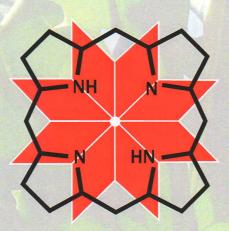
MINISTRY OF EDUCATION OF THE REPUBLIC OF BELARUS Educational Institution "BELARUSIAN STATE TECHNOLOGICAL UNIVERSITY"



INTERNATIONAL WORKSHOP ON PHOTOCHEMISTRY OF ORGANIC MOLECULES DEDICATED TO THE 85th ANNIVERSARY OF ACADEMICIAN G. P. GURINOVICH



PROGRAM AND BOOK OF ABSTRACTS

September 18–20, 2018 Minsk MINISTRY OF EDUCATION OF THE REPUBLIC OF BELARUS Educational Institution "BELARUSIAN STATE TECHNOLOGICAL UNIVERSITY"



International Workshop on Photochemistry of Organic Molecules

dedicated to the 85-th anniversary of academician G.P. Gurinovich

September 18-20, 2018

Program and Book of Abstracts

Minsk



September 18-20, 2018 Minsk, BELARUS

International Workshop on Photochemistry of Organic Molecules dedicated to the 85-th anniversary of academician G.P. Gurinovich: Program and Book of Abstracts. – Minsk: BSTU, 2018. – 54 p. – ISBN 978-985-530-699-4.

This issue consists of the Program and Abstracts of the lectures of the International Workshop on Photochemistry of Organic Molecules dedicated to the 85-th anniversary of academician G.P. Gurinovich, one of the founders of Belarusian School on the spectroscopy and photochemistry of tetrapyrrolic compounds. The lectures span a wide range of fundamental and applied problems where the tetrapyrrolic compounds involved.

This issue will be useful to scientists working in the field of biologically relevant compounds, biotechnology, spectroscopy and photophysics of organic compounds and their metallocomplexes, as well as for the graduate and Ph.D. students of corresponding fields of science.

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The Molecules of Life

Tetrapyrrolic compounds are ubiquitous pigments of Life, and the importance of the studies of their properties and functions cannot be overestimated. Photosynthesis, water reduction, oxygen transport and storage are the main roles they play in nature. Once can say, that without these molecules the Life in existing form would not be possible. All the energy processes that make Life on Earth possible at the fundamental molecular level are based mainly on the tetrapyrrolic compounds.

The subject of porphyrins embraces many scientific disciplines and due to this multidisciplinary significance tetrapyrrolic compounds have a high potential for using in the numerous modern technologies. On the base of these molecules highly sensitive nanosize molecular sensors are developed, they can be used for the noninvasive real-time monitoring, including the screening of air and water pollution. Tetrapyrrolic compounds and their metallocomplexes serve as efficient catalysts in numerous chemical reactions for laboratory and industrial use. These compounds are well known photosensitizers of singlet molecular oxygen and this feature gives rise to the application of these compounds in medicine. The pharmaceutical compositions based on the tetrapyrrolic sensitizers are approved for the clinical use in many countries for the cancer and age macular degeneration treatment with photodynamic therapy. The impressive results are obtained in design of dye sensitized solar cells with porphyrins as dye molecules.

In Belarus the problems related to the tetrapyrrolic compounds are studied in numerous Institutions of the National Academy of Sciences and Universities. The scientific school in the spectroscopy and photochemistry of tetrapyrrolic compounds founded by academician G.P. Gurinovich and member-correspondent K.N. Solovyov in the middle of sixties of the last century has a lot of achievements and is well-known over the world. The fruitful ideas put in by the founders allow keeping the scientific traditions over the generations and maintaining the high level of the research. Organizing this International Workshop on Photochemistry of Organic Molecules dedicated to the 85-th anniversary of academician G.P. Gurinovich is our bow to the huge efforts he made for the development of this scientific field. We hope that the sharing of the new scientific results and fruitful discussions during this Workshop will be useful for all the participants.

Rector of Belarusian State Technological University

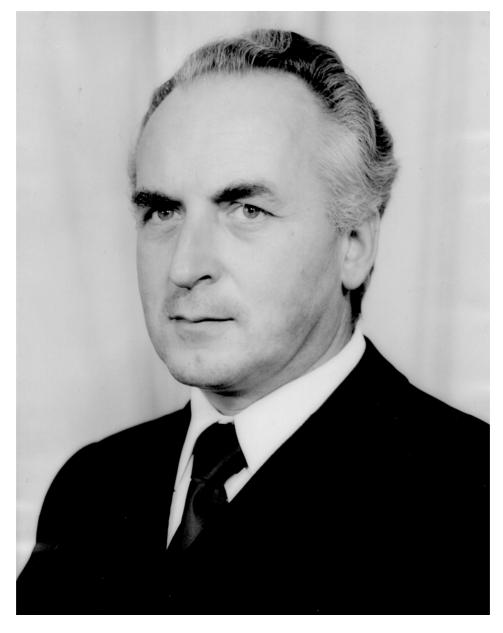
Igor V. Voitau

Head of the Physics Dept. of Belarusian State Technological University

Mikalai M. Kruk



September 18-20, 2018 Minsk, BELARUS



Academician Georgii Pavlovich GURINOVICH

(1933-1994)



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G.P. Gurinovich was born April 26, 1933 in Borisov, Minsk region. His very fruitful career in science has begun under the supervision of academician A.N. Sevchenko at the time of being a student of Belarusian State University. In 1956 Gurinovich G.P. graduated with honors from the Physics Department of Physics and Mathematics Faculty and on the recommendation of the department of physical optics he was accepted as a Ph. D student to the Institute of Physics, Academy of Sciences BSSR the same year. After finishing his Ph.D. studies he started to work at the Institute of Physics where he successfully defended his thesis for the degree of candidate of sciences (Ph.D.) in physical and mathematical sciences in 1960, and was soon elected to the position of senior researcher.

Dynamic and successful work of the Gurinovich C.P. led to his appointment as the head of the research group which has been reorganized into the Laboratory of Photochemistry in 1965, which he directed until his death. Since 1992, this laboratory was named as the Laboratory of Photonics of Molecules.

