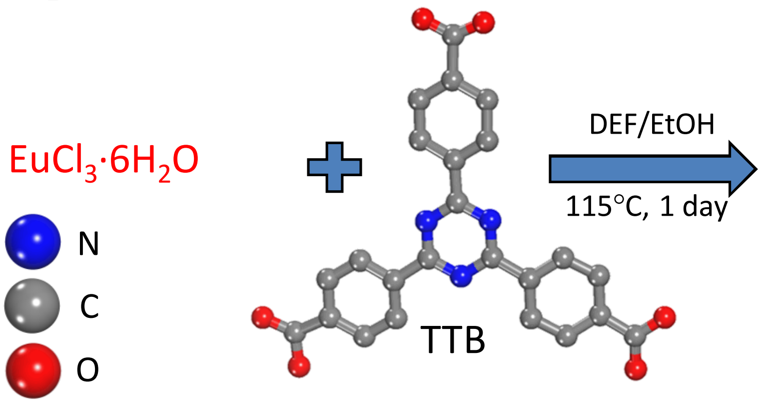



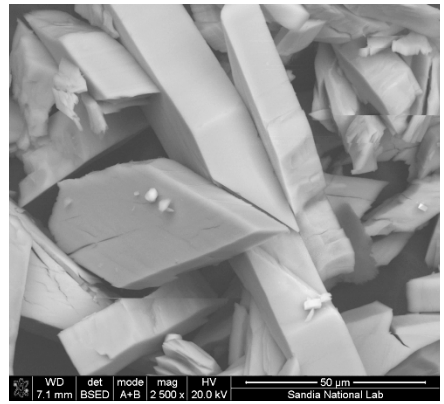
| Excitation wavelength, nm | 25°C | 100°C | 150°C |
|---|---|---|---|
| 340 | 18.8% | 11% | 14% |
| 394 | 27.4% | **41.8%** | **40%** |

Absolute QY increases to ~ 42 %

# SMOF-7: novel Eu-TTB red emitter with high efficiency and thermal stability

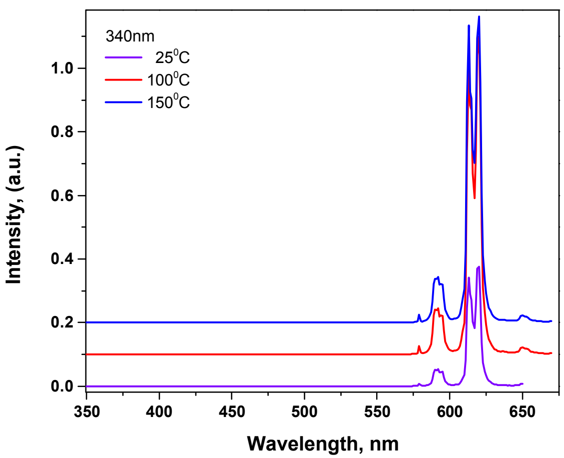
4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid

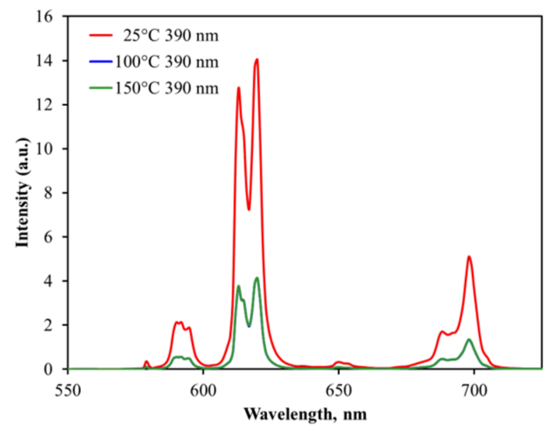



Single-crystal X-ray diffraction

Monoclinic, 3D framework
C2/c
a= 31.8177 Å
b= 13.9924Å
c= 19.3398 Å
α=γ= 90° β= 98.544°
V= 8514.56 Å$^3$



