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From Molecules to Materials: Collaborative Research at the Chemistry—Materials Science Interface and Lessons Learned in Cyclophane Chemistry

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In the spirit of pursuing collaborative research at the interface of chemistry and materials science for engineering cyclophane-based functional systems, the journey from molecules to materials and a portion of the accomplishments exploring technologically-relevant small-molecule organic emitters, polymer thin films, and supra-sensing through supramolecular host-guest interactions (molecular self-assembly) is shared. This report highlights diverse research trajectories and the importance of active collaboration within the chemistry community. It is also intended to serves young scientists who are committed to research in interdisciplinary domains. This inspires fostering global research networks and promoting industrial—academic symbiosis that bring innovations to the education environment and curriculum by sharing mutual experiences, knowledge, and specialized skills which may cut across several inter-related disciplines.

1. Introduction

Chemistry in all its facets has become an enabling partner throughout the molecular sciences, pharmaceuticals, agrochemicals, cosmetics, dyes, fine chemicals, polymer industries, functional materials, and other disciplines, because many of the distinctive features and functions of a functional system and materials are the province of molecular-level chemistry.[1] Chemistry if often called the central science because of its role in connecting multiple scientific disciplines. Collaboration with individual scientists, research laboratories, and top institutions worldwide has become increasingly more relevant. Capitalizing on collaborative research efforts within the chemistry community and ensuing holistic approaches of interdisciplinary research has been rewarding in countless ways. The true value of interdisciplinary research lies in fresh perspectives and melding interdisciplinary viewpoints. Synthetic chemists have been contributing to both their independent and collaborative research in the field of fundamentally important areas of chemical science and materials engineering by developing target-oriented synthesis methods and innovative concepts to craft (macro)molecular components with new or improved functions for designing "made-to-order" materials.[2] In material science, sometimes ambitious projects are crashed to a halt not because of a failure in achieving the ultimate objectives but because they confront a bottleneck in synthesis of the fundamental (macro)molecular precursors before ever studying them in functional systems and bulk of the time is usually spent trying to make particular precursors and understand the chemical aspects

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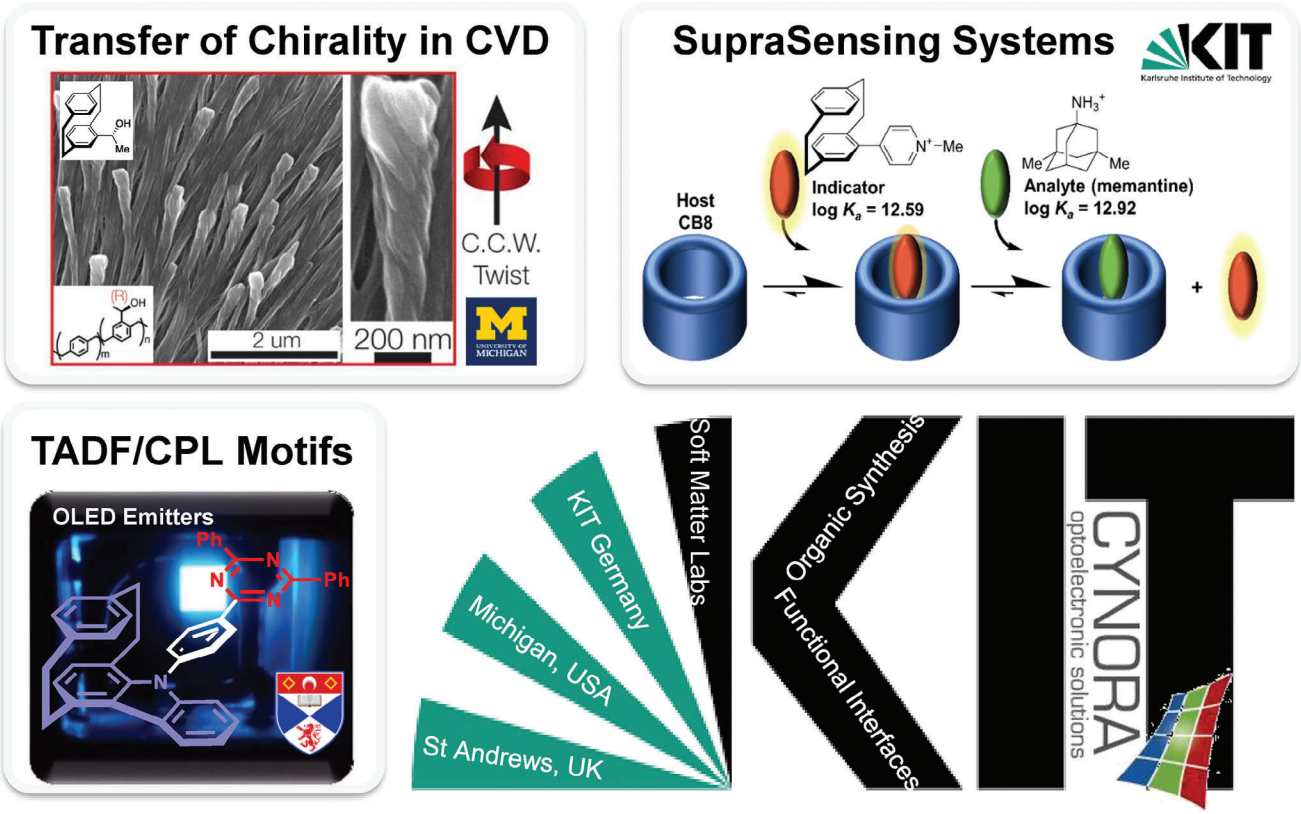


Figure 1. Capitalizing on collaborative research at the chemistry—materials science interface for engineering cyclophane-based functional systems. Images are partly reproduced from the authors own work ref. [13,22,42,64] KIT logo (without the text and Cynora logo) is formally adopted at the Karlsruhe Institute of Technology (KIT).

behind system-level functions. To harvest the multifold potential of chemical synthesis as an enabling science and to explore new terrains, chemists collaborate with experts from other areas of chemical sciences and materials engineering. Synthetic chemists provide seeds and materials scientists nurture it till the very end, thereby fruitful collaborations could serve a bigger purpose for the betterment of the community and the public interests.

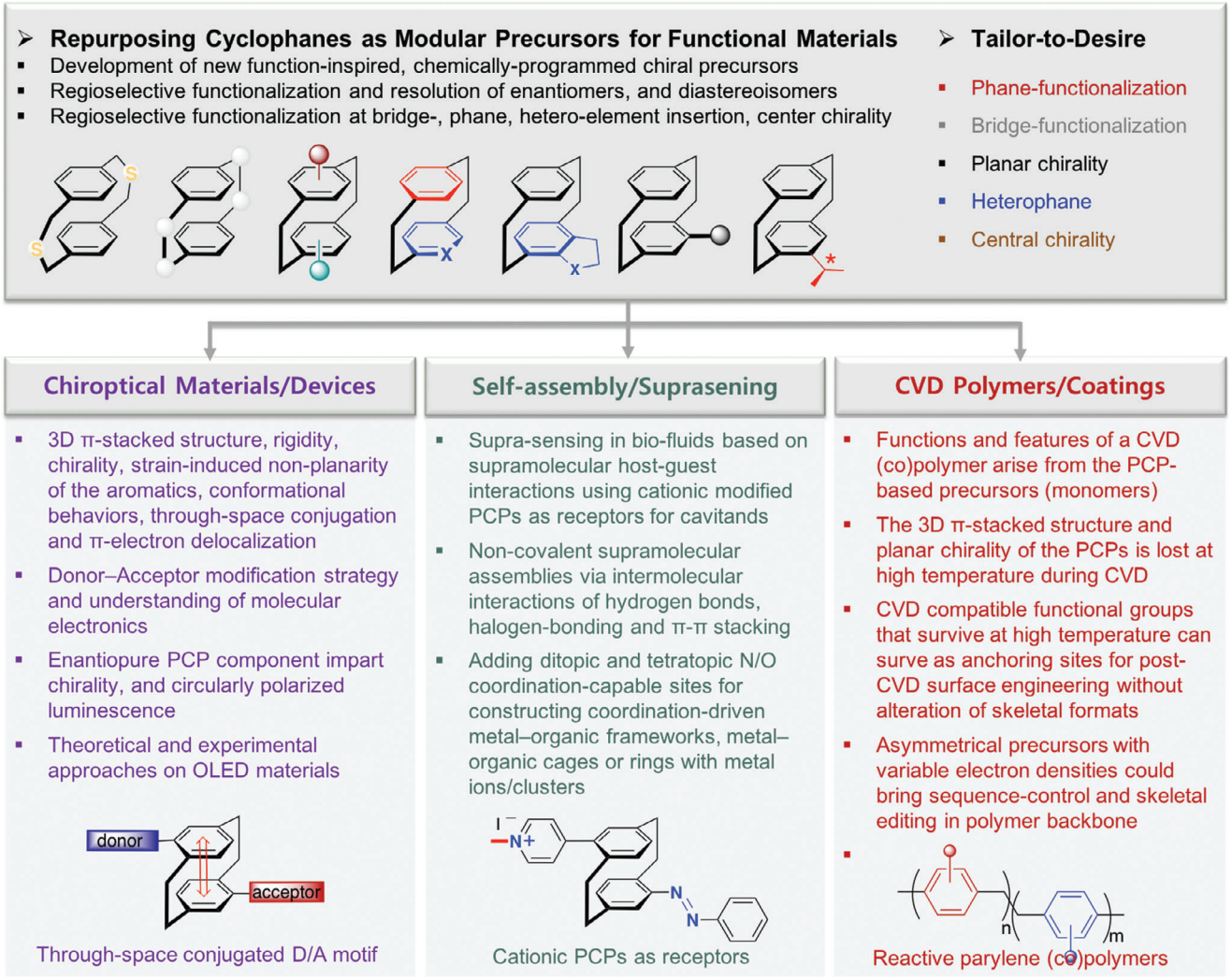
To design and explore cyclophanes as functional molecules for advanced materials and device fabrications, we have selected representative research projects to highlight our adventures in cyclophanes chemistry. We team up with key cooperation partners at institutes from international campuses, including researchers from Institute of Organic Chemistry (IOC), Soft Matter Lab (SML), Institute of Functional Interfaces (IFG), and Institute of Nanotechnology (INT) at the Karlsruhe Institute of Technology (KIT), Biointerfaces Institute at the University of Michigan, USA, and Organic Semiconductor Centre at the University of St Andrews, United Kingdom that enabled some of the achievements highlighted in this report focusing on developing through-space conjugated π-stacked small-molecule organic emitters, supra-sensing in bio-fluids, and surface-engineering of technologically-relevant polymeric parylenes that finds broad applications (**Figure 1**).

Choosing the Soft Matter Laboratory (SML) at the KIT as the focal point for our collaborative research program has been strategic. The SML offers interdisciplinary expertise bridging the gap between organic synthesis, polymers and materials as well as surface chemistry, providing extensive know-how in materials fabrication, characterization, and their emerging applications. In collaborative research at the chemistry—materials science interface, a synthetic chemist generally begins with synthesizing target molecules. In these endeavors, the SML labs at the KIT have devoted efforts exploring cyclophanes in molecular structuring of materials for applications ranging from developing cyclophane-based planar chiral ligands/catalysts to functional parylene coatings, TADF/CPL emitters, as well as other functional systems.

From the perspective of function-led design considerations of materials, everything starts with the judicious selection of molecular precursors that bring desired features and physicochemical functions once incorporated into materials.[3] Chirality has been a principal theme in our research program. Many chiral cyclophanes were prepared on a large scale and provided to the collaborators for further specific investigations in materials fabrication. The generalized design concept of the fundamental building blocks, i.e., chemically-programmed cyclophanes, their retrosynthetic analogy, and some of the key molecular features behind system-level functions as we successfully developed, are outlined in **Table 1**.

