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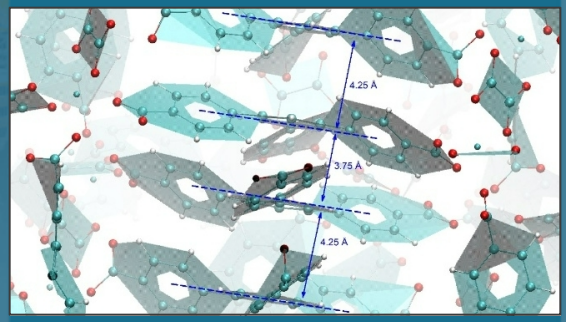
Ligand-based tunable light emission in non-REE MOF structures



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U.S. DEPARTMENT OF ENERGY NNSA

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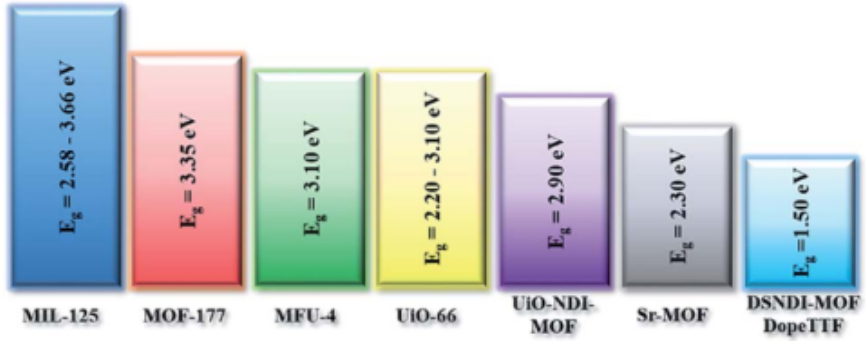
Introduction – Light Emission in MOFs

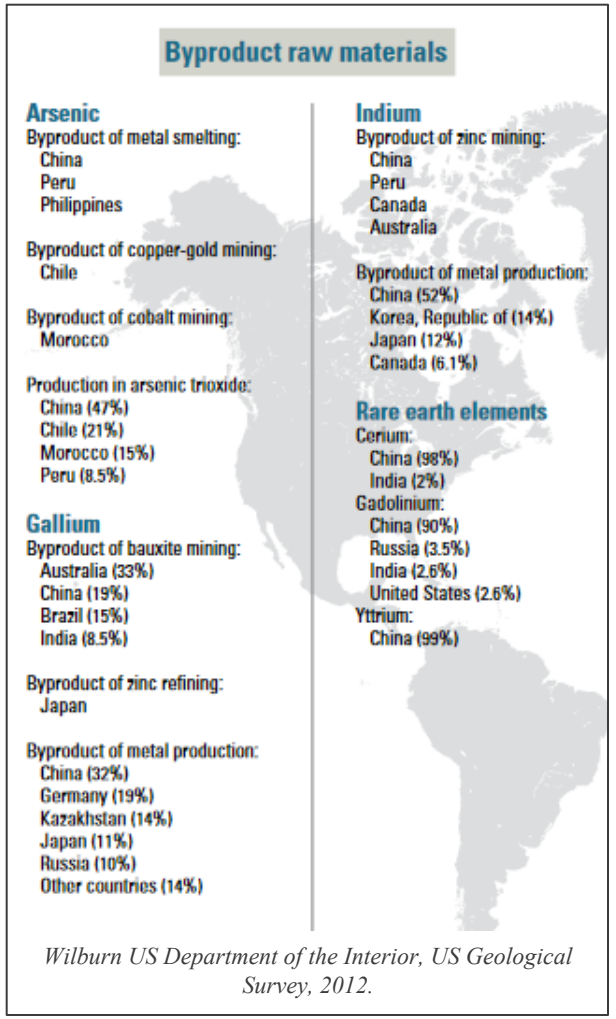
- Common light emitting materials rely on the use of rare-earth elements that are in limited supply and are inconsistently distributed globally.

- Metal-organic frameworks (MOFs) have already demonstrated tunable light emitting properties based on their composition, structure and incorporation of secondary species.



Bandgap comparison in reported MOF structures

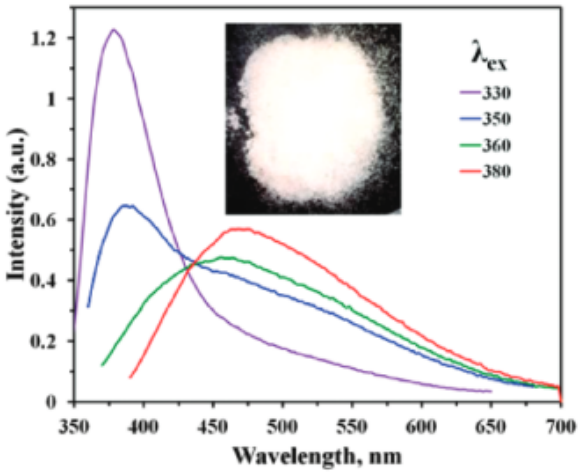
Chueh et al. J. Mater. Chem. A 7.29 (2019): 17079-17095.



