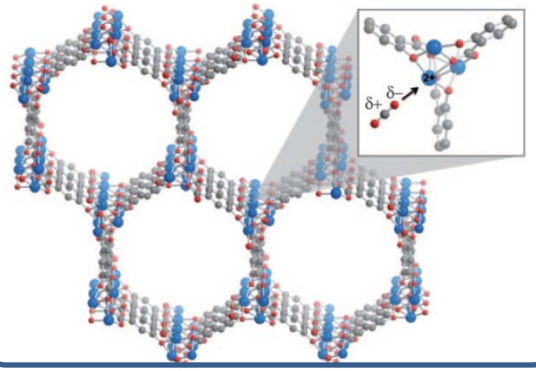
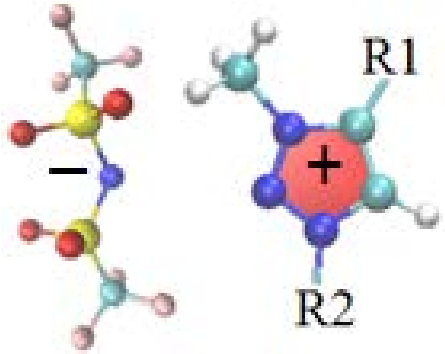
Taking Fundamentally New Materials for CO_2 Capture Toward Applications: A Synergistic Effort

Presented by Jeff Kortright, LBNL (for Berend Smit)

Metal Organic Frameworks (MOFs)



Ionic Liquids



BERKELEY LAB

EFRC Energy Frontier Research Center
for gas separations relevant to clean air technologies

NETL

Carnegie Mellon University

Acknowledgements

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DOE facilities

NERSCC, LBNL
Advanced Light Source, LBNL
Molecular Foundry, LBNL

Funding (to LBNL)

DOE, Fossil Energy, Carbon Capture Program
FWP MSKCBS
~250K$/year for 3 years

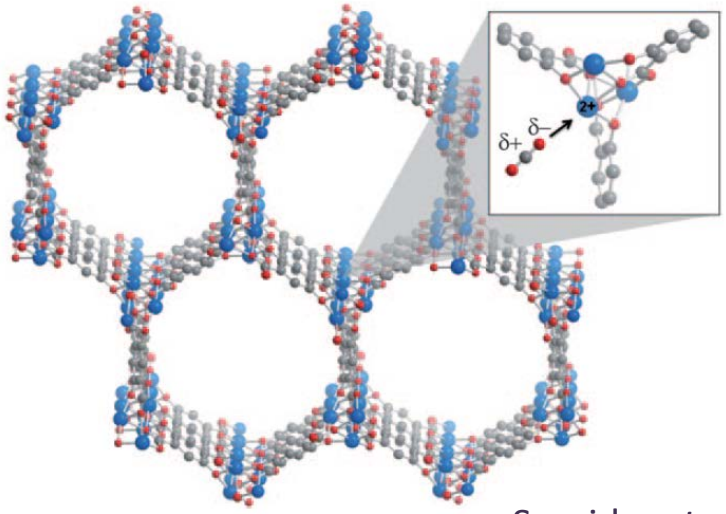
Combine strengths of Berkeley & NETL

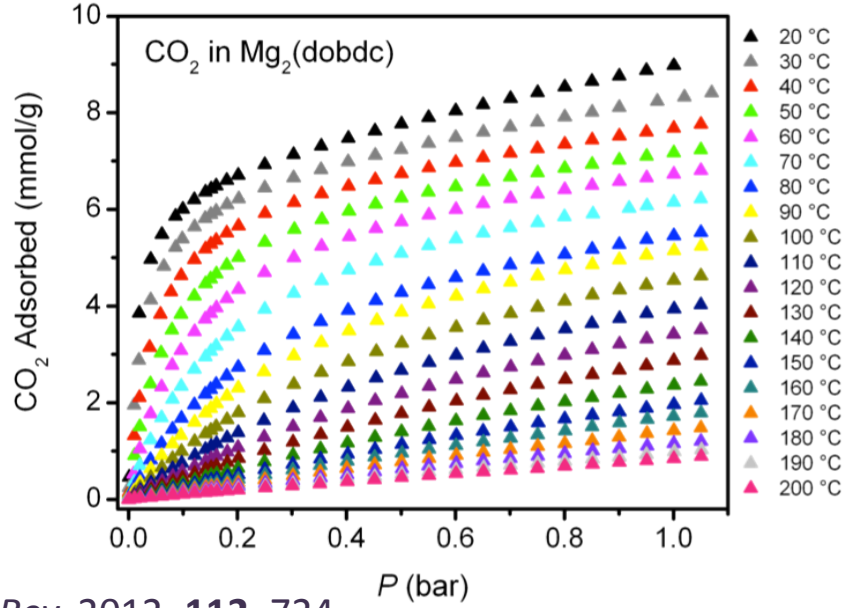
- Synthesis of MOFs tailored for gas separations & other applications
- Computational methods, *ab initio* theory
- Advanced characterization development (NMR, soft x-ray synchrotron techniques)
- National facilities (NERSCC, ALS, MF)

