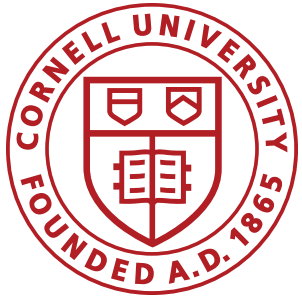


Investigating Organometallic Crosslinked Polymers with Density Functional Theory

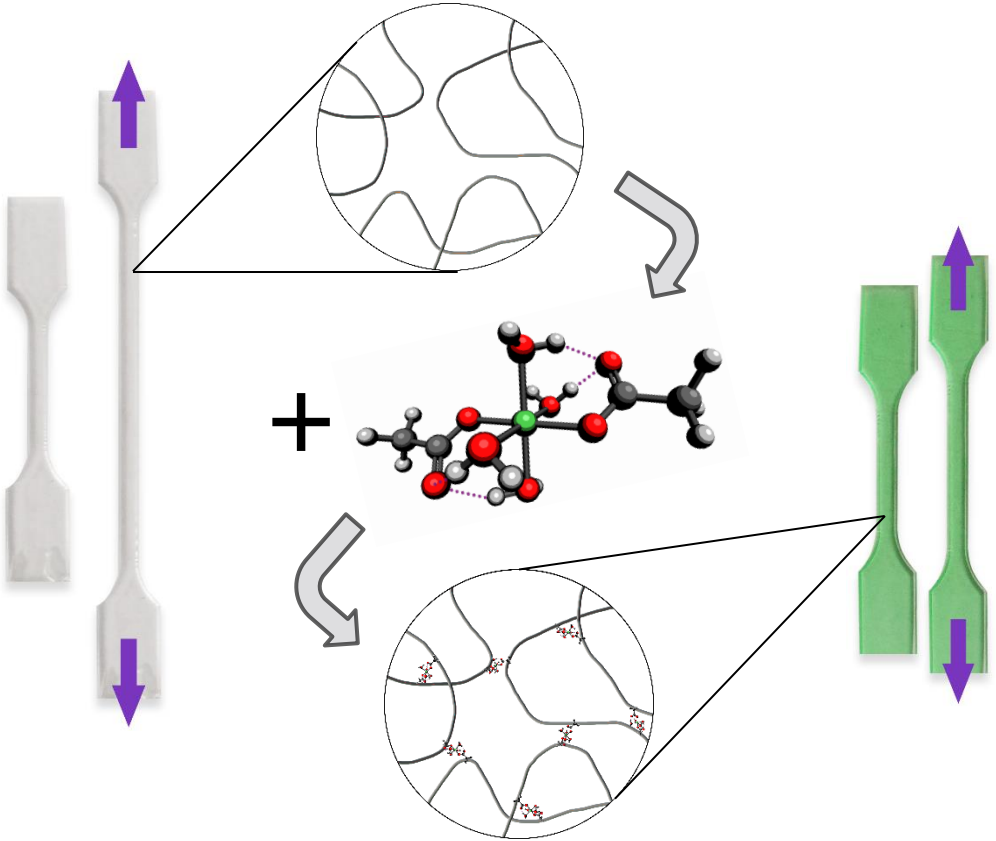
56th Annual Technical Meeting of the Society of Engineering Science

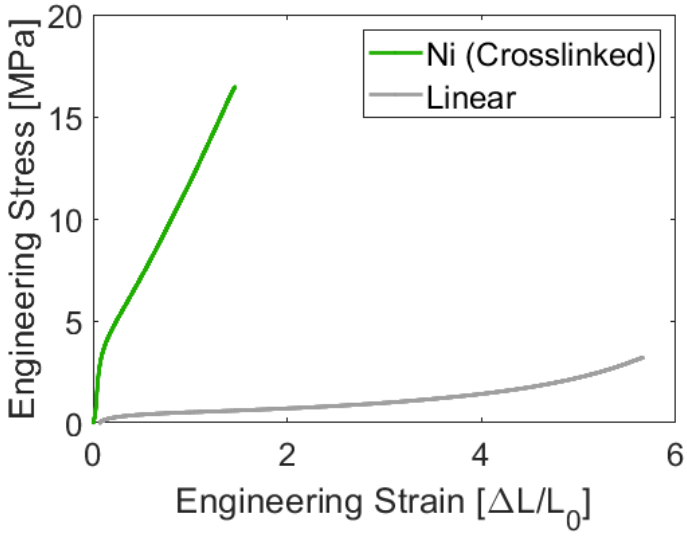
Presenter: Michael Buche

Authors: Michael Buche, Zachary Sparrow, Yuval Vidavsky, Robert DiStasio, Meredith Silberstein