[2.2]Paracyclophane (PCP) first discovered by C. J. Brown and A. C. Farthing in 1949,[4] is the smallest co-facially stacked prochiral 3D scaffold where two benzene rings are held together by

Table 1. Design concept of cyclophanes as chemically programmed precursors for functional systems with a particular focus on π-stacked small-molecule organic TADF/CPL OLED emitters are highlighted in purple, supramolecular host-guest interactions (molecular self-assembly) in green, and CVD polymers/surface coatings are highlighted in red.



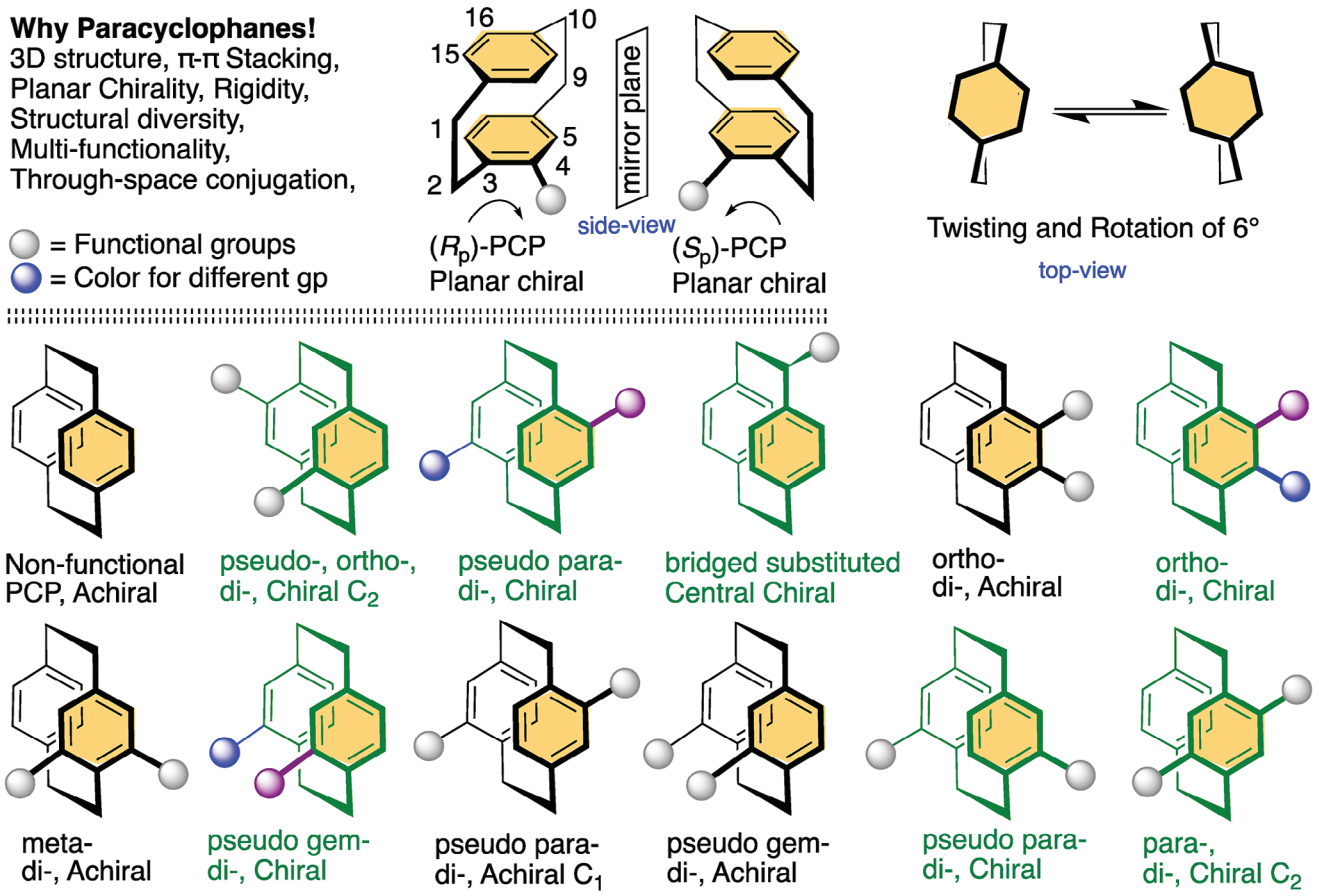


Figure 2. Common substitution pattern of the substituted PCPs with relative nomenclature and chirality descriptors exemplified by 4-substittuted-PCPs.

two short ethylene bridges -$[CH_2]_2$- in their *para*-positions which has been investigated for several decades because of the unusual physicochemical characteristics caused by the transannular π–π electronic interactions of the stacked benzene rings (short inter-ring distances between ≈2.83 and 3.09 Å in decks) that results the unique chemical properties (**Figure 2**).[5] PCP derivatives provide a promising platform to study through-space electronic interactions and the element of planar chirality as PCP exhibits unique stereochemical features (their planar chirality is represented by S_p- and R_p- for enantiomers) on selective functionalization. The small separation of the decks in PCP leads to a distorted geometric structure and an overlap of the π-electrons such that a single, over-both-rings extended π-system is formed.

The inherent planar chirality of cyclophanes led to its use as important scaffolds in catalyst/ligand design for asymmetric synthesis and material science applications, e.g., energy materials for photovoltaics, π-stacked polymers, and parylene coatings. Some of our investigations are discussed in the upcoming sections.

2. Interdisciplinary Research in Cyclophane Chemistry: Repurposing Cyclophanes as Functional Molecules for Functional Materials

Our journey of conducting joint research started with a humble beginning by sharing a "Wishlist" from Michigan in quest of conceptually novel cyclophanes and chemically-programmed heterophanes that could be used as precursor/monomers for the preparation of chemically and topologically-controlled surface coatings formed via cyclophane-based chemical vapor deposition (CVD) polymerization. In follow-up, at the first place, the research outcomes of chemical synthesis in the form of molecular archives, molecular libraries, and systematical span of the obtained chemical data generated over the years at the KIT for individual projects on cyclophanes were shared for specific investigations in CVD polymerization and surface coatings. Screening of synthetically accessible and available monomers in early-stage research has been of great help for a quick start toward optimal scaffolds.

2.1. Structurally-Controlled Polymer Surfaces via Cyclophane-Based Chemical Vapor Deposition (CVD) Polymerization and Post-CVD Fabrications

A longstanding challenge in polymer chemistry is synthesizing precisely controlled soft matter, especially at polymer surfaces. As a test case, CVD polymerization could be used to elucidate the principles of molecular control of structuring polymer over multiple hierarchical levels. This research was aimed on three major structural elements: a) the primary sequence of CVD (co)polymers, 2) topologically defined polymer architectures,

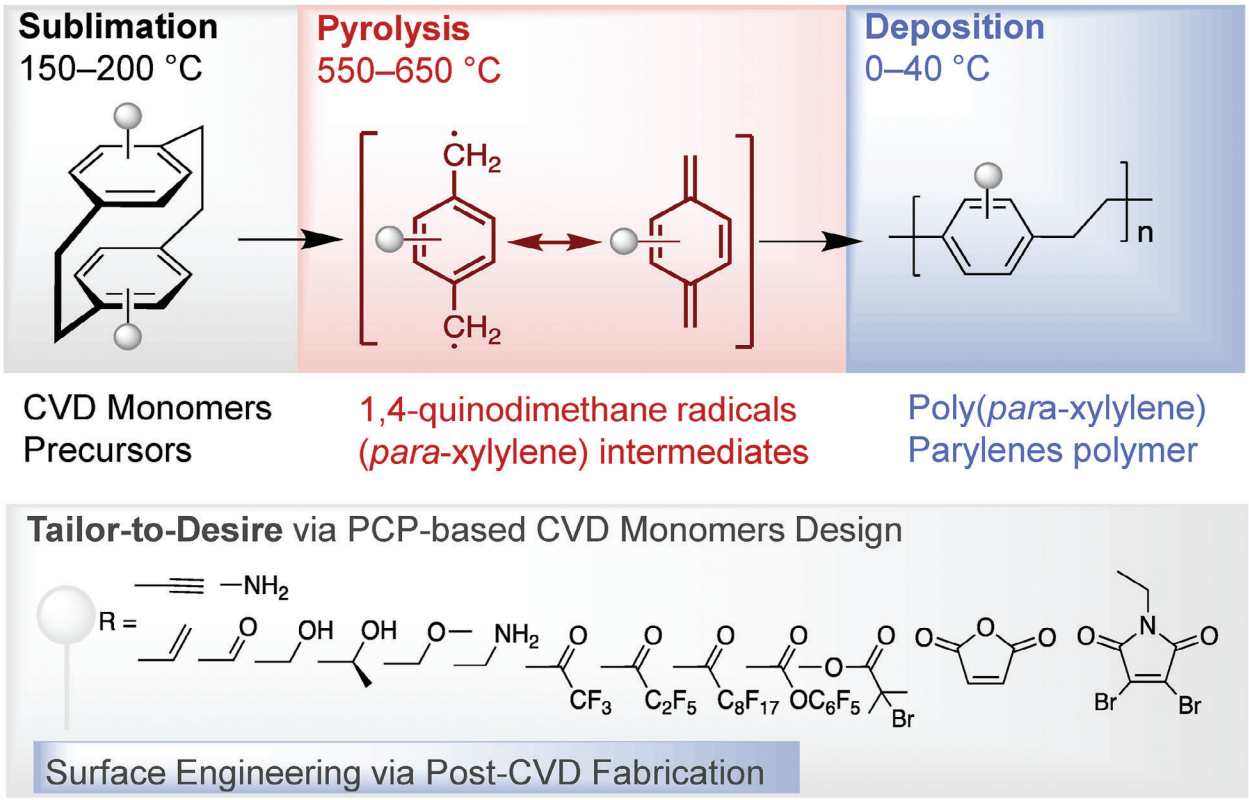


Figure 3. General concept of the Gorham process using PCP-based CVD polymerization into poly(*p*-xylylene) coatings in a custom-built CVD device setup and a general polymerization mechanism via *para*-xylylene radicals intermediates (top). Library of CVD compatible functionalized PCPs as precursors/monomers (bottom).

and 3) hierarchically controlled chirality transfer in nanofiber-decorated polymer surfaces. In particular, templated-CVD polymerization of chiral phane-type molecules was intended to further our understanding of multiscale chirality. The influence of using chiral substituents on the formation of twisted nanofibres by varying the asymmetric size of the chiral substituents on cyclophanes could lead to an understanding of the principles of the induced helical chirality. Synthetically, we aimed to diversify the range of CVD polymer structures via designing novel heterophanes,for instance, pyridophane, pyrazinophanes and pyrimidinophanes. Heterocyclophanes featuring a systematic variation of electron-rich and poor aromatic phane units may lead to strictly defined sequences in CVD (co)polymerization.

CVD polymerization is a widely practiced solvent-free method used for surface functionalization and thin-film polymer coatings via a range of polymerization modes, including a reaction pathway using cyclophanes as precursor molecules (this pathway is known as the Gorham process) which William F. Gorham first described at Union Carbide in 1966.[6] The general concept of the Gorham process consists of three main steps pursued in specifically design CVD device setups: 1) sublimation of the cyclophane precursors (at 150–200 °C, under vacuum at 0.2–0.3 Torr (this might be varying based on the chemical nature of the cyclophane and with bulkier groups attached to cyclophanes); 2) flow of the cyclophane precursors components into the pyrolysis zone at high temperature of (>550 °C) where the precursors are cleaved at the ethylene bridges -$[CH_2]_2$- generating reactive intermediates of 1,4-quinodimethane diradicals (*para*-xylylene) and finally; 3) the reactive species are transferred into a deposition chamber (typically at 0–40 °C temperatures) where they spontaneously polymerize into high-molecular weight polymers.[7] This general CVD process is depicted in **Figure 3**.

