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The Fuel Cycle Research & Development

Volatile Gas Adsorption in Metal-Organic Frameworks (MOFs)

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Materials Research Society:

Crystalline Nanoporous Framework Materials-Applications and Technological Feasibility

Gas Storage,

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The importance of capturing volatile radioactive iodine (I_2) gas

- Increased worldwide energy demands, balanced with the need to reduce greenhouse gas emissions have fueled research in *clean, safe, and responsible nuclear energy*

- *Appropriate nuclear waste management*: a main concern for safety associated with nuclear energy

- Particularly challenging is the capture of volatile gaseous fission products from nuclear fuel reprocessing or inadvertent environmental release: ^{129}I and ^{131}I, ^{3}H, $^{14}CO_2$, and ^{85}Kr

- Unique exposure problems for radio-I_2 isotopes:
  - ^{129}I: long-lived isotope (half-life of 1.57×10^7 years), requiring *capture and reliable storage while it decays*
  - ^{131}I: short-lived (half-life of 8.02 days), but *requires immediate capture* as it directly affects human metabolic processes

Metal-Organic Frameworks (MOFs): tunable and versatile new generation of porous materials

- Highly modular, a large set of materials available
- Highly tunable, amenable for modifications, supporting diverse chemistry
- Mild synthetic protocols
- Recent studies focus on new research topics

Chem Soc Rev

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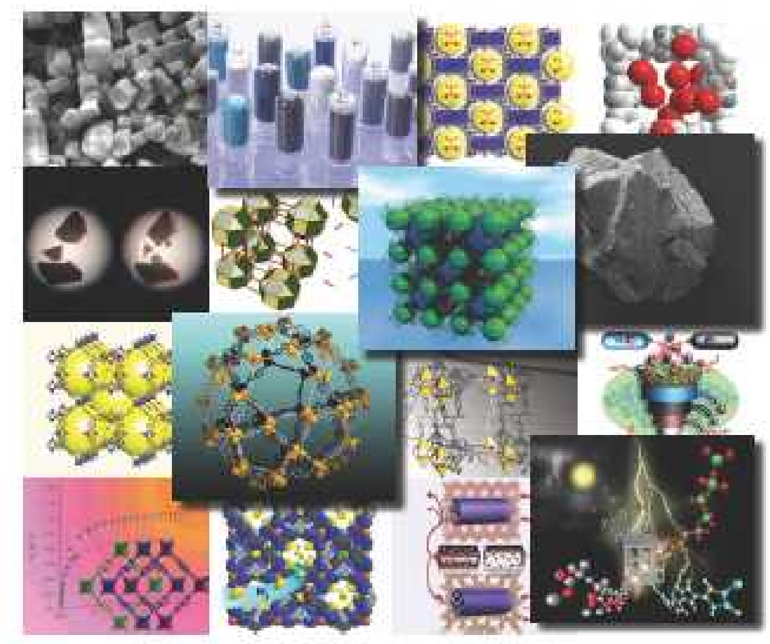

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Judicious selection of "ideal" candidate for selective I2 sorption

Pre-requisites

- Restrictive pore apertures to impart molecular selectivity for directional diffusion of iodine (~3.35 Å)
- Large surface area and pore volume
- High *chemical*, *thermal*, and *moisture* stability

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Park, K. S.et.al *Proc. Natl. Acad. Sci. U. S. A.* **2006***, 103,* 10186.

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ZIF-8

✓The β-cages, 11.6 Å in diameter, are connected via six-member ring (6 MR) apertures of ~3.4 Å

✓Surface area ZIF-8 = 1,947 m^2 g^{-1} and Pore volume= 0.663 cc g^{-1}

✓Chemically stable in boiling solvents (including water), and thermally stable up to 550°C

Park, K. S.et.al *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103,* 10186.

Challenges: structural characterization of adsorbed guest species within porous hosts

- Considerable effort has been devoted to *understanding guest binding within porous systems*

- The high symmetry of the ZIF-8 poses *challenges in locating guests*, which often can be crystallographically disordered

- Complete understanding of guest binding can only be obtained by *combining insights from local and long-range structural probes, and molecular simulations:*
  - XRD,
  - pdf ,
  - molecular simulations

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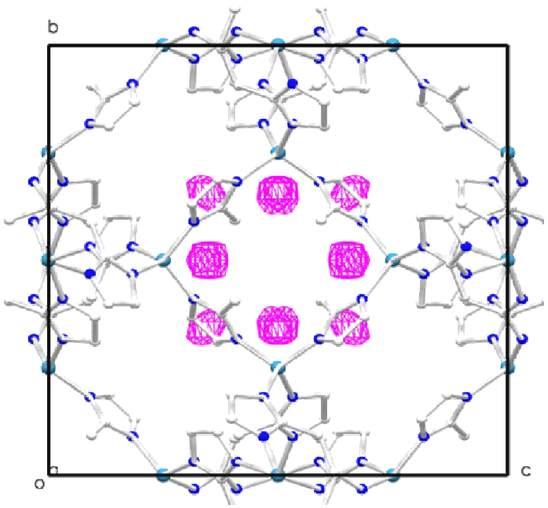
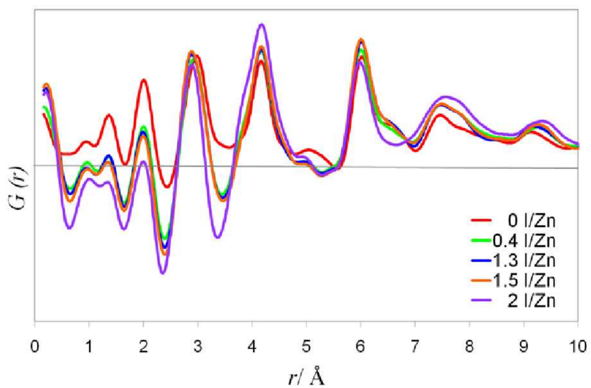
Integration of experiment and modeling to identify the preferred binding sites for I_2 in ZIF-8