10/15/2019

Organometallic Crosslinked Polymers





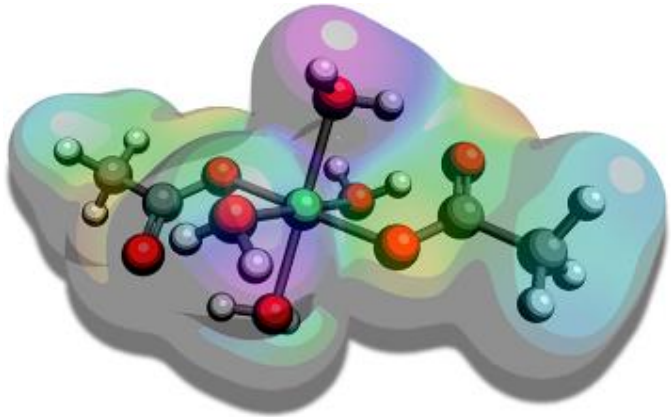
Vidavsky*, Buche*, et. al. (in preparation)

Scope of this Study

- Metal-coordination complexes as crosslinking structures in a polymer
  - Use ligands to modify crosslinking structures
    - Thereby modifying bulk mechanical properties

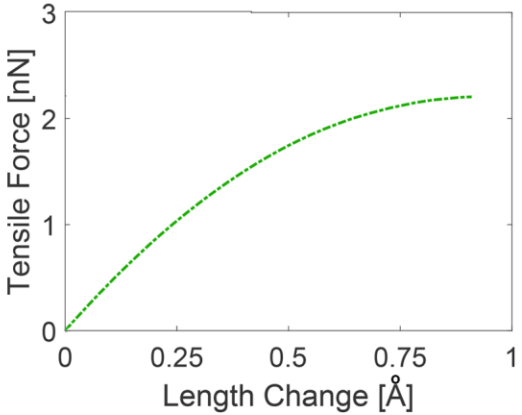
- Investigate the crosslinking using quantum chemistry simulation
  - Predict and interpret experimental results
  - Inform material design
  - Inform a constitutive model

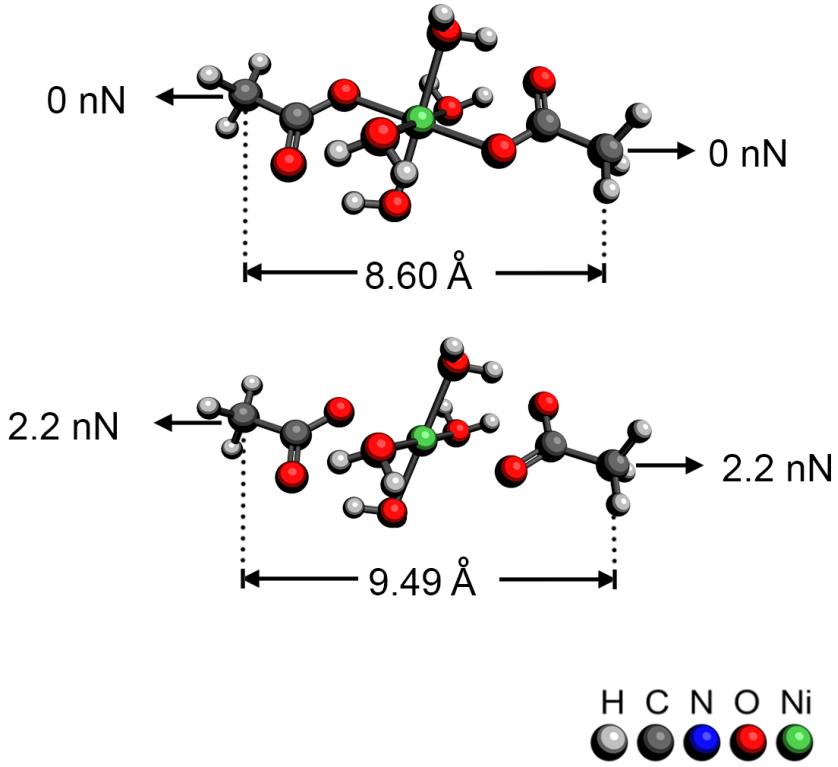
- Specifically, the crosslinking structure
  - Mechanical response
  - Free energy barriers
  - Population distributions



