# Direct Air Capture with Aqueous Amino Acids and Crystalline Guanidines

ERKCC08

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Oak Ridge National Laboratory

U.S. Department of Energy

National Energy Technology Laboratory

**Direct Air Capture Kickoff Meeting**

February 24-25, 2021

# Program Overview

**Funding:** BES, Chemical Sciences, Geosciences, and Biosciences Division, Separation Science ($1,400,000/year budget)

**Project Performance Dates:** 2019-2022

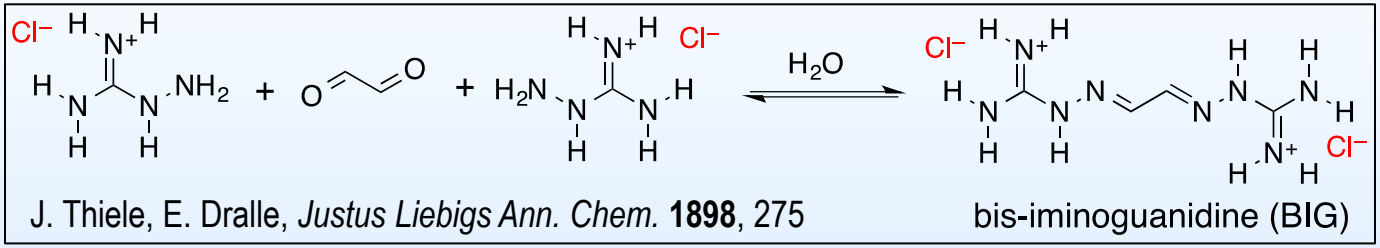
**Project Participants:** Radu Custelcean (lead PI), Slava Bryantsev, Santa Jansone-Popova, Bruce Moyer, Nikki Thiele

**Overall Project Objectives:** *Understand the structural, energetic, and mechanistic factors controlling the efficiency and selectivity of ion separations via constitutional dynamic chemistry*

**Aim 2:** *What are the structural, thermodynamic, and kinetic factors leading to strong, fast, and selective binding of anions (e.g., $SO_4^{2-}$, $CrO_4^{2-}$, $CO_3^{2-}$) by dynamic receptors, and to their energy-efficient release for sustainable separations?*

# Technology (Science) Background

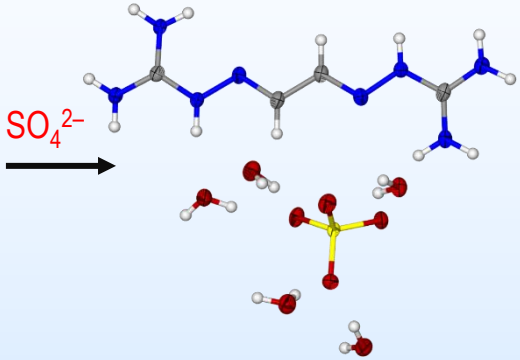
## Bis-iminoguanidine (BIG) receptors for oxyanion separations




J. Thiele, E. Dralle, *Justus Liebigs Ann. Chem.* **1898**, 275

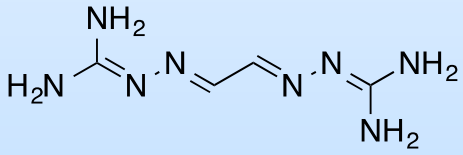
bis-iminoguanidine (BIG)

*Chem Commun* **2020**, *56*, 10272




Very low aqueous solubility
$K_{sp}$ = 3.2(5) x $10^{-7}$
(on a par with $SrSO_4$)

