SUPRA60

Celebrating **60 YEARS**
of
SUPRAMOLECULAR
CHEMISTRY
in
STRASBOURG

August 28-29, 2025 – ISIS, Strasbourg, France

WELCOME ADDRESS

The history of Supramolecular Chemistry began 60 years ago in Strasbourg, a topic and place which continue to be at the forefront of Chemistry.
To celebrate this remarkable longevity, we are honored to welcome you at "Supra 60: celebrating 60 years of Supramolecular Chemistry in Strasbourg", which is hosted at ISIS (Strasbourg).
These days are provided free of registration fees, and the participants have the possibility to deliver oral presentations (time slots were allocated by a lottery) or to present posters, and we are very pleased to present herewith the abstracts of the 23 oral communications and 22 posters which will be presented.
We are very happy to have you here in Strasbourg to celebrate all together this unique moment.

The organizing committee:
Annia Bertrand
Aline Chevalier
Wais Hosseini
Philippe Reutenauer
Gaël Schaeffer
Jean-Louis Schmitt
Sébastien Ulrich

PROGRAM

Supra60

		Thu 28 August 2025		Fri 29 August 2025
08:45		Welcome coffee		
09:00				*Morning coffee & poster session*
09:30		**PLENARY: Prof. Jean-Marie LEHN**		
10:00	*Chairwoman: Anna HIRSCH*	**OC1: Jean-François AYME**	*Chairman: Mir Wais HOSSEINI*	**OC13: Joe OTSUKI**
10:30		**OC2: Mihail BARBOIU**		**OC14: Anne PETITJEAN**
11:00		**OC3: Dario BASSANI**		**OC15: Zoe PIKRAMENOU**
11:30		**OC4: Michał CHMIELEWSKI**		**OC16: Gu RUIRUI**
12:00		*Lunch break & Poster session*		*Lunch break & Poster session*
12:30				
13:00				
13:30				
14:00	*Chairman: Sébastien ULRICH*	**OC5: Hicham FENNIRI**	*Chairwoman: Anne PETITJEAN*	**OC17: Hanadi SLEIMAN**
14:30		**OC6: Konstantina FYLAKTAKIDOU**		**OC18: Sébastien ULRICH**
15:00		**OC7: Nicolas GIUSEPPONE**		**OC19: Ghislaine VANTOMME**
15:30		**OC8: Jonathan HALL**		**OC20: Dirk VOLKMER**
16:00		*Coffee break & poster session*		*Coffee break & poster session*
16:30	*Chairman: Jack HARROWFIELD*	**OC9: Michael HANNON**	*Chairwoman: Ghislaine VANTOMME*	**OC21: Kenneth WARNMARK**
17:00		**OC10: Mir Wais HOSSEINI**		**OC22: Ulrich ZIENER**
17:30		**OC11: Petr KOVAŘÍČEK**		**OC23: Katharina FROMM**
18:00		**OC12: Meixia HE**		Closing ceremony
18:30		*Free evening*		*Farewell Dinner*
19:00				
19:30				
20:00				

ORAL

Autonomous mobile robots for exploratory synthetic chemistry

Tianwei Dai*, Sriram Vijayakrishnan*, Filip T. Szczypiński*, Jean-François Ayme*, Ehsan Simaei*, Rob Clowes, Caitlin E. Shields, Zhengxue Zhou, Peiying Wang, John W. Ward, Andrew I. Cooper[1]
*- equal contributions
[1]Research Centre for Functional Materials Design and Materials Innovation Factory, University of Liverpool, 51 Oxford St, Liverpool L7 3NY, UK.
Email: jfayme@liverpool.ac.uk

Abstract

Autonomous laboratories can accelerate discoveries in chemical synthesis, but this requires automated measurements coupled with reliable decision-making[1]. Most autonomous laboratories involve bespoke automated equipment, and reaction outcomes are often assessed using a single, hard-wired characterization technique[2]. Any decision-making algorithms must then operate using this narrow range of characterization data[3]. By contrast, manual experiments tend to draw on a wider range of instruments to characterize reaction products, and decisions are rarely taken based on one measurement alone. Here we show that a synthesis laboratory can be integrated into an autonomous laboratory by using mobile robots that operate equipment and make decisions in a human-like way. Our modular workflow combines mobile robots, an automated synthesis platform, a liquid chromatography–mass spectrometer and a benchtop nuclear magnetic resonance spectrometer. This allows robots to share existing laboratory equipment with human researchers without monopolizing it or requiring extensive redesign. A heuristic decision-maker processes the orthogonal measurement data, selecting successful reactions to take forward and automatically checking the reproducibility of any screening hits. We exemplify this approach in the three areas of structural diversification chemistry, supramolecular host–guest chemistry and photochemical synthesis.

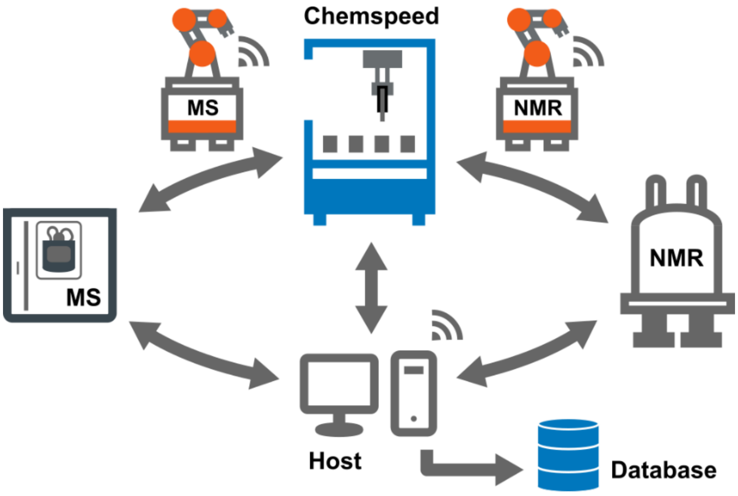

Figure 1. Workflow design for an autonomous synthesis platform utilizing two mobile robots for sample transportation between a Chemspeed synthesizer and a benchtop NMR spectrometer and an ESI-MS spectrometer.

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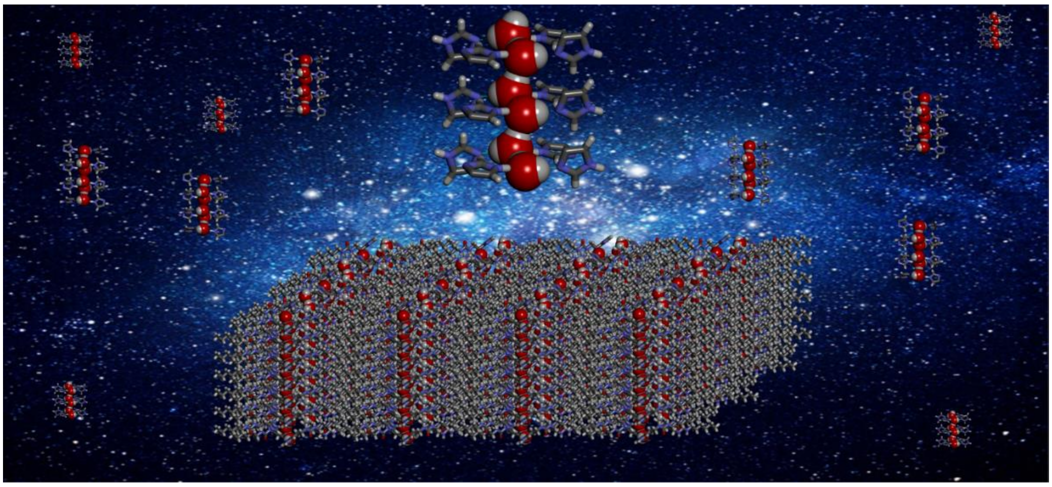
ARTIFICIAL WATER CHANNELS-
TOWARD BIOMIMETIC MEMBRANES FOR DESALINATION

Mihail Barboiu

Adaptive Supramolecular Nanosystems Group, Institut Europeen des
Membranes, ENSCM-UMII-UMR CNRS 5635, Place Eugene Bataillon CC047,
34095 Montpellier, France. Email: mihail-dumitru.barboiu@umontpellier.fr

Abstract

This lecture discusses the incipient development of the biomimetic artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding water structures useful for many biological scenarios. Moreover, they can be used for the preparation of highly selective membranes for desalination.



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How supramolecular chemistry will save Champagne, Riesling and Gewürztraminer from the nefarious effects of light

Dario M. Bassani,[1] Nathalie Langleron,[2] Clément Monsarrat,[2]

[1]Inst. of Molecular Sciences, CNRS UMR 5255, Univ. Bordeaux, 33400 Talence, France; [2] Martell,
Mumm, Perrier-Jouët, 51053 Reims, France.
Email: dario.bassani@u-bordeaux.fr

Abstract

Labo Lehn has a long tradition of sharing scientific breakthroughs around a glass of beer or wine, be it on late Friday afternoons or evening group meetings. Unfortunately, all of these drinks are very sensitive to light and rapidly develop what is known as the light-struck fault upon exposure to sunlight. In the case of white wines, crémant, and champagnes, the culprit is vitamin B2 (riboflavin) which is also responsible for the wine's vibrant yellow color. The reaction proceeds through the long-lived excited triplet state, which photooxidizes methionine and results in the formation of volatile organosulfur products such as thiomethanol and dimethyl disulfide. These smell pretty bad, mostly like rotten eggs and cooked cabbage. Do date, the only solution is to drink in the dark which is, of course, not good for bright ideas.

We will look at how careful examination of a few experimental results questioned the established reaction mechanism and suggested a stronger dependence of the oxidation products on methionine concentration.[1] From this, we can see that it is conceivable to design methionine receptors that selectively bind the flatulent amino acid and prevent the light-struck fault without altering the organoleptic properties of even the most fragrant of Alsatian white wines.[2] This application of supramolecular chemistry to highly societal challenges clearly demonstrates the potential of "chemistry beyond the bottle" to solve even the most odorous problems.

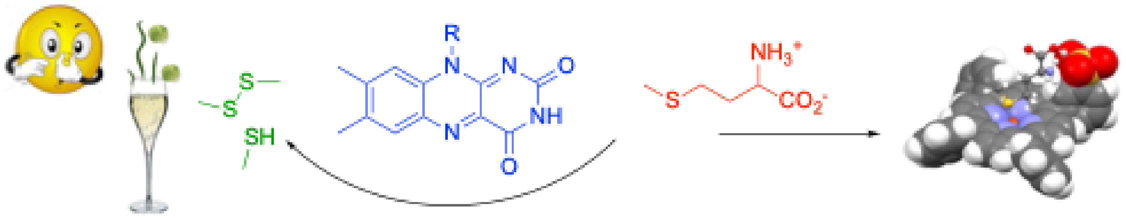

Figure 1. Riboflavin (in blue) photo-oxidizes methionine present many white wines and champagnes to induce the light-struck fault, characterized by the formation of volatile organosulfur species. A resin was developed to selectively sequesters methionine without altering the wine's taste or color. It is composed of metalated porphyrins mimicking the active site in cytochrome C.

Acknowledgements

Financial support and starting materials from many sources is gratefully acknowledged.

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SUPRAMOLECULAR TRANSPORTERS FOR BIOLOGICALLY ACTIVE ANIONS – FROM SIMPLE BUILDING BLOCKS TO ANION TRANSPORTING NANOMACHINES

Michał J. Chmielewski[1]

[1]Supramolecular Chemistry Laboratory, Biological and Chemical Research Centre, Faculty of Chemistry,
University of Warsaw, Warsaw, Poland.
Email: mchmielewski@chem.uw.edu.pl

Abstract

In this lecture, I will present an overview of our research journey spanning over two decades, which began with the discovery of 1,8-diaminocarbazole as a privileged scaffold for the construction of anion receptors, sensors, and transporters.[1] This journey has led us through a series of advances in supramolecular anion transport, culminating in the design of increasingly complex systems based on this simple building block.

In 2018, we demonstrated that simple diamidocarbazoles act as active and easily tunable chloride transporters.[2] By 2020, we have shown that they can also transport a variety of other biologically relevant anions, including anionic drugs.[3] In 2022, we further expanded their substrate scope to include amino acids,[4] and in the same year the transporters were also shown to display interesting antibacterial activity.[5] In 2024, we employed diaminocarbazole scaffold for the construction of a switchable, fluorescent catenane with sulfate sensing capabilities.[6] In a follow-up work, we developed related catenanes capable of transporting extremely hydrophilic anions.[7] Most recently, we introduced nanoparticles decorated with anion binding sites as a new class of artificial anion transporters.[7]

Together, these developments trace a trajectory from simple molecular scaffolds to sophisticated nanomachines for the transport of biologically active anions.

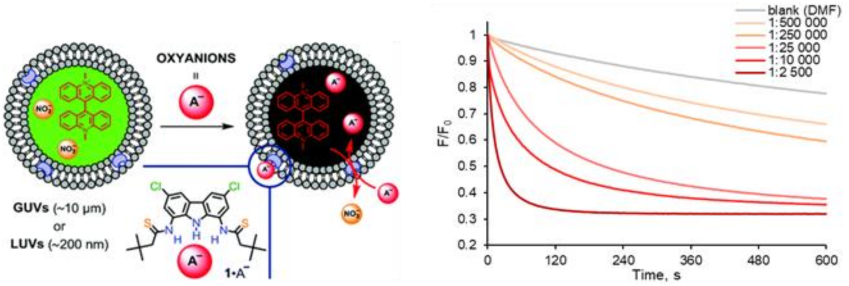

Figure 1.

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Setting the Groundwork for a World Class African University in Morocco

Hicham Fenniri[1]

[1]International Water Research Institute & Moroccan Foundation for Advanced Science Innovation and Research, University Mohammed 6 Polytechnique (UM6P), Benguerir, Morocco.
hicham.fenniri@um6p.ma

Abstract

The essence of technological ingenuity is the efficient and sustainable transfer of scientific knowledge to commercial use. This knowledge transfer is indeed the cornerstone of most innovative societies and is at the core of UM6P's R&D strategy.

The socio-economic challenges we face today, the climate and energy crises, global supply chain problems, demographic changes, and new geopolitical conflicts have changed our world and shaken the long-term stability of our security and prosperity. To join the industrialized world and lead Africa to prosperity, our community at UM6P embraces, practices, and spreads the spirit of innovation across all disciplines, academic endeavors, and entrepreneurial activities.

To achieve sovereignty in central areas of technology and transform our economy to a more sustainable system, from energy supply, food security, water sourcing and management, to artificial intelligence, UM6P has established colleges, institutes, nd dedicated R&D programs, as well as a culture of entrepreneurship dedicated to Morocco and Africa's pressing economic challenges with the aim of **bridging today's innovations with tomorrow's commercial products and services**.

In this brief presentation, I will present UM6P's vision and current R&D&I strategy along with some key milestones and performance indicators with the aim of fostering new partnerships and collaborations.

