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Cyclophanes as Emerging Materials — From Synthesis To Functions

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Cyclophanes, in general, are coined to name any small or larger cyclic system containing methylene-bridged -$[CH_2]_n$- aromatic ring (be they all-carbon or heteroaromatics); hence, a diverse class of molecular systems can be referenced as cyclophanes. It was Nobel laureate Donald James Cram who first suggested the name "cyclophane" for this class of compounds, which have since become more sophisticated with increased functionality (as chiral ligands/catalysts, precursors/monomers, materials, and functional systems, molecular devices) and morphed with time. The aesthetically appealing and stereochemically remarkable molecular architecture of cyclophanes, their mechanisms of formation, and unusual physicochemical functions are of substantial importance from the perspective of fundamental scientific curiosity to a wide range of applications-driven research across chemical sciences and technology. In recent years, meeting the demands of an ever-changing research landscape, cyclophane chemistry has inevitably evolved from molecules to new materials that involve cyclophanes, as witnessed by the dramatic increase in breakthrough research which prompted this dedicated Special Issue of Advanced Functional Materials' Cyclophanes as Emerging Materials — From Synthesis to Functions' highlighting research contributions from best-known leading experts in the field that beautifully illustrates the ever-expanding scope of cyclophanes from a materials sciences perspective. The spectacular and fast-growing developments in the field, which are truly multi-disciplinary and cut across several interrelated disciplines at the chemistry–material science interface, are propelled by inputs from experts in synthetic chemistry, polymer chemistry, surface science, optoelectronics, photophysics, and material engineering.

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This Special Issue highlights new paradigms and covers global developments focusing on technologically-relevant cyclophane-based material applications. The progress is reflected in the following thematic collection of 22 inspirational articles, each providing instructive details of the most recent research in the fast-moving field of cyclophanes and an assessment of a future to look forward to expanding the bounds of this exciting field is provided. This collection includes Perspectives, Reviews, and Personal Account-type reports presenting extensive and insightful discussions and several inspiring research articles describing collaborative interests in emerging applications that offer a hopeful vision of where research might be heading.

Our Guest Editorial is not intended to be exhaustive; we refrain from providing in-depth details of all the articles as our authors have undertaken strenuous work capturing the inspiring science for this Special Issue. This rich collection of thematic articles appropriately starts with an insightful overview of the cyclophane-based materials provided by Z. Hassan, outlines molecular insights and chemical aspects behind functions associated with molecular features of planar chirality, conformational behaviors, strain-induced non-planarity, and the profound impacts of through-space conjugation on properties of the of cyclophanes (2311828). N. Abbott, J. Lahann, and colleagues update the latest emergent properties, functions, and applications of phane-based polymers formed via the chemical vapor deposition polymerization (CVD) process and introduce novel techniques for templated CVD processes (2315891). CVD is a widely used technology in surface science, providing a substrate-independent platform for bioactive surface functionalization strategies. F. Y. Chou, Y. C. Chiang, H. Y. Chen, and colleagues review research progress and advancements in the vapor-phase synthesis of poly(*para*-xylylene) technology ranging from coatings to porous and hierarchical materials (2313511). Cyclophanes are classified as being neutral, cationic, or anionic. Y. Beldjoudi provides an overview of the zwitterionic viologen-based cyclophanes functional systems owing to their unique electrochemical properties (2315267). In a perspective article, Z. Hassan, E. Z. Colman, J. Lahann, and S. Bräse share lessons and prospects of coordinated interdisciplinary efforts at the chemistry and materials science interface for engineering cyclophane-based functional systems (2403365). Below, we briefly highlight the contents (subtopics) of the Special Issue.

A) *Optoelectronic Materials Applications*: A rapidly emerging focus of cyclophane chemistry centers on small molecules of optoelectronic materials dealing with chirality, conformational behaviors, through-space conjugation, and π-electron interactions/delocalization as decisive factors in tuning emergent chiroptical and electronic functions of the