Complementary local and long-range structural probes

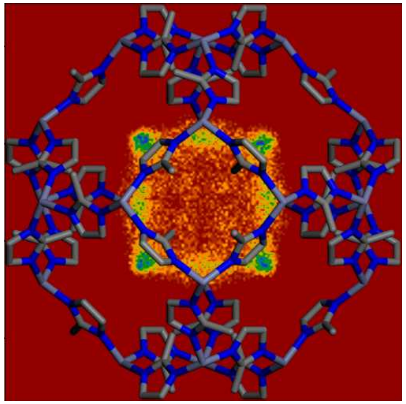


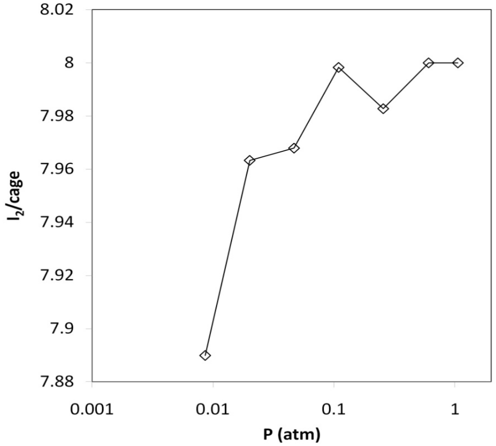
Difference-Fourier analysis map



Pair Distribution Function analysis

Molecular modeling





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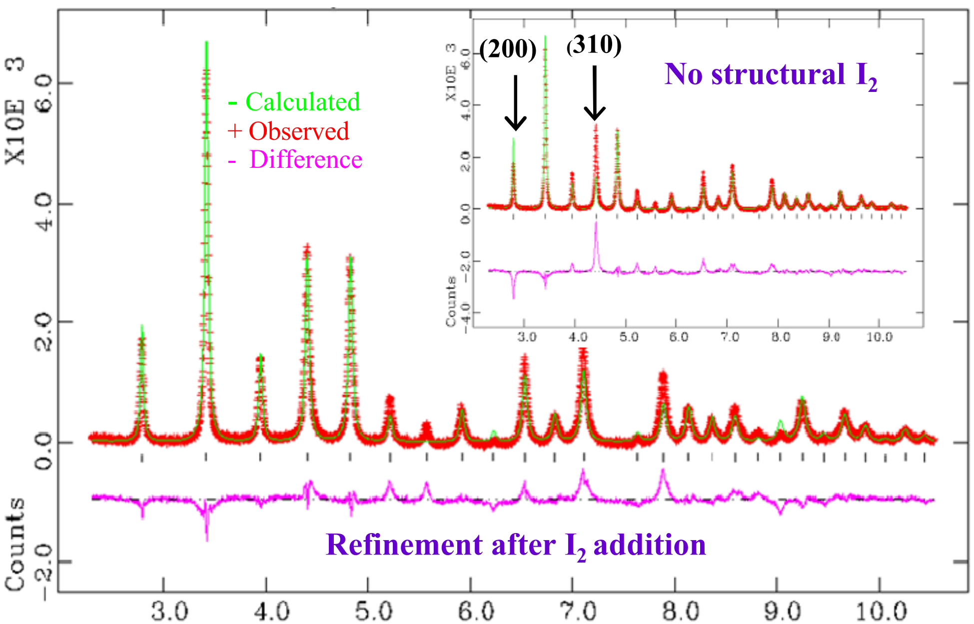
High-resolution synchrotron-based XRD



Calculated, observed and difference spectrum of 0.4 I/Zn loading of I_2@ZIF-8 after I_2 inclusion in structure refinement by Rietveld analysis (inset: before I_2 inclusion).

- Sample crystallinity is maintained up to ~1.3 I/Zn loadings
- Bragg reflections broaden significantly beyond this value and are difficult to distinguish from the pronounced diffuse features in the “background”
- A small contraction of the lattice with increased I_2 loadings is noted, (17.029 Å to 16.933 Å between the 0.4 I/Zn and 1.3 I/Zn loadings)

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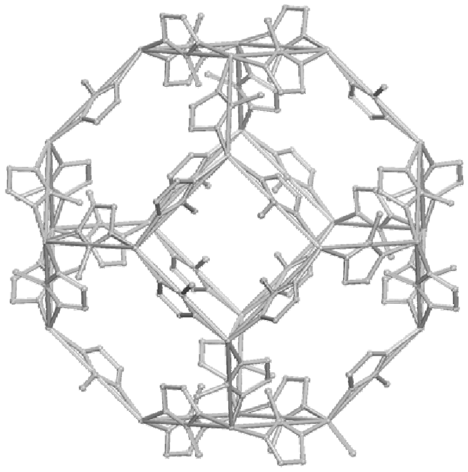
Determining the I_2 binding locations