The increasing recognition of the green chemistry and biocompatibility as guiding principles in materials manufacturing favor solvent-free process such as CVD polymerization. CVD polymerization does not require catalysts, and initiators, is intrinsically solvent-free, and reduces side products and waste materials relative to solvent-based coating processes. Advances in CVD (co)polymerization for developing reactive surfaces, evolving trends of programmable covalent immobilization of biorelent motifs, and their emerging applications in biointerface engineering have been summarized in several focused reviews, and inspiring book chapters are available in the literature.[8]

For structurally-controlled parylene (co)polymer surfaces and their post-CVD modifications at the molecular level for tuning specific properties and functions, the structure and functional design of the precursor components are of utmost relevance.[9] A parylene polymer's chemical composition determines its application sphere which can be varied by altering the polymer backbone skeleton or by cross-linking specific functional moieties to tune their physicochemical properties.[10] PCP-based monomers bearing synthetically tunable groups, such as OH, SH, F, Br, Cl, NH_2, NO_2, CHO, COR, CO_2R, $COCF_3$, COC_2F_5,

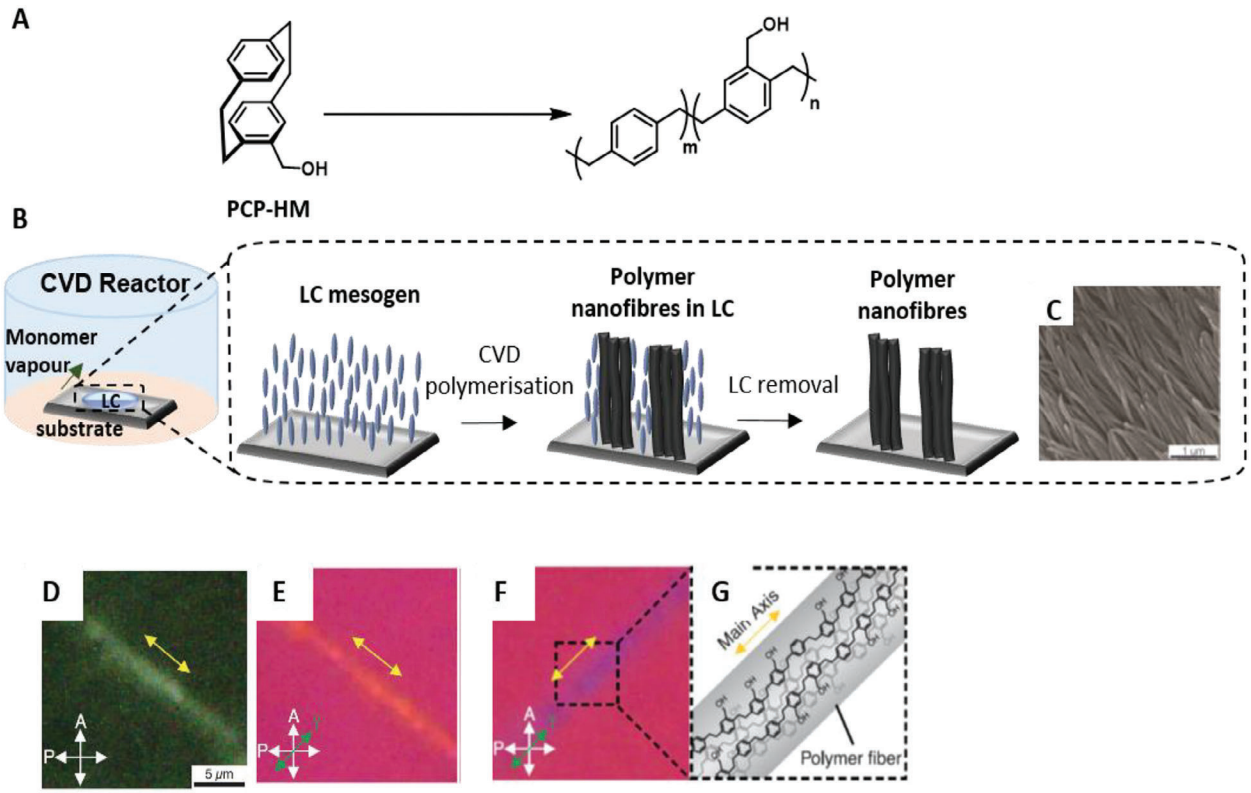


Figure 4. Templated synthesis of polymeric nanofibres into anisotropic media using surface-anchored LC phases as templates: A) CVD of 4-hydroxymethyl-PCP to yield the respective polymer; B) Fabrication of polymer nanofibres via CVD into LCs (after the nanofiber synthesis, the LC template was removed); 3C) Scanning electron microscopy image of nanofibres after LC removal; D) Optical micrograph (cross polarisers) of a nanofiber, where A and P are the orientations of the polarizers; E,F) Micrographs of a nanofiber with a quarter-wave plate with its slow axis; G) Alignment of the polymer chains along the axis of the fiber. Reproduced with permission from ref. [12] Copyright **2018** *Science*, American Association for the Advancement of Science.

ethynyl, vinyl, maleimide, 2-bromoisobutyryl, and anhydride functional components are compatible with CVD polymerization conditions. Parylene properties depend on the cyclophane monomer functional groups used in CVD process that can also serve as anchoring sites for post-CVD surface fabrication through biorthogonal strategies without altering the polymer's skeletal formats, which brings new capabilities at bioinstructive interfaces. Through feeding differently functionalized multiple cyclophanes into the CVD co-polymerization process, reactive polymer coatings carrying multiple functional groups can be prepared, which have been demonstrated for immobilizing proteins, peptides, DNA, polyethylene glycol (PEG), sugar, and other biomolecules of bio-related interests.[11]

2.1.1. Shape-Controlled Nanofibers Synthesis via Templated Chemical Vapor Deposition Polymerization into Liquid Crystalline Films: Multi-scale Chirality, Precisely Defined Structures and Compositions

Despite the spectacular advances, one of the longstanding objectives has been the development of CVD polymerization with preserved 3D morphology and inherit distinct features such as stereochemistry, chirality and responsiveness that are crucial for certain practical applications, including chiroptical sensing or responsiveness. In fundamental contrast to previous work, we demonstrated that CVD polymerization of 4-hydroxymethyl-PCP into thin films of liquid crystals phases (LC) resulted in the formation of surfaces decorated with aligned arrays of shape-controlled polymeric nanofibres, emphasizing the role of the template in dictating the morphology of the CVD nanofibers (**Figure 4**).[12] The LC layer acted as a template for the polymerization, and the anisotropic molecular arrangement in the LC layer guided the polymerization to form an array of aligned polymer nanofibers. The polymer chains preferentially grow along the alignment direction of the LC, creating well-organized nanofibers with programmable geometry, alignment, and chemistry. This has significantly advanced scientific capabilities for molecularly controlled structuring of soft matter surfaces with a wide range of shapes and sizes. Most notably, linear fibers were obtained by using nematic LCs, while blue-phase LCs yielded nanostructures with pores of ≈500 nm in diameter. The chirality of the LC influenced the handedness of the nanofibers. Using cholesteric LCs, the 3D helical chirality could be transferred to the obtained nanofiber as a spiraling of the fiber in the μm range. Thus, the molecular arrangement of the LCs organized on a solid support can determine the morphology of the polymeric structures prepared by CVD polymerization. For example, a nematic LCs can

template assemblies of vertically grown nanofibres (Figure 4C). Initial studies on the growth mechanism of nanofibres templated by LCs suggest that the thermally generated radicals partition into the LC fluid, molecularly arrange along the solid-LC interface, and initiate polymer growth following topological defect lines (i.e., disclinations) of the LC phase. Hence, it can be expected that the LC matrix (mesophases) and the type of monomer used for CVD polymerization will affect molecular ordering and, ultimately, the structure of the resulting polymer films. After removing the LCs, the nanofibres of poly-*p*-xylylene were anchored to the underlying substrate, structurally amorphous yet optically birefringent (Figure 4D). We inserted a quarter wave plate between two crossed-polarisers (Figure 4E,F) and found that the refractive index was highest along the fiber axis. Electron diffraction patterns of the nanofibres were investigated and alignment of the polymer chains along the main axis of the nanofibres was identified, which is consistent with the structure based on polarization microscopy (Figure 4G). Using the inherent variability in molecular arrangements presented by LCs, surfaces decorated with diverse nanofiber morphologies were prepared. Depending on the LC matrix, overall, it was possible to alter the nanofiber chirality that allows for control of adhesion between two surfaces and demonstrates a molecular control of properties including wettability, intrinsic photoluminescence, biodegradability, and surface charge. The LCs used to control the growth of nanofibres during CVD polymerization provide unprecedented control over molecular structure, macroscopic morphology, and long-range lateral organization in soft matter surfaces.

At high temperature, PCP precursors are cleaved at the ethylene bridges in pyrolysis into diradicals. Hence, the innate planar chirality of the appropriately functionalized-PCPs cannot be sustained during the CVD polymerization process. We conjectured that adding another stereogenic element, by adding central chirality in the side-group to the PCP precursors, can transcript conformational features of the PCP monomers into corresponding polymeric nanofibers, achieving hierarchically controlled chirality in polymers. After carefully screening of various chiral PCP monomers and the CVD conditions for the chiral precursors into supported films of LCs, our approach successfully demonstrates enabling chirality transfer in the corresponding parylenes. A pre-weighted amount (4 mg) of the PCP precursor bearing a stereogenic center as side-group, namely (S_p,*S*)−1-(4-[2.2]paracyclophanyl)ethanol or its counterpart of (S_p,*R*)−1-(4-[2.2]paracyclophanyl)ethanol enables the formation of chirality-defined enantiomorphically pure nanohelices formed from achiral nematic templates via CVD polymerization into a (10–12 µm) thick nematic LC template E7 film pre-loaded into TEM grid wells placed on a homeotropically aligning glass substrate (**Figure 5**).[13] Using chiral PCP derivatives as CVD monomers, allowed that chirality can be transferred from the molecular level to a micrometer environment. The morphology and structural regularity of the template are strictly preserved, even upon removal of the LCs template. The enantiomeric excess of the chiral precursor could control the twisting of nanofibers rather than the templating LC medium, which remains achiral. The chiral information is directly encoded into the PCP precursors rather than the templating into supported films of liquid crystalline (LC) phases. The presence of a stereogenic center in the CVD precursors appeared to be a prerequisite for the templated synthesis of nanohelices, suggesting a chirality transfer across the continuum of molecular, macromolecular, and microscopic scales. Depending on the chirality of the PCP-monomer, CVD fiber reflects twists into right- or left-handness (*S* or *R*), and this opposite helicity shows a mirrored signal in the CD spectrum. The CVD polymerization of chiral precursors ranging from 0% e.e. to 100% e.e. of the *S*-configured precursor was studied. SEM revealed the morphology of the nanofibers prepared with different % e.e. of the chiral precursor, which was markedly different. The e.e. defines the contour length, the pitch, the twist angle, and the mesoscale morphology of the nanohelices.

With 0% e.e. chiral precursor, the resulting nanofibers remained un-twisted. The absence of CD signals indicates minimal helicity on the nanofibers prepared with 0% e.e. chiral precursor. Strong bisignate CD signals were found for twisted nanofibers at 242 nm. It is hypothesized that as the molecular size of the chiral center increases, the degree of the steric effect should increase, and thus, the degree of twisting should increase as well. However, the effect of insolubility seems to be more prominent—further systematic studies using bulkier PCPs are to be examined, justifying the hypothesis. These enantiomorphically pure topologies may serve as model surfaces toward a deeper understanding of nature's way to create homochirality via multiscale chirality transfer.