$HCO_3^-$

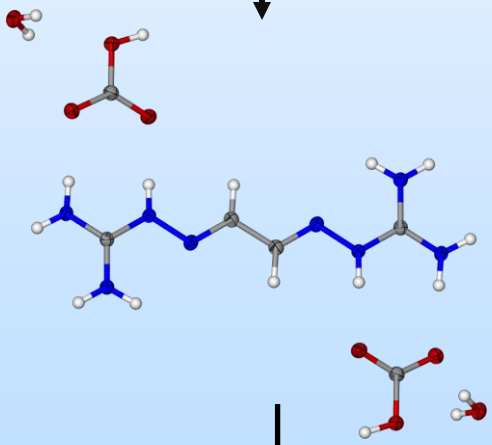


glyoxal-bis(iminoguanidine)
**GBIG** (10 mM aq)

13% $CO_2$ + 87% $N_2$
0.4 L/min

30 min, 91%

$\Delta H_{abs}$ = – 61.3 kJ/mol $CO_2$



Phase-change (reactive cryst) $CO_2$-capture process, combining the characteristics of aqueous solvents and solid sorbents

120 °C, 60 min
– $CO_2$, – 2 $H_2O$

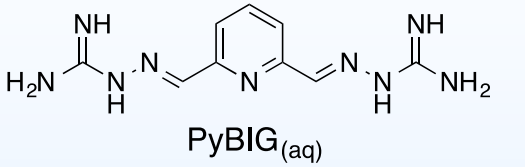
$\Delta H_{des}$ = 121.5 kJ/mol $CO_2$



*Chem* **2019**, *5*, 719 (highlighted in Science)

# Technical Approach/Project Scope

**DAC cycle**




PyBIG$_{(aq)}$

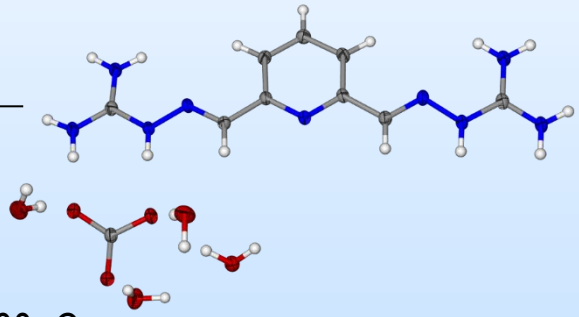
**release**

80-120 °C
– $CO_2$
– 5 $H_2O$

**absorption**

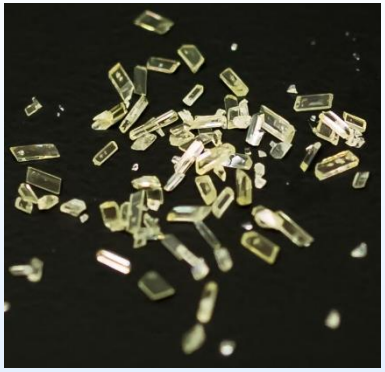
$CO_2$ (air)

$K = 10^5$ atm$^{-1}$
$\Delta H$ = – 71 kJ/mol



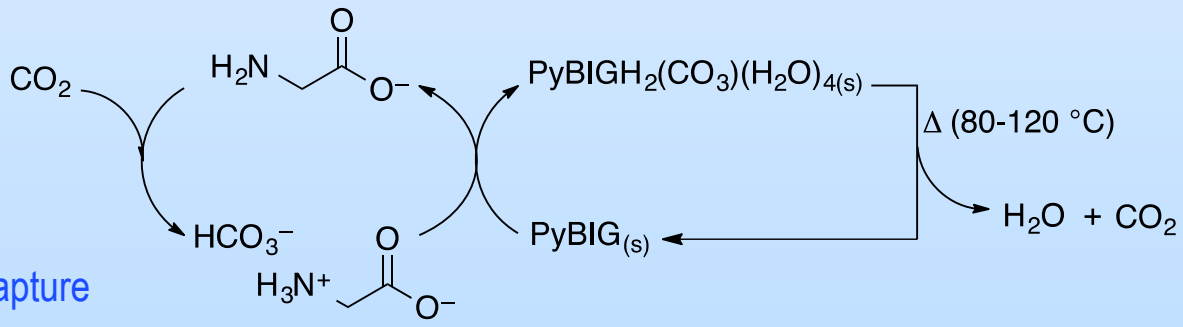
$\Delta H$ = 223 kJ/mol
$H_2O$: 148 kJ/mol

