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Swiss Science Concentrates

A CHIMIA Column

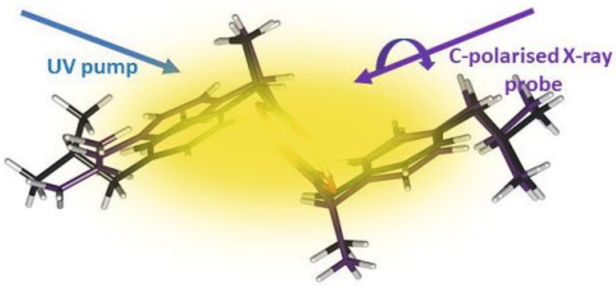
Short Abstracts of Interesting Recent Publications of Swiss Origin

Element- and enantiomer-selective visualization of molecular motion in real-time

R. Mincigrucci*, J. R. Rouxel*, B. Rossi, E. Principi, C. Bottari, S. Catalini, J. S. Pelli-Cresi, D. Fainozzi, L. Foglia, A. Simoncig, A. Matruglio, G. Kurdi, F. Capotondi, E. Pedersoli, A. Perucchi, F. Piccirilli, A. Gessini, M. Giarola, G. Mariotto, M. Oppermann, S. Mukamel, F. Bencivenga, M. Chergui*, and C. Masciovecchio*
Nat. Commun. **2023**, *14*, 386,
https://doi.org/10.1038/s41467-023-36047-5
École Polytechnique Fédérale de Lausanne

Monitoring in real-time the motion of nuclei in molecules has been made possible by using ultrafast optical-domain spectroscopies. Element-selectivity is achieved by using ultrashort X-ray pulses from X-ray free electron lasers. However, detecting light elements encountered in organic molecules has remained elusive. Here, the authors report an impulsive stimulated Raman scattering. (ISRS) pump/carbon K-edge absorption probe study, allowing the observation of the low-frequency vibrational modes, involving specific selected carbon atoms in the Ibuprofen *R*/*S* dimer. By controlling the X-ray pulse circular polarization, the authors can access the enantiomer of the dimer to which the selected carbon atoms belong and thus, achieve enantio-selectivity.

Authors' comments:
"We demonstrated that low-frequency atomic motion can be monitored in real-time with element- and enantio-selectivity in a racemic mixture. Low-frequency modes are often those participating in biochemical reactions."

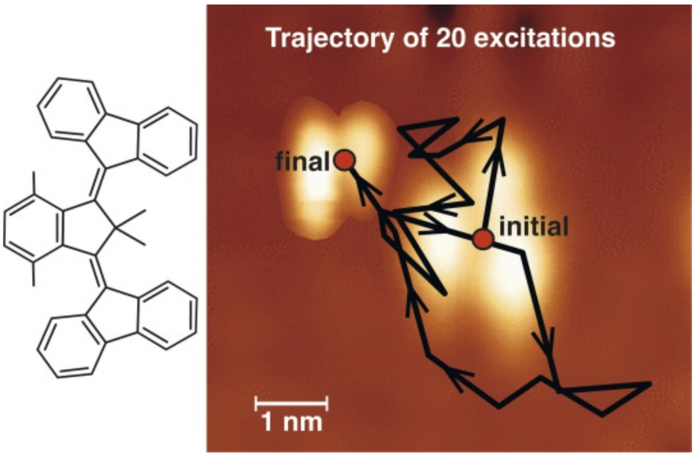


Driving a Third Generation Molecular Motor with Electrons Across a Surface

Gitika Srivastava, Peter Štacko, Jesús I. Mendieta-Moreno, Shayan Edalatmanesh, Jos C. M. Kistemaker, G. Henrieke Heideman, Laura Zoppi, Manfred Parschau, Ben L. Feringa*, and Karl-Heinz Ernst*
ACS Nano **2023**, *17*, 3931,
https://doi.org/10.1021/acsnano.2c12340
Empa / University of Zurich / University of Groningen

Molecular motors can be activated with a broad set of stimuli such as light, temperature, redox potentials and more. In their publication, Ernst and co-workers described the development of an indene-based molecular motor that can be driven by electrons across a surface. The study demonstrates that the electron transfer rate between the tip and the motor is controlled by adjusting the voltage, which in turn affects the speed and directionality of the motor rotation. By using STM and spectroscopy it was possible to monitor and manipulate the rotation of the motor providing insights into the fundamental mechanisms of these systems and opening new possibilities for the development of more efficient and controllable nanoscale devices.