In a different setting, recently Chen and co-workers have introduced sublimating-ice particles as a dynamic template for PCP-based multicomponent CVD (co)polymerization that enable accessing poly(*p*-xylylene) (co)polymer 3D porous particles replicating the ice particle template.[14] These findings outline a new approach for polymer nanostructures, aiming for engineered 3D soft-matter architectures.

2.1.2. Multifunctional Surfaces through CVD of Substituted Heterophanes: Going Beyond All-carbon Poly(p-xylylene)s and Controlling Molecular Sequence

Cyclophanes employed in CVD polymerization largely contain simple all-carbon backbones. However, by integrating heteroaromatics such as pyridophane, pyrazinophanes and pyrimidinophane derivatives in cyclophane, an entirely new class of functionalized polymers can be prepared by CVD process. In our proof-of-concept study going beyond all-carbon poly(*p*-xylylene)s, we have demonstrated poly(lutidine)s multifunctional surfaces through CVD by employing substituted pyridinophanes precursors (**Figure 6**).[15] These polylutidine films have shown higher isoelectric points owing to the nitrogen atoms in the polymer backbone than the corresponding poly-xylylene surfaces that supported an increased adhesion of primary human umbilical vein endothelial cells. Further accessibility to synthetically-tunable alkyne functional moieties on the surface of poly(4-ethynyl-2,5-lutidinylene-co-*p*-xylylene) coatings enables spatially-controlled surface modification for immobilization of biomolecules in post-CVD fabrication using Huisgen 1,3-dipolar cycloaddition.

With the heteroaromatics in the polymer backbone, on the one hand, we are targeting precise structural control in polymerization. On the other the nitrogen-rich chelating sites lead to a novel class of metal-chelating surfaces capable of interacting with metal ions/clusters of different chemical nature that can be used

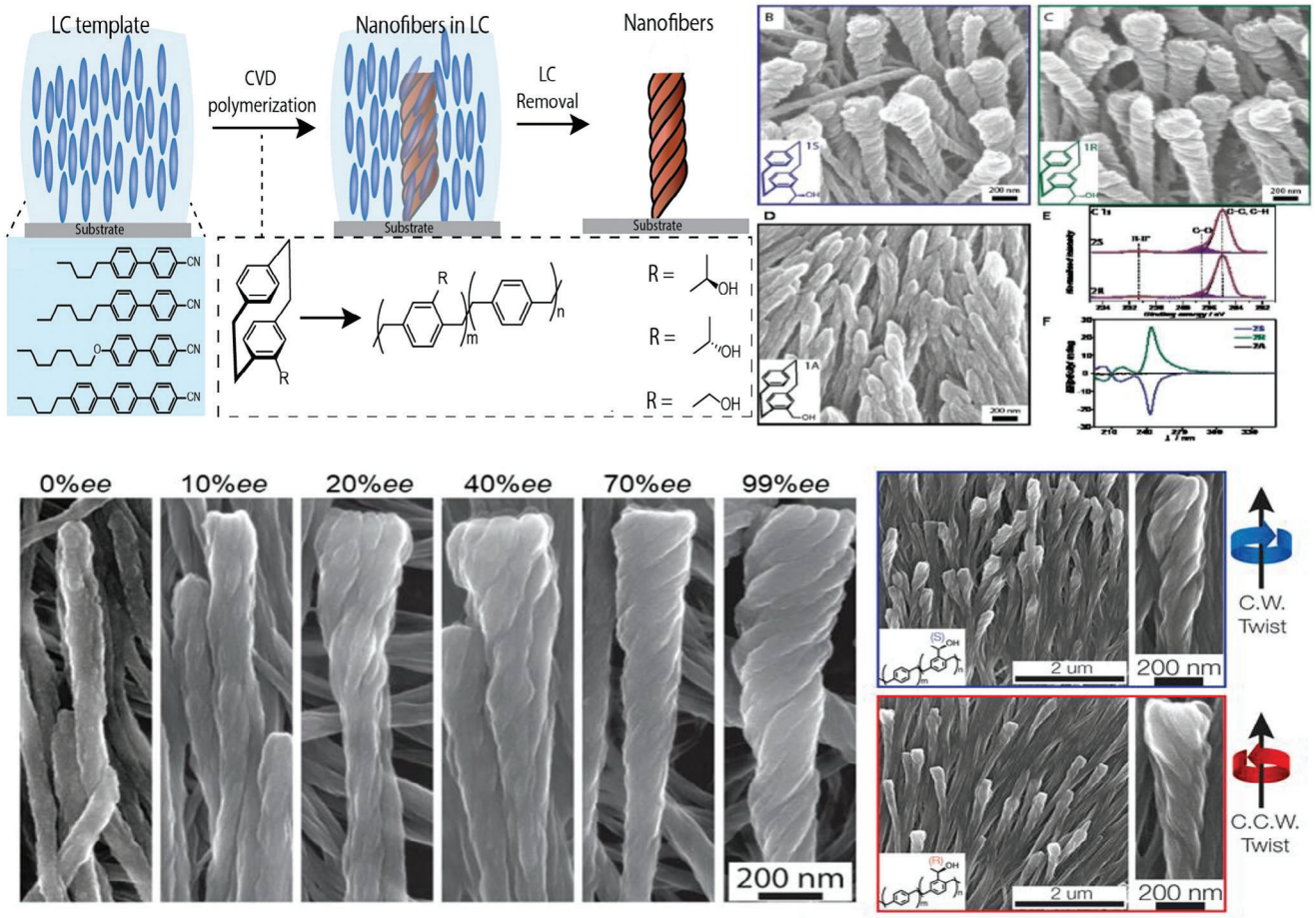


Figure 5. A) Templated synthesis of chirality-defined enantiomorphically pure polymer nanohelices via CVD polymerization into a nematic LC film (top). Inset: CVD polymerization of chiral and achiral PCP precursors B–D) SEM images of nanohelices *S* and *R* and achiral nanofibers prepared by CVD polymerization of 1*S* B), 1*R* C), and 1A D), respectively (the LCs are anchored on a surface before polymerization and removed after CVD polymerization). E) High-resolution C1s XPS spectra of *S* and *R* confirming identical chemical composition for nanohelices with opposite handedness; these spectra are identical to the achiral nanofibers. F) Circular dichroism spectra of nanohelices *S* (blue) and *R* (green) and achiral nanofibers A (black). Bottom: Enantiomeric purity of the molecular precursors defines the pitch of nanohelices during templated CVD polymerization. SEM images of the nanofibers and the induced mesoscale chirality of (+)-(S_p,*S*)-PCP and (+)-(S_p,*R*)-PCP with varying % enantiomeric excess upon polymerization into nematic E7. (blue) *S*-configured or (red) *R*-configured into a thin film of LC (MDA-98-1602). Reproduced with permission from ref. [13] Copyright 2021, Wiley-VCH.

for certain applications, for instance, heterogeneous green catalysts. This pioneering research on metal-ions immobilization onto the polymer surfaces has been of fundamental understanding. We aim to enable new catalytic functions and learn whether modifying the surfaces by immobilizing metal ions of different natures could enhance the existing efficiency in broadly useful challenging organic reactions by comparing their reactivities and efficiencies in several transformations. Their easy recyclability, reusability, and complete recovery from the reaction products could contribute to sustainable research efforts.

Furthermore employing cyclophanes with a systematic variation of electron-rich and poor aromatic phane units in CVD (co)polymerization may lead to strictly defined sequences. To achieve this control, we focus on four major process parameters: i) sublimation of the heteroaromatic cyclophane, ii) pyrolysis into two *p*-xylylenes, iii) adsorption/desorption to the cooled surface, and iv) the polymerization itself. Sequence control during CVD polymerization could result in alternating copolymer sequences or forming two individual homopolymers. By employing asymmetric cyclophanes, the repetition units can be connected in various ways giving sire to many possible CVD copolymers sequences. Besides the statistical copolymer structures, alternative structures, such as alternating copolymers or even the formation of two individual homopolymers can be contemplated.

2.2. Cyclophane-Based Small-Molecules Organic OLEDs: Thermally Activated Delayed Fluorescence (TADF) and Circularly Polarized Luminescence (CPL) Emitters

Organic light-emitting diodes (OLEDs), one of the most promising electroluminescent technologies, are widely used in numerous applications, such as smartwatches, mobile phones and televisions.[16] By avoiding costly platinoid metal elements that trigger environmental concerns, we aim to develop TADF

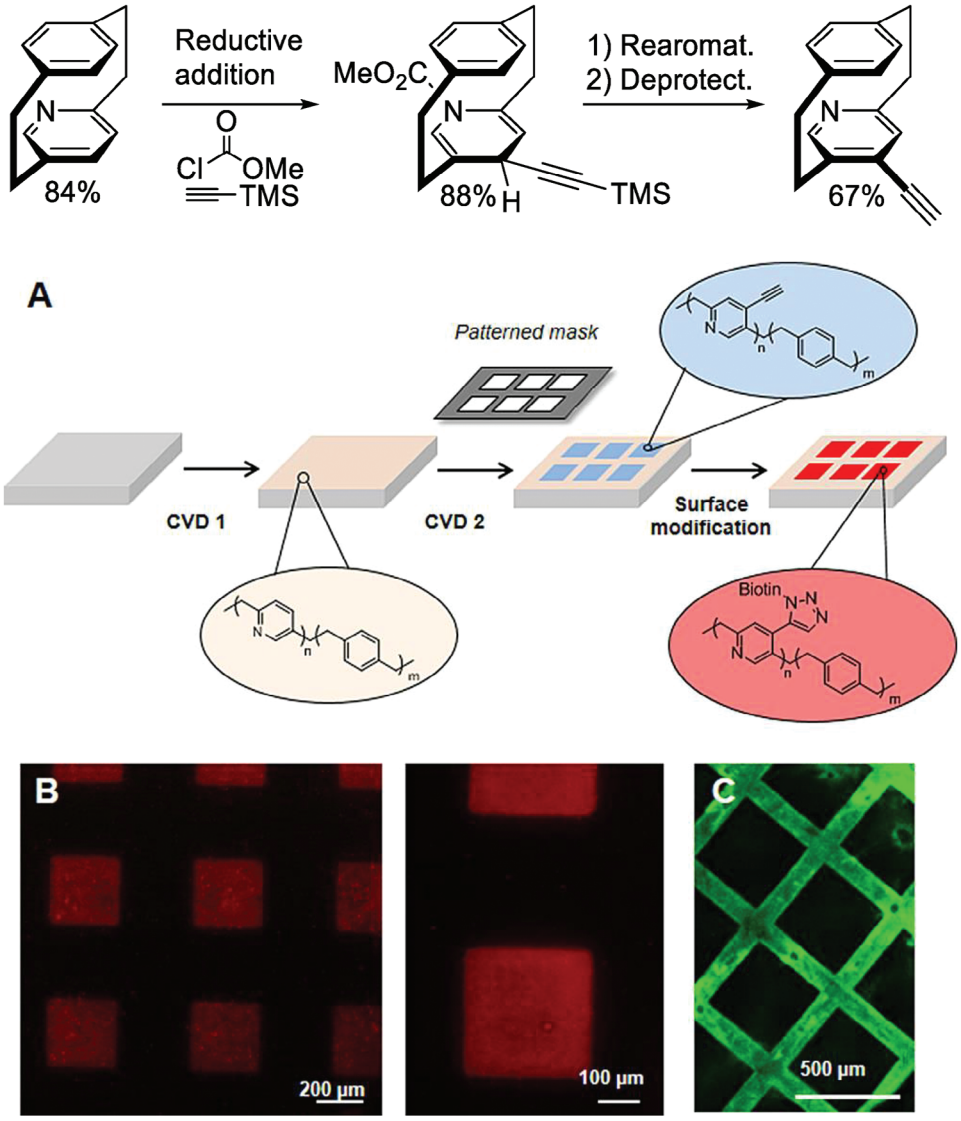


Figure 6. Function-oriented synthesis of acetylene-tagged pyridophane and formation of functional polylutidine-co-polymers. A) Schematic representation of the protocol for biotin immobilization on the functional coating. B) Fluorescence images after streptavidin incubation and c) fluorescence image after azido-PEG microcontact printing on polymer coating (PEG is located on a square pattern) and BSA-FITC incubation. Reproduced with permission.[15] Copyright 2017, Wiley-VCH.