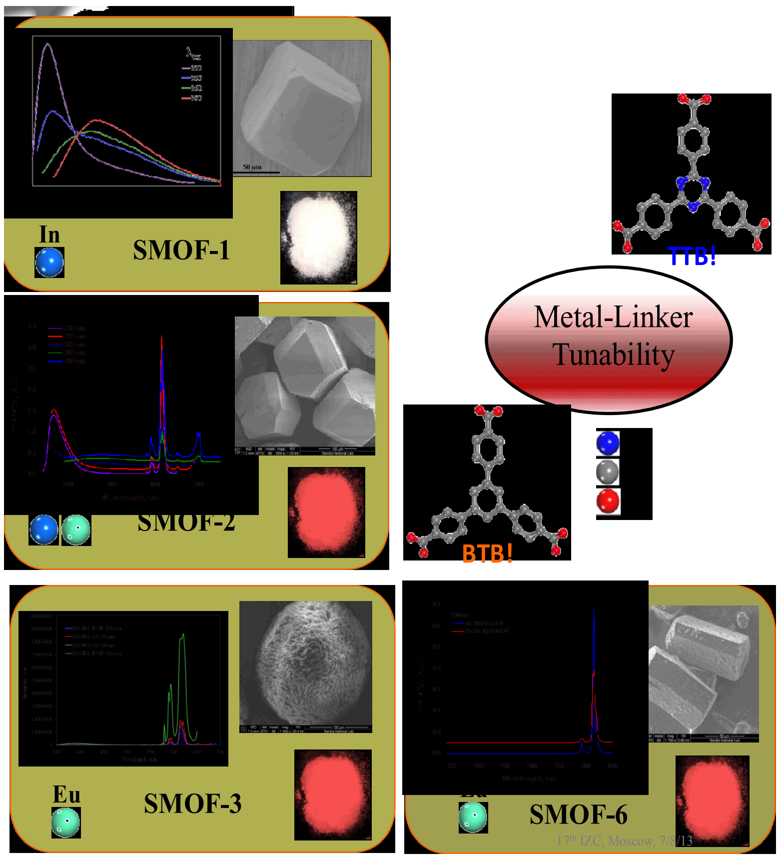



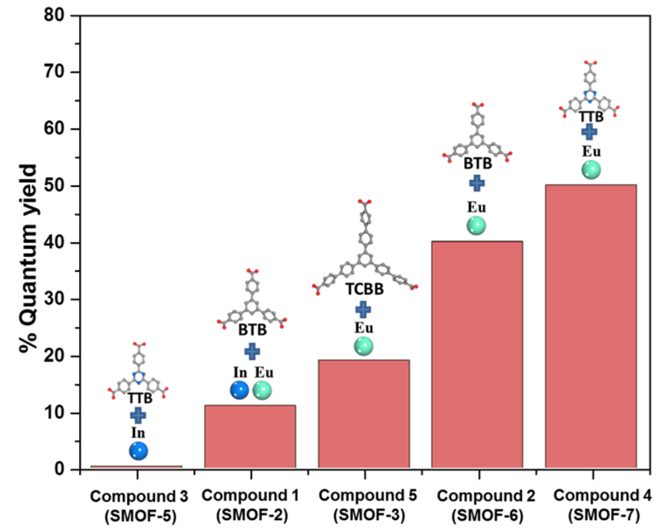

Absolute QY increases to ~ 50 %

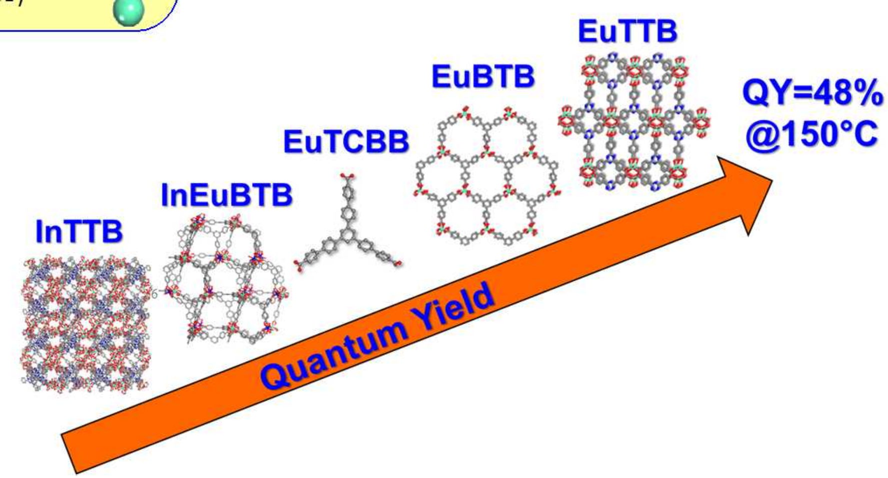
| Excitation wavelength, nm | 25°C | 100°C | 150°C |
|---|---|---|---|
| 340 | 46% | 50% | 48% |
| 394 | 22% | 22.3% | 19% |