GREEN APPROACHES TO ACHIEVE COMPLEXITY AND CHEMICAL DIVERSITY IN BORON CHEMISTRY

Konstantina Fylaktakidou,[1,*] Polynikis Paisidis,[1] Antigoni Kotali[2]

[1]Laboratory of Organic Chemistry, Chemistry Department and [2]Laboratory of Organic Chemistry,
Department of Chemical Engineering, AUTH, 54124 Thessaloniki, Greece.
Email: kfylakta@chem.auth.gr

Abstract

Boronic acids are able to be merged with *in situ* formed or preformed linkers that contain OH terminal arms and an *N*-donor located in a suitable position to occupy the vacant boron *p* orbital. As a result, the construction of bridged boron heterocycles, most commonly [4.4.0] (Figure, **A**) and [4.3.0] occurs, the properties of which include luminescent and photosensitizing activity, drug delivery, enzyme modulation and DNA binding activity.[1] Interestingly, the formation of [5.4.0] bridges (Figure, **B**) is extremely rare, represented in the literature by only three examples derived from inorganic boron derivatives.[2] A variety of such [4.4.0] and [5.4.0] boron bridged compounds have been synthesized in our laboratories using green chemistry in reactions that lock three or two components together with only H_2O as the byproduct.[1],[3] Any hydrolytic dissociative attack of H_2O in these heterocycles rules their applications which are ultimately based on the nature and the position of the substituents of the organic frames. In addition, boron chemistry seems to offer more opportunities in synthesis, via hydrolysis and dehydration reactions, like the formation of 5 or 6 membered heterocyclic rings (Figure, **C**) via green, multicomponent diversity-oriented synthesis using 2-aminobenzonitrile derivatives as starting materials.[4]

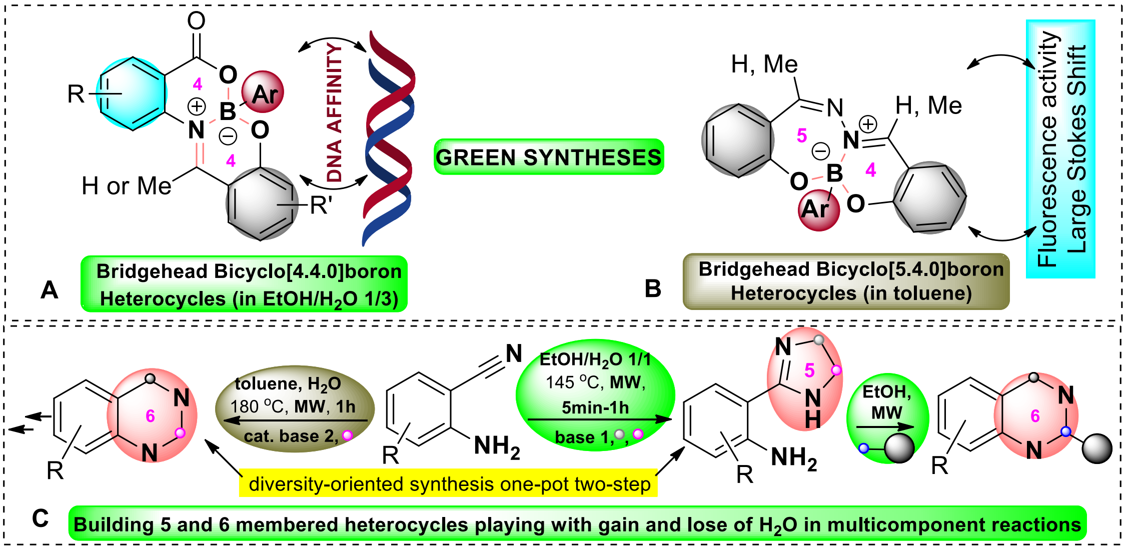

Figure. **A** & **B**: Structures of [4.4.0] and [5.4.0] bridgehead bicycloboron heterocycles; **C**: Schematic green diversity-oriented synthesis of 5 and 6 membered heterocycles from 2-aminobenzonitriles.

Acknowledgements

The authors thank Alan and Linde Katritzky Foundation, USA, for financial support.

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Using artificial molecular motors to drive complex chemical systems out-of-equilibrium

Nicolas Giuseppone[1]

[1] University of Strasbourg, Institut Universitaire de France (IUF)
Institut Charles Sadron - CNRS, 23 rue du Loess, BP 84047
67034 Strasbourg Cedex 2, France
E-mail: giuseppone@unistra.fr

Abstract

Inspired by the protein machinery found in biological systems, and based on the theoretical understanding of the physics of motion at nanoscale, organic chemists have developed a number of molecules that can actuate when triggered by various external chemical or physical stimuli. In particular, basic molecular switches that commute between (meta)stable states, and more advanced molecular motors that produce unidirectional cyclic motions, have been reported. However, the integration of individual molecular motors in a continuous out-of-equilibrium mechanical process that can produce mechanical work at various length scales and up to the macroscale remains an important area to explore. We will discuss advances developed by our group on the collective actuation of artificial molecular motors, which involve their mechanical coupling with polymer and supramolecular self-assemblies. We will show how it becomes possible to integrate them and to make use of their autonomous mechanical work to drive endoenergetic processes in complex systems and active materials.

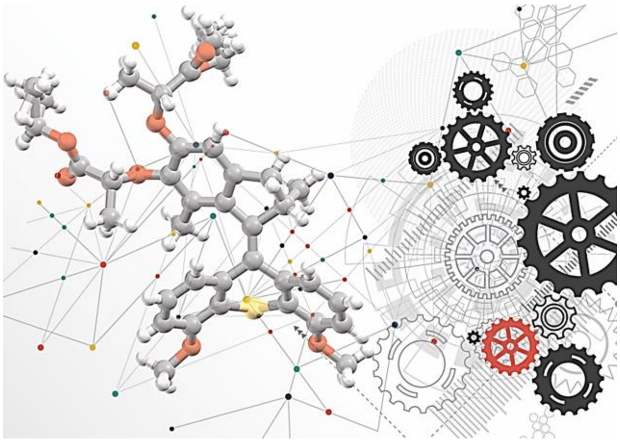

Figure1. Motor$\subset$System.

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RNA G-Quadruplexes Regulate the Polyamine Biosynthesis Pathway

Jonathan Hall[1]

[1] ETH Zurich, Vladimir-Prelog-Weg 4, 8093 Zürich, Switzerland.
Email: jonathan.hall@pharma.ethz.ch

Abstract

Nature makes extensive use of metal-ligand interactions to control gene expression. G-quadruplexes are naturally occurring structures found in RNAs (and DNAs), in which a guanine tetrad wraps around cations such as potassium to form stacked planar arrangements connected by short loops, as part of a highly stable conformation. This motif is found in the untranslated regions of messenger RNAs where it influences gene expression in various ways, usually by suppressing translation. We identified a group of G-quadruplex-motifs in the messenger RNAs (mRNAs) of enzymes and factors involved in polyamine biosynthesis. We confirmed their structures with comprehensive biophysical characterization of their properties, comparing them to a reference G-quadruplex. Using cellular reporter assays, we discovered how some of these motifs regulate and sense polyamine levels, creating feedback loops during polyamine biosynthesis[1].

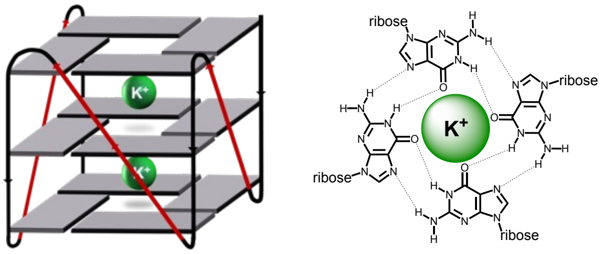

Figure 1. Schematic of a canonical RNA G-quadruplex.

Acknowledgements

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SUPRAMOLECULAR RECOGNITION OF DNA AND RNA JUNCTION STRUCTURES FOR ANTI-VIRAL AND ANTI-CANCER THERAPY

M.J. Hannon,[1]

[1]School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.
Email: m.j.hannon@bham.ac.uk

Abstract

We use the outer surfaces of metallo-supramolecular cylinders (helicates) to create a perfect match for the central cavities of DNA and RNA junctions (Fig. 1). They bind strongly to DNA and RNA Y-shaped junctions, forks and bulges - nanomolar to picomolar affinities - and modulate their dynamic behaviour.[1] We can control the activity of these agents by encapsulating them in a curcubituril ring to create a rotaxane structure, with release from the rotaxane switching on the junction-binding activity.[2] Recognition of a specific nucleic acid shapes is a powerful approach: In RNA-viruses the ends of the genome are non-coding parts which fold into specific structures and regulate viral replication. The same structures are common to many different viruses and an exciting new anti-viral target. We have shown that some of our agents can bind junction and bulge structures in the untranslated regions of both SARS-CoV-2 and HIV-1 and show potent anti-viral activities at concentration levels where they are not cytotoxic to mammalian cells.[2]

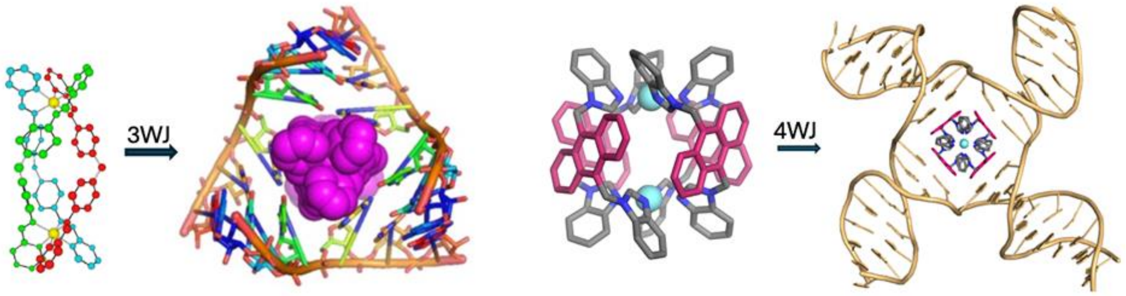

Figure 1. Supramolecules recognising 3-way and 4-way junctions.

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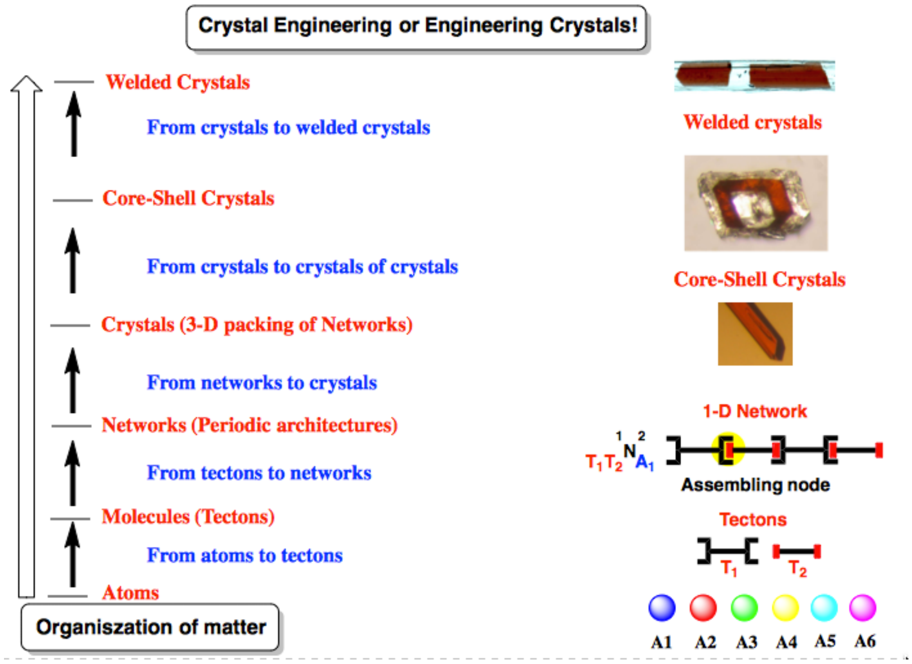
Perspectives in Molecular Tectonics: from molecules to crystals, mosaics of crystals and crystal welding

Mir Wais Hosseini [1]

Institut Le Bel, University of Strasbourg, 4, rue Blaise Pascal, 67000 Strasbourg, France
Email: hosseini@unistra.fr

Abstract

Bridging the gap between microscopic (atoms and molecules) and macroscopic (materials) worlds is challenging and requires construction strategies. At the intersection of supramolecular and solid-state chemistry and material sciences, we have developed an approach called molecular tectonics. This approach is based on supramolecular synthesis of crystalline materials seen as extended periodic molecular networks. Their construction by selfassembly processes results from repetitive molecular recognition events between programmed tectons or building blocks. The approach is operational and versatile and allows, not only the design and construction of a variety of organic or hybrid complex architectures and core-shell crystals, but also the welding, under mild condition, of crystals into networks of crystals.



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CATALYSIS AS THE DRIVING PRINCIPLE FOR PHOTOREDOX CATALYST FORMATION

Petr Kovaricek,[1]

[1]University of Chemistry and Technology Prague, Dpt. of Organic Chemistry Technicka 5, 16628 Prague.
Email: Petr.Kovaricek@vscht.cz

Abstract

2*H*-chromeno[2,3-d]pyrimidines are referred to as deazaoxaflavins (DAOFs) due to their structural analogy with flavins, known cofactors of enzymes and artificial redox catalysts. They are formed by a sequence of reversible condensation reactions from derivatives of barbituric acid and salicylaldehyde. DAOFs are highly active in photoredox catalysis which is benchmarked on the photosulfoxidation model reaction. Engagement of the DAOF molecule in a catalytic cycle is, although very brief, removal of a reversible cascade product and thus shifts the equilibrium in favor of DAOF catalyst formation. This work describes reversibly formed DAOF catalysts that autonomously assemble from their components. Their formation is governed thermodynamically by employment in a catalytic cycle; therefore, the catalytic function is the driving principle for catalyst formation.

MODULATING PHOTOLUMINESCENCE AND PHOTOCHROMICM OF SALIZYLALDIMINE IN THE SOLID STATE THROUGH MOLECULAR ENGINEERING

Meixia HE,[1] Zhiyuan Han,[1] Jean-Marie Lehn,[2] Quan Li[1]

[1]Institute of Advanced Materials and School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China. Email: meixiahe@seu.edu.cn
[2]Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université de Strasbourg, 8 allée Gaspard Monge, Strasbourg 67000, France

Abstract

Photoluminescence and photochromism play crucial roles in the development of solid-state photoresponsive materials.[1] However, achieving precise tuning through molecular modifications remains a challenge. Herein, we synthesized a series of salicylaldimine molecules using salicylaldehyde derivatives and amines.[2] Notably, the incorporation of a bulky naphthalimide group into salicylaldimines resulted in visible-light-driven solid-state photoswitches, exhibiting triple fluorescence switching from green to yellow to orange. Additionally, the introduction of a urea group facilitated versatile adaptations across three distinct stacking states in response to light, mechanical, and thermal stimuli, enabling controllable transitions between photochromism and photoluminescence. Furthermore, by substituting salicylaldehyde hydrazone derivatives, either excitation-dependent emission or pronounced photochromism was achieved with minimal structural changes. The exceptional photophysical properties highlight the potential applications in anticounterfeiting, smart coatings, and encrypted information storage, offering insightful strategies for developing solid-state photoresponsive materials.

