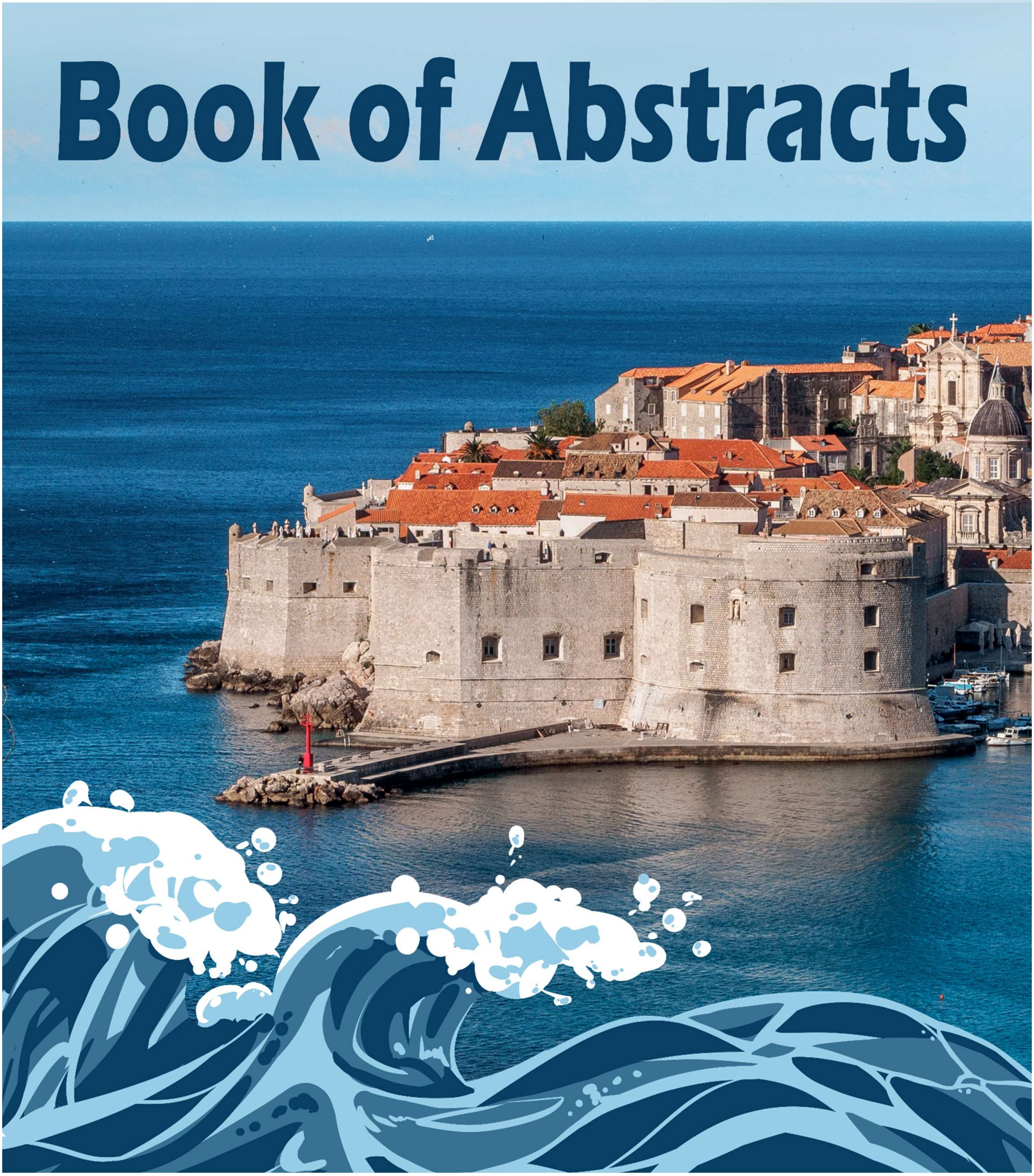
icesaa3

July 7 – 10, 2024, Dubrovnik, Croatia

International Conference on Excited State Aromaticity and Antiaromaticity

Book of Abstracts



GOLDEN SPONSOR:

MAGNITUDE
INSTRUMENTS™

SILVER SPONSORS:

TURBOMOLE

ישראל

PLIVA | teva

ISRAEL

IZRAELSKO PRIJATELJSTVO - ZAGREB, HRVATSKA

OTHER SPONSORS:

chemistry
an Open Access Journal by MDPI

REPUBLIC OF CROATIA
Ministry of Science,
Education and Youth

Journal of Physical
Organic Chemistry

ACADEMIA SCIENTIARUM ET ARTIUM CROATICA
MDCCCLXI
ZAKLADA

3rd International Conference
on
Excited State Aromaticity
and
Antiaromaticity

Book of Abstracts

ICESAA3
July 7 – 10, 2024
Dubrovnik, Croatia

ORGANIZED BY:

The Croatian Chemical Society and the Israel Chemical Society

Impressum

Proceedings

Title:

3rd International Conference on Excited State Aromaticity and Antiaromaticity Book of Abstracts

Subtitle:

ICESAA3 July 7 – 10, 2024, Dubrovnik, Croatia

Publisher:

Institut Ruđer Bošković, Bijenička cesta 54, 10000 Zagreb Croatia
Hrvatsko kemijsko društvo, Horvatovac 102/A, 10000 Zagreb Croatia

Year:

2024

ISBN:

978-953-7941-52-9

Editors:

Ivana Antol, Ruđer Bošković Institute, Zagreb

Renana Gershoni-Poranne, Technion-Israel Institute of Technology, Israel

Front page cover design:

Jelena Glasovac

Format:

pdf

Language:

engleski

Subjects:

prirodne znanosti, kemija

Pages:

89

GENERAL INFORMATION:

Since the discovery of benzene over 150 years ago, aromaticity has become one of the most fundamental concepts in chemistry, forming the basis for the properties and reactivity of many compounds. For most of its long history, aromaticity has been studied in the ground state of compounds. However, it is now recognized that aromaticity and antiaromaticity in the excited state also play key roles, particularly in photochemical reactions.

Over the past decade or so, the concept of excited state aromaticity and antiaromaticity has been further refined and many breakthrough examples have surfaced. The ICESAA meetings are the premier venue for disseminating and discussing recent advances related to excited state aromaticity and antiaromaticity, exemplifying its importance in a variety of photophysical and photochemical properties and processes. It is clear that both fundamental and applicative aspects remain underexplored, with great potential yet to be tapped.

The ICESAA conference series is devoted to fundamental aspects and applications of excited state aromaticity and antiaromaticity in chemistry and materials science, as well as other fields, such as biology and biomedicine. The 1st ICESAA conference was organized in Sigtuna, Sweden, from July 30 to August 2, 2019, and the second on Kauai, U. S. A., from December 16 until December 21, 2022.

INTERNATIONAL SCIENTIFIC COMMITTEE:

- **Renana Gershoni-Poranne**, Technion-Israel Institute of Technology, Israel
- **Henrik Ottosson**, Department of Chemistry, Ångström Laboratory, Uppsala University, Sweden
- **Judy I.-Chia Wu**, Department of Chemistry, University of Houston, USA
- **Arthur Winter**, Department of Chemistry, Iowa State University, USA
- **Shohei Saito**, Department of Chemistry, Graduate School of Science, Kyoto University, Japan

LOCAL ORGANISING COMMITTEE:

- **Danijel Namjesnik**, Faculty of Science, University of Zagreb, Croatia
- **Ivana Antol**, Ruđer Bošković Institute, Zagreb, Croatia
- **Renana Gershoni-Poranne**, Technion—Israel Institute of Technology, Israel
- **Nikola Basarić**, Ruđer Bošković Institute, Zagreb, Croatia

CONFERENCE OFFICE:

- **Danijela Hus Mustić**, Croatian Chemical Society, Zagreb, Croatia

COVER DESIGN:

- **Jelena Glasovac**

CONFERENCE VENUE:

- **Lecture hall** - University of Dubrovnik, Branitelja Dubrovnika 41, Dubrovnik, Croatia, https://www.unidu.hr/
- **Poster session & lunches** - Inter-University Centre Dubrovnik, Don Frana Bulića 4, Dubrovnik, Croatia, https://iuc.hr/

CONFERENCE SITE:

The 3rd ICESAA conference will be organized in Dubrovnik in Croatia, often coined as a pearl of Adriatic. The city is a well-known tourist destination owing to its rich culture and history and picturesque medieval architecture. Moreover, rich culinary experience and mild Mediterranean climate bring tourists from all over the world to Dubrovnik during all seasons.

The Dubrovnik City Walls are the major attraction for any visitor, being one of the best preserved fortification systems in Europe. The 1940-metre long walls include five fortresses and sixteen towers and bastions. The Walls are open for visitors all year round.

SPECIAL ISSUE:

A special Issue of the *Journal of Physical Organic Chemistry* will be published in connection with the Conference.

Journal of Physical
Organic Chemistry

icesaa3

July 7 – 10, 2024, Dubrovnik, Croatia

PARTICIPANTS

PARTICIPANTS:

Manabu Abe, Hiroshima University, Japan, mabe@hiroshima-u.ac.jp	IL7
Igor Alabugin, Florida State University, USA, alabugin@chem.fsu.edu	IL36
Itay Almog, Technion - Israel Institute of Technology, Israel, itayal@campus.technion.ac.il	P1
Ivana Antol, Ruđer Bošković Institute, Croatia, iantol@irb.hr	
Liudmil Antonov, Bulgarian Academy of Sciences, Bulgaria, lantonov@tautomer.eu	P2
Jean-Luc A. Ayitou, University of Illinois, Chicago, USA, aayitou@uic.edu	IL33
Mercedes Alonso Giner, Vrije Universiteit, Brussel, Belgium, Mercedes.Alonso.Giner@vub.be	IL30
Marija Baranac-Stojanović, University of Belgrade, Serbia, mbaranac@chem.bg.ac.rs	IL17
Mario Barbatti, Aix-Marseille University, France, mario.BARBATTI@univ-amu.fr	IL19
Fabien Barrois, Aix-Marseille Université, CNRS-ISM2, fabien.barrois@etu.univ-amu.fr	P3
Glib Baryshkinov, Linköping University, Sweden, glib.baryshnikov@liu.se	P4
Nikola Basarić, Ruđer Bošković Institute, Croatia, nbasaric@irb.hr	
Rémi Bonald Giner, Uppsala University, Sweden, remi.bonald-giner@kemi.uu.se	
Dan Cairnie, Magnitude Instruments, USA, dan.cairnie@maginsts.com	S
Irene Casademont Reig, Vrije Universiteit Brussel (VUB), Belgium, irene.casademont.reig@vub.be	CT2
David Casanova, Donostia International Physics Center (DIPC) & IKERBASQUE - Basque Foundation for Science, Spain, david.casanova@dipc.org	IL10
Juan Casado Cordón, University of Málaga, Spain, casado@uma.es	IL13
Sabyasachi Chakraborty, Technion, Israel Institute of Technology, Israel, sabyasachi@campus.technion.ac.il	CT9
Chunyan Chi, National University of Singapore, Singapore, chunyan@nus.edu.sg	IL26
Susannah Coote, University of Bath, UK, scc98@bath.ac.uk	
Soumyajit Das, Indian Institute of Technology Ropar, India, chmsdas@iitrpr.ac.in	IL6
Catherine S. P. De Castro, King Abdullah University of Science and Technology, Saudi Arabia, catherine.decastro@kaust.edu.sa	CT4
Eline Desmedt, Vrije Universiteit Brussel, Belgium, Eline.Louise.Desmedt@vub.be	CT7
Nađa Došlić, Ruđer Bošković Institute, Croatia, nadja.doslic@irb.hr	CT1
David Dunlop, Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Charles University, Czech Republic, david.dunlop@uochb.cas.cz	CT8
Bo Durbeej, Linköping University, Sweden, bo.durbeej@liu.se	IL25
Jochen Eeckhoudt, Vrije Universiteit Brussel, Belgium, jochen.pedro.eeckhoudt@vub.be	P5
Shany Erez, Technion City, Israel, erezshany@campus.technion.ac.il	P6

Marc Hamilton Garner, Technical University of Denmark, Denmark, marchamiltongarner@hotmail.com P7

Renana Gershonei-Poranne, Technion, Technion - Israel Institute of Technology, Israel, rporanne@technion.ac.il

Ori Gidron, The Hebrew University of Jerusalem, Israel, Ori.Gidron@mail.huji.ac.il IL27

Zoran Glasovac, Ruđer Bošković Institute, Croatia, zglasovac@irb.hr P8

Ganna Gryn'ova, Heidelberg Institute for Theoretical Studies, Germany, ganna.grynova@h-its.org IL16

Anna D. Gudmundsdottir, University of Cincinnati, USA, annag@uc.edu IL29

Michael M. Haley, University of Oregon, USA, haley@uoregon.edu IL5

Johannes Hennemann, Institut für Organische Chemie Universität Würzburg, johannes.hennemann@uni-wuerzburg.de P9

Yoshimitsu Itoh, The University of Tokyo, Japan, itoh@chembio.t.u-tokyo.ac.jp IL11

Michal Juríček, University of Zurich, Switzerland, michal.juricek@chem.uzh.ch IL12

Peter B. Karadakov, University of York, UK, peter.karadakov@york.ac.uk IL32

Amir Karton, University of New England, Australia, Amir.Karton@une.edu.au IL9

Eric Kennehan, Magnitude Instruments, USA, erkennehan@maginsts.com S

Fatimah Khaleel, Technion, Technion - Israel Institute of Technology, Israel, fatimah.kh@campus.technion.ac.il P10

Dongho Kim, Yonsei University, Korea, dongho@yonsei.ac.kr IL20

Oskar Kristinsson, University of Iceland, Reykjavik, Iceland, ogk2@hi.is

Croix J. Laconsay, University of Houston, United States, croix.laconsay1@gmail.com P11

Stiv Llenga, School of Chemistry, University of Birmingham, United Kingdom, stiv.llenga@h-its.org P12

Gábor London, Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungary, london.gabor@ttk.hu IL34

Eduard Matito, Donostia International Physics Center, Spain, ematito@gmail.com IL31

Péter J. Mayer, Uppsala University, Sweden, peter.mayer@kemi.uu.se P13

Eduardo Mayo Yanes, Technion - Israel Institute of Technology, Israel, eduardomayoyanes@gmail.com P14

Ognjen Miljanić, University of Houston, USA, miljanic@uh.edu P15

Katarzyna Młodzikowska-Pieńko, Technion Israel Institute of Technology, Israel, kasiamp@campus.technion.ac.il P16

Jean-François Morin, Université Laval, Canada, Jean-Francois.Morin@chm.ulaval.ca IL15

Danijel Namjesnik, University of Zagreb, Croatia, danijel.namjesnik@chem.pmf.hr

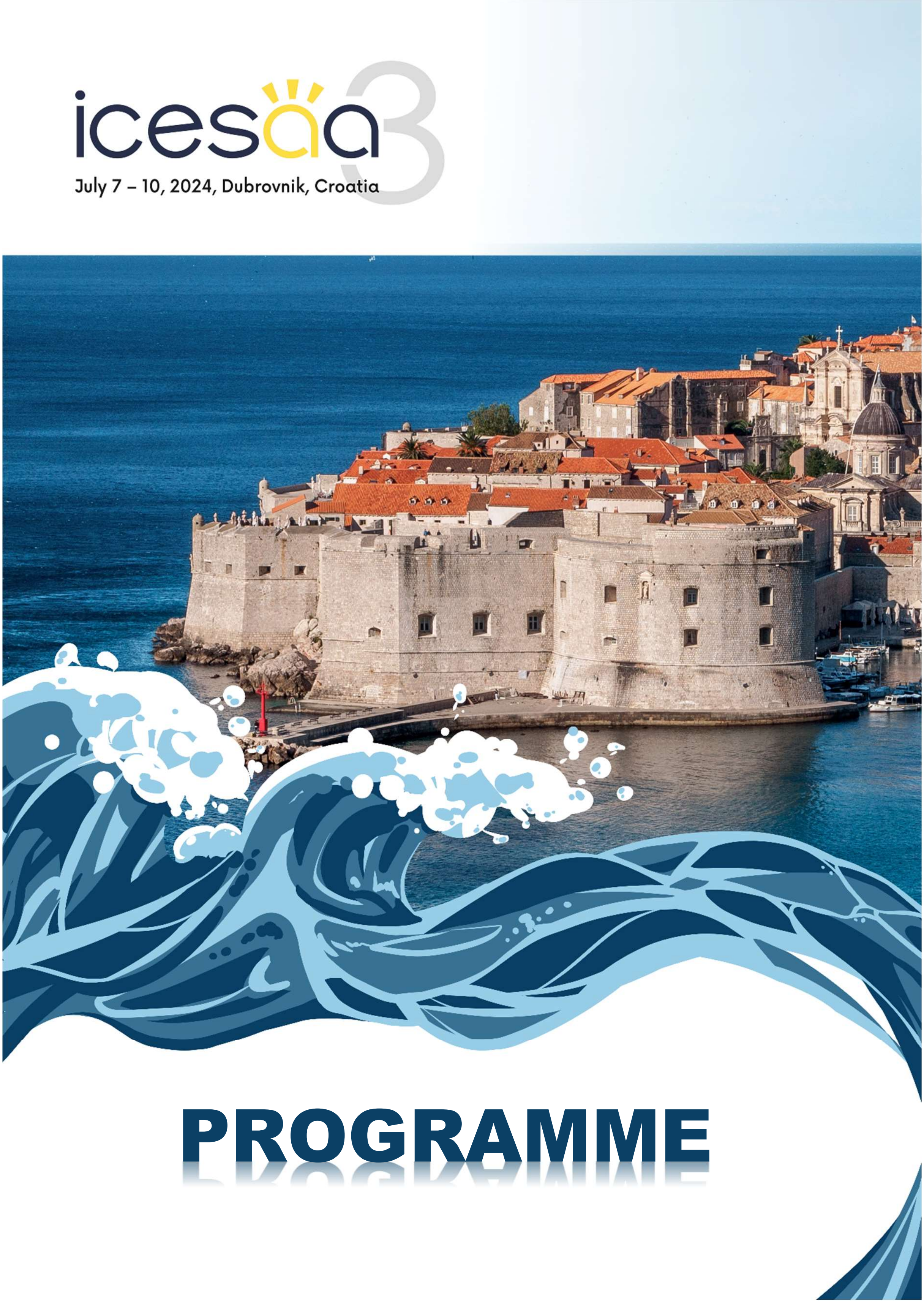
Juwon Oh, Soonchunhyang University, Korea, juwoh933@sch.ac.kr IL28

Mesías Orozco-Ic, Donostia International Physics Center (DIPC), Spain, mesias.orozco@dipc.org CT10

Martin Peeks, University of New South Wales Sidney, Australia, m.peeks@unsw.edu.au	IL22
Dawid Pinkowicz, Jagiellonian University, Krakow, Poland, dawid.pinkowicz@uj.edu.pl	CT5
Michael Pittelkow, University of Copenhagen, Denmark, pittel@chem.ku.dk	IL23
Felix Plasser, Loughborough University, UK, F.Plasser@lboro.ac.uk	IL18
Nathalie Proos Vedin, Uppsala University, Sweden, nathalie.proosvedin@kemi.uu.se	P17
Prince Ravat, Universität Würzburg, Germany, princekumar.ravat@uni-wuerzburg.de	CT3
Amisadai Lorenzo Reyes, CNRS-ISM2, Aix Marsielle Université, France, amisadai.LORENZO-REYES@etu.univ-amu.fr	P18
Luisa Rzesny, Institute of Organic Chemistry II and Advanced Materials, Germany, luisa.rzesny@uni-ulm.de	P19
Michel Rickhaus, University of Geneva, Switzerland, michel.rickhaus@chem.uzh.ch	IL15
Emil Säbb, Uppsala University, Sweden, emil.sabb@kemi.uu.se	P20
Shohei Saito, Kyoto University, Japan, saito.shohei.4c@kyoto-u.ac.jp	IL21
Maria Eugenia Sandoval Salinas, University College London, UK, m.salinas@ucl.ac.uk	P21
Himanshu Sharma, IIT Ropar, India, himanshu.19cyz0021@iitrpr.ac.in	P22
Piotr de Silva, Technical University of Denmark, Denmark, pdes@dtu.dk	IL3
Jayaraman Sivaguru, Bowling Green State University, USA, sivagj@bgsu.edu	IL35
João Soares, University of Houston, USA, joaovitoros159@gmail.com	P23
Miquel Solà i Puig, University of Girona, Spain, miquel.sola@udg.edu	IL1
Luis Soriano-Agueda, Donostia International Physics Center, Spain, lsorianoagueda@gmail.com	P24
Amnon Stanger, Technion, Haifa, Israel, stanger@technion.ac.il	IL2
Marcin Stępień, Wrocław University, Poland, marcin.stepien@uwr.edu.pl	IL14
Haruna Sugimura, Osaka University, Japan, sugimurah20@chem.sci.osaka-u.ac.jp	
Dariusz Szczepanik, Jagiellonian University, Poland, dariusz.szczepanik@uj.edu.pl	CT6
John D. Tovar, Johns Hopkins University, USA, jtovar1@jhu.edu	IL24
James Turner, Loughborough University, Loughborough, United Kingdom, j.turner2@lboro.ac.uk	P25
Renan Vidal Viesser, University of Houston, USA, renan.viesser@gmail.com	P26
Judy I-Chia Wu, University of Houston, USA, judyicwu@gmail.com	IL8

icesaa3

July 7 – 10, 2024, Dubrovnik, Croatia



PROGRAMME

PROGRAMME:

Sunday July 7th 2024. INTER-UNIVERSITY CENTRE DUBROVNIK **Don Frana Bulića 4, HR-20000 Dubrovnik, Croatia**	
19:00 -	Welcome Reception

MondayJuly 8th 2024., LECTURE HALL University of Dubrovnik **Branitelja Dubrovnika 41, HR-20000 Dubrovnik, Croatia**		
		Chairman: Renana Gershoni-Poranne
9:00-9:30	IL1	**Miquel Solà i Puig**: Aromaticity of Annulenes, Acenes, Phenacenes, and Osmaacenes in their Lowest-lying Triplet States
9:30-10:00	IL2	**Amnon Stanger**: Singlet Fission and Aromaticity
10:00-10:30	IL3	**Piotr de Silva**: Singlet-Triplet Inversion in Photoactive Molecules
10:30-11:00	Coffee break	
11:00-11:30	IL4	**Jean-François Morin**: π-Extended Azuleno[2,1,8,*ija*]azulenes: an Interplay Between Local and Global Aromaticity
11:30-12:00	IL5	**Michael M. Haley**: Adventures With Indenofluorenes
12:00-12:30	IL6	**Soumyajit Das**: π-Extended Indenofluorenes: Syntheses, (Anti)aromaticity and Diradical Properties
12:30-13:00	IL7	**Manabu Abe**: Substituent Effect on Triplet Ground State of Indenyl Cations
13:00-15:00	Lunch break	
		Chairman: Igor Alabugin
15:00-15:30	IL8	**Judy I.-C. Wu**: Photoswitching Transformations Triggered by Aromaticity Gain and Antiaromaticity Relief
15:30-16:00	IL9	**Amir Karton**: Reversible Nonaromatic/Antiaromatic Molecular Switch by Graphene-Induced Planarization of Highly Curved π-Systems
16:00-16:30	IL10	**David Casanova**: Unveiling (Anti)aromaticity in the Excimer State
16:30-17:00	Coffee break	
17:00-17:30	IL11	**Yoshimisu Itoh**: Molecular Assembly and Function Inspired by Excited State Aromaticity
17:30-17:45	CT1	**Nađa Došlić**: The Ring-Opening Reaction of 1,3-Cyclohexadiene: Identifying the True Reactive State
17:45-18:00	CT2	**Irene Casademont Reig**: Exploiting Excited States via Inverse Design
18:00-18:15	CT3	**Prince Ravat**: Helically Twisted Nanoribbons Employing [7]Helicene as a Molecular Wrench
18:15-18:30	CT4	**Catherine S. P. De Castro**: Exploring Exciton Dynamics in NFAs
18:30-18:45	CT5	**Dawid Pinkowicz**: Tris(dioxothiadiazole) - a Molecule with Five Redox States and Varying Aromaticity
18:45-19:00	CT6	**Dariusz Szczepanik**: Cyclic Delocalization vs Ring Current: Facts and Myths
19:00 -	P1-P26	Poster session

Tuesday July 9th 2024. LECTURE HALL University of Dubrovnik
Branitelja Dubrovnika 41, HR-20000 Dubrovnik, Croatia

		Chairman: Judy I.-C. Wu
9:00-9:30	IL12	**Michal Juríček**: What Makes the Thermal, Formally Forbidden Electrocyclization of Cethrene so Facile?
9:30-10:00	IL13	**Juan Casado Cordón**: "*Apolar*" Diradicals with Charge Resonant Forms
10:00-10:30	IL14	**Marcel Stępień**: π-Conjugated Oligoradicaloids and Anions: Aromaticity, Magnetism, and Non-covalent Interactions
10:30-11:00	Coffee break	
11:00-11:30	IL15	**Michel Rickhaus**: The Strategic Design of Curved Polyaromatics Opportunities for Organization
11:30-12:00	IL16	**Ganna Gryn'ova**: Property Patterns in *N*-Heteropolycycles from Chemical Intuition and Machine Learning
12:00-12:30	IL17	**Marija Baranac-Stojanović**: Effect of Heteroatoms on Triplet State Energies and Antiaromaticity of Benzene and some Polycyclic Aromatic Compounds
12:30-13:00	IL18	**Felix Plasser**: Harnessing Aromaticity for Molecular Materials Design a Computational Approach
13:00-15:00	Lunch break	
		Chairman: Manabu Abe
15:00-15:30	IL19	**Mario Barbatti**: Perspectives in Excited-State Dynamics for Modeling Photoprocesses
15:30-16:00	IL20	**Dongho Kim**: Site-specific Coordination Chemistry and Photophysical Behaviors by Hückel-Möbius Aromatic Switching
16:00-16:30	IL21	**Shohei Saito**: ESA-induced Reversible Photomelting of π-Stacked Soft Materials
16:30-17:00	Coffee break	
17:00-17:30	IL22	**Martin Peeks**: Manifestations of (Anti)aromaticity in Porphyrinoids Big and Small
17:30-18:00	IL23	**Michael Pittelkow**: Molecular Engineering Using Croconic Acid
18:00-18:15	CT7	**Eline Desmedt**: Exploring the Relationship Between Aromaticity and (Non)linear Optical Properties for Hexaphyrins
18:15-18:30	CT8	**David Dunlop**: The Relationship Between Aromaticity and Anti-Kasha Fluorescence of (6+5)Fused 10π-S-Heterocycles
18:30-18:45	CT9	**Sabyasachi Chakraborty**: The Effect of B, N Substitution on Cata-condensed Polybenzenoid Hydrocarbons: A Computational Investigation
19:00 -	Conference dinner	

Wednesday July 10th 2024. LECTURE HALL University of Dubrovnik Branitelja Dubrovnika 41, HR-20000 Dubrovnik, Croatia		
		Chairman: Michael M. Haley
9:00-9:30	IL24	**John D. Tovar**: Unusual Conjugation Topologies and their Impact on Delocalization within π-electron Materials
9:30-10:00	IL25	**Bo Durbeej**: Geometry-based Probing of Excited-State Aromaticity and Antiaromaticity
10:00-10:30	IL26	**Chunyan Chi**: Molecular Carbons with Different Topologies and Size
10:30-11:00	Coffee break	
11:00-11:30	IL27	**Ori Gidron**: Helitwistacenes and Furan Macrocycles: Inversion of Circularly Polarized Light Emission and Excited-State Global Aromaticity
11:30-12:00	IL28	**Juwon Oh**: Aromaticity in Multicyclic Macrocycles and its Change in the Triplet State
12:00-12:30	IL29	**Anna Gudmundsdottir**: Photophysical Characteristic and Photoreactivity of Coronene and Corannulene Derivatives in Solution and the Solid State
12:30-13:00	IL30	**Mercedes Alonso Giner**: Exploiting Excited-State Aromaticity for Tuning the Excited State Energies
13:00-15:00	Lunch break	
		Chairman: Nikola Basarić
15:00-15:30	IL31	**Eduard Matito**: Efficient Assessment of Aromaticity through Electron-Delocalization Metrics
15:30-16:00	IL32	**Peter B. Karadakov**: Aromaticity and Antiaromaticity in Low-Lying Electronic States Other than S_1 and T_1
16:00-16:30	IL33	**Jean-Luc A. Ayitou**: Controlling Non-Linear Photophysical Processes and Photochemical Transformations using Aromaticity Reversal in Heterocyclic Thioamides
16:30-17:00	Coffee break	
17:00-17:30	IL34	**Gábor London**: Chasing (Anti)aromaticity Effects in the Ground and Excited States with Molecular Switches
17:30-18:00	IL35	**Jayaraman Sivaguru**: Uncovering Novel Photochemical Reactivity from the Excited State
18:00-18:30	IL36	**Igor Alabugin**: Interplay Between Aromaticity and Antiaromaticity in Cyclizations
18:30-18:45	CT10	**Mesías Orozco-Ic**: Core-electron Contributions to the Magnetic Response of Molecules with Heavy Elements
18:45 -19:00	Closing ceremony	

July 7 – 10, 2024, Dubrovnik, Croatia

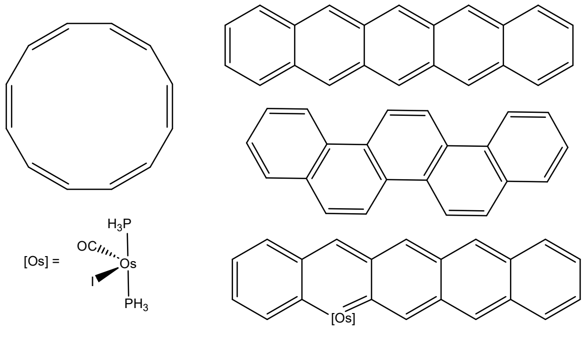
INVITED LECTURES

Aromaticity of Annulenes, Acenes, Phenacenes, and Osmaacenes in their Lowest-Lying Triplet States

Miquel Solà[1], Louis A. M. Van Nyvel[2], Rodrigo Báez-Grez[3], Mercedes Alonso[2],
Slavko Radenković[4] and Ricardo Pino-Ríos[3]

[1]*Institute of Computational Chemistry and Catalysis and Department of Chemistry, University of Girona, C/ M. Aurèlia Capmany, 69, 17003 Girona, Catalonia, Spain*
[2] *Department of General Chemistry (ALGC), Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels, Belgium.*
[3] *Laboratorio de Química Teórica, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Región Metropolitana, Chile*
[4]*University of Kragujevac, Faculty of Science, P. O. Box 60, 34000 Kragujevac, Serbia*
E-mail: miquel.sola@udg.edu

The first rule of aromaticity to be established was the famous ‘$4n+2$ π-electron’ rule, which states that a planar, cyclic, conjugated molecule with $4n+2$ π-electrons is aromatic. In 1972, Colin Baird showed [1] that cyclic D_{nh} annulenes with $4n$ π-electrons in their lowest triplet excited state (T_1) have an aromatic character, whereas those with $4n+2$ π-electrons possess an antiaromatic character. The Hückel rule holds strictly only for monocyclic π-conjugated systems such as benzene and cyclooctatetraene. It was noticed early on that polycyclic aromatic hydrocarbons (PAHs) do not obey this rule. The π-sextet rule, proposed in 1972 by Clar to describe aromaticity in PAHs [2], proved to be a more versatile model. In this work, we start analyzing the aromaticity of the T_1 state in cyclic annulenes to then move to PAHs such as acenes and phenacenes. Using several measures of aromaticity, we show how Baird’s and Hückel/Clar’s rules can be combined to explain the triplet state energies of PAHs with fused $(4n+2)\pi$-rings [3]. Finally, we apply the same tools to a particular case of metallic PAHs, the osmaacenes [4].