Overview of Simulation Steps

- Mechanical Response
  1. Minima search (OPT)
  2. Diagonalize Hessian (FREQ)
  3. Apply external forces (EFEI)





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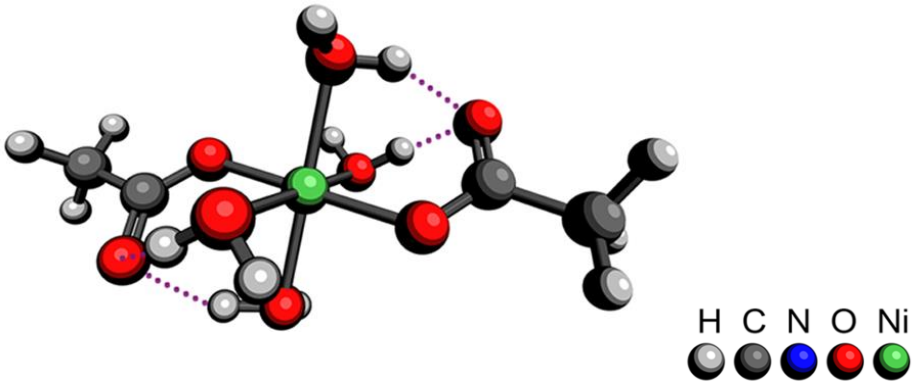
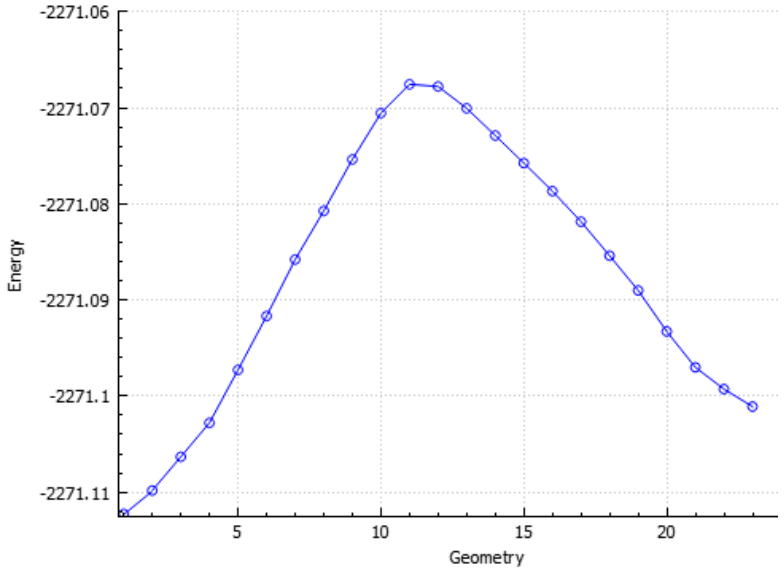
Overview of Simulation Steps

- Free Energy Barriers
  1. EFEI-informed “product” (OPT)
  2. Approximate reaction path (FSM)
  3. Transition state search (TS)





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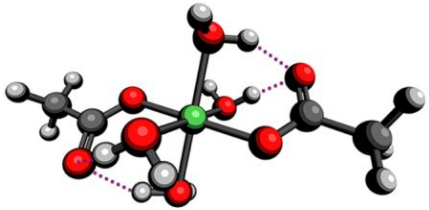
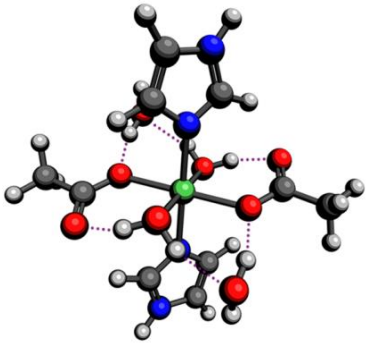
Effects of Added Ligands