compounds that emit light with high photoluminescence quantum yields, show high color purity due to their narrowband emission, and are easy to synthesize. The potential of TADF emitters for OLEDs was first demonstrated by Adachi and colleagues in 2012 who showed how twisted donor-acceptor compounds consisting of carbazolyl donors and dicyanobenzene acceptors could be used as emitters in devices that achieved efficiencies comparable to phosphorescent devices.[17] Since this pioneering research, thousands of reports have demonstrated the wide breadth of chemical space populated by TADF materials.[18]

Our contributions to this field include different TADF emitter designs with a π-stacked chiral 3D PCP scaffold. The design concept and retrosynthetic strategy to develop cyclophane-based TADF emitters, aided by computational simulations, are depicted in **Figure 7**. The distance within the two bent phenyl rings of the PCP core (3.09 Å) is shorter than the known π-stacking distance (3.35 Å) between two aromatic units; thus, unusual transannular electronic communications can be expected.[19] The physicochemical characteristics of the rigid 3D skeleton and stereochemical features arising on appropriate substitution, planar chirality, chemical and photostability, structural diversity with functionalization at strategic positions, and spatial electronic communications within the stacked benzene rings make it a promising scaffold for organic semiconductor materials and optoelectronic devices. Electron-donating moieties, such as carbazole-based groups, triphenylamines and acridine-based structures like phenoxazines, phenothiazine and 9,9-dimethyl-9,10-dihydroacridine are usually employed as donors while electron-accepting moieties, such as benzonitriles, triazines, benzophenones, sulfones,

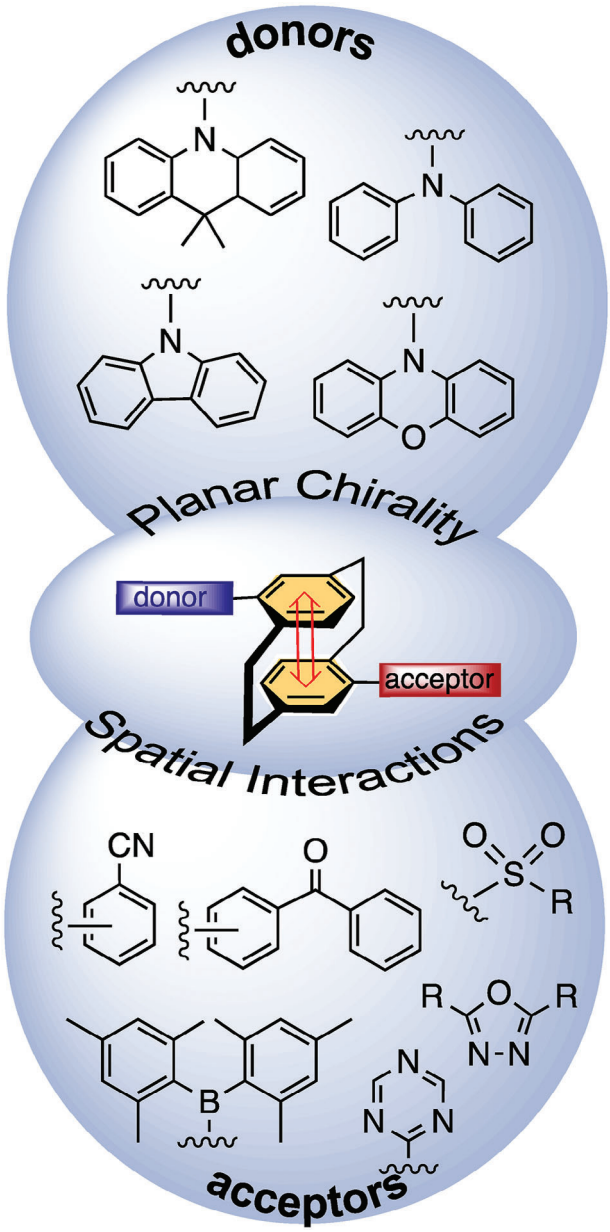


Figure 7. Design concept and retrosynthetic strategy to develop cyclophane-based TADF/CPL emitters featuring typical donor and acceptor moieties bridged by PCP scaffold to explore through-space electronic communications and tuning photophysical functions.

dimesitylboranes and others are predominantly decorated as acceptors.

We first reported TADF emitters where the donor resides on one deck and the acceptor on the other using the PCP scaffold to mediate electronic communication between the two.[20] We employed donors (4′-*N*,*N*-diphenylamino)phenyl and (4′-*N*-carbazolyl)phenyl and benzoyl groups as the acceptor (varying in their regiochemistry), which showed blue TADF emission with photoluminescence maxima, λ_{PL}, at 480 and 465 nm, respectively, in 15 wt% doped films in mCP (**Figure 8**). The photoluminescence quantum yields, Φ_{PL}, were low at 12% and 15%, thus no devices were fabricated. The presence of the enantiopure PCP component imparts planar chirality, and emissive analogs can generate circularly polarized luminescence (CPL).[21] We demonstrated that the incorporation of an annelated chiral carbazolophane (Czp) as an electron-donor combined with a triazine-based (TRZ) acceptor produce emitters that possess a ΔE_{ST} of 0.16 eV, λ_{PL} at 480 nm and Φ_{PL} of 70% in 10 wt% doped films in bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO).[22] Compared with carbazole, Czp adopts a more twisted conformation in donor–acceptor systems due to its larger size. This leads to a smaller ΔE_{ST} and turns on TADF in donor-triazine compounds. Enantiomerically pure R_P- and S_P- emitters showed mirror image circular dichroism and CPL spectra, the latter with g_{lum} of 1.3×10^{-3}. Sky blue-emitting OLEDs shows a maximum EQE (EQE_{max}) of 17% at CIE coordinates of (0.17, 0.25). We have demonstrated that the emission color could be tuned to the blue by incorporating electron-withdrawing cyano (CN) and trifluoromethyl (CF_3) groups onto the Czp moiety in CNCzpPhTRZ and CF_3CzpPhTRZ.[23] CNCzpPhTRZ and CF_3CzpPhTRZ emit at 458 and 456 nm and have Φ_{PL} of 65% and 70%, respectively in 10 wt% doped films in 2,8-bis(diphenylphosphoryl)dibenzo[*b*,*d*]thiophene (PPT). Blue OLEDs with CNCzpPhTRZ showed an EQE_{max} of 7.4% at 456 nm while the devices with CF_3CzpPhTRZ showed an EQE_{max} of 11.6% at 460 nm. In each of these TADF emitters, only a single deck of the PCP was initially elaborated.

We have disclosed a new class of [2]paracyclo[2](1,7)carbazolophanes that involve one of the ethylene bridge -$[CH_2]_2$ breakage and atypical rearrangement that triggers carbazole heterocycle formation/insertion within the [2.2]paracyclophane skeleton.[24] Here, a comparative study of the photophysical and optoelectronic properties of two cyclophane emitters, (1,7)*t*BuCzpPhTrz and its isomer (1,4)*t*BuCzpPhTrz, was performed. The carbazolophane-triazine compound (1,7)*t*BuCzpPhTrz, obtained via an unprecedented intramolecular rearrangement, is the first example of a planar chiral TADF emitter deviating from the PCP scaffold. Significant geometrical change of the enclosed carbazole in (1,7)*t*BuCzp results in an attenuation of the donor strength, while the merits of rigidity and steric bulk remain intact. In particular, the full width at half maximum of the photoluminescence spectrum in toluene of (1,7)*t*BuCzpPhTrz is reduced by 34% and the emission blue-shifted by 20 nm compared to that of (1,4)*t*BuCzpPhTrz. In doped films, the compounds reach high Φ_{PL} of 91 and 81%, respectively. The chiroptical properties reveal dissymmetry factors $|g_{PL}|$ of up to 5×10^{-4}.

To address the broadness of the emission, we have explored the strategy of directly decorating PCP and Czp with a multi-resonant TADF (MR-TADF) carbonyl (C=O)/N-based (quinolino[3,2,1-de]acridine-5,9-dione) core (known as DiKTa or QAO), and synthesized two pairs of chiral MR-TADF materials namely PCP-DiKTa and Czp-DiKTa.[25] The OLEDs with PCP-DiKTa and Czp-DiKTa showed narrowband emission at 489 and 518 nm and high EQE_{max} of 25.7 and 29.2%. Enantiomerically pure samples of both compounds show chiroptical properties in the ground state while only Czp-DiKTa exhibited chiroptical activity in the excited state, with dissymmetry factors ($|g_{PL}|$) of 4×10^{-4}. This study serves as an illustrative example of how a CP-TADF emitter can be tailored to be used in devices that showed narrowband