**Benchmark:**
$CaCO_3$ 179 kJ/mol, 900 °C



PyBIG-$CO_3$: $K_{sp} = 1.0 \times 10^{-9}$
$CaCO_3$: $K_{sp} = 3.4 \times 10^{-9}$

**DAC bi-cycle with amino acid/PyBIG**



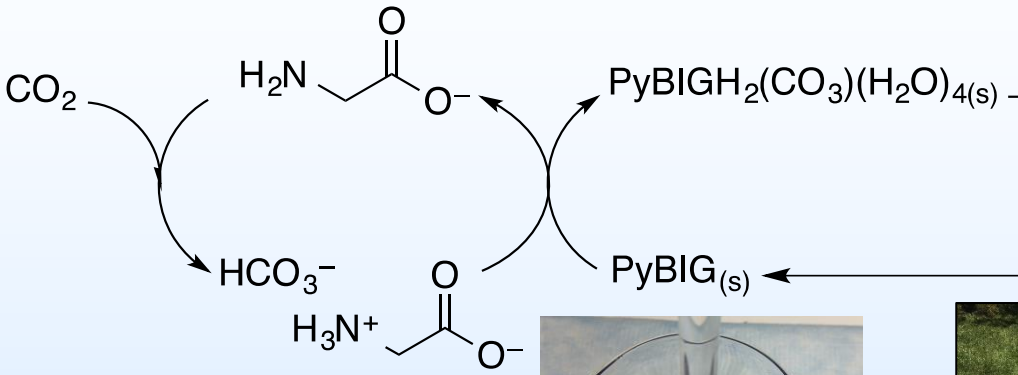

**Fundamental questions:**

- What factors determine the efficacy of $CO_2$ capture and the energy efficiency of $CO_2$ release?
- How important is the water in the crystals (enthalpy vs entropy)?
- What is the synergy between the amino acids and BIGs?


*Angew. Chem. Int. Ed.* **2017**, *56*, 1042
*Nature Energy* **2018**, *3*, 553
*Ind. Eng. Chem. Res.* **2019**, *58*, 23338
*ChemSusChem* **2020**, *13*, 6381