Activated β-cage

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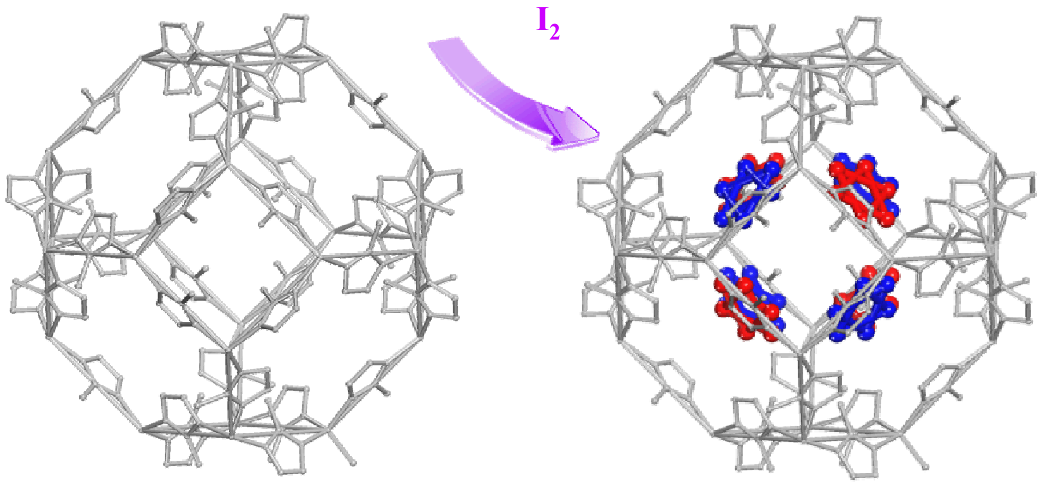
Determining the I_2 binding locations



Activated β-cage

Dynamically disordered I_2 molecules

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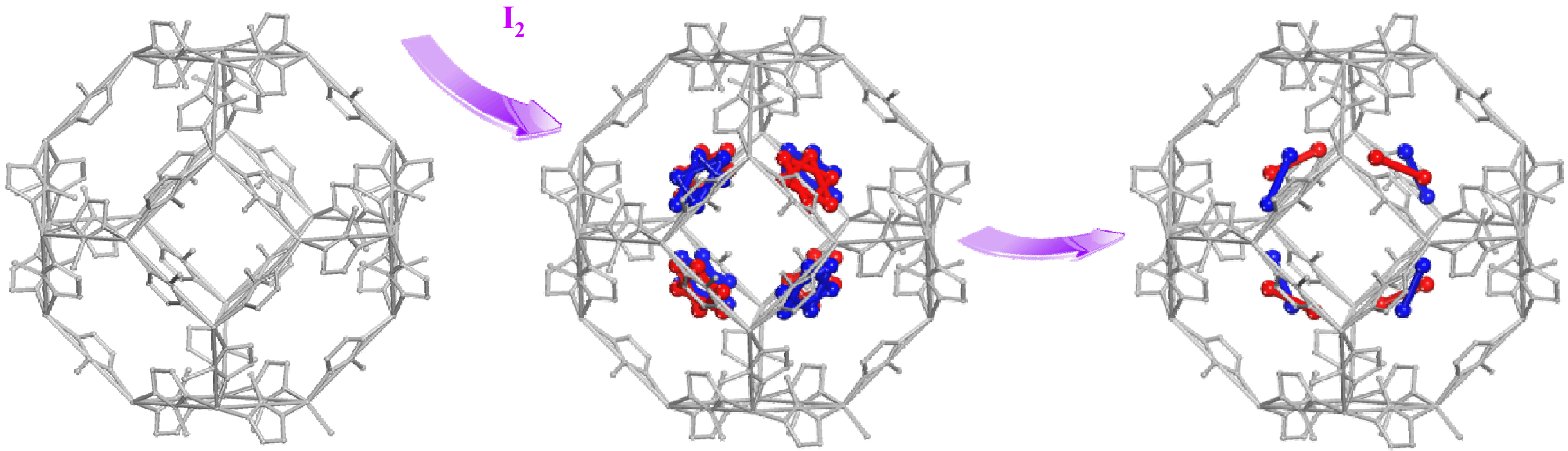
Determining the I_2 binding locations



Activated β-cage

Dynamically disordered I_2 molecules

Refined I_2 sites:
I_a (blue) and I_b (red)

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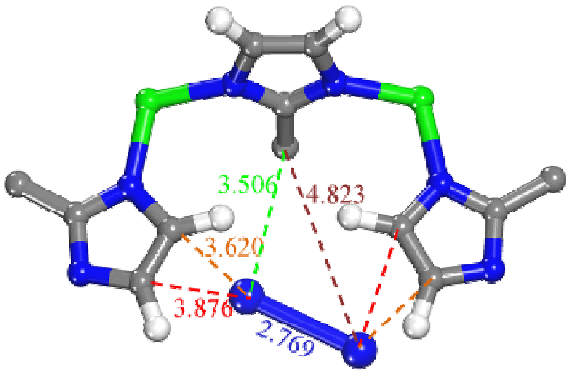
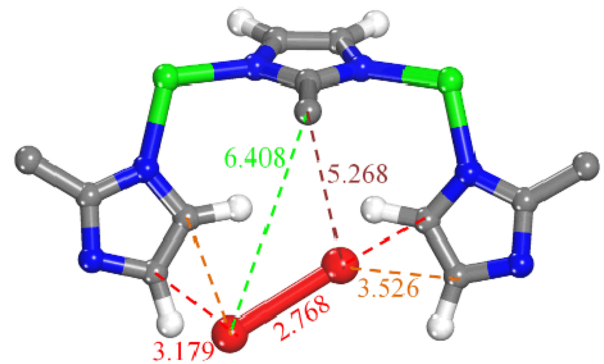
Two distinct I_2 binding site: I_a and I_b

I_a site



I_b site



I_2 site occupancy and I_2···MeIM close contacts in I_2@ZIF-8

I_2 site	**Site occupancy**		**Contacts with MeIM**	
	0.4 I/Zn	**1.3 I/ Zn**	**C (CH_3)**	**C(H=CH)**
I_a	0.28	0.88	3.506 Å; 4.823 Å	3.620 Å; 3.876 Å
I_b	0.14	0.38	5.268 Å; 6.408 Å	3.179 Å; 3.526 Å