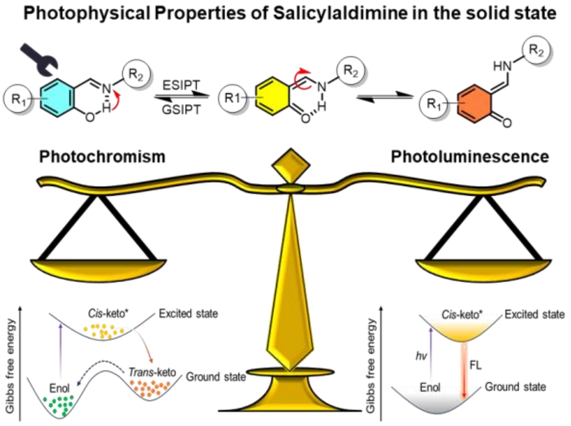

Figure 1. The modulation of photophysical properties of salicylaldimine including photochromism and photoluminescence in the solid state through molecular engineering strategy.

Acknowledgements

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GENERATION AND FUNCTIONS OF PORPHYRIN ASSEMBLIES BASED ON COORDINATION INTERACTIONS

Joe Otsuki

[1]Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University,
Tokyo, Japan
Email: otsuki.joe@nihon-u.ac.jp

Abstract

Porphyrins, including chlorophylls, represent a prototypical photo-, electro- and chemofunctional compounds, and serve as key building blocks in supramolecular chemistry. Supramolecular porphyrin assemblies are found in natural light-harvesting antenna systems of photosynthetic molecular devices [1]. We have developed zinc porphyrin assemblies via axial coordination by introducing pyridyl groups at strategically chosen positions and orientations. Some of these assemblies exhibit double-helical structures in the solid state [2]. Incorporation of a fullerene or ferrocene unit into these assemblies has led to artificial light-harvesting and charge-separation models [3,4].

More recently, we synthesized porphyrins bearing 2,2'-bipyridine (bpy) units. Upon the addition of Zn^{2+} ions, tetrahedral $Zn(bpy)_2$-type complexes form, bringing two porphyrins into close proximity and generating face-to-face porphyrin dimers (Figure 1, left) [5]. Notably, the binding of Zn^{2+} ions proceeds in a highly cooperative manner. Newer designs have enabled the formation of a cavity formation between the two porphyrin macrocycles (Figure 1, middle and right) and the host capabilities of these porphyrin dimers are currently under investigation.

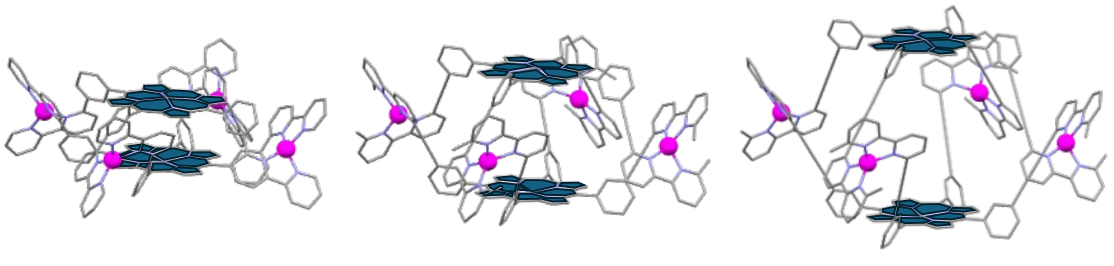

Figure 1. Face-to-face porphyrin dimers generated by Zn-ion coordination.

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LESSONS FROM LABO LEHN 1998-2002

Anne Petitjean,[1] Caitlin Miron,[1] Katie Manas,[1] Jean-Louis Mergny,[2]

[1]Department of Chemistry, Queen's University, Kingston ON, Canada; [2] École Polytechnique, Laboratoire d'Optique et de Biosciences, Palaiseau, France.
Email: anne.petitjean@chem.queensu.ca

Abstract

In a non-canonical presentation blending individual anecdotes and science, we will touch on snippets of scientific topics ranging from supramolecular polymers, folding of artificial and natural oligomers, molecular machines and medicinal chemistry.

Four lessons from the *labo Lehn* at the turn of the millennium will be used as guidelines, and the audience will be invited to provide their own lessons from their time (technology allowing…).

Some recent developments in the design and study of nucleic acid binders will conclude the presentation.[1,2]

Acknowledgements

The friendship and energy of all members of Labo Lehn from 1998-2002 and 2004-2005 are greatly acknowledged. Funds from the French *Ministère de l'Éducation Nationale, de la Recherche et de la Technologie* made this unique experience possible. More recently, funding from Queen's University, the Natural Sciences and Engineering Research Council, the Ontario Institute for Cancer Research, and Mitacs have allowed pursuing a line of research inspired by the above experience.

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LIGHT- AND ULTRASOUND- ACTIVATED NANOPROBES IN DETECTION AND LOCALISED THERAPY

Professor Zoe Pikramenou,[1]

[1]School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.
Email: z.pikramenou@bham.ac.uk

Abstract

Gold and silica nanoparticles present ideal scaffolds to incorporate multiple molecular probes into a single nanoscale architecture for targeting cellular and tissue environments without engaging in lengthy, multi-labelling synthetic procedures.

Gold nanoparticles are popular multimodal agents with characteristic surface plasmon resonance and interesting therapeutic potential due to their photothermal properties. To introduce the attractive characteristic properties of photoactive metals into nano-designs we have developed gold nanoprobes decorated with photoactive metal complexes based on Ru(II), Ir(III) and Eu(III) (Figure 1a).[1] The visible luminescence with long lifetimes of the metal provide ideal detection and cellular tracking in cells and blood flows.[2] Additionally, osmium-decorated particles show localised production of Reactive Oxygen Species, underlying their potential for localised, light activated therapies.[3]

Silica nanoparticles are attractive vehicles for encapsulation of drugs due to their excellent biocompatibility. Encapsulation of a drug within the framework provides a *Trojan Horse* strategy for localised delivery and targeted release. We have used this approach to study controlled antimicrobial agent release by low frequency ultrasound enabling imaging and penetration in bacterial biofilms (Figure 1b).[4]

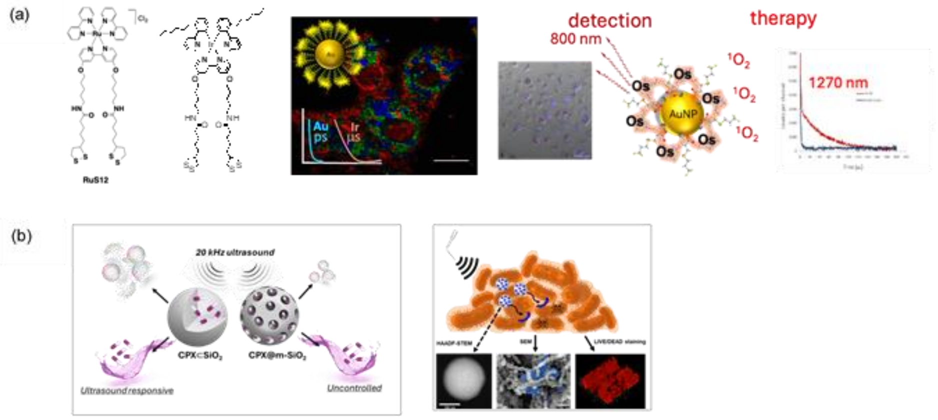

Figure 1. (a) Metal complexes for gold nanoparticles in two-photon lifetime imaging and therapeutic cellular activity. (b) Silica nanoparticles for localised delivery of antimicrobial agents in bacterial biofilms.

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Light-Driven Constitutional Pump Powers a Dynamic Covalent System Far from Equilibrium

Ruirui Gu,[1] Jean-Marie Lehn[3], Ben L. Feringa[1,2], Da-Hui Qu[1]
[1]Feringa Nobel Prize Scientist Joint Research Center, East China University of Science and Technology, 200237 Shanghai, P. R. China; [2]Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands; [3]Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université de Strasbourg, 67000 Strasbourg, France
Email: guruirui@ecust.edu.cn

Abstract

Accessing non-equilibrium states in dynamic covalent reactions presents an intriguing task to emulate biomimetic energy-dissipative behaviors through the controlled reshuffling of covalent bonds, enabling reversible yet energy-dissipative constitutional variations. However, achieving such states remains fundamentally challenging due to microscopic reversibility and rapid equilibration inherent to these reactions. Inspired by kinetic asymmetry mechanisms prevalent in living organisms, we introduce a light-driven constitutional pump that establishes a unidirectional kinetic pathway beyond intrinsic equilibria, autonomously driving a dynamic covalent C=C/C=N metathesis reaction far from equilibrium. This pump operates through a three-step kinetic ratchet mechanism under single-wavelength photonic control, demonstrating how reaction outcome can be kinetically manipulated by elevating energy barriers, in stark contrast to catalysis. The resulting strong directional bias drives the system to a non-equilibrium steady state, achieving a significant constitutional selection towards metathesis products, while preserving closed-system reversibility.

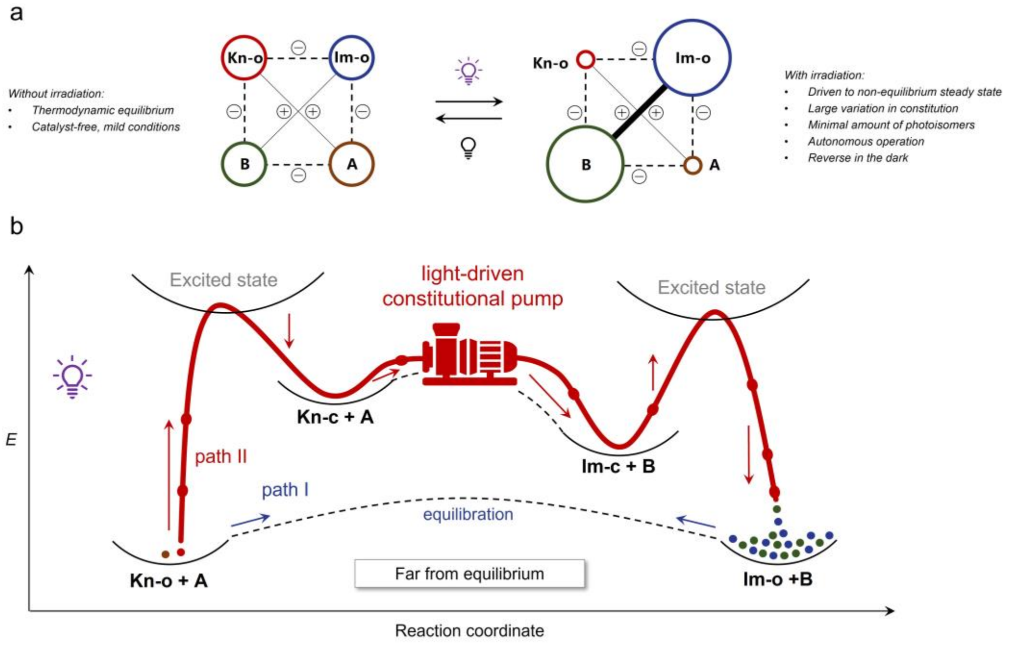

Figure 1. a) Constitutional dynamic networks; b) Light-driven constitutional pumping mechanism.

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Supramolecular DNA Materials as Precision Therapies

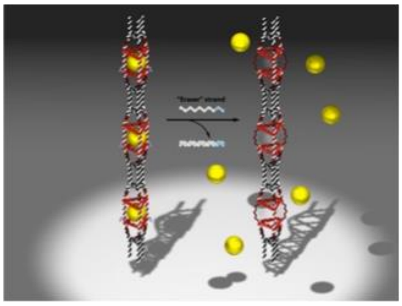
Hanadi Sleiman[1]

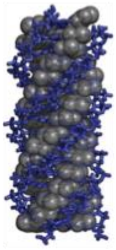
[1]affiliation: Dept. of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, QC, H3A 0B8, Canada
Email: Hanadi.sleiman@mcgill.ca

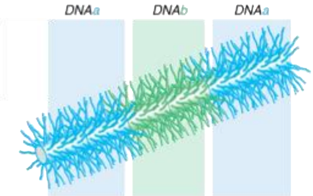
Abstract

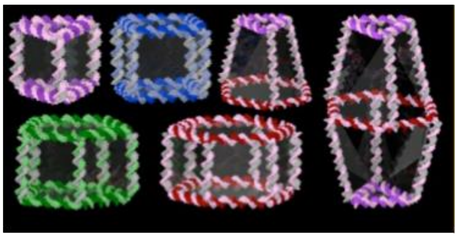
Our group applies supramolecular chemistry principles to build DNA-based materials with precise, responsive, and programmable function. By combining DNA with synthetic molecules and polymers, we create DNA nanostructures such as cages, nanotubes, and nanoparticles for the delivery of nucleic acid therapies. These structures use minimal components and respond to biological triggers, such as cancer-specific markers, releasing drugs precisely at target sites.

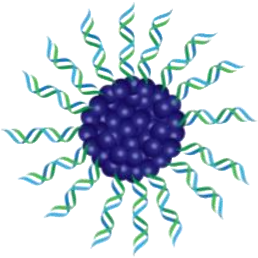
We find that they resist nuclease degradation, silence gene expression to a significantly greater extent than their component oligonucleotides and have a favorable in vivo distribution profile. They achieve effective in vivo gene silencing in multiple organs, unlike other nucleic acid treatments that only target the liver. Our DNA nanostructures can be applied to drug and gene delivery, tissue regeneration and materials science.