# Platforms for Tuned Light Emissions, SMOF-7 Max QY = 48% @ 150°C

- Second Generation Materials. Tuned MOF frameworks (metal centers & ligands)
- Results: MOF framework chemistry (charge transfers: ligand-ligand, ligand-metal; metals; temperature stability) dictates the Quantum Yield, Thermal Stability, and Processability




*Chem. Mater.* **2014**, *26* (9), 2943
US Patent Application #14/319,675, Nov 17, 2014

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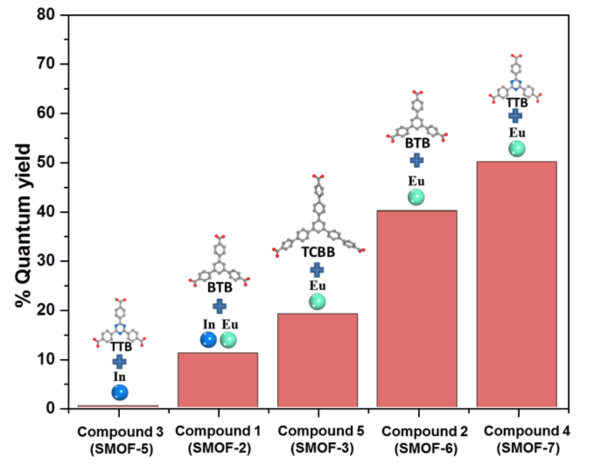
# Summary

- Introduced a prototype novel MOF material featuring intrinsic broadband direct white light emission

- Tunable platform which allows for the significant enhancement of the associated color properties upon $Eu^{3+}$ co-doping, approaching values required for SSL applications

- Quantum yields: structure property relationship
  highest values for MOFs at high temperatures: maintained coordination environment around the metal center, plus electronic configuration of the organic linker




- SMOF-7 (compound 4): structural integrity is not affected by temperature; strong $Eu^{3+}$ emission is retained. Ligand – metal charge transfer is retained.

| | % QY compd **2** | | % QY compd **4** | | % QY compd **5** | |
|---|---|---|---|---|---|---|
| excitation wavelength (nm) | AS | TT | AS | TT | AS | TT |
| 340 | 18 | 14 | 46 | 50 | | |
| 350 | | | | | 14 | 15 |
| 394 | 27 | 40 | 22 | 19 | 19 | 19 |

- Future research is directed towards pre- or post-synthesis framework functionalization for enhanced SSL properties

# Sandia National Laboratories

Kauai Test Facility
Hawaii

Tonopah Test Range,
Nevada

Albuquerque, New Mexico

Livermore,California

Yucca Mountain,
Nevada

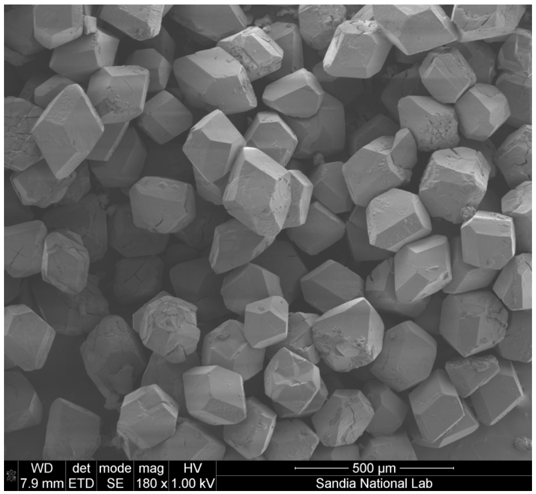
WIPP,
New Mexico

Pantex, Texas

# Extra slides

# On-going studies SMOF-2: A Novel In-30% Eu- BTB Framework

$In(NO_3)\bullet H_2O + EuCl_3\bullet 6H_2O$ + 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) + oxalic acid + (DEF)/EtOH
115° C, 4 days




