Book of Abstracts



 $17^{\text{th}} - 18^{\text{th}}$ September 2021



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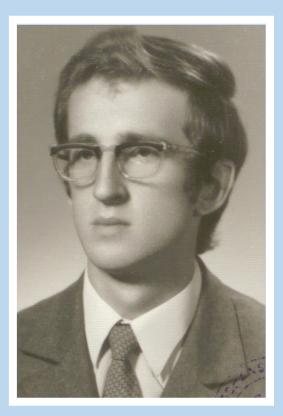
THE SYMPOSIUM WAS ORGANIZED TO CELEBRATE PROFESSOR L. LATOS-GRAŻYŃSKI'S 70[™] BIRTHDAY.

Professor Latos-Grażyński was born on April 7, 1951. He grew up and received his early education in Żagań. In 1969 he began to study chemistry at the University of Wrocław and received his M.Sc. degree in 1974. His Ph.D. thesis, presented in 1978, was entitled *Nuclear Magnetic Resonance in the Investigations of Systems Containing a Metal Ion [Co(II), Hg(II), Ni(II)] and Polyaminoacetic Acids* (mentor: prof. B. Jeżowska-Trzebiatowska). From 1979 to 1981 he worked as a post-doc with professors Gerd N. La Mar and Alan L. Balch at the University of California, Davis.

On his return to Poland prof. Latos-Grażyński resumed his work at the University of Wrocław, frequently revisiting Davis during summers. Further steps in his scientific career were the D.Sc. degree (1986) and professorship (since 1992). He became full professor in 1998. In 2004 prof. Latos-Grażyński was elected a corresponding member of the Polish Academy of Sciences (PAN) and in 2016 became an ordinary member.

Professor Latos-Grażyński received the prestigious award of the Foundation for the Polish Science (1998), the M. Skłodowska-Curie award of the Polish Academy of Sciences (2000), the Humboldt Research Award (2005), the Japan Society for Promotion of Science (JSPS) Fellowship for Research (2010), award of Polish Prime Minister for Scientific Achievements (2010), Jędrzej Śniadecki Medal of Polish Chemical Society (2014). Marie Skłodowska-Curie – Wilhem Klemm Vorlesung, GDCh-Wissenschaftsforum Chemie, Dresden 2015 or Order of Polonia Restituta, the Officer's Cross (Krzyż Oficerski Orderu Odrodzenia Polski).

Jubilee has authored or co-authored over 280 scientific publications, which have been cited more than 12000 times (H-index – 58).

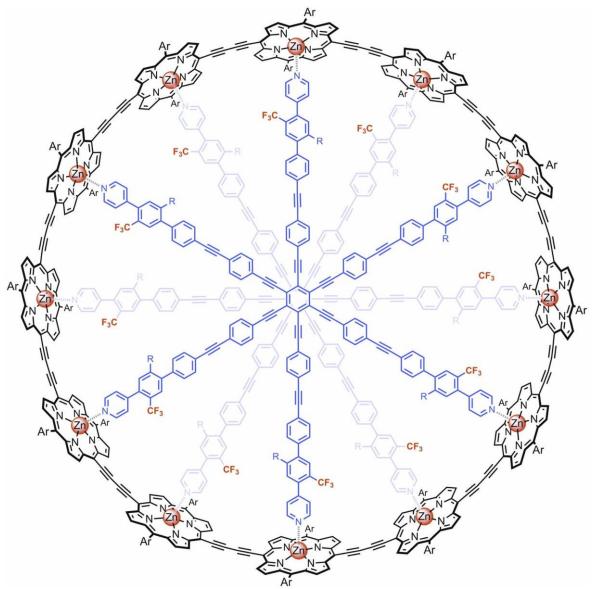


SYNTHESIS & ELECTRONIC DELOCALIZATION IN π -CONJUGATED MACROCYCLES: DOES AROMATICITY HAVE A SIZE LIMIT?

Harry L. Anderson

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Template-directed synthesis can be used to create π -conjugated porphyrin rings as big as proteins.^[1] These systems mimic the light-harvesting behavior of photosynthetic chlorophyll arrays^[2] and they display global aromaticity in some oxidation states.^[3,4] For example, the 12-porphyrin nanoring template complex is globally aromatic in its 6+ oxidation state with a Hückel circuit of 162 π electrons.^[4] Recent work on related systems will be presented.



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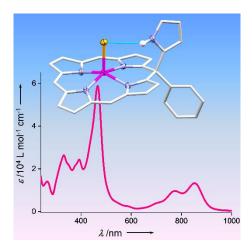
ISOPORPHYRINS AND THE TOP OF THE PYR(ROLE)AMID: NEWS FROM THE ADLER-LONGO REACTION

Prof. Dr. Martin Bröring

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One-pot reactions according to the Adler-Longo method are usually the most straightforward option for the preparation of tetra-*meso*-aryl porphyrins. Following a general rule in this strategy, dynamic mixtures of linear oligopyrroles are formed (so-called scrambling) from an aldehyde and pyrrole in an acid-induced manner in a first condensation step. In the second oxidative step, these oligopyrroles then irreversibly react to the desired macrocycles and to many other macrocyclic and linear oligomeric by-products.

The newest addition to the porphyrinoids obtained in this fashion are the isoporphyrins.^[1] These species show a unique optical behaviour, but have hitherto been difficult to obtain and handle. We have now successfully opened the field of isoporphyrin preparation and manipulation.^[2,3] This contribution will highlight recent results and some surprises of this new chemistry.