Authors' comments:
"A two-rotor molecule runs only forward but with low degree of directionality. For the first time, the efficiency of molecular motor action induced by inelastic electron tunneling has been evaluated."



Prepared by Cesare Berton, Patrick A. Cieslik, Fan Liu, Stanislav Prytuliak, Simon Klinger, Jonas Genz, Dominik Roth, Samy Kichou, and Jason P. Holland*

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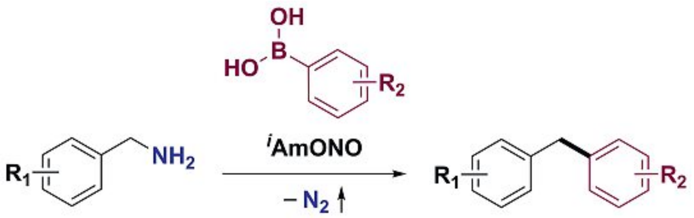
Deaminative Coupling of Benzylamines and Arylboronic Acids

Giedre Sirvinskaite, Julia C. Reisenbauer, and Bill Morandi*
Chem. Sci. **2023**, *14*, 17009,
https://doi.org/10.1039/d2sc06055h
ETH Zurich

Amines are appealing functional handles due to their common occurrence in both natural and industrially made products, but direct removal of the nitrogen atom with concomitant functionalisation remains a challenge. To overcome the difficulty of breaking the strong C–N bonds, the authors developed a method to enable deaminative coupling of benzylamines with arylboronic acids using inexpensive isoamyl nitrite as a nitrosating reagent, forging a new C–C bond. The reaction demonstrated a broad functional group tolerance under metal-free conditions. Substituted arylboronic acids were shown to furnish isomeric diarylmethane products. Based on preliminary mechanistic investigations, the authors proposed that Friedel-Crafts reaction of substituted arylboronic acids with subsequent hydride shift and deboronation might be one of the mechanistic pathways responsible for isomeric product formation.

Authors' comments:
"Unexpected isomeric product formation using substituted arylboronic acids as coupling partners led us to perform detailed mechanistic studies, revealing the complex reaction manifold operating under reaction conditions."



BODIPY-Based Photothermal Agents with Excellent Phototoxic Indices for Cancer Treatment

Lukas Schneider, Martina Kalt, Samuel Koch, Shanmugi Sithamparanathan, Veronika Villiger, Johann Mattiat, Flavia Kradolfer, Ekaterina Slyshkina, Sandra Luber, Mathias Bonmarin, Caroline Maake, and Bernhard Spingler*
J. Am. Chem. Soc. **2023**, *145*, 4534–4544,
https://doi.org/10.1021/jacs.2c11650
University of Zurich

Photodynamic therapy (PDT) is a widely used method for the treatment of numerous cancers. It relies on a photosensitizer, which once delivered into the cell, can be excited by irradiation with visible light followed by the generation of cytotoxic reactive oxygen species (ROS). However, this method rapidly loses its efficiency under hypoxic conditions, common in large tumors. Alternative approaches like Photothermal Therapy (PTT) apply nanomaterials to kill cells via local light-to-heat conversion, but biodegradation and toxicity issues remain unresolved. In this work, the authors developed six BODIPY-based agents with molecular structures that aggregate upon administration to the cells of interest and efficiently convert the absorbed light into heat under hypoxic conditions. Experiments showed unprecedented dark-to-light toxicity ratios (phototoxic indices) both in normoxic and hypoxic cells.

Authors' comments:
"Small molecule-based agents with a photothermal mechanism of action, such as the reported BODIPY-based compounds, may overcome the barrier of oxygen-dependency of conventional photosensitizers for PDT, and provide a new avenue to cancer therapy."