In 1968, Gurinovich G.P. defended his Doctoral thesis (Habilitation) "Spectroscopy and photochemistry of porphyrins" for the degree of Doctor of Physical and Mathematical Sciences. In the same year he published a monograph "The spectroscopy of chlorophyll and related compounds", written in collaboration with A.N. Sevchenko and K.N. Solovyov. This monograph has become for many years a handbook for professionals of different profiles involved in the study of tetrapyrrolic compounds, and was almost immediately translated into English in USA. This year there are 50 years from the publication of this seminal book.

Gurinovich G.P. was awarded the title of Professor in 1970. In the same year he was elected a Corresponding member of the Academy of Sciences of the Belorussian SSR. On February 25, 1994, the day before his untimely death, George Pavlovich Gurinovich has been elected a full member of the Academy of Sciences of Belarus by General meeting of the Academy of Sciences of Belarus.

The main scientific direction, which began to develop by Gurinovich G.P. was related to the luminescence and photochemistry of chlorophyll and related tetrapyrrolic compounds. In 1980, Gurinovich G.P. and Solovyov K. N. were awarded the State Prize of the BSSR in the field of science and technology for the work "Photonics of biologically important pigments and their analogues". Fruitful cooperation of G.P. Gurinovich and K.N. Solovyov continued for many years. The world scientific community recognized that these two scientists put the founding stone to the Belarusian school of spectroscopy and photochemistry of macroheterocyclic tetrapyrrolic compounds.

Lot of efforts G.P. Gurinovich put into the studies of singlet molecular oxygen sensitization by triplet state populated photosensitizers and applications of this phenomenon in the medicine for photodynamic therapy of cancer.

Academician Gurinovich G.P. supervised 6 doctors and 25 candidates of sciences, which continue the research on the tetrapyrrolic compounds in Belarus, Tajikistan, Poland, Germany, Syria, Lebanon, USA.



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Workshop Program



September 18-20, 2018 Minsk, BELARUS

Tuesday, September 18

8.30-9.15	Registration of Participants			
9.15-9.40	Opening Ceremony			
Session 1. Chairmans: Mikalai Kruk, Wim Dehaen				
9.40-10.00	Eduard Zenkevich Minsk, Belarus	Electronic Energy Relaxation Processes in Chlorophyll and its Analogs: From Concentrated Solutions to Structurally- Organized Nanoassemblies		
10.00-10.20	Alexander Krasnovsky Moscow, Russia	Absorption and photoreceptor properties of dissolved oxygen molecules under natural conditions. Review of currently available results		
10.20-10.40	Vladimir Zorin Minsk, Belarus	Evaluation of photodynamic activity and physico-chemical determinants of sensibilization of transformed tissues and cells by chlorine type photosensitizers: molecular and cellular aspects		
10.40-11.10	Coffee Break			
11.10-11.30	Jacek Waluk Warsaw, Poland	Tautomerism in Porphyrin Isomers		
11.30-11.50	Wouter Maes Hasselt, Belgium	Porphyrinoid Materials for Organic Electronics and Advanced Healthcare		
11.50-12.10	Pavel Stuzhin Ivanovo, Russia	Spectral-Luminescent and Photochemical Properties of Subporphyrazines with Fused Electron-Deficient Heterocycles		
12.10-14.00	Lunch			
14.00-19.30	Excursions			



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Wednesday, September 19

9.00-9.20	Organizing Committee Announcements			
Session 2. Chairmans: Alexander Krasnovky, Jacek Waluk				
9.20-9.40	Wim Dehaen Leuven, Belgium	Fluorescing BOPHY, BODIPY and Triazapentalene Derivatives		
9.40-10.00	Danuta Gryko Warsaw, Poland	Light Induced Reactions Catalyzed by Porphyrinoids		
10.00-10.20	Alexey Lyubimtsev Ivanovo, Russia	Synthetic aspects of preparation of hydrogenated porphyrins		
10.20-10.40	Martin Presselt Jena, Germany	Supramolecular structures of amphiphilic dyes for photochemical and photophysical applications		
10.40-11.10	Coffee Break			
11.10-11.30	Jacek Dobkowski Warsaw, Poland	Excited state energy degradation paths in the case of porphycene and dibenzo-porphycene isolated in low temperature matrices		
11.30-11.50	Lev Gladkov Minsk, Belarus	DFT Calculations of IR Spectra of Phthalocyanine, Zn-Phthalocyanine and its Deuterated Derivatives		
11.50-12.10	Valery Kuzmitsky Minsk, Belarus	The Use of the DFT PBE/TZVP and INDO/SM Quantum Chemical Methods in the Calculations of Molecules of Porphyrazine and Phthalocyanines		
12.10-14.00		Lunch		



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Wednesday, September 19

Session 3. Chairmans: Eduard Zenkevich, Wouter Maes				
14.00-14.20	Mikalai Kruk Minsk, Belarus	On the Shift of Equilibrium Between the Free Base Corroles and Their Deprotonated Forms in Solution		
14.20-14.40	Piotr Fita Warsaw, Poland	Optical Spectroscopy Revealing Unusual Cis- diprotonated Metallophthalocyanines		
14.40-15.00	Sergey Syrbu Ivanovo, Russia	Photophysical Properties and Photodynamic Activity of Zinc Diazaporphyrinate		
15.00-15.20	Beatrice Berionni Berna Rome, Italy	Joining Corroles and Phthalocyanines in Functional Porphyrinoid Arrays		
15.20-15.50	Coffee Break			
15.50-16.10	Lizaveta Liulkovich Minsk, Belarus	Spectral Signature of the Equilibrium Distribution of the Free Base 5,10,15,20- tetrakis-(3- <i>N</i> -methylpyridyl)-porphyrin Atropisomers in Solution		
16.10-16.30	Dmitry Klenitsky Minsk, Belarus	Substitution Architecture Control of the Macrocycle Nonplanarity in the Free Base Corroles		
16.30-16.50	Tatiana Karlovich Minsk, Belarus	Temperature Control of the NH- tautomerization Rate and Photophysical Properties of Free Base Corroles		
17.00-18.00	Visiting Museum and Exposition Hall of Belarusian State Technological University			
18.30-22.00	Workshop Dinner/Closing Ceremony			



