CHIMIA Column Short Abstracts of Interesting Recent Publications of Swiss Origin

Shape-assisted Self-assembly

Joseph F. Woods, Lucía Gallego, Pauline Pfister, Mounir Maaloum, Andreas Vargas Jentzsch, and Michel Rickhaus*, *Nat. Commun.* **2022**, *13*, 3681, https://doi.org/10.1038/s41467-022-31482-2 University of Zurich, University of Strasbourg

Self-assembly and molecular recognition are important processes both in life and material sciences, such as enzyme-substrate recognition, sensing or nanofabrication. In this article the authors analyze carpyridine, a saddle-shaped macrocycle containing carbazole and pyridine groups. The results obtained with a hexyl substituted derivative showed that it is possible to obtain highly ordered, self-assembled nanosheets from monomers without strong interaction sites. This work demonstrates that the shape of a molecular unit can influence order by guiding the monomers into micrometer-long stacks which then self-assemble into 2D sheets of single-molecular thickness and very defined boundaries. The two-dimensional sheets can only be assembled as a result of a fine equilibrium between entropic gains and the competition of dipolar π - π and hydrophobic interactions. In conclusion, the article highlights the crucial role that topography can have in molecular assembly and sets the tone for future rational designed systems of increased complexity.

Authors' comments:

"This simplistic approach showcases the overlooked and underappreciated role of topography in self-assemblies without strong or highly directional interactions that are more commonly used in the field of supramolecular chemistry."

Porous Covalent Organic Nanotubes and their Assembly in Loops and Toroids

Kalipada Koner, Shayan Karak, Sharath Kandambeth, Suvendu Karak*, Neethu Thomas, Luigi Leanza, Claudio Perego, Luca Pesce, Riccardo Capelli, Monika Moun, Monika Bhakar, Thalasseril G. Ajithkumar, Giovanni M. Pavan*, and Rahul Banerjee*, *Nat. Chem.* **2022**, *14*, 507–514, https://doi.org/10.1038/s41557-022-00908-1

University of Applied Sciences and Arts of Southern Switzerland

In this article the authors explored the challenging synthesis of covalently bonded porous structures, using organic building blocks designed to assemble into covalent organic nanotubes (CONTs) through dynamic covalent chemistry. Looking at their application in electronic devices, energy storage, catalysis and biosensors, CONTs were obtained *via* a one-pot reaction strategy, where the spatial orientation of the functional groups promotes the growth of the framework in one dimension. The strong covalent bonds between carbon, nitrogen and oxygen, attribute high thermal and chemical stability to the CONTs. Combining spectroscopy, microscopy and computational modelling the authors obtained insight into the interactions between the CONTs and the surrounding solvent. Driven by such interactions, upon ultrasonication, the CONTs assemble into intertwined structures that go on to coil and form toroidal superstructures.

Authors' comments:

"We presented efficient synthesis of porous nanotubes with high potential for applications. Spectroscopy, microscopy and computational modelling techniques allowed fine characterization of the properties and self-assembly behavior of such structures."



Prepared by Gordon Honeyman, Stefania Gianolio, Lucia Robustini, Pablo Díaz-Kruik and Francesca Paradisi* **Do you want your article to appear in the SWISS SCIENCE CONCENTRATES highlight?** Please contact francesca.paradisi@unibe.ch

Synthesis of Cyclometalated Gold(iii) Complexes *via* Catalytic Rhodium to Gold(iii) Transmetalation

Jaime Martín, Enrique Gómez-Bengoa, Alexandre Genoux, and Cristina Nevado*, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116755, https://doi.org/10.1002/anie.202116755 University of Zurich

Gold(III) complexes have found application in a broad range of fields. In particular, cyclometalated gold(III) complexes containing bidentate (C^N) ligands have been intensely investigated, owing to their antitumoral activity, photochemical properties and catalytic competence. However, only a handful of strategies tackling their synthesis are available to date. Herein the authors report a catalytic, environmentally friendly method to synthesize a broad array of cyclometalated (C^N)gold(III) complexes. Their approach relies on catalytic Csp²-H bond activation, utilizing a commercially available bench-stable rhodium catalyst, followed by an unprecedented Rh-to-Au^{III} transmetalation step. An investigation of the reaction mechanism reveals a rate-determining stepwise (C, then N) ligand transfer process. The methodology tolerates a variety of 2-phenylpyridine derivatives and more complex substrates based on different N-donor heterocycles.

Authors' comments:

"This straightforward method overcomes the severe drawbacks of strategies typically used in the preparation an essential type of gold(III) complexes by an unprecedented Rh-to-Au^{III} transmetalation step. The one-pot reaction employs commercially available precursors and proceeds under mild and toxic waste-free conditions."





- ✓ 1st Example of Rh-to-Au(III) transmetalation
- Rate-determining stepwise ligand transfer (first C- then N)

Synthesis of Mucin O-Glycans Associated with Attenuation of Pathogen Virulence

Giulietta Minzer and Rachel Hevey*, *ChemistryOpen* **2022**, e202200134, https://doi.org/10.1002/open.202200134 University of Basel

Mucosal infections are a major source of concern due to a rise in antibiotic resistance and limited therapeutic options. Mixtures of O-glycans isolated from mucus have been shown to effectively down-regulate virulence gene expression in diverse pathogens, therefore this class of compounds are of interest to identify active structures and elucidate their mechanism of action. This work is the first to describe a synthetic approach to obtaining a small library of mucosal O-glycans of interest. Through mass spectrometry analysis of mucus samples and activity studies, the most promising glycans were identified. Using common building blocks, individual glycans were prepared in >20 mg scale to facilitate future biological testing.

Authors' comments:

"Individual glycans are virtually impossible to isolate from mucus samples using current technologies. Therefore, obtaining these glycans *via* a synthetic approach is critical for understanding how they regulate pathogen virulence, and we are very excited to explore this further."

