CAPTURE AND CONVERT CO_2

COVALENT ORGANIC FRAMEWORKS COMPRISING COBALT PORPHYRIN CATALYST

Adriana Tucker

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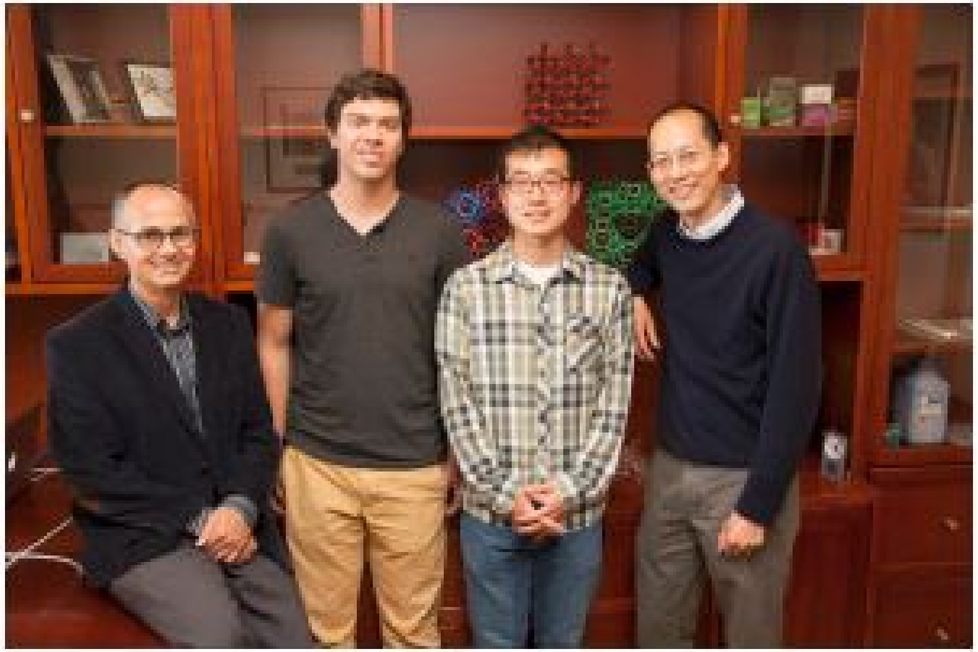
MOTIVATION

- Power production from combustion of fossil fuels, such as coal and natural gas, releases carbon dioxide (CO_2) and contributes to rising greenhouse gas (GHG) levels in the atmosphere.
- Technologies capable of cost-effective CO_2 capture and reuse would help stabilize atmospheric GHG levels and provide an opportunity to turn CO_2 into a feedstock for valuable products, such as chemicals and fuels
- Reductions in greenhouse gases
  - Only one part of the fight against climate change
- Prevents any additional emissions
  - Capture and re-use the gases already out there

RESEARCH

- Many attempts to develop homogeneous or heterogeneous catalysts for carbon dioxide
- U.S. Department of Energy (DOE)'s Lawrence Berkeley National Laboratory (Berkeley Lab)
- Incorporated molecules of carbon dioxide reduction catalysts into the sponge-like crystals of covalent organic frameworks (COFs)
  - Mainly been used for carbon capture and separation
  - Molecular control by choice of catalysts plus the robust crystalline nature of the COF
- Molecular system that not only absorbs carbon dioxide, but also selectively reduces it to carbon monoxide



From left, , Omar Yaghi, Christian Diercks, Song Lin and Chris Chang,. (Photo by Michael Barnes, UC Berkeley)

WHAT ARE COVALENT ORGANIC FRAMEWORKS (COFs)?