Scheme 1. Type of systems studied.

REFERENCES

[1] N. C. Baird, *J. Am. Chem. Soc.* **1972**, *94*, 4941-4948.

[2] E. Clar, *The Aromatic Sextet*, Wiley, New York, **1972**.

[3] R. Pino-Rios, R. Báez-Grez, M. Solà, *Phys. Chem. Chem. Phys.* **2021**, *23*, 13574-13582.

[4] S. Radenković, M. Solà, *Inorg. Chem.* **2023**, *62*, 9578-9588.

Singlet Fission and Aromaticity

Amnon Stanger

Schulich Department of Chemistry, Technion, Haifa 3200003, Israel
E-mail: stanger@technion.ac.il

Singlet fission (SF) is a phenomenon where a molecule in its first excited singlet state can transfer part of the energy to a second molecule, forming two molecules in their first excited triplet state (i.e., S(1)→2T(1)) that eventually end up as two pairs of electron-hole. The energy requirements stem from the law of energy conservation; $\Delta E[S(1)-S(0)] \geq 2\Delta E[T(1)-S(0)]$ and $\Delta E[T(1)-S(0)] \leq \Delta E[T(2)-T(1)]$. The practical problem with calculating these energies is that DFT methods do not yield dependable energies, so that high level *ab-initio* methods have to be used, limiting the size of the systems that can be studied.

Fowler[1] has shown that induced ring currents can be understood as transition between occupied and unoccupied MOs. The direction (diatropic or paratropic) and the intensity of the induced current depends on the relative symmetries and is inversely proportional to the energy gap between the involved MOs, respectively. Thus, the induced current and the resulting induced magnetic field (as expressed by NICS-X-scan) can be viewed as spectra, yielding information about transitions from the calculated state (e.g., S(0), T(1)) to its excited states. NICS is not sensitive to the level of theory, therefore reliable results can be obtained for large (practical) systems.

In the paper I will introduce a NICS(1.7)$_{\pi,zz}$-X-scan based method to identify SF compounds.

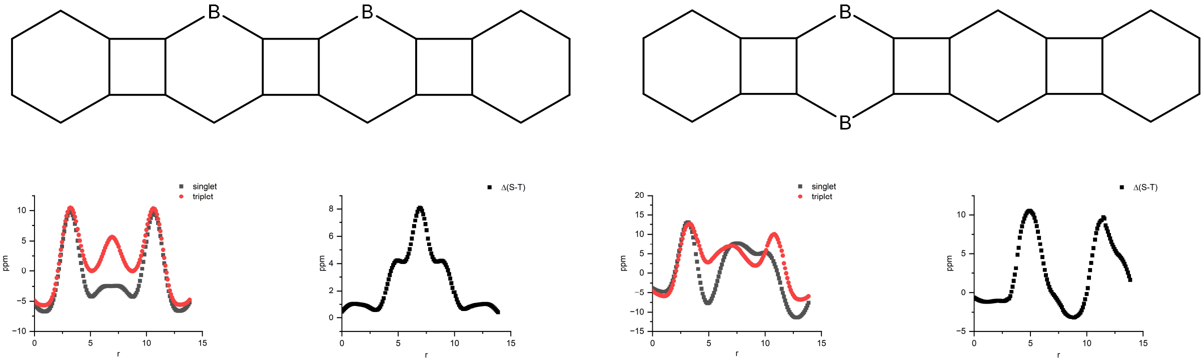


Figure 1. NICS(1.7)$_{\pi,zz}$ of singlet and triplet 9,11-(left) and 9,10-(right) dibora[4]phenylenes. Left – SF characteristics. Right – No SF characteristics

REFERENCES

[1] (a) P. W. Fowler, E. Steiner, *Chem. Phys. Lett.* **2002**, *364*, 259–266. DOI: 10.1016/S0009-2614(02)01244-7. (b) P. W. Fowler, E. Steiner, R. W. A. Havenith, L. W. Jenneskens, *Magn. Reson. Chem.* **2004**, *42*, S68–S78. DOI: 10.1002/mrc.1445. (c) E. Steiner, P. W. Fowler, *J. Phys. Chem. A* **2001**, *105*, 9553–9562. DOI: 10.1021/jp011955m. (d) E. Steiner, P. W. Fowler, *Chemical Communications* **2001**, 2220–2221. DOI: 10.1039/b104847n.

Singlet-Triplet Inversion in Photoactive Molecules

Piotr de Silva

Department of Energy Conversion and Storage, Technical University of Denmark,
2800 Kongens Lyngby, Denmark.
E-mail: pdes@dtu.dk

The well-established Hund's rule predicts that the state of higher spin multiplicity has lower energy for a given electronic configuration. Consequently, the singlet-triplet (ST) gap is predicted to be always nonnegative. For a long time, there was little to no evidence that Hund's rule could be violated in molecules. This ground was broken in 2019 when two independent theoretical studies demonstrated ST inversion in azaphenalenes [1, 2]. They also showed that ST inversion is due to electron correlation and requires a substantial contribution of double excitations in the lowest-lying excited states, an effect that had not been explicitly considered before in molecular design. Such ST-inverted photoactive organic materials have potential applications in a host of technologies, including light-emitting devices and photocatalysts.

I will analyze the problem of gap inversion from the perspective of the electronic structure theory. I will demonstrate that inversion is possible but requires a substantial contribution of double excitations in the lowest-lying states. I will also show that adiabatic TD-DFT, the workhorse excited states electronic structure method, fails to predict negative singlet-triplet gaps and, in general, has questionable accuracy for the calculations of small-gap systems. Further, I will discuss the kinetics of electronic transitions in azaphenales, focusing on the nuclear-ensemble-based calculations of fluorescence and intersystem crossing rate constants [3,4].

REFERENCES

[1] P. de Silva, *J. Phys. Chem. Lett.,* **2019**, *10*, 5674–5679.

[2] J. Ehrmaier, *et al., J. Phys. Chem. A*, **2019**, *123*, 8099–8108.

[3] L. E. de Sousa and P. de Silva, *J. Chem. Theory Comput.*, **2021**, *17*, 5816-5824.

[4] L. E. de Sousa and P. de Silva, *J. Phys. Chem. A*, **2023**, *127*, 8200-8208.

π-Extended Azuleno[2,1,8,*ija*]azulenes: an Interplay Between Local and Global Aromaticity

Jean-François Morin, Pierre Mathey, Frédéric Lirette, Jérémie Ouellette
and Manamba Dite Sisse Traoré

Department of Chemistry, Université Laval, Quebec (QC) Canada G1V0A6
E-mail: jean-francois.morin@chm.ulaval.ca

Non-alternant non-benzenoid hydrocarbons consisting of an assembly of odd-membered (mostly 5 and 7) carbocycles have become highly sought synthetic targets due to their unique electronic properties and the synthetic challenge they represent. The most prevalent examples, namely azulene, pentalene and heptalene, have been known and studied for many decades and continue to attract a big deal of attention as new opportunities for these molecules keep arising. One major challenge in the field of non-alternant non-benzenoid hydrocarbons is to extend the π-conjugation by fusing several odd-membered rings in a longitudinal and/or lateral fashion to form new carbon allotropes with unique sets of properties that are difficult to obtain with common benzenoid hydrocarbons. One very interesting yet not well-studied fused azulene dimer is the azuleno[2,1,8-*ija*]azulene (or dicyclohepta[*cd,gh*]pentalene **1**, Figure 1), a stable non-alternant hydrocarbons possessing a peripheral 14 π-electron annulene. Herein, we report the synthesis and properties of a new series of annulated azuleno[2,1,8-*ija*]azulene whose periphery has been modulated to change both the local and global aromaticity of the molecules, the goal being to extend the conjugation as much as possible without promoting the formation of a diradical that leads to dimerization. The electronic and optical properties of these molecules will also be discussed. Recent efforts to prepared bowl-shaped molecules from the azuleno[2,1,8-*ija*]azulene scaffold will be presented.

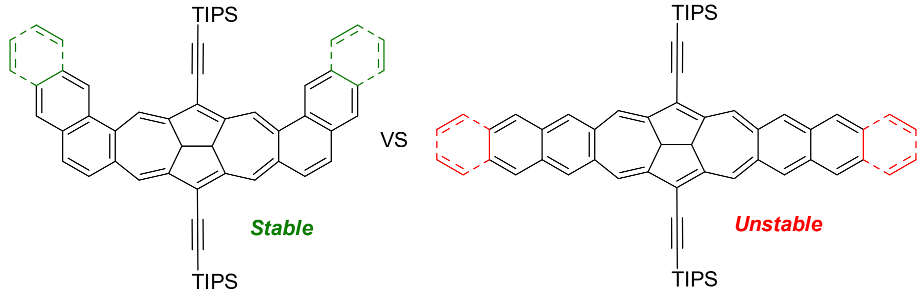


Figure 1. Example of stable and unstable azuleno[2,1,8-*ija*]azulenes

REFERENCES

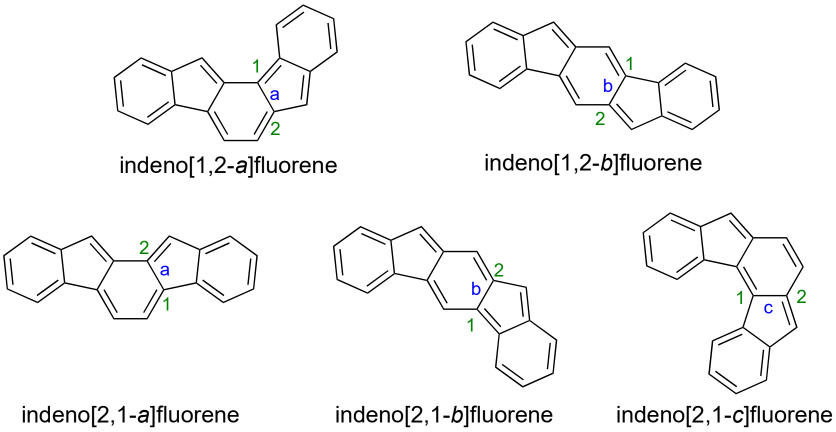
[1] P. Mathey, F. Lirette, I. Fernandez, L. Renne, T. R. Weitz, J.-F. Morin, *Angew. Chem. Int. Ed.* **2023**, *62*, e202216281.

Adventures with Indenofluorenes

Michael M. Haley

Department of Chemistry & Biochemistry, University of Oregon, Eugene, Oregon 97403-1253, USA
E-mail: haley@uoregon.edu

This talk will present our synthetic, structural, computational and materials studies of a class of carbon-rich molecules based on the indenofluorene (IF) skeleton (Figure 1).[1] Access to the fully conjugated, 20 π-electron, formally antiaromatic ring systems is accomplished via a variety of intermediate diones, which in turn can be prepared via a simple three-step process (Suzuki cross-coupling, benzylic oxidation, Friedel-Crafts acylation). Optimization of their syntheses now permits access to IF derivatives in multigram quantities. We have shown that thin films or single crystals of several different IF scaffolds can serve as an active layer in organic field effect transistors (OFETs).[2] Current studies are focused on varying the antiaromaticity of the indacene core in [1,2-*b*]IFs by systematic alteration of the outer benzene groups with other aromatic motifs to generate a wide variety of “diarenoindacene” structures. Investigations into other indenofluorene regioisomers resulted either in stable antiaromatic systems ([2,1-*c*]IFs) [3], reactive molecules ([2,1-*a*]IFs) that rearranged to benzocyclobutadiene derivatives [4], or unstable compounds ([1,2-*a*]IFs) that only could be confirmed upon reduction with alkali metals.[5]



indeno[1,2-*a*]fluorene indeno[1,2-*b*]fluorene

indeno[2,1-*a*]fluorene indeno[2,1-*b*]fluorene indeno[2,1-*c*]fluorene

Figure 1. The five possible regioisomers of indenofluorene.

REFERENCES

[1] C. K. Frederickson, B. D. Rose and M. M. Haley, *Acc. Chem. Res.* **2017**, *50*, 977-987.

[2] A. M. Zeidell, L. Jennings, C. K. Frederickson, Q. Ai, J. J. Dressler, L. N. Zakharov, C. Risko, M. M. Haley and O. D. Jurchescu, *Chem. Mater.* **2019**, *31*, 6962-6970.

[3] T. Jousselin-Oba, P. E. Deal, A. G. Fix, C. K. Frederickson, C. L. Vonnegut, A. Yassar, L. N. Zakharov, M. Frigoli and M. M. Haley, *Chem. Asian J.* **2019**, *14*, 1737-1744.

[4] J. E. Barker, T. Kodama, M. K. Song, C. K. Frederickson, T. Jousselin-Oba, L. N. Zakharov, J. Marrot, M. Frigoli, R. P. Johnson and M. M. Haley, *ChemPlusChem* **2019**, *84*, 665-672.

[5] J. J. Dressler, Z. Zhou, J. L. Marshall, R. Kishi, S. Takamuku, Z. Wei, S. N. Spisak, M. Nakano, M. A. Petrukhina and M. M. Haley, *Angew. Chem. Int. Ed.* **2017**, *56*, 15363-15367.

π-Extended Indenofluorenes: Syntheses, (Anti)aromaticity and Diradical Properties

Soumyajit Das

Department of Chemistry, Indian Institute of Technology (IIT) Ropar, Rupnagar 140001, Punjab, India
E-mail: chmsdas@iitrpr.ac.in

Indeno[1,2-*b*]fluorene, indeno[2,1-*a*]fluorene and indeno[2,1-*c*]fluorene are stable closed-shell regioisomers of 4nπ indenofluorene (IF) series,[1] which motivated us to explore some of their unknown π-extended derivatives. In our group, we developed a new synthetic approach for [2,1-*c*]IF and used this approach to construct a curved (4n+2)π *s*-indacenodifluorene (*s*-IDF) isomer that absorbed in the NIR-region and displayed small HOMO-LUMO energy gap.[2] Further we developed the synthesis of a *S*-heterocyclic *as*-IDF that displayed dominant antiaromatic character for the *as*-indacene subunit.[3] While [1,2-*b*]IF and [2,1-*a*]IF were traditionally synthesized by nucleophilic addition of aryl groups to the benzo-fused diketone precursor and followed by $SnCl_2$-mediated reduction of the hydroxy groups,[1] we developed a new steric-promoted synthetic approach that utilizes DDQ oxidation in the final step to generate [1,2-*b*]IF and [2,1-*a*]IF derivatives.[4] We utilized this approach to further construct the first open-shell diradicaloid 6,6'-biindenofluorene (6,6'-BIF).[5] Accidental synthesis of tetrabenzoindeno[2,1-*a*]fluorene (TBz[2,1-*a*]IF) derivative will also be discussed, that displayed an open-shell singlet ground state (EPR, NMR and DFT) despite the dominance of a *ortho*-quinoidal *as*-indacene subunit, as evident from x-ray crystallographic analysis.[6] Our TBz[2,1-*a*]IF is a unique diradicaloid with small diradical character despite displaying a small singlet-triplet energy gap.

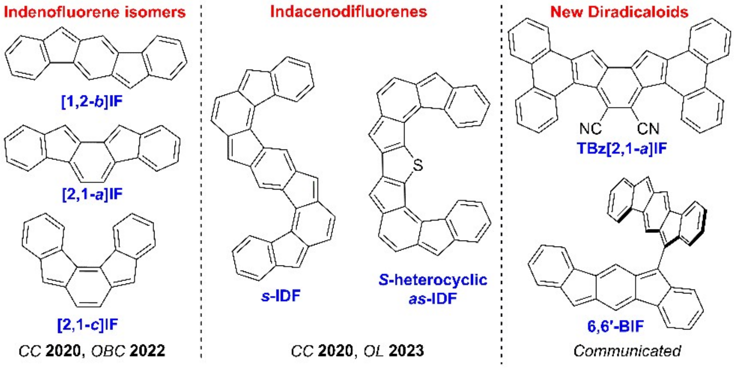


Figure 1. Conjugated backbones of isomeric indenofluorenes and their π-extended derivatives

REFERENCES

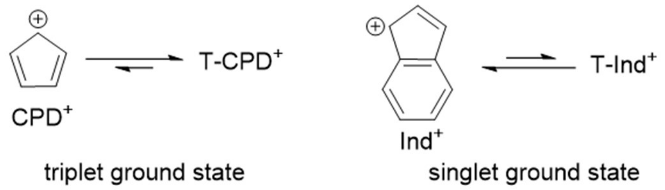
[1] C. K. Frederickson, B. D. Rose, M. M. Haley, *Acc. Chem. Res.*, **2017**, *50*, 977–987.
[2] H. Sharma, P. K. Sharma, S. Das, *Chem. Commun.*, **2020**, *56*, 11319–11322.
[3] P. K. Sharma, D. Mallick, H. Sharma, S. Das, *Org. Lett.* **2023***, 25,* 2201–2206.
[4] H. Sharma, N. Bhardwaj, S. Das, *Org. Biomol. Chem.*, **2022**, *20*, 8071−8077.
[5] *Unpublished.*
[6] *Unpublished.*

Substituent Effect on Triplet Ground State of Indenyl Cations

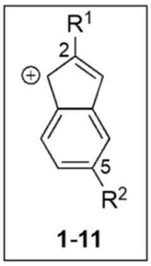
Ma-aya Takano,[1] Ivana Antol,[2] Manabu Abe[1]

[1]Departmentof Chemistry, Graduate School of Science, HiroshimaUniversity,1-3-1 Kagamiyama,
Higashi-Hiroshima, Hiroshima 739-8526 (Japan);
[2]Institut RuđerBošković, Bijenička cesta 54, 10000 Zagreb (Croatia)
E-mail: mabe@hiroshima-u.ac.jp

Cyclopentadienyl cation (CPD^+) is well known as one of the triplet ground state carbocations. Due to the Hückel anti-aromaticity in closed-shell singlet (CS) and Baird aromaticity in triplet (T) of CPD^+, T(T-CPD^+) is $\Delta E_{ST} = 8.7$ kcal mol^{-1} more stable than the singlet.[1-4] On the other hand, although indenyl cation (Ind^+) which fused one benzene ring to CPD^+ also has Hückel anti-aromaticity in its CS and Baird aromaticity in T, CS is a ground state ($\Delta E_{ST} \approx -9.2$ kcal mol^{-1}). The resonance stabilization of the positive charge (22.0 kcal mol^{-1}) by the fused benzene ring is key in stabilizing the CS state.[5]



In this study, the substituent effect on the electronic ground state was investigated about Ind^+ derivatives **1-11** which introduced substituent R^1 and R^2 at C2 and C5 of Ind^+, respectively, by density functional theory (DFT) and complete active space multiconfiguration (CAS) second-order perturbation theory (CASPT2/CASSCF) calculations to demonstrate a strategy for control the electronic ground state of indenyl cation.[6] We also report the experimental study on the direct detection of triplet cation species.



1-11

	R^1,R^2		R^1,R^2
1	H,H	**8**	4-$MeOC_6H_4$,H
2	Me,H	**9**	4-$NO_2C_6H_4$,H
3	OMe,H	**10**	4-$MeOC_6H_4$,NH_2
4	Ph,H	**11**	4-$MeOC_6H_4$,NO_2
5	NH_2,H		
6	CN,H		
7	NO_2,H		

substituents effects
singlet *vs* triplet

REFERENCES

[1] Baird, N. C. *J. Am. Chem. Soc.*, **1971**, *53* (4), 4941–4948.

[2] Ottosson, H. *Nat. Chem.* **2012**, *4* (12), 969–971.

[3] Breslow, R.; Chang, W.; Hill, R.; Wassermanlc, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112–1119.

[4] Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffmann, J. M.; Perchonock, C.; Wasserman, E.; Al., *J. Am. Chem. Soc.* **1973**, *95*, 3017–3018.

[5] Jiao, H.; Von Ragué Schleyer, P.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119* (30), 7075–7083.

[6] Takano, M.; Antol, I.; Abe, M. *Eur. J. Org. Chem.* **2024**, *27*, e2023012.

Photoswitching Transformations Triggered by Aromaticity Gain and Antiaromaticity Relief

Judy I. Wu, Joao V. Soares, Francisco A. Martins

University of Houston, Houston, TX, USA
E-mail: jiwu@central.uh.edu

Photoswitches are molecules that can show reversible changes in geometry and chemical property when irradiated by light. For many of such systems, the chromophore is an aromatic ring which can lose aromaticity or gain antiaromatic character in the lowest ππ* (or nπ*) state. We surmise that the concepts of excited-state aromaticity and antiaromaticity may be integral to many of these light-triggered transformations. Two classes of photoswitches, the dibenzoborole derivatives and a series of azobenzene derivatives, are discussed in this talk. Boroles are [4*n*] antiaromatic in the ground state and aromatic in the lowest ππ* state. Computations reveal that Lewis coordination to the empty *p* orbital of boron maybe modulated by a switch in (anti)aromatic character of the borole core. Azobenzenes are an important class of photoswitches—*E* to *Z* isomerization is triggered by light, and the reverse process can occur thermally. It was proposed the thermal *Z* to *E* isomerization of azobenzenes is facilitated by a crossing between the S_0 and T_1 (nπ*) state. We recognize that the T_1 of azobenzene involves a change in the (anti)aromatic character of the two arenes, and further discuss the role of spin-orbit coupling in this process.

Reversible Nonaromatic/Antiaromatic Molecular Switch by Graphene-Induced Planarization of Highly Curved π-Systems

Amir Karton

School of Science and Technology, University of New England, Armidale, NSW 2351, Australia
E-mail: amir.karton@une.edu.au

Highly curved π-systems exhibit altered electronic properties upon planarization. This has inspired intense research into inducing planarity by incorporating curved polycyclic aromatic hydrocarbons (PAHs) into rigid π-systems. Here, we present an alternative strategy: planarizing PAHs through adsorption onto a graphene monolayer. Dispersion-corrected density functional theory calculations show that strong π–π stacking interactions between graphene and PAHs enforce a planar structure, transforming nonaromatic PAHs into antiaromatic ones.[1,2] This reversible graphene-induced planarization offers a novel approach for a nonaromatic/antiaromatic molecular switch.

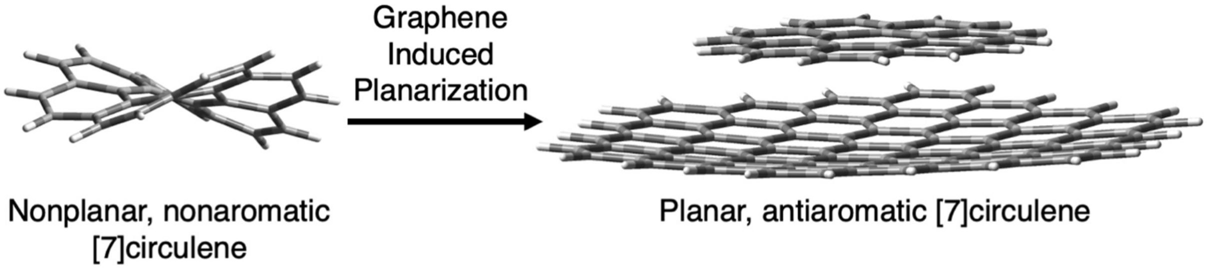


Figure 1. Planarization of negatively curved [7]circulene on a graphene monolayer.[2]

REFERENCES

[1] A. A. Kroeger, A. Karton, *J. Comput. Chem.*, **2022**, *43*, 96.
[2] A. Karton, *Chem. Phys.*, **2023**, *569*, 111853.

IL10

Unveiling (Anti)Aromaticity in the Excimer State

David Casanova

Donostia International Physics Center (DIPC), 20018 Donostia, Euskadi, Spain
E-mail: david.casanova@dipc.org

An excimer is an electronically excited state of a molecular homodimer, arising from the interaction between a ground-state molecule and an excited counterpart [1]. Although the properties of excimeric states and their involvement in a variety of photophysical and photochemical processes have been largely investigated, much less is known about their (anti)aromatic character or the role that excited state (anti)aromaticity might play in their formation. To elucidate these issues, in this talk I will delve into the intricate forces guiding the formation of the benzene excimer, scrutinizing its electron structure and (anti)aromatic characteristics. Our investigation extends to various facets [2], including excited states within molecular aggregates, the differences between singlet and triplet excimers, and the benzene-tricyanobenzene exciplex. Employing a diabatization strategy, we dissect electronic wave functions into localized excitations and ion-pair configurations. Notably, our analysis unveils the excimer's (anti)aromaticity as a composite of ground, excited, and ionic molecular states. We assert the benzene excimer's classification as antiaromatic, albeit with a lesser degree of antiaromaticity compared to the molecular excited singlet state. Furthermore, we present a model electronic Hamiltonian for the excimer state, serving as a foundational tool for extrapolating electronic Hamiltonians in molecular aggregates. Intriguingly, benzene multimers exhibit a nuanced (anti)aromatic character, with the central column manifesting antiaromaticity while the peripheries display aromatic behavior. Beyond its immediate focus on the excimer, our work establishes a versatile framework for elucidating and characterizing excited states within aggregates, promising broader implications for the field.

REFERENCES

[1] B. Stevens, *Nature*, **1961**, *192*, 725-727.
[2] A. Diaz-Andres, D. Casanova, *J. Phys. Chem. Lett.*, **2021**, *12*, 7400-7408.

Molecular Assembly and Function Inspired by Excited State Aromaticity

Yoshimitsu Itoh

Department of Chemistry and Biotechnology, The University of Tokyo
E-mail: itoh@chembio.t.u-tokyo.ac.jp

Controlling molecular assembly and functions using light is one of the most important topics in developing photo-responsive materials. Previously, we reported the first experimental demonstration of the energetics of excited-state aromaticity (Baird aromaticity) using thiophene-fused cyclooctatetraene derivatives [1]. This molecule undergoes ring inversion through a planar transition state. Under photo-irradiation, the inversion kinetics was significantly enhanced due to the emergence of aromaticity at the [4*n*]annulene core in the planar transition state. By comparing the activation barrier with and without photo-irradiation, we successfully estimated the energetic impact of Baird aromaticity to be 21–22 kcal/mol.

Inspired by this result, we reported several unique photofunctional molecular assemblies. For example, by using thiophene-fused cyclooctatetraene derivatives, we successfully made the first example of an alternating heterochiral supramolecular polymer [2]. As expected, this supramolecular polymerization can be initiated by photo-irradiation to the optically resolved monomer through racemization. Interestingly, we found that the polymerization can proceed only after the removal of the photo-irradiation, even the racemization was completed, due to the rapid fluttering motion of the monomer under photo-irradiation that prevent the monomers to interact with the growing end of the polymer [3]. In fact, we can temporary suspend the polymerization by irradiating light even after the polymerization was initiated. This is the first example of photo-suspendable supramolecular polymerization.

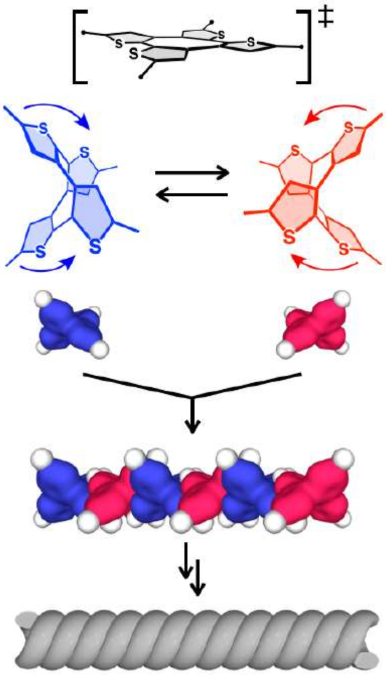


Figure 1. Functional molecular assembly of thiophene-fused cyclooctatetraene.