# Team and Facilities

Air humidifier




$CO_2$ loading monitored by
NMR, IC, Coulometric titration

Solar oven

Charles Seipp

Neil Williams

Katie Garrabrant

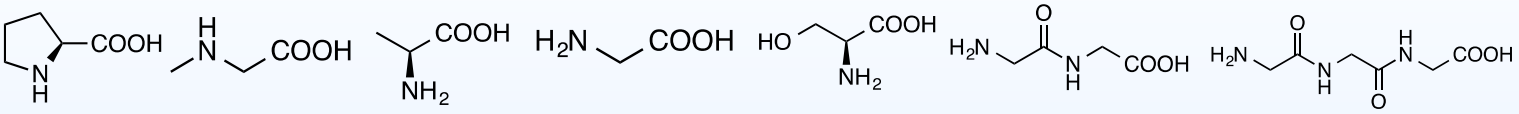
Flavien Brethomé

Pierrick Agullo

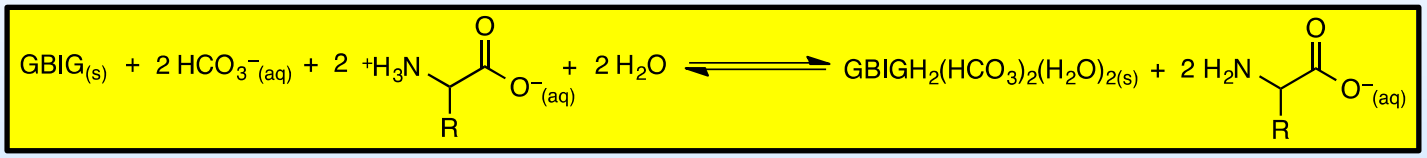
Diana Stamberga

# Progress and Current Status

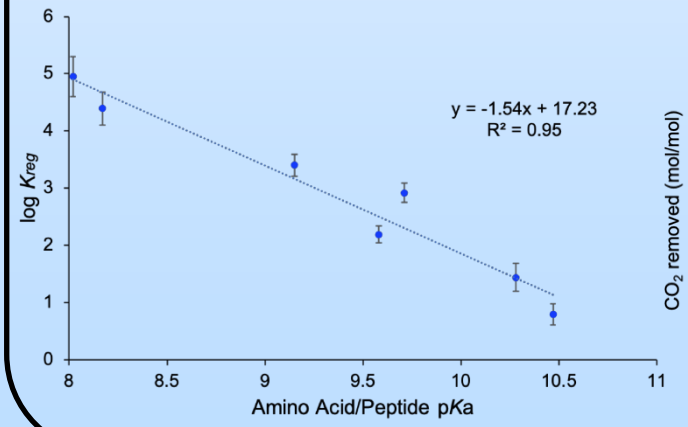
**Amino acids/Peptides** (p$K_a$)



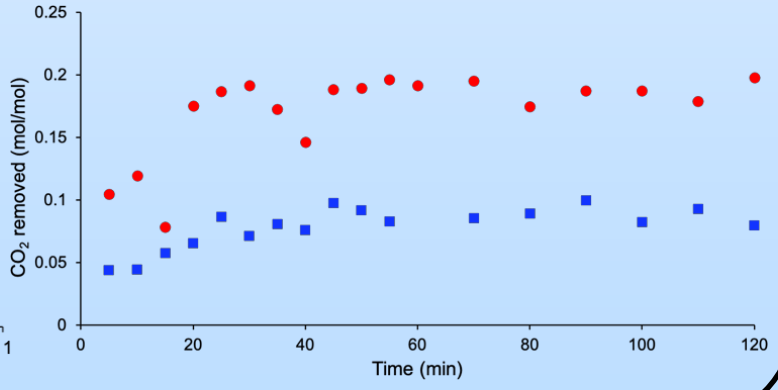
| Pro | Sar | Ala | Gly | Ser | GlyGly | GlyGlyGly |
|---|---|---|---|---|---|---|
| 10.47 | 10.28 | 9.71 | 9.58 | 9.15 | 8.17 | 8.02 |