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DYNAMIC SYSTEMS FOR DRUG DELIVERY

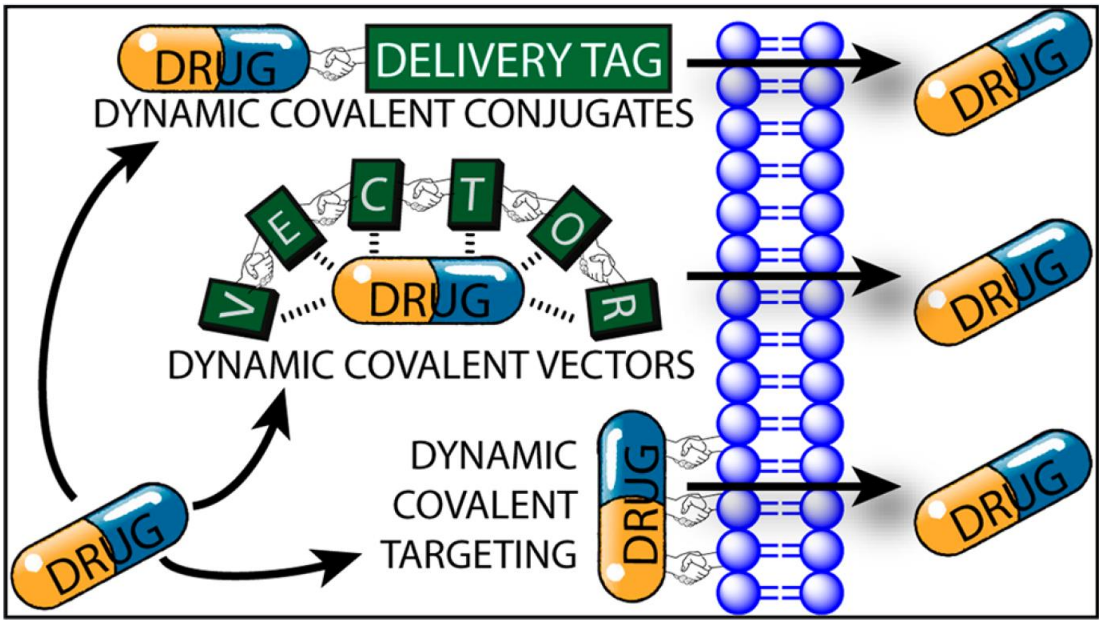
Sébastien ULRICH[1]

[1]IBMM, CNRS, Université de Montpellier, France.
Email: sebastien.ulrich@cnrs.fr

Abstract

Chemistry has grown to become a science of *complex organized systems*, which are made of molecular components in *dynamic interactions*, and from which *functions emerge*. The integration of dynamic features in chemical systems is therefore a prominent and promising approach toward life-like materials, and we propose it bears also a strong potential for drug delivery applications.[1]

The central goal of our research activity is to design smart dynamic systems for the specific and challenging issue of nucleic acid delivery. In this presentation, I will showcase our recent efforts implementing *dynamic covalent chemistry* for the generation of RNA vectors that self-assemble and degrade in a controlled manner.[2-6]



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SYNTHESIS AND ASSEMBLY OF LIGHT-RESPONSIVE SUPRAMOLECULAR NANOSTRUCTURES:

STEP TOWARD ADAPTIVE MATERIALS

Ghislaine Vantomme

Institute for Complex Molecular Systems, Eindhoven University of Technology, the Netherlands.
Email: g.vantomme@tue.nl

Abstract

The need for functional supramolecular systems is growing, driven by interest in device miniaturization, the emergence of smart materials, and efforts to mimic biological processes. Mastering the non-covalent synthesis of these supramolecular architectures requires control over their structure, dynamics, and function at all length scales. In particular, the precise positional arrangement of molecules facilitates the control of supramolecular interactions and the design of materials with unconventional responses. However, the construction of these systems is challenging due to their inherent complexity resulting from their sensitivity to small perturbations, the large number of interacting components, and the multiple aggregation pathways by which the systems can evolve. In the lecture, we will illustrate our approach to functional supramolecular materials.[1] The focus is on the synthesis of highly ordered morphologies that will change their properties upon exposure to light, coupling cooperative molecular events to macroscopic function.

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FUNCTIONAL $K_{3,3}$ (“KURATOWSKI”) BUILDING UNITS IN MATERIALS CHEMISTRY: PAST, PRESENT, AND FUTURE.

Dirk Volkmer[1]

[1]University of Augsburg, Institute of Physics, Augsburg, Bavaria – D-86159, Germany.
Email: dirk.volkmer@uni-a.de

Abstract

The first metal-organic framework (MFU-4, Metal-organic Framework Ulm University) comprising “*Kuratowski*-type” coordination units was reported in 2009.[1] Its strictly orthogonal geometry has inspired chemists to develop a diverse range of functional materials. Owing to a combination of nano-sized cavities and ultra-narrow pores, MFU-4 features kinetic gas trapping allowing for quantum sieving of light hydrogen isotopologues,[2] or high-capacity/slow-release entrapment of noble gas atoms.[3] Gas-specific uptake rates allowed us to construct the first MOF@SAW surface acoustic wave-based sensor.[4] In contrast to MFU-4, the isoreticular MFU-4*l*(arge) features framework-anchored metal sites resembling the iconic scorpionate complexes (Fig.1).[5] Cu^{I}-MFU-4*l* shows reversible chemisorption of O_2, N_2, and H_2 with record-breaking isosteric heats of adsorption of $32–53\,\mathrm{kJ\,mol^{-1}}$.[6] Biomimetic generation of catalytically active $Fe^{IV}{=}O$ species in Fe-exchanged MFU-4*l* has recently been demonstrated by Hou et al.,[7] indicating the huge potential of MFU-4-type metal–organic frameworks as catalytic materials. Apart from the above mentioned applications, framework materials containing Kuratowski-type building units, such as simple M(II)-triazolate frameworks, often show fascinating physical properties, ranging from cooperative large-hysteresis spin-crossover in $[Fe^{II}(ta)_2]$ to spin-liquid behaviour in $[Mn^{II}(ta)_2]$, to name only a few examples.[8, 9] Research activities in our group have recently turned to photoactive metal complexes and frameworks for which the programmable self-assembly of $K_{3,3}$ units offers an efficient bottom-up approach toward artificial photoantenna systems.

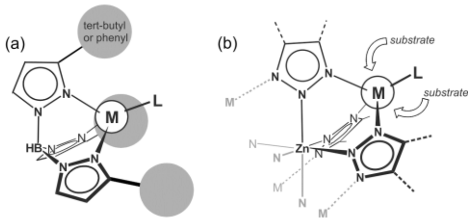

Figure 1. (a) Scorpionate complex; (b) Secondary building (“Kuratowski-type”) unit from MFU-4*l* comprising open metal sites. (M = transition metal, L = ligand)

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PHOTOREDOX CATALYSIS USING THE CHARGE-TRANSFER STATE OF IRON COMPLEXES

Kenneth Wärnmark

Centre for Analysis and Synthesis, Department of Chemistry, Lund University, Lund, Sweden.
Email: Kenneth.Warnmark@chem.lu.se.

Abstract

The introduction of saturated octahedral iron *N*-heterocyclic carbene (FeNHC) complexes,[1,2] has made iron photofunctional.[3] Hence, FeNHC complexes have allowed iron to function as photosensitizers in dye-sensitized solar cells (DSSCs),[4] and in hydrogen evolutions reactions (HERs),[5] and as photocatalysts in photoredox catalysis,[6] challenging the archetypical complexes of ruthenium and iridium for these purposes. This has been made possible by raising the energy of the metal-centered (MC) states of iron by attaching it to NHCs, resulting in the prolongation of the lifetime of iron's charge-transfer (CT) state by several orders of magnitudes compared to traditional iron polypyridyl complexes. In this lecture, the photophysical background and the use of the second generation of FeNHC complexes,[2] (**Fig. 1**) as effective photocatalysts in photoredox catalysis to produce chemicals, will be presented and discussed.

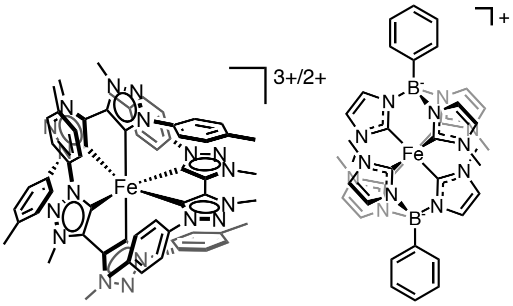

Figure 1. The second-generation of photoactive iron *N*-heterocyclic (FeNHC) complexes.

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2D SUPRAMOLECULAR POLYMERIZATION OF OLIGOPYRIDINES: STM STUDIES

Ulrich Ziener,[1] Felix D. Goll[1]

[1]Institute of Organic Chemistry III, Ulm University, Ulm, Germany.
Email: ulrich.ziener@uni-ulm.de

Abstract

Oligopyridines represent a versatile class of synthetically accessible molecular building blocks, well suited for the controlled self-assembly of highly ordered two-dimensional (2D) structures on graphite surfaces.[1] Even minor modifications at the molecular periphery significantly alter the resulting 2D packing motifs, which are governed by a delicate balance of weak hydrogen bonding and van der Waals interactions. Introducing electron-donating units into the electron-deficient scaffold expands the diversity of intermolecular interactions and enables tailored assembly behavior. The supramolecular polymerization of a donor–acceptor bisterpyridine (BTP) functionalized with an electron-rich carbazole unit is investigated using scanning tunneling microscopy (STM) at the solution|HOPG interface.[2] The results reveal the formation of 2D supramolecular (co-)polymer crystals via a chain-growth polymerization process. This growth can be quantitatively described using copolymerization statistics. Concentration-dependent STM studies, combined with derived copolymerization parameters and DFT calculations, support a self-assembly mechanism in which kinetically driven polymerization is followed by thermodynamically controlled 2D crystallization.

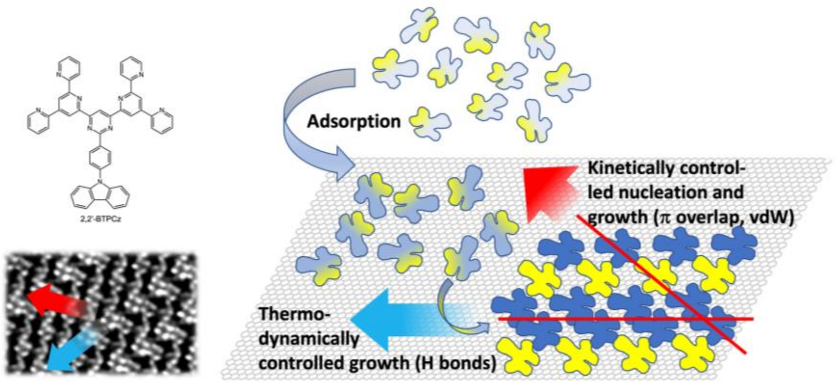

Figure 1. Mechanism of 2D self-assembly of a donor-acceptor bisterpyridine on HOPG.

Acknowledgements

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SILVER AND BACTERIA: TRANSPORTING, BREATHING AND KILLING SOFTLY

Katharina M. Fromm,[1] Valentin Chabert,[1] Alexandre Bianchi,[1] Salem Majouri,[1] Maxym Karamash,[1] Bernd Giese[1]

[1]: Department of Chemistry, University of Fribourg, Fribourg, Switzerland.
Email: Katharina.fromm@unifr.ch

Abstract

The bioinorganic chemistry of silver and its ions is heavily connoted with its antimicrobial properties. While phenomenologically well described the exact molecular mechanisms of its toxicity toward bacteria and its relatively weak toxicity with respect to eukaryotic cells are scarcely understood.

Yet, some Gram-negative bacteria, initially growing in silver rich mining areas, seem to survive higher silver ion concentrations than other bacteria. This is due to the presence of a silver efflux pump system, which is quite similar (ca- 40-50%) to the copper efflux pump, except for one protein, SilE, which has no equivalent in the copper system. We studied the protein and model peptides thereof to understand the role of this protein and its structural changes upon silver ion binding. It turns out that the protein itself adopts a random coil structure, folding up into an alpha-helical structure when silver ions are added. This change is however quite subtle, and we thus analyzed how the different amino acids and their sequence in the proteins may change the outcome of the protein function. The peptide sequences influence not only the binding constants, but also the folding of the peptide (or not) into alpha helices, and hence the functioning of the SilE as such.[1]

An alternative way of handling toxic silver ions is their extracellular reduction into much less soluble silver nanoparticles. Such a mechanism is adopted by the anaerobic *Geobacter surfurreducens* and is also called mineral respiration, as electrons which are produced by anaerobic respiration are dumped on insoluble minerals such as Fe_2O_3 to form Fe_3O_4 for example. We have studied the process of reduction with soluble and insoluble metal ions and found that the electron outflux is constant and can be regulated by the ratio of the Fe(III)/Fe(II) concentration in periplasmic and outer membrane cytochromes.[2]

Acknowledgements

The authors thank the University of Fribourg for generous support, as well as the Swiss National Science Foundation, which covered also parts of the subprojects which were carried out in collaboration with Carlos Salgueiro from the University of Lissabon, Jörn Dengjel from the University of Fribourg, Maggy Hologne from the University of Lyon, Peter Broekmann from University of Bern and Martin Spichty from the University of Mulhouse.

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POSTERS

Dynamic Electromerism: Correlated Rotational and *cross*-Conjugation Dynamics in DAMN (DiAminoMaleoNitrile) and DAFN (DiAminoFumaroNitrile) Derivatives

María-Jesús Aguilera-Roldán, Pablo Roseiro,† Ferran Esteve, Nicolas Giuseppone, Vincent Robert, Jean-Marie Lehn*

ABSTRACT: Conformational dynamics play a key role in molecular reactivity and the development of functional molecular machines. In this study, we investigate the competitive correlation between internal rotation about the C-NR_2 and *cross*-conjugation dynamics in DAMN, DAFN, and their derivatives. Using a combination of NMR spectroscopy, crystallographic analysis, and computational studies, we demonstrate that conjugation in one of the two push-pull π-systems restricts its own C-N bond rotation while suspending conjugation and facilitating rotation in the other system, leading to a synchronized rotation-conjugation oscillation. Variable Temperature (VT)-NMR spectroscopy revealed that the presence of competing *cross*-conjugated pathways dramatically lowers the C-N rotational barriers of the amino groups compared to those of reference compounds presenting a single π-system (12–13 kcal/mol). Density functional theory (DFT) studies yielded rotational barriers as low as ~2 kcal/mol for the tetra-methylated DAMN, with a disrotatory mechanism. The introduction of steric effects increased the rotational barriers, yielding measurable NMR values of 7–8 kcal/mol in the bulkiest DAMN derivative. Additionally, modulation of the structural de-symmetrisation of the coupled push-pull systems in mono-imine derivatives of DAMN allowed the determination of rotational barriers within the range of those of the reference compounds. These effects were in agreement with the presence of *cross*-conjugation, which was also supported by X-ray diffraction. The findings provide insight into the structural factors governing rotational barriers in *cross*-conjugated systems exhibiting correlated molecular motion. Thus, DAMN and DAFN present a dynamic electromerism process where oscillation between two different *cross*-conjugation pathways is regulated by the C-N rotation frequency.

POSITIONAL ELECTRONIC DIRECTIONALITY IN THE GENERATION OF DYNAMIC COVALENT LIBRARIES OF *BIS*-IMINES FROM THE SUBSTITUTED AROMATIC COMPONENTS

Bamaprasad Bag [1,2], Jean-Marie Lehn[2]

[1]Materials Chemistry and Interfacial Engineering Department, CSIR-Institute of Minerals and Materials Technology, P.O.: R.R.L.; Bhubaneswar-751013, India; [2]Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université de Strasbourg, 8 allée Gaspard Monge, BP 70028, F-67000 Strasbourg Cedex, E-mail: bpbag@immt.res.in

Abstract

The intricacies of dynamic covalent chemistry (DCC)[1-2] provide a basis for the principles of adaptation processes[3] in component generation through self-sorting of constituents, where changes in constitution depending upon the nature, number and arrangement of the interacting components contribute to constitutional dynamics. In this context, reversible reactions between components containing complementary functional groups have been the prima facie domain of DCC, where component exchange generates dynamic covalent libraries (DCLs). The thermodynamic and kinetic features of interconvertible reactions are the crucial parameters that affect the composition of DCLs as a function of time. For example, the thermodynamic and kinetic features of reversible formation of imine type C=N linkages from the reaction of amines and carbonyl compounds have been crucial in developing DCC, and have successfully been implemented in material development. The structural effects on imine formation and reaction rates have been investigated for various aldehydes and amino- components. In this investigation[4], the control of electronic directionality on the reactivity of the components in preferential generation of *bis*-imines from bis-amines in the aldehyde-(*bis*-amine)-aldehyde scaffold has been explored. The simultaneous reaction of *bis*-amine (*p*-phenylenediamine) where the amino groups are in *para*-position of a conjugated system, with two different nitro-benzaldehydes, where the electron-withdrawing group is in either *p*-position or *m*-position to the carbonyl centre, therefore showed that conjugation in a *bis*-amine has favoured the formation of a cross *bis*-imine over the formation of homologous *bis*-amines. The comprehension of reactivity preferences through this study as a control of positional electronic directionality in respective *bis*-imine formation puts forth the basis of kinetic control and thermodynamic selections of the imine components in generating their constitutional covalent libraries. Such reactivity modulation also promotes exploration in reaction mixtures of higher complexities of amine and aldehyde components that contribute to the adaptive behaviour of constituents formed for a selection in constitutional dynamic systems.