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Thursday, September 20

9.00-12.10	Transfer to Minsk National Airport/Minsk Sightseeing Tour	
12.10-14.00	Lunch	
14.00-19.00	Minsk Sightseeing Tour/Free Time	
19.00-21.00	Visiting Theaters (optional)	



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Workshop Lectures Abstracts



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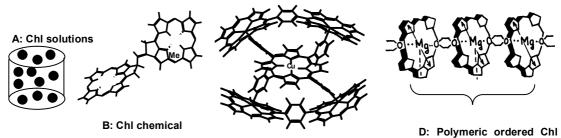
Electronic Energy Relaxation Processes in Chlorophyll and its Analogs: From Concentrated Solutions to Structurally-Organized Nanoassemblies

E. Zenkevich

National Technical University of Belarus Prospect Nezavisimosti 65, 220013 Minsk, Belarus e-mail: zenkev@tut.by

The seminal importance of chlorophylls as Nature's chief light absorbers has elicited vast studies encompassing biology, chemistry, and physics. Chlorophylls along with heme and bacteriochlorophylls are the most abundant members of the so-called "pigments of life", which constitute a subset of the large class of tetrapyrrole macrocycles. The investigations of the primary light-harvesting reactions in natural photosynthetic systems have improved appreciably our understanding of the mechanisms involved in the transfer and trapping of solar energy. Nevetheless, up to now the interpretation of the spectral-kinetic parameters of *in vivo* photosynthetic light-harvesting systems and reaction centers is met with considerable difficulties due to the combined effects of the pigment–pigment and pigment–protein interactions taking place in natural objects. In this respect, the formation of artificial complexes containing chlorophyll and other tetrapyrrolic compounds followed by comprehensive analysis of mechanisms of photoinduced relaxation processes seems to be considered as a necessary and important step in order to understand detailed pathways and specificity of natural photoprocesses taking place in living systems.

This review talk presents main results being obtained by Byelorussian scientific school of academician G.P. Gurinovich and his followers devoted to the study of spectral-kinetic properties and photonics of pigment-pigment interactions for chlorophyll and its immediate analogs *in vitro* (from highly concentrated solutions to structurally-organized heterogeneous nanoassemblies of various morphology, see Figure below). The combination of modern experimental spectroscopic approaches has been used in this study in a temperature range of $4.2 \div 300$ K: steady-state and time-resolved (ns-ps-fs) spectroscopy, optical activity and polarization measurements, fluorescence line narrowing and spectral hole burning, etc. The adequacy was validated for various theoretical models describing the primary processes of photosynthesis (the electronic excitation energy transfer and the photoinduced charge transport) at small interchromophore distances subject to surrounding properties the conformational dynamics of interacting subunits.



C: self-assembled multiporphyrin complexes

Application-oriented aspects were considered concerning the use of multicomponent nanostructures based on photostable tetrapyrrolic compounds with controllable electron-transport properties and conformation mobility for the development of elemental base in molecular electronics, photonics, medicine and nanobiotechnology. Here, we review possible strategies for designing nanoscale light-harvesting systems based on tetrapyrrolic pigments and nanoassemblies on their basis. In fact, understanding the evolutionary constraints imposed on bioenergetic systems is not only an intellectual pursuit but may be a key to unlock our energy future.



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Absorption and photoreceptor properties of dissolved oxygen molecules under natural conditions. Review of currently available results A.A. Krasnovsky, A.S. Benditkis, A.S. Kozlov

Federal Center of Biotechnology, Russian Academy of Science, 117071, Moscow, Russian Federation, phoal@mail.ru

It is known that molecular oxygen has the triplet ground state and two relatively low-lying singlet states, whose zero and higher vibrational sublevels can be populated upon oxygen excitation. However, triplet-singlet transitions in oxygen molecules are highly forbidden. Therefore, corresponding absorption bands are extremely weak. As a result, until recent time, nothing was known about the absorption properties of oxygen dissolved in natural systems under ambient conditions. Apparently, this information is of basic importance for oxygen photonics and understanding the state and function of oxygen molecules in chemical and biological systems. Interest to this problem is also stimulated by the suggestion that oxygen molecules might serve as photoreceptors causing biological and therapeutic action of laser and LED radiation. A decade ago our group started a project, which allowed us to strongly approach the solution of the above problems. We have shown that formation of singlet oxygen can be reliably detected upon direct laser excitation of oxygen in air-saturated solutions using oxygenation of singlet oxygen traps [1]. From kinetic analysis of oxygenation rates accurate absorption coefficients were obtained for oxygen absorption maxima at 765, 1070 and 1270 nm in several common organic solvents and water. Recently, we extended our photochemical studies to oxygen excitation in red and dark red regions and compared the results with those obtained from detection of singlet oxygen phosphorescence upon direct oxygen excitation by laser radiation (see refs. in paper [9]). The present paper is aimed to summarize and discuss all currently available results of our group. Major experimental papers of our group are indicated in the reference list.

ACKNOWLEDGMENTS

This work was supported the Russian Foundation for Basic Research (project No 15-04-05500) and the program "Basic science for medicine" of the Russian Academy of Science.

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Spectral-Luminescent and Photochemical Properties of Subporphyrazines with Fused Electron-Deficient Heterocycles <u>Pavel Stuzhin</u>,^a Mahmoud Khandoush, Ivan Skvortsov, Yuriy Zhabanov^a Veronika Novakova,^b Pavel Kubat,^c Nikolai Somov^d

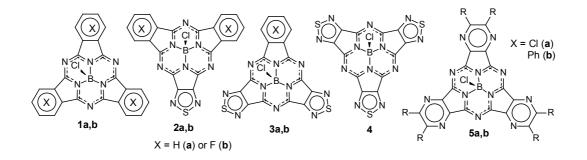
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Peculiarities of spectral luminescence and photochemical properties of boron(III) subphthalocyanines (1) and their heterocyclic analogues – subporphyrazines containing annulated electron-deficient 1,2,5-thiadiazole fragment (2, 3, 4) or pyrazine rings (5) - are considered.