a= b= 43.671 Å

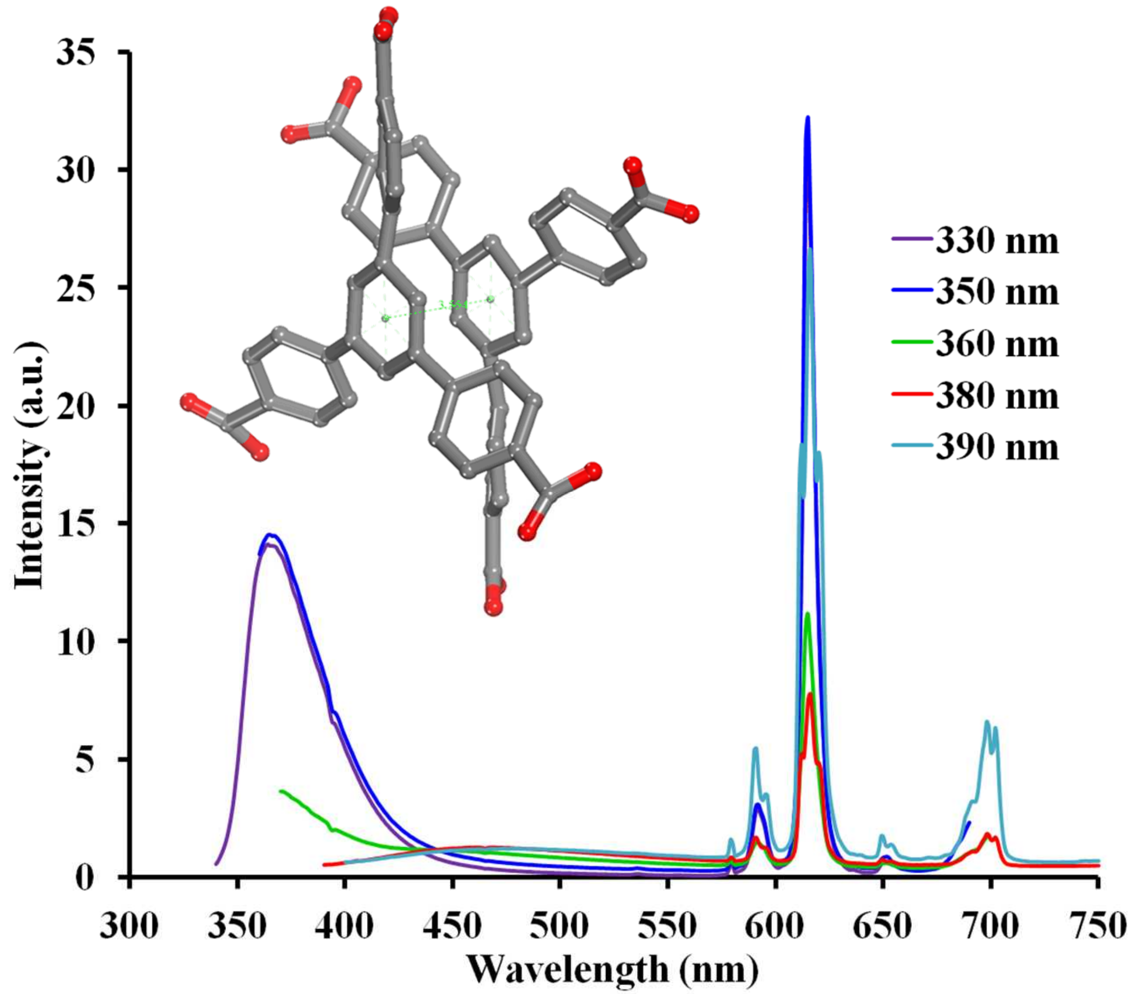
c = 41.867 Å

α= β= 90°

γ= 120°

Volume= 69149.5 $Å^3$

Absolute QY increases to ~ 11.2 %



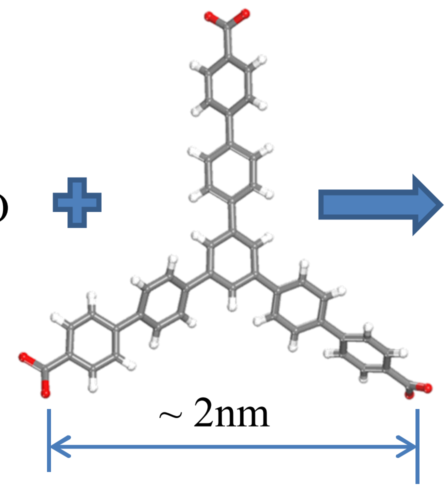

Sava, D.F. et.al, 2012, in preparation

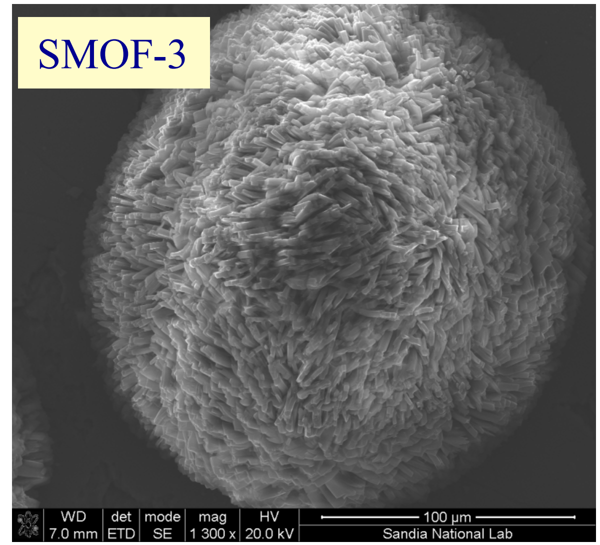
# Advanced Materials: SMOF-3
## Novel MOF red light emitters

Another platform for tuning light emissions