Acknowledgements

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LANTHANIDE CRYPTATES AND TR-FRET BIOASSAYS

ALPHA-BAZIN Béatrice[1], BAZIN Hervé[2]

[1] Université Paris-Saclay, CEA, INRAE, Département Médicaments et Technologies pour la Santé (DMTS), SPI/Li2D, F-30200, Bagnols-sur-Cèze, France. [2]Villeneuve-les-Avignon, France; Email: herve.bazin00@gmail.com

Abstract Since the fluorescence lifetime of a Ln-complex is far longer than that of biological autofluorescence background, time resolution can easily separate signal from noise. This property is well suited to the design of high sensitivity FRET based bioassays [1]. Such assays became the gold standard in HTS as HTRF$^{\text{TM}}$ and TRACE$^{®}$ using initially the Eu$^{3+}\subset$TBP cryptate [2 , 3, 4] (Fig 1) as FRET donor. The Eu$^{3+}\subset$TBP cryptate is characterized by a 10% quantum yield and a luminescence lifetime *ca.* 1ms in presence of fluoride ion optimizing the FRET efficiency. The high quantum yield for Tb-hydroxyisophthalamide cryptate, allowed the development of Lumi-4-Tb [5] (Fig 2). The respective advantages and specificites of Eu$^{3+}\subset$TBP and Lumi-4-Tb cryptates will be discussed in respect of cell based assays.

1, Ln = Eu
2, Ln = Tb

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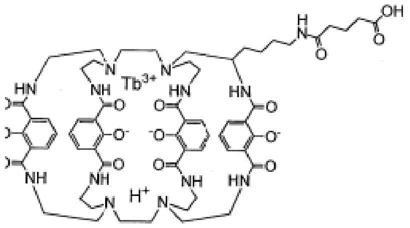

Figure 1. TBP (Ln^{3+}) Cryptates [2 , 3]

Figure 2. Lumi4(Tb) [5]

Such cryptates can be used as donor in TR-FRET experiments using APC (AlloPhycoCyanine) as FRET acceptor [4]. Cell membrane proteins can be selectively labeled using SNAP-TAG [6] and O-Alkyl-Guanine labelled with Lumi-4-Tb allowing cell based bioassays.

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Non-Stochastic Chiral Crystallization of Epsomite ($MgSO_4 \cdot 7H_2O$)

Louis A. Cuccia[1], Tsion Abebe[1], Ziqiao Zhong[1], Evelyn Huaman[1], Reajean Sivakumar[1], Cameron Lennox[2], Devonté Brefo[1], Vilaylak Sukhaseum[1], Pui Shan Monica Cheung[1], Jeanne Paquette[3] and Scott Bohle[2]

[1]Department of Chemistry and Biochemistry, Concordia University, Montréal, Canada; [2]Department of Chemistry, McGill University, Montréal, Canada; [3]Department of Earth and Planetary Sciences, McGill University, Montréal, Canada.
Email: louis.cuccia@concordia.ca

Abstract

A remarkable manifestation of chirality occurs when achiral molecules crystallize in non-centrosymmetric space groups to form enantiomorphic crystals.[1] When this occurs, one expects a stochastic distribution of left- and right-handed crystals (*i.e.*, 50:50). Epsomite ($MgSO_4 \cdot 7H_2O$) is a chiral sulphate mineral ($P2_12_12_1$) made up of achiral building blocks.[2][3] Remarkably, non-stochastic chiral distributions (left-handed preference when specified) have been reported in five historic reports: Pasteur (1854), Dufet (1904), Pocklington (1906), Longchambon (1922) and Belyustin & Rogacheva (1966).[4][5] It is believed that this biased chiral crystallization is due to a cryptochiral environment as proposed by Pocklington almost 120 years ago. Herein, epsomite crystals were resolved according to their distinguishable morphologies by identifying the orientation of the hemihedral faces with respect to the sphenoidal faces. The absolute configuration of epsomite was confirmed with the Flack parameter obtained from single crystal X-ray diffraction of each enantiomorph. A student laboratory exercise was developed to expose students to classical *'resolution by triage'* introduced by Pasteur in 1848 to resolve sodium ammonium tartrate tetrahydrate.[6] In our lab a significant bias towards left-handed crystals was once again observed: 1100 left *vs* 288 right (lab/home grown) and 156 left *vs* 45 right (commercial crystals). This was facilitated by indexing the faces of epsomite using visual inspection, contact angle goniometry, etch figures and preferential cleavage along the {010} hemihedral planes. We also observed that dehydration occurs preferentially at the hemihedral and prism faces (in this order), whereas the sphenoidal faces are the most resistant to dehydration to the hexahydrite. Finally, enantiomorphic epsomite crystals were readily modelled with paper and additive manufacturing using Vesta software tools. Experiments exploring the chiral crystallization of epsomite in the presence of chiral additives are ongoing.

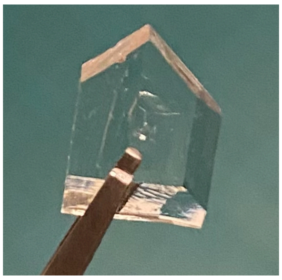

Figure 1. Left-handed epsomite crystal

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Write-Read-Erase: Macrocyclic Effectors Regulate Imine Expression in Water

Ferran Esteve,[1] Martina Mazzaferro,[1,2,3] Jean-Marie Lehn[1]

[1] Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université de Strasbourg, 8 allée Gaspard Monge, 67000 Strasbourg, France.
[2] Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale F. Stagno d'Alcontres, 31, 98166 Messina, Italy.
[3] Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto, 8, 06123 Perugia, Italy

Email: estevefranch@unistra.fr

Abstract

Enzymatic molecular recognition and post-modification of specific amino acid residues on target proteins allows for *writing*, *reading* and *erasing* processes that regulate a wide range of biological processes [1,2]. In this work, we investigate minimalistic chemical systems based on reversible imine formation reactions that adapt their expression in response to macrocyclic effectors. The *writing* action relies on the formation of the host:guest supramolecular adduct between the macrocycles and the components/constituents. The dynamic condensation reaction *reads* each action and changes the expression of the imines accordingly, giving a specific constitutional pattern. The strength of the up-regulating or down-regulating effect can be tuned depending on the supramolecular match between the guests and the microenvironments provided by the different macrocycles. Addition of a better guest for the host *erases* the action and reestablishes the initial equilibrium state, regulating the whole process. Complex behaviors like constituent selection, (non-)selective amplification/inhibition, and sorting-to-scrambling transitions emerge from the orthogonal action of different macrocycles on dynamic covalent libraries[3]. These results represent a remarkable step in increasing the applicability of dynamic imine chemistry in water and contribute to the development of chemical systems of higher complexity that mimic biological mode-of-actions found in biology[4].

Acknowledgements

This work was supported by the Agence Nationale de la Recherche in France (ANR-20CE07-0031), University of Strasbourg Institute for Advanced Study, and Fondation Jean-Marie Lehn. This project has also received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 101151945.

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FROM COORDINATION CHEMISTRY TO NUCLEIC ACID TARGETING: G-QUADRUPLEX STABILIZATION BY Ln^{3+} MACROCYCLIC COMPLEXES

Marta A. Fik-Jaskółka,[1] Ernest Ewert,[1] Dawid Marcinkowski,[1] Izabela Pospieszna-Markiewicz,[1] Zbigniew Hnatejko,[1] Maciej Kubicki,[1] Violetta Patroniak,[1] Giovanni N. Roviello[2]

[1]Faculty of Chemistry, University of Adam Mickiewicz in Poznań, Poland; [2]Institute of Biostructures and Bioimaging, Italian National Council for Research, Naples, Italy.
Email: martafik@amu.edu.pl

Abstract

Cancer remains the second most common cause of death worldwide [1]. This is why researchers do not cease designing, developing and studying new potential anti-cancer drugs. One promising approach involves stabilizing G-quadruplexes (G4) – four-stranded, non-canonical nucleic acid structures formed by guanine-rich sequences [2] – found in telomeres and promoter regions of oncogenes [3].

This study explores the synthesis and characterization of two 18-membered hexaaza macrocyclic complexes formed from pyridine-2,6-dicarbaldehyde and trans-1,2-diaminocyclohexane, coordinated with La^{3+} and Dy^{3+} ions. Using UV-melting and circular dichroism (CD) spectroscopy, we demonstrate that the $[LaL]^{3+}$ complex exhibits superior stabilization of these G4 structures compared to $[DyL]^{3+}$. Further *in silico* docking studies reveal significant binding interactions between $[LaL]^{3+}$ and hTERT G4 DNA occurring through the coordination of the metal ion with the O6 atom of G15 residue in the central cavity of the G4 structure. Moreover, the TDS and CD spectra of the randomly coiled Tel26 sequence incubated with $[LaL]^{3+}$ indicate its folding into a G4-like structure. Overall, these findings position $[LaL]^{3+}$ as a promising candidate for further investigation in cancer treatment strategies.

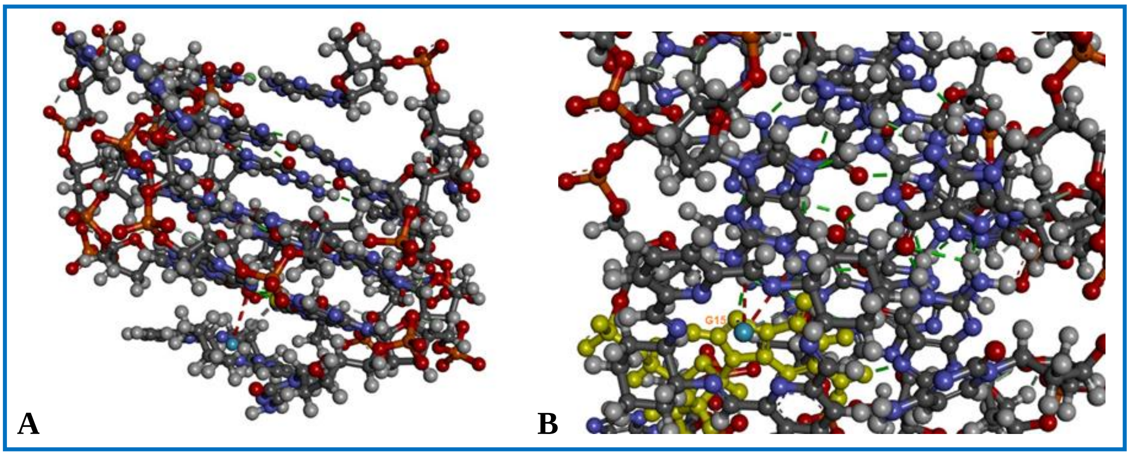

Figure 1. (A) Pose view of the model obtained for the $[LaL]^{3+}$/hTERT complex and (B) detailed view of the same complex showing the intermolecular interactions occurring between $[LaL]^{3+}$ and the G4 DNA. The metal cation is displayed in cyan while the residue G15 is represented in yellow colour for clarity.

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New Photochemistry for Complexes of Amidine-*N*-Oxide Ligands

Garry S. Hanan,[1] Mihaela Cibian,[1,2] Jessica Castro,[1] Elizabeth Lamothe,[1] Arindam Saha,[1] Francesco Nastasi,[3] Sebastiano Campagna,[3]

[1] Université de Montréal, Montréal, Québec Canada; [2] Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada; [3] Università di Messina, Messina, Italy.
Email: garry.hanan@umontreal.ca

Abstract

The coordination compounds of AMidine-*N*-OXide (AMOX) ligands present interesting photophysical,[1] redox, and magnetic properties,[2] granting further developments toward functional materials and their potential application in optoelectronic devices and catalysis.

Structure-properties relationships were determined in a series of complexes of the same metal but with different AMOX ligand substitution pattern, reflecting the important role of ring substituents and their electronic and steric effects. The type of substituents determines the degree of electron-density delocalization within the chelate ring and onto the ligand, allowing the modulation of the σ-donation, π-donation, and π-acceptance capacity, with direct effect on the metal-ligand interaction, and hence on the properties of the complex.

Acknowledgements

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Transforming Materials into Shapes: Harnessing the Out-of-Equilibrium State of Dual-Color Photoinitiators to bring Volumetric 3D Printing to Life

Martin Herder

xolo GmbH, Berlin, Germany.
Email: martin.herder@xolo3d.com

Abstract

Bringing complex functionality to living or non-living matter involves deploying energy in a time- and spatially-controlled manner, pushing a chemical system into an out-of-equilibrium state. In this state, new functionalities may emerge, and highly dynamic processes can be driven, which are not possible at the system's thermodynamic minimum. In this context, molecular photochemistry is a powerful tool, as energy can be delivered in a highly controlled manner using photons. While typically photochemical processes occur in short-lived excited states, there is also the possibility to harness light energy to generate an out-of-equilibrium (metastable) ground state, where the system possesses a different constitution and, consequently, different functionality than when in equilibrium.[1]

We invented the so-called dual-color photoinitiator (DCPI), which harnesses the alternated properties of a photo-generated, metastable ground state to create functionality, i.e. the three-dimensional spatial confinement of a photopolymerization. While conventional photoinitiators lead to polymerization wherever light is present, the DCPI confines the polymerization zone precisely to the intersection point of two light beams having two different wavelengths. With this approach, any volume element within a photopolymer material can be selectively polymerized simply by shining two beams of light into the bulk material, ultimately allowing a solidified object to emerge "out-of-nothing."