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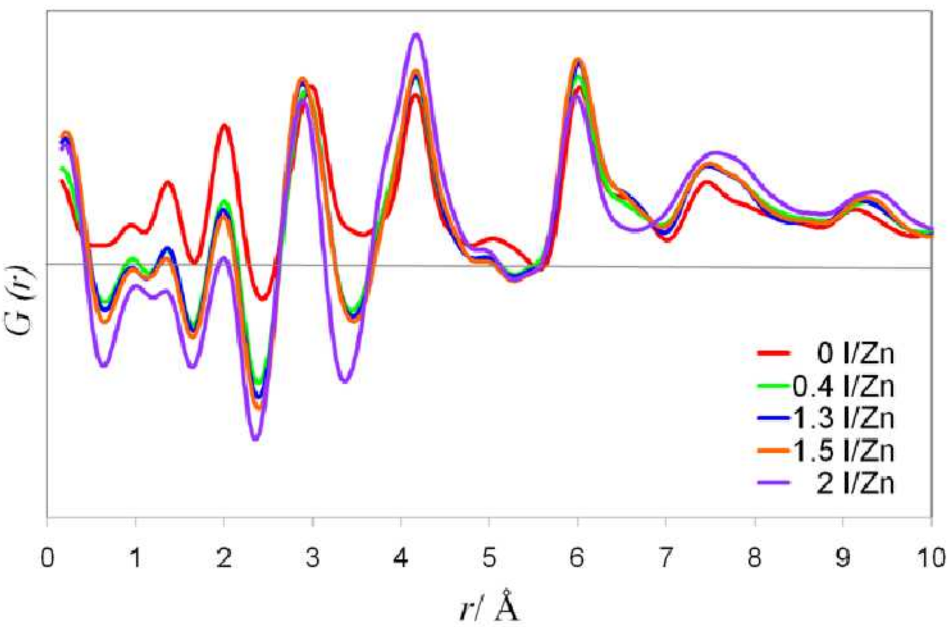
Pair Distribution Function analysis: local structure probe



- The PDF method- a weighted histogram of the atomic distances, independent of sample crystallinity
- Below ~6 Å, the *general features in the PDF are retained at all I_2 loading levels*
- The persistence of the peak at ~6 Å, corresponding to the Zn-(MeIM)-Zn′ distance, indicates that *short-range order and the framework connectivity are still maintained*

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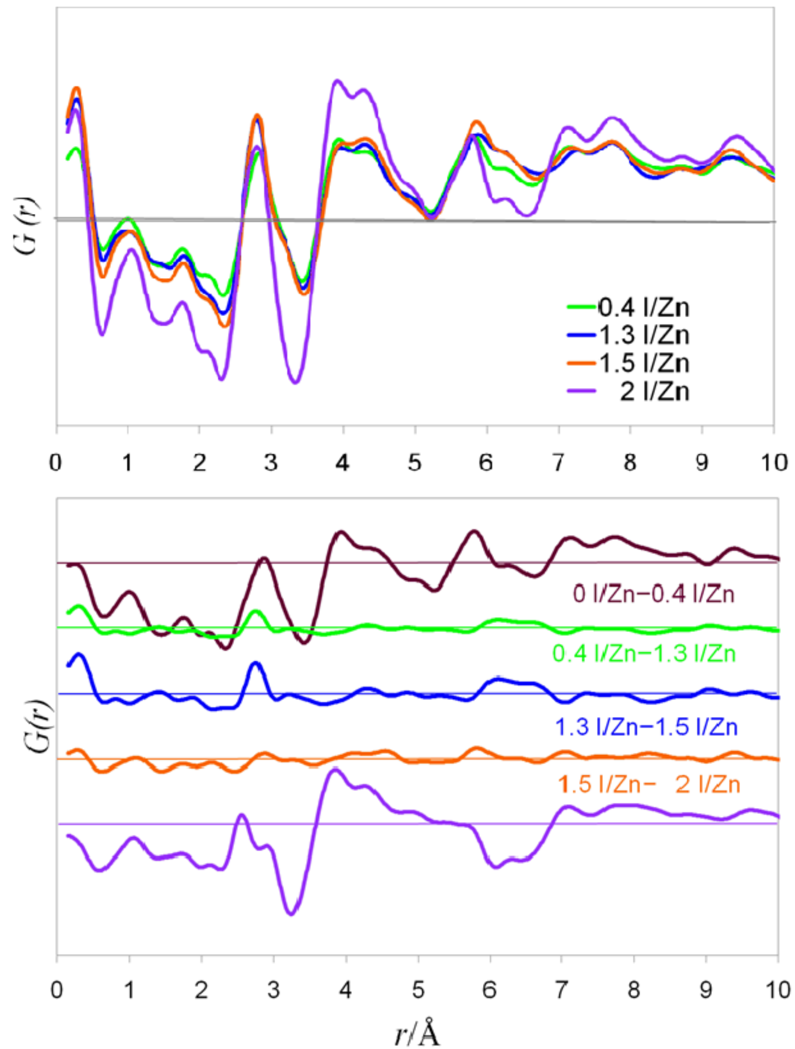
Pair Distribution Function analysis: local structure probe



- Differential analysis applied to isolate I_2 guest molecules contributions
- Incremental I2 loading up to 1.3 I/Zn
  peaks at 2.75 Å, 3.23 Å, 4.29 Å, 4.91 Å, 5.46 Å, 6.01 Å, and 6.61 Å
- I2 loading >1.3 I/Zn: new peaks at 2.56 Å, 2.94 Å, and 3.79 Å, increased intensity of the peaks at ~4.29 Å and ~4.91 Å, and reduced intensity of the peak at 3.23 Å