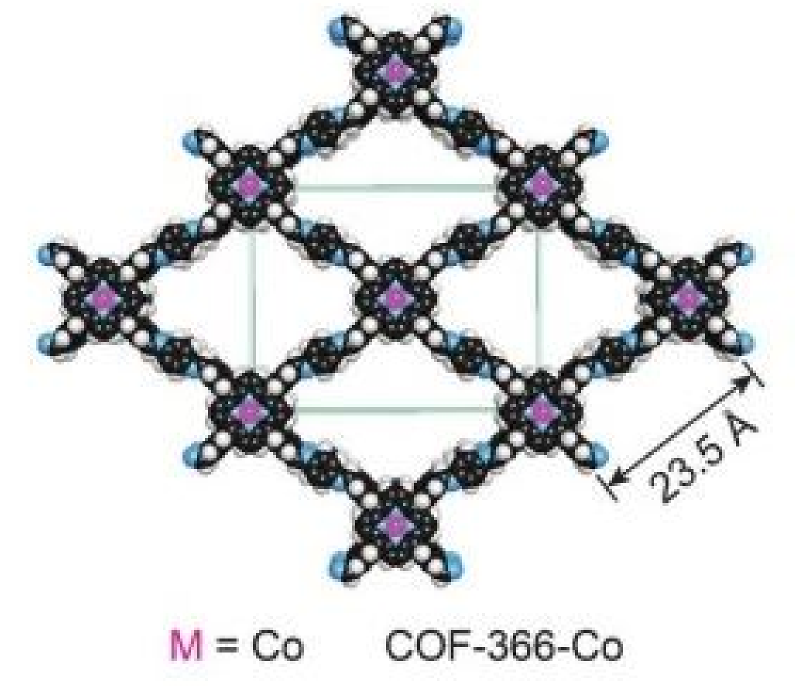
- Porous three-dimensional crystal consisting of a tightly folded, compact framework that features an extraordinarily large internal surface area
  - COF the size of a sugar cube were it to be opened and unfolded would blanket a football field
- Sponge-like quality of a COF's vast internal surface area enables the system to absorb and store enormous quantities of targeted molecules, such as carbon dioxide

WHY USE COFs?

- COFs could potentially combine advantages of both molecular and heterogeneous catalysts:
  - Construction with molecular building blocks would enable precise manipulation of the spatial arrangement of catalytic centers within the predetermined COF structure
  - The frameworks could be expanded and functionalized without changing the underlying topology of the structure
  - The conserved pore environment around the active sites within the COF could be tuned electronically and sterically while providing ready access for the substrate