- Mitigating strategies for fossil fuel use
- Novel membranes for CO_2 capture
- Ionic liquids for CO_2 capture

Open metal site & functionalized MOFs

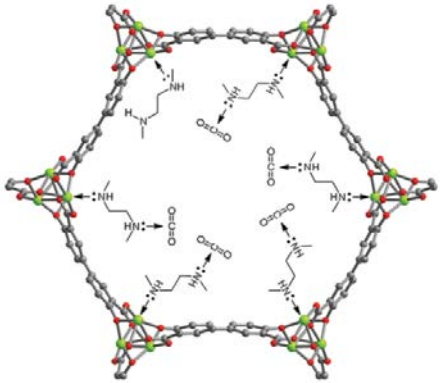
Mg^{2+}-MOF-74





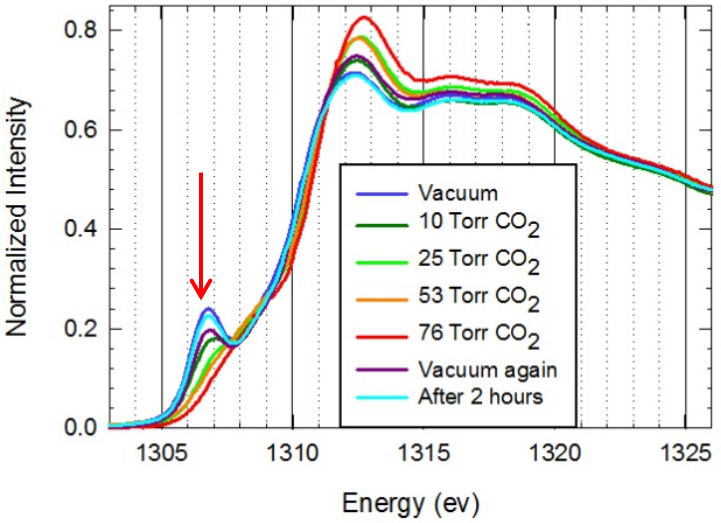
Sumida, *et al.*, *Chem. Rev.* 2012, **112**, 724

Amine-functionalized variant exhibits phase-change isotherm relevant to CO_2 capture.

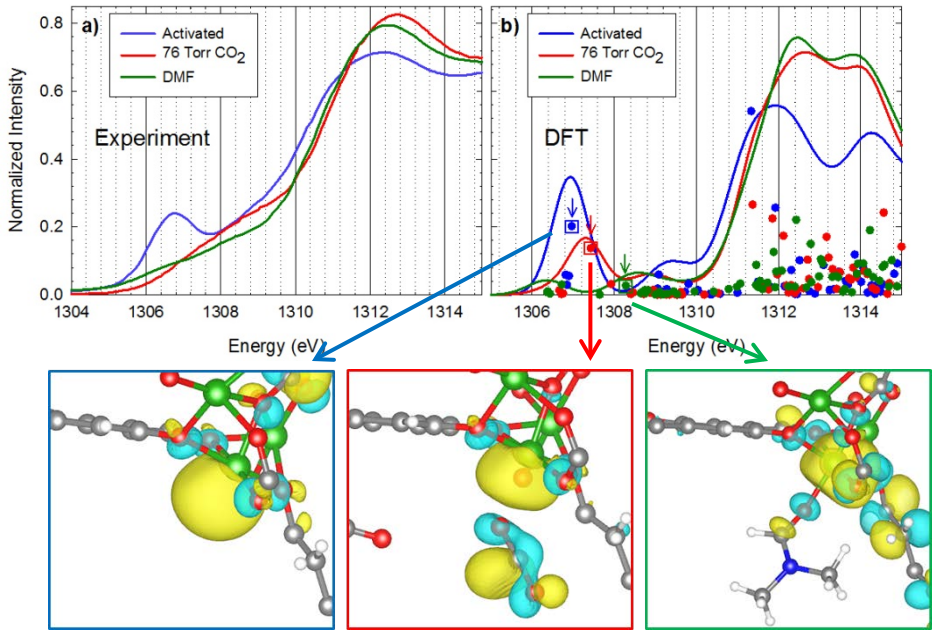


Tom McDonald, *et al.*, *JACS* 2012, **134**, 7056 (see poster)

