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Swiss Science Concentrates

A CHIMIA Column

A Rapid, Highly Sensitive and Selective Phosgene Sensor Based on 5,6-Pinepyridine

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Phosgene is a highly reactive gas that finds numerous applications as a building block in the chemical industry. However, due to its high toxicity, it is essential to have sensitive phosgene detection to prevent its severe effects on health. In the highlighted paper, Solea et al. developed a highly sensitive compound based on a carboxylic derivative of 5,6-pinenepyridine, which reacts with phosgene to form a visible and fluorometrically detectable isoindolone. Their newly developed sensor can detect concentrations as low as 9.7 nM phosgene in solution and 0.1 ppm airborne phosgene. Additionally, the sensor displays high selectivity and a fast response time (about 5 s) which is almost 3 times faster than the sensing reactions already reported.

Authors' comments:

"The sensing molecule immobilized on a solid support preserves its excellent detection abilities and possess all the prerequisites for developing a portable detector, which is currently underway at HES-SO."



Triple Regioselective Functionalisation of Cationic[4] Helicenes via Iridium-Catalysed Borylation and Suzuki **Cross-Coupling Reactivity**

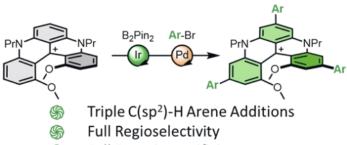
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Lucas Frédéric, Bibiana Fabri, Laure Guénée, Francesco Zinna, Lorenzo Di Bari, Jérôme Lacour* Chem. Eur. J. 2022, 28, e202201853. https://doi.org/10.1002/chem.202201853 University of Geneva

Cationic [n]helicenes constitute an original class of helical molecules with peculiar properties which permit applications in many domains, spanning from asymmetric synthesis and organic electronics, to supramolecular and biological chemistry. The absorption and emission properties of these molecules can be addressed by varying the functional groups on the outer rim of the helicenes. In particular, the development of methods for late-stage functionalization is attractive. Herein, the authors demonstrate an elegant one-pot synthesis of tris(arene)-functionalized cationic [4]helicenes, using Ir and Pd-catalysis, with full regioselectivity and enantiospecificity. Products obtained with this procedure show great improvements in fluorescence quantum yields and lifetimes. The enhancements observed in spectroscopic properties prime these molecules as potential candidates for a new series of biological probes.

Authors' comments:

"This new protocol establishes the first triple post-functionalization at activated positions - para to the formal positive charge. Consequently, many future derivatizations of such cationic [4]helicenes can be envisaged for diverse applications."



- **Full Enantiospecificity**
- Improved PLQY and Lifetimes
- CPL in the far red spectrum

COLUMNS CHIMIA 2023, 77, No. 1/2 67

CO₂ Conversion at High Current Densities: Stabilization of Bi(III)-Containing Electrocatalysts under CO₂ Gas Flow Conditions

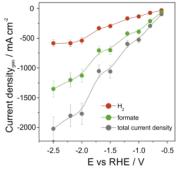
Iván Zelocualtecatl Montiel, Abhijit Dutta, Kiran Kiran, Alain Rieder, Anna Iarchuk, Soma Vesztergom, Marta Mirolo, Isaac Martens, Jakub Drnec, Peter Broekmann* *ACS Catal.* **2022**, *12*, 10872–10886. https://doi.org/10.1021/acscatal.2c02549 University of Bern; NCCR *Catalysis*

The electrochemical conversion of CO, into valuable chemicals such as formate is a promising approach for mitigating the ecological imbalance caused by the ever-growing levels of greenhouse gases. Among the catalysts required to accelerate the kinetically hindered CO₂ reduction reaction (CO₂RR), bismuth has demonstrated high selectivities towards formate in classical H-type cells. However, under these experimental conditions, practical applications remain limited. Herein, the authors demonstrate the superior performance of bismuth subcarbonate ((BiO)₂CO₃) layer catalysts readily formed in situ from a CO₂ absorbing Bi₂O₃ precursor material using a fluidic CO₂-fed-electrolyzer. The accelerated mass transport of CO, gas in this device boosts formate production beyond PCD_{formate} values of -1 A cm⁻² and lead to a substantial stabilization of the Bi(III) catalyst (see Figure below). Overall, this study paves the way to profitable and sustainable processes for CO₂ conversion in aqueous environment with facile downstream processing following primary electrolysis.

Authors' comments:

"This work was carried out within the frame of the NCCR *Catalysis* which aims at developing new carbon-neutral value chains for the production of fuels and platform chemicals *via* (electro)catalytic processes starting from renewable and abundant resources."





Nanoscale Chemical Imaging of Human Cell Membranes Using Tip-Enhanced Raman Spectroscopy

Dušan Mrđenović, Wenjie Ge, Naresh Kumar, Renato Zenobi* *Angew. Chem.Int. Ed.* **2022**, *61*, e2022102. https://doi.org/10.1002/anie.202210288 ETH Zurich

The aim of this work was to tackle the lack of label-free non-destructive diagnostic techniques for imaging of cells and cells membrane with nanoscale resolution. Tip-enhanced Raman spectroscopy (TERS) is a combination of scanning probe microscopy (SPM) and Raman spectroscopy and has already been applied to relatively 'simple' systems, but hardly ever to biological membranes, due to their complex composition. In TERS analysis of pancreatic cancer (BxPC-3) cells, 200 μW of excitation laser power was enough to achieve a decent signal. The spatial resolution was excellent (2.5±2.3 nm), showing the distribution of macromolecules like lipids, proteins, and DNA.

Authors' comments:

"In TERS, the intense electric field under the tip sometimes leads to decomposition and spurious bands that are easily misinterpreted. This was avoided here by the use of low power."

