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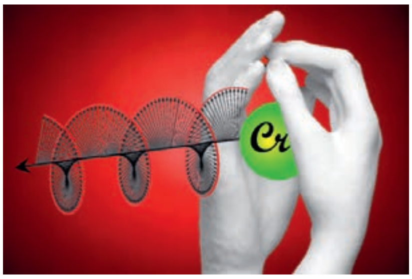
Short Abstracts of Interesting Recent Publications of Swiss Origin

Bright Long-Lived Circularly Polarized Luminescence in Chiral Chromium (III) Complexes

J.-R. Jiménez,* M. Poncet, S. Míguez-Lago, S. Grass, J. Lacour, C. Besnard, J. M. Cuerva, A. G. Campaña, and C. Piguet*, *Angew. Chem. Int. Ed.* **2021**, 60, 10095, https://doi.org/10/1002/anie.202101158
Department of Inorganic and Analytical Chemistry University of Geneva, Switzerland.

Chiral chromophores displaying efficient circularly polarized luminescence (CPL) are promising candidates for bio-applications, photonics and advanced security inks. The authors report the preparation and characterization of a series of highly emissive inert and chiral Cr^{III} complexes displaying circularly polarized luminescence within the NIR region. The helical $[Cr(dqpR)_2]^{3+}$ (dqp = 2,6-di(quinoline-8-yl)pyridine; R = OCH_3, Br or C≡CH) complexes were synthesized as racemic mixtures and resolved into the respective PP and MM enantiomers by chiral stationary phase HPLC. The octahedral geometries of the six-membered chelate rings provide high quantum yields (>14%) and long-lived excited lifetimes of up to 1.35 ms at room temperature in aqueous solution. Functionalization of the dqp ligand can improve the chiral resolution and is the focus for future work.

Authors' comments:
"Cheese and dessert! Inert and chiral emissive organic molecules or complexes with rarest metals (Pt, Pd, Ru, Os, Ir) provide high quantum yields but poor dissymmetry factors. Chiral inert Cr(III) complexes match the two jackpots".



Replacing DMF in solid-phase peptide synthesis: varying the composition of green binary solvent mixtures as a tool to mitigate common side-reactions

S. Jadhav, V. Martin, P. H. G. Egelund, H. Johansson Castro, T. Krüger, F. Richner, S. T. Le Quement, F. Albericio, F. Dettner, C. Lechner, R. Schönleber*, D. Sejer Pedersen*, *Green Chem.* **2021**, *23*, 3312, https://doi.org/10.1039/D0GC03171B
Bachem AG, Novo Nordisk

The ongoing need to identify greener processes has led to a considerable amount of research dedicated towards discovering benign solutions. Such is the case where DMF, a solvent conventionally used in SPPS, is yet to find a suitable substitute that matches criteria with respect to polarity and viscosity. Here, the authors report an elegant screen and profile of various binary solvent mixtures and outline how these permutations affect Fmoc-cleavage, coupling reactions, and common side reactions, exemplified in the synthesis of the peptide therapeutic Bivalirudin. Such a broad repertoire of solvent combinations should allow the identification of conditions best suited for industrial manufacturing processes.

Authors' comments:
"The toolbox of alternative solvents for DMF, developed in collaboration with Novo Nordisk, can be easily customized for target peptide synthesis using solid-phase peptide synthesis (SPPS). Moreover, the simple platform to mitigate detrimental side-reactions described in this report unlocks the potential of the binary solvents in green SPPS".