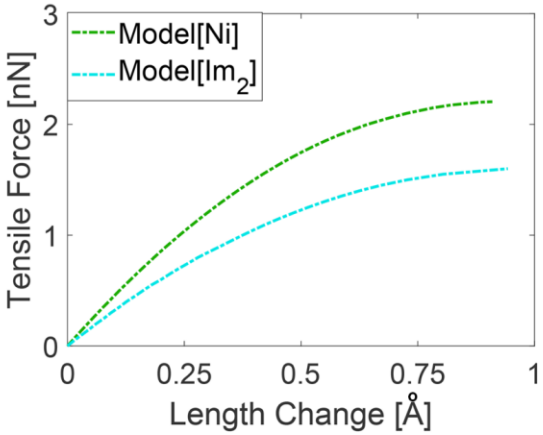
Model[Ni]



+2( )

Model[Im$_2$]

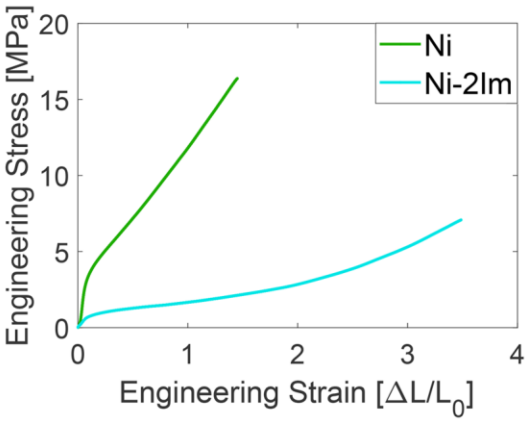


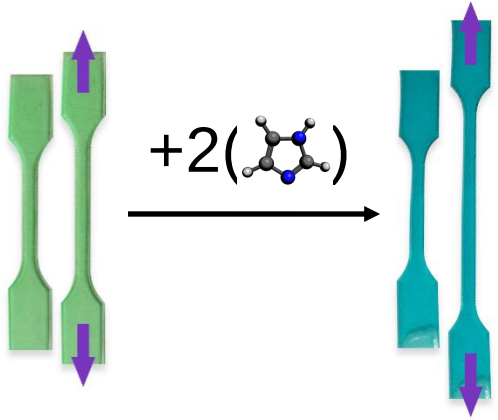


H C N O Ni

Model	[Ni]	[Im$_2$]
ΔG (kcal/mol)	5.06	6.29
ΔG‡(kcal/mol)	18.13	15.60

Experiment





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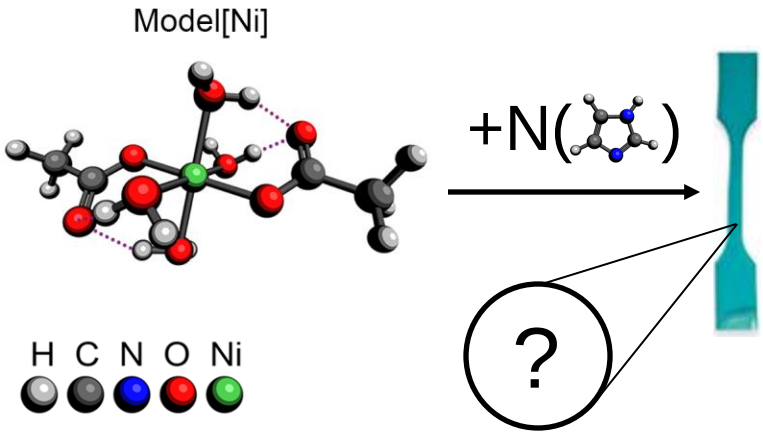
Varying Ligand Amount

Does adding *n* ligands necessarily correspond to getting *n* on each crosslink? **No!**