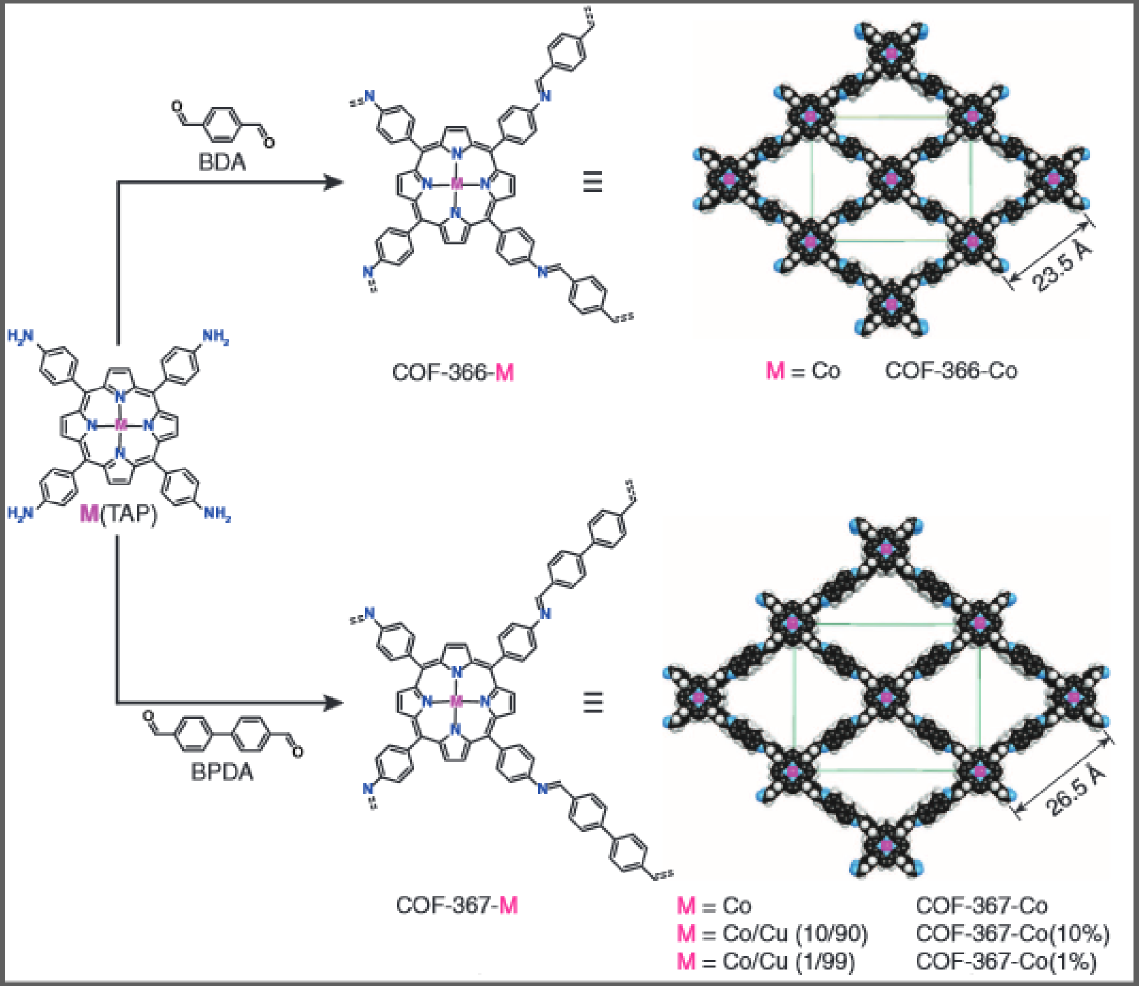
CONCEPT

- Molecular backbone of COFs is embedded with a porphyrin catalyst, a ring-shaped organic molecule with a cobalt atom at its core
  - Porphyrins are electrical conductors that are especially proficient at transporting electrons to carbon dioxide
  - Cobalt is naturally abundant and relatively inexpensive material (environmentally friendly)
- The catalysts, which are organic molecules containing cobalt, are suspended in the porous structure, preventing them from contacting one another and deactivating
- Reticular chemistry enables molecular systems to be "stitched" into netlike structures that are held together by strong chemical bonds



Structural model showing a covalent organic framework (COF) embedded with a cobalt porphyrin.

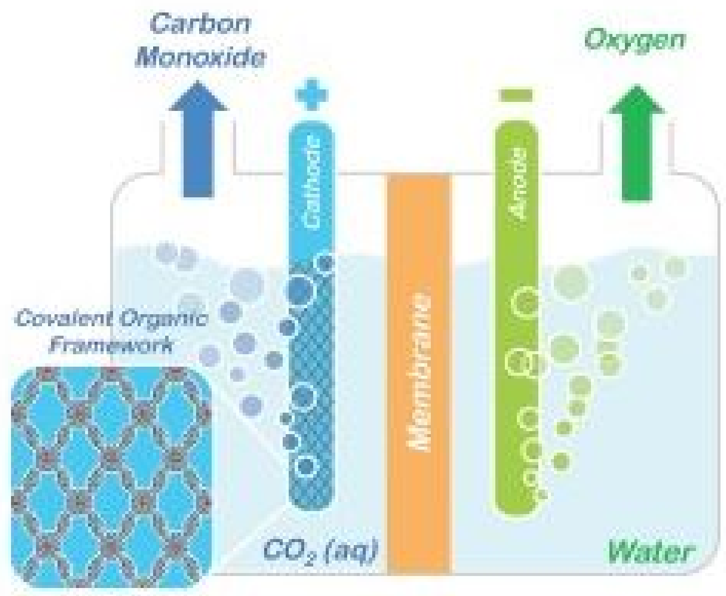
STRUCTURE



BDA
COF-366-M
M = Co
COF-366-Co
23.5 Å
M(TAP)
BPDA
COF-367-M
26.5 Å
M = Co
M = Co/Cu (10/90)
M = Co/Cu (1/99)
COF-367-Co
COF-367-Co(10%)
COF-367-Co(1%)