CO_2 adsorption isotherm via Mg *K*-edge absorption in Mg-MOF-74

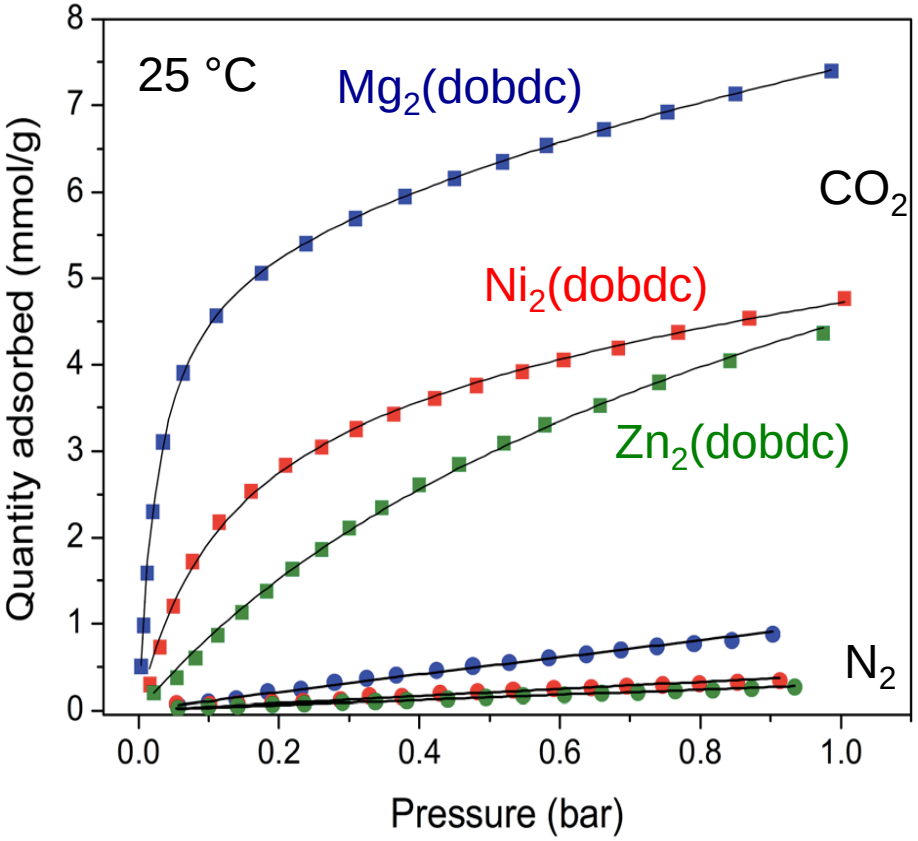


- Reversible spectral changes as CO_2 adsorbs & desorbs at open Mg^{2+} sites.
- *Ab initio* theoretical & experimental spectra agree.
- *Direct* confirmation of 1st principles description of MOFs that includes VdW interactions.



W. S. Drisdell, R. Poloni, T. M. McDonald, J.R. Long, B. Smit, J.B. Neaton, D. Prendergast, J.B. Kortright, *J. Am. Chem. Soc.* 2013, **135**, 18183

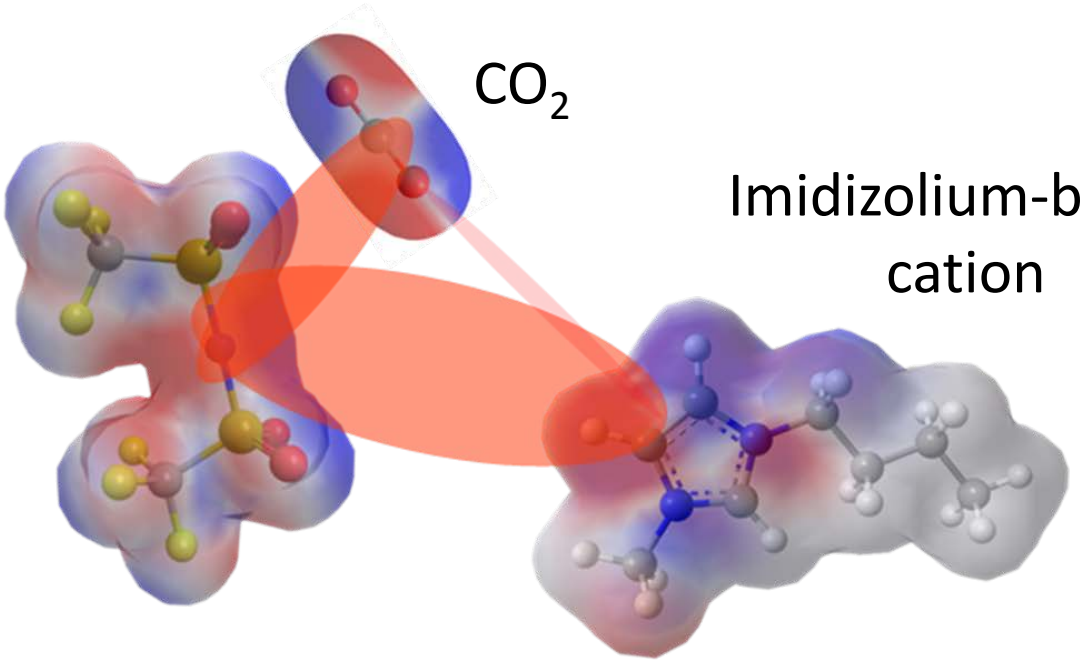
Mixed matrix membranes incorporating Mg-MOF-74



- Mg-MOF-74 nanocrystals in polyimide membranes perform nearly as well as bulk material.
- CO_2/N_2 selectivity maintained.
- Rubbery polymers reduce CO_2 adsorption by blocking access to pores.
- Possible approach to implement MOFs in CO_2 capture.