Nth Imidazole	1	2	3	4
ΔG (kcal/mol)	-4.60	-8.34	-0.80	0.53



Imidazole Equivalents	[Ni]	[Im_1]	[Im_2]	[Im_3]	[Im_4]
0	100	0	0	0	0
1	49	2	49	0	0
2	0	0	100	0	0
3	0	0	21	61	18
4	0	0	16	60	24

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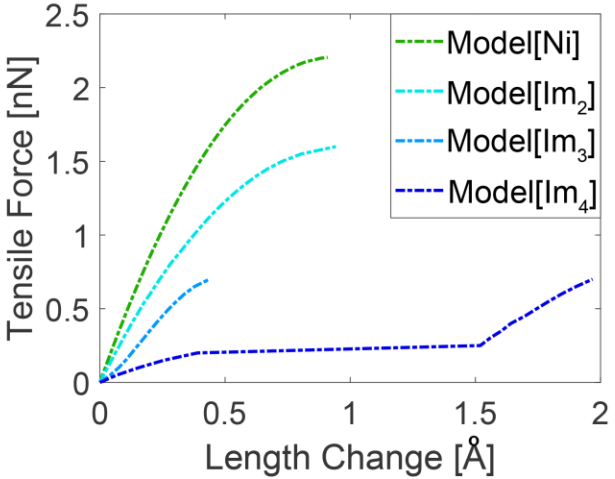
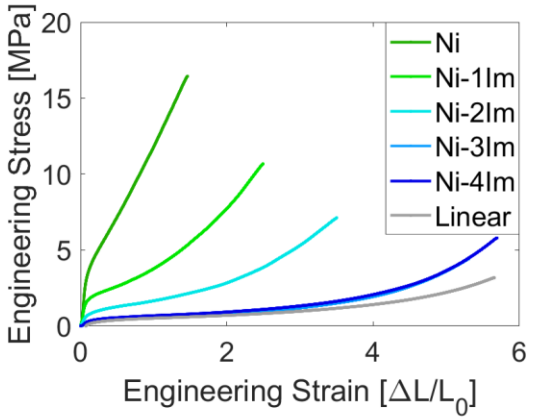
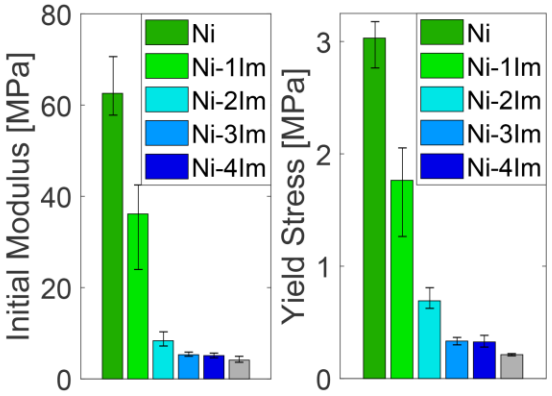
Varying Ligand Amount



Model	[Ni]	[Im_2]	[Im_3]
ΔG (kcal/mol)	5.06	6.29	2.12
ΔG‡(kcal/mol)	18.13	15.60	11.57

Experiment





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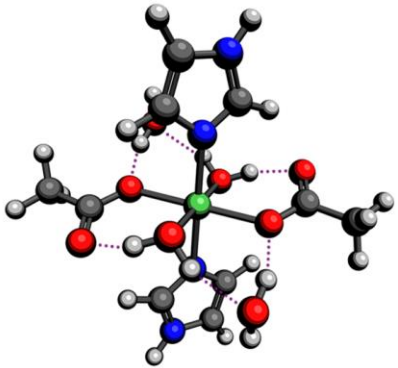
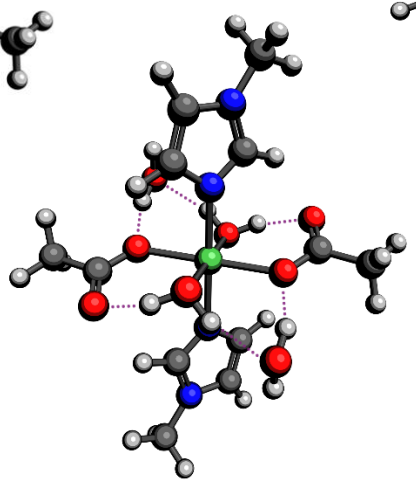
Varying Ligand Type