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chiral cyclophanes. Several research articles discuss the impacts of structural, chemical, and photophysical properties, chirality, and through-space conjugation between individual chromophores coupled with organic light-emitting diodes (OLED)s device process approaches for (opto)electronic applications. Enantiopure cyclophane component impart planar chirality and emissive analogs can exhibit circularly polarized luminescence (CPL). M. Hasegawa, Y. Mazaki, and colleagues describe chiroptical properties of radially extended carbazole and chiral induction ability in achiral π-conjugated polymers featuring chiral [2.2]paracyclophane core, which undergoes electropolymerization to produce an insoluble thin film on the electrode (2315215). E. Z. Colman, Ifor D. W. Samuel, and colleagues present [2.2]paracyclophane-substituted chiral multi-resonant thermally activated delayed fluorescence (TADF) emitters for efficient organic OLEDs. This work demonstrates how the donor strength modulates the energy state, thereby influencing the photophysics of the emitter and ultimately affecting the corresponding device's performance (2402036). Y. Morisaki and colleagues report two kinds of optically active A-shaped cyclic π-conjugation systems based on enantiopure planar chiral [2.2]paracyclophanes emitting bright circularly polarized luminescence with high anisotropy factors (2310566). I. D. W. Samuel, E. Z. Colman, S. Bräse, and colleagues present a comparison of the performance of planar chiral cyclophane-based TADF emitters with modified donor design, (1,7)tBuCzpPhTrz and its isomer (1,4)tBuCzpPhTrz. In this work, an unprecedented carbazolophane-triazine compound is introduced (2401956). Y. X. Zheng, W. H. Zheng, and colleagues disclose TADF materials for circularly polarized electroluminescence, showcasing the useful utility of chiral di[2.2]paracyclophane-based scaffolds (2314205). H. Röhm, S. Bräse, and colleagues report the principal application of substituted [2.2]paracyclophanes for hole transport in perovskite solar cells (2309226). H. Bettinger, D. M. Guldi and colleagues focus on a full-fledged family of π-stacked conjugated oligo-tetracene fine-tuning interactions to control molecular down conversion by choosing different [2.2]paracyclophane substitution patterns and by varying the degree of substitution (2313576). H. Röhm and colleagues report different doping strategies for tetrasubstituted paracyclophane hole transport layers in perovskite solar cells (2402110).

B) *Supramolecular and Non-Covalent Systems*: Beyond the most conventional covalent bonding concept and by employing reversible non-covalent interactions, using chemically-programmed cyclophanes, supramolecular materials can be assembled with controlled arrangements (ranging from 1D to 3D) and emerging properties. In these endeavors, the research work by A. J. Attias, S. F. L. Mertens, and colleagues on electrochemically switching between a 2D crystal and an amorphous cyclophane monolayer at the solid-liquid interface between highly oriented pyrolytic graphite and an electrolyte solution represents an impressive display. On-surface 3D nanoarchitectures, host-guest behavior with cyclodextrin, and electrochemically gated transistor function open avenues to 2D, 3D, and 4D nanoarchitectures with advanced functions (2315861). Darren W. Johnson and colleagues envision a self-assembly route to perylene diimide-bridged cyclophanes utilizing a pnictogen-assisted dynamic covalent chemistry, which shows enhanced properties over monomers and linear congeners and can serve as hosts for electron-rich guests (2314262). T. Zheng, M. Runowski, S. Bräse, and colleagues report an ultrasensitive optical fluorescent-phosphorescent thermometer involving host-guest-supramolecular-complexation-and polymerization of [2.2]paracyclophane-based molecules with cucurbit[8]uril to suppress the molecular motion and promote bright, long-lasting phosphorescence (2313517). S. Bräse and colleagues demonstrate photolysis of [2.2]paracyclophane aryl azide in a supramolecular host for potential application in bioimaging (2401938). Bridging cyclophane chemistry with the still-developing field of supramolecular chemistry points to exciting new possibilities in (multi)functional systems and materials applications.

C) *Phane-Based Chemical Vapor Deposition Polymerization*: Next is a series of contributions focused on cyclophane-based CVD polymerization. H. Y. Chen, Y. C. Chiang, and colleagues describe parylene-based porous scaffolding materials by vapor sublimation and deposition polymerization process to fabricate a directional scaffold for guiding tubular dentin regeneration (2313056). H. Y. Kim, H. S. Kim, K. J. Lee, and colleagues report on a novel intrinsically photo-patternable high-k Parylene-based thin film (Parylene-OH) via a chemical vapor deposition process that can be photo-patterned by UV crosslinking without further lithography processes that could be used in the future of state-of-the-art flexible electronic devices (2405530). J. Lahann and colleagues introduce phosphonate-functionalized polymers with exceptional stability and notable electronic properties through UV-induced Photo-Arbuzov chemistry of halogenated polymer coatings readily available via CVD polymerization (2403408).

