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Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Coupling of Unactivated Alkyl Electrophiles Using Frustrated Ion Pairs

Sven Roediger, Emilien Le Saux, Philip Böhm, and Bill Morandi*

Nature **2024**, *636*, 108
https://doi.org/10.1038/s41586-024-08195-1
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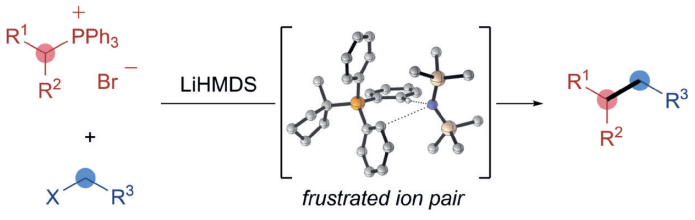
The formation of C(sp^3)–C(sp^3) bonds, central to many organic compounds, remains a significant challenge in organic synthesis, particularly in cross-electrophile coupling reactions. Traditional approaches rely heavily on transition-metal catalysis and preformed organometallic intermediates, often facing limitations in functional group compatibility and substrate scope. Here, the researchers report a novel, transition-metal-free platform for C(sp^3)–C(sp^3) bond formation, enabled by an unconventional single-electron transfer within a frustrated ion pair. This strategy circumvents the need for activating or stabilizing groups on the coupling partners and exhibits remarkable functional group tolerance, allowing the coupling of fragments traditionally challenging in transition-metal-catalyzed processes. Furthermore, this mechanistic innovation provides a foundation for designing new reactions, showcasing its potential to address long-standing challenges in organic synthesis. Their findings highlight a broadly applicable reactivity pattern that could expand the toolkit for constructing complex organic molecules in a more efficient and versatile manner.

Authors' comments:
"In this work, we introduce a new approach for cross-electrophile coupling reactions. We hope that the underlining mechanistic concept will inspire further reaction development."



unactivated substrates — transition metal-free — unusual mechanism

Photoreceptor-Like Signal Transduction Between Polymer-Based Protocells

Lukas Heuberger, Maria Korpidou, Ainoa Guinart, Daniel Doellerer, Diego Monserrat López, Cora-Ann Schoenenberger, Daela Milinkovic, Emanuel Lörtscher, Ben L. Feringa,* and Cornelia G. Palivan*

Adv. Mater. **2024**, *2413981*
https://doi.org/10.1002/adma.202413981
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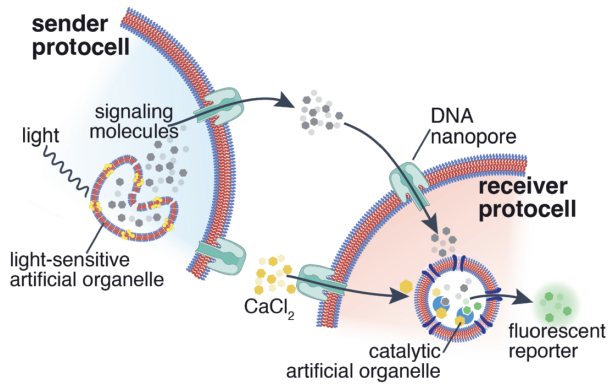
Deciphering signaling pathways is key to understanding cellular communication. This study presents modular polymer-based protocells that mimic retinal photoreceptor signaling, offering a robust model for spatiotemporally defined signal transduction. Using microfluidics, protocells are constructed with specialized artificial organelles enabling hierarchical organization. In one protocell population (sender), light-activated molecular motors embedded in organelle membranes release signaling molecules, into the sender cavity. From there, these signals are transferred intercellularly to receiver protocells containing catalytic organelles, where signal conversion takes place and is modulated by environmental calcium. By segregating different organelles in distinct protocells, a sequential signaling chain is achieved, mimicking natural communication pathways. This approach provides insights into cellular signaling and advances integration between synthetic and living systems, with precise bio-relevant control over individual steps. The model offers a valuable tool for exploring signaling dynamics and developing bioinspired technologies.

Authors' comments:
"Our strategy advances bio-inspired artificial organelles and protocells by combining diverse and carefully selected synthetic (*e.g.* amphiphilic copolymers, molecular motors) and natural (enzymes, proteins, peptides, DNA) building blocks to achieve multifunctionality and adaptability that replicate cellular communication."