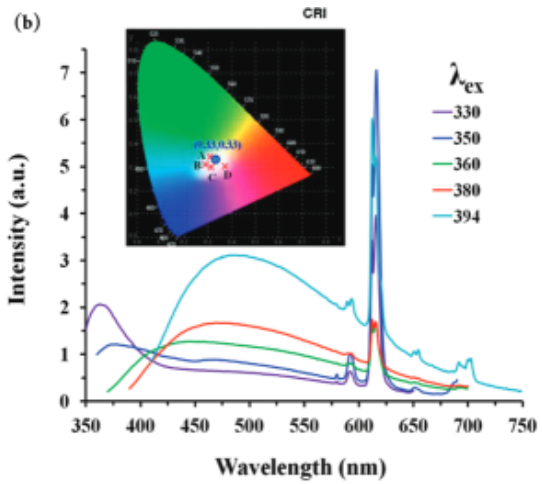
Wilburn US Department of the Interior, US Geological Survey, 2012.

- Sava Gallis and Nenoff (SNL) pioneered single component warm white light photoluminescence MOFs via the formation of interpenetrating frameworks.

Sava Gallis et al. Chem. Mater. 26.9 (2014) 2943-2951



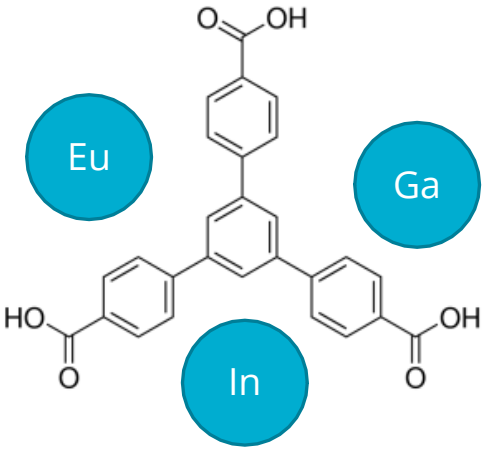
Emission spectra of SMOF-1, (inset) optical image of white light emission



Emission spectra of 10% Eu-doped SMOF 1 (inset) CIE chromaticity diagram

Sava et al. J. Amer. Chem. Soc. 134.9 (2012): 3983-3986

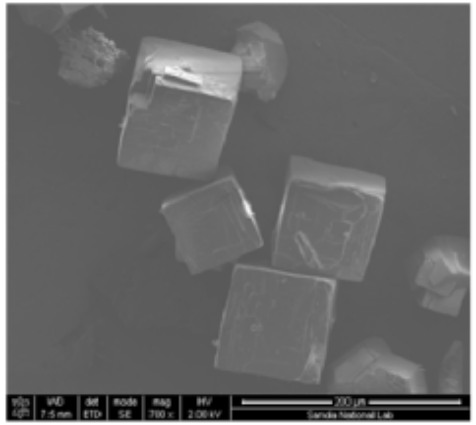
How can crystal design elements control and tune photoluminescence properties of MOFs?



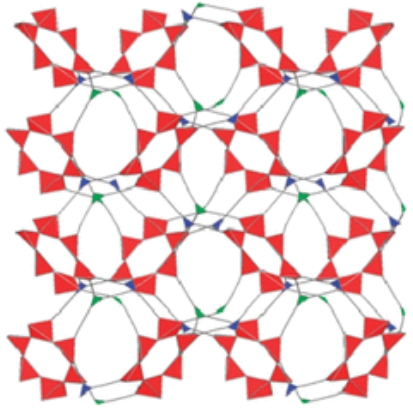
- Focus on initial success in SMOF-1 series

Sava et al. J. Amer. Chem. Soc. 134.9 (2012): 3983-3986

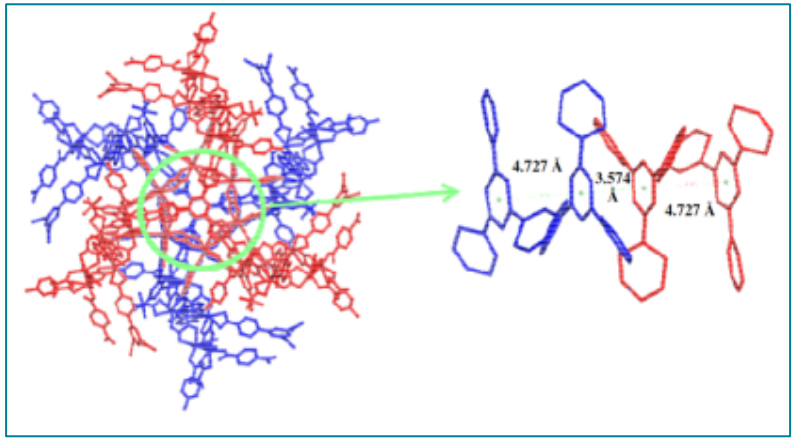
- Interpenetrated MOF structure with four stacked 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) linkers
- In, Ga, Eu, or mixed-metal centers to influence additional emission



SEM images of single crystals of as-synthesized SMOF-1



Molecular building blocks in SMOF-1 topological representation of single net



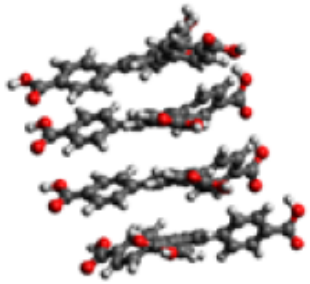
Unique stacked arrangement of BTB linkers in SMOF-1

Computational methods can probe individual features of the MOF structure to identify the impact on photoluminescence properties.