REFERENCES

[1] M. Ueda, K. Jorner, Y.-M. Sung, T. Mori, Q. Xiao, D. Kim, H. Ottosson, T. Aida, Y. Itoh, *Nature Commun*. **2017**, *8*, 346.

[2] M. Ueda, T. Aoki, T. Akiyama, T. Nakamuro, K. Yamashita, H. Yanagisawa, O. Nureki, M. Kikkawa, E.Nakamura, T. Aida, Y. Itoh, *J. Am. Chem. Soc*. **2021**, *143*, 5121–5126.

[3] T. Aoki, M. Ueda, T. Aida, Y. Itoh, *J. Am. Chem. Soc*. **2022**, *144*, 7080–7084.

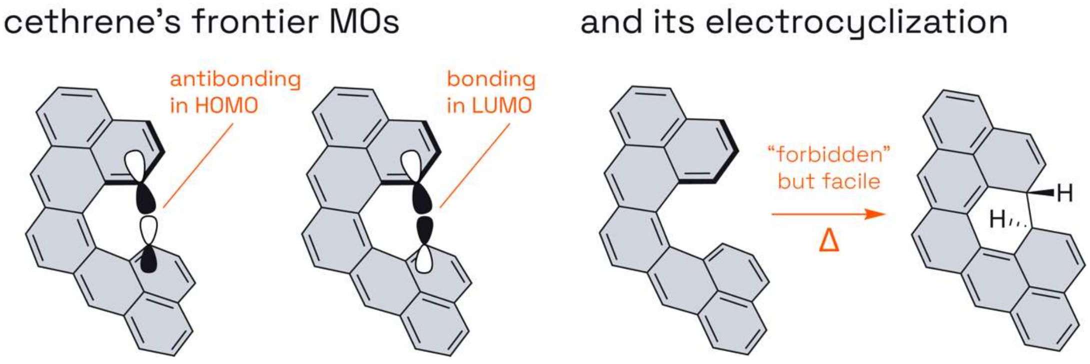
What Makes the Thermal, Formally Forbidden Electrocyclization of Cethrene so Facile?

Michal Juríček

Department of Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland
E-mail: michal.juricek@chem.uzh.ch

Thermal and photochemical pericyclic reactions are known to take place via aromatic transition states. The analysis of the aromaticity/antiaromaticity of their transition states complements the approach capitalizing on the Woodward−Hoffmann selection rules.[1,2] How about reactions that proceed both thermally and photochemically, that is, reactions where one of the pathways is formally symmetry-forbidden? An example of such reaction is electrocyclic ring-closure in singlet diradicaloid cethrene,[3–5] which proceeds both thermally and photochemically in a conrotatory mode. This feature is in stark contrast to most of other pericyclic reactions and places cethrene among a rare type of molecules like pleiadene and biphenalenylidene. In cethrene, the thermal conrotatory electrocyclization is formally a "forbidden" process according to the Woodward–Hoffmann rules. But because of its small HOMO–LUMO gap, the LUMO is partially occupied in the ground state and the thermal process thus displays a surprisingly low activation energy (~14 kcal mol^{-1}). We have shown that this is most likely due to decreasing the symmetry of the molecule along the reaction coordinate. Our most recent, unpublished studies indicate, however, that heavy-atom tunneling also significantly accelerates this reaction.

And what excited state aromaticity has got to do with it? Let's discuss on the symposium! :-)



REFERENCES

[1] M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, *Chem. Rev.*, **2014**, *114*, 5379–5425.

[2] R. C. Dougherty, *J. Am. Chem. Soc.*, **1971**, *93*, 7187–7201.

[3] P. Ravat, T. Šolomek, M. Rickhaus, D. Häussinger, M. Neuburger, M. Baumgarten, M. Juríček, *Angew. Chem. Int. Ed.*, **2016**, *55*, 1183–1186.

[4] T. Šolomek, P. Ravat, Z. Mou, M. Kertesz, M. Juríček, *J. Org. Chem.*, **2018**, *83*, 4769–4774.

[5] P. Ravat, T. Šolomek, D. Häussinger, O. Blacque, M. Juríček, *J. Am. Chem. Soc.*, **2018**, *140*, 10839–10847.

“*Apolar*” Diradicals with Charge Resonant Forms

Juan Casado

Department of Physical Chemistry, Faculty of Science, University of Málaga, 29071 Málaga, Spain
E-mail: casado@uma.es

Homosymmetric diradicals can be understood in the context of the 2 electrons 2 orbitals model (i.e., 2e-2o), by electron distribution in two singly occupied molecular orbitals (i.e., SOMO) of the same energy.[1] Heterosymmetric or asymmetric diradicals are known for quite long time, however, they have been scarcely studied compared to great number of symmetric cases. In a very simplistic way, one can see the asymmetric diradical with two SOMOs of different energy such as shown in Figure 1. We want to highlight, in the current communication, the role played by the ionic forms, which nicely emerge by applying the 2e-2o model, a relevance that becomes very important in the particular case of asymmetric diradicals when the two local ionic forms do not cancel each other in the charge resonant structure. The ionicity of diradicals has been considered in the analysis of their excited state properties in which imparts a decisive contribution in the appearance of photoluminescence.[2] This is important given that diradicals are mostly characterized by being efficient fluorescence quenchers and great efforts have been made to implement emission properties with magnetism in open-shell molecules, either monoradicals or diradicals.

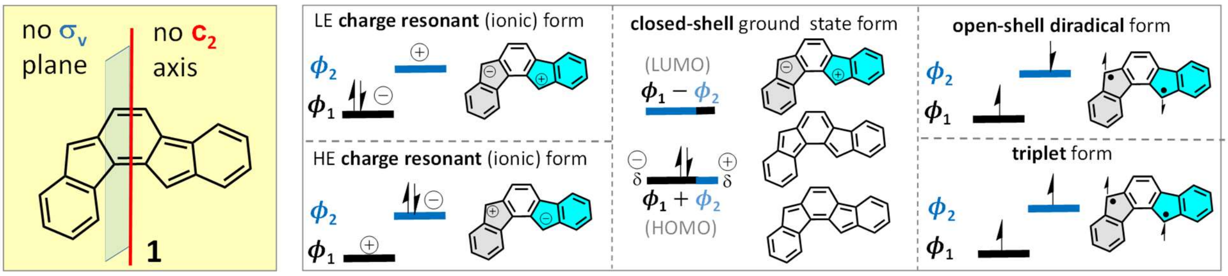


Figure 1. Anindenofluorene diradical studied, among others, in this presentation. Occupation, energies and distribution of the two electrons in the diradical state together with the main resonant structures.

In this communication, a series of diradicals will be presented all based on the formation of quinoidal pro-aromatic species able to evolve into the open-shell diradicals by the gaining of aromatic character. A dissection of the diradical wavefunction in the context of the 2 electrons 2 orbital model will be made from which the bonding, non-bonding and the ionic forms intuitively emerge. A series of quantum chemical calculations as well as the pertinent experiments will be carried out in order to highlight the role of the ionic forms in asymmetric diradicals.

REFERENCES

[1] L. Salem, C. Rowland, *Angew. Chem. Int. Ed.* **1972,** *11*, 92-111.
[2] A. Punzi, Y. Dai, ,C.N. Dibenedetto, E. Mesto, E. Schingaro, T. Ullrich, M. Striccoli, D.M. Guldi, F. Negri, G.M. Farinola, D. Blasi, D., *J. Am. Chem. Soc.*, **2023**, *145*, 20229−20241.

π-Conjugated Oligoradicaloids and Anions: Aromaticity, Magnetism, and Non-covalent Interactions

Marcin Stępień

Wydział Chemii, Uniwersytet Wrocławski, ul. F. Joliot-Curie 14, 50-383 Wrocław, POLAND
marcin.stepien@uwr.edu.pl

Charge and spin distribution in π-conjugated molecules depends in a complex fashion on the size topology of the ring system, placement of heteroatoms and molecular curvature. In large non-benzenoid systems, structure–property correlations become particularly intricate, showing effects of local and global aromaticity, mixed valence character, and non-equivalence of spin-interaction pathways. This talk will highlight some of the linear, macrocyclic, and 2D-fused systems recently developed by our group, with a focus on electron-deficient molecules obtained by peripheral fusion of naphthalimide subunits, and several pentannulated oligoradicaloid frameworks. We will show how these systems respond to changes in spin state and charge and how they can be used for coordination of cations and anions.

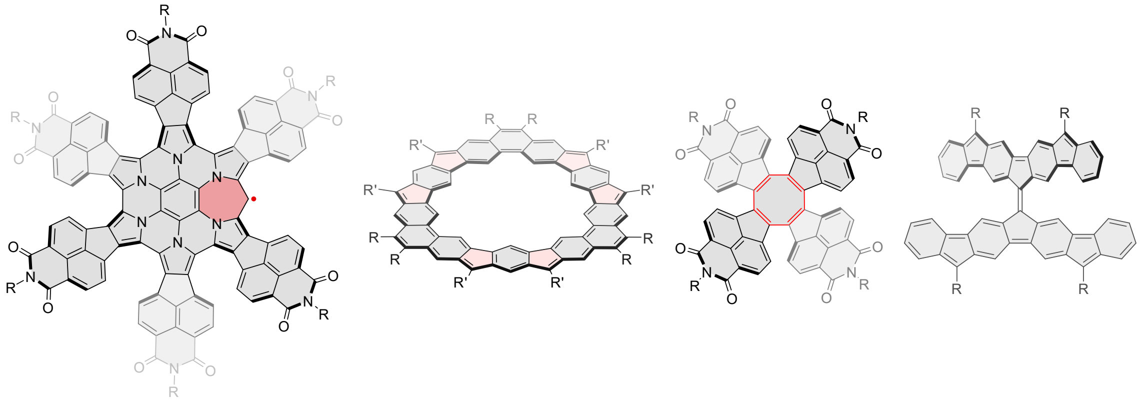


Figure 1

REFERENCES

1. L. Moshniaha, M. Żyła-Karwowska, P. J. Chmielewski, T. Lis, J. Cybińska, E. Gońka, J. Oschwald, T. Drewello, S. M. Rivero, J. Casado, M. Stępień, *J. Am. Chem. Soc.* **2020**, *142*, 3626–3635.
2. R. Kumar, P. J. Chmielewski, T. Lis, D. Volkmer, M. Stępień, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207486.
3. B. Prajapati, D.-K. Dang, P. J. Chmielewski, M. A. Majewski, T. Lis, C. J. Gómez-García, P. M. Zimmerman, M. Stępień, *Angew. Chem. Int. Ed.* **2021**, *60*, 22496–22504.
4. Prajapati, B.; Ambhore, M.; Dang, D.-K.; Chmielewski, P. J.; Lis, T.; Gómez-García, C. J.; Zimmerman, P. M.; Stępień, M. *Nat. Chem.* **2023**, *15*, 1541–1548.

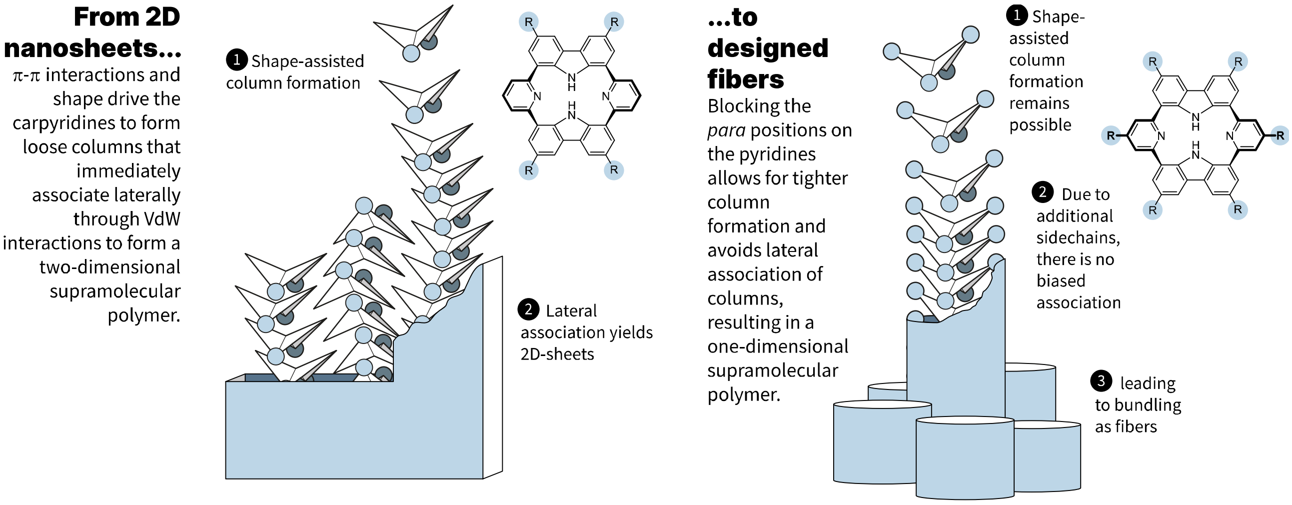
The Strategic Design of Curved Polyaromatics Opportunities for Organization

Michel Rickhaus

Department of Organic Chemistry, University of Geneva, Geneva, Switzerland

E-mail: michel.rickhaus@unige.ch

In a typical self-assembly setting, a core is decorated by suitable sidechains that induce supramolecular polymerization. While this approach has led to spectacular assemblies, the core has almost always been seen as a rigid platform from which to append functionality rather than as an integral, defining part of the unit. The core mission of our group is to investigate the role that molecular topography – the form– plays in the assembly process. With emphasis on synthetic solutions, we construct π-topographies that we think to be beneficial to supramolecular polymerization.



From 2D nanosheets... π-π interactions and shape drive the carpyridines to form loose columns that immediately associate laterally through VdW interactions to form a two-dimensional supramolecular polymer.

❶ Shape-assisted column formation

❷ Lateral association yields 2D-sheets

...to designed fibers Blocking the *para* positions on the pyridines allows for tighter column formation and avoids lateral association of columns, resulting in a one-dimensional supramolecular polymer.

❶ Shape-assisted column formation remains possible

❷ Due to additional sidechains, there is no biased association

❸ leading to bundling as fibers

We were recently[1-3] able to demonstrate that indeed, a simple negatively curved polyaromatic building block (about 2 nm wide, including sidechains) can instigate order on the micrometer(!) scale with astonishing aspect ratios (about 1:1000:100’000) and edge-definition by simple drop-casting (toluene). The paradigmatic shift is that these soft matter monolayered sheets/flakes are not held together by conventionally employed non-covalent interactions like hydrogen-, ionic, or coordinative bonding. By using curved π-systems, we succeeded in driving these assemblies to high order mainly by π–π interactions and demonstrated that rational tailoring yields different tertiary structures. I will share key (form)-concepts for π-systems to act as information carriers for curvature-induced self-assembly (CASA), insights into our current systems, and opportunities for “shape-shifting” molecular frameworks.

[1] J. F. Woods/L. Gallego, P. Pfister, M. Maaloum, A. Vargas Jentzsch, M. Rickhaus, *Nature Commun.* **2022**, *13*, 3681

[2] J. F. Woods, L. Gallego, A. Maisch, D. Renggli, C. Cuocci, O. Blacque, G. Steinfeld, A. Kaech, B. B. Spingler, A. Vargas Jentzsch, M. Rickhaus* *Nature Commun.* **2023**, 14, 4725

[3] L. Gallego, J. F. Woods, R. Butti, P. Szwedziak, A. Vargas Jentzsch*, M. Rickhaus* *Angew. Chem. Int Ed* **2024**, *63*, e202318879

Property Patterns in *N*-Heteropolycycles from Chemical Intuition and Machine Learning

Ganna Gryn'ova, Stiv Llenga

School of Chemistry, University of Birmingham, UK
E-mail: g.grynova@bham.ac.uk

As chemists, we pride ourselves on our ability to deduce chemical behaviour from the composition and structure of a molecule – an ability often referred to as chemical intuition. Yet, this skill is not without its limitations, particularly when the molecule in question is relatively large and complex. Such is the case of *N*-heteropolycycles (Fig. 1), widely used in organic electronics.

In this talk we will discuss our efforts toward better understanding the chemistry of these species and elucidating the property patterns across their chemical space. Using in-house datasets of diverse open- and closed-shell *N*-heteropolycycles, we will illustrate how dimensionality reduction, feature selection, and other machine-learning-inspired techniques allow discovering relationships between their structures and various chemical properties, including the extent of aromaticity and the ground state multiplicity. Finally, we will showcase how such relationships can be utilized in rational application-oriented design of new and improved systems.

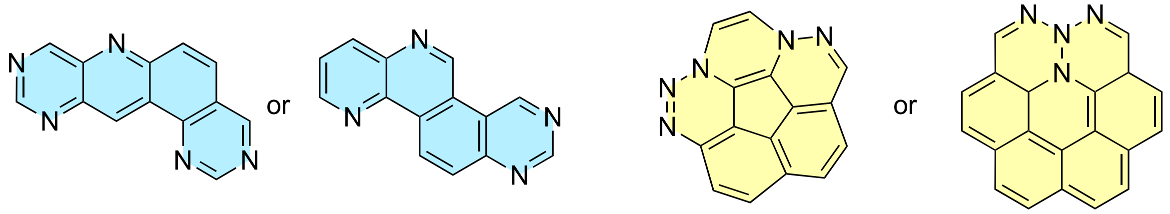


Figure 1. Which molecule in each pair has a higher HOMO-LUMO gap? What does your chemical intuition tell you?

Effect of Heteroatoms on Triplet State Energies and Antiaromaticity of Benzene and some Polycyclic Aromatic Compounds

Marija Baranac-Stojanović,[1] Milovan Stojanović,[2] Jovana Aleksić[2]

[1] *University of Belgrade – Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia*
[2] *University of Belgrade – Institute of Chemistry, Technology and Metallurgy – Center for Chemistry, Njegoševa 12, Belgrade, Serbia*
E-mail: mbaranac@chem.bg.ac.rs

The rules of (anti)aromaticity in the first excited triplet state are opposite to those in the ground state, which means that benzene and polycyclic aromatic hydrocarbons (PAHs) become antiaromatic upon $S_0 \rightarrow T_1$ excitation [1-3]. Incorporation of heteroatom(s) into these compounds is expected to affect triplet state energies and antiaromaticity. This issue has been investigated by means of theoretical calculations.

Calculations predict that in the case of benzene, naphthalene and anthracene containing one heteroatom (N, O, P, S and Si) the S_0-T_1 energy gaps are related to (anti)aromaticity degree, which is a function of spin density distribution. Systems with delocalized spin density are globally antiaromatic and have larger gaps. Localization of spin density to one ring in bi- and tricycles reduces global and creates local antiaromaticity, allowing other ring(s) to develop local aromaticity [4]. Particularly interesting are compounds containing silicon atom. They can be characterized as weakly aromatic in their triplet state (almost non-aromatic silacycle plus Hückel aromatic carbocycles). Varying the position of Si atom(s) in mono-, di-, tri- and tetracycles enables fine-tuning of triplet energies, which are related to the type of aromatic carbocyclic subunits and their degree of aromaticity [5].

REFERENCES

[1] N. C. Baird, *J. Am. Chem. Soc*, **1972**, *94*, 4941-4948.
[2] M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, *Chem. Rev.*, **2014**, *114*, 5379-5425.
[3] R. Papadakis, H. Ottosson, *Chem. Soc. Rev.,* **2015**, *44*, 6472-6493.
[4] M. Baranac-Stojanović, M. Stojanović, J. Aleksić, *New J. Chem.*, **2021**, *45*, 5060-5074.
[5] M. Baranac-Stojanović, M. Stojanović, J. Aleksić, *Chem. Asian J.*, **2022**, e202101261.

Harnessing Aromaticity for Molecular Materials Design a Computational Approach

Felix Plasser

Department of Chemistry, Loughborough University, LE11 3TU, United Kingdom
E-mail: f.plasser@lboro.ac.uk

Excited-state and charged-state (anti)aromaticity offer powerful design guidelines for modifying the optoelectronic properties of molecular materials. These guidelines can be applied on top of more traditional strategies such as donor/acceptor substitution or (de)planarisation to tune, e.g., redox potentials, excitation energies and Stokes shifts. However, it is often not clear how to characterise various types of aromaticity effectively. This talk presents strategies for characterising aromaticity and shows recent use cases in realistic molecular materials.

It is of particular interest how routine DFT and TDDFT computations can be used for characterising aromaticity. Here, we will contrast various approaches – geometric parameters, magnetic properties, delocalisation, and orbital shapes – in terms of their ease applicability and power to reveal non-trivial properties [1].

The approach will be first illustrated in the context of macrocycles with a formally antiaromatic ground state highlighting how those provide an ideal platform for many-electron accumulation [2]. Figure 1 presents an analysis of such systems using the visualisation of chemical shielding tensors (VIST) technique [3]. Subsequently, we will investigate the effect of (anti)aromaticity on excited-state proton transfer reactions.

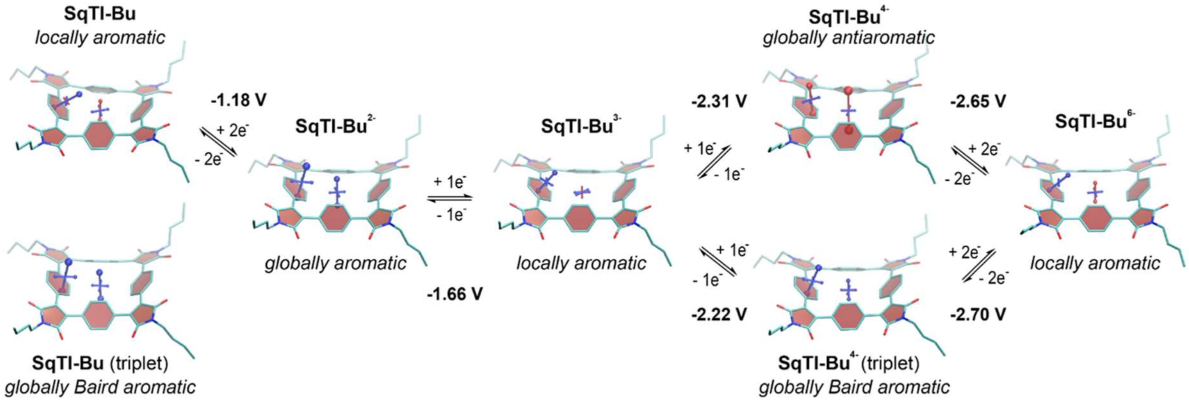


Figure 1. Analysis of multielectron reduction of a macrocyclic system using VIST plots.

REFERENCES

[1] Plasser, F. *Chemistry*, **2021**, 3, 532-549.

[2] Eder, S., Ding, B., Thornton, D. B., Sammut, D., White, A. J. P., Plasser, F., Stephens, I. E. L., Heeney, M., Mezzavilla, S., Glöcklhofer, F. *Angew Chemie Int Ed*, **2022**, 61, e202212623.

[3] Plasser, F., Glöcklhofer, F. *Eur J Org Chem*, **2021**, 2021, 2529–2539.

Perspectives in Excited-State Dynamics for Modeling Photoprocesses

Mario Barbatti

Aix Marseille University, CNRS, ICR, Marseille, France
Institut Universitaire de France, 75231, Paris, France
E-mail: mario.barbatti@univ-amu.fr Web: www.barbatti.org

Molecular excited electronic states are central to diverse fields, including biology, health, and technology. Upon photoexcitation, molecules are unequilibrated systems with multiple competing reaction pathways and time evolution from a few picoseconds to microseconds, depending on the processes involved. Moreover, they present highly complex electronic densities and often visit geometric conformations with multireference characters.

Mixed quantum-classical nonadiabatic dynamics help characterize these systems by providing insights into the physical-chemical phenomenon, delivering information for the deconvolution of experimental time-resolved data, and predicting properties before and after synthesis. However, these methods face challenges, including developing new functionalities, reliable research protocols, efficient computational methods, integration with experimental analysis, and a balanced description of the electronic correlation between states with different characters.

In recent years, my research group has proposed mixed quantum-classical nonadiabatic dynamics methods for treating open quantum systems, systems excited by incoherent light, and zero-point-energy leakage. We also created methodologies for propagating dynamics computing nonadiabatic couplings without wave functions and estimating the temperature of microcanonical quantum systems. I will overview some of these new approaches in this talk. I will also discuss case studies showing these methods in action.

Site-Specific Coordination Chemistry and Photophysical Behaviors by Hückel–Möbius Aromatic Switching

Juwon Oh[1] and Dongho Kim[2]

[1]*Department of Chemistry, Soonchunhyang University, Asan, 31538, Korea*
[2]*Department of Chemistry, Yonsei University, Seoul 03722, Korea*
E-mail: dongho@yonsei.ac.kr

In organometallic complexes featuring π-conjugated macrocyclic chelate ligands, conformational alterations exert a significant impact on the electronic interactions between the metal center and the ligands, thereby modulating the properties of the complexes. To explore this phenomenon, we scrutinized the metal–ligand interactions in hexaphyrin mono-Pd(II) complexes, namely Pd[28]M and Pd[26]H. These complexes manifest a redox-triggered transition between Hückel and Möbius aromaticity, accompanied by subsequent changes in molecular conformation, which profoundly influence their electronic structure and photophysical characteristics. In the Möbius aromatic Pd[28]M complex, the relatively weak metal–ligand interaction preserves the π electronic structure of the hexaphyrin ligand nearly intact. Consequently, this complex undergoes efficient intersystem crossing (ISC), facilitated by the heavy-atom effect of the Pd metal. Conversely, in the Hückel aromatic Pd[26]H complex, the substantial metal-ligand interaction induces ligand-to-metal charge-transfer (LMCT) dynamics in the excited state. These disparate metal-ligand electronic interactions were elucidated through comprehensive investigations employing time-resolved electronic and vibrational spectroscopies, complemented by time-dependent density functional theory (DFT) calculations. Our findings underscore the profound influence of Hückel–Möbius aromaticity switching on the modulation of metal-ligand interactions, offering an intriguing avenue for tailoring the properties of metal complexes. Moreover, this insight paves the way for fine-tuning metal–ligand interactions and the innovative design of functional organometallic materials. Furthermore, we present the synthesis of a Janus-type carbaporphyrin pseudo-dimer, characterized by antiaromatic features on one fused side and nonaromatic behavior on the other unfused side. To corroborate its unique characteristics, we prepared a tetraphenylene (TPE) linked bis-dibenzihomoporphyrin and a previously reported dibenzo[*g,p*]chrysene (DBC) linked bis-dicarbacorrole as controls. Through meticulous analyses encompassing 1H NMR spectral studies, single crystal X-ray diffraction analyses, and DFT calculations, we validated the mixed character of the Janus-type carbaporphyrin pseudo-dimer. Moreover, we highlight an intriguing facet of the Janus pseudo-dimer, wherein it can be transformed into a heterometallic complex. This transformation involves one side coordinating a Cu(III) center while the other stabilizes a BODIPY complex. This distinctive regiochemical reactivity underscores the versatility of carbaporphyrin dimers as frameworks, with electronic attributes and site-specific coordination chemistry finely controlled through asymmetry.

REFERENCES

[1] J. Oh, Y. M. Sung, Y. Hong, D. Kim, *Acc. Chem. Res*. **2018**, *51*, 1349–1358.

[2] Y. M. Sung, M.-C. Yoon, J. M. Lim, H. Rath, K. Naoda, A. Osuka, D. Kim, *Nat. Chem*. **2015**, *7*, 418–422.

[3] J. Kim, J. Oh, T. Soya, T. Yoneda, S. Park, M. Lim, A. Osuka, D. Kim, *Angew. Chem*. **2020**, *132*, 5167 – 5172; *Angew. Chem. Int. Ed*. **2020**, *59*, 5129–5134.

[4] J. Kim, J. Oh, S. Park, T. Yoneda, A. Osuka, M. Lim, D. Kim, *J. Am. Chem. Soc*. **2022**, *144*, 1, 582-589.

[5] H. He, J. Lee, Z. Zong, J. Kim, V.M. Lynch, J. Oh, D. Kim, J.L. Sessler, X.-S. Ke, *Nat. Commun*. **2024**, *15*, 2913, https://doi.org/10.1038/s41467-024-47239-y

ESA-Induced Reversible Photomelting of π-Stacked Soft Materials

Shohei Saito

Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, JAPAN
E-mail: saito.shohei@chem.sci.osaka-u.ac.jp

We have developed photoresponsive soft materials that shows ESA-induced reversible melting properties. These materials are composed of a PDMS polymer chain bearing COT-fused molecular units (FLAP) at both termini. The V-shaped molecules are columnarly π-stacked, and thus they work as a physical crosslink of the PDMS gels. On the other hand, under UV irradiation, the physical crosslink immediately melts by conformational planarization because of the excited-state aromaticity (ESA). Reversible and real-time viscoelasticity change was induced only by turning a UV light on and off. While various applications of the COT-fused flapping molecules (FLAP) have been reported (see Ref.), this presentation demonstrates the utility of FLAP π-stacks as a supramolecular photoresponsive element.