Influence of heterocyclic annulation on the electronic and geometrical structure is also discussed.

ACKNOWLEDGMENTS

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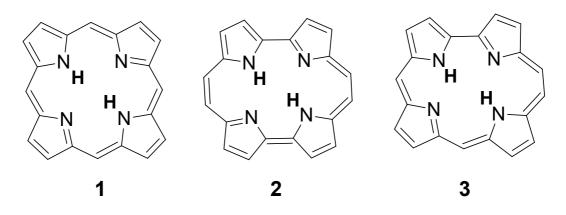
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Tautomerism in Porphyrin Isomers

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Our interests revolve around proton/hydrogen transfer processes, in both the ground and excited electronic states. Porphyrin (1) and its isomers: porphycene $(2)^1$ and hemiporphycene $(3)^2$ are used as models for studying intramolecular double hydrogen migration in a system with well-defined hydrogen bond geometry. I will present the results of investigations of 2 and 3 carried out in different experimental regimes, including (i) cold molecules isolated in supersonic beams;³ (ii) molecular ensembles in condensed phases;^{3,4} (iii) single molecules located in polymer matrices, plasmonic systems or on metal surfaces.^{3,5} These studies lead to a complex picture of a multidimensional reaction path, with the dominant role of hydrogen tunnelling and the influence of several vibrational modes that can either promote or hinder the tautomerization.



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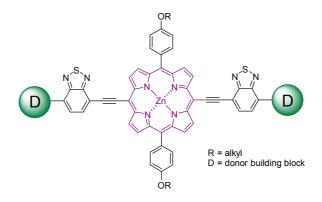


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Porphyrinoid Materials for Organic Electronics and Advanced Healthcare Mathias Kelchtermans, Sam Gielen, Jasper Deckers, Wouter Maes

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As Nature itself has developed porphyrin chromophores for solar light to energy conversion, it seems reasonable to pursue artificial systems based on the same types of molecules. In recent years, there have been substantial efforts to employ porphyrinoid materials in different types of organic solar cells and photodetectors, with reasonable success. On the other hand, porphyrins and their analogues are also well-established photosensitizers for photodynamic therapy. In the present contribution, different efforts from our group in these directions will be presented. A number of advanced push-pull type (low optical gap) porphyrinoid materials have been synthesized and analyzed in bulk heterojunction organic photovoltaics and (near-infrared) organic photodetectors. The same materials and smaller BODIPY derivatives are also explored for theranostic applications





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Evaluation of photodynamic activity and physico-chemical determinants of sensibilization of transformed tissues and cells by chlorine type photosensitizers: molecular and cellular aspects

<u>V.P. Zorin</u>^a, T.E. Zorina^a, I.E. Kravchenko^a, I.I. Khludeyev^a, T.V. Shman^b, M.V. Belevtsev^b

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Photodynamic therapy (PDT) efficacy strongly depends on the selectivity of photosensitizer (PS) accumulation and distribution in cellular and tissue targets, thus the search for new photosensitizers with optimal photophysical and pharmacokinetic characteristics is considered to be the main direction of PDT development. PS used in PDT accumulate in tumor tissue, although the fundamental mechanisms are less clear. Theoretically, once a molecule used for cancer detection or treatment is injected into blood stream, it encounters the following "resistance" before reaching the intracellular space: distribution through vascular space, transport across microvascular wall, transport through interstitial space, transport across cell membrane. Each of these stages involved into the control of sensitizer location and retention in tumor represents a complex process which depends on numerous parameters.

We have focused our researcher on understanding the physico-chemical parameters governing the distribution of porphyrin sensitizers among protein, cells and tissues structures. This work includes three lines of studies:

1. The kinetics of pigment transfer from protein carrier or biological membranes was analyzed by spectroscopic techniques;

2. The kinetics of porphyrin accumulation and redistribution between blood cells was studied by flow cytometry and fluorescent microscopy;

3. The kinetics of porphyrin accumulation and release from tissue was estimated ex vivo with several fluorescent techniques.

All measurements were carried out with chlorin-type photosensitizers (chlorin e6, monomethyl ester of chlorin e6, dimethyl ester of chlorin e6, trimethyl ester of chlorin e6 and temoporphin).

The results obtained show that the dynamics of the distribution of the studied pigments differs significantly and may be of certain value when the pharmacokinetic behavior of porphyrin sensitizer is analyzed. High capacity of porphyrin binding to blood cells may change the kinetics of pigment uptake by different tissues due to decreasing of pigment activity in plasma. In addition, the parameters of plasma/blood cells partitioning may be translated into blood/vessels endothelium distribution of sensitizer. Therefore, our finding may be helpful in defining the optimal therapeutic protocol for PDT application for malignant and vasculature diseases.

The studied compounds, like most second-generation photosensitizers are insoluble in water, thus requiring special drug formulations for their injection. The developed experimental approaches have been used to compare the rates of chlorins release from lipid vesicles in model systems and in vivo. According to the data obtained characteristic values of retention time changes in very wide range, from seconds for chlorin e6 to several hours for meta-tetra(hydroxyphenyl)chlorin. Our recent results show that the recovery kinetics may play significant role in the application of photosensitizer liposomal formulations and make possible to control of sensitizer biodistribution. Pharmacokinetic and fluorescent microscopy studies of photosensitizers distribution in several in vivo and in vitro models confirm this conclusion.



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Fluorescing BOPHY, BODIPY and Triazapentalene Derivatives

Bram Verbelen, Stijn Boodts, Tomas Opsomer, Yingchun Wang, Wim Dehaen

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The laboratory of organic synthesis in Leuven is interested in new synthetic methodologies leading to novel dye molecules. We will present our newest results on a variety of fluorescing dyes.