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CRAIG-TYPE MÖBIOUS METALLA(ANTI)AROMATICITY IN PLATINUM(II) AND PALLADIUM(II) DICARBAPORPHYRINOIDS

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The continual discovery of new molecular architectures has expanded the understanding of the multifaceted nature of the concept of aromaticity. For instance, the introduction of transition metals into the π -conjugated framework of organic molecules has led to fascinating metalla-aromatic structures, exhibiting properties distinct from their corresponding hydrocarbon analogs.¹ In comparison with various metalla-aromatics reported so far, the construction of antiaromatic metallacycles has remained a synthetic challenge due to thermodynamic instability.² Furthermore, the realization of a highly elongated π -conjugated carbon backbone in metalla-aromatics is rare due to the requirement of a higher planar coordination configuration around the metal ions.³

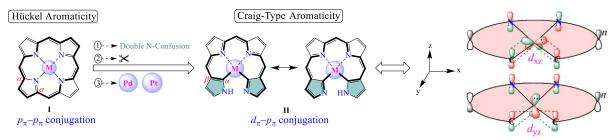


Figure 1. A Craig-type d_{π} - p_{π} global conjugation is envisioned in structure **II**, conceptually derived from metalloporphyrin **I**.

In this work, we envisioned that the pre-organized pyrrolic π -backbone of a hypothetical metalloporphyrin structure I can be utilized to obtain a Craig-type⁴ aromatic structure II (Figure 1). Implementing the double N-confusion (i.e., α,β -pyrrolic connectivity) can offer two strong metal(M)-carbon bonds. Furthermore, removing a *meso*-carbon in **II** ensures the complete elimination of the ligand dominating π -Hückel aromatic character. Thus, providing an alternative possible conjugation pathway through the metal-carbon bonds. Synthesis of these unique class of metallaporphyrinoids, their structural characterizations, and various computational indices such as NICS values, AICD plots and EDDB(H) to probe aromaticity will be discussed in detail. Interestingly, the implementation of diffuse 4d(Pd) and 5d(Pt)orbitals into the tetrapyrrolic π -backbone has significantly red-shifted the absorption in the near-infrared region and exhibited excellent photostability and photothermal conversion efficiency of 60–65% (λ_{ex} = 1064 nm).

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EXPECT THE UNEXPECTED!

Jacek Waluk

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Our investigations of porphyrin (1) and its isomers: porphycene (2), hemiporphycene (3), and corrphycene (4) (Figure 1) have frequently provided examples of uncommon or even surprising behaviour of these fascinating molecules. I will present some of these results, including unusual hydrogen bonding patterns,¹ tautomerism dominated by vibrational mode-selective tunnelling,² emission in plasmonic systems,³ single-molecule fluorescence⁴ and Raman⁵ spectroscopy or microscopy⁶ studies carried out in various environments, viscosity-dependent photophysics,⁷ and photostability.⁸

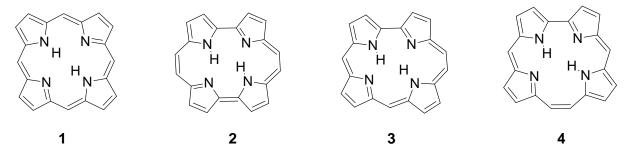


Figure 1. Porphyrin (1), porphycene (2), hemiporphycene (3) and corrphycene (4).

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NEW ERA IN THE CHEMISTRY OF DIKETOPYRROLOPYRROLES

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Discovered in the early seventies diketopyrrolopyrroles (DPPs) are one of the most recently developed groups of organic pigments.^[1] Due to their relatively simple synthesis and other advantageous properties, such as their intense color, excellent stability, and low solubility, DPPs have been rapidly adopted for numerous industrial applications. Over time it was revealed that, through *N*-alkylation, DPP pigments can be easily transformed into very soluble dyes showing strong fluorescence.^[1] This characteristics, combined with the possibility that DPPs can be easily modified, has attracted the attention of many researchers. Most of these reports concern the use of DPP derivatives in semiconductor electronic devices, such as organic field-effect transistors (OFET), solar cells and organic light-emitting diodes (OLED).^[1] In this presentation, we would like to report three major discoveries related to chemistry of diketopyrrolopyrroles made during the last year. Namely: (1) the entirely new method to synthesize unsymmetrical diketopyrrolopyrroles possessing three different substituents:^[2] (2) breakthrough methodology leading to novel type of π -expanded diketopyrrolopyrroles:^[3] and (3) boron-complexes of diketopyrrolopyrroles with superb emission properties.^[4] These three discoveries taken together ensure that diketopyrrolopyrroles will continue to attract attention for years to come.

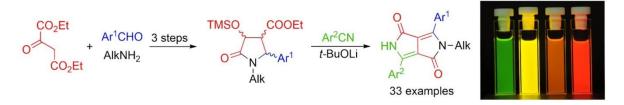


Figure. New methodology leading to unsymmetrical diketopyrrolopyrroles.

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SUPRAMOLECULAR ASSEMBLIES – FROM MOLECULAR COMPONENTS TO FUNCTIONAL NANOSTRUCTURES

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Supramolecular chemistry investigates chemicals systems and large architectures build from simple molecular components connected *via* weak, non-covalent and reversible interactions. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility, so as to allow a continuous modification in constitution by reorganization and exchange of building blocks. These features define a Dynamic Combinatorial Chemistry (DCC) on both the molecular and supramolecular levels.¹ The field of DCC is currently undergoing a revival, largely on account of our increased understanding of supramolecular phenomena and the subsequent development of self-assembly processes. The results obtained so far show the enormous potential of complex and functional chemical systems generated by implementation of supramolecular and DCC approach, however the full understanding of controlled synthesis of multicomponent molecular and supramolecular architectures (2D and 3D), with predicted physicochemical parameters was not yet achieved.