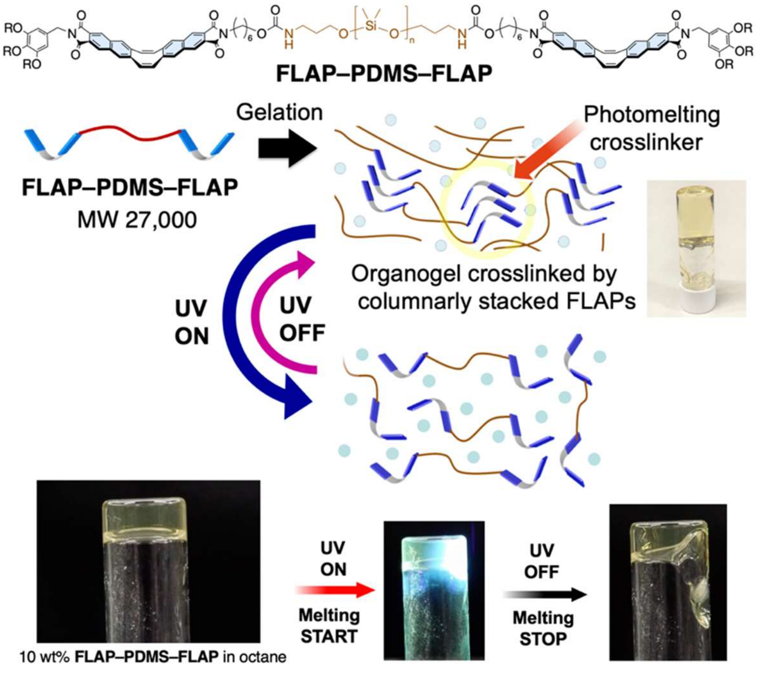


Figure 1. ESA of the π-stacked FLAP units triggers realtime photomelting of PDMS gel.

REFERENCES

References for FLAP: [1] First report (excited-state planarization, two-fold columnar π-stacking): *J. Am. Chem. Soc.* **2013**, *135*, 8842; [2] Light-melt adhesive: *Nat. Commun.* **2016**, *7*, 12094; [3] Molecular movie for a photoresponsive liquid crystal: *J. Am. Chem. Soc.* **2017**, *139*, 15792; [4] Fluorogenic viscosity probe: *Angew. Chem. Int. Ed.* **2020**, *59*, 16430; [5] Controlling the S_1 energy profile by excited-state aromaticity: *J. Am. Chem. Soc.* **2020**, *142*, 14985; [6] Monitoring polymer free volume by single-molecule spectroscopy: *J. Am. Chem. Soc.* **2021**, *143*, 14306; [7] Force probe for polymer physics: *Nat. Commun.* **2022**, *13*, 303; [8] Real-time stress imaging of gels/elatomers: *J. Am. Chem. Soc.* **2022**, *144*, 2804; *J. Am. Chem. Soc.* **2023**, *145*, 26799-26809.

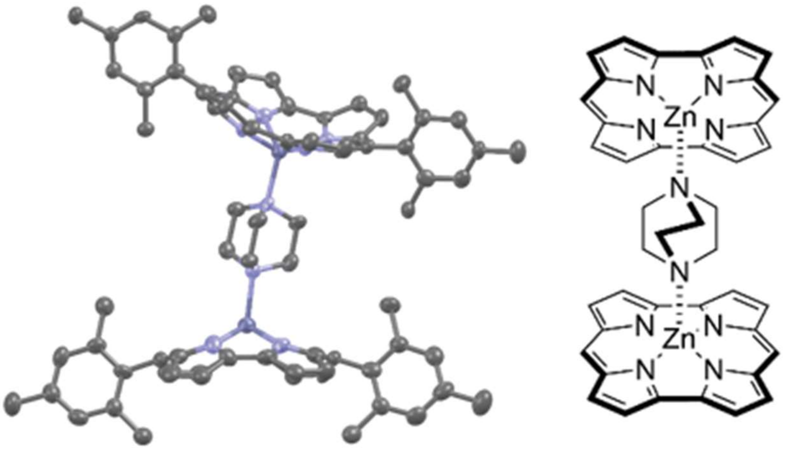
Manifestations of (Anti)aromaticity in Porphyrinoids Big and Small

Martin D. Peeks

School of Chemistry, University of New South Wales, UNSW Sydney NSW 2052 Australia
E-mail: m.peeks@unsw.edu.au

One of the most attractive features of aromaticity as a concept is that it seems to offer a common and simple origin for properties spanning stability, structure, magnetism, and photochemistry. By exploring the extremes of (anti)aromaticity we might evaluate to what extent chemists' "working definitions" of aromaticity compare to reality. We have recently shown, and will discuss, how aromaticity in oxidised porphyrin nanorings[1] is associated with some increase in electronic delocalization compared to non-aromatic rings,[2] but to a much lesser than might be seen in a smaller cycle.

In the much smaller size regime, we explore the differences between aromaticity and antiaromaticity by comparing porphyrin (aromatic) and its ring-contracted sibling norcorrole,[3,4] which has a 16 π-electron circuit and is antiaromatic. We have synthesised zinc norcorrole and its supramolecular complexes.[5] Surprisingly, zinc norcorrole has almost the same ring current strength (in nA/T) to that in zinc porphyrin, albeit of opposite sign. It has approximately 100-fold higher binding constants to N-containing axial ligands (DABCO crystal structure shown in Figure) than porphyrin, likely due to the norcorrole's extreme curvature, which exposes the norcorrole's Zn^{2+} for binding.



REFERENCES

[1] M. Jirásek, H. L. Anderson and M. D. Peeks, *Acc. Chem. Res.*, **2021**, *54*, 3241–3251.
[2] D. Bradley, B. K. Hillier and M. D. Peeks, *Chem. Commun.*, **2023**, *59*, 13438–13441.
[3] M. Bröring, S. Köhler and C. Kleeberg, *Angew. Chem. Int. Ed.*, **2008**, *47*, 5658–5660.
[4] T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi and H. Shinokubo, *Angew. Chem. Int. Ed.*, **2012**, *51*, 8542–8545.
[5] D. Bradley, R. Tian, M. Bhadbhade, L. Macreadie, C. Sarowar and M. D. Peeks, *Inorg Chem*, **2024**, DOI:10.1021/acs.inorgchem.4c01146.

Molecular Engineering Using Croconic Acid

Michael Pittelkow

Department of Chemistry, University of Copenhagen,
E-mail: pittel@chem.ku.dk

In this presentation, I will discuss the synthesis of croconic acid derivatives, and describe how we have used them in a variety of applications: as NIR absorbers (for laser welding of plastic),[1-3] as anion binders,[4] as UV-absorbers (for sunscreen) and as a novel building block for cyclic carbon-rich structures.[5]

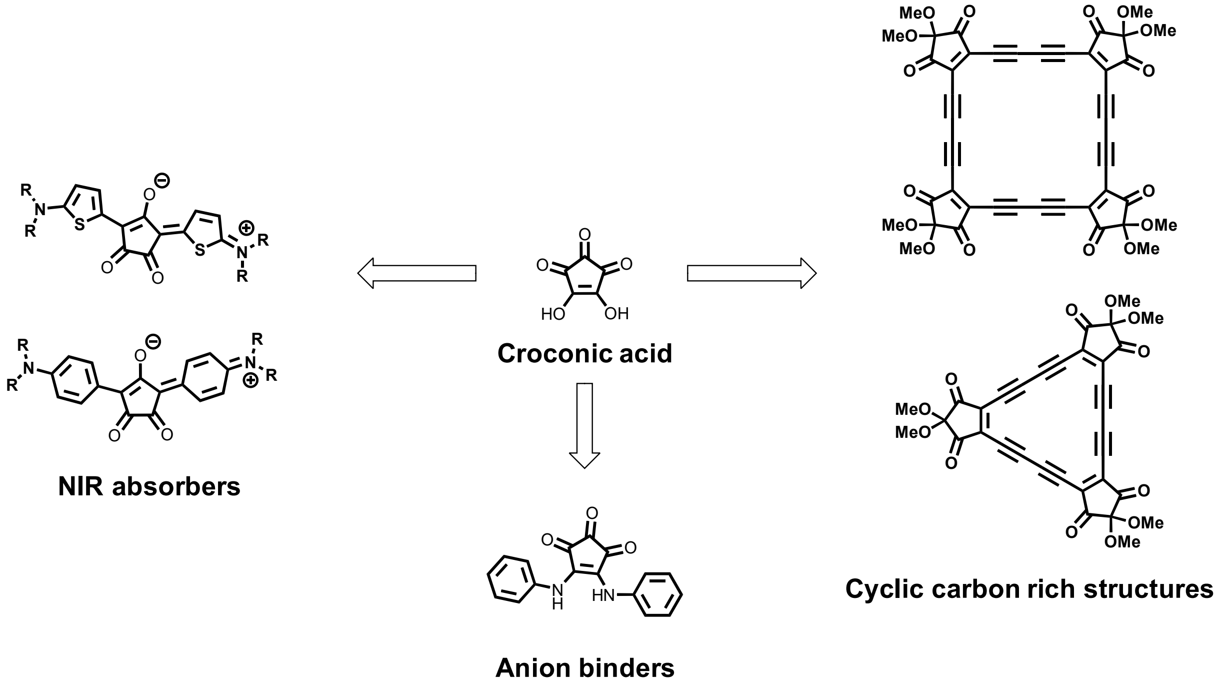


Figure 1. Directions in croconic acid chemistry.

REFERENCES

[1] H. Ø. Bak, T. Brock-Nannestad, M. Pittelkow, WO 2014/166506.
[2] A. Jeppesen, B. E. Nielsen, T. Brock-Nannestad, M. Pittelkow, WO 2019/154974 A1.
[3] B. E Nielsen, PhD Thesis, UCPH, 2021.
[4] A. Jeppesen, B. E. Nielsen, D. Larsen, O. M. Akselsen, T. I. Soelling, T. Brock-Nannestad, M. Pittelkow, *Org. Biomol. Chem.*, **2017**, 15, 2784-2790.
[5] Y. Lie, G. Baryshnikov, M. Pittelkow, *Manuscript in preparation*, 2024.

Unusual Conjugation Topologies and their Impact on Delocalization within π-Electron Materials

John D. Tovar

Johns Hopkins University, Department of Chemistry, Department of Materials Science and Engineering, and Institute for NanoBioTechnology, 3400 N. Charles St. (NCB 316)
E-mail: jtovar1@jhu.edu

The palate used to create high performance organic electronic materials is rich in aromatic building blocks, including numerous variations of benzene, thiophene and pyrrole rings. Although these materials can be photoexcited leading to subsequent exciton migration or subjected to redox processes to inject charge carriers, they all are formed from "static" ground electronic states. This presentation will highlight two new avenues in conjugated material design. The first entails the use of photoswitchable structural units that undergo electrocyclizations leading to subtle but electronically dramatic alterations of π-electron conjugation topology. This is achieved through the photochemical creation and disruption of local aromatic substructures along the polymer backbone as a way to externally attenuate electronic properties thus providing a way to toggle between two distinct electronic ground states. The second will introduce prospects for radial topologies and their impact on linear conjugated polymer electronics. Our understanding of cyclic conjugation remains far behind the much more studied linear π electron delocalization, especially in exotic systems maintaining both cyclic and linear conjugation pathways. We describe the synthesis and electronic properties of small-molecule and polymeric cycloparaphenylenes (CPPs) as part of extended linearly π-conjugated frameworks, showing the unique nature of hybrid radial and linear π electron delocalization operative in these new conjugation pathways.

REFERENCES

[1] G. M. Peters, J. D. Tovar, *J. Am. Chem. Soc.*, **2019**, *141*, 3146-3152.

[2] G. M. Peters, G. Grover, R. Maust, C. Colwell, H. Bates, W. Edgell, R. Jasti, M. Kertesz, J. D. Tovar, *J. Am. Chem. Soc.*, **2020**, *142*, 2293-2300.

[3] E. Peterson, R. L. Maust, R. Jasti, M. Kertesz, J. D. Tovar, *J. Am. Chem. Soc.*, **2022**, *144*, 4611-4622.

[4] N. P. Adams and J. D. Tovar, "Torsional influences on cross-conjugated thieno[3,4-b]thiophene photochromes," submitted.

Geometry-Based Probing of Excited-State Aromaticity and Antiaromaticity

Enrique M. Arpa and Bo Durbeej

Division of Theoretical Chemistry, IFM, Linköping University, SE-581 83 Linköping, Sweden
E-mail: bo.durbeej@liu.se

Excited-state aromaticity (ESA) and antiaromaticity (ESAA) are by now well-established concepts for rationalizing photophysical properties and photochemical reactivities of cyclic, conjugated molecules. However, a hurdle for the use of the ESA and ESAA concepts as rational design tools is that both the experimental measurements and the quantum chemical calculations with which aromatic and antiaromatic features are usually probed, are generally more difficult to perform for excited states than for ground states. Against this background, I will here describe our recent efforts to reliably probe ESA and ESAA on geometric grounds by means of the harmonic oscillator model of aromaticity (HOMA) index, which possibly offers the easiest route to computational quantification of aromaticity. In particular, I will show that a new parameterization of HOMA outperforms the standard parameterization of HOMA in describing the ESA and ESAA of a large set of carbocyclic and heterocyclic compounds, as assessed by the degree of agreement attained with other types of aromaticity indices considered more accurate [1]. Furthermore, I will present results demonstrating that the same parameterization strategy also improves the description of ground-state aromaticity and antiaromaticity in a similar way [2].

REFERENCES

[1] E. M. Arpa and B. Durbeej, *Phys. Chem. Chem. Phys*., **2023**, *25*, 16763.

[2] E. M. Arpa and B. Durbeej, To be submitted.

Molecular Carbons with Different Topologies and Size

Chunyan Chi

Department of Chemistry, National University of Singapore, Singapore
E-mail: chmcc@nus.edu.sg

Carbon-based nanostructures have shown revolutionary influence in the area of chemistry, physics and materials science. Recent efforts have been focused on novel topological structures of sp^2-carbons such as carbon nanohoops, nanobelts, molecular cages, and open-shell nanographenes, which provoked new chemistry and materials. However, synthesis of this kind of molecules is extremely challenging mainly due to strain or intrinsic high reactivity. Another issue is that most of these carbon nanostructures have a localized aromatic character; that means, the π-electrons are not globally delocalized along the backbone, which limits their optical and electronic properties and applications. Herein, the synthesis of a series of novel π-structures with different topologies will be introduced, and their physical properties, aromaticity and diradical character will be discussed.[1-7] Some structures are shown in Figure 1.

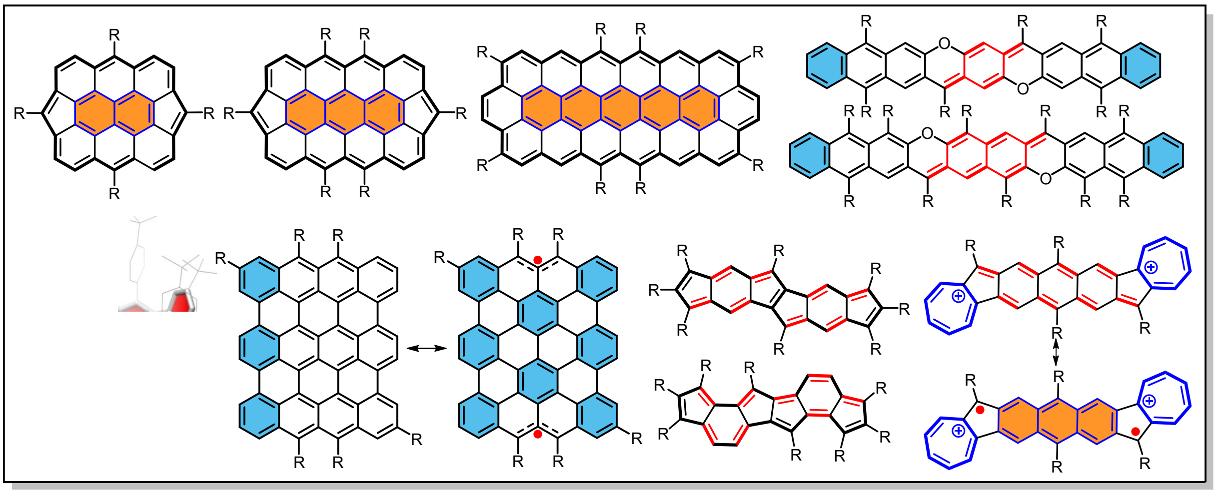


Figure 1. Some examples of π-structures made in Chi group.

REFERENCES

[1] T. Xu, X. Hou, Y. Han, H. Wei, Z. Li, C. Chi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304937.

[2] Q. Jiang, H. Wei, X. Hou, C. Chi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202306938.

[3] A. Ong, T. Tao, Q. Jiang, Y. Han, Y. Ou, K.-W. Huang, C. Chi, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209286.

[4] T. Xu, Y. Han, Z. Shen, X. Hou, Q. Jiang, W. Zeng, P. W. Ng, C. Chi, *J. Am. Chem. Soc.* **2021**, 143, 20562-20568.

[5] J.-J. Shen, Y. Han, S. Dong, H. Phan, T. S. Herng, T. Xu, J. Ding, C. Chi, *Angew. Chem. Int. Ed.* **2021**, *60*, 4464-4469.

[6] Y. Han, S. Dong, J. Shao, W. Fan, C. Chi, *Angew. Chem. Int. Ed.* **2021**, *60*, 2658-2662.

[7] S. Dong, T. Y. Gopalakrishna, Y. Han, H. Phan, T. Tao, Y. Ni, G. Liu, C. Chi, *J. Am. Chem. Soc.* **2019**, *141*, 62-66.

Helitwistacenes and Furan Macrocycles: Inversion of Circularly Polarized Light Emission and Excited-State Global Aromaticity

Ori Gidron

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Edmond J. Safra Campus, 9190401, Jerusalem, Israel
E-mail: ori.gidron@mail.huji.ac.il

The excited state properties of aromatic materials are strongly affected by their structure. In the current work, I will focus on the investigation of the excited-state properties in two systems: Helitwistacenes and furan macrocycles.

In the first part, I will discuss the combination of helicene with lateral helicity and twistacene with longitudinal helicity, with tunable twisting. We found that both the absorption and emission of circularly polarized light in these molecules exhibits sign inversion when subjected to external factors such as different solvent polarities.[1] We also found that twisting affects the excited state properties such as intersystem crossing.[2]

In the second part, I will discuss the excited state properties in the first series of furan macrocycles.[3] The alternating number of π-electrons (4n+2 and 4n) in these series, results in alternating global (anti)aromaticity.[4] Our recent transient-absorption studies indicate that this alternating excited state aromaticity behavior continues in higher excited states.

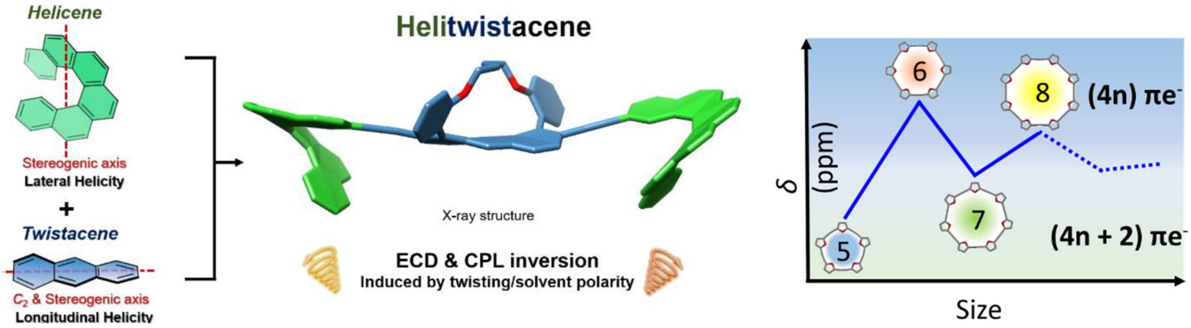


Figure 1. Left: Combining lateral and longitudinal helicity to form helitwistacenes with a tunable twist. Right: Alternating global (anti)aromaticity in furan macrocycles.

REFERENCES

[1] I. Shioukhi, H. Batchu, G. Schwartz, L. Minion, Y. Deree, B. Bogoslavsky, L. W. Shimon, L., J. Wade, R. Hoffman, M. J. Fuchter, G. Markovich, O. Gidron, *Angew. Chem. Int. Ed.* **2024**, e202319318.

[2] A. Bedi, A. Manor Armon, Y. Diskin Posner, B. Bogoslavsky, O. Gidron, *Nat. Commun*. **2022**, *13*, 451.

[3] O. Dishi, Y. Rahav, O. Gidron *Chem. Commun.* **2024** *60, 522.*

[4]. Y. Rahav, S. Rajagopalan, O. Dishi, B. Bogoslavsky, O. Gidron, *Commun. Chem.* **2023**, *6,* 100.

Aromaticity in Multicyclic Macrocycles and its Change in the Triplet State

Juwon Oh[1] and Dongho Kim[2]

[1]*Department of Chemistry, Soonchunhyang University, Asan, 31538, Korea*
[2]*Department of Chemistry, Yonsei University, Seoul 03722, Korea*
E-mail: juwoh933@sch.ac.kr

Aromaticity is one of the key fundamental concepts in organic chemistry. As cyclic π-conjugated molecules increase in size, local or global cyclic π-conjugation can form, which has a significant effect on their π-electron structures and aromaticity. This further provides important information for understanding the characteristics and designing functional macrocyclic compounds. From this perspective, research on aromaticity has intensively focused on monocyclic [n]annulene-like systems or polycyclic aromatic hydrocarbons.[1] Recently, there has been growing interest in the π-electronic structure and aromaticity in fully π-conjugated multiple macrocyclic systems.[2,3] For fully π-conjugated multicyclic macrocycles, there are many possibilities in a formation of π-delocalization, and we should also consider that the electronic coupling between the individual constitutional macrocycles would lead to unique electronic structures and aromaticity.[4] Herein, we have focused on fully π-conjugated multicyclic porphyrinoids for investigating their aromaticity in their multicyclic macrocycle structures with a change of aromaticity in the triplet state. The geometry, aromaticity, and electronic properties of these macrocycles at different oxidation states were also scrutinized experimentally and theoretically, revealing how the constitutional macrocycles interact with each other and contribute to unique aromatic/antiaromatic character. This study provides new insights into the complex aromaticity in π-conjugated multicyclic macrocycle systems.

REFERENCES

[1] J. Oh, Y. M. Sung, Y. Hong, D. Kim, *Acc. Chem. Res*. **2018**, *51*, 1349–1358.

[2] W. Y. Cha, et. al. *Nat. Chem*. **2017**, *8*, 1243-1248.

[3] Y. Ni, T. Y. Copalakrishna, H. Phan, T. Kim, T. S. Herng, Y. Han, T. Tao, J. Ding, D. Kim, J. Wu, *Nat. Chem*. **2020**, *12*, 242-248.

[4] L. Ren, Y. Han, Y. Hou, Y. Ni, Y. Zou, T. Jiao, J. Wu, *J. Am. Chem. Soc.* **2023**, *145*, 12398-12406.

Photophysical Characteristic and Photoreactivity of Coronene and Corannulene Derivatives in Solution and the Solid State

Anna D. Gudmundsdottir

University of Cincinnati, 821 Rieveschl Hall, PO Box 210172, Cincinnati, Ohio 45221, USA
E-mail: annag@uc.edu

Over the past two decades corannulene and its derivatives have found numerous applications in the area of host-guest chemistry, metal-organic frameworks, and porous organic polymers, to name a few. Despite these broad applications, there is a lack of detailed understanding at the molecular level regarding how curvature influences their chemical and physical properties. Corannulene and its derivatives provide us with a curved aromatic platform which remains largely unexplored with regards to the reactions that are well-documented for planar aromatic hydrocarbons. Corannulene and its derivatives present a unique curved aromatic structure that contrasts with reactions of planar aromatic hydrocarbons, making it an intriguing area for further exploration. Herein, we report the photophysical properties and photoreactivity of corannulene, nitro-corannulene and coronene in solution and the solid state. Ultrafast transient spectroscopy and nanosecond laser flash photolysis in solution and the solid state revealed that coronene reacts differently in solution than corannulene derivatives, whereas in the solid state they have similar properties. Analysis of the aromaticity of the triplet configuration of the corannulene and coronene derivatives assists in understanding how their structure affects their physical properties and reactivity.

Exploiting Excited-State Aromaticity for Tuning the Excited State Energies

Mercedes Alonso[1], Luis Leyva-Parra[2], Irene Casademont-Reig[1], Eline Desmedt[1], Freija De Vleeschower[1], William Tiznado[2]

[1] *Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB), Brussels, Belgium*
[2] *Centro de Química Teórica & Computacional, Universidad Andrés Bello, Santiago, Chile*
E-mail: mercedes.alonso.giner@vub.be

Excited-state aromaticity has been invoked as a driving force in photochemistry [1], but solid computational assessments are required to render the Baird-aromaticity concept as a useful tool to tune the energies of molecular excited states. In this talk, I will introduce different measures of aromaticity to assess ground- and excited-state aromaticity in polycyclic aromatic hydrocarbons. Such systems pose a challenge for conventional magnetic descriptors due to the superposition of local magnetic responses [2]. Recently, we established a meticulous analysis of the magnetically induced currents, which allows for determining the most appropriate combination of ring current circuits (local, semilocal and global) in both the ground (S_0) and lowest triplet (T_1) states [3]. Our aromaticity study is complemented with advanced electronic and geometric descriptors to consider different aspects of aromaticity, particularly important for the evaluation of excited-state aromaticity due to the lack of studies concerning the performance of aromaticity indices on excited states. These descriptors are combined to unveil the impact of ground- and excited-state aromaticity on the singlet-triplet energy difference [4] and devise fulvene chromophores for singlet fission with enhanced stability assisted by inverse design.

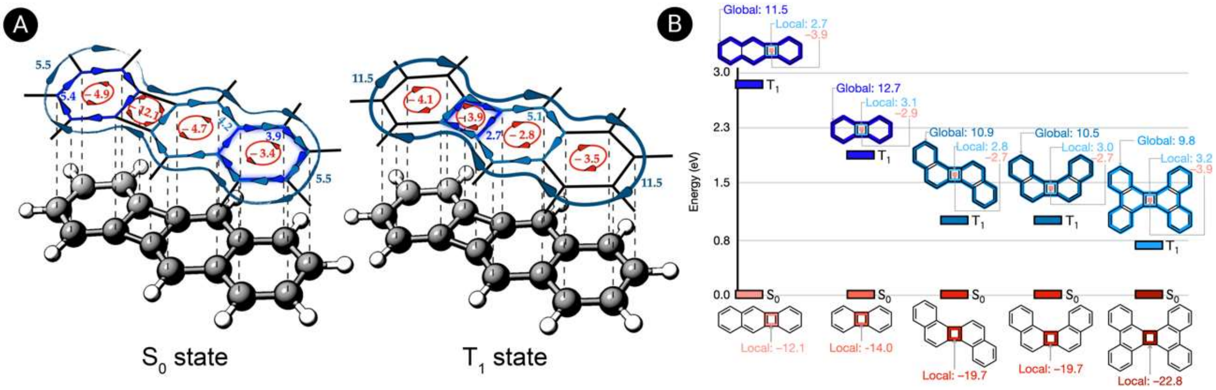


Figure 1. Schematic representation of local, semilocal and global currents in PAHs with their ring current strengths (A) and the connection with the singlet-triplet energy difference (B).

REFERENCES

[1] J. Yan, T. Slanina, J. Bergman, H. Ottosson, *Chem. Eur. J.* **2023**, *29*, e202203748.

[2] D. Inostroza, V. García, O. Yañez, J. J. Torres-Vega, *et al*, *New J. Chem.* **2021**, *45*, 8345-8351.

[3] L. Leyva-Parra, R. Pino-Rios, D. Inostroza, M. Solà, M. Alonso, W. Tiznado, *Chem. Eur. J.* **2024**, *30*, e202302415.

[4] L. Leyva-Parra, I. Casademont-Reig, R. Pino-Rios, L. Ruiz, M. Alonso, W. Tiznado, *ChemPhysChem*, **2024**, *Early view*, e202400271.

IL31

Efficient Assessment of Aromaticity through Electron-Delocalization Metrics

Eduard Matito,[1,2] Joan Grèbol,[1,3] Luis Soriano-Agueda,[1] Pedro Salvador[3]

[1] *Donostia International Physics Center (DIPC), Donostia, Euskadi, Spain*
[2] *Ikerbasque Foundation, Bilbao, Euskadi, Spain*
[3] *Institute of Computational Chemistry and Catalysis, University of Girona, Girona, Catalonia, Spain.*
E-mail: ematito@dipc.org

Electronic aromaticity indices focus on electron delocalization as the primal signature of aromaticity and are among the most reliable measures for assessing it [1]. They depend on how we define an atomic partition, *i.e.*, on how we define an *atom-in-the-molecule* (AIM). Real-space atomic partitions are often preferred for their accuracy, however, they come with two significant drawbacks: high computational cost and an increase in numerical errors as the size of the ring grows [2]. Consequently, indices link I_{ring} or MCI are restricted to medium-sized molecules and relatively small rings (up to 12-14 atoms). This limitation significantly impedes the study of aromaticity in large conjugated systems, such as porphyrins and nanorings, which prompted us to develop indices more robust to numerical errors [2-4].

In this talk, we explore the use of AIMs based on Hilbert-space partitions and introduce three *robust* Hilbert-space partitions—meta-Löwdin, Natural Atomic Orbitals (NAO), and Intrinsic Atomic Orbitals (IAO)—that combine the reliability of real-space partitions without their associated disadvantages [5]. These partitions are devoid of numerical errors and are capable of effectively replacing the quantum theory of atoms in molecules (QTAIM) partition [6] to evaluate the aromatic character of molecules. We also introduce ESIpy, an open-source code to compute aromaticity indices from Hilbert-space partitions [7]. Finally, we analyze the performance of various electron-delocalization measures for assessing aromaticity.

REFERENCES

[1] F. Feixas, E. Matito, J. Poater, M. Solà, *Chem. Soc. Rev.* **2015**, *44*, 6434.

[2] E. Matito, *Phys. Chem. Chem. Phys.* **2016**, *18*, 11839.