PROCESS

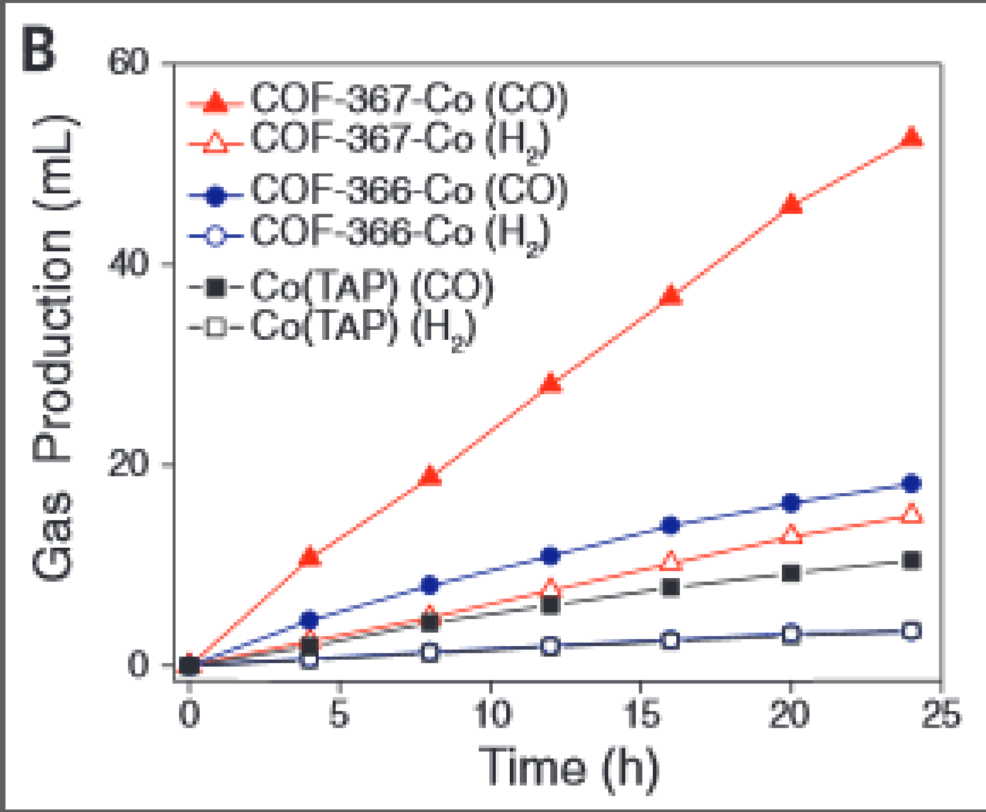
- Ability to modify chemically active sites at will with molecular-level control by tuning the building blocks constituting a COF's framework
- Because the porphyrin COFs are stable in water, they can operate in aqueous electrolyte with high selectivity over competing water reduction reactions, an essential requirement for working with flue gas emissions
- Electrolytic approaches benefit from using water as the reaction medium, as it is a cheap, abundant, and environmentally benign solvent that facilitates proton and electron transfer