Taking into account the big potential of supramolecular and dynamic covalent chemistries in the creation of functional architectures² we decided to investigate the formation of complex chemical systems by means of dynamic/reversible covalent and non-covalent bonds.³ The purpose of our studies is the development of new complex supramolecular and molecular dynamic systems of different topologies and functions.⁴⁻ The influence of the employed dynamic bonds on the structural, physicochemical and functional properties of the synthesized architectures is of our main interest.



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BIOINSPIRED CATALYSIS FOR SUSTAINABLE LIGHT-INDUCED PROCESSES

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Nature constructs and decomposes complex molecules with the help of enzymes and light as the ultimate energy source. However, despite enzyme's fundamental benefits, their industrial application can be limited by their availability, instability towards certain reaction conditions, cost, scale, lack of suitable enzyme etc. A complementary approach to sustainable methodologies relies on the formation or cleavage of chemical bonds using bioinspired methods (methods imitating the efficient and elegant designs of biology) and recruiting light, the most abundant free energy source.

Vitamin B₁₂ - a cofactor of many enzymes seems inspirational.^[1,2] This type of catalysis has been successfully translated into the laboratory and used in a small collection of reactions.^[2] The advantage of using vitamin B₁₂ as a catalyst lays in the complete stability of the central cobalt ion and by the definition it is nontoxic. It has also been well documented that the reaction mechanism usually follows a radical pathway, bringing a new dimension to this already interesting field.

Along this line, we have developed new vitamin B_{12} -catalyzed reactions involving reduction of Co(III) to Co(I) or Co(II) and subsequent reactions with electrophiles, SOMOphiles, or radicals.^[3-5] Light-induced vitamin B_{12} -catalyzed methods are also suitable for C-O bond cleavage.^[6] These key findings emphasize the unique feature of vitamin B_{12} as a catalyst to achieve something unachievable with other methodologies or to find a greener approach.

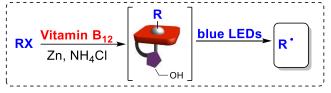


Figure 1: Vitamin B₁₂ - catalysis

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RE-ENGINEERING THE PIGMENTS OF LIFE – FREE BASE PORPHYRINS AS ORGANOCATALYSTS AND SENSORS

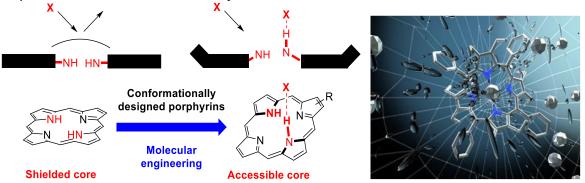
Mathias O. Senge

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Porphyrins are nature's cofactors par excellence. Next to oxygen transport and storage, their role in electron transport and as photosynthetic pigments, they catalyze a multitude of chemical reactions.^{1,2} All these catalytic functions depend on the presence of a central metal which is intricately involved in the catalytic processes. Thus, all known catalytically active porphyrins are metalloporphyrins. However, we have discovered that, upon appropriate manipulation of the porphyrin macrocycle conformation, the core nitrogen atoms in free base porphyrins can be involved in catalysis as well.

Distorted porphyrins are able to activate small molecules via general base catalysis by participation of the imine groups or through hydrogen bonding catalysis involving the pyrrole units. To make the "active center" more accessible to substrates, the degree of outwards orientation of the pyrrole groups can be fine-tuned depending on the peripheral substitution pattern using *peri*-interactions or core substitution.³ Various distortion modes exist, and saddle distorted porphyrins have been shown to have an increased basicity which qualifies these tetrapyrroles for catalytic screening.⁴ Additionally, it is possible to enhance the basicity via electronic modulation of the β -and meso-substituents through the introduction of electron-withdrawing groups.

An extensive screening of a number of nonplanar porphyrins and substrates, as well as reaction conditions, has been used to develop design criteria for optimizing the catalytic properties of distorted porphyrins. Notably, certain free base porphyrins have been found to function as organocatalysts in Michael addition reactions, indicating a new mode of catalytic action for porphyrins which does <u>NOT</u> require a central metal ion. In addition, similar concepts have been used to develop switchable porphyrin receptors for the detection of analytes.^{5,6}



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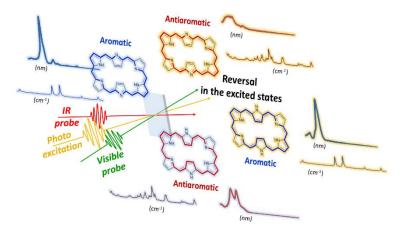
EXCITED-STATE AROMATICITY IN EXPANDED PORPHYRINOIDS: ELECTRONIC STRUCTURES AND CONFORMATIONS UPON AROMATICITY REVERSAL

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Aromaticity, the special energetic stability derived from cyclic $[4n+2]\pi$ conjugation, has been the topic of intense interest in chemistry. Recently, the pioneering work by Colin Baird on aromaticity reversal, postulating that aromatic (antiaromatic) character in the ground state reverses to antiaromatic (aromatic) character in the lowest excited triplet state, has attracted much attention. The completely reversed aromaticity in the excited states provides direct insight into understanding the properties of photoactive materials. However, most studies on excited state aromaticity have been based on the theoretical point of view. The experimental evaluation of excited state aromaticity is still challenging and strenuous because the assessment of aromaticity with conventional magnetic, energetic, and geometric indices is difficult in the excited states.

Time-resolved optical spectroscopies can provide a new and alternative avenue to experimentally evaluate excited state aromaticity. With monitoring ultrafast changes in the excited states, they can provide valuable information for excited state aromaticity. In this regard, recent breakthroughs in experimentally assessing aromaticity reversal in the excited states with time-resolved optical spectroscopic measurements are introduced. To scrutinize this intriguing and challenging scientific issue, expanded porphyrins have been utilized as the ideal testing platform because they exhibit perfect aromatic and antiaromatic congener pairs, having the same molecular framework but with different numbers of π -electrons, which facilitates the study of the pure effect of aromaticity. Time-resolved electronic and vibrational absorption spectroscopies capture the change of electronic structure and molecular conformations driven by the change of aromaticity and provide clear evidence for aromaticity reversal in the excited states. These approaches will pave a way for the development of new experimental indices for the evaluation of excited state aromaticity and its applications.