Firstly, we will present our results on the substitution of BODIPY dyes by radical addition, and the properties of some of the substituted derivatives will be disclosed.[1]

Secondly, we will report the use of dichloroBOPHY dyes to extend the variety of this novel class of dye molecules, including fused derivatives.[2]

Thirdly, we will include an application of our new triazolization method towards the synthesis of fluorescing aryltriazapentalene dyes. [3] To end, some other applications of the triazoles will also be reported, including applications in porphyrin chemistry.[4]

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Synthetic aspects of preparation of hydrogenated porphyrins

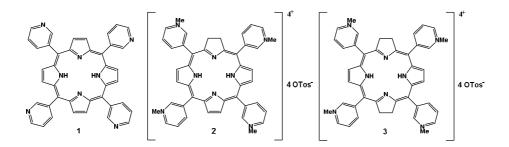
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Tetrapyrric macroheterocycles are representatives of organic compounds that are widely used in medicine and ecology. Existing drugs based on porphyrins and related compounds have proven to be effective photosensitizers in the diagnosis and treatment of cancer. The number of publications in the world scientific journals devoted to the search for even more effective compounds in a number of macroheterocycles is steadily growing.

No less urgent problem is the development of methods to improve the effectiveness of existing drugs, which are based on the design of new supramolecular systems with improved characteristics, compared with individual components. The combination of several compounds in the active component of the drug, each of which has individual characteristics and contributes to an increase in the total effectiveness of the action, also determines the actual direction of research.

In this study, we have conducted a detailed study of experimental aspects of the reduction reaction of 5,10,15,20-tetrakis(pyridine-3-yl)porphine (1) with subsequent quaternization of the obtained hydrogenated derivatives.



For the first time from a mixture of chromatographically isolated and fully characterized 5,10,15,20 tetrakis(pyridine-3-yl)chlorine and 5,10,15,20 tetrakis(pyridine-3-yl)bacteriochlorin, which allowed to obtain on the basis of their respective individual water-soluble derivative 2 and 3. A complex study of the properties of synthesized hydrogenated porphyrins was carried out.

ACKNOWLEDGMENTS

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Optical Spectroscopy Revealing Unusual Cis-diprotonated Metallophthalocyanines

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Photophysical studies of protonation of a series of zinc and magnesium metallophthalocyanines non-peripherally substituted with various alkoxy groups (Fig. 1) revealed unusual behaviour of molecules containing magnesium ions, strongly contrasting with properties of their zinc analogues. Whereas protonation of the studied zinc metallophthalocyanines lead to a bathochromic shift of their absorption and fluorescence spectra and shortening of their fluorescence lifetimes to a degree reflecting the number of attached protons, shifts of the spectra of the magnesium derivatives and changes of their fluorescence lifetimes are a non-monotonic function of the protonation degree: the bathochromic shift of the doubly protonated form is smaller than that of the monoprotonated one (Fig 2). Similarly, the fluorescence lifetime of the doubly protonated magnesium derivative is longer than that of its monoprotonated form. This observation can be explained in terms of the four-orbital Gouterman model by formation of the *cis*-diprotonated form of the doubly protonated molecule (with protons attached to adjacent bridging nitrogen atoms) [1]. Such a protonation pattern is untypical for metallophthalocyanines and observation of a *cis*-diprotonated form has not been reported in the past.



Fig. 1. Structures of studied metallopthalocyanines.

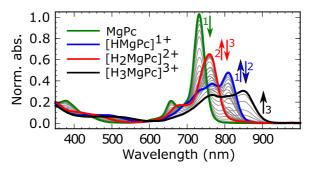


Fig. 2. Changes of absorption spectra of a magnesium metallophthalocyanine nonperipherally substituted with trioxanonyl groups observed during titration with acid.

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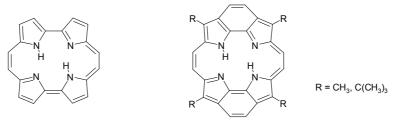
Excited state energy degradation paths in the case of porphycene and dibenzoporphycene isolated in low temperature matrices

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Picosecond time-resolved spectroscopy in emission and absorption was used to study excited state deactivation processes of porphycene and dibenzoporphycene incorporated in solid argon and nitrogen matrices as well as embedded in rigid methyltetrahydrofuran (MTHF).



Porphycene

Dibenzoporphycene

For the matrix-isolated porphycene, excitation into the Soret band, located about 11000 cm⁻¹ above the lowest singlet state, results in major spectral evolution of the time-resolved fluorescence (TRF) as well as transient absorption (TA) spectra on the time scale 100 ps. No such evolution is detected for excitation into the Q band.

In the case of dibenzoporphycene, when the molecule is excited into the Soret band, the relaxation to S_1 is faster than the temporal resolution of the apparatus (2.5 ps). The depopulation of the S_1 occurs in 10-20 ps, leading directly to S_0 .



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Light Induced Reactions Catalyzed by Porphyrinoids

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"Do as nature, work as nature, and produce as nature" (Bao-Lian Su) Photocatalysis has recently emerged as powerful tool for the formation of C-C bonds mainly catalyzed by ruthenium and iridium complexes.[1,2] But, they are both very expensive and undesirable by pharmaceutical industry. On the other hand, organic dyes exhibit considerable advantages and in fact they have been shown to act as photoredox catalysts with eosin Y being the most widely studied.[3]

Our life depends on porphyrinoids - pigments of life. They are responsible for oxygen transport (heam), electron transport (cytochrome c), and photosynthesis (chlorophyll a). Chlorophylls are, in the first instance, responsible for transforming light energy into the chemical reactivity with the ultimate production of starch (photosynthesis). We follow nature and exploit the potential of pigments of life.



This presentation will highlight a successful application of porphyrinoids as catalysts for visible-light induced selective functionalizations. In particular, these compounds are effective in catalyzing C-C bond forming reactions involving the reductive or oxidative quenching. Employing dual catalytic system – photocatalysis merged with enamine-iminium catalysis alkylation of carbonyl compounds at the α position was accomplished.[4,5] Porphyrins with tuned

physicochemical properties, via tailoring various substituents at the periphery of the macrocycle, are also effective in catalyzing light-induced direct arylation of heteroarenes with diazonium salts [6] or deaminative alkynylation [7].