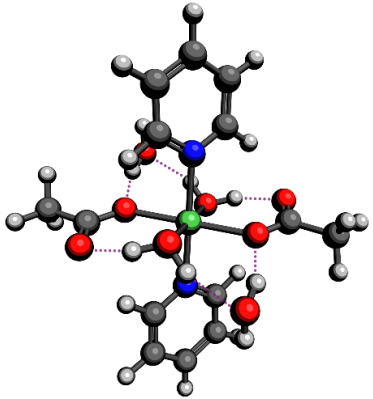
Model[Im_2]



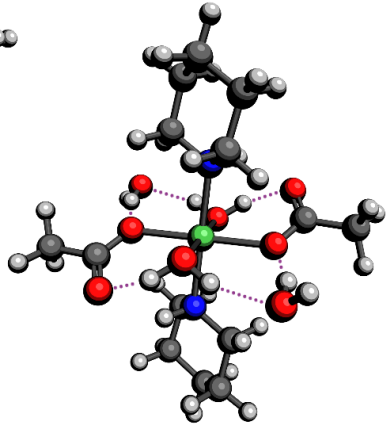
Model[$MeIm_2$]



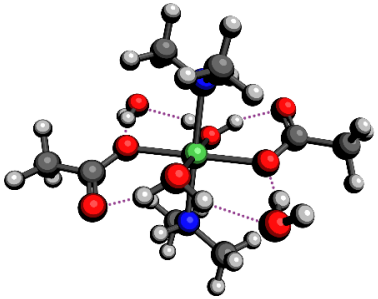
Model[Py_2]

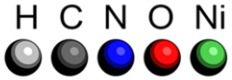


Model[$Pipe_2$]



Model[DMA_2]





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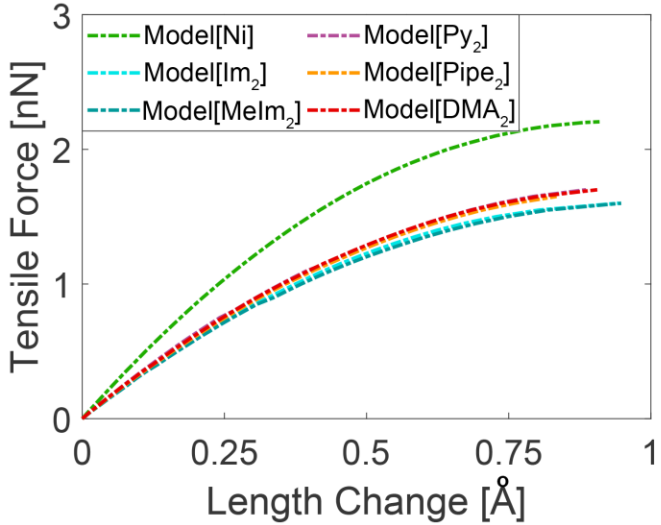
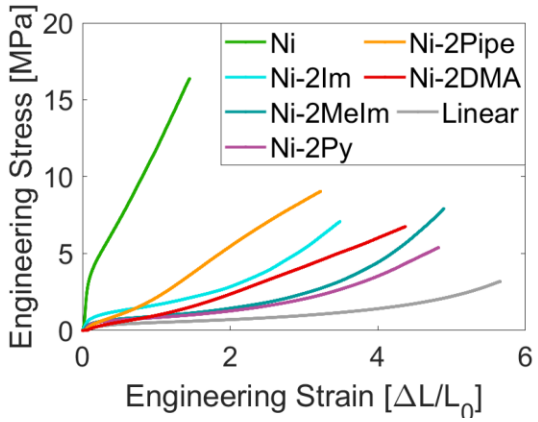
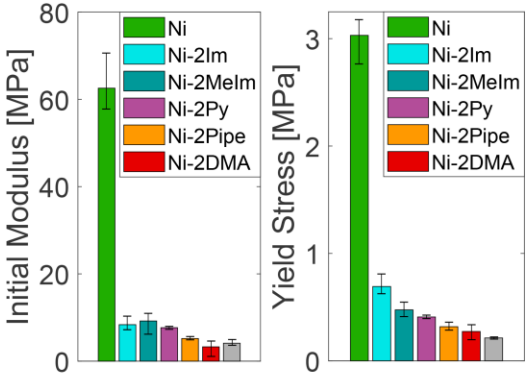
Varying Ligand Type