Computational approach

Evaluate Emission from Stacked Linkers

- Evaluation of UV-vis emission from stacked BTB linkers *only*
- The number (2-4) and stacking distance (3.0-4.0 Å) was varied
- Simulated via electronic structure gas phase calculations



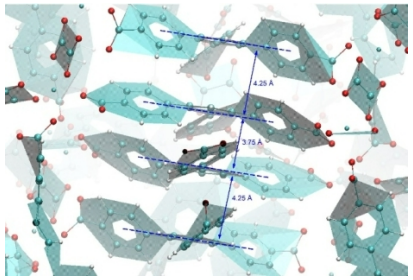
Calculation Details:

- B3LYP hybrid-functional with 6-31G(d,p) basis set
- Gaussian 16 Revision B.01
- Following optimization time-dependent DFT (TD-DFT) was performed
- UV-Vis spectra calculated via calculated electronic transitions (300-800 nm)
- Singlet and triplet states were both calculated

Refs: Frisch et al. Gaussian16 ***2016****., Hanwell et al. J. Chem. Phys.* ***1982****, 77, 3654, Lee et al. Phys. Rev. B* ***1988****, 37, 785, Becke et al. J. Chem. Phys.* ***1993****, 98, 1372, Stratmann et al. J. Chem. Phys.* ***1998****, 109, 8218, Furche et al. J. Chem. Phys.* ***2002****, 117, 7433, O'Boyle et al. J. Comput. Chem.* ***2008****, 29, 839., Boyle et al. Dalton Trans.* ***2018****, 47, 4162.*

Compositional Control of Stacking Distance

- Evaluation of change in stacking distance based on metals with different ionic radii
- Multiple compositions were evaluated (100% In, 100% Ga, 10% Eu-90% In, 25% Ga – 75%In)



- Simulated via periodic density functional theory (DFT) simulations

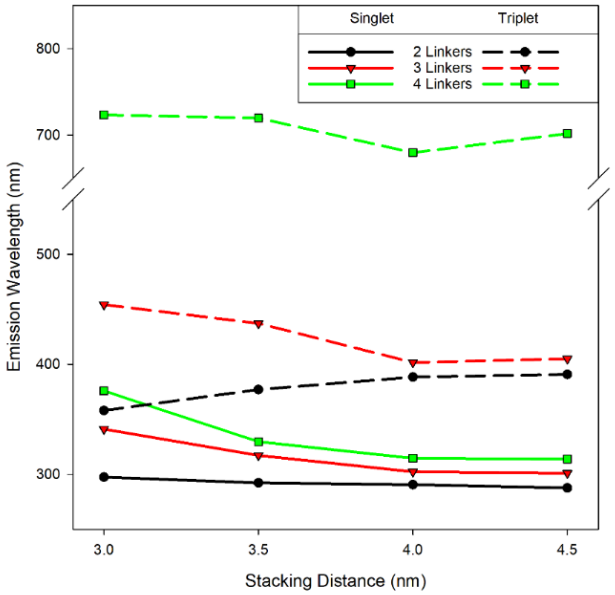
Calculation Details:

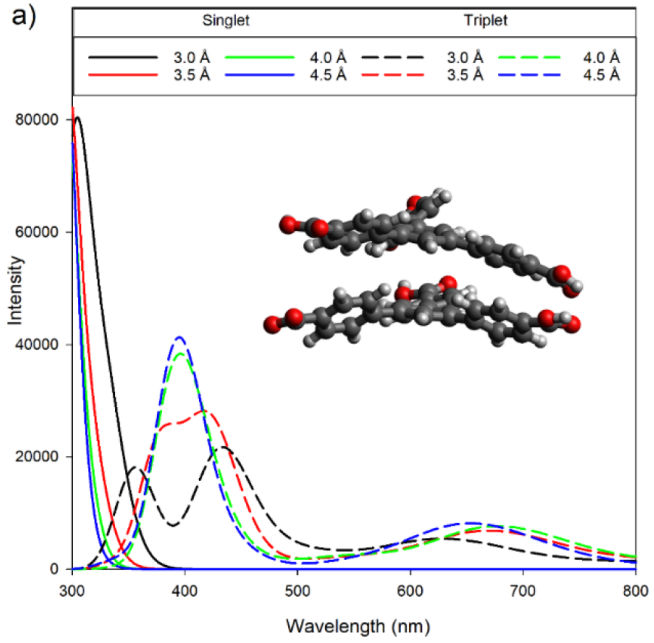
- PBE exchange correlation functional for solids (PBEsol), non-spin polarized, gaussian smearing of 0.01 eV, gamma k-point, converged to 0.01 eV/atom, dispersion correction of DFT-D3
- Vienna *ab initio* Simulation Program (VASP)
- Following metal replacement relaxed via three step protocol (relax atomic positions, relax cell volume, relax atomic positions)