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Supramolecular structures of amphiphilic dyes for photochemical and photophysical applications

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Beyond molecular properties the supramolecular structures essentially determine photonic¹ and electric² material properties. One of the approaches to control the supramolecular structure is by means of interface assembly of dyes that have been made amphiphilic. This assembly is utilized in the Langmuir-Blodgett (LB) technique^{3, 4} as well as in the Liquid-Liquid Interface Precipitate $(LLIP)^2$ technique. In our work we utilize both methods for the fabrication of model layers with tunable supramolecular

MPEGC₆₀ p⁺ a-Si:H intrinsic a-Si:H Ev =4.0 eV CB -4.26 ٩ ح Ag °< ≥ ~5.40 UMO -4.35 =1.60 1111111111 5 20 a Al-ZnO E 9 Щ HOMO VB SC_{220°C} SC_{165°C} LLP 9 8 ပ္ထိ 80

structure for optoelectronic devices and self-healing membranes. This supramolecular structural tuning enables variation of the LUMO energy of fullerene films by 120 meV, that translate to 70 mV variation in open circuit voltage of corresponding pi-Si-hybrid solar cells.²

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b. Band Diagram (without contact)



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Photophysical Properties and Photodynamic Activity of Zinc Diazaporphyrinate

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5,15-Diazaporphyrins (DAP) with β -alkyl substituents are promising macroheterocyclic compounds for creating new materials for sensors, photovoltaic devices, and potential photosensitizers in photodynamic therapy. However, at the moment, their practical application is limited due to the difficult availability and poor knowledge of their properties. In connection with this, a promising task is the synthesis and study of a number of properties of these compounds.

The object of this study is a zinc complex of 3,7,13,17-tetramethyl-2,8,12,18-tetraamyl-5,15-diazaporphyrin (ZnDAP), which was obtained by the [2+2]-condensation of the corresponding dipyrromethenes with sodium azide in pyridine with the addition of lead acetate. The resulting lead complex (PbDAP) is labile, and in chromatographic purification gives the free base diazaporphyrin. Subsequent boiling of DAP with zinc acetate in dichloromethane with a small addition of methanol gives a zinc complex.

ZnDAP is characterized by a narrow Q-band of absorption ($\lambda_Q = 590 \text{ nm}, \Delta v_{1/2} = 287 \text{ cm}^{-1}$, $\epsilon \sim 10^4 \text{ M}^{-1}\text{cm}^{-1}$), wide Soret band ($\lambda_B = 376 \text{ nm}$) and intense fluorescence with $\lambda_{em} = 593 \text{ nm}$ in a neutral medium. The efficiency of generation of singlet oxygen upon irradiation of a solution of ZnDAP in DMF by visible light in the wavelength range 500-800 nm was evaluated by the spectrophotometric method based on measuring the concentration of 1,3-diphenylisobenzofuran (DPBF). Solution of zinc phthalocyanine in DMF ($\Phi_{\Delta} = 0.55$) was used as a standard. The obtained data prove the high efficiency of ZnDAP for photosensitized generation of singlet oxygen.

Aggregation of ZnDAP takes place in water-organic media containing more than 40% of the water. This process is accompanied by a shift and broadening of both bands in the absorption spectrum ($\lambda_B = 352 \text{ nm}$, $\lambda_Q = 592 \text{ nm}$), as well as a decrease in extinction and complete fluorescence quenching. In aqueous solutions of surfactants with a concentration above critical concentration of micelle formation, solubilization of the monomeric form of the chromophore in the surfactant micelles is not observed, which indicates a high stability of the aggregates being formed. When the ZnDAP solution is acidified, diprotonization occurs along the *meso*-nitrogen atoms, which does not affect the central metal atom. This form is distinguished by the bathochromic shift of both bands in the ESP ($\lambda_B = 382 \text{ nm}$, $\lambda_Q = 623 \text{ nm}$) and less intense fluorescence in the 630 nm region compared to the neutral monomeric form of the chromophore.



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DFT Calculations of IR Spectra of Phthalocyanine, Zn-Phthalocyanine and its Deuterated Derivatives

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Normal modes (NM) of free base phthalocyanine (Pc), Pc-d₂, Pc-d₁₆, Pc-d₁₈, ZnPc and Zn Pc-d₁₆, AlPc with Cl have been calculated by the DFT method. The detail interpretation of IR spectra of this compounds has been made. The results of the calculations are in good agreement with the experimental data, although the scaling of the force field was not carried out.

A total 28 in-plane NM of E_u symmetry and 8 out-of-plane NM of A_{2u} symmetry can be active in the IR spectrum of ZnPc, which belongs to point symmetry group D_{4h} .

According to the calculations, the Zn atom was shifted most from the equilibrium position in the out-of-plane NM with frequency 119 cm⁻¹ and the in-plane NM with frequency 238 cm⁻¹. Namely, these frequencies will be sensitive to isotopic substitution of the Zn atom. These NM were assigned to IR bands at 98 and 258 cm⁻¹, the frequencies of which depended more strongly on the nature of the central atom of the Pc complexes [1]. The ZnN bonds also contributed greatly to inplane NM 118 and 298 cm⁻¹ (IR bands 116 and 303 cm⁻¹ [1]). The frequencies of NM 498 and 887 cm⁻¹ involving deformations $C_aN_mC_a$ angles depends on the nature of the central atom also. Stretching C_aN_m bond changing make significant contributions in the NM 1457 and 1480 cm⁻¹. The

IR bands 780 and 955 cm⁻¹ corresponds to out-of-plane CH vibrations. The frequencies of these NM lowered down upon deuteration to 580 and 744 cm⁻¹ respectively. In-plane bending vibrations of CH groups predominantly participate in NM 1007, 1099, 1164 and 1287 cm⁻¹ (IR bands 1003,1089,1166 and 1284 cm⁻¹). NM of ZnPC-d₁₆ of analogues form have frequencies 850, 831, 808 and 999 cm⁻¹.