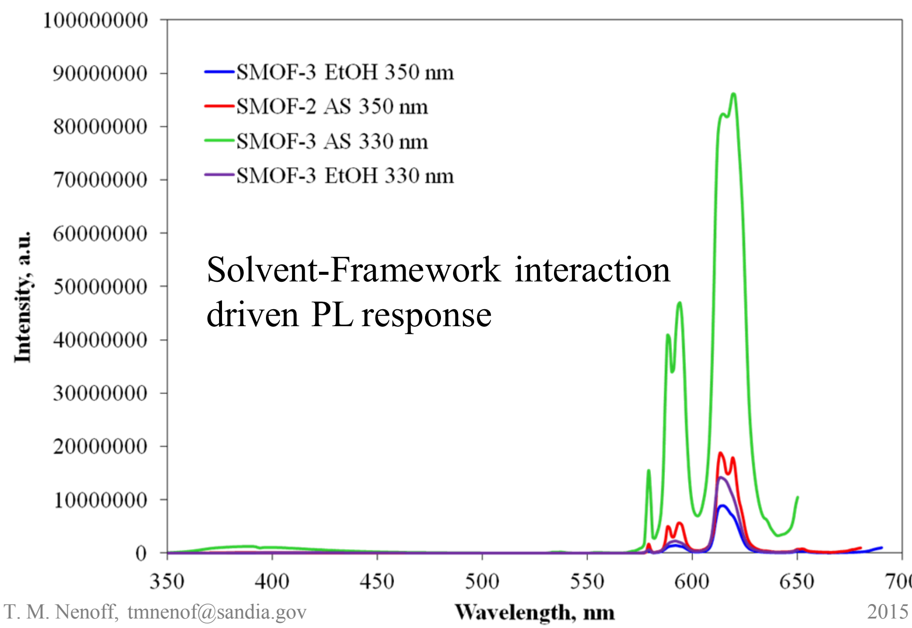
Sava, D.F. et.al, 2012, in prep

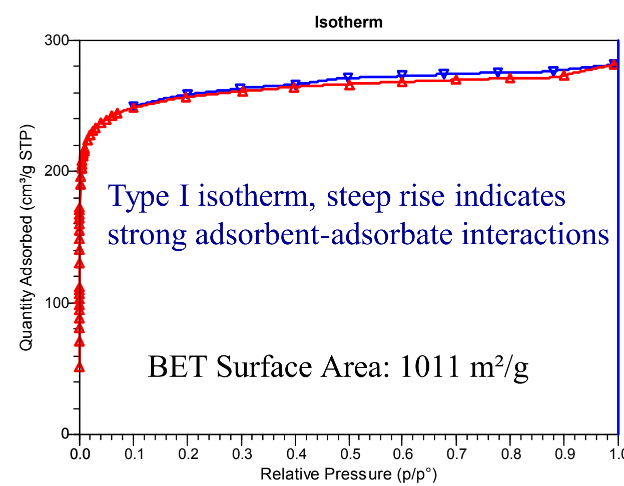
$EuCl_3 \cdot 6H_2O$




Absolute QY increases to = 21 %



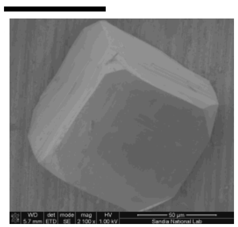



# Sandia Metal-Organic Frameworks (MOFs): Platforms for Tuned Light Emissions

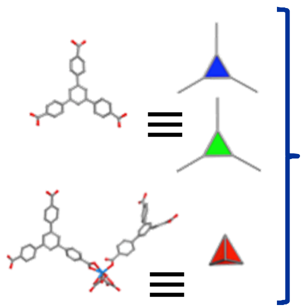
Tina Nenoff, Dorina Sava, Lauren Rohwer, Mark Rodriguez