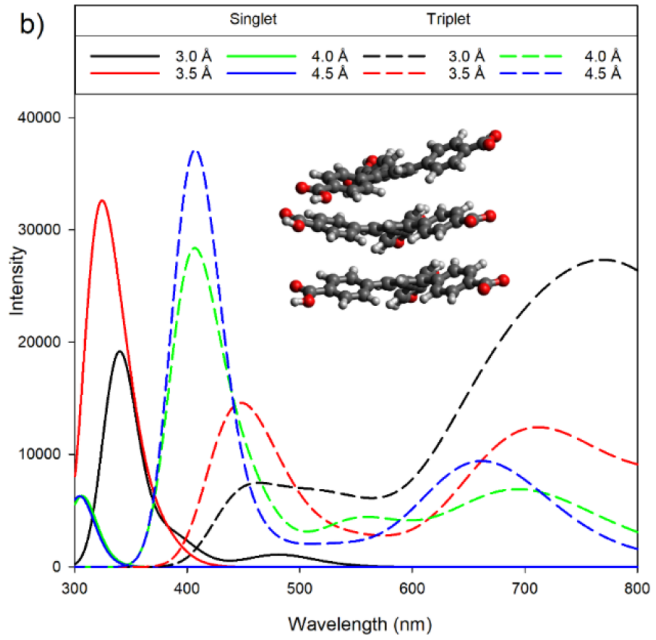
Refs: Kresse et al. Phys. Rev. B ***1993****, 47, 558, Perdew et al. Phys. Rev. Lett.* ***2008****, 100, 136406., Grimme et al. J. Chem. Phys.* ***2010****, 132, 154104, Grimme et al. J. Phys. Chem. C.* ***2020****, 124, 26801, Vogel et al. Phys. Chem. Chem. Phys.* ***2019****, 21, 23085, Henkelis et al. ACS Appl. Mater. Interfaces.* ***2020****, 12, 19504.*

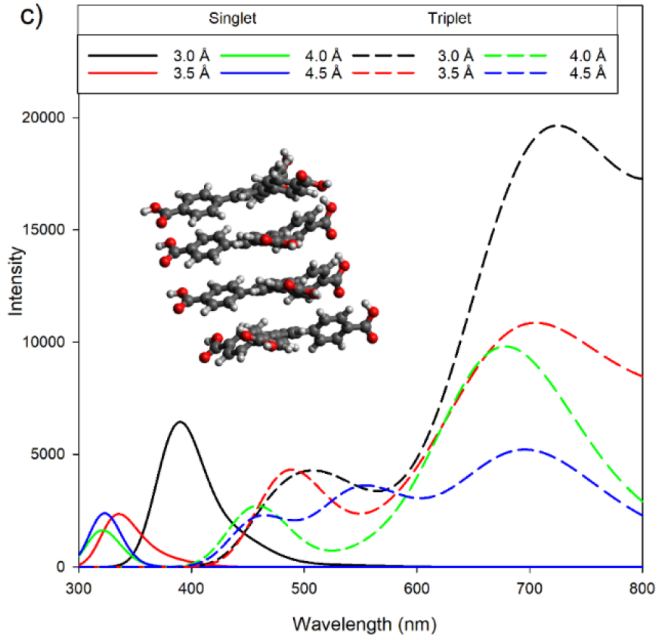
Stacking distance and number of linkers alters emission wavelength

- Increasing # of linkers:
  - Moves emission from single to triplet states
  - Decreases the strength of the emission
- Increasing stacking distance:
  - Shifts to longer wavelengths
  - Creates one primary peak