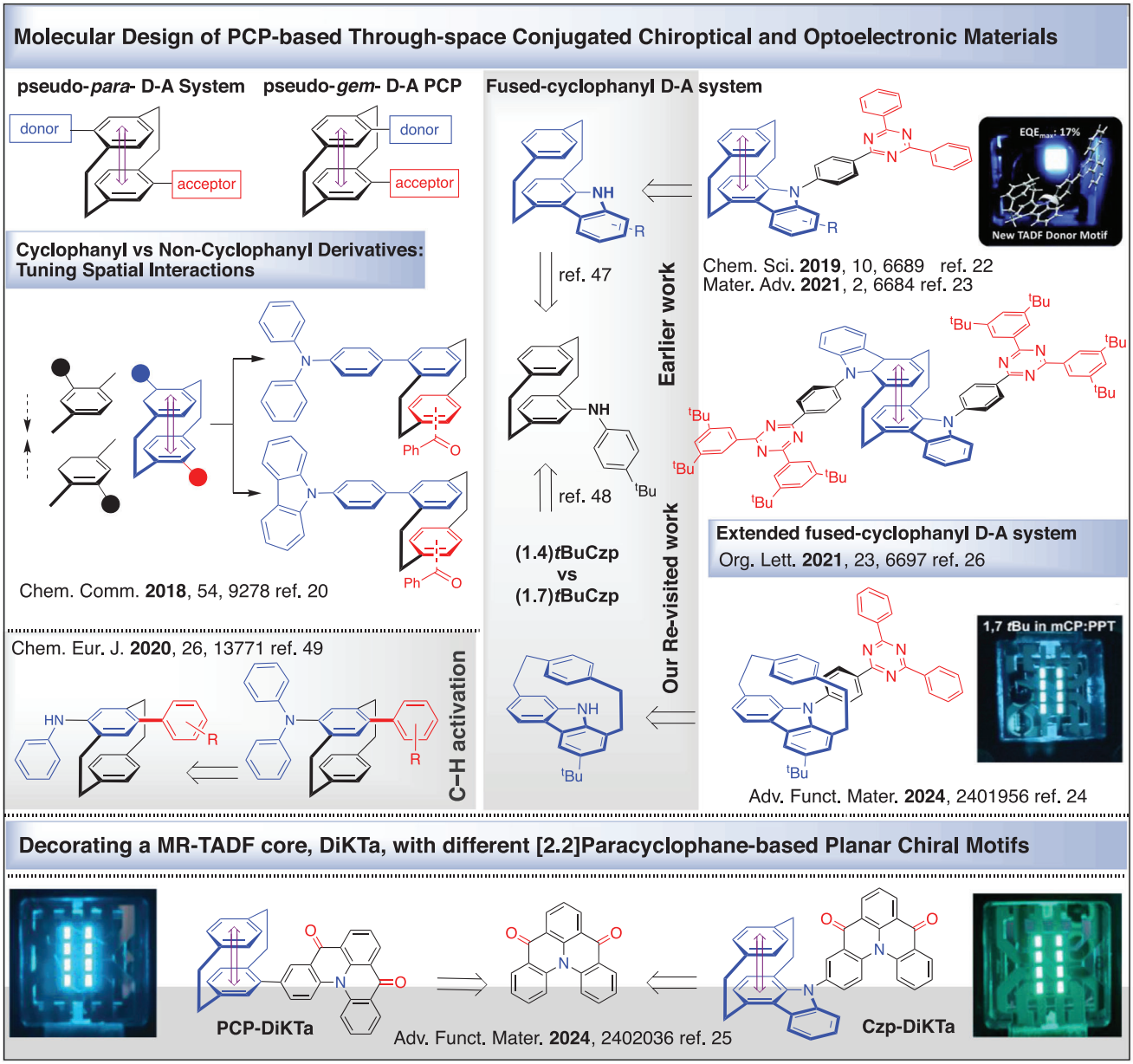


Figure 8. Cyclophane-based small-molecule TADF/CPL emitters: Exploring donor–acceptor modification strategy and through-space conjugation. Retrosynthetic analogy shows serendipitous synthetic disclosures including an unprecedented preferential C–H activation versus N-arylation,[49] and (1,7)carbazolophane formation versus (1,4)carbazolophane by atypical rearrangement and oxidative cyclization.[48] OLED images courtesy of the Zysman-Colman group at the University of St Andrews, UK. Adapted with permission from Ref. [22–26].

emission and superior device performance, mitigating efficiency roll-off concerns.

A second strategy to tune the photophysics of cyclophane-based TADF compounds is to elaborate both decks, which we demonstrated in a family of emitters possessing dicarbazolophane-based centrosymmetric donors.[26] The solution-processed OLEDs showed EQE_{max} of 8.2%. Tertiary butyl groups were introduced onto the triazine acceptor to improve the solubility of targeted emitters in organic solvents, which is important for producing high-quality solution-processed films. Other research groups worldwide have also made impressive contributions in recent years to the design of cyclophane-based TADF CPL emitters and their use in OLEDs.[27–34]

With ever-growing numbers of diverse chiral scaffolds being reported for TADF organic emitters, exploring new concepts and designing strategies offer the opportunity for improvements in performance to further progress. One of our ongoing research efforts for the realization of new organic optoelectronic materials lies under the umbrella of an Integrated International Core-to-Core joint research program headquartered in Japan https://www.scl.kyoto-u.ac.jp/~hirose/NCDc2c/index.html). The

Core-to-Core program aims to establish specialist-dependent collaboration with the best-known experts as diverse research hubs, with researchers from Germany, the United Kingdom, Canada, and Japan participating in this research program. This initiative aims at the synthesis of conceptually novel scaffolds aided by computational theory and simulations, which includes the development of new TADF materials. With these efforts, we hope organic electronics will become more "colorful" in the upcoming years.

2.3. Cyclophanyl-Derived Indicators Dyes for Host–Guest Supramolecular Sensing Assays: Developing New Fluorescent Chemosensors

Moving beyond covalent bonds, this research cooperation involves supramolecular synthesis and host–guest approaches for molecular sensing. We are intrigued by the behavior of small-charged molecules (guests) in confined molecular spaces (synthetic macrocyclic hosts). We aimed to develop model cationic-charged pyridium- and vinylpyridinium-modified cyclophanes as fluorescent guest molecules (indicator dyes) for supramolecular host–guest complexation in combination with several macrocyclic molecular hosts with in-depth studies of mechanism and function. This research is performed in cooperation with the Biedermann group and colleagues at the Institute of Nanotechnology (INT) at the KIT.

Developing new analysis methods and chemosensors with high levels of sensitivity and specificity for bio-relevant small molecule analytes (for instance, drug molecules, toxins, steroids, neurotransmitters, and hormones) and ions in aqueous media and complex biofluids (e.g., urine, and blood) hold high promises from application perspectives in medical diagnostics.[35] For developing chemosensors that exhibit high affinity toward such biomolecules, supramolecular sensing-driven approaches have become one of the prime candidates.[36] Synthetic molecular systems with discrete confined cavities, such as flexible crown ethers, cryptands, pillararenes, cucurbiturils, molecular boxes, and other macrocycles, display a combination of specific chemical reactivity, recognition, and complexation properties with external guests entities that have vital implications for host–guest supramolecular chemistry.[37]

We introduce the concept of "Suprasensing", i.e., supramolecular host-guest systems using cationic cyclophanes as guest indicators in combination with macrocyclic cucurbit[*n*]uril-based assay in aqueous environments or complex bio-fluids. Cucurbit[*n*]urils (CB[*n*], n = 5–8, 10, 13–15) and derivatives are glycoluril-based pumpkin-shaped (the name is given because of resemblance to a pumpkin of the *cucurbitaceae* family) synthetic macrocyclic hosts capable of remarkable guest-binding and exquisite recognition in aqueous environments (**Figure 9**).[38] CB[*n*], first reported in 1905, and related macrocycles display specific chemical reactivity and unique host–guest complexation properties attributed to the rigid molecular structure of CB[*n*]s, consisting of hydrophobic inner confined cavities surrounded by two symmetric polar carbonyl-lined portals.[39] A wide range of guests molecules and ions, for instance, amino acids, peptides, steroids, drug molecules, hydrocarbons, and certain proteins such as insulin, can fit into the hydrophobic inner cavity via charge–dipole interactions with the carbonyl portals of CB[*n*]s, form strong and stable host–guest complexes in water that can serve useful functions including molecular sensing, recognition, delivery and controlled release of drug molecules for diagnosis and therapy which has been summarized in several focused-reviews and inspiring articles.[40] The varying sizes of the portal diameter, cavity diameter, cavity volume, outer diameter and yet constant height of the cucurbit[*n*]urils (CB[*n*]) lead to remarkable recognition properties and supramolecular host-guest chemistry in confined spaces.

Modular PCP-containing mono-, and di-cationic pyridinium and vinylpyridinium modified cores as receptors in CB[*n*]-based host–guest supramolecular systems were prepared by regioselective functionalization, chiral resolution, and followed by successive transformations via Pd-catalyzed cross-coupling reaction with various pyridyl and vinylpyridinium derivatives (**Figure 10**).[41] On *N*-methylation, the PCPs bearing (cationic) pyridyl and vinylpyridyl functionalities were demonstrated as useful molecular receptors in host-guest supramolecular assays.

In preliminary explorations, methylpyridinium-modified PCP has been certificated a great affinity guest to CB[8] macrocyclic host for CB-based supramolecular sensing assay (**Figure 11**).[42] In this approach, an indicator is precomplexed in a supramolecular host, and if an analyte with a higher binding affinity is present, the indicator is displaced. A quantifiable spectroscopic analysis can follow the analyte's gradual indicator displacement. Methylpyridinium-modified PCP was the highest binding constant with CB[8] ($K_a = 2 \times 10^{13}$ M^{-1} in unbuffered water; $K_a = 5 \times 10^{11}$ M^{-1} in buffer). In aqueous media, these chromophoric and fluorescent indicator dyes showed characteristic emission bands in the visible (500−700 nm), could be excited with common light sources and lasers (up to 450 nm), and have large Stokes shifts which enable easy detection of optical changes (on complexation and dissociation) desirable for sensing applications. Fluorescence-detected circular dichroism is demonstrated for CB-based supramolecular chiral host–guest complexes exploiting planar chirality of the enantiopure PCP as a molecular guest.[43] The CB[*n*]-based complexation and high-affinity bindings were investigated by direct-binding assays (DBA), indicator displacement assays (IDA), and guest displacement assays (GDA) that exhibit high sensitivity, fast response time, and technical simplicity. A new strategy of guest displacement assay as a complementary method to IDA, capable of determining the binding affinity of spectrally silenced host-guest has been envisioned.[44] In contrast to IDA, the GDA method involves replacing the analyte with a dye to re-equilibrate and detect signal enhancement changes. It can permit the application to insoluble guests, typically hydrophobic and weakly bound guests.

This research on CB[*n*]-based host–guest supramolecular assays has been predominantly spanning molecular design and optimizing CB[*n*]-based host–guest binding pathways. It remains to be explored whether PCP-derived chromophore extended-conjugation, their relative orientation, and substitution patterns of the differently-functionalized cyclophanyl scaffolds could have critical effects on modulating/enhancing sensing properties of the CB[*n*] host–guest supramolecular system. This work is

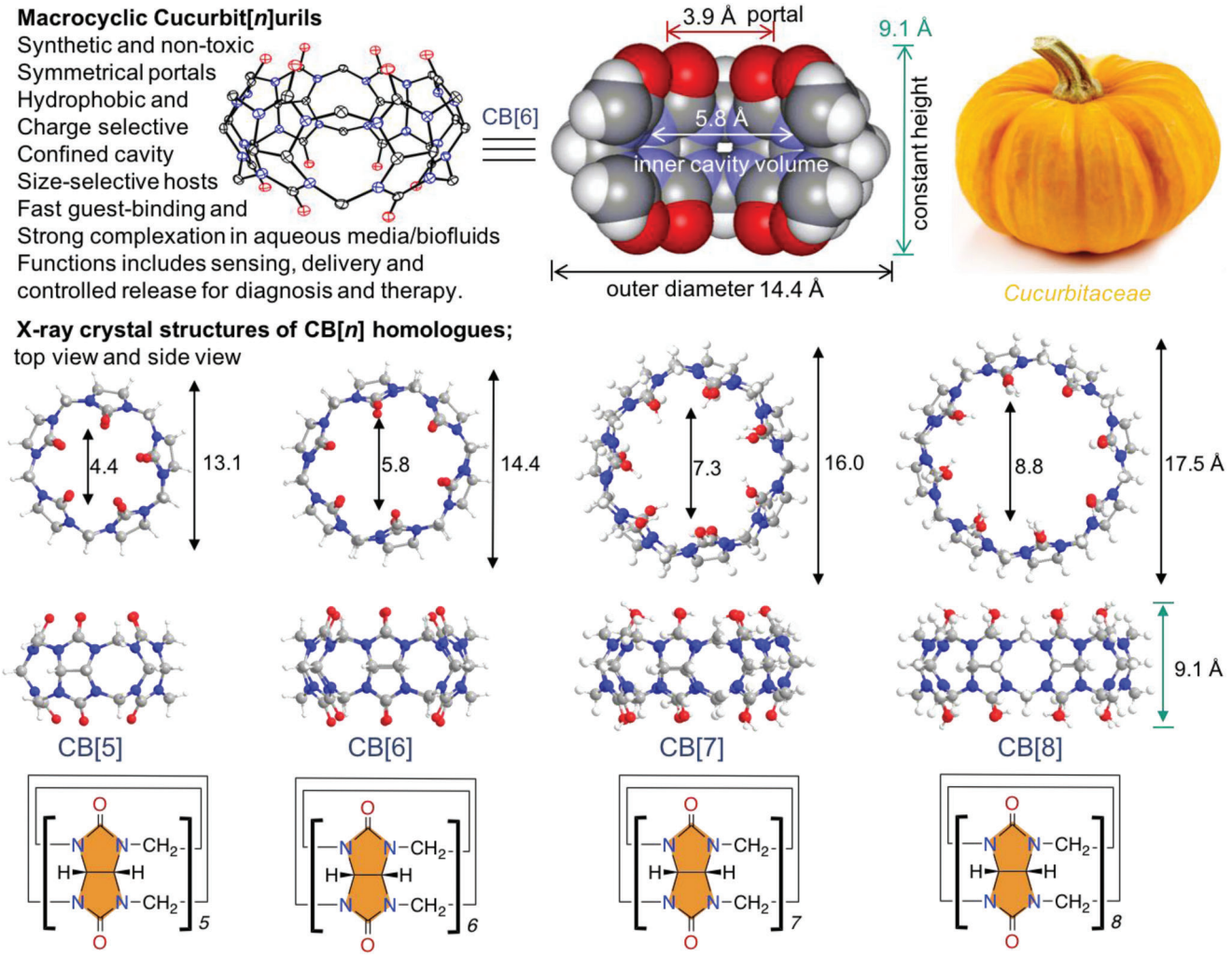


Figure 9. The chemical structures of known cucurbit[*n*]urils (CB[*n*], $n = 5–8$). In the crystal structures of CB[*n*], solvent/water molecules encapsulated inside (CB[*n*] cavities are removed for clarity. Color codes: oxygen, red; nitrogen, blue and carbon, gray. Crystal images are adopted with permission from the work of Kim labs, Mock, Isaacs and others whose names appear and cited in the ref. [38,39] Kürbis/cucurbitaceae image is reproduced from open resources.

