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A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

3D vs. turbostratic: controlling metal-organic framework dimensionality via N-heterocyclic carbene chemistry

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<https://doi.org/10.1039/d2sc01041k>

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An azolium ligand was used to construct a Cu-metal-organic framework (MOF); the work demonstrates that using such building blocks is an effective way to immobilize N-heterocyclic carbenes (NHC) or NHC-derived species inside MOF pores.

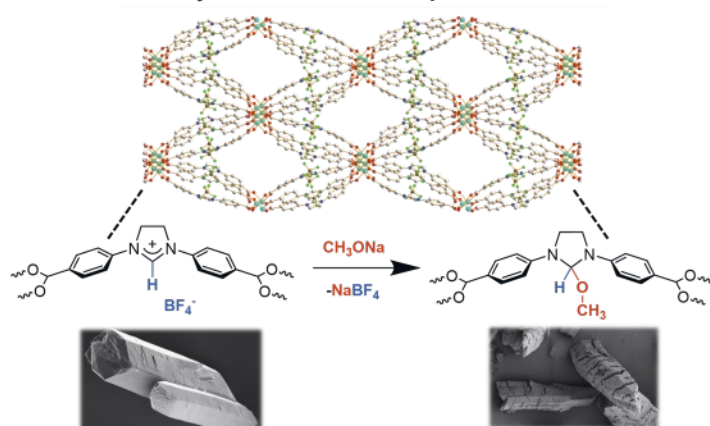
After synthesis of the novel Cu-MOF, denoted Cu-Sp5-BF₄, the C² carbon of the ligand was post synthetically modified with methoxide units, significantly altering the dimensionality of the material. In fact, the material passes from a 3D porous material to a 2D turbostratic phase, referred to as Cu-Sp5-OMe, during the modification.

Next, Cu-Sp5-BF₄ and the turbostratic Cu-Sp5-OMe, were modified with Ir, which was appended to the NHC ligand. Both Ir-containing materials, were then tested in the hydrogenation of stilbene, and it was shown that the catalytic performance is improved when using the turbostratic phase.

Authors' comments:

"In this work, we show how the structure of a MOF can be controlled by simply changing the counterion of the copper salt used during the MOF synthesis. Further, by virtue of N-heterocyclic carbene chemistry performed on the MOF ligand, combined with accessible Ir-NHC species inside the MOF pores, the catalytic hydrogenation of stilbene could be demonstrated."

NHC chemistry enables turbostratic phase formation in a MOF



Electrocatalytic metal hydride generation using CPET mediators

Subal Dey, Fabio Masero, Enzo Brack, Marc Fontecave, and Victor Mougél*

Nature, **2022**, *607*, 499

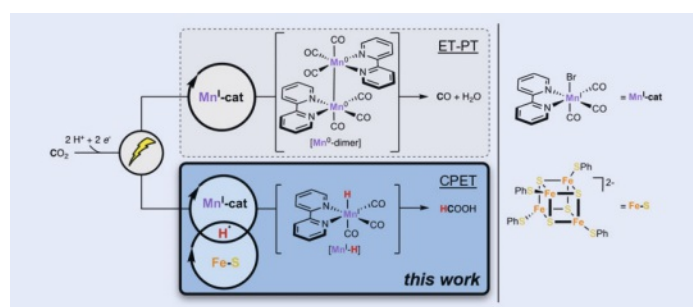
<https://doi.org/10.1038/s41586-022-04874-z>

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Transition metal hydrides (M-H) are ubiquitous intermediates in a wide range of enzymatic processes and catalytic reactions. A critical challenge to address is the ability to form M-H bonds easily. Herein, the authors propose an alternative strategy for the electrochemical generation of M-H, involving the overall transfer of an electrogenerated hydrogen atom to the metal centre in one kinetic step, called concerted proton-electron transfer (CPET). Enabling higher rates and lower driving forces, moderate reducing potentials and weak acids, therefore lowering the risk of the hydride species being quenched. Such a concerted process necessitates the use of a mediator in the process. They report that the use of an iron-sulfur cluster (Fe-S) can be used as a CPET mediator, owing to their low reorganization energy and the tuning of their redox potential on modulation of the ligand framework, in the presence of (Mn^I-cat) to promote the electrocatalytic formation of Mn-H species.