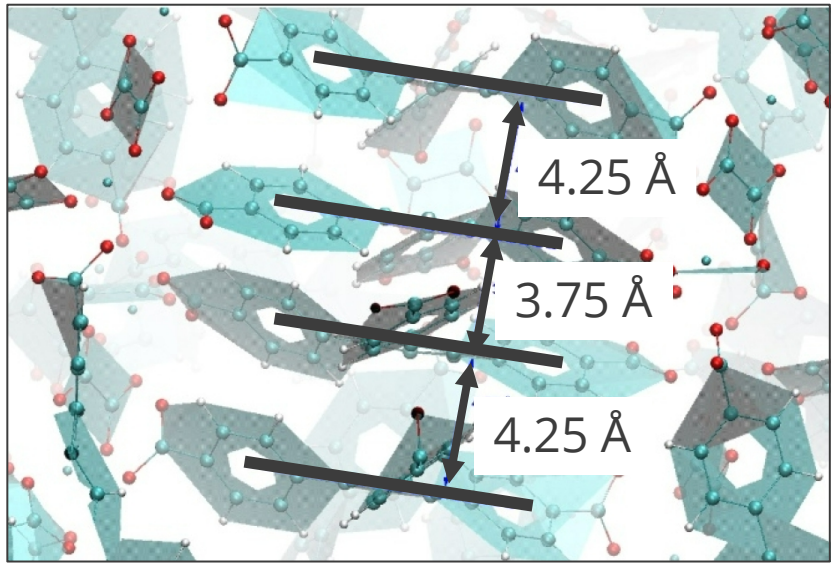




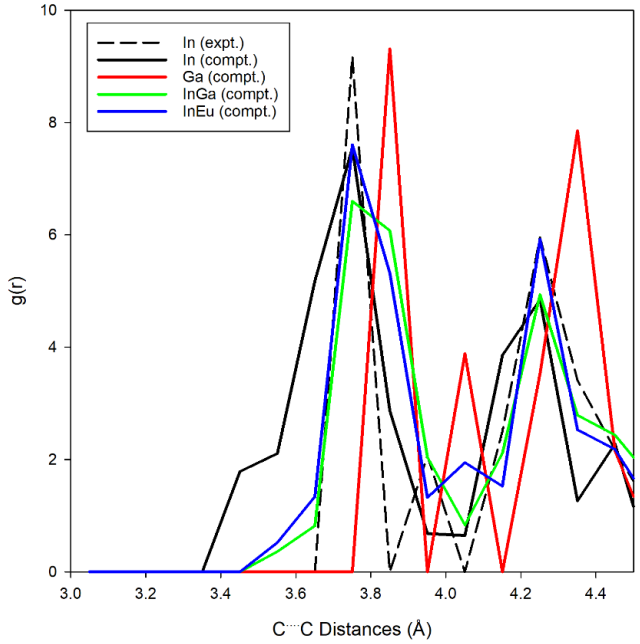


How can the stacking distance be controlled in the full periodic MOF framework?

Stacking distances can be controlled by the radii of the metal



Stacking distances are *not* uniform



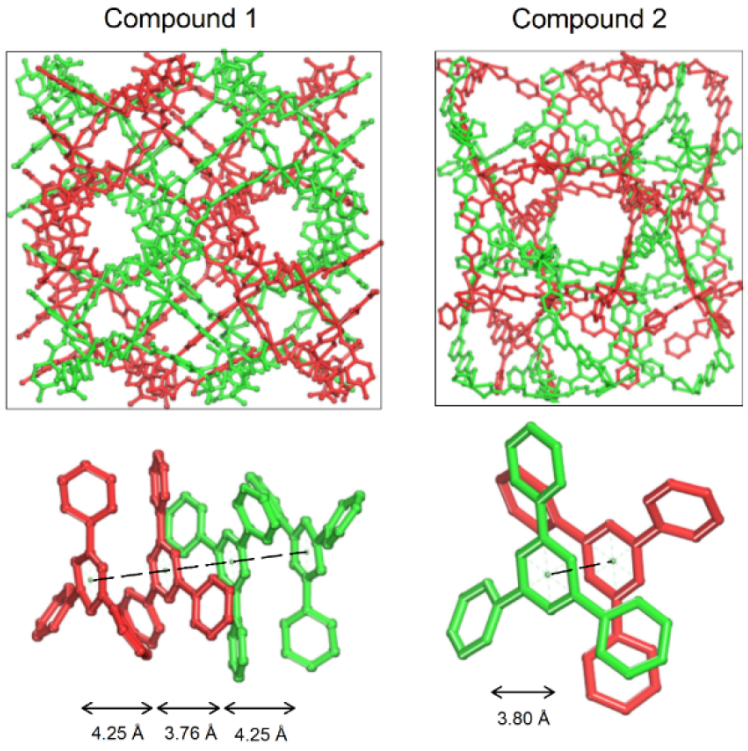
- 100% Ga causes shifts to *longer* stacking distances
- Partial Ga replacement adds in *some* longer distances
- Partial Eu replacement adds *smaller* stacking distances

		a=b=c (Å)	α=β=γ (°)	Density (g/cm³)	M-O Distance (Å)		
					Ga	In	Eu
In	Calc.	33.78	90	1.019	-	2.26	-
	Expt.	33.98	90	1.002	-	2.21	-
Ga	Calc.	33.62	90	0.939	1.91	-	-
GaIn	Calc.	33.57	90	1.007	2.02	2.22	-
EuIn	Calc.	33.77	90	1.028	-	2.25	2.35