Prepared by Gordon Honeyman, David Lim, Stefania Gianolio, Pablo Díaz Kruik and Francesca Paradisi*
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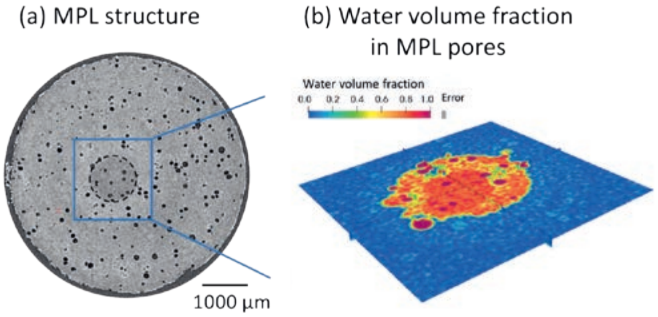
A Method for Spatial Quantification of Water in Microporous Layers of Polymer Electrolyte Fuel Cells by X-ray Tomographic Microscopy

Y.-C. Chen, A. Berger, S. De Angelis, T. Schuler, M. Bozzetti, J. Eller, V. Tileli, T. J. Schmidt, and F. N. Büchi*, *ACS Appl. Mater. Interf.* **2021**, *13*, 16227–16237, https://doi.org/10.1021/acsami.0c22358
PSI Applied Materials and Interfaces, Villigen

Polymer electrolyte fuel cells (PEFCs) have raised interest recently because of the global pressure for reducing CO_2 emissions. In this study, the authors shed light on water transport mechanisms inside the microporous layer (MPL) to rationally optimize their performance: water saturation in the cathode gas diffusion layer (GDL) leads to constricted oxygen transport from the gas channels to the catalyst layer, limiting the cell efficiency. Using a laboratory computed tomography (CT), a new X-ray tomographic imaging methodology is presented and validated to quantify the liquid in the unresolved pores of nanopore materials.
Exploiting X-ray tomography with a polychromatic X-ray source for *operando* laboratory-scale measurements, the presented method quantitatively characterizes the spatial variation of porosity and water sorption properties of MPL materials for PEFCs, without *a priori* knowledge of the material's structure or composition. The larger field of view bridges the gap between the nanoscale microporous layer pore description and the macroscale fuel cell performance evaluation.

Authors' comments:
"X-ray tomographic imaging has proved to be a versatile tool to characterize water management in the micro-porous materials fuel cells and the development of novel materials. Here we expand the methodology to nano-porous MPL materials".



(a) X-ray tomographic image of MPL; (b) Water volume fraction in this MPL based on greylevel analysis.

Rationalizing Photo-triggered Hydrogen Evolution Using Polypyridine Cobalt Complexes: Substituent Effects on Hexadentate Chelating Ligands

F. Lucarini, D. Bongni, P. Schiel, G. Bevini, E. Benazzi, E. Solari, F. Fadaei-Tirani, R. Scopelliti, M. Marazzi*, M. Natali*, M. Pastore*, and A. Ruggi*, *ChemSusChem.* **2021**, *14,* 1874–1885, https://doi.org/10.1002/cssc.202100161
Université de Fribourg, Università di Ferrara, Ecole Polytechnique Fédérale de Lausanne, Universidad de Alcalà, Université de Lorraine & CNRS

The water splitting reaction consists of two separate half reactions, the reduction of protons to produce hydrogen and the oxidation of water to give oxygen. In this paper the authors have developed four different polypyridine Co(II) complexes to study the impact of substituents on the hydrogen evolution reaction. The results indicate that the modification of the hexadentate ligand scaffold with electron- withdrawing ($-CF_3$) or with electron-donating ($-OCH_3$) groups does not affect the performance of the catalyst. In contrast, the crucial factor for a high catalytic efficiency was the location of these substituents. The complexes were able to produce hydrogen, under light-driven conditions in the presence of $Ru(bpy)_3^{2+}$ and ascorbic acid at pH 4, obtaining quantum yields between 3.5% and 11.3%, turnover numbers between 5520 and 591, and maximum turnover frequencies between 86.1 and 26.7 min^{-1} depending on the catalyst, consequently opening the door to long-term solar energy storage.

Authors' comments:
"The structure–activity effect on the efficiency of photochemical hydrogen production in substituted polypyridyl cobalt catalysts is a highly debated topic. In this work, we prove that the position of the substituents, rather than their electronic nature, plays a more substantial role. In fact, the presence of substituents on the pyridine opens new and more favorable mechanistic pathways, whilst the same substituents on the bipyridine decrease the catalyst efficiency".