T.H. Bae, T. McDonald, J.R. Long, *Energy Environ. Sci.* 2013, ***6***, 3565

Intermolecular interactions in ionic liquids for CO_2 capture



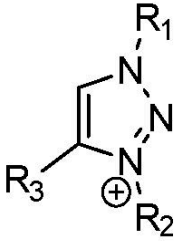
- Major interaction between CO_2 and anion
- Cation interacts strongly with anion
- Tuning cation may indirectly but significantly affect CO_2 solubility

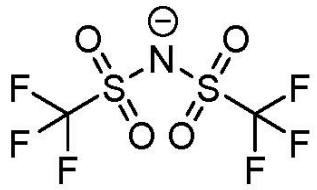
Towards a Materials Genome Approach for Ionic Liquids: Synthesis Guided by *Ab Inito* Property Maps

F. Yang, M. Lartey, K. Jariwala, S. Bowser, K. Damodaran, E. Albenze, **D. Luebke**, **H. Nulwala**, **B. Smit**, **M. Harancyzk**,

J. Phys. Chem. (submitted for publication)

Consider unexplored triazolium based ILs





Tf_2N^-

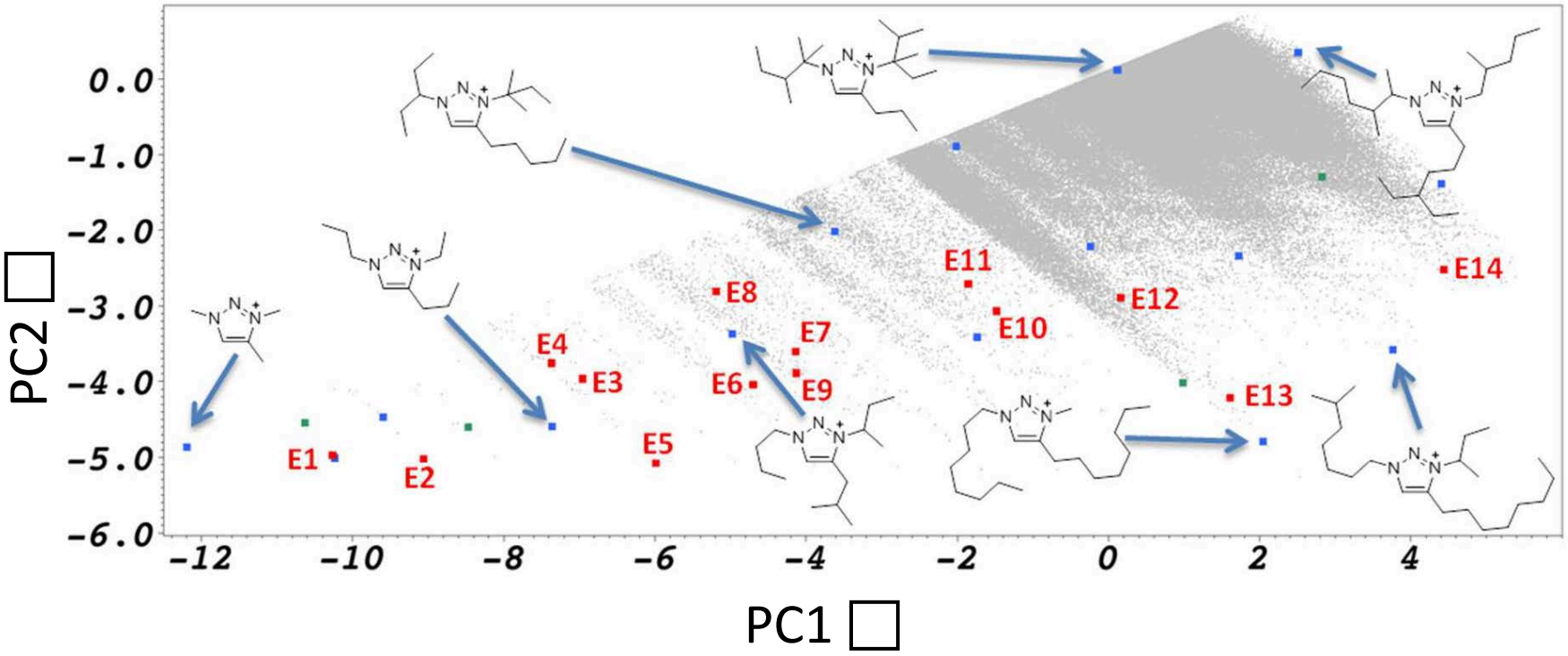
- Limit R_1, R_2, R_3 to hydrocarbons C1 – C8
- 33 common anions in including Tf_2N^-
- Limit IL combinations to ~200,000 (from ~2M)
- Develop *ab initio* force fields for 20 ILs spanning large set, calculate:
  - Density
  - Ion diffusivity, viscosity
  - Henry coefficients for CO_2, etc.