The result is a new volumetric 3D printing technology called Xolography,[2] which we employ to create unprecedented shapes and advance real-world applications such as optics and photonics[3] as well as bioprinting and tissue engineering.[4]

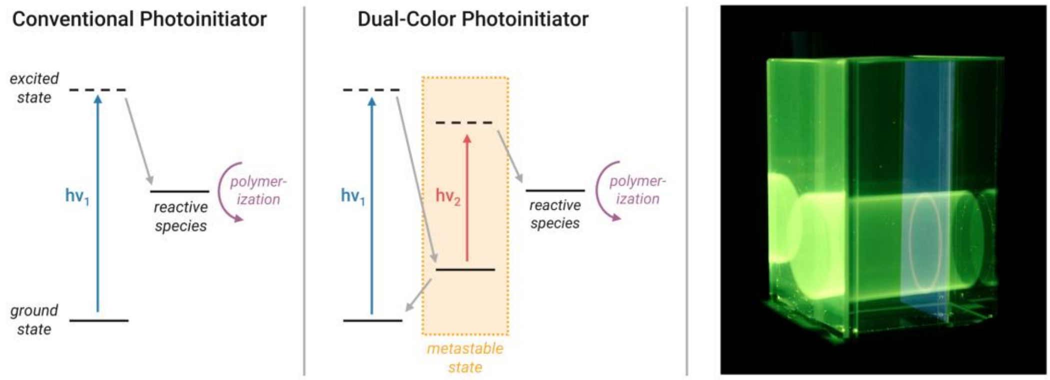

Figure 1. Left: A conventional photoinitiator reacting with UV ($h\nu_1$) light only. Center: A dual-color photoinitiator being activated via a metastable state in the presence of UV ($h\nu_1$) *and* visible ($h\nu_2$) light. Right: Xolography volumetric 3D printing by intersecting a UV light sheet (blue) with a visible light projection (white) within the bulk of a photopolymer.

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Supramolecular polymers with strong adhesion combining non-covalent self-assembly and covalent cross-linking

Shimei Jiang,[1] Yan Shao,[1] Wen Li,[1] Massimo Cametti[2]

[1]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China; [2]Department of Chemistry, Politecnico di Milano, Via Luigi Mancinelli 7, 20131, Milano, Italy.
Email: smjiang@jlu.edu.cn

Abstract

Constructing high-strength adhesives based on a single small molecule presents a significant challenge. Herein, a novel tripodal multifunctional molecule BTA-C7 was designed to be able to exploit a synergistic self-assembling and photo-crosslinking strategy to reach high adhesive performances. BTA-C7 molecule is constituted of a central benzene-1,3,5-tricarboxyamide core, from which cyanostilbene moieties stems, ending each arm with a benzo-crown-ether macrocycle. Under ambient conditions, BTA-C7 self-assembles into one-dimensional (1D) fibers, exhibits strong adhesion (2.3 MPa). Furthermore, under UV irradiation, additional covalent photo-crosslinking can enhance the strength to 5.2 MPa due to the [2+2] cycloaddition reactions of cyanostilbene moieties. At the same time, we were also able to ascertain how irradiation affects the aggregates morphology, thus establishing a direct connection between BTA-C7 macroscopic performance and its microscopic molecular arrangement. Our approach ingeniously leverages the synergistic advantages of three functional groups to develop a robust and efficient supramolecular adhesive.

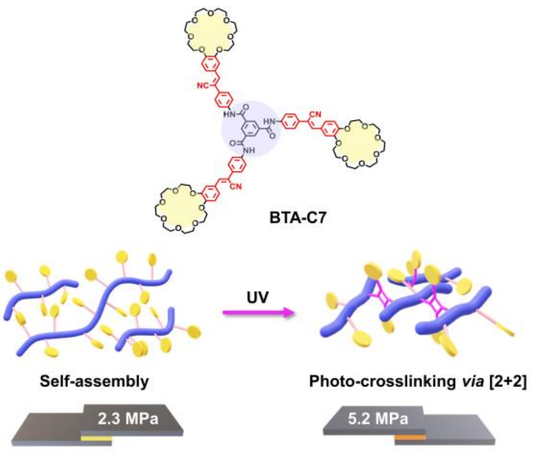

Figure 1. (a) Molecular structures of customized compound **BTA-C7**. (b) Schematic diagram of a synergistic supramolecular and covalent polymerization strategy to achieve remarkable adhesive performance based on **BTA-C7**.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (52173167).

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Innovative Hydrogel Composites Incorporating Andrographolide and Sterculia-Derived Silver Nanoparticles for Accelerated Wound Healing and Infection Control

Sirinan Kulchat[1], Chanon Talodthaisong[1], Apichart Saenchoopa[1], Kittiya Plaeyao[1], Rina Patramanon[2], Wonn Shweyi Thet Tun[2], Sarawut Lapmanee[3], James A. Hutchison[4],

[1]Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand;
[2]Department of Biochemistry, Faculty of Science, Khon Kaen University, Khon Kaen, Thailand;
[3]Department of Basic Medical Sciences, Faculty of Medicine, Siam University, Bangkok, Thailand;
[4]School of Chemistry and Centre of Excellence in Exciton Science, The University of Melbourne, Victoria, Australia.
Email: sirikul@kku.ac.th

Abstract

This study introduces two innovative hydrogels designed for accelerated wound healing and infection prevention. The first is a gelatin-based, self-healing hydrogel crosslinked with vanillin and Fe^{3+} ions, exhibiting high swelling, shear-thinning, and quick self-repair within 10 minutes. Silver nanoparticles (AgNPs) stabilized by andrographolide, a natural anti-inflammatory agent, were embedded, resulting in a bio-nanocomposite with potent antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, and *Burkholderia pseudomallei*. In vivo tests confirmed enhanced wound healing and tissue regeneration compared to the hydrogel alone. The second hydrogel combines aloe vera, gelatin, and sodium alginate (AGS), optimized at a 1:5:3 ratio (AGS-3), demonstrating excellent water absorption, rheology, thermal stability, pH and temperature responsiveness, and suitability for injection. Incorporating Sterculia monosperma-silver nanoparticles (SM-AgNPs) and curcumin-loaded nanoliposomes (NLPs), this composite exhibited strong antibacterial effects against both E. coli and S. aureus. Overall, these multifunctional hydrogels offer rapid self-healing, high swelling, and effective antimicrobial properties, making them promising candidates for wound healing, infection control, and targeted drug delivery. The integration of natural products, nanotechnology, and biopolymers paves the way for sustainable and efficient biomedical applications.

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Generation of a Virtual Dynamic Combinatorial Coordination Library of Silver (I) grid complexes that exhibit preferential heteroligand recognition.

A. Lehchilli,[1] S. Flanagan,[1] N. Grüber,[2] Corinne Bailly,[2] P. N. W. Baxter,[3] J.-M. Lehn[1]

[1] Laboratory of Supramolecular chemistry, Institute for Supramolecular Science and Engineering, Strasbourg, France; [2] Radiocrystallography service, University of Strasbourg, Strasbourg, France; [3] Laboratory of Chemistry of Informational Macromolecules, Institute for Supramolecular Science and Engineering, Strasbourg, France.
Email: adam.lehchilli@etu.unistra.fr

Abstract

Grid-type coordination complexes comprising 2-D arrays of metal ions arranged in symmetric [n×n] ($n \geq 2$) or asymmetric [m×n] ($m,n \geq 2$; $m \neq n$) arrays are structurally unusual materials that have been the subject of continued interest within the fields of inorganic and supramolecular chemistry.[1] Within the context of the rapidly evolving fields of nanotechnology and materials science, the dimensional similarity between large multinuclear 2-D ion dot arrays and pixelated information storage materials introduces the intriguing future possibility that large coordination grids and polymer analogues may find applications in these areas.[2]

In this work, a virtual dynamic combinatorial coordination library (VCCL) of Ag(I) grid complexes was generated, incorporating a variety of structurally differing di- and tritopic heterocyclic N-donor ligands. Coordination grids arising from Homo- and Heteroligand recognition were identified in solution within the library and revealed an overall preference for Heteroligand assembly, giving 2×2, 2×3 and 3×3 mixed-ligand grid species. This was attributable to specific structural features of the differing ligands within the Ag(I) grids, that cooperatively interact via π-π interactions to afford enhanced stabilization in the Heteroligand systems relative to their Homoligand-speciated counterparts. The structural design principles that emerged open up the possibility for the creation of more complex structures by judicial choice of ligands and combinations. Further studies into their physicochemical properties will be anticipated to lead to interesting applications in materials science and adaptive chemistry.

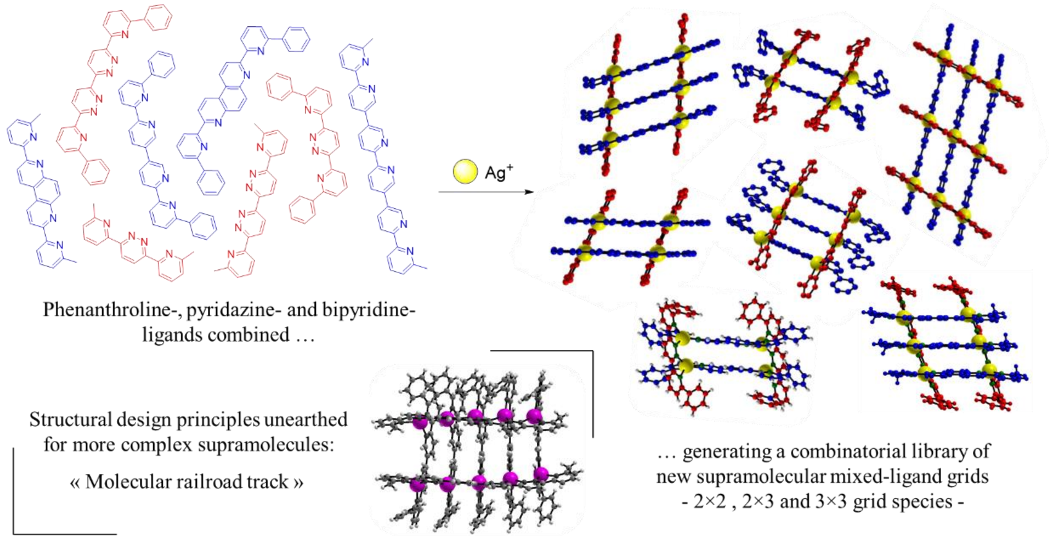

Figure 1: Creation of a Virtual Combinatorial Library of Ag(I) heteroligand 2×2, 2×3 and 3×3 grid complexes.

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Self-assembling hydrogels release therapeutics as potential treatments for acute brain injury

Andrew Marsh,[2] Ishwarjeet U. S. Dhillon,[2] Shuyu Liu,[2] Rachel A. Hand,[2]
Paulina Michór,[4] Andrew Bottrill,[4] Bruno G. Frenguelli,[4] Jeffery T. Davis[1]

[1]Department of Chemistry and Biochemistry, University of Maryland, Maryland 20742-4454, USA
[2]Department of Chemistry, University of Warwick, Coventry CV4 7AL UK
[3]Polymer Characterization RTP, University of Warwick, Coventry, CV4 7AL UK
[4]School of Life Sciences, University of Warwick, Coventry, CV4 7AL UK.
Email: a.marsh@warwick.ac.uk

Abstract

We compare guanosine-borate with sodium alginate hydrogels and calcium chloride cross-linked beads as delivery vehicles for ribose-adenine mixtures (RibAde) in order to explore potential treatments for acute brain injury.

Acute brain injury events such as stroke result in the depletion of cellular adenosine triphosphate (ATP) through the formation of neuroprotective adenosine, and its release with its metabolites into the bloodstream. This impairs ATP synthesis via the dominant purine salvage pathway that requires these metabolites. Delivery of ATP precursors via RibAde has been previously shown in tissue and animal models of stroke to improve both ATP synthesis and outcome after stroke.[1] The major challenges in developing a therapeutic are:

- solubilizing adenine in a biocompatible system;[2]
- time-dependent release to tissue with its therapeutic partner, ribose.

We gathered rheology, UV and CD spectroscopic data for potassium and sodium 50 mM guanosine (G)-quartet hydrogels, prepared using established procedures,[2] loaded with ribose (R), adenine (A) and 1:1 admixtures (A+R) each at total drug concentrations of 0, 4, 8, 16, 20, 24 and 32 mM. Sodium alginate gels and calcium chloride cross-linked beads[3] were prepared as water or artificial cerebrospinal fluid (aCSF) mixtures and each similarly loaded with drug. Time-dependent released drug concentration was followed from gels and beads using UV spectroscopy and where possible, hydrophilic interaction liquid ion chromatography (HILIC) mass spectrometry.[4]

Acknowledgements

We thank: the University of Warwick for support and access to facilities, in particular the Polymer Characterisation Research Technology Platform (RTP; Drs Daniel Lester and James Town) and Proteomics RTP. We thank Dr Nikola Chmel for instrument training, access and discussion of CD and LD data. SL thanks the University of Warwick for Undergraduate Research Scholarship Scheme funding (2021).

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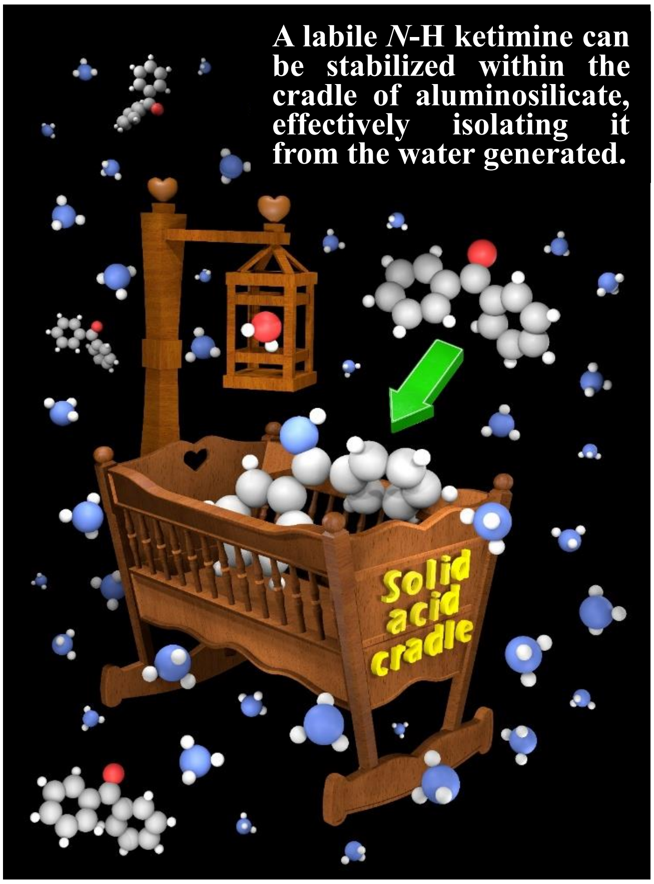
Simple Synthesis of Labile *N*–H Unprotected Ketimines from Ketones and Ammonia Using Porous Aluminosilicates

ONAKA Makoto
Professor Emeritus, The University of Tokyo, Tokyo, Japan
Email: conaka@g.ecc.u-tokyo.ac.jp


A labile *N*-H ketimine can be stabilized within the cradle of aluminosilicate, effectively isolating it from the water generated.

Abstract

I have been interested in performing organic synthesis using porous solid materials. Today, I would like to present one of our recent studies.

The most atom-efficient method for synthesizing *N*-unprotected ketimines (*N*–H ketimines) from ketones is the direct dehydration-condensation reaction with ammonia (NH_3). However, versatile synthetic methods for *N*–H ketimines have been limited until now.

We found that *N*–H diaryl ketimines bearing a range of functional groups on the aryl rings could be synthesized in high yields from the corresponding diaryl ketones and NH_3 under solvent-free conditions using aluminosilicates such as silica-alumina (SiO_2–Al_2O_3) and proton-exchanged Y-type zeolite (H–Y) [1]. Solid-state ^{13}C and ^{15}N NMR measurements indicated that the *N*–H ketimines formed within the acidic zeolite pores were coordinated to NH_4^+ species on the pore surfaces. Our quantum chemical calculations further revealed why the dehydration-condensation reaction between ketones and NH_3—an endothermic process in a vacuum—proceeds toward product formation under the experimental conditions.