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TEXAS-INSPIRED DRUG DISCOVERY EFFORTS

Jonathan L. Sessler

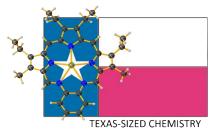
The University of Texas at Austin

This lecture will present the development of expanded porphyrins as potential drug leads. The presentation will begin with a personal story of a 3x cancer survivor and how with the assistance of great coworkers and collaborators an effort has been made to fight back against this disease by studying the chemistry and anti-cancer biology of gadolinium(III) texaphyrins.

Texaphyrins were the first of the so-called expanded porphyrins--larger analogues of heme pigments--to stabilize a 1:1 complex with a metal cation. Subsequently, and continuing as a focus today, an effort has been made in our laboratories and those of many others, including that of Lechosław Latos-Grażyński and other speakers in this symposium, to create additional expanded porphyrins. Hundreds are now known. Several from our laboratory have proved useful at stabilizing actinide cation complexes.

Recently, efforts have been made to create so-called immunogenic cell death promoters designed to prevent cancer recurrence based on redox-active gold(I) carbenes. An introduction to this new research direction will serve to close the lecture.

Collaborations with a number of groups, including those of Profs. Dongho Kim, Andrew Gaunt, John Arnold, Stosh Kozimer, Jong Sung Kim, Shunichi Fukuzumi, T.K. Chandrashekar, Dirk Guldi, Changhee Lee, Jan Jeppesen, Steffen Bähring, Zahid Siddik, Rick Finch, Zhengrong Cui, and Tomas Torres, are gratefully acknowledged. Special thanks also go to Jonathan F. Arambula, Gregory Thiabaud, Sajal Sen, Xiaofan Ji, James Brewster, and Daniel Mangel. Early funding came from the US NIH and the CPRIT, with current support provided by OncoTEX, Inc. (disclaimer: JLS is a non-executive board member of OncoTex, Inc.) and the Robert A. Welch Foundation.



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PORPHYRINS AND FULLERENES

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This talk will consider the utility of flat metal porphyrins, particularly Ni(II)(octaethylporphyrin), as cocrystallization agents for structural characterization of fullerenes, metallofullerenes, and other related rather round molecules.^{1,2}

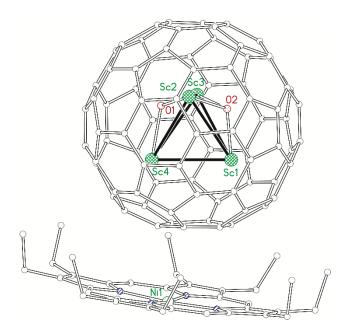


Figure 1. The structure of $Sc_4(\mu_3-O)_2 @ I_h-C_{80} \cdot Ni^{II}(OEP) \cdot 2C_6H_6$ from Stevenson, S., M. A. Mackey, M. A. Stuart, J. P. Philips, M. L. Easterling, C. J. Chancellor, M. M. Olmstead, A. L. Balch. A Distorted Tetrahedral Metal Oxide Cluster inside an Icosahedral Carbon Cage, Synthesis, Isolation, and Structural Characterization of $Sc_4(\mu_3-O)_2@I_h-C_{80}$. *J. Am. Chem. Soc.* **2008**, *130*, 11844-11845.

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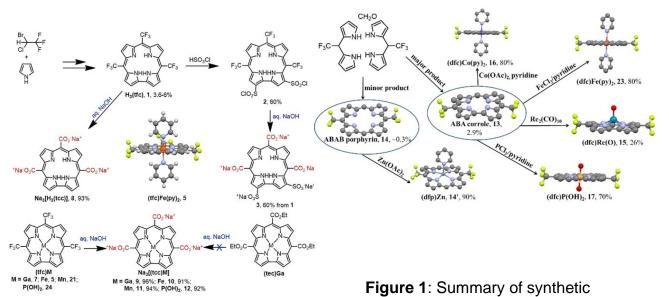
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THE JOURNEY TOWARDS LESS SUBSTITUTED CORROLES AND SAPPHYRINS

Zeev Gross and Atif Mahammed

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The last 20 years have evidenced an enormous increase of activity on introducing corroles as drug candidates for fighting various diseases and as sustainable catalysts for clean production of energy from renewable resources. While triarylcorroles were used almost exclusively for those purposes, ongoing research also exposed the demand for corroles that are much smaller in size. We now report the progress in that direction, which already resulted in derivatives within the molecular weight limit characteristic of orally available drugs (Figure 1, left) and metal complexes of the size required for strong absorbance onto electrodes used for fuel cells (Figure 1, right).¹



approaches.

Parallel efforts are devoted to the design of new sapphyrins and novel metal complexes thereof.²

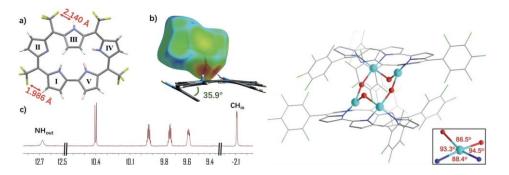


Figure 2: New Sapphyrins and new coordination chemistry.