F. Yang, M. Lartey, K. Jariwala, E. Albenze, R.L. Thompson, J. Kim, M. Haranczyk, N.B. Nulwala, D. Luebke, B. Smit, *Phys. Chem. Chem.Phys* 2013, **15**, 3264

- Find most strongly correlated chemical descriptors (maximum projection area, maximum projection volume , VdW volume)
- Use neural network and other methods to extrapolate properties over entire IL set.

Property maps for ρ, k_H, D_+, *etc*.

Projected onto 2 strongest principal components, PC1, PC2



Blue = full force field simulation for training algorithms

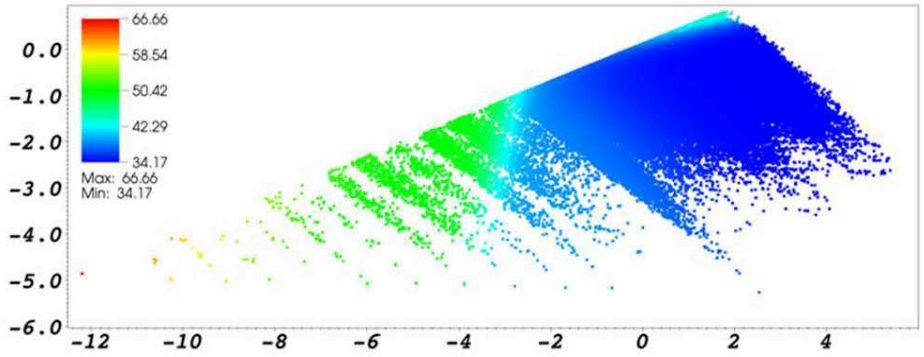
Red = experimental calibration (synthesize & test)

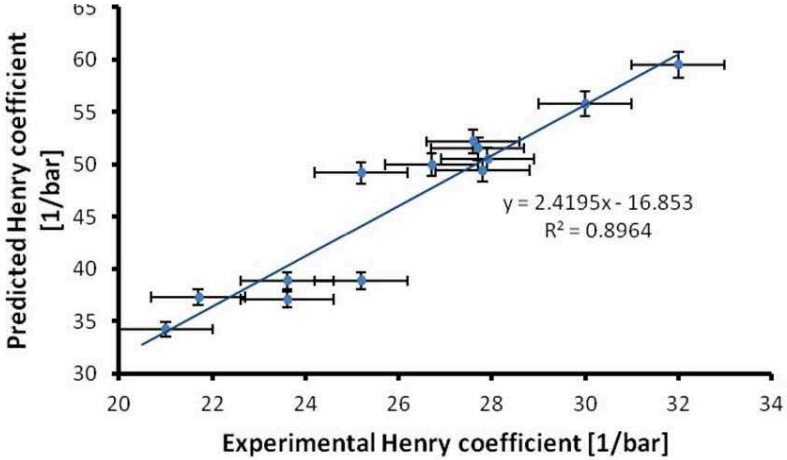
Comparison with experiment

Simulated property maps

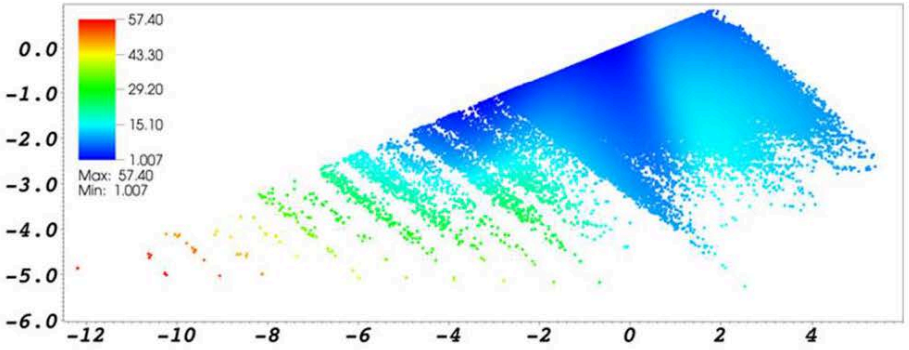
Experimental verification (E1-E15)