[3] C. García-Fernández, et al. *J. Phys. Chem. C* **2017**, *121*, 27118.

[4] I. Casademont-Reig, T. Woller, J. Contreras-García, M. Alonso, M. Torrent-Succarrat, E. Matito, *Phys. Chem. Chem. Phys.* **2018**, *20*, 2787.

[5] J. Grèbol, E. Matito, P. Salvador, *Chem. Eur. J.*, **accepted**.

[6] R.F.W. Bader, *A Theory of Atoms in Molecules. A Quantum Theory.* Oxford University Press, **1990**.

[7] https://github.com/jgrebol/ESIpy

Aromaticity and Antiaromaticity in Low-Lying Electronic States Other than S_1 and T_1

Peter B. Karadakov

Department of Chemistry, University of York, Heslington, York YO10 5DD, U.K.
E-mail: peter.karadakov@york.ac.uk

Low-lying electronic states of cyclic conjugated hydrocarbons other than T_1 (which is addressed by Baird's rule) and S_1 can also exhibit magnetic properties such as nucleus-independent chemical shifts (NICS) and variations in off-nucleus isotropic magnetic shielding, $\sigma_{\text{iso}}(\mathbf{r}) = ⅓[\sigma_{xx}(\mathbf{r}) + \sigma_{yy}(\mathbf{r}) + \sigma_{zz}(\mathbf{r})]$, within molecular space, that suggest certain levels of aromaticity or antiaromaticity. Calculations utilizing state-optimized full π space complete-active-space self-consistent field wavefunctions involving gauge-including atomic orbitals (CASSCF-GIAO) have shown that the second singlet excited states (S_2) of benzene [1], regular octagonal cyclooctatetraene [2] and naphthalene [3], corresponding to vertical excitations, exhibit NICS values that are significantly more negative than those for the S_0 state of benzene; the interior of the carbon framework in these states is well-shielded all over, but the carbon-hydrogen bonds are less shielded than in the corresponding S_0 states. While it is tempting to classify these S_2 states as aromatic, it is questionable whether, based on comparisons between NICS values, it would be justified to assume that these S_2 states are more aromatic than the S_0 state of benzene. It should be noted that state-optimized full π space CASSCF-GIAO calculations on anthracene also predict a "strongly aromatic" vertical singlet excited state, however, in contrast to naphthalene, this state is S_1, whereas the lowest singlet antiaromatic state is S_2 [3]. This talk discusses the properties of these low-lying "strongly aromatic" vertical excited states and their importance when analyzing excited state aromaticity reversals.

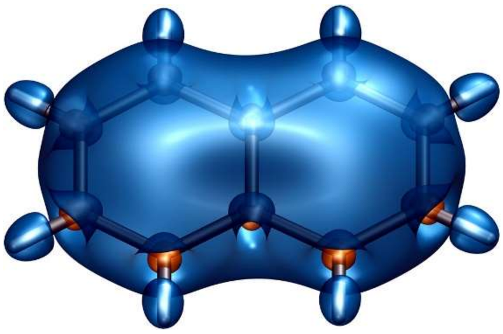


Figure 1. Isotropic shielding isosurfaces for the S_2 states of naphthalene at $\sigma_{\text{iso}}(\mathbf{r}) = \pm 16$ ppm (positive/negative isovalues in blue/orange), CASSCF(10,10)-GIAO/6-311+G(d) results [3].

REFERENCES

[1] P.B. Karadakov, P. Hearnshaw, K. E. Horner, *J. Org. Chem.*, **2016**, *81*, 11346-11352.
[2] P.B. Karadakov, N. Preston, *Phys. Chem. Chem. Phys.*, **2021**, 24750-24756.
[3] P.B. Karadakov, M. A. H. Al-Yassiri, *J. Phys. Chem. A*, **2023**, *127*, 3148-3162.

Controlling Non-Linear Photophysical Processes and Photochemical Transformations Using Aromaticity Reversal in Heterocyclic Thioamides

A. Jean-Luc Ayitou

Department of Chemistry, University of Illinois Chicago, Chicago, IL 60607, USA.

E-mail: aayitou@uic.edu

Aromaticity is an intrinsic property of π-conjugated annulenes and their heterocyclic congeners, and this feature/property has been used to explain favorable and unfavorable thermal chemical transformations. Light-initiated conversion of pro/non-aromatics to excited-state aromatic systems (or vice-versa) could help in rapid interconversion from one reactive spin state to the other. Hence, creating novel light-harvesting systems that can become metastable excited state aromatic species could open new horizons in photophysical energy transfer and photochemical transformations. Our laboratory is currently focused on creating a library of new pro-aromatic organic heterocyclic thioamides, which are prepared through a process of "chemical perturbation" that allows the modification of the local and global resonance energy stabilization of their molecular framework. Fundamentally, our main objective is to exploit the unique aromaticity of these thioamides for applications that lie at the interface of solar energy conversion/modulation, non-linear photophysical processes, and photochemical reactions. Practically, the thioamides of our interest are employed as photometric sensors of heavy metal ions and photo-auxiliaries for chemical transformations and drug discovery.

My presentation will detail the synthesis of several heterocyclic thioamides with modulable aromaticity. I will also discuss the photophysics of these compounds, which can be used as light-harvesting antennae for triplet photochemical/photophysical processes. Lastly, I will highlight our ongoing effort to tame the unique properties of the thioamide compounds for drug discovery and synergistic medicinal applications.

Chasing (Anti)aromaticity Effects in the Ground and Excited States with Molecular Switches

Gábor London

Institute of Organic Chemistry, HUN-REN Research Centre for Natural Sciences,
1117 Budapest, Hungary
E-mail: london.gabor@ttk.hu

Dithienylethenes are a popular class of molecular switches both for applications and fundamental studies. Most of them contain the same type of ethene bridge: an isolated double bond embedded in a five-membered ring. Molecules having ethene bridges in electronically more complex environments have been the focus of less investigations.

Our research interests include the study of dithienylethenes interfaced with rings and ring systems that have (anti)aromatic character [1-3]. With such structures fundamental effects of (anti)aromaticity on photoswitching processes can be studied, and, possibly, novel applications could be developed.

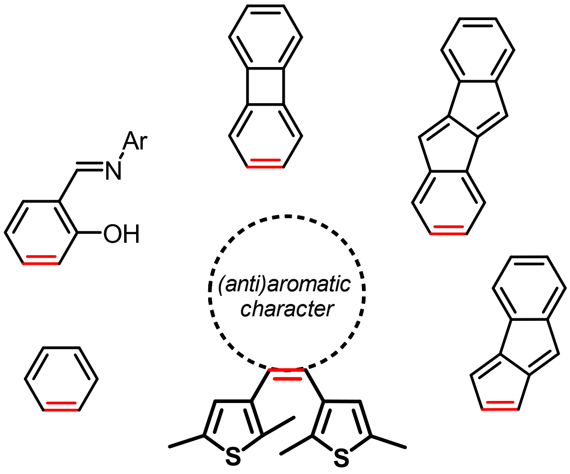


Figure 1. Dithienylethenes with conjugated backbones.

REFERENCES

[1] B. Oruganti, P. P. Kalapos, V. Bhargav, G. London, B. Durbeej, *J. Am. Chem Soc.*, **2020**, *142*, 13941−13953.

[2] P. P. Kalapos, P. J. Mayer, T. Gazdag, A. Demeter, B. Oruganti, B. Durbeej, G. London, *J. Org. Chem.*, **2022**, *87*, 9532−9542.

[3] P. P. Kalapos, A. Kunfi, M. M. Bogner, T. Holczbauer, M. A. Kochman, B. Durbeej, G. London, *J. Org. Chem.*, **2024**, *89*, 16−26.

Uncovering Novel Photochemical Reactivity From the Excited State

Jayaraman Sivaguru

Center for Photochemical Sciences and Department of Chemistry,
Bowling Green State University, Bowling Green OH, 43403. United States.

E-mail: sivagj@bgsu.edu

Manipulating dynamics in the excited state provide avenues to develop novel photochemical reactivity there by offering access to build complex molecular architectures often with unique stereochemistry. A fundamental challenge in developing such processes involve controlling excited state reactivity of organic molecules due to the short lifetimes of the reactive species. We have been interested in developing strategies for controlling the excited state reactivity as well as stereochemistry of products where the reactants reach the excited state(s) upon UV and/or visible light irradiations. This presentation will highlight our methodology of employing UV and/or visible light for performing photoreactions with excellent control over reactivity and selectivity. Based on photochemical and photophysical investigations, the presentation will highlight novel excited state reactivity of organic molecules, how to influence their excited state behavior towards productive reaction pathways and provide a mechanistic rationale for the observed reactivity.[1]

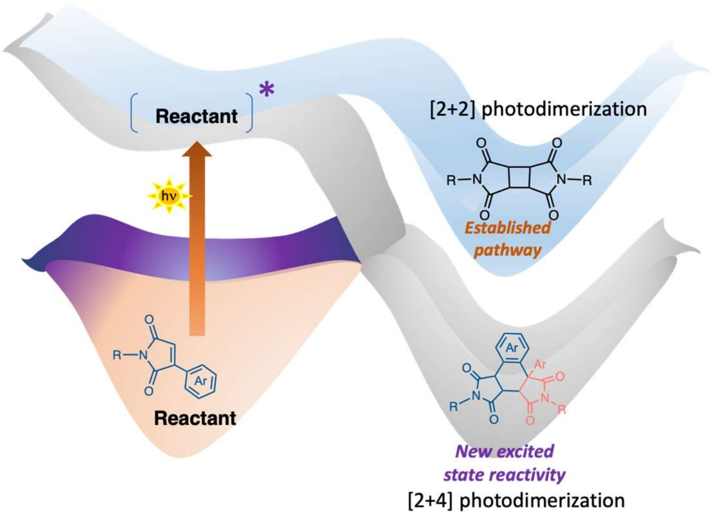


Figure 1. Novel photochemical reactivity from the excited state.

REFERENCES

[1] Ahuja, S.; Baburaj, S.; Valloli, L. K.; Rakhimov, S. A.; Manal, K.; Kushwaha, A.; Jockusch, S.; Forbes, M. D. E.; Sivaguru, J., *Angew Chem Int Edit* **2023**, e202316662.

Interplay Between Aromaticity and Antiaromaticity in Cyclizations

Igor V. Alabugin

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Fl 32306, USA

e-mail: alabugin@chem.fsu.edu

Is aromaticity a property of only cyclic molecules?

What if the cycle is in the process of its formation?

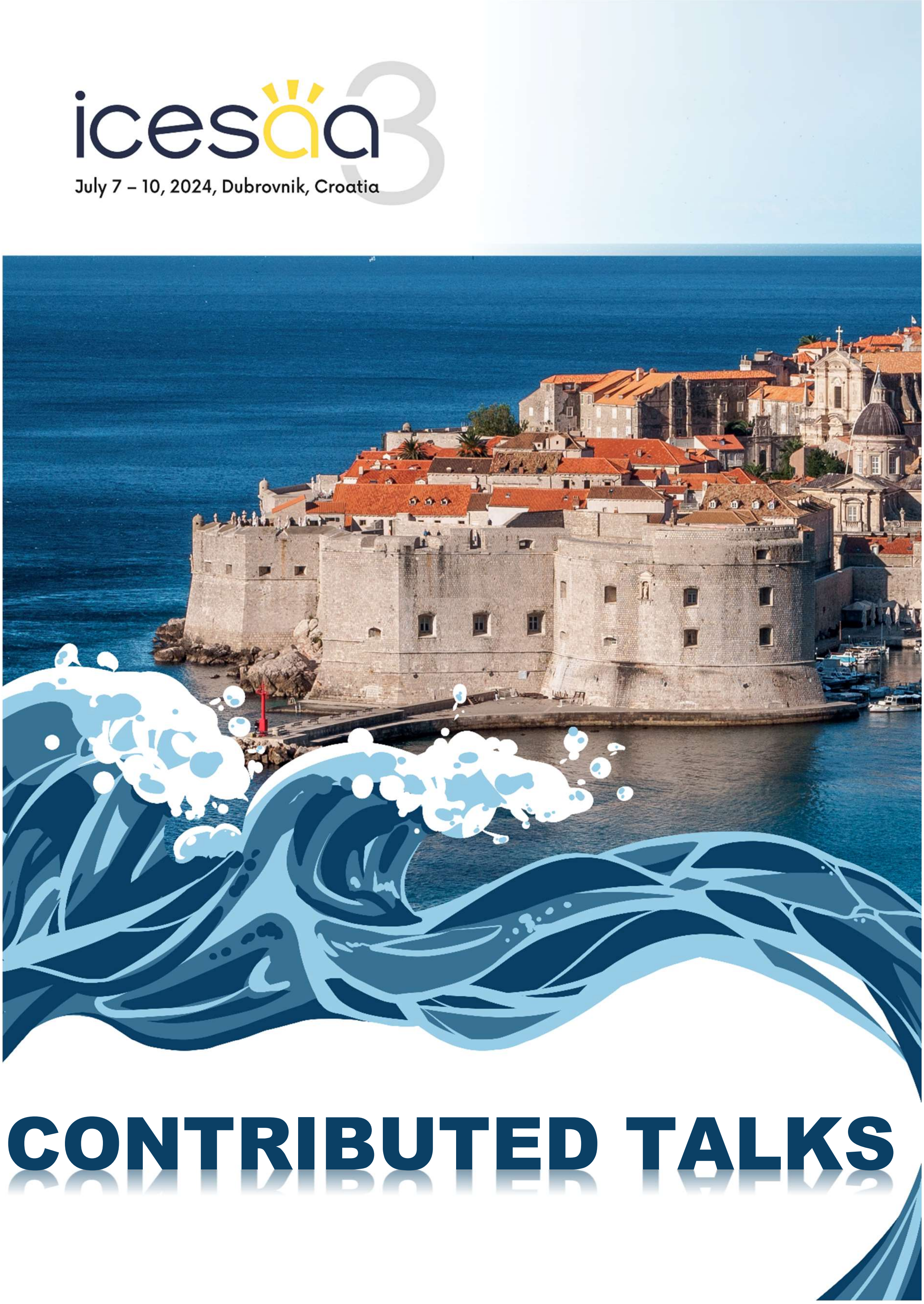
Or there is no cycle at all?

Can we still use this concept for the molecular design and control reactivity?

Hope that we can answer these questions!

icesaa3

July 7 – 10, 2024, Dubrovnik, Croatia



CONTRIBUTED TALKS

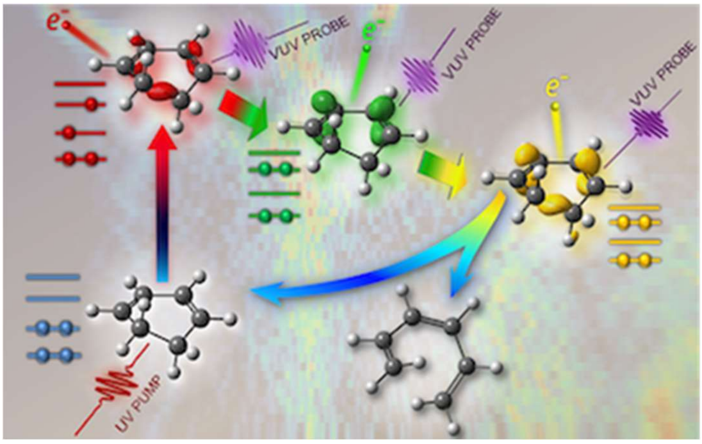
The Ring-Opening Reaction of 1,3-Cyclohexadiene: Identifying the True Reactive State

Tomislav Piteša and Nađa Došlić

Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
E-mail: nadja.doslic@irb.hr

The photochemically induced ring-opening isomerization reaction of 1,3-cyclohexadiene (CHD) to 1,3,5-hexatriene (HT) is a textbook example of a pericyclic reaction [1]. The conceptual framework to understand the photochemistry of CHD is provided by the Woodward–Hoffmann rules [2], extended by van der Lugt and Oosterhoff [3] and stating that the conrotatory ring opening reaction is mediated by a doubly excited electronic state of the same symmetry as the ground state (1^1A^-).The generally accepted sequence of events starts with a valence excitation to the first (S_1) bright state, labelled 1^1B, followed by a passage through a conical intersection (CoIn) to a dark state, labelled 2^1A^- The following step is a branching between two pathways at a second CoIn, either the return to the ground state of the cyclic molecule or the actual ring-opening reaction leading to the open-chain isomer.

To address the problem of the true reactive state we ask a seemingly simple question: is there any other electronic state of symmetry A and partial double excitation character that may be involved in the ring-opening reaction in CHD? We show that the evolution of the process is more complex than usually described and that a high-lying state with a pronounced double-excitation character, labeled 3^1A^-, plays a key role in the ring-opening reaction. [4] The translocation of electron density in the 3^1A^- state and the importance of antiaromaticity relief in the ring opening reaction will be discussed.



Scheme 1. Translocation of electron density in the ring opening reaction of CHD

REFERENCES

[1] S. Deb, P. M. Weber, *Annu. Rev. Phys. Chem.* **2011** *62*, 19–39.

[2] R. B. Woodward, R. Hoffmann. *Angew. Chemie Int. Ed.* **1969**, *8*, 781–853.

[3] W. T. A. M. Van der Lugt, L. J. Oosterhoff *J. Am. Chem. Soc.* **1969**, *91*, 6042–6049.

[4] O. Travnikova *et al. J. Am. Chem. Soc.* **2022**, 144, 21878–21886.

Exploiting Excited States via Inverse Design

Irene Casademont-Reig,[1] Roger Monreal-Corona,[1,2] Eline Desmedt,[1]

Freija Vleeschouwer,[1] Mercedes Alonso[1]

[1]*General General Chemistry-Eenheid Algemene Chemie (ALGC), Department of Chemistry, Vrije Universiteit Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium*
[2]*Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany 69, 17003 Girona, Catalonia, Spain*

E-mail: irene.casademont.reig@vub.be

Electron excitation by photons is a key fundamental process to enhance the efficiency of photovoltaic devices.[1] Singlet-fission (SF) materials have the potential to surpass the efficiency of such devices as they can generate two excitons from a single photon, affording quantum efficiencies up to 200%.[2] A central bottleneck in this field is the limited number of suitable SF chromophores beyond linear acenes which are susceptible to photochemistry degradation.

In this project, we used fulvenes[3] as a test bed to establish a robust and innovative inverse design[4] protocol that will be later applied to accelerate the discovery of new promising porphyrinoids as SF chromophores.[5] These computational strategies can be efficiently used to manipulate the excited state energies of fulvenes, generating a diverse library of systems that fulfil the strict energetic requirements for singlet fission. On the generated database, general design criteria spanning a wider chemical space are devised, including the role of ground- and excited-state aromaticity and the diradical character.

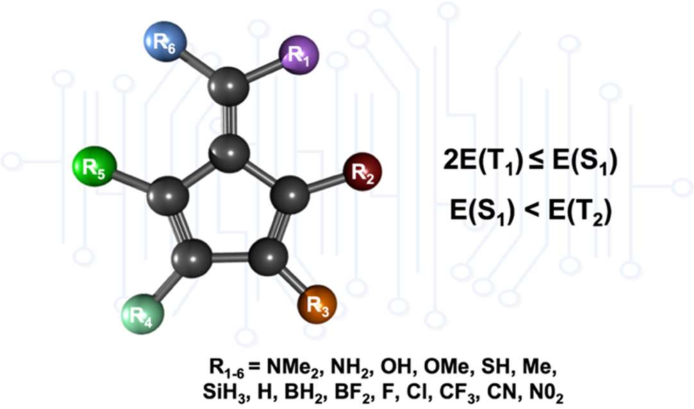


Figure 1. Targeted fulvenes for developing novel SF chromophores with enhanced stability.

REFERENCES

[1] A. J. Baldacchino, M. I. Collins, M. P. Nielsen, T. W. Schmidt, D. R. McCamey, M. J. Y. Tayebjee, *Chem. Phys. Rev.* **2022**, *3*, 021304

[2] T. Ullrich, D. Munz, D. M. Guldi, *Chem. Soc Rev.* **2021**, *50*, 3485-3518

[3] O. El Bakouri, J. R. Smith, H. Ottosson, *J. Am. Chem. Soc.*, **2020**, *142*, 5602-5617

[4] E. Desmedt, D. Smets, T. Woller, J. L. Teunissen, M. Alonso, F. De Vleeschouwer, *Phys. Chem. Chem. Phys.* **2023**, *25*, 17128-17142; E. Desmedt, L. Serrano Gimenez, F. De Vleeschouwer, M. Alonso, *Molecules*, **2023**, *28*, 7371-7392

[5] I. Casademont-Reig, R. Monreal-Corona, E. Desmedt, F. Vleeschouwer, M. Alonso, *in preparation*

Helically Twisted Nanoribbons Employing [7]Helicene as a Molecular Wrench

Asim Swain, Prince Ravat

Julius-Maximilians-Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany

E-mail: princekumar.ravat@uni-wuerzburg.de

Controlling the stereoselective twisting of non-planar nanographene (NG) poses significant challenges, particularly in cove-edged NG, where the energy difference between conformations is minimal (<1 kcal mol^{-1}). The twists in NG are often regulated by bulkier substitutions at the edges. The three-dimensional geometry of [*n*]helicenes can serve as a strain inducer, by imposing chiral strain along the C_2 axis, a factor that is often overlooked. Herein, [7]helicenes were stitched to the terminal K-regions of the pyrene nanoribbon (NR) by employing a palladium-catalyzed, stereoselective and site-selective annulative π-extension (APEX) reaction. The induced strain from the [7]helicene results in a helical NR with an end-to-end twist of up to 171°, the second highest in acene cored molecule. The chirality of the NRs was dictated by the annulated [7]helicene, albeit in opposite direction. The helical conformation accounts for 99.9% of the molecular population. The NRs exhibit configurational stability, with an estimated Gibbs activation energy for diastereomerization ($\Delta G^{\ddagger}$(298 K)) of 37.7 kcal mol^{-1}. Furthermore, the NRs remain conformationally robust over temperature range of 278–333 K, showing no observable changes in chiroptical responses.

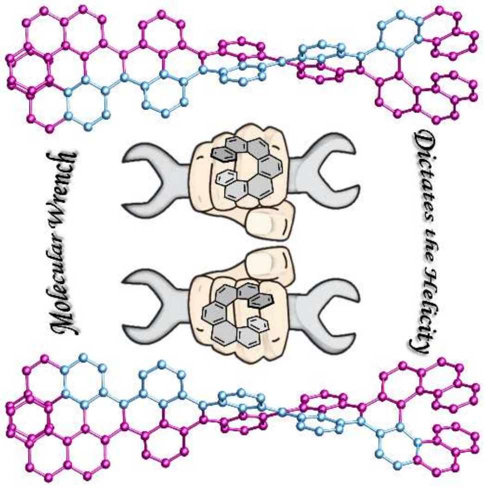


Figure 1. Helically twisted cove-edged pyrene nanoribbon locked by terminal [7]helicenes.

REFERENCES

[1] P. Ravat *et al., unpublished results* **2024**. *Org. Chem. Front.* **2023***, 10,* 3714. *J. Org. Chem.* **2022**, *87*, 993. *Org. Lett.* **2021**, *23*, 1339., *Chem. Eur. J.* **2021**, *27*, 3957.

[2] K. Itami *et al., Nat. Commun.* **2015**, *6*, 6251. *Angew. Chem. Int. Ed.* **2017**, *56*, 11144.

Exploring Exciton Dynamics in NFAs

Catherine S. P. De Castro, Wenchao Yang, Julien Gorenflot, C. Petoukhoff, N. Alsehri, S. Chen, Y. Firdaus, D. Villalva, S. Karutedath, T. Anthopoulos, D. Baran, Frédéric Laquai

King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, KAUST Solar Centre (KSC), Thuwal 23955-6900 Kingdom of Saudi Arabia

E-mail: catherine.decastro@kaust.edu.sa

Optimizing exciton diffusion length (L_D), *i.e.* the distance that excitons can travel before recombining, is crucial for enhancing device performance and reducing losses in organic solar cells. However, varying L_D values have been reported for the same non-fullerene acceptors (NFA) by different groups or methods. This study compares these methods and proposes the most meaningful approach. To do this, we first monitored exciton density decays of NFAs using transient absorption (TA) and time-resolved photoluminescence (TRPL) for pristine and polystyrene diluted NFA (PS:NFA) films. These decays were fitted considering exciton-exciton annihilation within the exciton lifetime (τ), with L_D as the fitting parameter. [1]

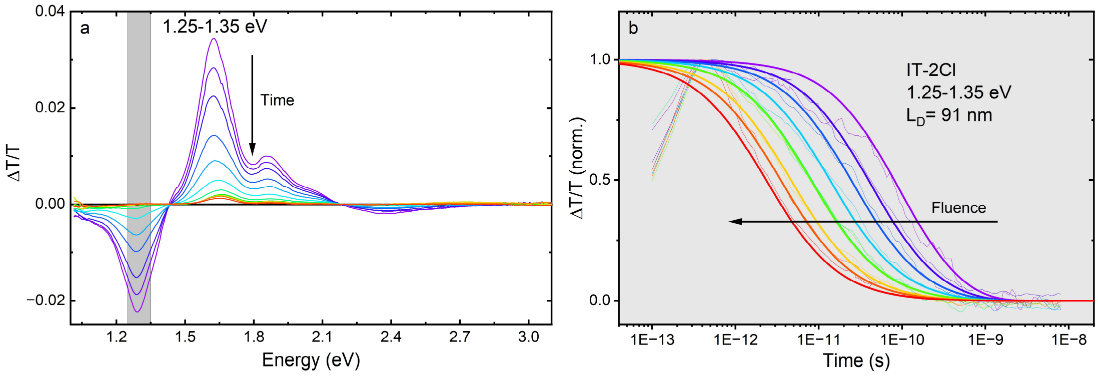


Figure 1. ps-ns TA (a) spectra and (b) kinetics of a NFA film, reproduced from ref. [2]. The fits in b were obtained using τ from low fluence TA of PS:NFA films.

Next, we used experimentally extracted parameters in a Kinetic Monte Carlo simulation (KMC) to reproduce the TA kinetics. By combining both macroscopic (TA fitting) and microscopic (KMC) in 4 similarly cored NFAs, we concluded that τ should be obtained *via* pristine NFA film TRPL at low fluence. We also found that employing a cubic lattice and Förster-based transfer rates in KMC adequately reproduces exciton dynamics, and established that a lattice constant near the π-stacking distance is essential for accurately representing exciton transport.

REFERENCES

[1] S. Chandrabose, et al., *J. Am. Chem. Soc.* **2019**, 141, 17, 6922-6929.

[2] Y. Firdaus, et al. *Nat. Commun.* **2020**, *11(1):5220*, 1-10.

Tris(dioxothiadiazole) - a Molecule with Five Redox States and Varying Aromaticity

Paweł Pakulski, Dariusz Szczepanik, Dawid Pinkowicz

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Cracow, Poland
E-mail: dawid.pinkowicz@uj.edu.pl

Organic molecules generally show limited redox activity, often with only two available valence states. Access to multiple reversible redox events within a compact organic structure remains a challenge. Herein, a completely new platform for molecular multivalency and multiple types of aromaticity is presented: benzo[1,2-c:3,4-c′:5,6-c″]tris([1,2,5]thiadiazole) 2,2,5,5,8,8-hexaoxide (**tripak**) [1]. **Tripak** molecule comprises only 21 non-H atoms forming a rigid triangular strucutre (Figure 1a), yet it is able to reversibly exchange up to six electrons (Figure 1b). **Tripak** could be isolated in five valence states, all characterized by single crystal XRD crystallography. Multivalency provides compartmentalization of multiple desirable functionalities and aromaticity types. The neutral **tripak^0** is non-aromatic and forms remarkably strong anion-π interactions with various anions. **Tripak^{1-}** and **tripak^{3-}** are radicals and can be used in spintronics as qubits. The native dianionic state **tripak^{2-}** shows Hückel aromaticity while **tripak^{4-}** is a diradicaloid facilitating the antiaromatic ground state and the Baird aromatic excited state which is only 2.9 kcal·mol^{-1} higher in energy.

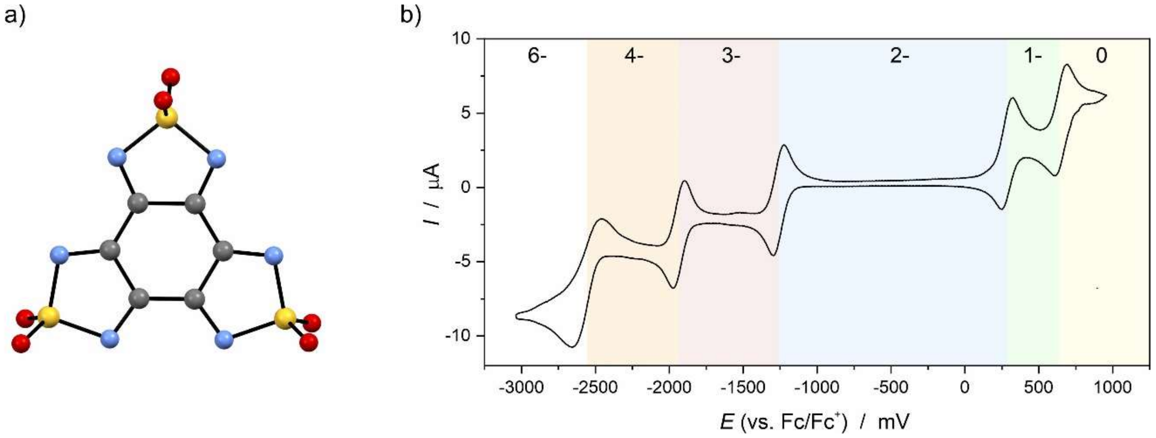


Figure 1. The structure of the **tripak** system (a) and an example of its cyclic voltammogram recorded in THF (b) demonstrating an extremely rich redox chemistry despite a very simple molecular structure.