Model	[$MeIm_2$]	[Py_2]	[$Pipe_2$]	[DMA_2]
ΔG (kcal/mol)	4.68	5.21	5.95	6.51
ΔG‡ (kcal/mol)	15.36	16.63	16.33	16.66

Experiment





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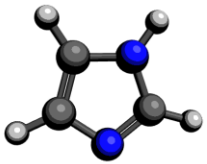
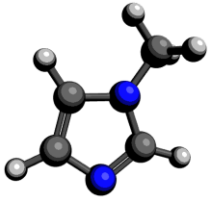
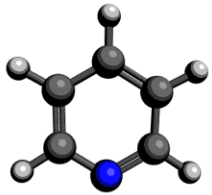
Varying Ligand Type



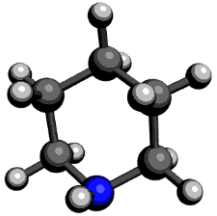
Im



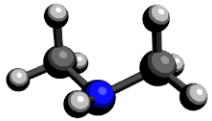
MeIm



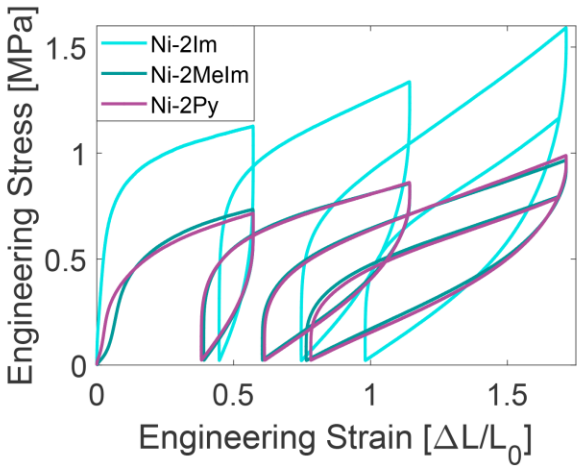
Py

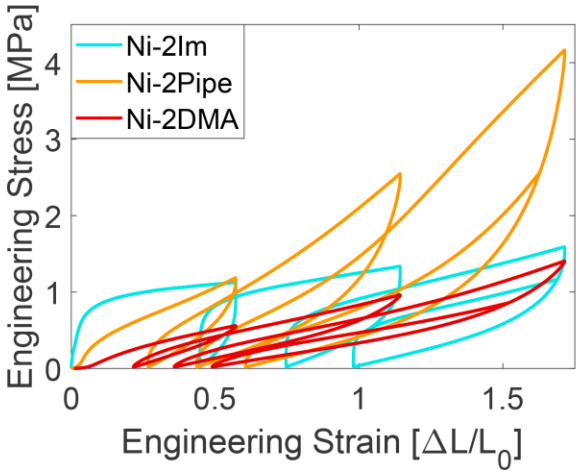


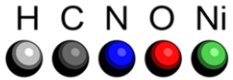
Pipe



DMA







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In Summary

- **Adding ligands** reduced crosslink stiffness and energy barrier
  - Manifested in reduced material stiffness and yield strength

- **Varying ligand amount** reduced crosslink stiffness and barrier
  - Manifested in excellent tunability from Ni to the Linear material

- **Varying ligand type** requires more in-depth analysis to predict
  - Material properties likely ruled by ligand-environment interactions
    - More comprehensive simulations

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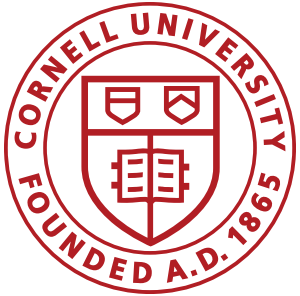

XSEDE
Extreme Science and Engineering Discovery Environment

Thank you

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