Very limited changes in cell volume

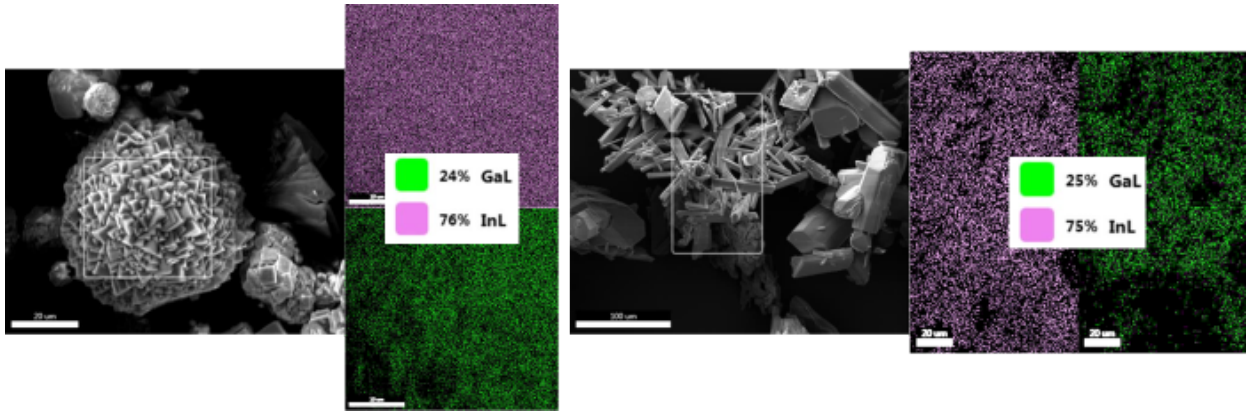
Multiple BTB-based MOFs were synthesized for validation of computational models

- 25% Ga – 75% In Compound 1 and Compound 2 structures were synthesized

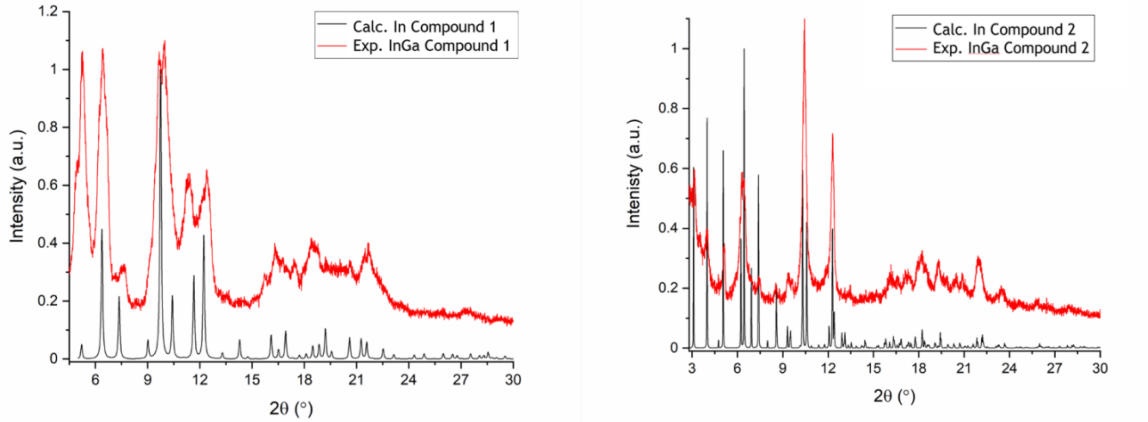


Four stacked BTB linkers

Two stacked BTB linkers



SEM images of InGa-Compound 1 at 20 µm (left) and InGa-Compound 2 at 100 µm (right) with elemental quantification shown for In (pink) and Ga (green).

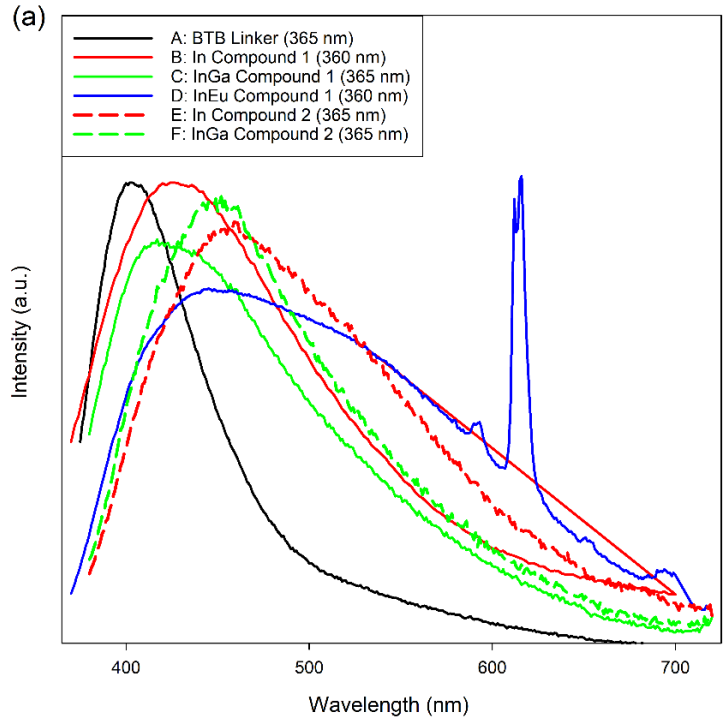


Powder X-ray diffraction patterns for the calculated In Compound 1 and 2 Compound 2(black) and the experimental InGa Compound 1 and 2 (red).