Moreover, this synthetic protocol is applicable to the preparation of *N*–H alkyl ketimines, such as *N*–H dicyclohexyl ketimine, with α-acidic hydrogens, which are generally less stable and more susceptible to hydrolysis and oligomerization than *N*–H diaryl ketimines.

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SELF-SORTING: AN ILLUSION?
A DISCUSSION ON CHEMISTRY, PERCEPTION, AND BEAUTY

Artem Osypenko

ADC PR&D, CARBOGEN AMCIS, Hauptstrasse 171, CH-4416 Bubendorf, Switzerland
Email: artem.osypenko@carbogen-amcis.com

Abstract

Self-sorting is one of the central emergent concepts in supramolecular chemistry, supported by numerous elegant studies from many groups, including Labo Lehn [1].

Wu and Isaacs questioned whether self-sorting is “the exception or the rule” [2], concluding that it may simply reflect general thermodynamic principles. Yet, the system they presented, in my view, cannot be described as self-sorted, due to the orthogonality of the chosen chemical processes.

Here, I invite you to go a step further and reflect: *to what extent is self-sorting a chemical phenomenon, and to what extent is it a construct of the mind?* Maybe self-sorting is about our cognitive need to impose order, find beauty, and hear music through the noise.

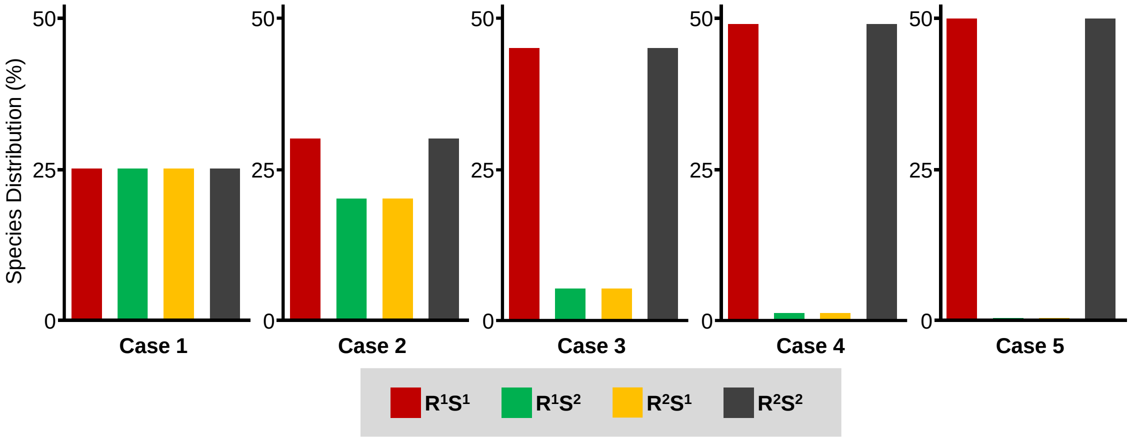

Figure 1. Simulated distributions of four receptor-substrate complexes (**R^1S^1**, **R^1S^2**, **R^2S^1**, **R^2S^2**) in five systems with varying stability constants under thermodynamic control. While the shift from “statistical” (Case 1) to “selective” distributions may be interpreted as “self-sorting”, all outcomes emerge solely from the interplay of thermodynamic parameters, raising the question of whether “self-sorting” is a distinct phenomenon or a convenient label.

Acknowledgements

I would like to warmly thank Prof. Lehn and all my colleagues from Labo Lehn for the unforgettable experience of science we shared together.

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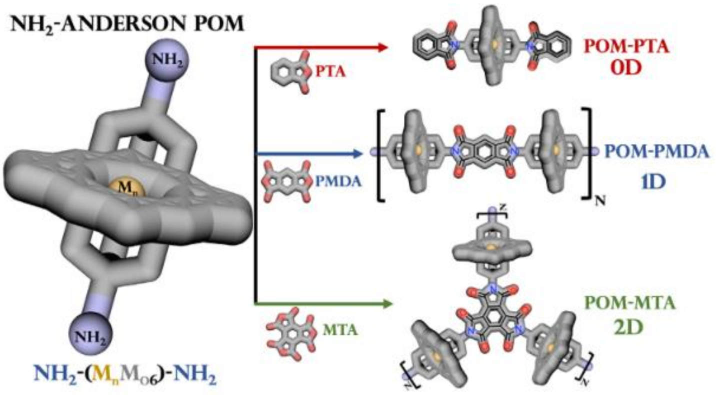
NEW MULTIFUNCTIONAL COMPLEXES OF *D*- AND *F*-METAL IONS WITH N-DONOR LIGANDS

Violetta Patroniak[1]

[1]Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.
Email: violapat@amu.edu.pl

Abstract

The synthesis of supramolecular complexes is currently one of the most explored areas of coordination chemistry due to their chemical and physical properties, unusual structures, and potential applications.[1] Characterization and study of the properties of new complexes of *d*- and *f*-metal ions are scientific goals pursued for many years by our research group. The presented topic of the talk will concern transition metal complexes with N-heterocyclic ligands, with special emphasis on their luminescent, magnetic, catalytic, photocatalytic, electrocatalytic and biological properties.[2-9]



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FROM CRYPTATES …TO PORPHYRINS
OR
FROM STRASBOURG…TO RENNES

Christine PAUL-ROTH, Olivier MONGIN, Fred PAUL
Univ Rennes, INSA Rennes, CNRS,
Institut des Sciences Chimiques de Rennes- ISCR
UMR 6226, F-35000 Rennes, France
Email: christine.paul@insa-rennes.fr

Abstract-In 2004, we synthesised a porphyrin possessing four fluorenyl arms (**TFP**), with a remarkable high fluorescence quantum yield (24%), compared to the reference **TPP** (11%), demonstrating the capacity of the fluorenyl units to enhance fluorescence.[1] Then, to exploite this efficiency, a series of Dendrimers based on **TPP** porphyrin core and bearing, in a non-conjugated way, fluorenyl dendrons was prepared.[2] Different applications were exploited: as the fabrication of red Organic Light Emitting Diodes (OLEDs),[3] and supramolecular assemblies.[4] In 2016, a family of conjugated Dendrimers, still based on **TPP** was obtained.[5] Then, another series of conjugated Dendrimers based on promising **TFP**-Bu was tried.[6] Recently these *Dendrimers* were compared with *Star-shaped* Porphyrins with fluorenyl arms,[7] and a new family of **super-power** star-porphyrins with reinforced fluorenyl arms has been synthesized.[8] Photophysical properties are discussed in the frame of two-photon-induced theranostics.

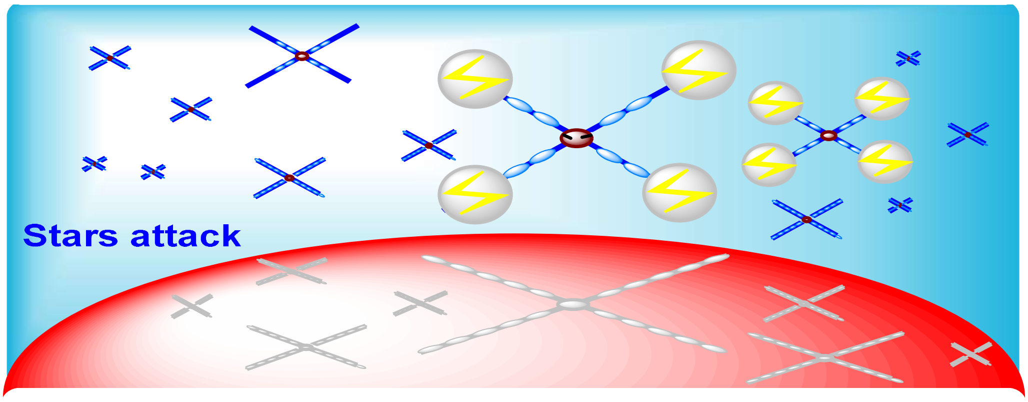

Figure 1. Star-shaped Fluorescent Porphyrins with impressive Two-photon Absorption Cross sections.

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TRANSFER OF STRUCTURAL UNITS THROUGH COVALENT SWITCHES: pH-MODULATED TRANSIMINATIONS

Juan Ramirez,[1,2] Adrian-Mihail Stadler,[1,2,3]

[1]Institut de Science et d'Ingénierie Supramoléculaires (ISIS), UMR 7006, CNRS - Université de Strasbourg, 8 Allée Gaspard Monge, 67000 Strasbourg, France; [2]University of Strasbourg Institute for Advanced Study (USIAS), 5 Allée du Général Rouvillois, 67083 Strasbourg, France; [3] Institut für Nanotechnologie (INT), Karlsruhe Institut für Technologie (KIT), 76344 Eggenstein-Leopoldshafen, Germany. Email: mstadler@unistra.fr

Abstract

Reversibility and lability[1] of covalent chemical bond are the foundations of the dynamic covalent chemistry[2] (DCC). These characteristics of certain covalent bonds make possible the replacement of constituent units of a molecular structure; in this way the chemical architecture becomes constitutionally dynamic. The assembly/disassembly of structural units within the framework of the DCC can allow the tuning of the properties of a molecular architecture. Imine C=N bond[3] is a reversible one, widespread used in various fields, comprising the development of new materials like dynamic polymers, sensors and adaptive materials.

The present work deals with the implementation of transimination reactions based on imines generated by the dialdehyde **A** (Figure 1) and aromatic and aliphatic amines. Monoaldehyde **M** (Figure 1) was used as model for several studies. After a preliminary kinetic monitoring of the formation of imines, the work was focused on the conditions of pH-modulated transiminations, which work like covalent (non mechanical) switches between diimine **AR1**$_2$ (R1 = aryl) and diimine **AR2**$_2$ (R2 = alkyl).

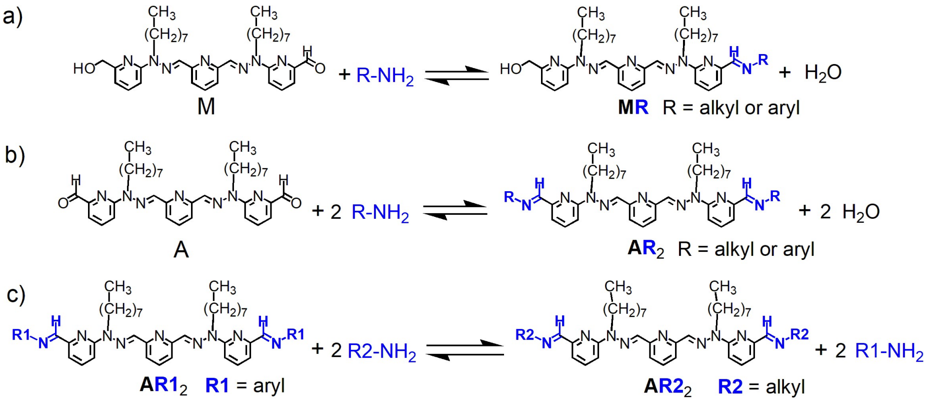

Figure 1. Formation of monoimine **MR** (a), of diimine **AR**$_2$ (b) and transimination (c).

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Self-Selection of Order by the Formation of Micro-Compartments Drives Adaptation, Catalysis, and Chemical Evolution in Constitutional Dynamic Networks

Tanguy Rieu,[1] Ferran Esteve,[1] Artem Osypenko,[2] Jean-Marie Lehn[1]

[1]Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université de Strasbourg, 8 allée Gaspard Monge, 67000 Strasbourg, France.[2] CARBOGEN AMCIS AG, Hauptstrasse 171, CH-4416 Bubendorf, Switzerland.

Email: tanguy.rieu@etu.unistra.fr

Abstract

The understanding of processes governing the transition from chaotic mixtures of molecules to systems of high compositional and functional complexity remains a challenge. The development of artificial models suggests that the formation of self-assemblies leading to increasing order may be the driving force for selection mechanisms that could rationalize the emergence of complexity.[1] However, the examples supporting such ‘‘cosmetic imperative’’ only passively relies on environmental factors and chemical reaction networks. Therefore, this work aims to shine light on the mechanisms of selection by self-assembly in adaptive networks with lipidic micro-environments—the only chemical entity that possesses the three hallmarks of complexity,[2] namely: catalysis, reproduction and containment. Gradual increase in complexity requires processes involving diversity and selection. Dynamic Covalent Libraries generate the compositional complexity for diversity affording a large variety of interconnected species defining Constitutional Dynamic Networks where competition for building blocks underlies the rules of selection.[3][4] To study such insights, dynamic covalent chemistry focused on imine bond is in presence of micellar micro-compartments demonstrates their selective propensity to prevent hydrolysis and that constitutional dynamic networks can be affected by micro-environments.[5] Such proof of concepts is extended to the formation of dynamic covalent micelles and vesicles in a mixture of constituents to unravel the selection mechanisms in the accretion of order, leading to dynamic mixed catalytic micelles capable to sustain complex functions such as catalysis and chemical evolution.

Acknowledgements

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HETEROGENIZATION OF CATALYTIC AND/OR PHOTOSENSITIZING UNITS ON NANOSTRUCTURED MATERIALS FOR ARTIFICIAL PHOTOSYNTHESIS

Francisco J. Romero-Salguero,[1] Miguel A. Pozo,[1] Raúl Rojas-Luna,[1,2] Juan Amaro-Gahete,[1,3] María A. Navarro,[1] Dolores G. Gil-Gavilán,[1] Marta Estrada-Ruiz,[1] Daniel Cosano,[1] Sara Garrido,[1] José R. Ruiz,[1] Souvik Roy,[2] Dolores Esquivel[1]

[1]Departamento de Química Orgánica, Instituto Químico para la Energía y el Medioambiente (IQUEMA), Facultad de Ciencias, Universidad de Córdoba, Córdoba, Spain; [2]School of Natural Science, University of Lincoln, Green Lane, Lincoln, UK; [3]UGR-Carbon – Materiales Polifuncionales Basados en Carbono, Departamento de Química Inorgánica, Universidad de Granada, Granada, Spain
Email: fjromero@uco.es

Abstract

One of the challenges facing humanity today is the production of chemical compounds that can be used as fuels and raw materials for the chemical industry from sources other than oil and coal. A possible alternative is to use the abundant solar energy for the transformation of H_2O and CO_2 into chemical compounds such as H_2, CO, CH_4 and CH_3OH, among others. Nature carries out this process through photosynthesis. In an attempt to mimic natural processes, the first papers on artificial photosynthesis were published in the late 1970s [1]. These systems consist of three components: a photosensitizer, which absorbs visible light, a catalyst, where protons or CO_2 are reduced, and a sacrificial electron donor agent.