IR bands of Pc 999, 1089, 1150, 1272 and 1295 cm⁻¹ [1] we assign to δ (CH). According to the calculations, in-plane bending NH vibrations are delocalized and participates in number of NM (728, 820, 1035, 1150, 1219 and 1532 cm⁻¹). Such motion has maximal amplitude in NM 1035 and 1219 cm⁻¹. Out-of-plane bending NH vibration is more characteristic. Its calculated frequency is equal 703 cm⁻¹ (507 for PC-d₂). These calculated data are supported by experimental data ([2] and our unpublished results).

The proposed interpretation of IR spectra enable bands in IR spectra of dimeric and trimeric Pc compounds to be assigned and changes in spectra of different crystal modifications upon formation of dimers with rare-earth ions and during certain intermolecular interactions to be explaned.

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The Use of the DFT PBE/TZVP and INDO/SM Quantum Chemical Methods in the Calculations of Molecules of Porphyrazine and Phthalocyanines

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A modified version of the quantum-chemical method INDO/S, specially designed for the calculations of the excited electronic states of molecules of the class of tetrapyrroles, INDO/Sm, was proposed in paper [1]. The set of parameters of the INDO/Sm method was obtained by the variation of one- and two-electron matrix elements and comparison of calculation results with experimental data for the parent molecule of the series of porphyrins – porphyrin (H₂P) and its magnesium complex (MgP). The INDO/Sm method was applied to a number of fundamental tetrapyrrole structures, including porphyrazine (tetraazaporphyrin) (H₂TAP) as well as chlorin and bacteriochlorin. It was used for the consideration of the experimental data on the electronic absorption and luminescence spectra of a number of new compounds of the class of tetrapyrroles, in particular, phenyl-substituted porphyrazines with a chalcogen-containing heterocycle, bacteriochlorophyll analogs, phenyl-substituted tetraazachlorins and their analogues with annelated benzene rings (see [2] and references therein). It was also found that the use of the geometry of molecules obtained as a result of its optimization in the framework of the DFT PBE/TZVP method [3] gives for INDO/Sm spectroscopic data improved agreement with experiment.

The geometrical structure of the porphyrazine (MgTAP, H_2TAP) and phthalocyanine (MgPc, H_2Pc) molecules and their octaphenyl derivatives has been calculated by the DFT PBE/TZVP method, and the calculations of the excited electronic states have been carried out by the INDO/Sm method. A detailed analysis of the bond lengths has been performed for the series of compounds MP – MTAP – MTAPPh₈ – MPc – MPcPh₈, M=Mg, H₂. It has been shown that the weight of the internal 16-atom macroheterocycle in the electronic structure of MgPc and MgPcPh₈ increases as compared to MgTAP, while the contribution of the 18-atom azacyclopolyene for the free bases H₂Pc and H₂PcPh₈ becomes weaker as compared to H₂TAP.

For the phthalocyanine molecules, the two lowest unoccupied MOs and the highest occupied MO are 70% localized on the internal 16-atom macrocycle; as to the lower-energy filled MOs, there is strong mixing of the π AOs of 16-atom macrocycle with the π MOs of the annelated benzene rings (MgPc and H₂Pc) and additionally with the π MOs of the phenyl rings (MgPcPh₈ and H₂PcPh₈). The Q state energies calculated by the INDO/Sm method agree with the experimental values with an accuracy of 200–400 cm⁻¹. It is emphasized that the observed broad absorption spectrum in the region of 27000–37000 cm⁻¹ (Soret band) of phthalocyanines should be primarily assigned to several $\pi\pi^*$ transitions for which both local excitation of the 16-atom macrocycle and electron transfer of the type of the 16-atom ring \leftrightarrow the benzene fragments are characteristic. If only two most intense $\pi\pi^*$ transitions are taken into account, there is a qualitative agreement between the calculation and experiment, but the calculated energies are overestimated by ~3000 cm⁻¹.

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On the Shift of Equilibrium Between the Free Base Corroles and Their Deprotonated Forms in Solution

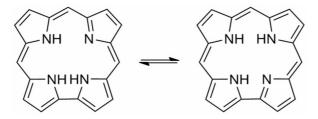
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Corroles constitute the family of tetrapyrrolic macrocycles, differing from regular porphyrins by the absence of one *meso*-carbon atom, resulting in direct bridging of two neighbouring pyrrole rings via a C_a - C_a linkage. Such structural change promotes substantial reorganization in the electronic structure to fulfil the macrocycle's aromaticity requirements. The free base corrole macrocycle consists of three pyrroles and one pyrrolenene ring. There is not enough space for three pyrrolic hydrogens to allow the planar conformation of the macrocycle and steric repulsion induces the formation of a nonplanar macrocycle conformation. The asymmetry of the macrocycle and the presence of three protons in its core provide the basis for the formation of non-equivalent NH-tautomers, whose electronic structures differ noticeably. Thus, all properties of free base corroles must be considered taking into account that free base corroles inherently exist as mixture of NH-tautomers with a nonplanar macrocycle.



We report the summary of our results which indicate that spectral-luminescent and physicochemical properties of the free base corroles need to be considered taking into account the inherent macrocycle nonplanarity and the formation of NH-tautomers [1-4]. The easy shift of the equilibrium between the free base and deprotonated forms in solution was proposed to explain on the same basis.

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Joining Corroles and Phthalocyanines in Functional Porphyrinoid Arrays

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Among the chromophores that have been used as molecular components in artificial photosynthetic systems, phorphyrinoids have been the preferred, due their intense optical absorption and rich redox chemistry.[1-3]

Amidst them, phthalocyanines (Pcs) and corroles (Corr) enjoy a privileged position. These chromophores, which have a two-dimensional 18 π -electron aromatic system isoelectronic with porphyrins, possess in fact unique physico-chemical properties which render these macrocycles valuable building blocks in materials science.[4,5]

Additionally, these tetrapyrroles can be peripherally modified to improve their light-harvesting ability and to tune their redox potentials.

In the present study, we have synthesized a donor-acceptor Corrole-Phthalocyanine dyad via a Sonogashira copper free cross coupling reaction. The presence of a different number of methoxy groups on the corrole framework is expected to improve the electron-donor properties of such a macrocycle thus enhancing the electron transfer to the linked zinc phthalocyanine, bearing electron-withdrawing groups.