above 1.3 I/Zn, rearrangement of I2 molecules required inside cage

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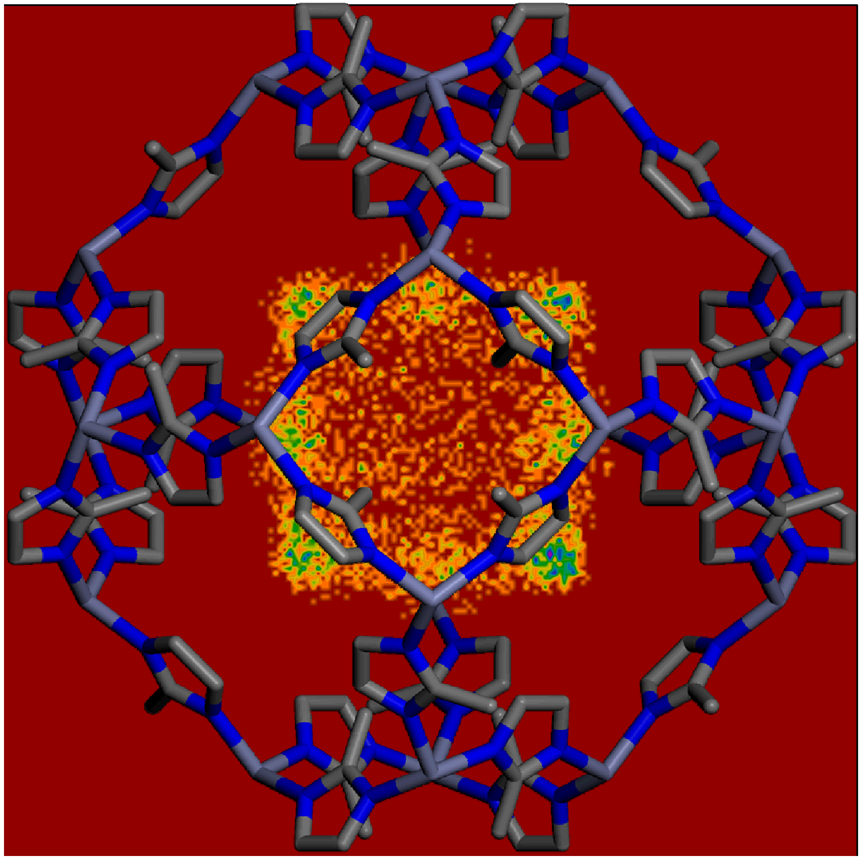
MD simulations predict I2 location and loading capacities per cage

0.5 I/Zn (~1.5 I_2 per cage)



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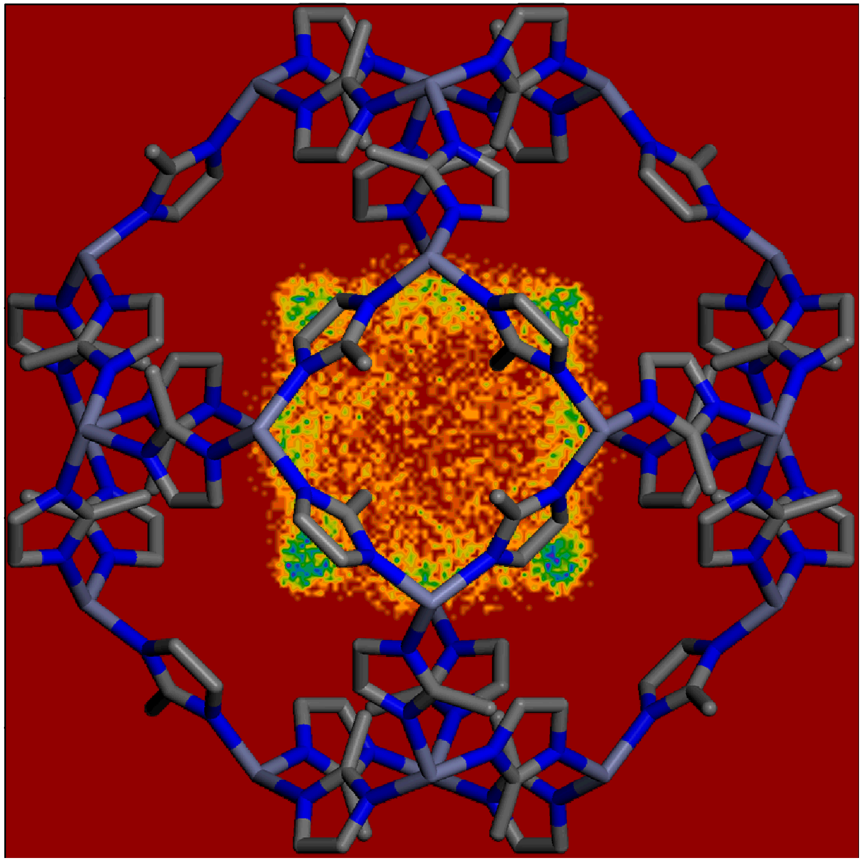
MD simulations