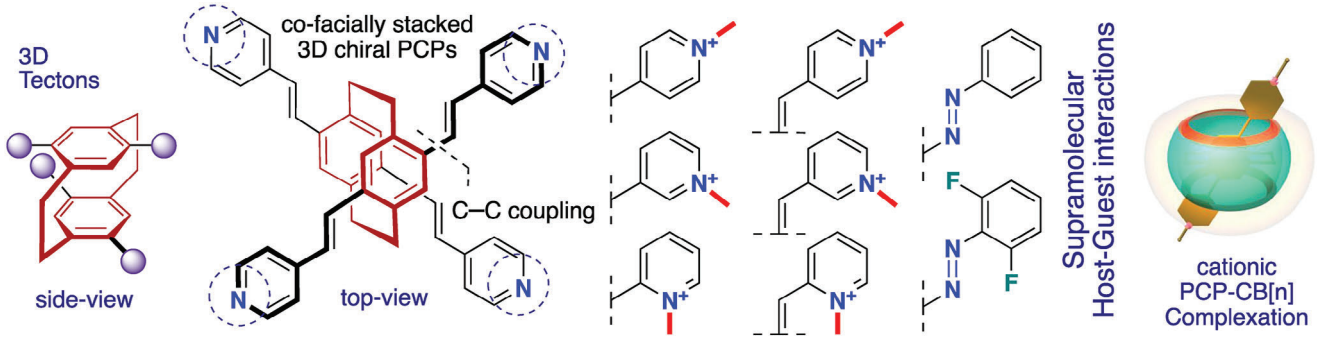


Figure 10. Mono-, di-, tri-, and tetra-cationic pyridinium and vinylpyridinium modified PCPs as modular receptors (a high affinity guests) for CB[n] macrocyclic hosts for CB-based supramolecular sensing assay. PCP-CB[*n*] complexation image courtesy of the Biedermann group and Dr. Yichuan Wang (a former PhD student) at the KIT. Reproduced from the authors own work Ref. [41].

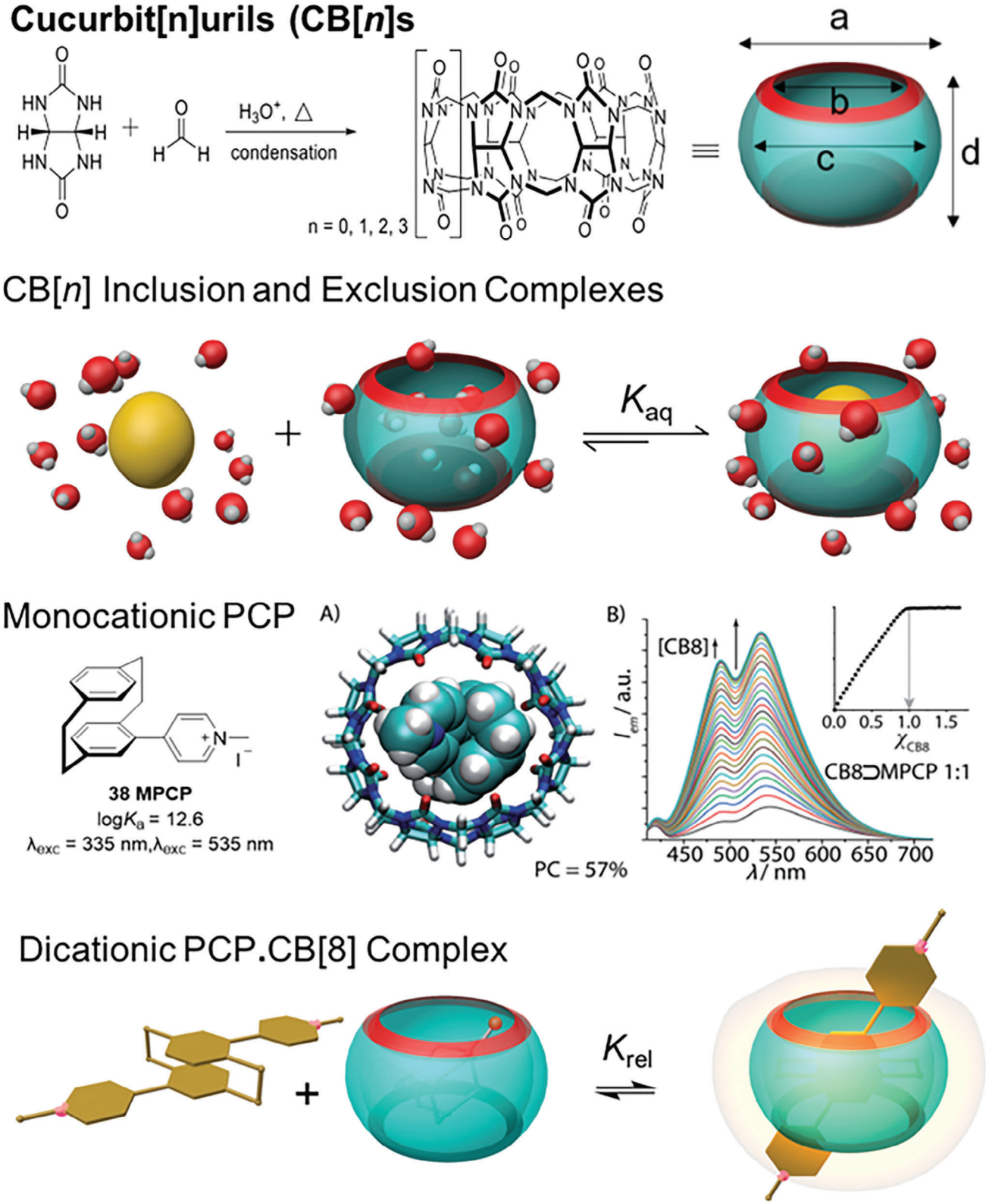


Figure 11. Cyclophanyl-derived pyridyl- and vinylpyridyl-modified cationic indicator dyes for host–guest supramolecular sensing. Parameters (a,b,c,d) demonstrating the varying sizes of the portal diameter, cavity diameter, cavity volume, outer diameter and yet constant height of the cucurbit[*n*]urils (CB[*n*]). Schematic illustration of the release of high-energy water molecules upon guest-binding, DFT model, and fluorescence spectra of the affinity showing the cationic methylpyridinium-modified PCP in indicator/analyte/host system. Reproduced with permission ref. [42] Copyright 2019, Royal Society of Chemistry and ref. [44] Copyright 2024, Wiley. PCP-CB complexation images courtesy of Biedermann group and Dr. Yichuan Wang at the KIT.

important in integrated planning because it investigates central and fundamental questions of chirality and chirality-based sensing. Supramolecular and bio-inspired systems are prime examples where the chirality of a molecule has a decisive influence on the whole system's behavior.

Beyond the concept of host-guest molecular assays, the N containing moieties at the peripheries onto the PCP derivatives have enormous potential to serve as coordination-capable molecular tectons for engineering function-inspired diverse noncovalent assemblies with tailored topologies, properties, and functions as like many other non-cyclophanyl building blocks.[45] For instance, pyridyl-substituted PCP derivatives as ditopic and tetratopic 3D tectons are particularly appealing for exploring cyclophane-based advanced material synthesis via molecular self-assembly inheriting the innate planar chirality and layered structure of the PCPs. Bridging cyclophane chemistry with supramolecular chemistry strategies to form supramolecular assemblies points to exciting new possibilities in cyclophane-based materials applications.

3. Few Lessons Learned in Cyclophane Chemistry via Multidisciplinary Research Initiatives from Molecules to Functional Materials and Prospects

Two of the authors of this report (ZH and SB) are synthetic chemists, "molecular makers" with special interests in developing function-inspired new organo(metallic) molecules and (macro)molecular scaffolds that could perform useful functions. Although researchers at large, doing independent science, pursue topics and specific interests based on understanding and familiarity to a particular domain, chemistry research is much more interdisciplinary. We have observed that what could be more obvious to synthetic chemists (molecular details) may not be obvious to material engineers, physicists, or bio-scientists (and vice versa). Multidisciplinary collaborations have become an integral part of research, and as part of research and expertise in organic synthesis, we are equally keen and have contributed as the "molecular foundry" to support interdisciplinary collaborations by designing innovative (macro)molecular building blocks that could be used as components for materials application. We share a few lessons learned during our research partnerships in engineering cyclophane-based materials and functional systems. This may serve a purpose in placing our research into a broader perspective and even stimulating new research perspectives.

3.1. Searching for New Reactivity and Methods in Designing Strategies: A Synthetic Chemists Perspective

"No molecule, no matter its structural type, is out of the reach of chemical synthesis. The real question, however, is how elegantly and efficiently we can synthesize such complex molecules, and it is here that the synthetic chemists have to concentrate their efforts the most."[46] Exploring new concepts and designing strategies offer the opportunity for improvements to further progress to show their benefits compared to the earlier reported work.

During our journey in cyclophane chemistry, we learned that despite 75 years of research and development, cyclophane still holds many surprises due to unusual chemical reactivity. Even in certain cases, the results may not be predictable under the classic and established reaction conditions. During our target-oriented synthesis for cyclophane-based TADF emitters development, the serendipitous formation of several unprecedented cyclophanes that had never been observed or overlooked in several earlier reports was disclosed. For instance, upon revisiting the earlier work on reporting the synthesis of planar chiral carbazole derivatives by oxidative cyclization of the 4-*N*-phenylamino-PCP,[47] a new class of [2]paracyclo(1,7)carbazolophanes[24] was disclosed that involve one of the ethylene bridge -$[CH_2]_2$- breakage and atypical rearrangement which triggers carbazole heterocycle formation/insertion within the PCP skeleton.[48] Several earlier reports had never identified this novel class of carbazolophanes featuring a differently-functionalized carbazole heterocycle insertion. Well-grown crystals of [2.2]paracyclo(1,7)carbazolophane were obtained and single-crystal X-ray analysis confirmed the molecular structure. There are very few examples of molecular re-arrangements reported that alter the PCP skeleton through C–C bond breakage. These findings tell us, "One can discover new things by carefully reviewing old work". These results are important for the future design of the conceptually novel molecular system and potentially useful molecules for organic optoelectronic materials dealing with steric strain, conformational behavior, and exploring the interplay of through-space electronic interactions/delocalization in tuning optoelectronic functions. Similarly, installing donor/acceptor-type motif onto the PCP as TADF precursor components, an unanticipated reactivity and preferential selectivity of regioselective C–H activation/aryl–aryl coupling of 4-phenylamino-PCP was observed.[49] The C–H activation/aryl–aryl coupling of amines under the Buchwald–amination reaction condition is not common in literature.