In this work we present our results in the heterogenization of catalytic and/or photosensitizing units in solid materials [2]. The materials used as supports include periodic mesoporous organosilicas (PMOs) and metal-organic frameworks (MOFs). Active sites inspired by [FeFe]-hydrogenase enzymes or vitamin B12 structure, such as diiron complexes, cobaloximes and cobalt phthalocyanines, have been successfully integrated on the pore walls by grafting, co-condensation and functionalization procedures. Additionally, various layered double hydroxides (LDHs) of different composition, alone or as part of composites, have also been used as catalysts. As photosensitizers, those based on ruthenium complexes with bipyridine-type ligands stand out, although other organic dyes have also been tested (Table 1).

Table 1. Some results on artificial photosynthesis

Catalyst	PS	ED	Irradiation	Conditions	Activity	TON
[Fe2S2]-PMO	$Ru(bpy)_3^{2+}$	Ascorbic acid	LED (475-750 nm)	Acetate buffer, pH=5	0.6 mmol H_2 g^{-1} at 6 h	5.2
Cobaloxime Im-PMO	Eosyn Y	TEOA	Xe lamp (λ>400 nm)	H_2O/CH_3CN	95 mmol H_2 g^{-1} at 2.5 h	138
CoN5-PMO	4CzIPN	BIH	Solar simulator (λ>400 nm)	CH_3CN	3.8 mmol CO g^{-1} at 3 h 75% CO sel	92
Ru-CoPc-PMO	Ru-CoPc-PMO	BIH	Xe lamp (λ>400 nm)	CH_3CN	1.5 mmol CO g^{-1} at 6 h 76% CO sel	50

Acknowledgements

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Progress is linked to the Past

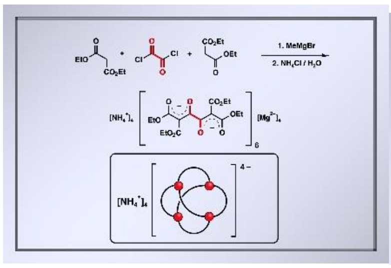
Presenting Author[1], Rolf W. Saalfrank[1] # Dedicated to J.-M. Lehn on the occasion of supra60

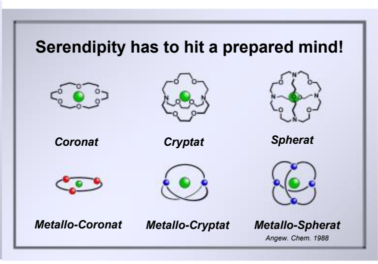
Institut für Organische Chemie, Universität Erlangen-Nürnberg, Germany

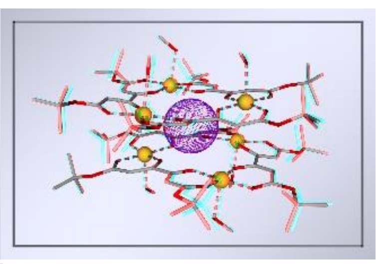
Email: rof.saalfrank@fau.de

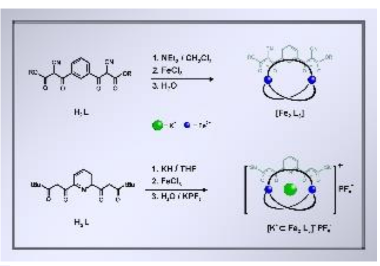
Abstract:

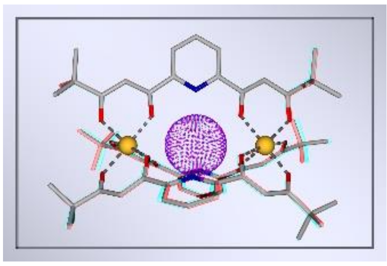
With completely different goals in mind, we reacted malonic ester with MeMgBr and oxally chloride and isolated a crystalline product [M_4L_6]. With the X ray in hands, I was singing in the corridor. Serendipity has hit a prepared mind[1,2]. This one pot procedure is generally valid for the synthesis of M-bridged metallo topomers[1,2] of the well known N-briged systems.

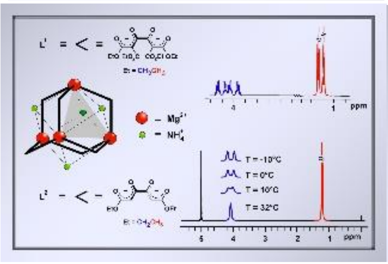


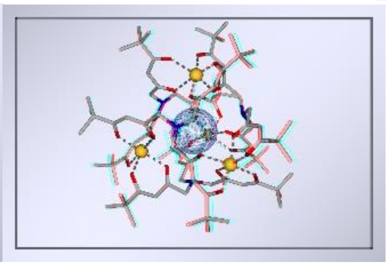


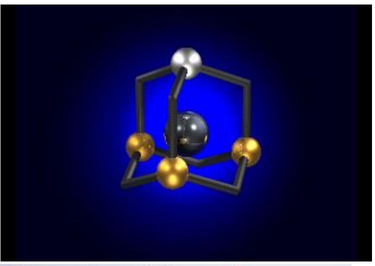


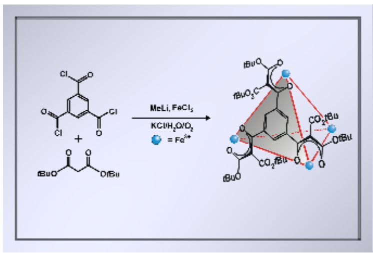


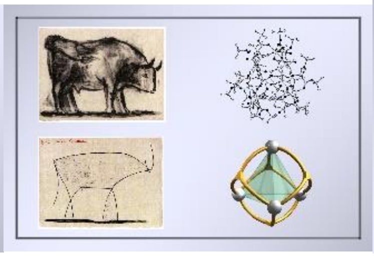


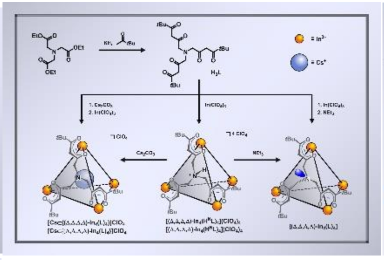


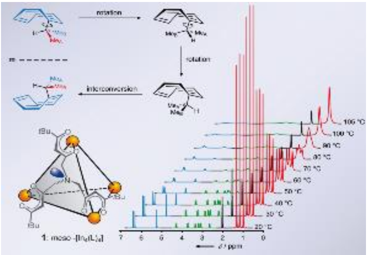


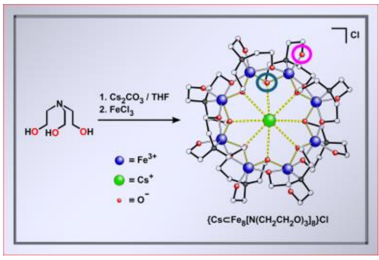


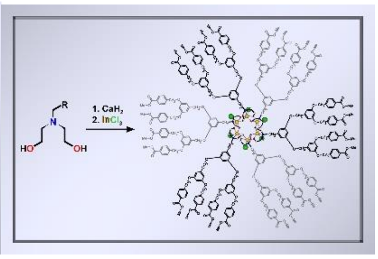












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For acknowledgements cf. [1], [2]. For generation of the artwork: Andreas Scheurer, Harald Maid

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ORGANIC REDOX FLOW BATTERY ASSISTED BY SUPRAMOLECULAR PHENOMENON

Yasutaka TANAKA

Laboratory of Molecular Recognition, Shizuoka University, Hamamatsu 432-8561, JAPON

Email: tcytna@shizuoka.ac.com

Abstract

A post-lithium ion battery has extensively focused attention. An organic redox flow battery is advantageous in view of the innocent aqueous electrolyte, wide options of inexpensive organic redox active materials, and flexibility of system construction (**Figure 1**). Quinones are the potential candidate of the active material here due to their availability, diverse adoption, and stable redox cycle (**Figure 2**). The decisive drawback however is the irreversible dimerization of quinones with their reduced forms via two point hydrogen-bonds resulting in water-insoluble and redox inactive dimer (**Figure 3**).

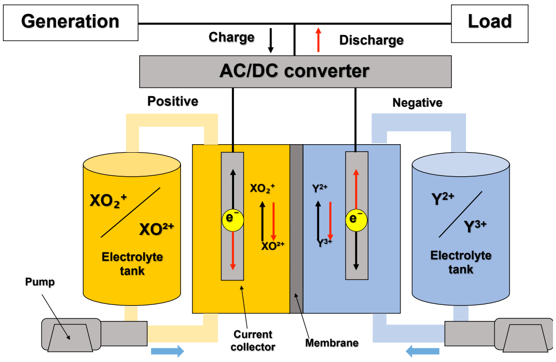

Figure 1 Schematic dialog of redox-flow battery

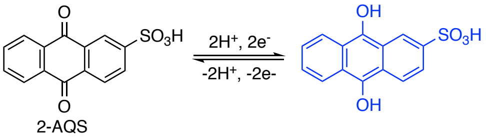

Figure 2 Redox reactions of 2-anthraquinone sulfonic acid (2-AQS)

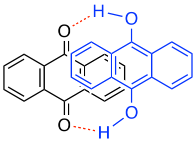

Figure 3 Quinone dimerization. The red dotted lines stand for hydrogen-bond.

We have thus adopted the highly water-soluble cyclodextrin ((2-hydroxypropyl)-β-cyclodextrin: HP-β-CD) into the system: thus the comlexation of a quinone and HP-β-CD would suppress the dimerization. HP-β-CD has the higher water-solubility (1.0 g/mL) than the parent β-CD (0.0019 g/mL). In particular the reversible redox reactions of 2-AQS took place in the presence of HP-β-CD while the capacity reduced with redox cycles in the absence (**Figure 4**, **5**). The ^{1}H-, ^{13}C-, COSY, ROESY, HMQC, DOSY evidenced the inclusion 1:1 complex of 2-AQS in HP-β-CD.

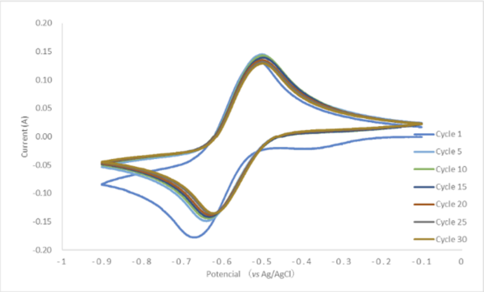

Figure 4 Circular voltammogram (*vs.* Ag/AgCl) of 2-AQS in the presence of HP-β-CD

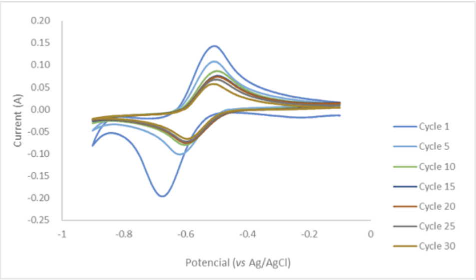

Figure 5 Circular voltammogram (*vs.* Ag/AgCl) of 2-AQS in the absence of HP-β-CD

The identification and commercial development of broad-spectrum antimicrobial theranostic leads based on luminescent ruthenium(II) complexes

Jim A THOMAS,[1,2] Simon Fairbanks[2] Kirsty Smitten,[1,2] Richard Senior,[2] Michael Murray[2]

[1]Chemistry, School of Mathematics and Physical Science, University of Sheffield, S3 7HF, UK,
[2]MetalloBio Ltd, The Innovation Centre, 217 Portobello,Sheffield, S1 4DP
Email: james.thomas@shef.ac.uk; jim.thomas@metallobio.com

Abstract

Luminescent polypyridyl ruthenium(II) complexes that interact with biomolecules are much studied for their biological potential. Using such architectures, we identified non-toxic super-resolution imaging probes, such as **1**, for live eukaryotic cells – Fig 1 A.[1–4] Complex **1** provided a platform to develop derivatives with medical potential; eg, as anticancer therapeutics[5] and phototherapeutic.[6,7] Recently, analogues that function as broad spectrum antimicrobials against AMR pathogens, such as **2** (Fig 2B), have been identified[8–10] and the most promising structures and their derivatives are being developed by the University spin-out MetalloBio ltd.

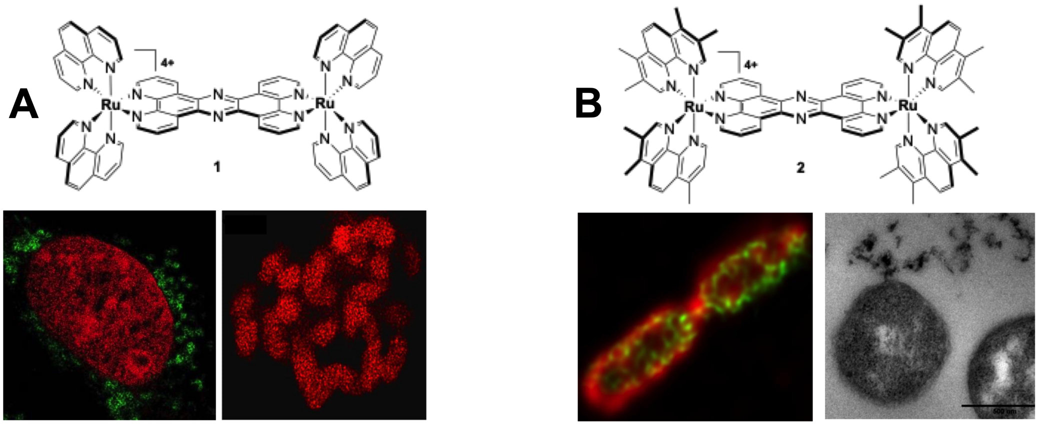

Figure 1. **A** Structure **1** and examples of STED nanoscopy images obtained using its probe capabilities. Left: single life cell, right: heterochromatin detail. **B** Structure of antimicrobial derivative **2** and bacterial images. Bottom left: STED nanoscopy shows outer membrane disruption of pathogenic *E coli* within 10 minutes. Bottom right: Using **2** as contrast stain, TEM reveals total lysis within 1 hour.

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Network Complexity Drives Selectivity Switching in Dynamic Covalent Libraries of Cages

Zhaozheng Yang[1,2], Cheng-Yi Zhu[1,2], Ferran Esteve[1], Jean-Marie Lehn[1,2]

[1]Laboratoire de Chimie Supramoléculaire, Institut de Science et d'Ingénierie Supramoléculaires (ISIS),
Université de Strasbourg, 67000 Strasbourg, France
[2]Lehn Institute of Functional Materials (LIFM), Sun Yat-Sen University, 510006 Guangzhou, China
Email: zhaozheng.yang@unistra.fr

Abstract

Controlling the reaction pathway and product selectivity of chemical reactions is a major challenge in synthetic chemistry. This challenge becomes more pronounced with systems of higher complexity containing an increasing number of reacting species, due to the exponential rise in possible constitutional outcomes. In contrast, a number of biological processes give high-fidelity sorted states from exceedingly complex mixtures as a result of favored structural topologies and interconnected network relationships. Inspired by this principle, we investigate if constitutional dynamic networks of imine cages can exhibit distinct selectivity preferences at different orders of complexity. Our results demonstrate how topological and constitutional complexities can affect the equilibrium landscape of reaction networks. Moreover, they represent an unprecedented synthetic strategy for programming constitutional selectivity in dynamic chemical systems, without the need for external energy inputs or stimuli.

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