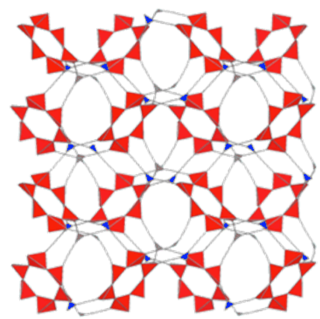
- Designed Materials for tuned light emissions with NO/Little rare earth metals, tuning of org ligand, metal, crystal frameworks
- Modeling, Design, Synthesis, PL studies of MOFs for light emissions Framework is a platform
- improved manufacturing, soft/low temp synthesis, little metal, processable organics due to durability +200°C
- unique SNL tools: combination/integration of modeling for design with proven synthesis/characterization capabilities for light emitting MOFs and PL measurements
  feedback loop to optimize materials

*JACS*, 2012, *134* (9), 3983

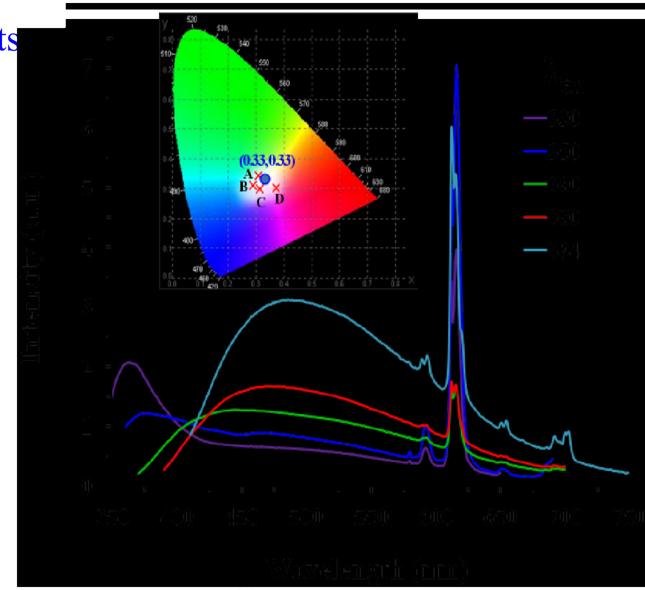


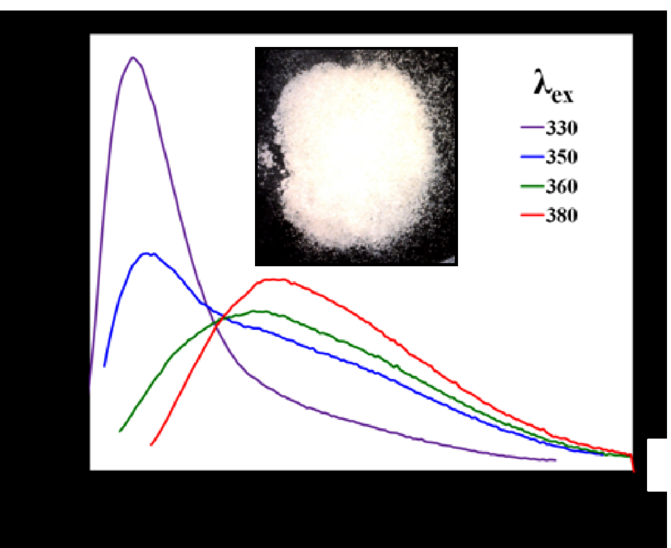
SMOF-1

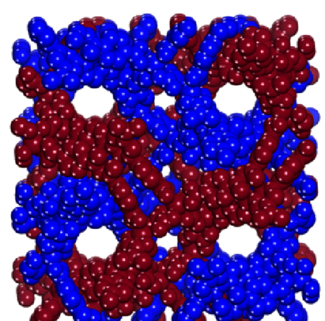


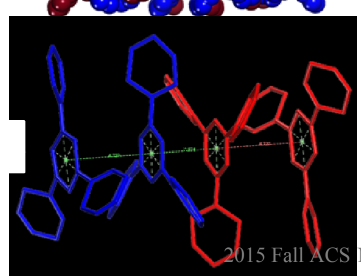


Doped SMOF-1





SMOF-2