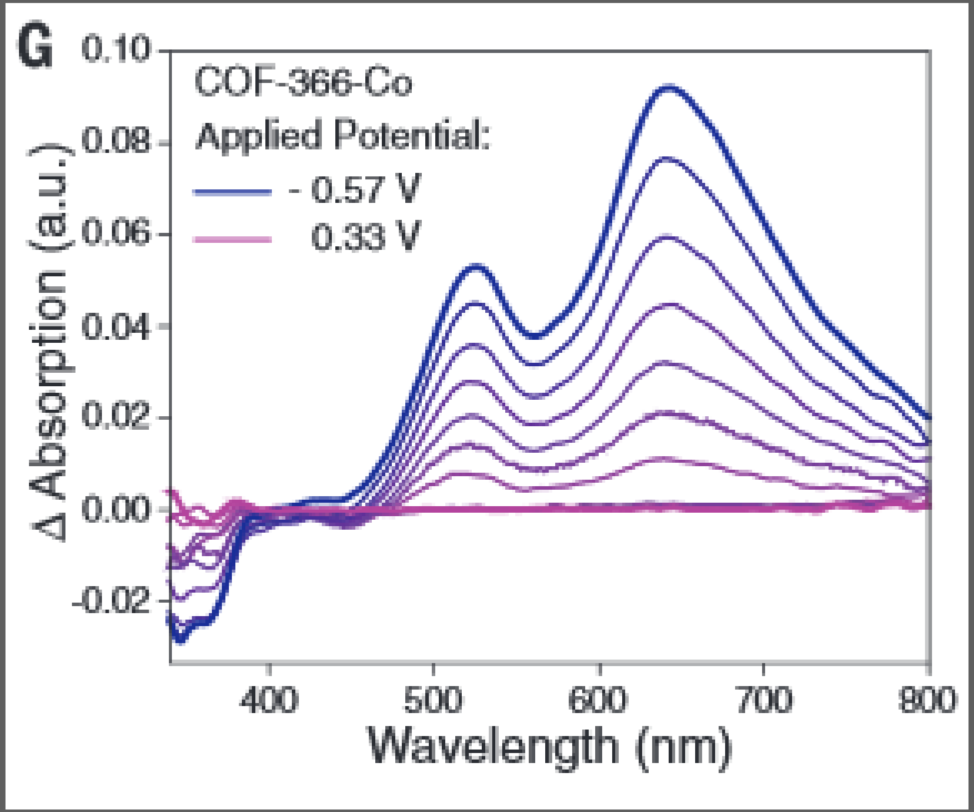
Conceptual model showing how porphyrin COFs could be used to split CO2 into CO and oxygen . (courtesy of Omar Yaghi)