Authors' comments:

"We demonstrated that a kinetically advantageous formation of M-H species was possible *via* a CPET step to a singly reduced metal centre and applied it to promote the electrochemical reduction of CO₂. We expect this approach to be applicable to a broad range of reactions involving M-H intermediates."



Site-Specific Protein Labeling and Generation of Defined Ubiquitin Protein Conjugates Using an Asparaginyl Endopeptidase

Maximilian Fottner, Johannes Heimgärtner, Maximilian Gantz, Rahel Mühlhofer, Timon Nast-Kolb, and Kathrin Lang*

J. Am. Chem. Soc. **2022**, *144*, 13118

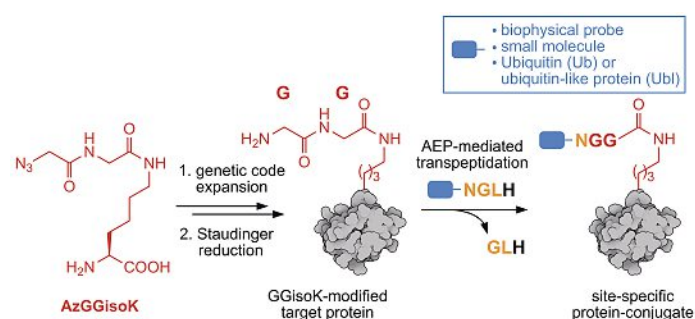
<https://doi.org/10.1021/jacs.2c02191>

Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

To label proteins at internal sites and generate protein–protein conjugates, in this work, the authors combine genetic code expansion and enzyme-mediated transpeptidation. Using genetic-code expansion they introduce a lysine residue bearing an isopeptide-linked glycyglycine moiety site-specifically into target proteins. This serves as an acceptor nucleophile in an Asparaginyl endopeptidase (AEP)-mediated transpeptidation reaction with various proteins and probes containing a tripeptidic recognition motif (NGL). A recently engineered AEP-variant allowed the facile generation of user-defined protein conjugates connected by a minimal, entirely peptidic linkage (NGG). The approach was used for attaching different fluorophores and small molecules to target proteins such as nanobodies and for creating defined ubiquitin–target protein conjugates displaying a native isopeptide bond.

Authors' comments:

“Our approach allows us to site-specifically label recombinant proteins at diverse sites with various probes and to generate defined protein–protein conjugates. Importantly, and different from other enzyme-mediated approaches, the obtained conjugates contain a minimal, completely peptidic linkage.



Advantages:

- flexible protein labeling at user-defined internal sites
- diverse probes, dual labeling
- minimal, tripeptidic linkage (NGG)
- generation of defined Ub/Ubl-protein conjugates

Ketenes in the Induction of the Methanol-to-Olefins Process

Xiangkun Wu, Zihao Zhang, Zeyou Pan, Xianguo Zhou, Andras Bodi, and Patrick Hemberger*

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<https://doi.org/10.1002/anie.202207777>

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The conversion of methanol-to-olefin over zeolites has become a promising alternative to the oil-based production of light olefins. While ketene has been postulated as a key intermediate in the zeolite-catalysed process, a detailed understanding of the reaction mechanism is still lacking. Using *operando* synchrotron photoelectron photon coincidence (PEPICO) spectroscopy and methyl acetate as a reactant, the authors successfully detected methylketene as a crucial intermediate, formed *via* methylation of ketene, confirming a so far only computationally predicted ketene-to-ethylene route. The detection of methylketene answers a long-standing question on how initial C-C bond intermediates are converted into light olefins.

Authors' comments:

“In heterogeneous catalysis, advanced technologies to identify reactive intermediates are crucial to unveil complex reaction networks. *Operando* PEPICO combines mass spectrometry and photoelectron spectroscopy as sensitive, selective and multiplexed analysis tool.”