REFERENCES

[1] P. Pakulski, M. Magott, S Chorazy, M. Sarewicz, M. Srebro-Hooper, D. Tabor, Ł. Łapok, D. Szczepanik, S. Demir, D. Pinkowicz, *Chem*, **2024**, *10*, 971-997, DOI: 10.1016/j.chempr.2023.12.024

Cyclic Delocalization *vs* Ring Current: Facts and Myths

Dariusz W. Szczepanik

Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Kraków, Poland.
E-mail: dariusz.szczepanik@uj.edu.pl

Cyclic delocalization of π-electrons in molecular systems containing conjugated bonds has been regarded as a source of unusual thermodynamic stability that can be rationalized by means of electron bookkeeping rules arising from the molecular orbital theory by Hückel. These rules adequately relate topology, symmetry, and degeneracy of molecular orbitals and they can be used to predict/explain reactivity and different ground-state and molecular-response properties. For simple monocyclic structures the electron counting rules "$4n$+2" and "$4n$" have been known to coincide with the four- and two-electron Fowler-Steiner selection rules that rationalize the magnetic-response properties within the framework of the ring-current model. In this study we prove for the very first time that in large poly- and macrocyclic structures the rules by Hückel and Fowler-Steiner no longer coincide with each other and the widely accepted interpretation of the ring-current pathways as the most aromatic ones is misleading. Additionally, we propose a profound paradigmatic shift for the definition of the ground/excited-state aromaticity regarded strictly as a concept of the chemical bonding theory rather than the molecular-response theory.

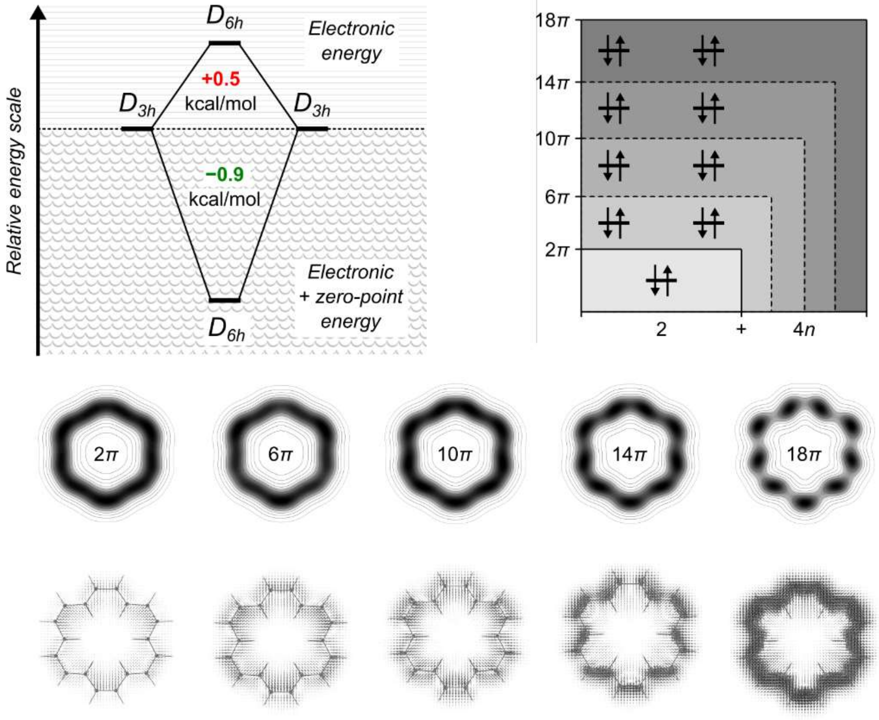


Figure 1. Chemical bonding patterns vs magnetically-induced ring currents in [18]annulene.

REFERENCES

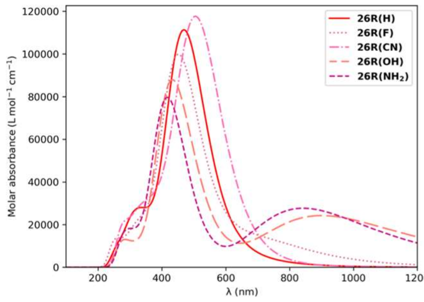
[1] G. Merino, M. Solà, I. Fernández, C. Foroutan-Nejad, *et al.*, *Chem. Sci.*, **2023**, *14*, 5569-5576.

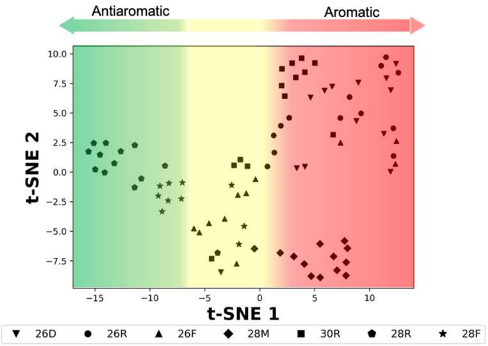
Exploring the Relationship Between Aromaticity and (Non)linear Optical Properties for Hexaphyrins

Eline Desmedt,[1] Irene Casademont-Reig,[1] Roger Monreal-Corona,[2] Freija De Vleeschouwer[1] and Mercedes Alonso[1]

[1]Department of General Chemistry: Algemene Chemie (ALGC), Vrije Universiteit Brussel, Pleinlaan 2 1050 Brussels, Belgium. [2]Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany 69, 17003 Girona, Catalonia, Spain
E-mail: Eline.Louise.Desmedt@vub.be

Owing to their tunable chemical and photophysical properties, porphyrins and their expanded analogs are put forward as promising candidates for new nonlinear optical (NLO) materials and NIR-red dyes.[1] In our previous works, we used an inverse molecular design algorithm to obtain functionalized [26]- and [30]hexaphyrin-based molecular switches with high NLO contrasts.[2,3] To further understand why different functionalizations yield higher NLO properties for [26]hexaphyrins than [30]hexaphyrins, we constructed structure-property relationships from structural, energetic, aromaticity, orbital, and charge-transfer-based features with machine-learning (ML) models and explainable ML techniques.[4] We concluded that the prominent contribution of orbital and charge-transfer-based features differs between the two types of hexaphyrins. Next, we extended our search to other linear spectroscopic properties which are usually connected to the macrocyclic aromaticity within expanded porphyrins.[5] By selecting a diverse set of functionalized [26]-, [28]-, and [30]hexaphyrin macrocycles with both Hückel and Möbius topologies, we studied the relationship between their aromaticity indices based on different criteria and absorption spectra. Finally, by visualizing the established chemical compound space, we identified different regions of aromaticity and connected these to certain important spectroscopical properties such as the absorbance of the Q- and B-band.





REFERENCES

[1] T. Tanaka & A. Osuka, *Chem. Soc. Rev.*, **2015**, 44, 943.

[2] E. Desmedt, D. Smets, T. Woller, M. Alonso, F. De Vleeschouwer, *Phys. Chem. Chem. Phys.* **2023**, *25*, 17128.

[3] E. Desmedt, L. Serrano Gimenez, F. De Vleeschouwer, M. Alonso, *Molecules* **2023**, *28,* 7371.

[4] E. Desmedt, M. Jacobs, M. Alonso, F. De Vleeschouwer, in preparation.

[5] E. Desmedt, I. Casademont-Reig, R. Monreal-Corona, F. De Vleeschouwer, M. Alonso, in preparation.

The Relationship Between Aromaticity and Anti-Kasha Fluorescence of (6+5)Fused 10π-*S*-Heterocycles

David Dunlop, Aleš Machara, Lucie Ludvíková, Tomáš Slanina

Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo náměstí 542/2, Prague 6, 160 00 Czech Republic
E-mail: david.dunlop@uochb.cas.cz

Azulene is blue and naphthalene is colorless because of the difference in their S_1 inter-electron repulsion [1]. Recently, we contextualized this difference in color, as well as azulene's anti-Kasha properties, within the framework of (excited-state) (anti)aromaticity [2]. We found that azulene's anti-Kasha properties are a function of its 10π-electronic structure, and most importantly its local aromaticity. Therefore, we suspected that pseudoazulenes, compounds in which azulene's C=C bond is replaced by a heteroatom, will exhibit the same behavior. Anti-Kasha behavior was indeed ascribed to thialene, a *S*-pseudoazulene, and a constitutional isomer of benzo[b and c]thiophenes [3]. Thus, we expanded our framework to describe why, in these three globally isoelectronic constitutional isomers, the adherence to Kasha's rule changes with the position of their sulfur heteroatom. In this contribution, we will share these findings to further our thesis that anti-Kasha properties of azulene, its derivatives, and its heterocyclic analogues, are inherently linked to their local aromaticity.

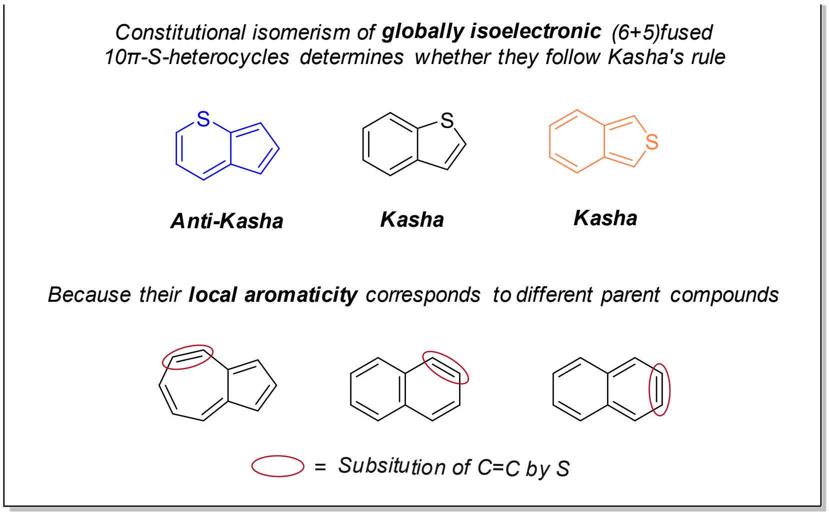


Figure 1. Thialene, benzo[b]thiophene and benzo[c]thiophene, classified by their adherence to Kasha's rule, and the parent compounds from which they derive their local aromaticity.

REFERENCES

[1] J. Michl, E. W. Thulstrup, *Tetrahedron*, **1976**, *32*, 205-209.

[2] D. Dunlop, L. Ludvíková, Ambar Banerjee, Henrik Ottosson, Tomáš Slanina, *J. Am. Chem. Soc.*, **2023**, *145*, 21569-21575.

[3] R. F.X. Klein, V. Horák, *J. Org. Chem*, **1986**, *51*, 4644-4651.

The Effect of B, N Substitution on *cata*-Condensed Polybenzenoid Hydrocarbons: A Computational Investigation

Sabyasachi Chakraborty, Itay Almog, Renana Gershoni-Poranne

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, 3200003, Israel
E-mail: rporanne@technion.ac.il

Cata-condensed polybenzenoid hydrocarbons (PBHs) are polycyclic aromatic molecules comprising multiple fused benzene units. Their optoelectronic properties are well documented and these properties are highly tunable based on functional group modifications or atomic substitutions to the scaffold. One such modification is substituting two carbon atoms with an isoelectronic B-N pair. Although the scaffold remains unchanged, this results in a large collection of molecules with diverse properties that are distinct from the unsubstituted PBHs, and may be promising as functional molecules [1,2]. Here, we describe a computational exploration of the chemical space of BN-substituted PBHs. We investigate the effect of various structural features on the molecular properties of the isomers and identify simple structural descriptors that allow for the prediction of these electronic properties. Furthermore, we study the effect of these substitutions on the aromaticity of these molecules in the ground and excited states and delineate guidelines for predicting these effects in a simple and easy manner.

REFERENCES

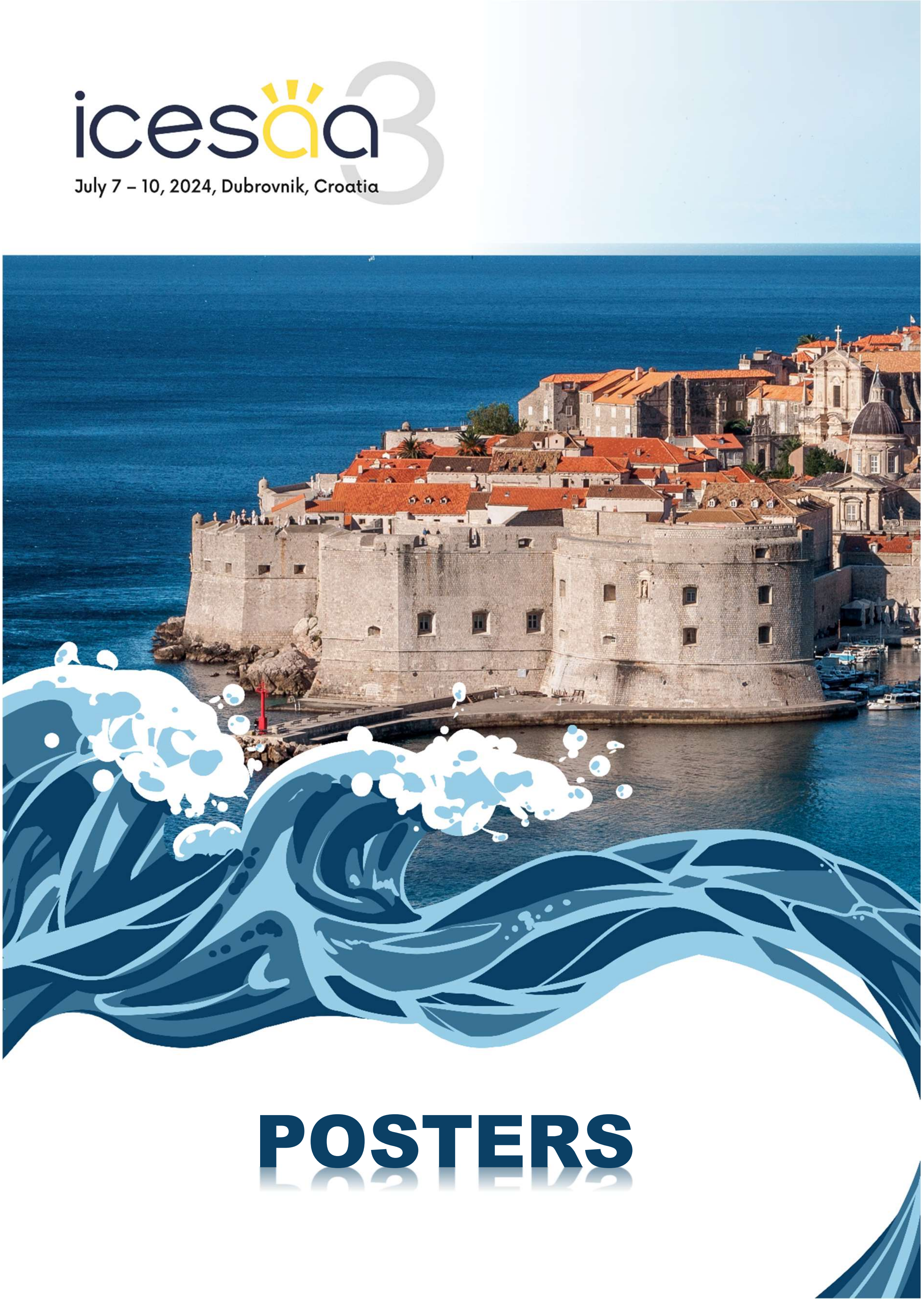
[1] Campbell, P. G., Marwitz, A.J.V., Liu, S.-Y., *Angew. Chem. Int. Ed.*, **2012**, *51*, 6074.
[2] Bosdet, M.J.D., Piers, W.E., *Can. J. Chem.*, **2009**, *87*, 1, 8.

Core-Electron Contributions to the Magnetic Response of Molecules with Heavy Elements

Mesías Orozco-Ic,[1*] Luis Soriano-Agueda,[1] Eduard Matito,[1] Dage Sundholm,[3]
and Gabriel Merino.[2]

[1] Donostia International Physics Center (DIPC), 20018 Donostia, Euskadi, Spain.
[2] Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados, Unidad Mérida. Km 6 Antigua Carretera a Progreso. Apdo. Postal 73, Cordemex, 97310, Mérida, Yuc., México.
[3] Department of Chemistry, Faculty of Science, University of Helsinki, P.O. Box 55, A. I. Virtasen aukio 1, FIN-00014 Helsinki, Finland.
E-mail: mesias.orozco@dipc.org

In this talk, we analyze the magnetic response of core electrons and its influence on the global magnetic response of systems containing heavy elements, employing the removing valence electron (RVE) approximation. We also explore electronic aromaticity indices to understand the potential role of core electrons. The analysis comprises planar and three-dimensional molecular systems, considering the applicability and limitation of the RVE approach. The study reveals that core electrons significantly contribute to the magnetic response, especially to the magnetic shielding, affecting the interpretation of aromaticity. The study emphasizes caution in labeling systems as strongly aromatic based solely on shielding function computations. Thus, the magnetic response of core electrons requires careful consideration, and multiple criteria complement each other for a comprehensive understanding, particularly in systems with heavy elements and intricate structures.



POSTERS

Linear Expanded Azulenes: Exploring the Electronic Properties in the Ground and Excited States

Itay Almog, Renana Gershoni-Poranne

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel
E-mail: itayal@campus.technion.ac.il

Linear expanded azulenes are molecules in which benzene rings are annulated between the five- and seven-membered rings of the azulene core. The members of this series of molecules, which are isomers of polyacenes, vary in the length of the chain of linearly fused benzene rings between the odd-numbered endcaps. Despite the relative structural similarity between expanded azulenes and polyacenes, the two families demonstrate different electronic properties and aromatic character. Expanded azulenes have small, or even inverted, singlet-triplet gaps [1], making them promising candidates for the design of opto-electronic devices that utilize the singlet fission phenomenon. They also show decreased aromatic stabilization, which may be related to high charge transfer abilities [2].

We report on a computational investigation aimed at characterizing the ground and excited states of linear expanded azulenes. The aromatic character is evaluated with NICS, EDDB, and BLA, and the relationship between these different metrics and the singlet-triplet gaps is studied. Natural Resonance Theory is employed to study the underlying electronic structure and to construct an intuitive model for understanding and predicting the behavior of this series of molecules.

Figure 1. Cyclohept-[*f*]indene (left) is an isomer of Anthracene (right).

REFERENCES

[1] Radenković, S., Marković, S., Milenković, V., *Chem. Phys. Lett*, **2012**, *545*, 132-137.

[2] Zhou, Kai-Ge, et al., PCCP, 2011, 13, 15882-15890.

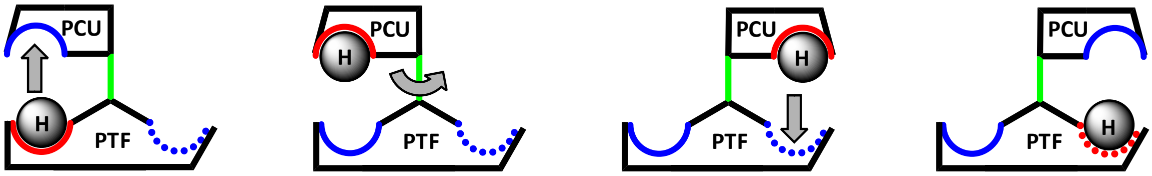
Long-Range Intramolecular Proton Transfer Mechanism of Photoswitching in Azodyes

Lidia Zaharieva,[1] Vera Deneva,[1,2] Fadhil S. Kamounah,[3] Nikolay Vassilev,[2] Ivan Angelov,[1] Daniela Nedeltcheva,[1,2] Michael Pittelkow,[3] Liudmil Antonov[1]

[1]Institute of Electronics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria
[2]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[3]Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark
E-mail: lantonov@tautomer.eu

The overall process of long-range intramolecular proton transfer (LRIPT) switching is outlined in Scheme 1 [1]. The proton, which is located at the proton donor site of a PT frame (PTF), undergoes ESIPT to the proton crane unit (PCU) upon irradiation. In this way, the proton is separated from the PTF, in which two free proton acceptor sites remain. The competition between them is the driving force of the rotation of the PCU, which can lead to the delivery and release of the proton to the other side of the PTF.

The structure of the PTF (7-OH quinoline or 4-OH coumarin) and the flexibility of the PCU (flexible or rigid) are the key parameters determining the mechanism of action and efficiency of switching [1-3]. In the current communication the switching in systems containing 7-OH quinoline as a PTF and azo group as a PCU will be considered in respect of efficiency, undesired side processes and possibilities for structural improvement.



Scheme 1. Sketch of the long-range intramolecular proton transfer mechanism of photoswitching.

Acknowledgements: The Bulgarian National Science Fund within the National Science Program VIHREN by project T-Motors (contracted as KP-06-DV-9/2019) is acknowledged for the financial support for this investigation.

REFERENCES

[1] C.Rehhagen, M.A.A.Cordero, F.S.Kamounah, V.Deneva, I.Angelov, M.Krupp, S.W.Svenningsen, M.Pittelkow, S.Lochbrunner & L.Antonov, *Journal of The American Chemical Society*, **2024**, 146, 2043−2053.

[2] S.Slavova, L.Antonov, *Physical Chemistry Chemical Physics*, **2024**, 26, 7177−7189.

[3] A.Georgiev, D.Yordanov, N.Ivanova, V.Deneva, N.Vassilev, F.S.Kamounah, M.Pittelkow, A.Crochet, K.M.Fromm, L.Antonov, *Dyes and Pigments*, **2021**, 195, 109739.

Valence Bond Like Wave Function on Small Acenes

Fabien Barrois, Stéphane Humbel, Denis Hagebaum-Reignier

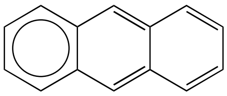
52 Avenue Escadrille Normandie Niemen 13013 Marseille
E-mail: fabien.barrois@univ-amu.fr

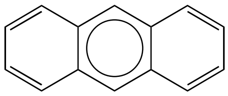
Benzenoids are molecules with fused benzene rings. They usually obey the Clar rule, where the structures with large number of sextets are preferred. They have been subject to major interest for decades. However, the synthesis of benzenoids can be challenging for unusual cases.

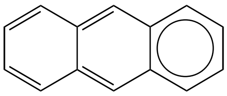
Among these, non-Kekulean benzenoids are those that cannot be described by Single/Double bond alternation: at least one radical appears in their Lewis structures. Hence, their open-shell character gives them peculiar magnetic properties. It is noteworthy that the synthesis of their most famous representative, called the Clar Goblet, has been made possible only in the recent years. As such, this synthesis and characterization opened the way to more studies on those non-Kekulean benzenoids and other radical benzenoids, mainly through theoretical studies. [1]

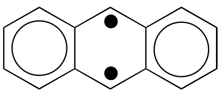
Here, we present a study on acenes as a preamble to the study of other benzenoids. [2] It is known in the literature that the longer the acenes are, the greater their biradical character is, showing thus properties similar to non-Kekulean benzenoids.

First, we propose a benchmark of the acene series using well-known methods like DFT and CASSCF and compare it with existing state-of-the art calculations in the literature. Also, we used Valence Bond (VB) wave functions [3] in order to describe aromaticity and resonance effects in anthracene. Specific VB-like wave function, that accounts for a single Clar sextet (**I**, **II**, **III**) will be discussed. The behavior of biradical structures that allow more sextets (**IV**) will be evaluated.


I


II


III


IV

REFERENCES

[1] S. Gil-Guerrero, M. Melle-Franco, A. Peña-Gallego, M. Mandada, *Chem. Eur. J.*, **2020**, *28*, 16138-16143
[2] H.F. Bettinger, C. Tönshoff, M. Doerr, E. Sanchez-Garcia, *J. Chem. Theory Comput.*, **2016**, 12, 305-312
[3] J. Gu, Y. Lin, B. Ma, W. Wu, S. Shaik, *J. Chem. Theory Comput.*, **2008**, 4, 2101-2107
[4] C. Ji, F. Ying, P. Su, C. Zhou, W. Wu, *J Chinese Chemical Soc*, **2023**, 70, 341-348

Aromaticity of Odd-Number Cyclo[n]carbons

Glib V. Baryshnikov

Laboratory of Organic Electronics, Department of Science and Technology,
Linköping University, Norrköping SE-60174, Sweden
E-mail: glib.baryshnikov@liu.se

Odd-number cyclo[n]carbons (n = 5, 7, 9, ..., 29) were studied computationally at density functional theory (DFT) and ab initio complete active space self-consistent field (CASSCF) levels of theory to get insight into their electronic structure and aromaticity [1]. DFT calculations predict a strongly delocalized carbene structure of the cyclo[n]carbons and an aromatic character for all of them in singlet state. In contrast, calculations at the CASSCF level yield geometrically bent and electronically localized carbene structures leading to an alternating double aromaticity of the odd-number cyclo[n]carbons. CASSCF calculations yield a singlet electronic ground state for the studied cyclo[n]carbons except for C_{25}, whereas at the DFT level the energy difference between the lowest singlet and triplet states depends on the employed functional. The BHandHLYP functional predicts a triplet ground state of the larger odd-number cyclo[n]carbons starting from n=13. The ground triplet state of C_{13} was also confirmed by CASPT2 and explicitly correlated coupled clusters calculations simulations in Ref. 2. Current-density calculations at the BHandHLYP level using the CASSCF-optimized molecular structures show that there is a through-space delocalization in the cyclo[n]carbons. The current density avoids the carbene carbon atom, leading to an alternating double aromaticity of the odd-number cyclo[n]carbons satisfying the antiaromatic [4k+1] and aromatic [4k+3] rules. C_{11}, C_{15}, and C_{19} are aromatic and can be prioritized in future synthesis. The bond-shift phenomenon for the triplet state of the cyclo[n]carbons was predicted that could lead to resonance structures that have different reactivity toward dimerization.

REFERENCES

[1] G. V. Baryshnikov, R. R. Valiev, L. I. Valiulina, A. E. Kurtsevich, T. Kurtén, D. Sundholm, M. Pittelkow, J. Zhang, H Ågren, J. Phys. Chem. A, 2022, 126, 2445-2452.

[2] F. Albrecht, I. Roncevic, Y. Gao, F. Paschke, A. Baiardi, I. Tavernelli, S. Mishra, H. L. Anderson, L. Gross, Science, 2024, 384, 677–682.

Aromaticity of Benzene under Isotropic Pressure

Jochen Eeckhoudt[1], Alexander Dellwisch[2], Tim Neudecker[2], Mercedes Alonso[1], Frank De Proft[1]

[1] ALGC, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Elsene, Belgium
[2] Institute for Physical and Theoretical Chemistry, University of Bremen, Leobener Str. 6, D-28359 Bremen, Germany
E-mail: jochen.pedro.eeckhoudt@vub.be

High pressure has long played an important role in chemical synthesis, material science and mechanistic investigations. Assisted by periodic DFT calculations and molecular dynamics simulations, modelling of high pressure chemistry has been made possible, but at a considerable computational cost which has limited the practical applications. With this in mind, static models have recently been developed based both on mechanochemical models (e.g. X-HCFF [1]) and the confinement of the electron density (e.g. XP-PCM, GOSTSHYP [2]). These models not only allow to study the structure and properties of molecular ensembles, but can also apply various effects of pressure to single molecules, effectively eliminating explicit environment effects. This has been exploited by us in the past when studying conceptual DFT properties of atoms. [3]

Aromaticity is one of these elusive properties that have been considered only sparsely under pressure.[4,5] The role of aromaticity as a guiding principle in reactivity and chemical properties provides the motivation to study it's evolution under pressure as quantified by distinct aromaticity descriptors. In this work, both X-HCFF and GOSTSHYP are used to put pressure on benzene as the archetypal aromatic model system and the response of some structural, electronic, magnetic, energetic and reactivity-based indices are evaluated. Their evolution with pressure can often be linked to intuitive concepts, but the conservation of symmetry imposed by the isotropicity of the pressure models complicates the study of the structural properties and results in limited changes for many other indicators such as multicenter indices, delocalization indices and the linear response function. Additionally, difficulties in the interpretation can arise due to the need for an atomic partition for the evaluation of the electronic indices and the use of reference values for certain descriptors.

REFERENCES

[1] T. Stauch, *J. Chem. Phys.*, **2020**, *153*, 134503.

[2] M. Scheurer, A. Dreuw, E. Epifanovsky, M. Head-Gordon, T. Stauch, *Chem. Theory Comput.*, **2021**, *17*, 583-597.

[3] J. Eeckhoudt, T. Bettens, P. Geerlings, R. Cammi, B. Chen, M. Alonso, F. De Proft, *Chem. Sci.*, **2022**, *13*, 9329-9350

[4] T. Novoa, J. Contreras-Garcia, P. Fuentealba, C. Cárdenas, *J. Chem. Phys.*, **2019**, *150*, 204304

[5] N. Casati, A. Kleppe, A.P. Jephcoat, P. Macchi, *Nat. Commun.,* **2016**, 7, 10901

Characterization of Open-Shell *peri*-Condensed Polybenzenoid Hydrocarbons

S. Erez and R. Gershoni-Poranne
Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel
E-mail: erezshany@campus.technion.ac.il

Peri-condensed polybenzenoid hydrocarbons (PBHs) are an important class of compounds that feature in many different functions. They are often used as models for graphene nanoflakes, but also help to understand molecular properties like conductivity and magnetism. PBH molecules with open-shell radical character are particularly interesting, as their unpaired electrons lead them to have unusual electronic structures and magnetic properties.