Amino acid/peptide regeneration by GBIG-$HCO_3$ crystallization

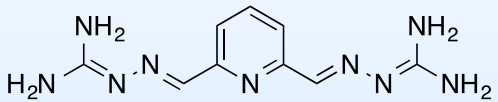



DAC with Gly vs GlyGly and GBIG



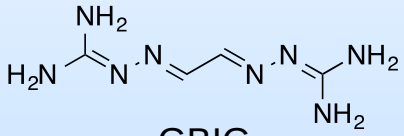

**BIGs**

reg. energies



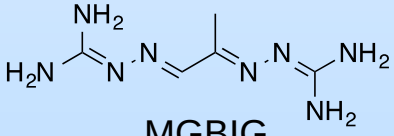
PyBIG

288 kJ/mol



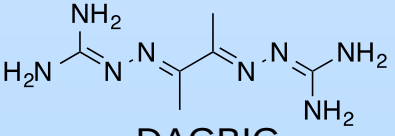
GBIG

152 kJ/mol



MGBIG

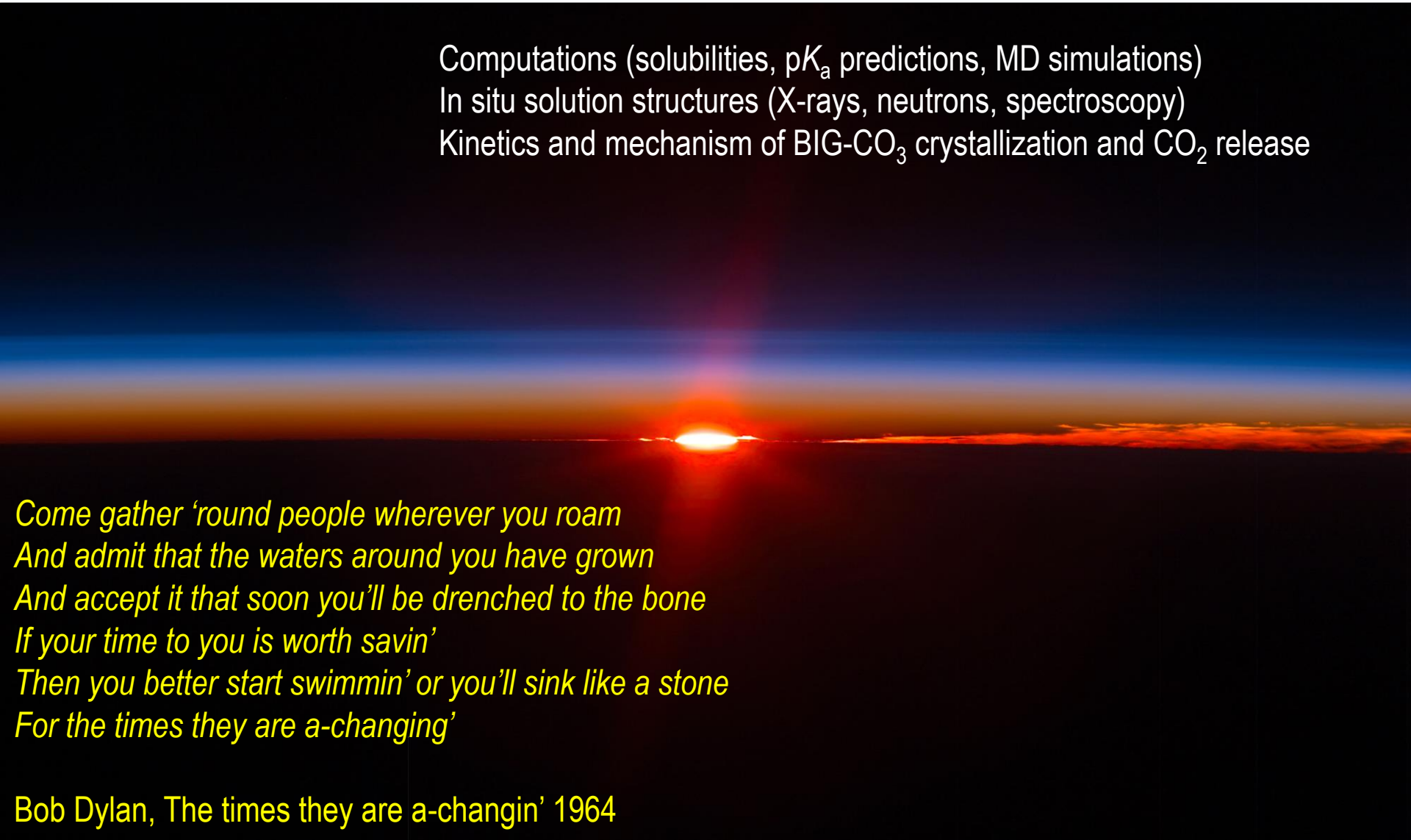
323 kJ/mol



DAGBIG

422 kJ/mol

# Opportunities for Collaboration



Computations (solubilities, p$K_a$ predictions, MD simulations)
In situ solution structures (X-rays, neutrons, spectroscopy)
Kinetics and mechanism of BIG-$CO_3$ crystallization and $CO_2$ release

*Come gather 'round people wherever you roam*
*And admit that the waters around you have grown*
*And accept it that soon you'll be drenched to the bone*
*If your time to you is worth savin'*
*Then you better start swimmin' or you'll sink like a stone*
*For the times they are a-changing'*

Bob Dylan, The times they are a-changin' 1964