Chirality has been a principal theme in our collaborative research program. We aim to find innovative, selective, and effective concepts to prepare enantiomerically pure planar and central chiral cyclophane monomers. For instance, aiming for CVD polymerization with chirality trasnfer via enantiomerically pure derivatives, a new and efficient protocol toward kinetic resolution of PCPs employing a ruthenium-catalyzed enantioselective hydrogenation process has been proved crucial.[50] This method can be performed on a multigram scale and gives access to enantiomerically pure derivatives with planar and central chirality of (R_p)-4-acetyl-PCP (≥97% e.e., 43%) and (S_p,*S*)-PCP derivatives (≥97% e.e., 46%). Beyond developing a new synthesis method, the final products have useful utility as precursor components; we have successfully demonstrated for the structuring of chiral polymers via cyclophane-based monomer design strategies.[51]

In our explorations toward developing broadly applicable surface modification strategies using CVD and post-CVD, we recently introduced a new platform though phosphorylation using UV-induced photo-Arbuzov reaction as a versatile portal to phosphonate-grafted scaffolds.[52] The phosphonylated PCPs were exclusively obtained by de-sulfurization/phosphonylation. While under similar reaction conditions, thio-cyclophanyl analogs solely undergo sulphur-extrusion and no C–P bond

formation occurs. Beyond developing new synthesis method for C–P bond formation, utility of this synthetic approach and final products as precursor components, we have successfully demonstrated in molecular structuring of phosphorylated polyparylenes and protein absorption properties of the developed surfaces.[53]

In a similar way, to access polylutidines multifunctional surfaces throught CVD polymerization, developing synthesis route toward the foundamental precursors of the rarely investigated class of the N-heterocyclic pyridinophanes is a pre-requisite. The synthesis of the pyridinophane scaffolds featuring a pyrazole, trizol, tetrazol, and pyrimidine heterocycle was successfully developed.[15b]

In search of new reactivity and methods as well as designing strategies, implementation of multiscale theoretical simulations and advanced modeling guide experimental chemists in designing strategies to understand and select superior-performing components. To correlate experimental data with high-level calculations has a transformative effect, and provide insights into how to design new and more efficient molecular building blocks and system-level functions. The breadth of methods, strategies, and techniques currently being applied to computational design.[54] Computer-aided methods and design strategies can provide a predictive role to rationalize and better understand experimental observations. Predictions are becoming more useful to experimentalists, information technology, computations, and automation in synthesis have a limitless future. Machine-learning approaches and computer-aided methods assist in designing strategies.[55]

We have an established protocol for our research that is "First ask to build molecules" guided by the concept of "First calculate then synthesize". These tools have been incredibly useful in guiding through synthesis.

3.2. Both "Hot data" and "Cold data" shall be Available on All Levels with Scientists' Agreement on a Sharing Policy

Access to online searchable journals and databases has been a significant scientific advance. However, research articles largely report "Hot data" and successful procedures that have been part of the publications. The focus is largely on the positive outcomes. Although synthetic procedures are optimized after numerous trials and errors and are called "Cold data" that largely remain unpublished. The causes of errors in optimization are left unreported due to word count policy within average limits or information can only be accessible/available after publication. Cold data could be a valuable information source that can guide colleagues to save their precious time and resources during their research in other laboratories and expedite scientific discoveries. We (obviously as a personal opinion) advocate that the research outcomes of all tested procedures and chemical data, both Hot data and Cold data should be available on all level with scientists agreements on a sharing policy for further specific investigation. Our cooperation has greatly benefited from the chemical data generated over the years at the KIT for individual projects. We have initiated a community-driven repository at the KIT (called Chemotion, https://chemotion.net) for extracting, re-using (ability), and sharing the chemistry research data for physically preserved research materials among our cooperation partners.[56] We developed Chemotion ELN, an open-source electronic lab notebook.[57] The ELN supports collecting, storing, processing, analyzing, disclosing, re-using research data, and managing the routine work of synthetic chemists and materials scientists that helps in situations, especially in early-stage research for screening synthetically accessible molecular libraries. This web-based application is an Open Source that offers modern solutions for chemical researchers, including access to previously-performed trials and errors as "Cold data".

The "Molecule Archive" established at the KIT is a service facility that registers and preserves chemical compounds from academic research institutions and distributes them for further re-use by scientists in collaborative projects. The service is provided to not-for-profit projects. This serve research cooperations aiming for applications in materials sciences and bio-related fields. For instance, our collaboration with S. Özbek and colleagues at the Department of Molecular Evolution and Genomics, Centre for Organismal Studies, University of Heidelberg deserves special mention that benefited from research data with physically preserved research materials. 700 small molecules screen identifies 1,5-triazole-substituted PCPs as novel inhibitors of mechanosensory nematocyst discharge in *Hydra magnipapillata*.[58] Several other PCPs are identified that cause inhibition of nematocyst discharge in the low micromolar range. [2.2]Paracyclophane linked two benzimidazole-octahydroindole ligands has been developed for commercial Odalasvir, a selective inhibitor of Hepatitis C virus NS5A protein entering Phase 3 clinical trials.[59] The enantioselective effect of planar chiral PCPs decorated with immunostimulatory small-molecule resiquimod/Res has been demonstrated in SARS-CoV-2 vaccine-induced immune response.[60] For SARS-CoV-2 vaccine, in comparison to *R*-ResPCP, *S*-ResPCP exhibited a 4.05-fold enhancement for vaccine-induced cross-neutralization against various viral strains. These findings demonstrate the enantioselectivity effects of small molecules on regulating vaccine-induced immune responses and emphasize the significance of chirality in designing small molecular adjuvants.

3.3. Nurturing Young Scientists via Multidisciplinary Research Initiatives, Joint Supervision and Mobility of Scholars

The most important aspect of research is training young minds and skilled scientists in a creative process. Today's realities point not only to highly specialized chemists such as those, for example, who know how to synthesize molecules rapidly and efficiently or those who can perform precise analyses but also to experts with interdisciplinary knowledge and skills who may be poised to solve different kinds of problems and define new ones.[61] Interdisciplinary research programs contribute to broadening and diversifying expertise and acquiring new capabilities.

Scientific research is becoming more global, and mobility could be the seeds for a mutually rewarding collaboration and building a strong network for research excellence/innovations. To foster an open scientific and interdisciplany exchange of knowledge, mobility of scholars provides outstanding opportunities for sharing mutual experiences, knowledge and skills. In

the context of our cooperation and research under the Joint Supervision of mentoring young scholars, several participating synthetic chemists at the KIT had the opportunity of study and perform research abroad with whom we collaborated, particularly at the Biointerfaces Institute, University of Michigan (https://www.lahannlab.com) via exchange programs for advancing their research projects and at the Organic Semiconductor Centre, University of St Andrews (http://www.zysman-colman.com) for special training and expertise in the development of organic and organometallic compounds for OLED materials used in optoelectronic products. Several materials scientists from the participating institutions were hosted at the KIT (https://www.ioc.kit.edu) through special initiatives to get familiar and work on synthesis methods development, chiral cyclophane building blocks, and materials synthesis for technologically relevant applications. This opportunity offers a broad scale of complimentary competencies through sharing experiences and new learning necessary to broaden and diversify expertise, acquiring new capabilities and exposure to enrich transferrable skills.

In addition to the mobility of young scholars, KIT has established to support Associated Group leadership program (one of the coauthor; J. Lahann is serving as co-director of the Institute of Functional Interfaces (IFG) while have main research activities in the USA). For know-how of synthetic chemists about CVD lab set-up and polymerization techniques as well as to discuss the progress of the CVD-PCP collaboration, in-person chalk talks at IFG, when time permits, has been always encouraging fostering better communication between the scientists. This collaborative research has led to several cooperation-related cutting-edge articles in interdisciplinary journals (>40 original articles cited in this report highlight a small portion of our recent joint research).

3.4. Training Objectives via Industrial–Academic Collaboration and Translational Journey from Academia to Innovative Entrepreneurship

Industrial partnership is a healthy development and should be promoted to strengthen collaborations and build partnerships for academic-industry symbiosis since both could benefit from it.[62] Acedemia is consulted for its opinion on future technologies. Through the interest of both academia and industry, cross-disciplinary research is expected providing an intellectual environment to prepare researchers with useful talents and skills to be employed in academia and industry. Industrial-academic collaborative research provides ideal environments for promoting young scientists as a key element that contains i) subject-specific and interdisciplinary education that drive innovation and development, ii) promotion of professional skills, and iii) targeted supervision of researchers. On successful completion of projects, graduates and students are likely to continue in universities and/or join industries and, thus, are expected to contribute to advancing research culture and developing technologies. Joint projects enable students to interface with future employers, providing a path to the industrial workforce. In this way, young scientists-engineers-entrepreneurs are trained for their future career in academia and industry. Overall, these consortia are excellent platforms for networking and identifying academic and industrial collaborators necessary for breakthroughs from labs to commercialization. Although collaborations mostly involving one-to-one academic group-company relationships still have significant impacts on the corresponding fields, larger consortia leverage the full capabilities of their constitutive institutions to address interdisciplinary challenges.[63] Cooperation with partners from science and industry represents a key success factor for stepping forward.

While academic research is fundamental in nature and the science necessarily basic, by setting joint priorities to meet shared needs, it is hoped and expected that certain application-driven outcomes, including translational research that spawns start-ups, might emerge. One prominent venture company bridging academic and industrial research is CYNORA GmbH, which has close ties and roots in academia (led by organic chemistry professionals/alumni at the IOC/KIT).[64] This inspires a translational journey from academia to end-product-driven research and the economic role of chemistry in entrepreneurship. SB, one of the authors of this report, has been serving as Co-Founder and Member of the advisory Board of Cynora GmbH. CYNORA innovates advanced OLED materials (with a portfolio of large number of patents) to enable a new generation of foldable, flexible, and transparent displays. The company is a leading global pioneer of novel TADF-based blue and green emitter systems that aim to improve OLED displays' power efficiency and color purity.

In collaborative research, synthetic chemist mostly begins the work by synthesizing molecules for specific investigations (scale-up synthesis, and sometime grams to multi-grams scales are required). These synthetic procedures are optimized after substantial trials and errors, or very specific procedures are figured-out that is a time-demanding task and need enormous efforts. On the other side, materials scientists aim for certain breakthroughs by ensuing collaborative research that need a lot of persistent effort, time, and patience. Many scientists recognize the importance of this as a team to struggle and succeed together. Synthetic chemists provide seeds and materials scientists nurture it till the very end, thereby fruitful collaborations is mutually win-win for all professionally that everyone get fair recognition as deserved which are sometime unnoticed. Sometime research projects may not work well as initially planned or might take longer than initially expected which is not unusual in scientific research and explorations. In such situations, this is certainly important to clearly communicate with trust and mutual respect.

The motto "Citius, Altius, Fortius – Communiter" not only motivates Olympics, it equally inspires scientists to be "Faster, Higher, Stronger – Together" for progressing scientific innovations and technological advancements. Together we are strong!

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Conflict of Interest

The authors declare no conflict of interest.

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