Identifying whether a PBH will have open-shell character or not is often non-trivial and requires multireference calculations. However, in a simplified sense, this can be traced to two aspects: a) the HOMO-LUMO gap, which shows the energy difference between a molecule's highest occupied and lowest unoccupied molecular orbitals, and b) the geometry of the PBH and its frontier orbitals, which dictates the facility of promoting an electron to a virtual orbital. Molecules with narrower gaps generally have an increased open-shell character, which significantly impacting their reactivity and photophysical traits.

We investigate approximate 16,000 PBH molecules with confirmed open-shell character (as determined by computational diagnostics such as NFOD and y value [1]). We study the relationship between the structural attributes, the HOMO-LUMO gap values, and the tendency (and extent) of diradical character. Through this analysis, we aim to provide valuable insights into predicting the behavior and energy transitions of these molecules.

REFERENCES

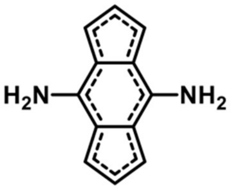
[1] Weiss, T., Wahab, A., Bronstein, A., Gershoni-Poranne, R. *J. Org. Chem* **2023**, *88*, 14, 9645–9656

Inverted Excited-State Singlet-Triplet Gaps in Polycyclic Non-Alternant Hydrocarbons

Marc H. Garner, Piotr de Silva

Department of Energy Conversion and Storage, Technical University of Denmark,
2800 Kongens Lyngby, Denmark.
E-mail: mhfga@dtu.dk

Organic molecules where the first excited singlet state is lower in energy than the first excited triplet state hold great potential as emitters in the next generation of light emitting diodes.[1-3] These molecules that violate Hund's rule of maximum spin multiplicity roughly fall into two classes: azaphenalenes and polycyclic non-alternant hydrocarbons. We have recently uncovered several molecular design rules for the latter class, for example through alleviation of antiaromaticity via substituents (Figure 1).[4-6] Here, we examine the potential of excited-state aromaticity as an additional factor to consider in molecular design of inverted gap emitters. This covers the structural effects of ground-state and excited-state (anti-)aromaticity, which can be both advantageous and disadvantageous. We further investigate how excited-state aromaticity affects the photophysical properties through the vibrational modes in the excited singlet and triplet states,[7] and we compute the related rates of intersystem-crossing and fluorescence. In our search for molecules where singlet-triplet inversion is retained in the relaxed excited-state structures, excited-state aromaticity provides a useful perspective on molecular design.



$E(S_1-T_1) = -90$ meV

Figure 1. Antiaromaticity is alleviated in the ground-state structure of indacene when appropriately substituted.[5] In this D_{2h} structure the excited-state singlet-triplet gap is inverted.

REFERENCES

[1] J. Ehrmaier, *et al., J. Phys. Chem. A*, **2019**, *123*, 8099–8108.
[2] P. de Silva, *J. Phys. Chem. Lett.,* **2019**, *10*, 5674–5679.
[3] N. Aizawa, *et al., Nature*, **2022**, *609*, 502–506.
[4] J. T. Blaskovits, *et al., Angew. Chem., Int. Ed.,* **2023**, *62*, e202218156.
[5] M. H. Garner, *et al.*, *Chem. Sci*., **2023**, *14*, 10458–10466.
[6] M. H. Garner, *et al.*, *Chem. Commun*., **2024**, *60*, 2070-2073.
[7] L. E. de Sousa and P. de Silva, *J. Phys. Chem. A*, **2021**, *17*, 5816-5824.

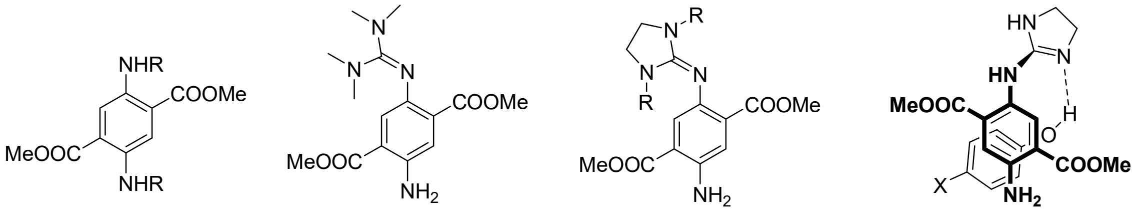
Structure and Properties of Guanidine Containing Single Benzene Fluorophores

Zoran Glasovac, Ivana Antol, Davor Margetić

Division of organic chemistry and biochemistry, Ruđer Bošković Institute, Zagreb, Croatia.
E-mail: glasovac@irb.hr

Fluorescence emission in the visible part of the electromagnetic spectrum is nowadays a hot topic and single benzene fluorophores (SBFs) are interesting molecules due to their low molecular weight, simplicity of synthesis, tunability and, in some cases, the tendency to form flexible crystals [1]. Two crucial features determine the properties of SBFs: accessibility of the charge transfer state within the single benzene ring and switch in the aromaticity upon excitation [1-3]. Observed large Stokes shifts were attributed to alleviating the antiaromaticity through the geometry relaxation [3]. Such systems, if equipped with proper functionality like guanidines, have great potential as fluorescent sensors for the anions or polar groups [4].

As a continuation of our interest in guanidine sensors [5], we present the results on the impact of the guanidine subunit on the fluorescence and aromaticity/antiaromaticity of the new SBF (Figure 1) with an emphasis on the role of protonation. The computational study using TDDFT and CASSCF approaches indicates a significant blue shift of the fluorescence band upon protonation. Additionally, the influence of π-complexation is tackled. The results are interpreted regarding change in acid/base properties and (anti)aromaticity of the first excited state, and compared with those obtained for the diamino analogs (SBF-R, Figure 1).



(R = H or alkyl) | (R = H or CH_3) | (X = H, OMe, NO_2)

SBF-R **SBF-TMG** **SBF-Im** **SBF-Cplx**

Figure 1. Structures of the investigated SBFs with SBF-R [1] being reference systems.

REFERENCES

[1] Y. Kim, J. H. Oh, D. Kim, *Org. Biomol. Chem.*, **2021**, *19*, 933-946.

[2] M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, *Chem. Rev.*, **2014**, *114*, 5379-5425.

[3] H. Kim, W. Park, Y Kim, M. Filatov, C. H. Choi, D. Lee, *Nat. Commun.*, **2021**, *12*, 5409.

[4] P. J. Pacheco-Liñán, C. Alonso-Moreno, F. Carrillo-Hermosilla, A. Garzón-Ruiz, C. Martín, C. Sáez, J. Albaladejo, I. Bravo, *ACS Sens.* **2021**, 6, 3224–3233.

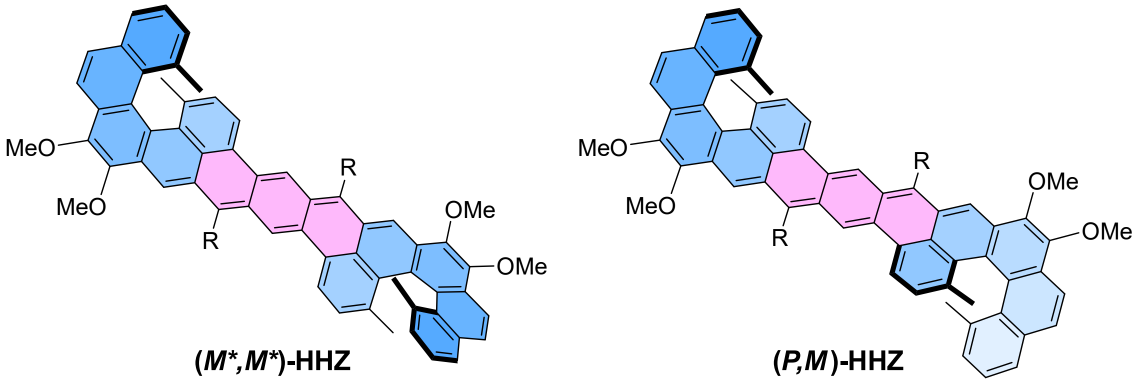
[5] Z. Glasovac, L. Barešić, I Antol, D. Margetić, *ChemPlusChem*, **2018**, *83*, 845– 854.

Effect of Molecular Conformation on the Physical Properties of Three-dimensional Biradicaloids

Johannes Hennemann and Prince Ravat

University of Würzburg, Institute of Organic Chemistry, Am Hubland, Würzburg, Germany
E-mail: princekumar.ravat@uni-wuerzburg.de

The marriage of a biradicaloid heptazethrene structure with helicenes leads to novel three-dimensional helically chiral biradicaloids, namely Helical Heptazethrenes (HHZ). This fusion results in a unique combination of physical properties of both classes of molecules. Our molecular design includes a straightforward synthesis, as well as an optimized strategy to separate the emerging stereoisomers. The outer edges of the helicene units of the enantiomers (*M*,M**-HHZ) face in the same direction, while a continuous helical structure is formed in the meso-compound (*P,M*-HHZ). In this context, the effect of molecular conformation on the singlet–triplet energy gap, biradical character and chiroptical properties was investigated in particular. Although there are already a few representatives of chiral biradicaloid polycyclic aromatic hydrocarbons, the full potential of these materials needs to be further investigated.



(*M,*M**)-HHZ** **(*P*,*M*)-HHZ**

Figure 1. Emerging conformational diastereomers as result of the unique combination of biradicaloid heptazethrene and three-dimensional helicene structures.

REFERENCES

[1] P. Ravat, T. Šolomek, M. Rickhaus, D. Häussinger, M. Neuburger, M. Baumgarten, M. Juríček, *Angew. Chem. Int. Ed.*, **2016**, *55*, 1183-1186.

[2] Z. Sun, S. Lee, K. H. Park, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, S. Das, Y. Li, C. Chi, R.-W. Li, K.-W. Huang, J. Ding, D. Kim, J. Wu, *J. Am. Chem. Soc.*, **2013**, *135*, 18229-18236.

[3] J. J. Dressler, M. Teraoka, G. L. Espejo, R. Kishi, S. Takamuku, C. J. Gomez-Garcia, L. N. Zakharov, J. Casado, M. M. Haley, *Nat. Chem.*, **2018**, *10*, 1134-1140.

Polybenzenoid Hydrocarbons in the S_1 State – The Effects of Annulation Geometry

Fatimah Khaleel, Renana Gershoni-Poranne

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel
E-mail: Fatimah.kh@campus.technion.ac.il
E-mail: rporanne@technion.ac.il

The design of functional organic electronic compounds has gained significant attention in recent years, with a focus on understanding the properties of singlet excited states [1,2]. In this study, we investigate the relationship between the structure of polybenzenoid hydrocarbons (PBHs) and their electronic properties, in the first singlet excited state. By breaking down PBHs into their tricyclic components and classifying them according to their annulation sequences, we uncover new patterns and regularities. These provide insights into the singlet excited state properties, enable prediction of properties of S_1-state PBHs, and can be used as design principles in the synthesis of new compounds. We establish guidelines for qualitatively predicting the S_0-S_1 energy gap, aromaticity, and spin location in larger PBHs, solely based on their smaller tri- and tetracyclic components. This research advances our understanding of singlet excited states in organic compounds and offers valuable insights for the design and characterization of functional electronic materials.

REFERENCES

[1] Anthony, J. E. *Chem. Rev.* **2006**, *106,* 5028–5048.
[2] Aumaitre, C.; Morin, J.-F. *The Chem. Rec.* **2019**, *19,* 1142–1154.

Excited-State Antiaromaticity-Relief Driven Azide Alkyne 1,3-Dipolar Cycloadditions

Croix J. Laconsay,* Nikolas R. Dos Santos, João V. Soares, Igor V. Alabugin,* Judy I. Wu*

Department of Chemistry, University of Houston, Houston, Texas 77204, United States
E-mail: croix.laconsay1@gmail.com

That aromatic compounds become highly reactive and antiaromatic in their first singlet or triplet π-π^* excited state—a concept known as Baird's rules—offers an opportunity to turn photons into useful reagents for chemical transformations.[1] Antiaromaticity is not commonly used as a reaction design principle for guiding synthetic campaigns, but Baird's rules offers an opportunity to do so. In the first π-π^* excited state, aromatic 4n+2 π-rings become excited-state antiaromatic and vice versa for 4n π-rings. In this work, we show that Baird's rules can be used as a design principle for click reactions (1,3-dipolar cycloadditions) between alkynes and azides. This work departs from previous photoclick reactions[2-3] in that it would not involve single-electron transfer events and would be designed and guided by excited-state antiaromaticity relief. Density functional theory calculations suggest that excited-state antiaromaticity relief drives acceleration of click reactions in 4n+2 π-systems, an effect that is absent in 4n π-systems.

REFERENCES

[1] N. C. Baird, *J. Am. Chem. Soc.*, **1972**, *94*, 4941-4948.

[2] Z. G. Wu, X. J. Liao, L. Yuan, Y. Wang, Y. X. Zheng, J. L. Zuo, Y. Pan, *Chem. Eur. J.* **2020**, *26*, 5694-5700.

[3]. Y. Fu, G. Alachouzos, N. S. Simet, M. D. Donato, M. F. Hilbers, W. J. Buma, W. Szymanski, B. L. Feringa, *Angew. Chem. Int. Ed.* **2024**, *e202319321*, (accepted) DOI: 10.1002/anie.202319321.

What Machines Can Teach Us About the Chemistry of *N*-Heteropolycycles?

Stiv Llenga[1], Ganna Gryn'ova[1]

[1]*School of Chemistry, University of Birmingham, Edgbaston B15 2TT, United Kingdom*

Address: *Edgbaston B15 2TT, United Kingdom*

E-mail: stiv.llenga@h-its.org

Polycyclic hydrocarbons possess remarkable catalytic, electronic, and optical properties. Although all-carbon polyaromatic hydrocarbons (PAHs) has been exhaustively investigated, the compound space of their N-doped counterparts is less explored. *N*-heteropolycycles demonstrate rich chemical behaviour and are particularly promising organic semiconductors and OLEDs because of the stable open-shell compounds they produce.

Benefitting from diverse data science approaches, in this contribution we explore the global patterns that govern chemistry of these species using in-house datasets of N-doped PAH molecules totalling over 100,000 datapoints. We utilise the capabilities of machine learning in general, and feature importance in particular, to investigate global chemical trends in these datasets. To assess the reliability of feature importance, we present a technique called "triad of models", which produces consistent predictions independent of the machine learning model used to perform the feature importance. Embedding this technique in pre-trained machine learning models, we provide guidelines for bespoke multi-objective molecular design of N-doped PAH.

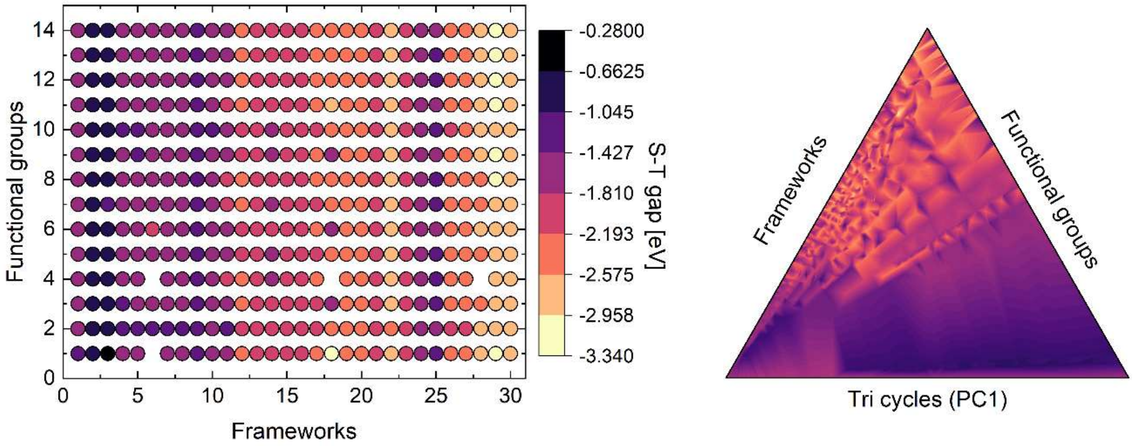


Figure 1. (Left) Big data patterns on how frameworks and functional groups affect N-doped PAH compounds' singlet-triplet gap. (Right) An illustration depicting the complex and extensive chemical space that is being used by machine learning to uncover the underlying chemistry within large datasets.

REFERENCES

This project is ongoing and includes unpublished results.

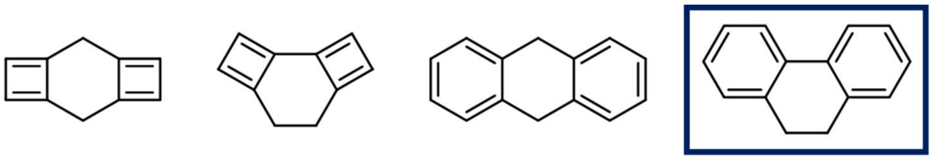
All That Glitters is not Gold – A Case Study of Aromaticity Where There Should Be None

Péter J. Mayer, and Henrik Ottosson

Department of Chemistry – Ångström, Uppsala University, Box 523, Uppsala, 751 20 Sweden
E-mail: peter.mayer@kemi.uu.se

Aromaticity is one of organic chemistry's most basic and fuzzy concepts, as no direct measurement exists.[1] Based on the Hückel definition of aromaticity, many methods are derived for quantifying it.[2] The most popular ones can be considered black boxes as they produce a number, which is used to determine whether a molecule is aromatic, non-aromatic, or antiaromatic. These methodologies can be used for molecules in excited state as it has been found that aromatic nature changes upon π-π* excitation from aromatic to antiaromatic and *vice versa*.[3] We designed a series of systems where false "aromaticity/antiaromaticity" may be observed in a partially π-conjugated system with non-aromatic rings with saturated C atoms.

For the study, the simplest aromatic and antiaromatic annulenes, benzene and cyclobutadiene, were chosen and connected via saturated cyclohexane and cyclooctane rings. Planarity was forced on the species. The most generally used geometric (HOMA), electronic (MCI, FLU), and magnetic (NICS) indices were chosen. The species were studied in their singlet ground state, first triplet excited state, and first quintet excited state. In these species, HOMA, MCI, and FLU gave consistent results for the partially saturated middle rings when going with increased multiplicity, while with NICS, one can observe false "aromatic or antiaromatic" characters.



	Middle ring			Aromaticity		
	HOMA	MCI	NICS$_{\pi zz}$(1)	Geometric	Electronic	Magnetic
S_0	-1.89	0.0008	7.59	Non-Aromatic	Non-Aromatic	**Antiaromatic?**
T_1	-1.87	0.0008	-2.39	Non-Aromatic	Non-Aromatic	Non-Aromatic
Q_1	-1.54	0.0009	-10.54	Non-Aromatic	Non-Aromatic	**Aromatic?**

Figure 1. Studied systems and aromaticity description of the highlighted species.

REFERENCES

[1] G. Merino, *et al.*, *Chem. Sci.*, **2023**, *14*, 5569-5576; H. Ottosson, *Chem. Sci.*, **2023**, *14*, 5542-5544.

[2] I. Fernandez, **2021**, *Aromaticity – Modern Computational Methods and Applications*, Elsevier.

[3] N. C. Baird, *J. Am. Chem. Soc.*, **1972**, *94*, 4941-4948.

Hetero-Polycyclic Aromatic Systems: a Data-Driven Analysis

Eduardo Mayo Yanes, Renana Gershoni-Poranne

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel
E-mail: rporanne@technion.ac.il

Polycyclic aromatic systems (PASs) are organic molecules containing multiple fused aromatic rings, endowed with unique electronic, optical, and chemical properties. These molecules are ubiquitous, found in diverse environments ranging from combustion byproducts to interstellar space, and they constitute the predominant class of compounds in various applications, including fluorescent emitters, catalysts, organic semiconductors, light-emitting diodes, field-effect transistors, and organic photovoltaics. In the pursuit of functional organic materials, identifying molecules that meet specific criteria such as stability, conductivity, and optical properties is a daunting task. However, the traditional trial-and-error approach to molecule design is inefficient and costly. Data-driven approaches offer a promising alternative, enabling the discovery of novel relationships between structural properties. Moreover, chemical data stands as the foundation for the application of powerful artificial intelligence systems to tackle the inverse design of functional molecules. Our group has taken the challenge of creating the first large-scale computational database of Polycyclic Aromatic Systems (COMPAS)[1]. In this work, we present the second installment of the COMPAS database that includes heteroatom-substituted PASs[2]. This new dataset comprises 500k molecules, spanning up to 10 cata-condensed rings and including 11 unique heterocycles ranging in size from 4 to 6 atoms, with different heteroatom compositions and aromatic characters. We calculated electronic properties using the semi-empirical GFN1-xTB method. Additionally, we developed a correction scheme based on values obtained from the CAM-B3LYP-D3BJ/def2-SVP DFT method for a subset of 50k molecules. In this poster, we will showcase the enumeration algorithm and the subsequent workflow developed to sample this diverse chemical space. Exploring the dataset, we unveiled insights into the electronic properties of PASs and their dependence on structural features. Notably, the inclusion of heterocycles expanded the property space considerably. Through the COMPAS-2 database, we provide a valuable resource for researchers in the field of organic electronics, accelerating the discovery and design of functional materials.

REFERENCES

[1] A. Wahab, L. Pfuderer, E. Paenurk, and R. Gershoni-Poranne, *J. Chem. Inf. Model.,* **2022**, 62(16), 3704–3713.

[2] E. Mayo Yanes, S. Chakraborty, and R. Gershoni-Poranne, *Sci. Data*, **2024**, 11(1), 97.

Cyclotetrabenzoin Derivatives as Platforms for Aromaticity Switching

Ognjen Š. Miljanić, Yun-Hsien Lin

Department of Chemistry, University of Houston, 112 Fleming Building, Houston TX 77204, USA
E-mail: miljanic@uh.edu

Cyclotetrabenzoin (**1**, Figure 1) is a tetrameric macrocycle prepared by the benzoin condensation of terephthaldehyde [1]. Its facile synthesis, easy derivatization, and shape-persistent structure have enabled its use as a supramolecular host for linear π-electron rich species, including carbon dioxide [2]. The oxidation product of **1** is cyclotetrabenzil (**2**) which has been shown to act as an electroactive component of lithium-ion batteries, undergoing a reversible eightfold reduction [3].

The fourfold symmetry of cyclotetrabenzoin and its oxidized and/or condensed derivatives opens an interesting possibility of a global antiaromatic 4*n* current with 24 π-electrons. While compounds **1** and **2** have extensively deplanarized structures which prevent the study of such global aromaticity, we have recently prepared tetraimidazoles (**3**) and tetraoxazole (**4**) derivatives of **2** which exhibit nearly planar structures in the solid state. Their solid-state structures show bond delocalization in the four benzene rings but no evidence of a significant global antiaromaticity. We anticipate that these compounds may be exciting targets for observing aromaticity in their excited and/or doubly reduced states. The intent behind this presentation is to inspire and intrigue colleagues to consider such aromaticity switching.

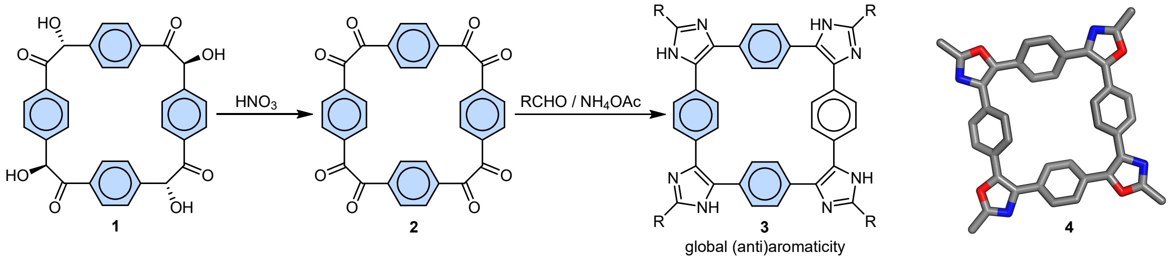


Figure 1. Cyclobenzoin (**1**) is a potential starting point for the preparation of numerous macrocycles which may exhibit (anti)aromaticity in their ground and/or excited states, including species such as **3** and **4**.

REFERENCES

[1] Q. Ji, H. T. M. Le, X. Wang, Y.-S Chen, T. Makarenko, A. J. Jacobson, O. Š. Miljanić, *Chem. Eur. J.*, **2015**, *21*, 17205–17209.

[2] Y.-T. Wang, C. McHale, X. Wang, C.-K. Chang, Y.-C. Chuang, W. Kaveevivitchai, O. Š. Miljanić, T.-H. Chen, *Angew. Chem. Int. Ed.*, **2021**, *60*, 14931–14937.

[3] J. Meng, A. Robles, S. Jalife, W. Ren, Y. Zhang, L. Zhao, Y. Liang, J. I. Wu, O. Š. Miljanić, Y. Yao, *Angew. Chem. Int. Ed.*, **2023,** e202300892.

Redox-Active Properties of Indenofluorene Ligands

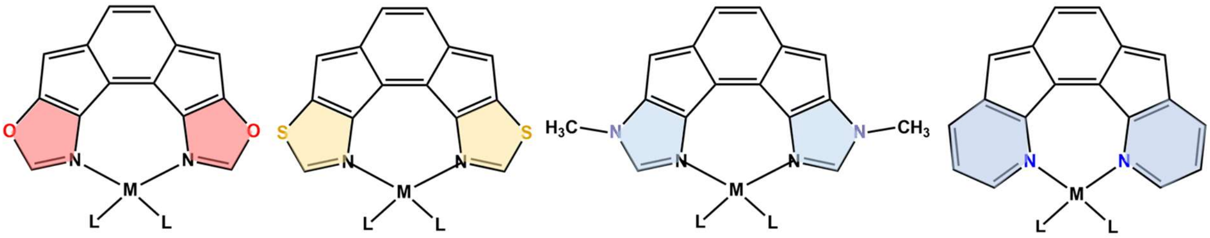
Katarzyna Młodzikowska-Pieńko and Renana Gershoni-Poranne

Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel
E-mail: kasiamp@campus.technion.ac.il

The ongoing endeavor to provide more sustainable prospects for future generations has spurred the application of earth-abundant metals for catalysis,[1] which have the advantages of abundant occurrence in nature and minimal toxicity. However, their tendency to engage in one-electron chemistry requires a unique approach to enhance their catalytic behavior.[2] The incorporation of redox-active ligands allows for the synergistic interplay between the metal core and the ligand, enabling efficient chemical transformations.[3]

In our work, we applied the antiaromatic indeno[2,1-c]fluorene (IF)[4] scaffold as a new type of redox-active ligand. To explore the range of potential of these IFs as redox-active ligands, we replaced the flanking benzenes with nitrogen-, oxygen-, and sulfur-containing heterocycles (Figure 1), which affect the electronic, aromatic, and geometric properties of the complex.

In our study, we identified a series of structure-property relationships and defined design principles, delineating the effect of various structural features on molecular properties and advancing towards the rational design of promising redox-active ligands.



M= metal
L= Cl, CO

Figure 1. Complexes of indeno[2,1-c]fluorene with metals investigated in this work.

REFERENCES

[1] A. Chirila, B. G. Das, P. F. Kuijpers, V. Sinha, B. de Bruin, Non-*Noble Metal Catalysis*, **2019**, *1*, 1-31.

[2] Z. You-Yun, U. Christopher, *Science* **2019**, *363*, 857–862.

[3] J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54* (42), 12236–12273

[4] A. G. Fix, P. E. Deal, C. L. Vonnegut, B. D. Rose, L. N. Zakharov, M. M. Haley, *Org. Lett.* **2013**, *15*, 1362–1365

The n,π* States of Heteroaromatics: When Are They the Lowest Excited States and in What Way Can They Be Aromatic or Antiaromatic?

Nathalie Proos Vedin [a], Sílvia Escayola [b,c], Slavko Radenković [d], Miquel Solà [b], Henrik Ottosson [a]

[a] Department of Chemistry - Ångström Laboratory, Uppsala University, 751 20 Uppsala, Sweden
[b] Institut de Química Computacional i Catàlisi, Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany, 69, 17003 Girona, Catalonia, Spain
[c] Donostia International Physics Center (DIPC), 20018 Donostia, Euskadi, Spain.
[d] University of Kragujevac, Faculty of Science, P. O. Box 60, 34000 Kragujevac, Serbia

E-mail: nathalie.proosvedin@kemi.uu.se

Over two-thirds of all known compounds are aromatic, and the majority of them are heteroaromatic [1]. Predictive rules like Hückel's and Baird's have proven valuable in assessing aromaticity in both ground and excited states [2-4]. Yet, it should be noted that Baird's rule specifically applies to excited states of π,π^* character. In contrast, many heterocycles have lower states of n,π^* character, which are often found to be of photochemical importance. The aromatic character of such states can instead be described using Mandado's $2n+1$ rule for aromaticity of separate spins [5], which explains that such species become π_α-antiaromatic and π_β-aromatic, or *vice versa*. Adding these contributions together gives rise to a residual, resulting in compounds with varying degrees of (anti)aromatic or non-aromatic character.

In this study, we explore the aromatic character of a range of important 6π-electron heteroaromatics in their lowest n,π^* states using qualitative theory and quantum chemical computations. While the majority are non-aromatic in their lowest n,π^* states, interestingly, there are also those that have residuals corresponding to aromatic or antiaromatic character. An aromatic residual is usually obtained for heteroaromatics with electropositive heteroatoms and/or for highly symmetric (D_{2h}) diheteroaromatics. For the complete compound set, there is a modest correlation between the (anti)aromatic character of the n,π^* state and the energy gap between the lowest n,π^* and π,π^* states ($R^2 = 0.42$), while it is stronger for monosubstituted pyrazines ($R^2 = 0.84$).