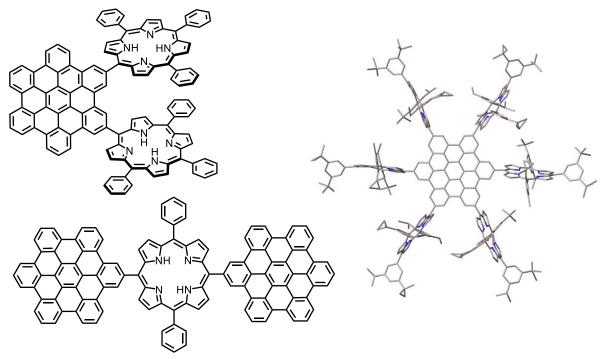
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PORPHYRIN-NANOGRAPHENE HYBRIDS

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Department of Chemistry & Pharmacy and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg

Novel architectures based on porphyrins and hexaarylbenzenes/ hexabenzocoronenes – nanographenes will be shown and their interactions with fullerenes will be discussed. Special emphasis is given to crystal packing phenomena. We report on the synthesis, characterization, and properties of some of these novel systems.^[1-4]



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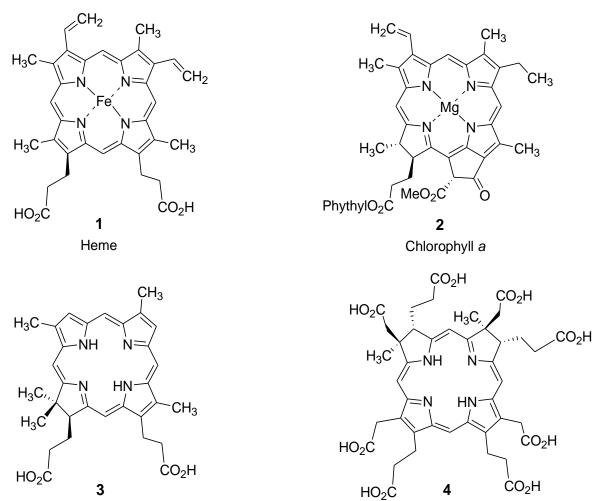
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PIGMENTS OF LIFE – A FASCINATING CHAPTER OF TETRAPYRROLE CHEMISTRY

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Every year more than one billion tons of heme **1** and chlorophyll **2** are produced by all kind of organisms in different environments. Therefore these ubiquitous tetrapyrroles form an ideal renewable feedstock for synthesis and less common natural porphyrinoid pigments. During the last four decades several of those less common pigments like bonellin **3** and sirohydrochlorin **4** were discovered in marine and terrestrial organisms. These hydroporphyrins are decorated by specific geminally dialkylated structural parts in their saturated rings. Construction of the geminally dialkylated parts by enantioselective routes poses a great challenge for synthesis.



Bonellin

Sirohydrochlorin

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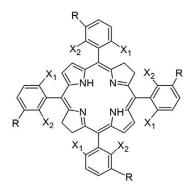
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SYNTHETIC BACTERIOCHLORINS – OPPORTUNITIES FOR PHOTODYNAMIC ACTIVITIES

Grażyna Stochel

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Photodynamic therapy (PDT) is considered as the credible alternative to surgery,



chemotherapy and radiotherapy in the management of cancer diseases. The key factors in this method are spectroscopic. photophysical and photochemical properties of the photosensitizer used, light dose and dioxygen concentration. Among many groups of photosensitizers studied up to now, synthetic bacteriochlorins (Fig.1) are unique in their photodynamic efficacy and possibilities of tuning the required properties. Engineering of their electronic and geometrical structures via rings substituents (R, X in Fig.1) allowed for receiving compounds interesting for applications, from photocatalysis various and

photodiagnosis to photodestruction. From the library of

meso-tetraphenyl bacteriochlorin

synthetic bacteriochlorins, after many biological (*in vitro* and *in vivo*) studies, the most promising photosensitizer for head and neck cancer PDT treatment entered the second clinical phase.

Acknowledgements:

Project ERA-Chemistry "Stable bacteriochlorins - Opportunities in Infrared Chemistry", project NCN no N185762 "Redox-cycling of metal-macrocycle complexes in the activation of small molecules (O2, NO) in homogeneous solutions: models, mechanisms and catalysis".

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ON COMMON DENOMINATORS: ABOUT RIGIDITY, FLEXIBILITY AND SURPRISES

Gerard van Koten

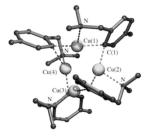
Organic Chemistry & Catalysis Utrecht University The Netherlands g.vankoten@uu.nl

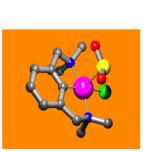
What are the factors that make a research line of interest? Is it a matter of aiming for intellectual satisfaction, or having an interest and motivation in solving a problem of societal or economical interest, or is it to create a context that supports teaching students the concepts of a discipline? Of course, there are many motivations but curiosity, knowledge, being sensitive to serendipity, being able and interested to collaborate, having had excellent mentors and colleagues, and sufficient financial support, all these aspects are prerequisites that are required to proceed. It is only in retrospect that one can make a judgement and discover and enjoy what really personal highlights were. I congratulate Professor **Lechosław Latos-Grażyński's** on a great scientific career (1983--), providing new life to porphyrinoid chemistry, for his ingenuity to develop novel syntheses and physicochemical analyses of small and extended, macrocyclic, porphyrin structures thereby uncovering new vistas for the synthesis of complex structures and metal complexes.