1.3 I/Zn (~4 I_2 per cage)



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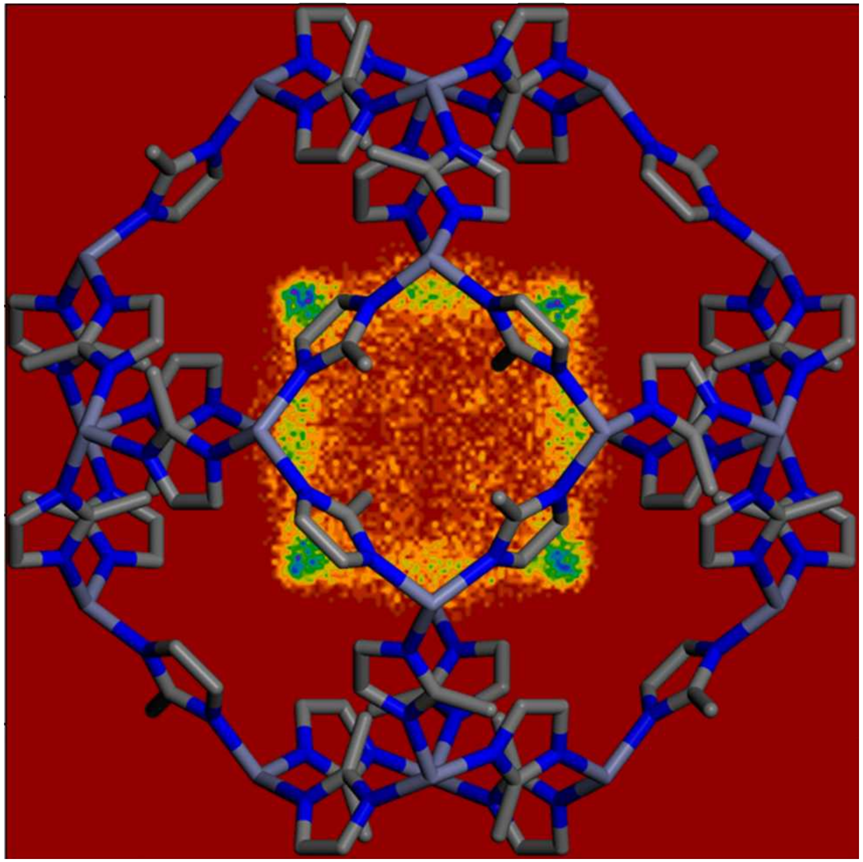
MD simulations

2 I/Zn (~6 I_2 per cage)



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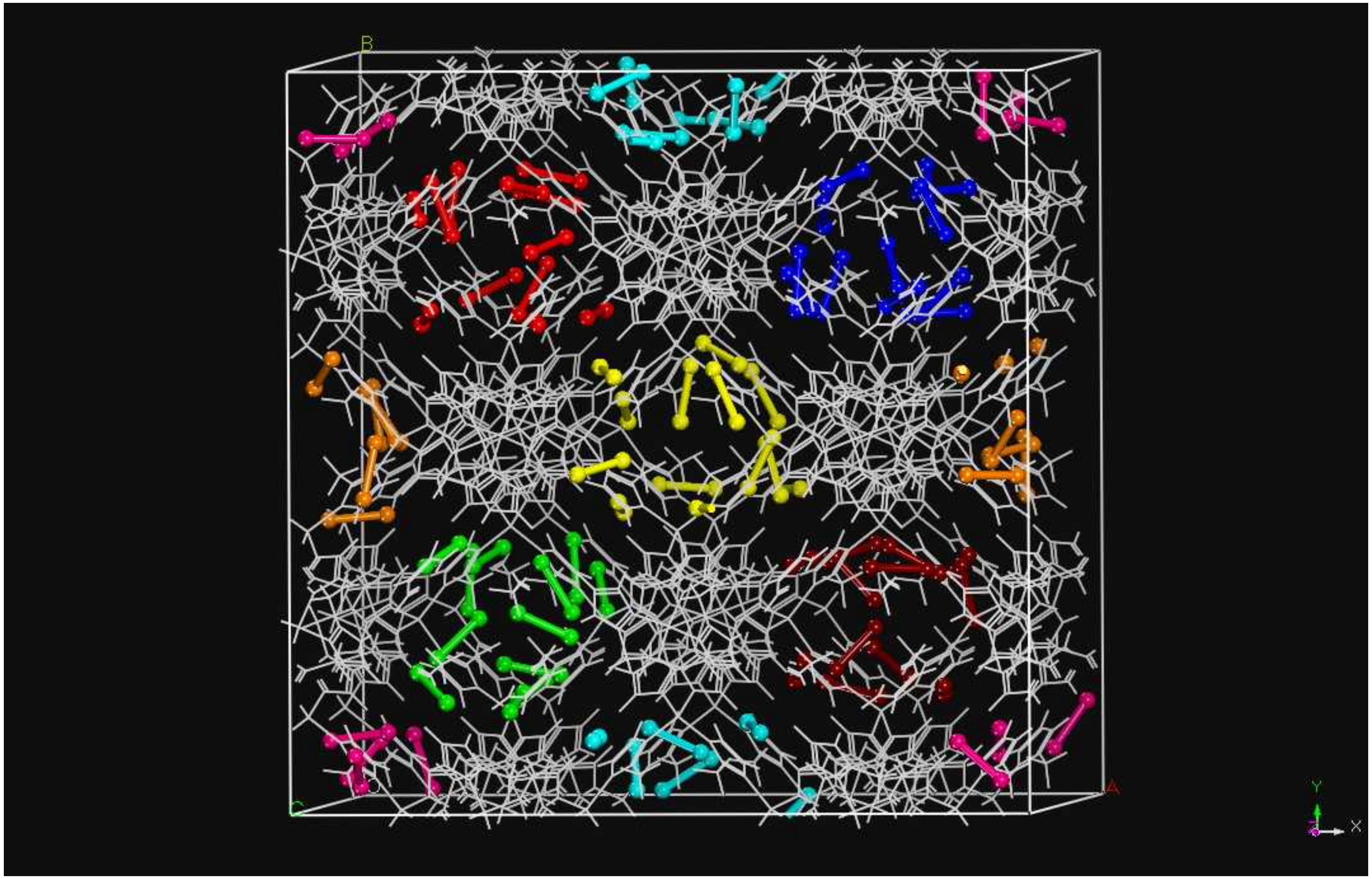
Dynamics of I_2 within cages