REFERENCES

[1] A. T. Balaban, D. C. Oniciu, A. R. Katritzky, *Chem. Rev.*, **2004**, *104*, 2777–2812.
[2] M. Rosenberg, C. Dahlstrand, K. Kilså, H. Ottosson, *Chem. Rev.*, **2014**, *114*, 5379–5425.
[3] N. C. Baird, *J. Am. Chem. Soc.*, **1972**, *94*, 4941–4948.
[4] J. Yan, T. Slanina, J Bergman, H. Ottosson, *Chem. Eur. J.*, **2023**, *29*, e202203748.
[5] M. Mandado, A. M. Graña, I. Pérez-Juste, *J. Chem. Phys.*, **2008**, *129*, 164114.

Ground and Excited State Aromaticity in Azulene-Based Helicenes

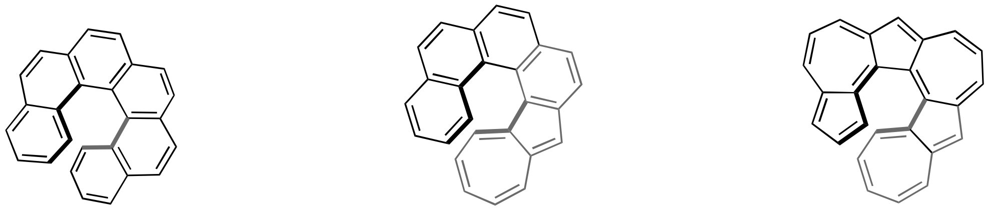
Amisadai Lorenzo Reyes, Fatim Ndeye Ndiaye, Albert Artigas, Yoann Coquerel, Denis Hagebaum-Reignier, Yannick Carissan

Address: 52 Av. Escadrille Normandie Niemen, 13013 Marseille, France
E-mail: amisadai.LORENZO-REYES@etu.univ-amu.fr

The combination of chirality and the peculiar photophysical properties of azulene looks like a promising strategy for the development of new chiroptical probes and sensors, spin filters or chiroptical switches. [1] Recently, new modified azulene helical systems have been successfully synthetized. [2] At the same time, theoretical studies have shown how azulene-containing compounds can modulate the excited state properties. [3] However, the understanding of how the presence of five- and seven-membered rings influences the properties remains limited.

We are interested in providing a comparative analysis of the aromaticity of azulene-based [n]-helicene[1] with its known classical benzenoid helicene analogues from a theoretical approach. Based on the analysis of magnetic properties (3D Isotropic Magnetic Shielding, IMS3D, Anisotropy of the Induced Current Density, AICD) and localization/delocalization of the wave function (Electron Density of Delocalized Bonds, EDDB), we study the ground and first triplet states of azulene-based helicenes at the B3LYP/6-311++G(d,p) level of theory.

We will show how the aromatic characters of helicenes with azulene units only ([n]-azu), differ from the behavior of the azulene and analogous benzenoid-azulene helicene hybrids ([n]-hel-azu). In particular, in azulene-based helicenes with 6 and 8 cycles the singlet and triplet states become closer in energy. We show that the triplet state is more prone to aromaticity than the isoelectronic analogues helicenes studied. This work resulted in a publication under review. [4]



[6]-hel [6]-hel-azu [6]-azu

Figure 1. Example of azulene-based isoelectronic helicene compounds under study.

[1] n: total number of *ortho*-fused cycles in the helicenes, here for n =4,6,8.

REFERENCES

[1] Huang, J.; Huang, S.; Zhao, Y.; Feng, B.; Jiang, K.; Sun, S.; Ke, C.; Kymakis, E.; Zhuang, X. *Small Methods* 2020, *4* (10), 2000628

[2] Duan, C.; Xin, H.; Gao, X. *Tetrahedron Letters* 2023, *123*, 154553.

[3] Yang, C.; Tian, W. Q. *ChemPlusChem* 2023, *88* (8), e202300279.

[4] A. Lorenzo Reyes *et al.*, *Chemistry a Europen Journal*, under revision.

Lemniscular Conjugated Hydrocarbons by Combining Cyclophanes with Cycloparaphenylenes

Luisa Rzesny[1], M. Rapp[2], H. F. Bettinger[2], B. Esser[1,]*

[1] Institute for Organic Chemistry II and Advanced Materials, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany
[2] Institute for Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-mail: luisa.rzesny@uni-ulm.de; birgit.esser@uni-ulm.de

Lemniscular conjugated hydrocarbons are intriguing compounds based on the distortion of their π-system and the radial orientation of the π-orbitals. Only few examples have been reported recently,[1–3] which are based on cycloparaphenylenes. Another class of compounds that has lately attracted much attention are such with in-plane oriented π-systems which are connected in a helical fashion.[4,5]

Here were present an approach to lemniscular conjugated hydrocarbons by combining cyclophanes with cycloparaphenylenes. These allow to study the interplay of through-space and through-bond conjugation. The syntheses and properties of these novel π-systems will be discussed.

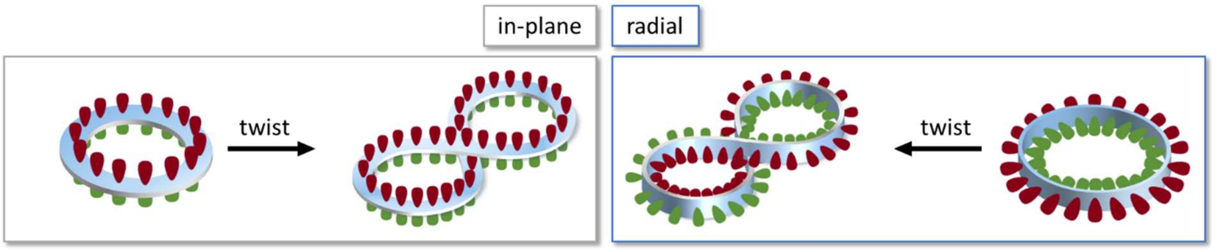


Figure 1. Topology of lemniscular conjugated hydrocarbons.

REFERENCES

[1] K. Senthilkumar, M. Kondratowicz, T. Lis, P.J. Chmielewski, J. Cybińska, J.L. Zafra, J. Casado, T. Vives, J. Crassous, L. Favereau, M. Stępień, J. Am. Chem. Soc. **2019**, *141*, 7421−7427.

[2] T. A. Schaub, E. A. Prantl, J. Kohn, M. Bursch, C. R. Marshall, E. J. Leonhardt, T. C. Lovell, L. N. Zakharov, C. K. Brozek, S. R. Waldvogel, S. Grimme, R. Jasti, *J. Am. Chem. Soc.* **2020**, 142, 8763−8775

[3] L. Zhan, C. Dai, G. Zhang, J. Zhu, S. Zhang, H. Wang, Y. Zeng, C.H. Tung, L.Z. Wu, H. Cong, Angew. Chem. Int. Ed. **2022**, *61*, e202113334.

[4] W. Fan, T. Matsuno, Y. Han, X. Wang, Q. Zhou, H. Isobe, J. Wu, *J. Am. Chem. Soc.* **2021**, *143*, 15924−15929.

[5] M. Krzeszewski, H. Ito, K. Itami, *J. Am. Chem. Soc.* **2022**, *144*, 862−871.

A Symmetry Problem Fixed by Heteroareno Annelation

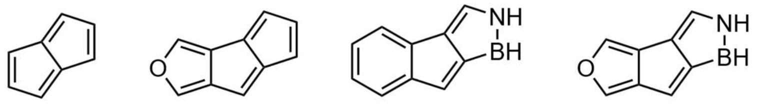
Emil Säbb [1], Péter J Mayer [1], Henrik Ottosson [1]

[1]*Department of Chemistry – Ångström Laboratory, Uppsala University, Lägerhyddsvägen 1 Uppsala, 752 37, Sweden.*
E-mail: emil.sabb@kemi.uu.se

Singlet fission (SF) is a process that can occur in organic molecules with favorable energetics, that, if fully realized, has the possibility to increase the efficiency of solar cells beyond the Shockley-Quisser limit of 33%. [1] However, one problem to the application of the SF process in photovoltaics has been that present SF chromophores are not sufficiently stable to illumination as they often photodegrade. A further problem has been the lack of rational design pathways for design of SF chromophores.

To address both these issues, Baird-aromatic chromophores have been investigated as possible SF chromophores. [2] Since they are aromatic in their lowest excited state, this should reduce the photodegradation aptitude and increase the lifetime of the excited state, allowing for efficient energy transfer to the single junction solar cell. Furthermore, this would allow for a rational design of chromophores based on an aromaticity index, where the energetics of the involved states can be tuned to fulfill the energetic criterion for SF. [2]

However, a problem with some proposed Baird-aromatic SF chromophores, specifically pentalene, is that they have forbidden $S_0 \rightarrow S_1$ transitions (zero oscillator strengths). A host of heteroareno-annelated and heteroatomic pentalenes were now investigated computationally in an effort to identify how to increase the oscillator strength of this transition so as to enhance the SF process. Can the oscillator strength of the forbidden transition be turned to nonzero via symmetry breaking, and at the same time maintain the excited state aromatic character of the pentalene core and the proper energy ordering of the S_1, T_1 and T_2 states for SF?



f	0.00	0.01	0.03	0.08
$E(T_1)$	0.63	1.19	1.50	1.59
$E(S_{1v})$	1.92	2.70	2.78	3.21
S_{1v}/T_1	3.06	2.35	1.78	2.02

REFERENCES

[1] M. B. Smith, J. Michl. *Chem. Rev.* **2010**, *110*, 6891-6936 DOI: 10.1021/cr1002613

[2] O. El Bakouri, J. R. Smith, H. Ottosson. *J. Amer. Chem. Soc.* **2020** *142*, 5602-5617 DOI: 10.1021/jacs.9b12435

Spin Control of Conjugated Systems in Inert Matrices

María Eugenia Sandoval-Salinas[1], Federico J. Hernández[1,2], Kseniya Gorbatenko[3], Enrique Mendez-Vega[3], Wolfram Sander[3], Rachel Crespo-Otero[1]

[1]University College London, London, United Kingdom
[2]University of Bristol, Bristol, United Kingdom
[3]Ruhr-Universität Bochum, Bochum, Germany
E-mail: m.salinas@ucl.ac.uk

Over the last decades, organic materials with unpaired electrons have arisen as promising building blocks for developing molecular magnets, memory and switching devices. Among them, carbenes are very versatile systems with the ability to stabilize either a triplet or singlet ground state, whose extended chemistry is spin-dependent [1]. In conjugated systems bearing a carbene center, tuning the spin with temperature and via substitution in different positions and substituents has been extensively explored [2]. Recently, their stability in inert matrices has been proved and their reactivity studied by some of the authors of us [2-4].

In this work, we studied the Benzo[b]fluorenyl Carbene (**BFC**), a fully planar carbene with a rigid framework and no substituents. Previously, **BFC** was reported to hold a triplet ground state in solution [5], our gas phase calculations agrees with that result. Nevertheless, we observe that different matrices stabilise the singlet or triplet ground state [6]. Here we present a computational study of **BFC** embedded in inert matrices of N_2, Ne and Ar. We consider the effect of the environment using an electronic embedded cluster model (QM:QM') as implemented our code *fromage* [7]. We combine DFT with a DFT tight binding Hamiltonian to describe the QM (**BFC**) and the QM' (the matrix) region, respectively.

We address the effect of the matrix in the selective stabilization of the multiplicity of the ground state, as well as the role played by the aromaticity in each state. Moreover, we also highlight how the environment affects the aromaticity of the system.

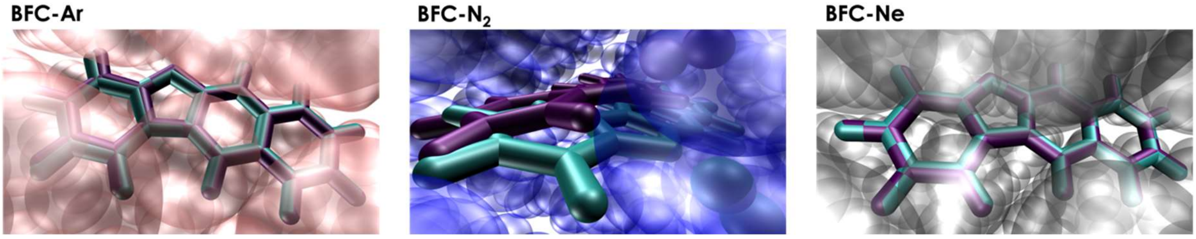


Figure 1. Minimum geometry of singlet (violet) and triplet (green) states of **BFC** embedded in Ar (pink, left), N_2 (blue, center) and Ne (silver, right) matrices.

REFERENCES

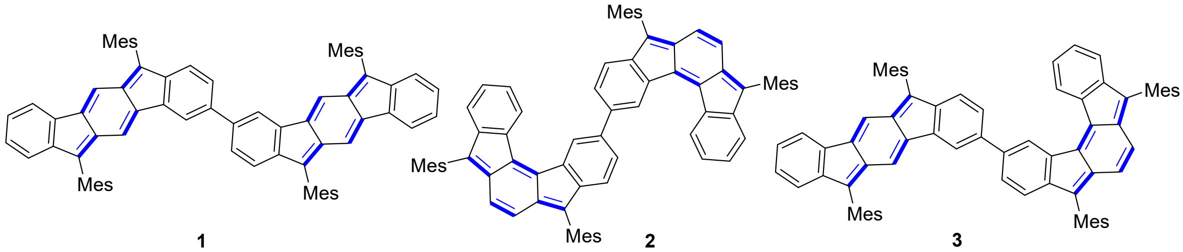
[1] P. Costa, W. Sander, *Angew. Chem. Int. Ed.*, **2014**, *53*, 5122-51225.
[2] P. Costa, I. Trosien, A. Savitsky, W. Lubitz, M. Fernandez-Oliva, E. Sanchez-Garcia, W. Sander, *J. Am. Chem. Soc.*, **2016**, *138*, 1622-1629.
[3] I. Trosien, E. Mendez-Vega, T. Thomanek, W. Sander, *Angew. Chem. Int. Ed.* **2019**, *58*, 14855-14859.
[4] Y. A. Tsegaw, P. E. Kadam, N. Totsch, E. Sanchez-Garcia, W. Sander, *J. Am. Chem. Soc.*, **2017**, *139*, 12310-12316.
[5] P.B. Grasse, J. J. Zupancic, S. C. Lapin. M. P. Hendrich, G. B. Schuster, *J. Org. Chem.* **1985**, *50*, 2352-2356.
[6] K. Gorbatenko, M. E. Sandoval-Salinas, F. J. Hernández, E. Mendez-Vega, R. Crespo-Otero, W. Sander, (in preparation).
[7] https://github.com/Crespo-Otero-group/fromage/tree/fromage2

Biindenofluorene Derivatives Comprising Formally Antiaromatic Indenofluorene Units

Himanshu Sharma, Soumyajit Das*

Department of Chemistry, IIT Ropar, Rupnagar, Punjab – 140001, India
Email: himanshu.19cyz0021@iitrpr.ac.in, chmsdas@iitrpr.ac.in

Fully conjugated indenofluorenes (IFs) and core-extended IFs have attracted significant attention in recent times due to their challenging synthesis, (anti)aromaticity, diradicaloid properties, and optoelectronic applications.[1] The wide band gap of 2.3 eV for an on-surface synthesized IF-based polymer, bearing antiaromatic IF units,[2] stimulated us to design and investigate new IF oligomers in the form of biindenofluorenes (BIFs), which are shown in Figure 1. We have synthesized and characterized three mesityl-substituted BIF derivatives, **1**, **2**, and **3**, which were formed by dimerizing formally antiaromatic IF units through the 3,3'- and 2,2'-carbons of indeno[1,2-*b*]fluorene and indeno[2,1-*c*]fluorene units, respectively. Our design has influenced the HOMO/LUMO energy levels for these IF-based dimers, resulting in much smaller HOMO-LUMO energy gaps than the previously reported IF-based polymer.[2] The hole-carrier mobilities of these BIFs are found to be in the order of 10^{-2} cm^2 V^{-1} S^{-1}.



1
3,3'-biindeno[1,2-*b*]fluorene

2
2,2'-biindeno[2,1-*c*]fluorene

3
[2,1-*c*]IF + [1,2-b]IF

Figure 1. Biindenofluorene derivatives **1**, **2** and **3**.

REFERENCES

[1] (a) C. K. Frederickson, B. D. Rose, M. M. Haley, *Acc. Chem. Res.*, **2017**, *50*, 977-987. (b) Y. Tobe *Physical Organic Chemistry of Quinodimethanes*, Springer, **2017**, *vol. 375*, 107.

[2] M. D. Giovannantonio, J. I. Urgel, U. Beser, A. V. Yakutovich, J. Wilhelm, C. A. Pignedoli, P. Ruffieux, A. Narita, K. Müllen, R. Fasel, *J. Am. Chem. Soc.* **2018**, *140*, 3532-3536.

Modulating Lewis Interactions by Excited-State Aromaticity and Antiaromaticity Concepts

João Vitor Soares,[1] Judy I. Wu[1]

[1]*Department of Chemistry, University of Houston, 3605, Cullen Blvd, Houston, 77004, United States.*
E-mail: jvoliveirasoares@uh.edu

Lewis interactions between pairs of electron donors and acceptors underlie many important reactions in organic catalysis, organometallic chemistry, and surface and electrochemistry. [1] Here, we apply Baird's rule,[2] i.e., a reversal of electron-counting rules for aromaticity and antiaromaticity in the lowest $\pi\pi^*$ state, to understand how photoexcitation can be used to modulate Lewis interactions in borole species. Borole is 4π-electron antiaromatic in the ground state, but becomes aromatic in the lowest triplet $\pi\pi^*$ excited state (Figure 1). Computations show that, in the ground state, coordinating borole to a Lewis base, X, relieves antiaromaticity. Yet, in the excited state, B–X bond cleavage restores aromaticity of the borole ring. This light-induced bond-breaking process has been observed in boron-doped polycyclic aromatic hydrocarbons[3,4] and many other photocleavage processes, and has relevance for the design of new photoresponsive materials. Several expanded borole systems will be discussed.

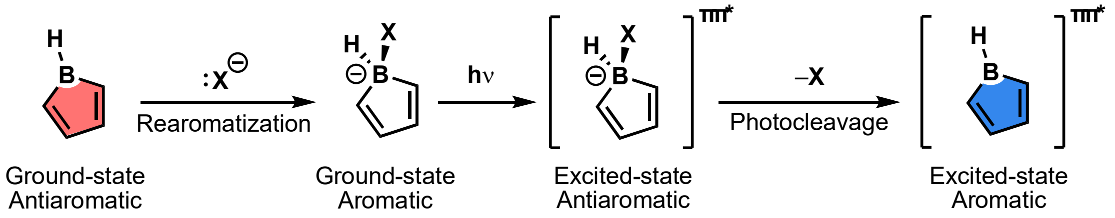


Figure 1. Schematic illustration showing light-induced changes in the (anti)aromatic characters of coordinated and uncoordinated borole.

REFERENCES

[1] Voegtle, M.; Dawlaty, M. J. Can Brønsted Photobases Act as Lewis Photobases? *J. Am. Chem. Soc.* **2022**, 144, 8178–8184.

[2] Colin Baird, N. A Molecular Orbital Theory of Organic Chemistry. II. The Structure of Mesomeric Systems. *J. Am. Chem. Soc*. **1952**, 74, 3345–3350.

[3] Naoki, A.; Yamada, T.; Narita, H.; Oehlmann, N.; Wagner, M.; Yamaguchi, S. Boron-Doped Polycyclic π-Electron Systems with an Antiaromatic Borole Substructure That Forms Photoresponsive B–P Lewis Adducts. *J. Am. Chem. Soc*. **2021**, 143, 9944–9951.

[4] Cassidy, S. J.; Brettell-Adams, I.; McNamara, L. E.; Smith, M. F.; Bautista, M.; Cao, H.; Vasiliu, M.; Gerlach, D. L.; Qu, F.; Hammer, N. I.; Dixon, D. A.; Rupar, P. A. Boranes with Ultra-High Stokes Shift Fluorescence. *Organometallics*, **2018**, 37, 3732– 37415.

Exhaustive Analysis of the New IDopp Aromaticity Index in Macro-Cycles. The Case of c-P6•T6^{6+} .

Luis Soriano-Agueda[1]* and Eduard Matito[1].

[1]Donostia International Physics Center, Euskadi, Spain
E-mail: e-mail address: lsorianoagueda@gmail.com

Recently Peeks, M. and collaborators have proposed a new index (ID opp) to estimate electronic delocalization.[1] In particular, they have studied the nanoring c-P6•T6^{6+} ,[1] a system that has caused controversy among the scientific community. [2,3] According to Peeks, ID opp suggests that the nanoring c-P6•T6^{6+} is aromatic, however we show that ID opp is an unreliable index to estimate aromaticity.

We use of the model shown in Figure 1, where we disconnect the porphyrins. In our model the ID opp index has to be zero, however this does not happen despite disconnections. All our analysis is based on Density Functional Theory.

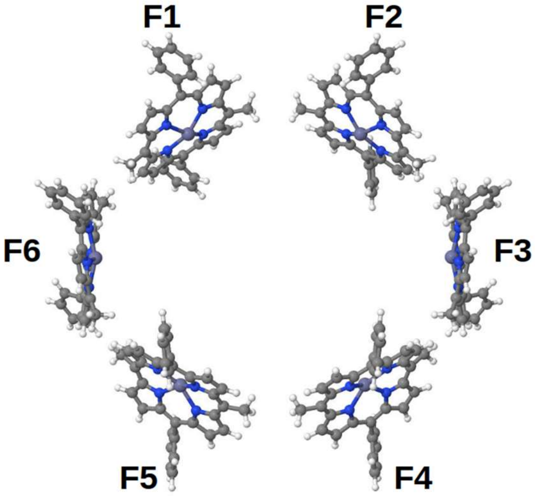


Figure 1. Fragments defined in the nanoring c-P6•T6^{6+} .

REFERENCES

[1] Bradley, D.; Hillier, B. K.; Peeks, M. Electronic delocalization in charged macrocycles is associated with global aromaticity. Chem. Commun. **2023,** 59, 13438.

[2] Deng, J. R.; Bradley, D.; Jirásek, M.; Anderson, H. L. Angew. Chem. **2022,** 134, e202201231.

[3] Casademont-Reig, I; Guerrero-Avilés, R.; Ramos-Cordoba, E.; Torrent-Sucarrat, M.; Matito, E. Angew.Chem. **2021**, 60, 24080-24088.

Modelling Conjugated Macrocycle Dimers in Various Excited and Charged States

James Turner, Felix Plasser

Department of Chemistry, Loughborough University, LE11 3TU, United Kingdom.
E-mail:J.Turner2@lboro.ac.uk

Aromatic macrocycles are large, conjugated ring structures with extended pi-electron systems which exhibit unique electronic properties [1] which become intriguing when they go into their excited and charged states. Following Huckel's rules, an organic molecule with a 4n+2 π-electron system is aromatic and a 4n system is antiaromatic. Applying Baird's rules to excited states the molecules reverse the Huckel's rules in their lowest lying singlet and triplet states [2]. Furthermore, global aromaticity can be affected by adding or subtracting two electrons.

A 4n molecule called paracyclophanetetraene (PCT) is the inspiration for this poster because it displays both aromatic and anti-aromatic properties giving rise to interesting photoredox applications [3]. PCT is a 4n π-electron system in its ground state making it a globally antiaromatic compound. Its ground-state properties are dominated by the local aromaticity of its four phenylene units effectively concealing the anti-aromaticity of the compound [4]. Within this poster, we investigate two PCT dimers linked by bi(thiophene) in various reduced and excited states. We use the visualisation of chemical shielding tensors (VIST)[5] method to elucidate the aromaticity of the different units involved.

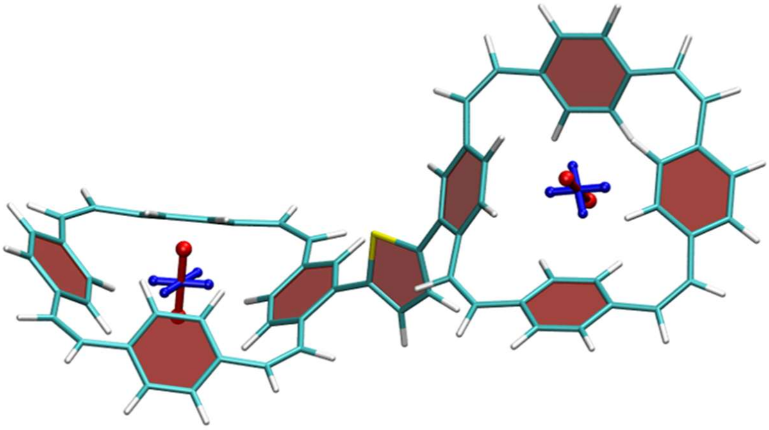


Figure 1: VIST plot neutral state PCT dimer.

REFERENCES

[1] M. Iyoda, J. Yamakawa and M. J. Rahman, ChemInform, 2012, 43.
[2] B. J. Lampkin, Y. H. Nguyen, P. B. Karadakov and B. VanVeller, Physical Chemistry Chemical Physics, 2019, 21, 11608-11614.
[3] M. Rimmele, W. Nogala, M. Seif-Eddine, M. M. Roessler, M. Heeney, F. Plasser and F. Glocklhofer, Organic Chemistry Frontiers, 2021, 8, 4730-4745.
[4] T. L. Bennett, A. V. Marsh, J. M. Turner, F. Plasser, M. Heeney and F. Glocklhofer, Molecular Systems Design Engineering, 2023, 8, 713-720.
[5] F. Plasser and F. Glocklhofer, European Journal of Organic Chemistry, 2021, 2021, 2529-2539.

Excited-State Antiaromaticity Relief Triggers Photoswitching in Multiply Hydrogen Bonded Motifs

Renan V. Viesser, Judy I. Wu

Department of Chemistry, University of Houston, Houston, Texas 77204, United States
E-mail: renan.viesser@gmail.com

Light irradiation can trigger proton transfer reactions and change the hydrogen bonding pattern in multiply hydrogen bonded arrays to promote a photoswitched association constant. Computations for ureidopyrimidinone homodimers (Upy) suggest that the quadruple H-bonded array AADD:DDAA (D: H-bond donor; A: H-bond acceptor) can undergo excited-state double proton transfer reaction (arrows in gray) and shift the tautomeric equilibrium to favor the array ADAD:DADA with a weaker association constant (Figure 1). NICS(1)$_{ZZ}$ values reveal that the dominant dimer tautomer is aromatic in the S_0 state (negative NICS, in blue). In the T_1 state, the photoexcited fragment becomes strongly antiaromatic (positive NICS, in red), but a double proton transferring relieves antiaromaticity. These photoswitchable quadruple H-bonding motifs have attracted considerable attention recently as potential building blocks of light-responsive supramolecular materials [1-3]. Several examples of phototautomerization reactions that weakens or strengthens the association constant will be discussed.

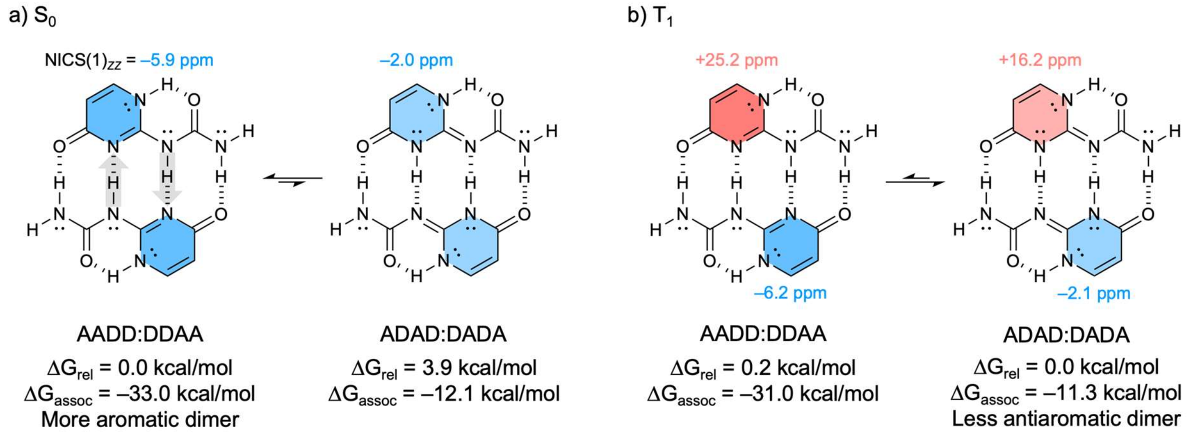


Figure 1. Phototautomerization in dimers of Upy. Relative energies (ΔG_{rel}), association energies (ΔG_{assoc}), and NICS(1)$_{ZZ}$ computed at B3LYP-D3/6-311+G(d,p) in a) S_0 and b) T_1 state indicate the weakening of H-bonding in the excited state trigger by the relief of antiaromaticity.

REFERENCES

[1] B. B. Mollet, Y. Nakano, P. C. M. M. Magusin, A. J. H. Spiering, J. A. J. M. Vekemans, P. Y. W. Dankers, E. W. Meijer, *J. Polym. Sci., Part A: Polym. Chem.*, **2016**, *54*, 81-90.

[2] B. Tang, M. Pauls, C. Bannwarth, S. Hecht, *J. Am. Chem. Soc.*, **2024**, *146*, 45-50.

[3] L. Wei, S.-T. Han, T.-T. Jin, T.-G. Zhan, L.-J. Liu, J. Cui, K.-D. Zhang, *Chem. Sci.*, **2021**, *12*, 1762-1771.

The organisers gratefully acknowlwdge the assistance given by:

Turistička zajednica
grada Dubrovnika
Dubrovnik
Tourist Board