Emission wavelength increased for InGa Compound 1 compositions and decreased for InGa Compound 2

- Photoluminescence excitation and emission spectra were measured for In-, InGa-, and In-Eu Compound 1, In- and InGa-Compound 2, and BTB linker excitation
- Addition of Ga or Eu to In-Compound 1 *decreased the intensity and broadened the emission*
- Quantum yield (QY) of the MOFs were lower than the linker alone and was consistent at different emission wavelengths
- Quenching of QY in MOFs is caused by Forster resonance energy transfers, a non-radiative mechanism from strong overlap in the absorption and emission spectra

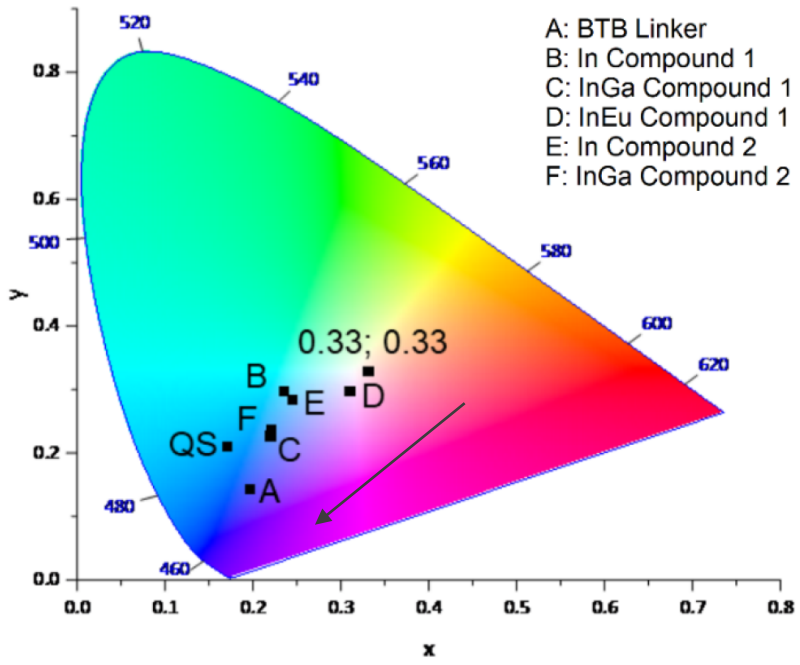
Yu et al. J. Amer. Chem. Soc. 142.25 (2020): 11192-11202.



Sample	Excitation λ (nm)	QY (%)	Emission λ (nm)
BTB Linker	340	9.5	409
	365	6	439
In-Compound 1[a)]	360	3.1	458
InGa-Compound 1	340	7	408
	365	3.3	471
InEu-Compound 1[a)]	330	4.3	449
	360	3.7	500
In-Compound 2	340	4.2	412
	365	1.5	496
InGa-Compound 2	340	4.8	409
	365	3.6	483

Ga and Eu addition results in a *blue shift* in emission

- Color properties are calculated from emission spectra
- Warm white light needs a x,y chromaticity coordinate of 0.33, 0.33
- Therefore, these structures are primarily *blue emitters* due to the absence of a red color component



Sample	Excitation λ (nm)	x	y	CRI	CCT (K)
BTB Linker	340	0.181	0.081	42	34,367
	365	0.195	0.145	68	34,367
In BTB	340	0.216	0.201	83	34,463
	365	0.244	0.285	56	16,174
InGa BTB	340	0.184	0.131	56	34,460
	365	0.220	0.238	82	34,463
InGa SMOF-1	340	0.190	0.124	62	34,367
	365	0.219	0.228	83	34,463
In SMOF-1	330	0.209	0.193	77.4	34,463
	360	0.234	0.298	85.1	33290
InEu SMOF-1	330	0.512	0.275	45	1,410
	360	0.309	0.298	81	7,068
Quinine Sulfate	365	0.170	0.212	46	34,463

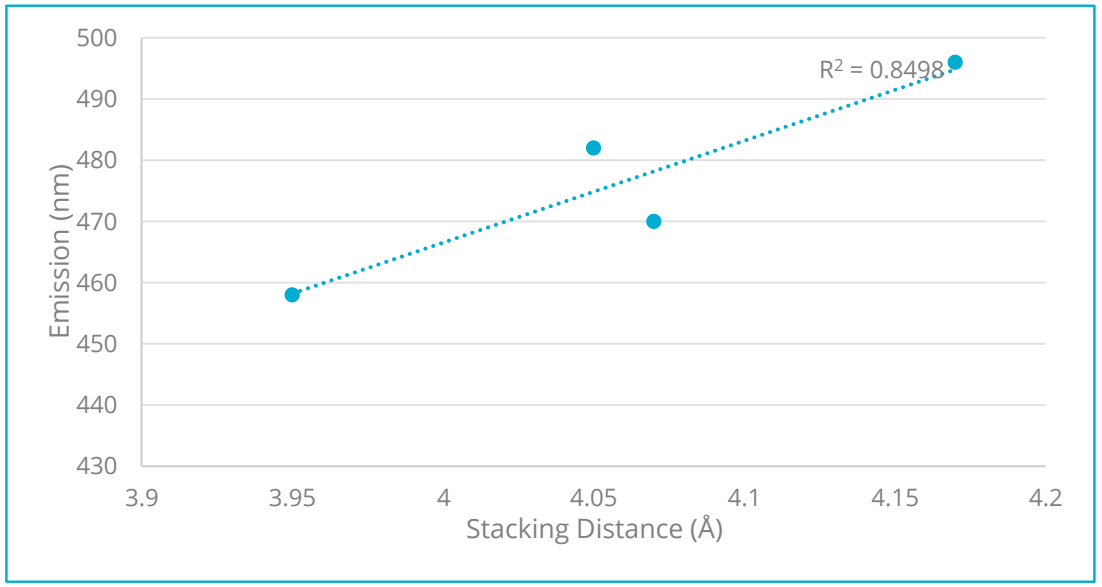
Calculated results (emission) are validated by experiential structures