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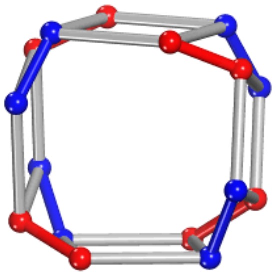
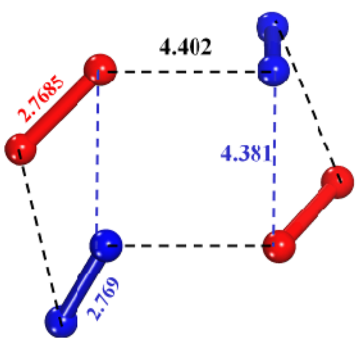
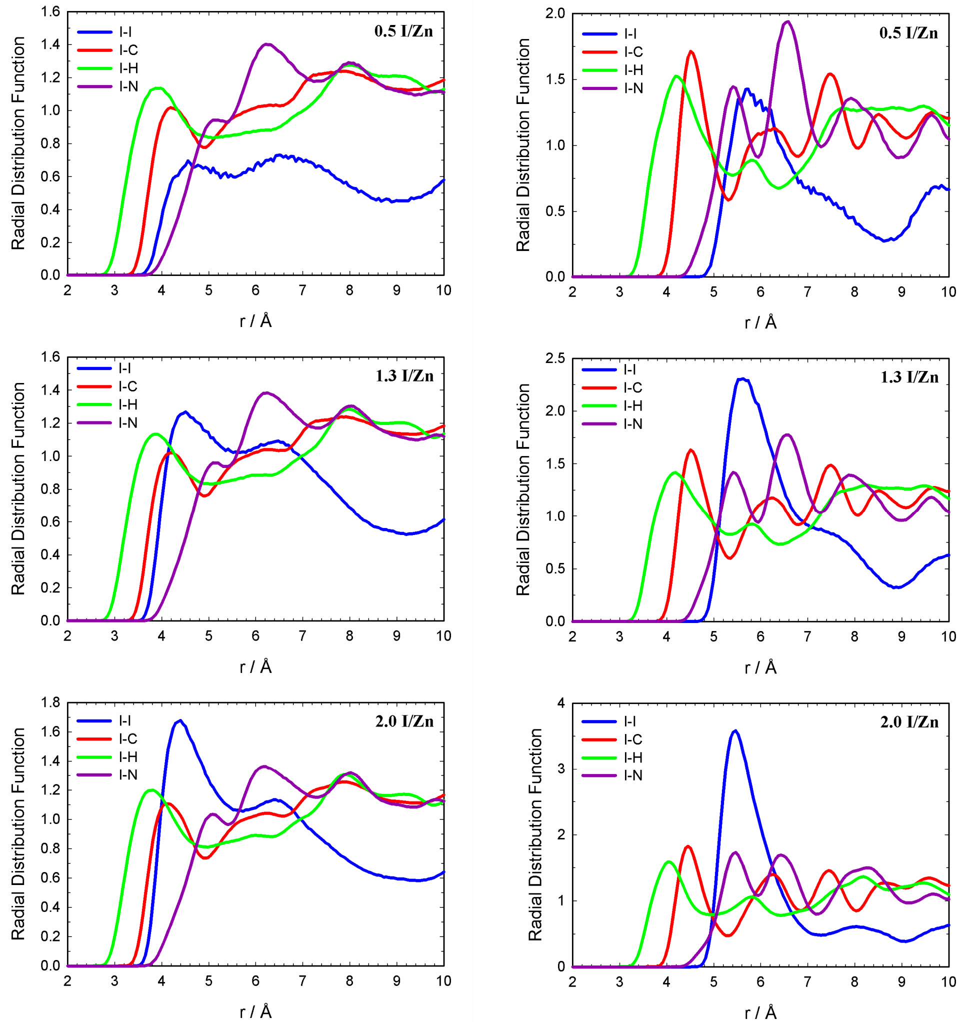
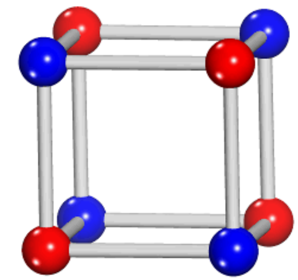
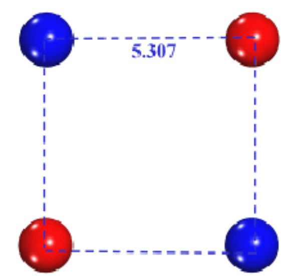
Experimental–modeling agreement
Radial Distribution Functions (RDFs) for the diatomic model and the united-atom approach