In my contribution, I will concentrate on a discussion of the differences and analogies between NCN-metal complexes, studied by talented students and coworkers in my group, and the great molecules developed here in Wrocław, which have "*A pincer motif etched into a meta-benziporphyrin frame*".¹

Figure 1 shows a timeline with some of my favorites.²

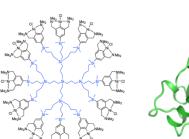
"My" Molecules, from small to large

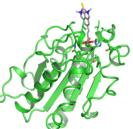




1972, R_4Cu_4

1986, NCN-PtBr(η¹-SO₂)





1994, CS-(NCN-NiX)₁₂ 2005, Cutinase-NCN-PtX

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CHEMISTRY OF HONEY

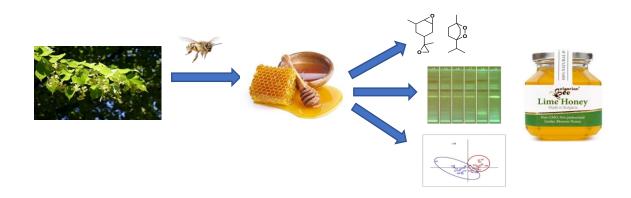
Izabela Jasicka-Misiak & Paweł Kafarski

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The honeybee is a highly sophisticated insect that has evolved over millions of years. The earliest recorded bee was found encased in amber and has been dated as 100 million years old [1]. Today bees live all over the world and there are approximately 20,000 species with honeybee being just one of these. Scientists believe that bees are responsible for the rich flower diversity we enjoy today. Most flowering plants cannot self-pollinate and pollination that relies on the wind or on pollinators.

Honey is one of the finest naturally made products that nature has to offer. Although its production is expanding and honey is becoming more widely available, the actual product that goes out to consumers tends to lose its authenticity after being processed and commercialized. Unfortunately, there are also more and more cases of honey adulteration and therefore, it is necessary to seek new methods that could be used in testing their quality, and botanical and geographical source.

The studies on such a characterization of honeys are directed towards: (i) search for specific compounds (markers) representing certain type of honey: (ii) building chemical profiles (also called fingerprints) for some classes of compounds (mostly phenolics and flavonoids) present in specific brands of honey and (iii) metabolomic studies. All the three research directions were carried out in our laboratory and proved their usefulness in authenticating different types of honey.



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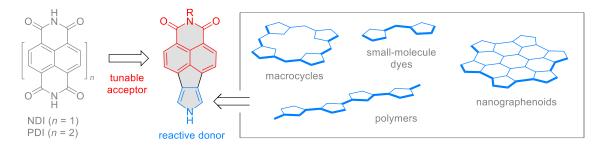
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DONOR-ACCEPTOR OLIGOPYRROLES: FROM MODULAR DYES TO SUPRAMOLECULAR SYSTEMS

Marcin Stępień

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Systematic tuning of optical bandgaps in organic molecules can be achieved by homologation (oligomerization) of linear π -conjugated motifs, by ring expansion of π -conjugated macrocycles, and by extension of fused ring systems in two dimensions. A complementary approach relies on combining donor and acceptor (D–A) moieties, with diverse recent applications in small-molecule and polymer chemistry. The D–A paradigm is particularly suitable for the development of tunable building blocks, which can be constructed by judicious merging of existing electron-deficient and electron-rich motifs. A simple and potentially productive design of such a hybrid structure is achieved by combining naphthalenemonoimide (NMI, red) and pyrrole (blue), as shown below.^[1,2] We will discuss the application of these and similar pyrroles as building blocks for the synthesis of diverse polycyclic aromatics, including macrocycles,^[2,3] heteroatom-doped nanocarbons,^[4–7] and small-molecule dyes,^[8,9] some of which are characterized by persistent helicene-like chirality. These systems reveal rich redox chemistry, spanning multiple oxidation levels, tunable optical signatures extending into the near infrared, and an ability to form complex supramolecular assemblies.



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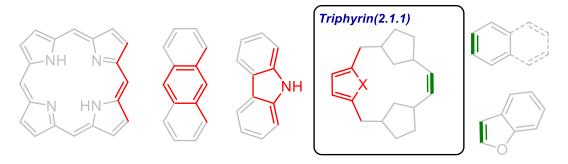
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CONJUGATION IN MACROCYLE BASED π -EXTENDED SYSTEMS

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Macrocyclic structures linking in one structural motif unsaturated carbo- or heterocyclic subunits remain important skeletons used for the fundamental studies broadening the understanding of the properties derived from efficiently delocalized π -cloud. Depending on the type of construction of novel skeletons the mutual interlacing of delocalisation paths – *global* and *local* – available in the complex structure substantially influence the final behaviour stabilizing currents characteristic for each subunit but also making possible observation of conjugation covering the whole molecule. Precisely planned structures create a set of factors leading to control of the delocalisation that can be modulated with different activators including the redox based modification of character from diatropic to paratropic, but also for switching on the global diatropic current in more complex structures.





Hybrid structures linking in one skeleton acene(s) or heteroacenes modulated by a presence of a specific macrocycle i.e. triphyrin(2.1.1) (Figure 1) show a potential for switching between diatropic and paratropic currents after redox activation.^[1,2,3] It results in, depending on the complexity of final molecule, observation of local effects of conjugation efficiently influencing properties of each subunit.^[2] A specific construction opens a possibility for observation of the reactivity characteristic for isolated unsaturated units^[4] in addition creating an opportunity for switching on the global diatropic currents.^[5] All those effects will be presented and discussed with a support of spectroscopic analysis performed for each structural motif.

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DEVELOPMENT OF ARTIFICIAL TRANSPORTERS FOR BIOLOGICALLY ACTIVE ANIONS

Michał J. Chmielewski

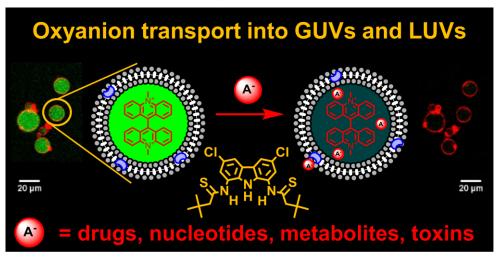
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Selective transport of various anions through biological membranes is fundamental to life. In particular, anion transport plays vital roles in pH and osmotic pressure regulation, intercellular communication, and cellular respiration. The latter process is particularly noteworthy because it involves facilitated transport of various oxyanions: carboxylates, phosphates, and bicarbonate.