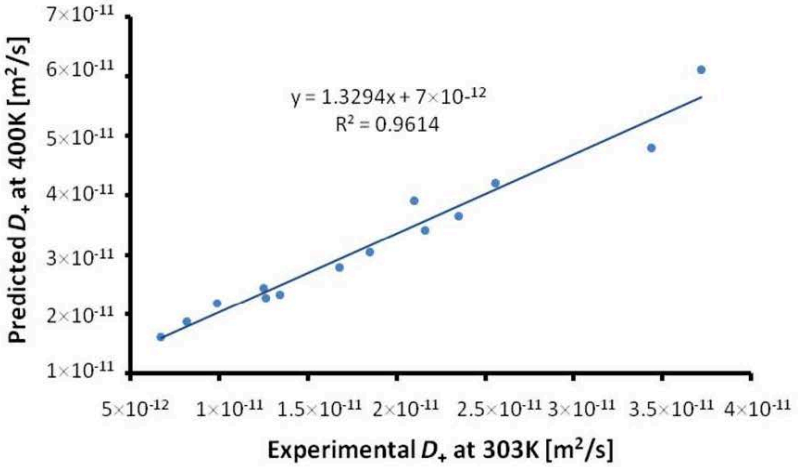
CO_2 Henry coefficient



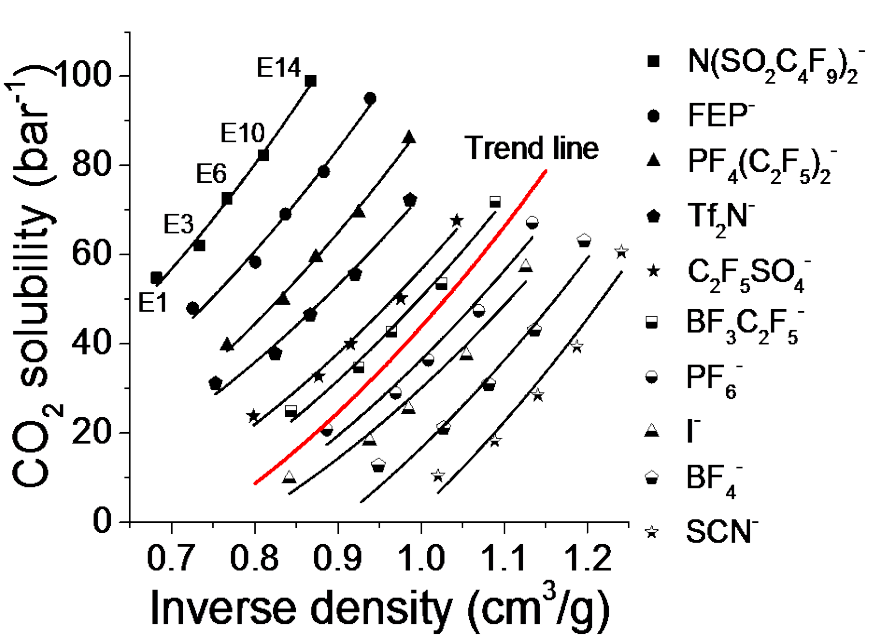


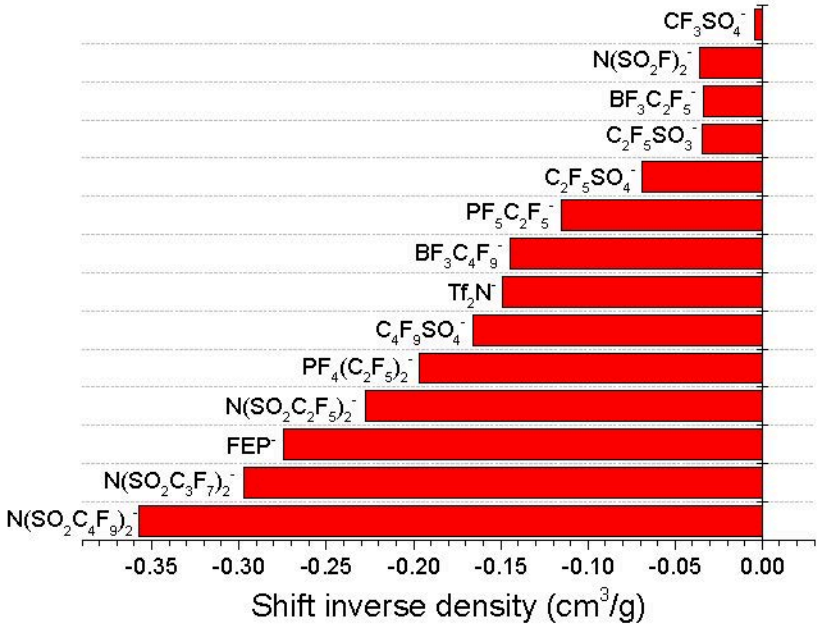
Cation diffusivity





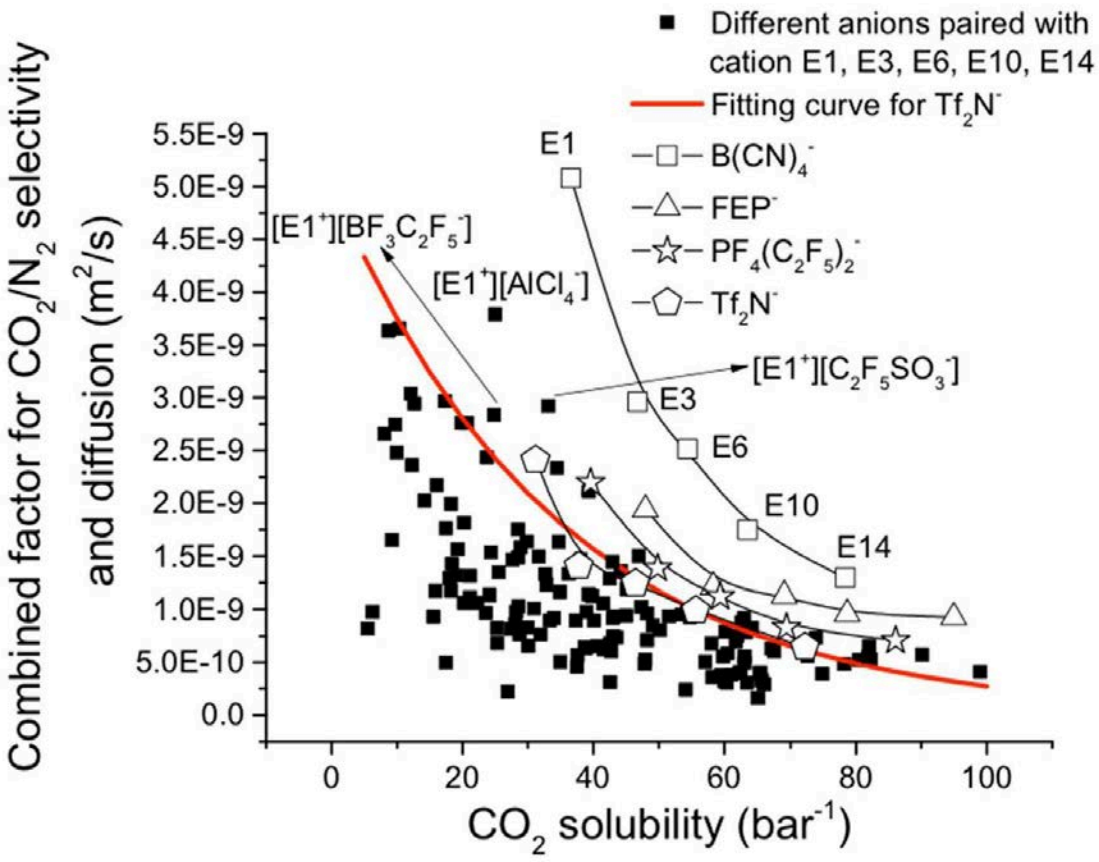
Further extrapolation of calculated properties w.r.t. trend lines



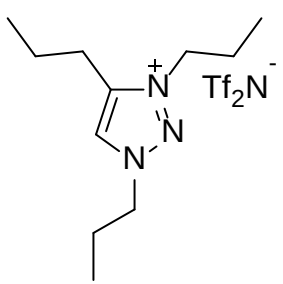


Final results: strong anion dependence

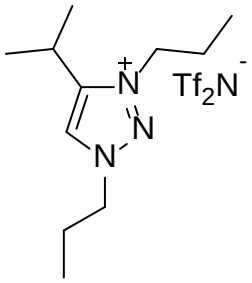
$B(CN)_4^- > FEP^- > PF_4(C_2F_5)_2^- > Tf_2N^-$



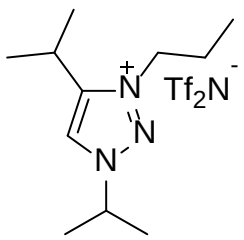
Comparative study of 4 ILs w/ Tf_2N^- anion: effect of isomeric cation branching



(I)



(II)



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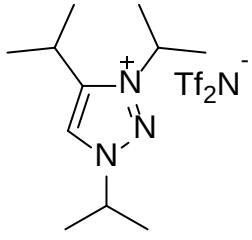
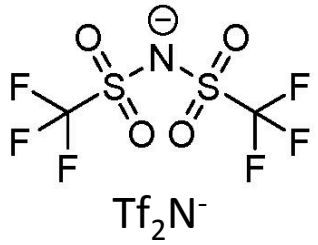