D) *Phane-Based Ring-opening Metathesis Polymerization and Others*: Cyclophanediene and related strained cyclophanes emerge as useful precursors for ring-opening metathesis polymerization to prepare poly(*p*-phenylene vinylene) conjugated polymers for emerging electronic and optical applications. M. Weck and colleagues envision folded well-defined 3D architecture from synthetic sheet-helix block copolymer of poly(*p*-phenylene vinylene) via the ring-opening metathesis polymerization of a thymine-bearing alkoxy-substituted [2.2]paracyclophane-1,9-diene (2313734). Finally, R. Vuurin, M. Carta, and S. Bräse report polymers of intrinsic microporosity via a Tröger's base formation mechanism featuring [2.2]paracyclophane moieties for applications in gas sorption (2401957).

The chemistry of cyclophanes is still under active investigation and will continue to blossom, which opens the possibility for a sequel in due time. We believe the future of cyclophane chemistry will benefit from interdisciplinary efforts and melding cross-disciplinary viewpoints with genuinely fresh perspectives. The partnership of scientists, engineers, and entrepreneurs will play a decisive role in bringing breakthroughs from labs to translational opportunities. This special issue of inspirational articles will be a valuable source in scientific research and teaching endeavors that will stimulate further explorations to keep pushing the boundries of the cyclophanes chemistry. It was the objective

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of the guest editors to create a one-stop reference for chemists, material scientists, and the broader scientific community interested in cyclophane chemistry. To understand the full scope, we encourage you to read it in full.

We are pleased to serve as the Guest Editors for this Special Issue and express our appreciation for this opportunity on the occassion of the 75th anniversary of the [2.2]paracyclophane and to highlight the recent achievements in cyclophanes chemistry. We thank all the individual authors for their outstanding research and contributions, making this up-to-date collection of articles possible. We are thankful to all the reviewers for their enormous support in evaluating research articles, and their input to the peer-review process is much appreciated. We also acknowledge the dedicated and excellent production team of Advanced Functional Materials of Wiley-VCH for their efforts in bringing together and spreading this Special Issue far and wide, especially the Editors Jörn Ritterbusch and Marc Zastrow; their assistance on the subject of this special issue is appreciated with thanks.

We welcome you to the amazing "World of Cyclophanes" and invite you to explore your fascinating interests in this exciting, diverse collection of articles: "Cyclophane as Emerging Materials — From Synthesis to Functions."

Thanks for reading!

Conflict of Interest

The authors declare no conflict of interest.



Zahid Hassan, Ph.D., studied chemistry at the HEJ Research Institute of Chemistry, at the Institut für Organische Chemie, Leibniz Universität Hannover, and received Ph.D., at the Institut für Organische Chemie (Leibniz-Institut für Katalyse), Universität Rostock, Germany. After an IBS Fellowship at the Centre for Self-Assembly and Complexity, POSTECH, he held a Faculty Position as Assistant Professor of Chemistry at the University of Nizwa, and then moved to Karlsruher Institüt für Technologie (KIT) in 2017, where he has led a research team at the Institut für Organische Chemie (IOC) and Institute of Functional Interfaces (IFG) at the KIT on synthesis methods development, chiral ligands/catalysts, materials synthesis via molecular self-assembly and understanding the chemical aspects behind system-level functions.



Joerg Lahann, Ph.D., is the Wolfgang Pauli Collegiate Professor of Chemical Engineering and Director of the Biointerfaces Institute at the University of Michigan. The Lahann Lab studies advanced polymers for drug and gene delivery and surface engineering. Current research areas include synthetic protein nanoparticles, CVD polymerization, and 3D jet writing. Lahann published over 300 research papers and contributed to 50 patents/patent applications. Lahann is an elected Fellow of the National Academy of Inventors and the American Institute of Medical and Biological Engineering, has been selected by Technology Review as one of the top 100 young investigators, and is the recipient of the Nanoscale Science and Engineering Award, an NSF-CAREER award, and two Idea Awards from the Department of Defense.



Stefan Bräse studied in Göttingen, Bangor (UK), and Marseille and received his Ph.D. with Armin de Meijere in Göttingen. After postdoctoral research at Uppsala University (Jan E. Bäckvall) and The Scripps Research Institute (K. C. Nicolaou), he began his career at the RWTH Aachen (with D. Enders). In 2001, he finished his habilitation and moved to the University of Bonn as a professor of chemistry. Since 2003, he has been a professor at KIT and director of the Institute of Biological and Chemical Systems-Functional Molecular Systems at KIT. His research interests include asymmetric processes, combinatorial methods for biologically active compounds, and synthetic functional materials.

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