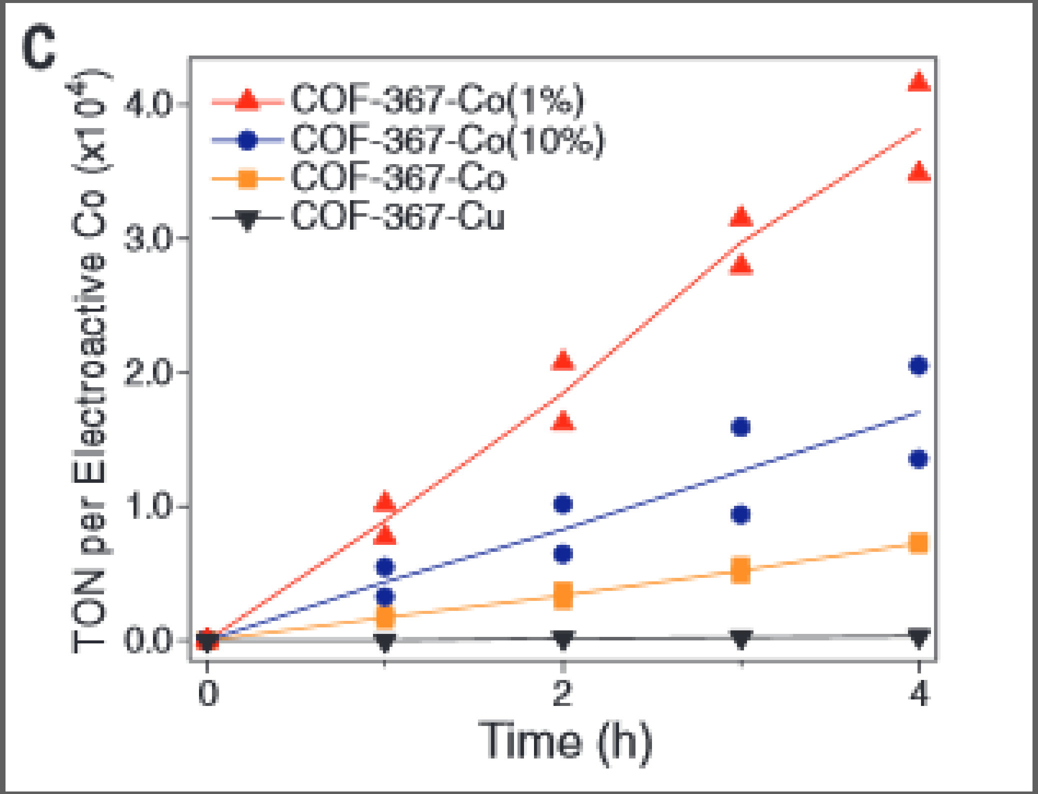
RESULTS

- In controlled potential electrolyses performed in carbon dioxide saturated aqueous bicarbonate buffer under applied potentials between 0.57 and 0.97 V (versus RHE), carbon monoxide was observed as the major reduction product with no other detectable carbon- based products
- At 0.67 V the catalyst displayed optimal performance
- More positive potentials led to sluggish carbon dioxide reactivity
- More negative potentials promoted off-pathway water reduction



RESULTS


G
COF-366-Co
Applied Potential:
- 0.57 V
0.33 V
Δ Absorption (a.u.)
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
400
500
600
700
800
Wavelength (nm)


C
COF-367-Co(1%)
COF-367-Co(10%)
COF-367-Co
COF-367-Cu
TON per Electroactive Co (x10^4)
4.0
3.0
2.0
1.0
0.0
0
2
4
Time (h)

RESULTS

- Porphyrin COFs displayed exceptionally high catalytic activity
- Turnover number up to 290,000, meaning one porphyrin COF can reduce 290,000 molecules of carbon dioxide to carbon monoxide every second
  - 26-fold increase over the catalytic activity of molecular cobalt porphyrin catalyst
  - Among the fastest and most efficient catalysts of all known carbon dioxide reduction agents
- Research indicates plenty of room for further improvement of porphyrin COF performances

IMPLEMENTATION

- Power plants
  - Absorb carbon dioxide and convert it into carbon monoxide
- Calcium carbonate ($CaCO_3$)
  - Construction material and whitening factory-produced paper
- Polycarbonates
  - Plastics used in products ranging from water bottles to spectacle lenses
  - Asia - 660,000 tonnes of polycarbonates annually, roughly 14% of the global total
- Polyols
  - Mattresses, adhesives, coatings, refrigerator insulation and spandex
- Hydrocarbons
  - Petrol, diesel, jet fuel and just about every other liquid energy source
  - ~14 times larger than that for non-fuel chemicals.

ADVANTAGES

- Reduction in GHGs
- Recycling carbon dioxide into fuels
  - Burying carbon dioxide at a cost of about $50 per ton
- Shift away from relying on fossil fuels as a source of carbon for materials and chemicals

DISADVANTAGES

- Expensive
- Energy intensive
- Difficulty with large scale implementation

POTENTIAL IMPACT

- Conversion process would change CO_2 from a waste product into a useful, economically viable feedstock, allowing renewable fuels and chemicals to be manufactured at costs comparable to more traditional processes
- Security
  - Converting CO_2 to synthesis gas and liquid fuels would help reduce amount of petroleum imports
- Environment
  - Carbon capture and reuse technology could help stabilize atmospheric GHG levels
  - Directly use ~300 million tonnes of CO per year
  - Indirectly reducing emissions by around a gigatonne per year ~5% of the total net emissions
- Economy
  - Economically viable carbon capture and reuse technology could promote the growth of new industries capable of utilizing synthesis gas as a feedstock for valuable products

WORLDWIDE SUPPORT

- Carbon XPRIZE
- German Ministry of Education and Research(2009) - €100 million (US$110 million)
- US Department of Energy(2011) - $106 million
- The European Union (2020) - Horizon Prize worth €1.5 million
- China(next 5 years) - 30 billion yuan ($4.7 billion)

CONCLUSION

- Carbon dioxide for its impact on the atmosphere and global climate change overshadow its value as an abundant, renewable, nontoxic and nonflammable source of carbon for the manufacturing of widely used chemical products
- Still a long way to go before the technology is ready for mass production
- If the cost of converting to fuels becomes low enough, then this idea would be important to controlling climate change

REFERENCES

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