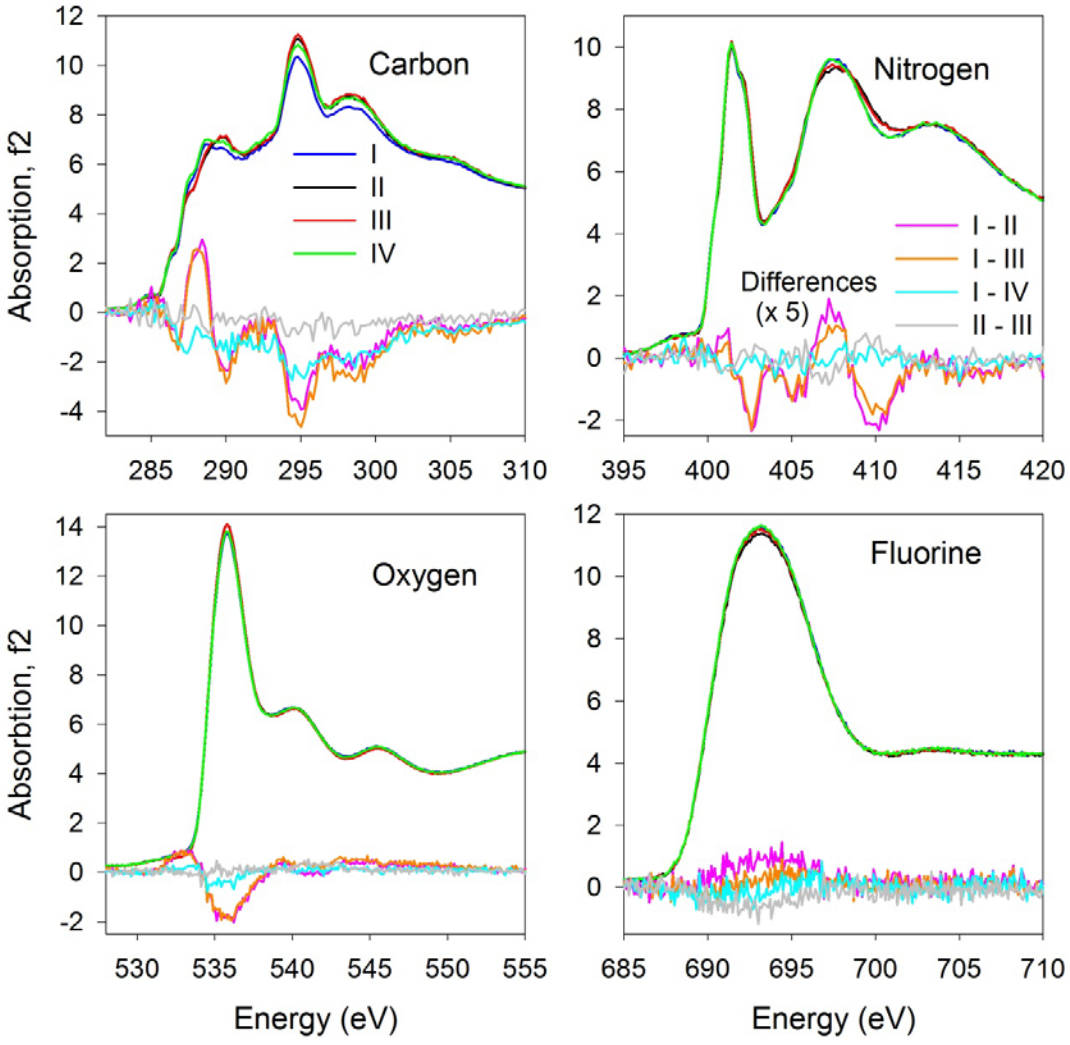
(IV)

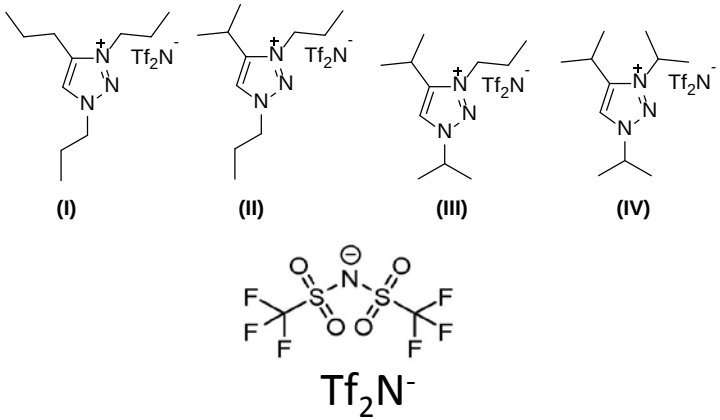


- ILs with various degree of branching were synthesized.
- Simulated density and CO_2 solubility do not match with experimental trends.
- Unusual thermodynamic trends not systematic w/ branching

IL	Number of branches	Density / g.cm^{-3}	Molar volume / cm^3.mol^{-1}	Henry's Law Constant CO_2 / bar	*H* / cP
(I)	0	1.366	348.7	28.8	57.6
(II)	1	1.347	353.9	29.9	66.1
(III)	2	1.347	353.9	28.6	81.5
(IV)	3	1.346	354.1	32.2	103.2

XAS at C, N, O, and F *K*-edges reveals unexpected dependence on branching





- Spectra of ILs I & IV (II & III) are nearly identical.
- Specific C-A interactions depend on *symmetry* of distribution of R groups.
- O & N differences may relate to Tf2N$^-$ conformational differences.
- C differences sense R-group C-H & C-C bonds; H bonding(?).

Summary

- Materials Genome approach combines many types of algorithms to screen ~ 200,000 ILs for their CO_2 capture potential. Impressive demonstration.
- Should be extendable to other well-defined problems.
- MGA relies on experimental calibration points.
- MGA effectively coarse-grains over fine details of intermolecular interactions.
- Experiments can observe trends that do not follow coarse-grained MGA predictions, evidently due to fine details of C-A interactions. Can *ab initio* theory capture these subtle trends?