Recently, the development of synthetic molecules that mimic the function of natural anion transporters has attracted significant attention. Many of these compounds have already been shown to display interesting biological activity, such as anticancer and antibiotic properties.

Thus far, however, research efforts in this area have mostly been focused on chloride transporters, despite the physiological importance of many oxyanions and the potentially detrimental effects of unselective anion transport on delicate ion homeostasis in cells.

In this contribution, we describe the development of small molecule artificial transporters for various biologically relevant oxyanions, such as drugs, metabolites, amino acids, and organic phosphates. We describe also new assays, which allow easy quantification of anion transport kinetics of a wide range of oxyanions using large unilamellar vesicles (LUVs) and giant unilamellar vesicles (GUVs) as models. Finally, we describe also the discovery of pH-switchable transporters and their potential applications in cancer therapy and drug delivery.



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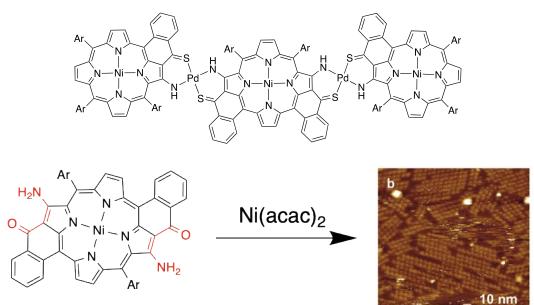
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COORDINATION-DRIVEN CONSTRUCTION OF OLIGOPORPHYRINS

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Peripheral functionalization of porphyrins represents an easy way to access extended porphyrins which bear hetero-atoms susceptible to be used as external coordination sites.^[1] Building dimers or oligomers containing porphyrinoids linked by metal ions is now a well-established field of research.^[2] Synthetic strategies leading to several different oligoporphyrins will be detailed.^[3] In addition, the coordination-driven assembly at a liquid-solid interface (HOPG = Highly Oriented Pyrolitic Graphite) of linear oligoporphyrins linked by metal ions will be presented.^[4]



In a phenyloctane solution, at the HOPG interface

Example of a triporphyrin prepared in solution (top) and coordination-driven assembly of oligoporphyrins at the HOPG/liquid interface and the resulting STM image (bottom).

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SURPRISING MANIFESTATIONS OF WEAK ISOTROPIC EXCHANGE INTERACTIONS IN HIGH-FIELD EPR

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The isotropic exchange in bi- or polynuclear transition metal systems give rise to a series of eigenstates of the coupled spin-squared operator \$2, where \$ is the sum of the spin operators of the metal ions. The isotropic exchange manifests itself typically in the magnetic susceptibility of a coupled transition metal system. Sometimes, spectra coming from several coupled spin states can be observed in EPR and the isotropic exchange determines the relative intensities of these spectra, while there is no effect of the exchange magnitude on the resonance fields. The above is valid when the exchange interactions are strong enough. The positions of the EPR features may become dependent on the isotropic exchange when it is so small that the microwave quantum energy can cause transitions between various S states. This is more likely to occur in HF EPR than in X or Q Bands, owing to high frequencies used. Transitions between different S states are nominally forbidden, but zero-field splitting on interacting moieties mixes different S states and relaxes the selection rules. This offers an interesting possibility of studying exchange interactions which are too weak to affect the bulk magnetic properties. Recently, such effects were observed.¹ An example of interacting copper(II) dimers (Fig. 1) will be discussed.

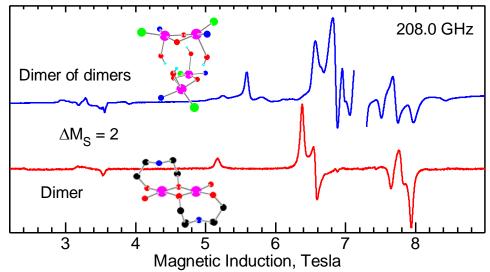


Figure 1. HF EPR spectra of a dimeric and of a tetranuclear Cu²⁺ complex.

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FROM SUPRAMOLECULAR CHEMISTRY TOWARDS ADAPTIVE CHEMISTRY INORGANIC ASPECTS

Jean-Marie Lehn

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Supramolecular chemistry aims at generating highly complex chemical systems from molecular components held together by non-covalent intermolecular forces, on the basis of the *molecular information* stored in the covalent framework of the components. A step beyond consists in the design of systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional architectures by self-assembly from their components.

Supramolecular chemistry is intrinsically a *dynamic chemistry* due to the lability of the interactions connecting the molecular components of a supramolecular entity. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibly. These features allow for a continuous change in constitution by reorganization and exchange of building blocks and define a *Constitutional Dynamic Chemistry* (CDC) on both levels. CDC takes advantage of dynamic diversity to allow variation and selection and operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

CDC generates networks of dynamically interconverting constituents, *constitutional dynamic networks*, presenting *agonistic* and *antagonistic* relationships between their constituents that may respond to perturbations by physical stimuli or to chemical effectors.

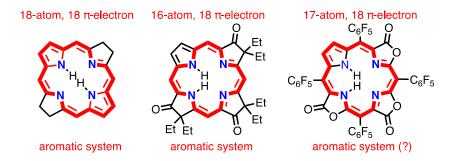
The implementation of these concepts points to the emergence of an *adaptive chemistry*. Inorganic aspects of these various features will be discussed in the context of *metallosupramolecular chemistry*.