The structural integrity of the multicomponent system has been confirmed performing spectral, electrochemical and computational studies.

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Spectral Signature of the Equilibrium Distribution of the Free Base 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin Atropisomers in Solution

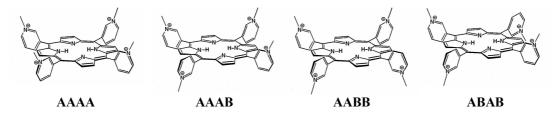
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It is known that the molecules of the *ortho-, meta-* and *para-*methyl substituted derivatives of the 5,10,15,20-tetrakis-pyridyl-porphyrin have pronounced photocytotoxic effect and are considered as promising candidates for inactivation of bacteria and viruses. The absorption and luminescence spectra of the *meta-*methyl substituted free base 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin was found to reveal large flexibility, in contrast to those reported for *ortho* and *para-*methyl substituted derivatives. We suggest that the most probable reason of such a behavior is the heterogeneity of the solutions appearing due to the formation of labile atropisomers, differing in the position of the substituted methyl group in the pyridine ring relative to the macrocycle mean plane (**A** – above , **B** – below, see scheme) due to weakly restricted rotation of substituents around the C_m-C₁ bond.



The detailed study of the spectral properties of the free base 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin has been carried out with elaboration of the absorption and luminescence spectroscopies [1]. The spectral changes was found to reflect the redistribution of the atropisomers concentrations upon establishing of the equilibrium distribution which ends approximately within 300 hours after the preparation of solution at the temperature 290 ± 2 K. The atropoisomerization is suggested to be inherent property of all the 5,10,15,20-tetraarylporphyrins with asymmetric substitution of aryl groups with respect to the axis passing through the C_m - C_1 bond, which does not relate with the sterical hindrances between the *ortho*-substituents in the aryl ring with tetrapyrrolic macrocycle. The prospects for the practical applications of revealed phenomenon are discussed.

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Substitution Architecture Control of the Macrocycle Nonplanarity in the Free Base Corroles

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It is well known, that the planar porphyrin macrocycle undergoes the transformation into the highly distorted nonplanar molecule upon the increasing loading with peripheral substituents is well known [1]. In case of the corroles the situation is more complicated upon increase in the crowding at the periphery of macrocycle since the corrole macrocycle is inherently nonplanar and it is able to adopt either the molecular conformation with the higher degree of nonplanar distortions of the same type or to undergo the conformational switch to the another type of macrocycle distortion when sufficient amount of the sterical strain accumulates at the macrocycle periphery.

The basis of the nonplanar distortions analysis is the deviation calculations of macrocycle atoms from the macrocycle mean plane. In the case of porphyrins the mean plane is selected as a plane with a minimum sum of mean square deviations of all the 24 macrocycle atoms. Almost all the macrocyclic atoms of the unsubstituted porphin molecule, tetraphenylporphyrin molecule or octaalkyl-substituted derivatives are in the mean plane. In case of corroles the selection of the macrocycle atoms are equivalent. In addition, the macrocycle mean plane must be the same for the two NH tautomers, i.e. it must remain invariant under NH tautomerization so that the analysis of geometric parameters of the molecule was carried out in the same basis. As a macrocycle mean plane we have proposed earlier the plane defined as one with minimal mean square deviations of C1, C4, C5, C6, C9, C16 and C19 carbon atoms (hereinafter – the 7C plane), according to IUPAC nomenclature [2].

Aiming to see how the corrole macrocycle conformation depends on the architecture of peripheral substitution the theoretical study has been carried out. Molecular conformation of the tetrapyrrolic macrocycle for the family of alkylated derivatives of the free base corroles has been calculated by quantum-chemical methods. The methyl groups have been chosen as substituents to impose the maximum steric constrains for the macrocycle neighborhood due to the sp^3 -hybridization of carbon atom. A number of the attached alkyl substituents and their positioning at the periphery of macrocycle determine the character and degree of the nonplanar macrocycle distortions. The degree of the nonplanar macrocycle distortions was treated as the $\Delta 23$ parameter, which is the average least-square deviation from the mean macrocycle plane C7 per one macrocycle atom [2]. The analysis of the obtained results will be presented in detail.

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Temperature Control of the NH-tautomerization Rate and Photophysical Properties of Free Base Corroles

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The NH-tautomers of the free base corroles are formed due to intrinsic asymmetry of the corrole macrocycle and presence of three protons in the macrocycle core. As a result, in addition to the radiative deactivation of the lowest singlet S_1 state and intersystem S_1 -T₁ crossing, the NH tautomerization needs to be considered as an additional channel of the excitation energy transport in the free base corroles [1]. In case of symmetrical AB_2 meso-substitution architecture two NHtautomers are formed. For the long wavelength T1 tautomer NH-tautomerization provides the additional nonradiative channel of the S_1 state population, and the photophysical properties of this tautomer do not depend on temperature. On the contrary, in case of the short wavelength T2 tautomer, tautomerization forms an efficient depopulation funnel for the S_1 state. For this tautomer the photophysical properties would depend on the temperature since the NH tautomerization rate constant distinctly increases with temperature. Since the NH tautomerization was found to be associated with overcoming the potential barrier in the lowest singlet S_1 state [1,2], therefore according to the Arrhenius equation a decrease/increase in temperature ultimately leads to a decrease/increase in the NH-tautomerization rate. The direct spectroscopic determination of the NH tautomerization rate and understanding of its pathway(s) is quite complicated task. At the same time there are several indirect data obtained with spectroscopic methods which allow shedding light on the NH tautomerization.

The energy level balance equations system is developed to describe the NH tautomerization rate constant. The set of the experimental data, consisting of the fluorescence spectra and quantum yields measured in the temperature range from 265 to 338 K are satisfactory reproduced with the theoretical solution of the above mentioned system of equations. The obtained theoretical temperature dependences of the fluorescence intensities for two NH-tautomers fit the experimental ones.

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