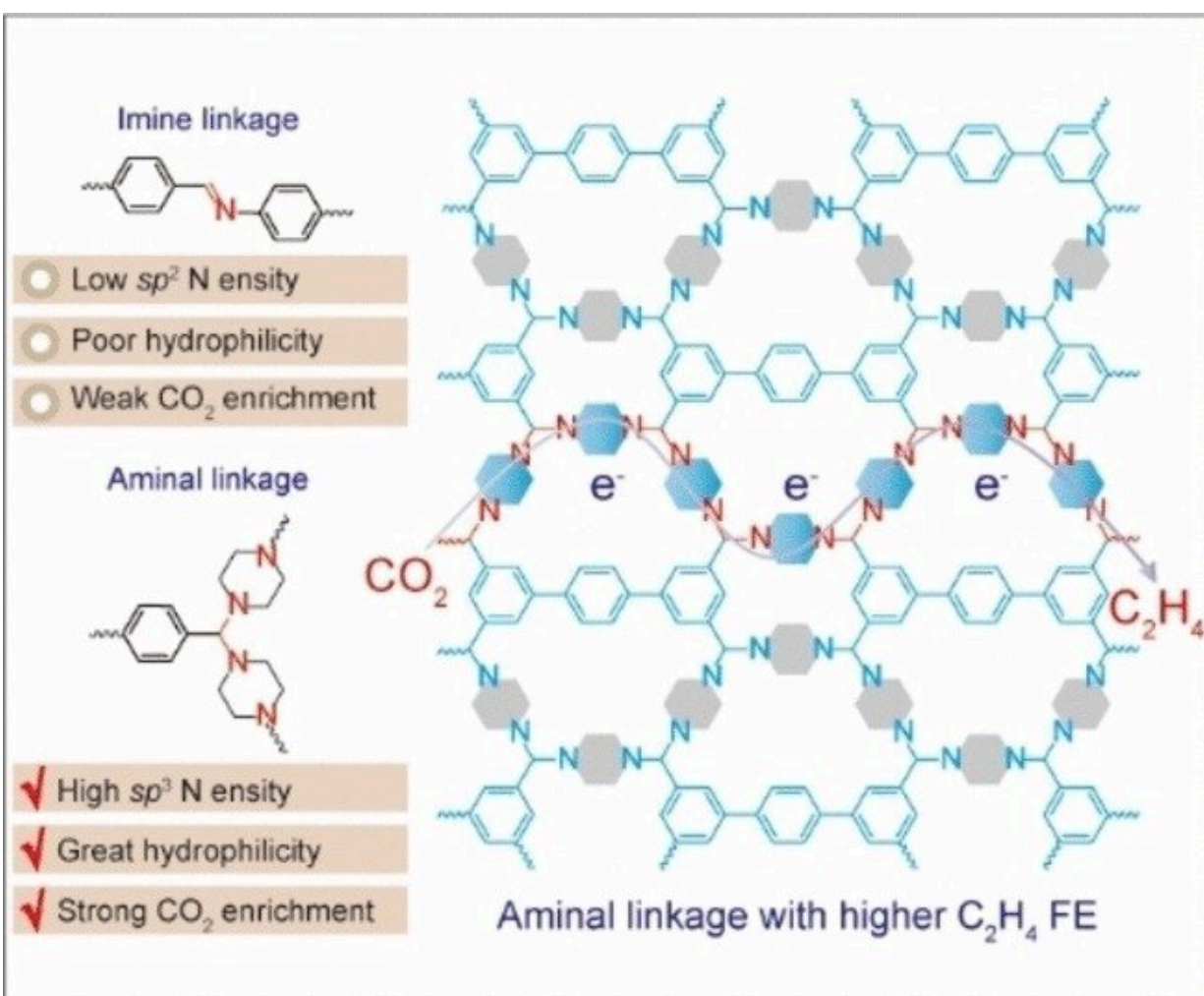


A metal-free organic framework for electrocatalytic production of ethylene from carbon dioxide

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Credit: *Angewandte Chemie International Edition* (2024). DOI: 10.1002/anie.202404738

Use of the greenhouse gas CO₂ as a chemical raw material would not only reduce emissions, but also the consumption of fossil feedstocks. A novel metal-free organic framework could make it possible to electrocatalytically produce ethylene, a primary chemical raw material, from CO₂.

As a team has [reported](#) in the journal *Angewandte Chemie International Edition*, nitrogen atoms with a particular electron configuration play a critical role for the catalyst.

Ethylene (ethene, C₂H₄) is an essential starting material for many products, including polyethylene and other plastics. Ethylene is produced industrially by the high-energy cracking and rectification of fossil feedstocks.

The electrochemical conversion of CO₂ to [ethylene](#) would be a promising route to reducing CO₂ emissions while also saving energy and fossil resources.

CO₂ is very stable, which makes it difficult to induce into reaction. With the use of electricity and catalysts, it is currently possible to convert it into C₁ chemicals such as methanol and methane.

The additional challenge in producing ethylene is that a bond must be formed between two carbon atoms. This has previously only been achieved with copper catalysts. Metal-free electrocatalysis would be advantageous because metals are a cost factor and can cause environmental problems.

A team led by Chengtao Gong and Fu-Sheng Ke at Wuhan University, China, has now developed a metal-free electrocatalyst for the conversion

of CO₂ to ethylene. The catalyst is based on a nitrogen-containing covalent organic framework (COF).

COFs are a new class of porous, crystalline, purely organic materials with defined topology. In contrast to [metal-organic frameworks](#) (MOFs), they require no metal ions to hold them together. Their pore sizes and chemical properties can be tuned over a wide range through selection of the building blocks.

The new COF contains nitrogen atoms with a special electron configuration (sp³ hybridization) as catalytically active centers. These sp³ nitrogen centers bind the individual building blocks into a framework through an aminal link (two amino groups bound to one carbon atom).

In contrast to COFs with a classic imine-linkage (–C=N–), aminal COFs have strict requirements regarding the lengths and angles of the bonds between building blocks, which causes the frameworks to be formed through ring closures.

The researchers found a suitable combination by using piperazine (a six-membered ring made of four carbon and two [nitrogen atoms](#)) and a building block made of three aromatic, six-membered carbon rings. When used as electrodes, their new COFs demonstrated high selectivity and performance (Faraday efficiency up to 19.1%) for the production of ethylene.

The success of the aminal COFs is due to the high density of active sp³-nitrogen centers, which both very effectively capture CO₂ and transfer electrons. This results in a high concentration of excited intermediates that can undergo C–C coupling.

In contrast, a variety of imine-linked COFs, which contain sp² nitrogen instead of sp³, were similarly tested and produced no ethylene. This

proves the importance of proper electron configuration for the electrochemical reduction of CO₂ to ethylene.

More information: Yang Xiao et al, Linkage Engineering in Covalent Organic Frameworks for Metal-Free Electrocatalytic C₂H₄ Production from CO₂, *Angewandte Chemie International Edition* (2024). [DOI: 10.1002/anie.202404738](https://doi.org/10.1002/anie.202404738)

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