Prepared by Cesare Berton, Jonas Genz, Stanislav Prytuliak, Fan Liu, Eda Nisli, Deborah Bäcker, Perle Hermant, Samy Kichou, Ben Boback, Dominik Ernst, Tiago Rosa de Araujo, Henrik Braband, and Jason P. Holland*
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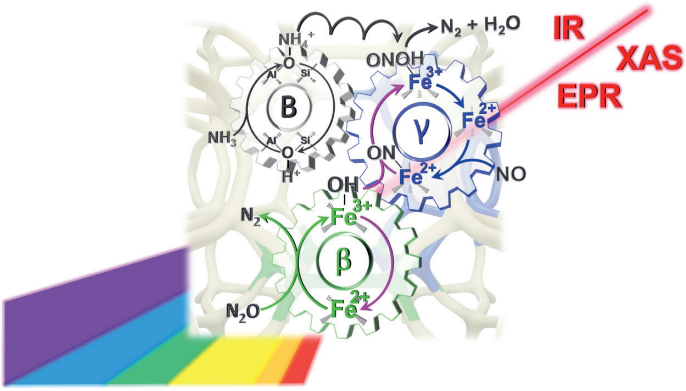
Iron-Catalysed Cooperative Redox Mechanism for the Simultaneous Conversion of Nitrous Oxide and Nitric Oxide

Filippo Buttignol, Jörg W. A. Fischer, Adam H. Clark, Martin Elsener, Alberto Garbujo, Pierdomenico Biasi, Izabela Czekaj, Maarten Nachtegaal, Gunnar Jeschke, Oliver Kröcher, and Davide Ferri*

Nat. Catal. **2024**, *7*, 1305
https://doi.org/10.1038/s41929-024-01231-3
PSI Center for Energy and Environmental Sciences, Paul Scherrer Institute, Villigen, Switzerland; Casale SA, Lugano, Switzerland; Cracow University of Technology, Cracow, Poland; ETH Zurich, Zurich, Switzerland; Institute of Chemical Sciences and Engineering, École polytechnique fédérale de Lausanne, Lausanne, Switzerland

Iron-exchanged zeolites are used industrially to mitigate nitric oxide (NO) and nitrous oxide (N_2O) emissions, but the active sites and mechanisms for their simultaneous removal are not well understood due to Fe species heterogeneity. Combining catalytic experiments with advanced spectroscopic techniques (XAS, DRIFTS, EPR), researchers identified square-planar Fe^{2+} sites at β-cationic positions as key for N_2O activation and redox cycling. These sites interact with tetrahedrally coordinated Fe^{2+} at γ-cationic positions, enabling NO adsorption and oxidation. NH_3 adsorbed on nearby Brønsted acid sites regulates the reaction rate by modulating the NO oxidation sequence. This dual-site mechanism enhances the cooperative redox processes, ensuring efficient conversion of both NO and N_2O.

Authors' comments:
"This work required multiple techniques, the collaboration with skilled individuals, and patience to gradually build up this reaction mechanism. It was immensely gratifying when we assembled all pieces of the puzzle and finally understood the full picture of what we investigated over four years."



Planar and Curved π–Extended Porphyrins by On-Surface Cyclodehydrogenation

Miloš Baljozović*, Joffrey Pijeat, Stéphane Campidelli*, and Karl-Heinz Ernst*

J. Am. Chem. Soc. **2024**, *146*, 34600.
https://doi.org/10.1021/jacs.4c12460
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Recent advances in on-surface synthesis have made it possible to produce atomically precise low-dimensional materials, some of which are not accessible to wet chemistry. Although porphyrins have been thoroughly investigated for their properties of peripheral functionalisation and central metal exchange in both on-surface and wet chemistry, extending the π-system of porphyrins with anthracenyl groups has remained a challenge. The authors report an *in vacuo* temperature-controlled cyclodehydrogenation of bis- and tetraanthracenyl Zn(II) porphyrins on an Au(111) surface. Gradual temperature increase induces sequential dehydrogenation, resulting in fused anthracenyl porphyrin products. At high molecular coverage, bowl-shaped porphyrins form, accompanied by Zn-Au transmetalation. These results enable the creation of a range of π-extended anthracenyl-containing porphyrins, with potential applications in molecular (photo/electro)catalysis, (opto) electronics, and spintronics.

Authors' comments:
"The possibility of utilizing on-surface dehydrogenation to fuse anthracenyl units with porphyrins was anticipated, but it was never imagined that a complete range of π-extended anthracenyl-containing porphyrins could be achieved."