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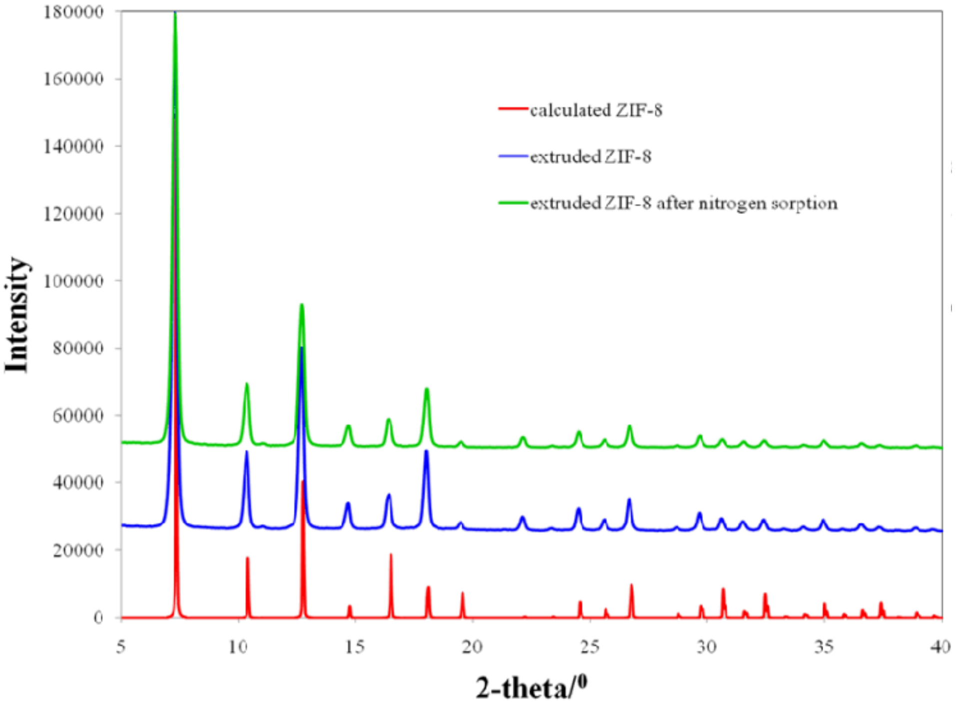
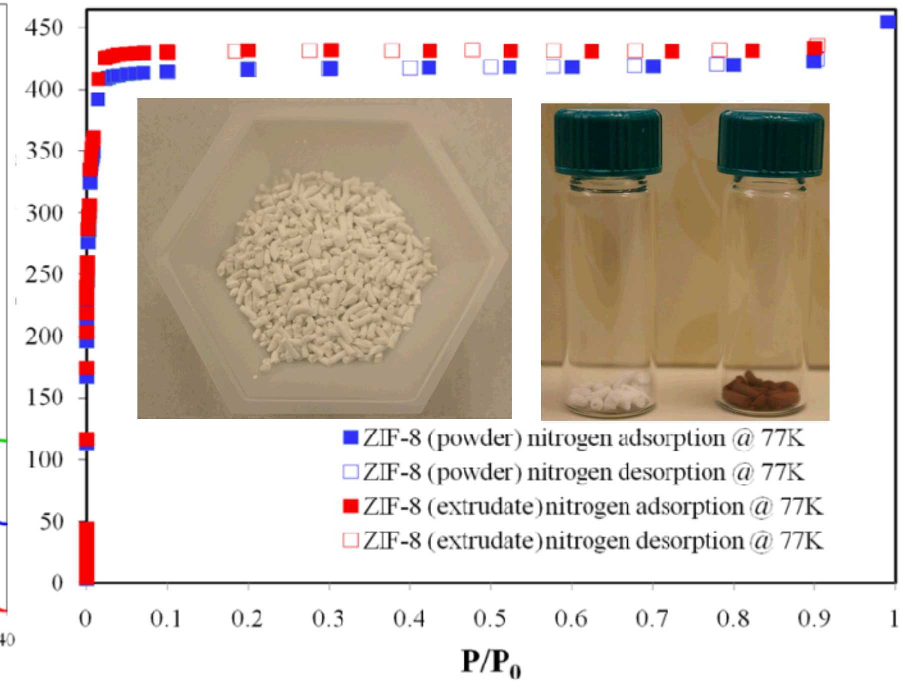
Sample pelletizing and characterization





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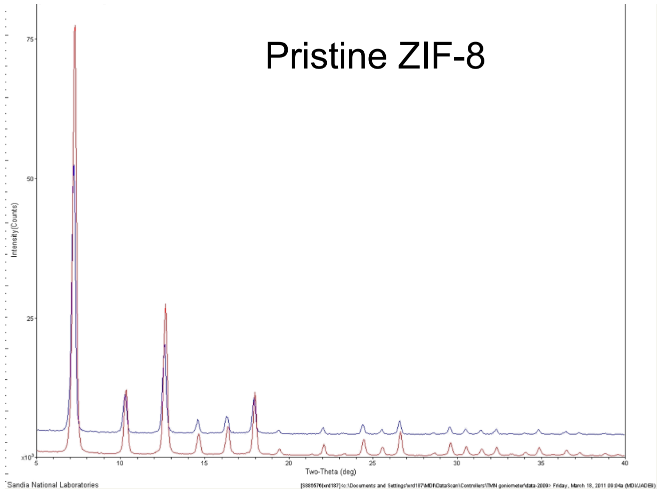
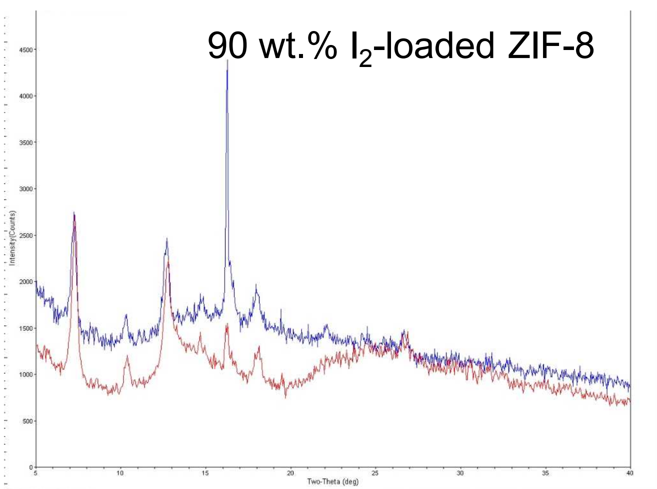
Irradiation studies at the Sandia Gamma Irradiation Facility (GIF)





Preliminary investigations

- Pristine and I_2-loaded ZIF-8 sample were exposed to Co-60 gamma irradiation at the Sandia Gamma Irradiation Facility (GIF)
- Dose rate= 0.1 Rads/sec; total dose= 2.59 x 10^5 Rads (2218 Gy); *samples maintain crystallinity*
- This irradiation study is a good approximation of an adequately shielded long-term disposal environment

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Summary and Future directions

- I_2 adsorption in ZIF-8 is mainly due to *favorable interactions with the 2-MeIM linker*
- Up to *6 I_2 molecules are captured* (2 I/Zn) inside each cage; complementary MD simulations confirm I_2 mobility is restricted within individual cages
- PDF analyses confirm that the *framework structure is retained beyond the loss of the long-range crystalline symmetry*
- High-adsorptive capacity is maintained in extruded pellet form
- Current studies focus on achieving selective adsorption capabilities from complex, multicomponent off-gas streams