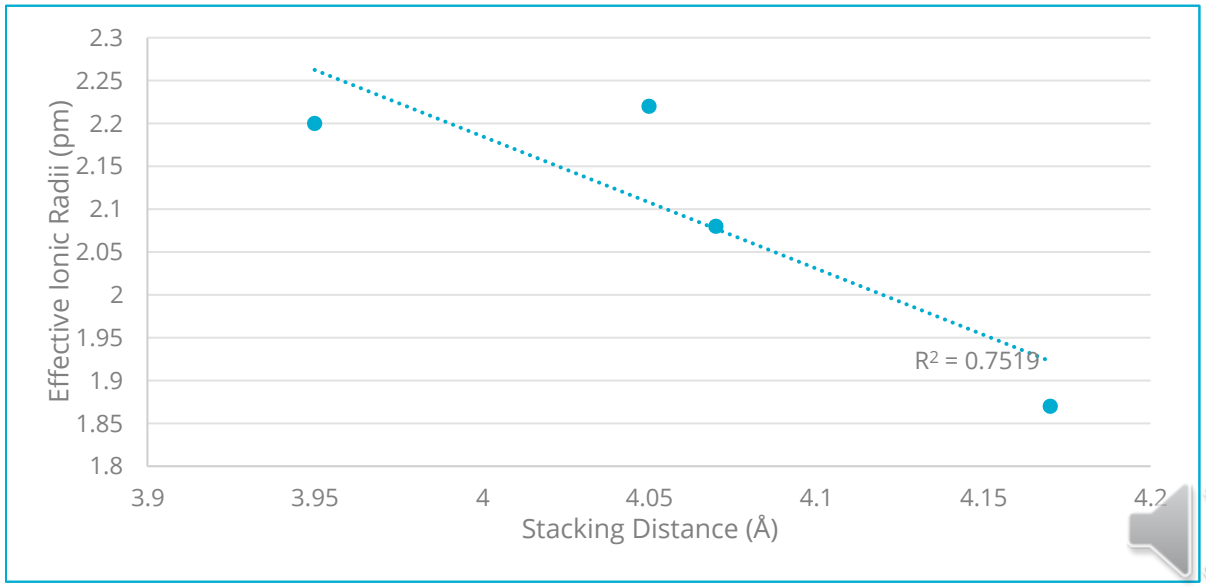
- Calculated InGa Compound 1 emission is within 1 nm of experimentally measured values
- Emission wavelength decreases with lower stacking distances
- Larger effective ionic radii decreases the stacking distances

Metal	Average Stacking Distance (Å)	Effective Ionic Radius[a] (Å)	Calculated Emission[b] (nm)	Experimental Emission (nm)
In – Expt.	4.16		458	-
In	3.95	2.20	458	-
Ga	4.17	1.87	496	-
InGa	4.07	2.08	470	471
InEu	4.05	2.22	482	500

[a] Effective ionic radius = mole % of metals in the Compound 1 structure (r_{In} = 2.2 Å, r_{Ga} = 1.87 Å, r_{Eu} = 2.40 Å)

[b] Predicted emission value from 45% triplet and 55% singlet contributions, with referenced to In-Compound 1





Conclusions

- Computational material design approach was used for identification of mechanisms of tunable light emission in a family of interpenetrated BTB MOF structures
- The number and distance of the stacked linkers controlled the emission wavelength and the intensity of the emission
- Metals with different ionic radii changes the stacking distance, identified as a mechanisms of controlling the emission wavelength
- Synthesis and characterization of InGa-based BTB confirmed the influence of Ga introduction in shifting emission wavelength to 470 nm, from 458 nm in In-BTB MOF
- The results demonstrate the use of computational methods to enable crystal design of MOF structures with *predictable* emission properties

More Information: Rimsza, J.M., Henkelis, S.E., Rohwer, L.E.S, Sava Gallis, D.F., and Nenoff, T.M. "Crystal Prediction and Design of Tunable Light Emission in Metal-Organic Frameworks" Advanced Optical Materials *under review*

Acknowledgements

- Project Team: Susan Henkelis, Dorina Sava Gallis, Lauren Rohwer, Tina Nenoff
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Questions?

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