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THE UNEXPECTED AROMATICITY OF TRIOXOPYRROCORPHINS AND PYRROCORPHINTRILACTONES

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All four isomers of the octaethyltrioxopyrrocorphins – two isomers prepared along known pathways,¹ two new isomers prepared by targeted synthesis, unexpectedly show macrocycle-aromatic properties, even though they might be expected to contain the macrocyclic π -system of the non-aromatic pyrrocorphins (hexahydroporphyrins).² Instead, all regioisomers possess broadly varying degrees of diatropicity that were experimentally determined using ¹H NMR spectroscopy and computationally verified. Bond length patterns in their crystal structures allow further conclusions to be made about the resonance structures present. Remarkably, the halochromic properties of the triketones differ also sharply from the 18-membered, 18 π -electron aromatic ring-current of regular (hydro)porphyrins,³ providing further support for the proposed 16-membered, 18 π -electron aromatic ring-current.

Three-fold OsO₄-mediated dihydroxylation of *meso*-tetrakis(pentafluorophenyl)porphyrin generated a single stereoisomer of a robust and non-macrocyle-aromatic hexahydroxypyrrocorphin. A single-step oxidative conversion of the hexahydroxypyrrocorphin generated three out of the four possible pyrrocorphinotrilactone regioisomers.⁴ We structurally, spectroscopically, and computationally characterized the trilactone isomers. Their UV-vis spectra and ring diatropicity, as measured by ¹H NMR spectroscopy and supported by DFT calculations, proves them also to be aromatic. Bond length analyses of their solid-state structures are less clear-cut, but we find indications for the presence of an unusual outer-inner-inner 17-membered, 18 π -electronic Hückel-aromatic system.

The work expands on the electronic structure of pyrrole-modified porphyrin analogues and highlights to which degree β -oxo-moieties can redirect porphyrinic aromatic ring currents.

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LLG – A MAN OF SCIENCE

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The short biography of the Jubilee, known to his friends and co-workers under the initials LLG, will be presented, with the focus of **periods** of his life, and research **groups** he worked in.



Author index

Harry L. Anderson, SYNTHESIS & ELECTRONIC DELOCALIZATION IN π-CONJUGATED MACROCYCLES: DOES AROMATICITY HAVE A SIZE LIMIT?
Prof. Dr. Martin Bröring, ISOPORPHYRINS AND THE TOP OF THE PYR(ROLE)AMID: NEWS FROM THE ADLER-LONGO REACTION
Biju Basumatary, Masatoshi Ishida and Hiroyuki Furuta, CRAIG-TYPE MÖBIOUS METALLA(ANTI)AROMATICITY IN PLATINUM(II) AND PALLADIUM(II) DICARBAPORPHYRINOIDS
Jacek Waluk, EXPECT THE UNEXPECTED!
Daniel T. Gryko, NEW ERA IN THE CHEMISTRY OF DIKETOPYRROLOPYRROLES8
Artur Stefankiewicz, SUPRAMOLECULAR ASSEMBLIES – FROM MOLECULAR COMPONENTS TO FUNCTIONAL NANOSTRUCTURES
Dorota Gryko BIOINSPIRED CATALYSIS FOR SUSTAINABLE LIGHT-INDUCED PROCESSES10
Mathias O. Senge, <i>RE-ENGINEERING THE PIGMENTS OF LIFE – FREE BASE PORPHYRINS AS ORGANOCATALYSTS AND</i> SENSORS
Dongho Kim, EXCITED-STATE AROMATICITY IN EXPANDED PORPHYRINOIDS: ELECTRONIC STRUCTURES AND CONFORMATIONS UPON AROMATICITY REVERSAL
Jonathan L. Sessler, TEXAS-INSPIRED DRUG DISCOVERY EFFORTS14
Alan L. Balch, <i>PORPHYRINS AND FULLERENES</i> 15
Zeev Gross and Atif Mahammed, THE JOURNEY TOWARDS LESS SUBSTITUTED CORROLES AND SAPPHYRINS
Norbert Jux, PORPHYRIN-NANOGRAPHENE HYBRIDS17
Franz-Peter Montforts, PIGMENTS OF LIFE – A FASCINATING CHAPTER OF TETRAPYRROLE CHEMISTRY
Grażyna Stochel, Synthetic Bacteriochlorins – Opportunities for Photodynamic Activities
Gerard van Koten, ON COMMON DENOMINATORS: ABOUT RIGIDITY, FLEXIBILITY AND SURPRISES
Izabela Jasicka-Misiak and Paweł Kafarski CHEMISTRY OF HONEY21
Marcin Stępień, DONOR–ACCEPTOR OLIGOPYRROLES: FROM MODULAR DYES TO SUPRAMOLECULAR SYSTEMS 22
Miłosz Pawlicki, CONJUGATION IN MACROCYLE BASED П-EXTENDED SYSTEMS23

Michał J. Chmielewski, DEVELOPMENT OF ARTIFICIAL TRANSPORTERS FOR BIOLOGICALLY ACTIVE ANIONS24
Romain Ruppert, COORDINATION-DRIVEN CONSTRUCTION OF OLIGOPORPHYRINS25
Andrzej Ożarowski, SURPRISING MANIFESTATIONS OF WEAK ISOTROPIC EXCHANGE INTERACTIONS IN HIGH-FIELD EPR
Jean-Marie Lehn FROM SUPRAMOLECULAR CHEMISTRY TOWARDS ADAPTIVE CHEMISTRY. INORGANIC ASPECTS 27
Christian Brückner, ^{*,a} Matthew J. Guberman-Pfeffer, ^a José Gascon, ^a Nevidita Chaudhury, ^a Nisansala Hewage, ^a Matthias Zeller ^b <i>THE UNEXPECTED AROMATICITY OF TRIOXOPYRROCORPHINS AND PYRROCORPHINTRILACTONES</i> .28
Jacek Wojaczyński, LLG – A MAN OF SCIENCE

