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Bending benzenes and twisting light

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Publication date
2026

[Link to publication](#)

Citation for published version (APA):

Kovida, K. (2026). *Bending benzenes and twisting light*. [Thesis, fully internal, Universiteit van Amsterdam].

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Summary

This thesis explores chiral π -conjugated macrocycles, focusing on chiral carbon nano hoops as potential candidates for circularly polarized luminescence (CPL) applications. It surveys strategies to achieve high emission dissymmetry factors and fluorescence quantum yields, the key parameters that define CPL performance. Particular attention is given to the influence of chirality, symmetry and strain on the chiroptical properties of these systems. Accordingly, the thesis is organized into two main parts. The first part focuses on the design and synthesis of chiral carbon nano hoops that incorporate chirality inducing units such as [2.2]paracyclophane (PCP) and helicene and investigates how exciton delocalization influences their chiroptical properties. The second part investigates the role of molecular strain in the stereodynamic behavior of helicene-based carbon nano hoops. Finally, an outlook discusses potential post-synthetic modifications aimed at building up strain through a π -extension strategy.

Chapter 1 lays the foundation by explaining the essential role of chirality in chemistry and introduces two key spectroscopic techniques, Circular Dichroism (CD) and Circularly Polarized Luminescence (CPL). It emphasizes the growing demand for high-performance chiral emitters for use in optoelectronics and defines the key parameters for quantifying CPL, such as dissymmetry factors of absorption and emission and emitter brightness. The chapter then discusses key strategies for designing bright emitters with large dissymmetry factors, highlighting the importance of placing the electric and magnetic transition dipole moments at an optimal angle. Following this, it reviews selected examples of π -conjugated macrocycles, specifically carbon nano hoops addressing the synthetic challenges involved in bending benzenes and surveys current methods for introducing chirality into otherwise achiral cycloparaphenylenes, thereby setting the stage for the molecular design approaches to chiral carbon nano hoops developed in later chapters.

Chapter 2 details the systematic preparation of chiral carbon nano hoops utilizing [2.2]paracyclophane (PCP) units as rigid, planar chiral building blocks. By integrating PCP units into cycloparaphenylene frameworks, chiral carbon nano hoops were developed with desirable photophysical properties. The chapter addresses key synthetic challenges, including the complex macrocyclization and aromatization steps, establishing an optimized protocol for making strained conjugated nano hoops described in later chapters. Additionally, it explores structural modification by introducing an acceptor group, which red shifts the emission but reveals a crucial balance between molecular strain and chemical instability.

Chapter 3 presents the synthesis of carbon nanohoops that incorporate both a planar chiral PCP unit and a highly fluorescent acceptor group into a cycloparaphenylene framework. The resulting macrocycles exhibit a pronounced redshift in their emission while maintaining high fluorescence quantum yields. Although the measured dissymmetry factors of absorption and emission were modest, this study enabled the first systematic investigation into how exciton delocalization influences the chiroptical properties in these nanohoop structures. The insights gained establish key structure–property relationships that serve as guidelines for maximizing chiroptical performance in future nanohoop designs.

Chapter 4 modifies the above design strategy by replacing the PCP unit with a [5]helicene moiety as the chiral element. The resulting fully conjugated helicene carbon nanohoop exhibits significantly red-shifted emission extending into the near-infrared (NIR) region with appreciable fluorescence quantum yield. Detailed steady-state spectroscopic studies of the separated enantiomers were performed to strengthen the hypothesis linking π -conjugation, exciton delocalization and the magnitude of dissymmetry factors. Furthermore, the high correlation between experimental results and theoretical calculations validates the computational model, opening the door for a large-scale computational screening to identify potential CPL candidates.

Chapter 5 delves into the stereodynamic properties of chiral nanohoops containing helicene units. A series of helicene nanohoops of varying sizes were successfully synthesized and their enantiomers were resolved. This systematic study investigates how the strain within the nanohoops influences the stereodynamic behavior of the embedded helicene. Extensive racemization kinetics experiments reveal a direct structure–property relationship, providing clear design guidelines for controlling the configurational stability of helicene nanohoops, a tool for developing stable chiral materials for chiroptical applications.

Finally, **Chapter 6** offers an outlook on a strategy for post-synthetic π -extension and strain increase within an already strained nanohoop. The approach involves the synthesis of strained macrocycles that incorporate both a helicene and a perylene diimide (PDI) unit, followed by an attempted photocyclization reaction designed to significantly increase molecular strain. Computational analysis strongly supports this strategy, predicting a substantial increase in strain upon π -annulation. Preliminary photophysical measurements show a large hypsochromic shift in absorption and emission upon π -annulation, which is consistent with the predicted widening of the energy gap, thereby validating the design concept.

Samenvatting

Dit proefschrift beschrijft onderzoek aan chirale π -geconjugeerde macrocyclische moleculen, in het bijzonder chirale koolstof-nanohoepels. Dit zijn grote ringstructuren die op hun beurt zijn opgebouwd uit kleinere ringen die met koolstof-koolstofbindingen aan elkaar zijn geknoopt. De nanohoepels worden beschouwd als potentiële kandidaten voor toepassingen in circulaire gepolariseerde luminescentie (CPL), een vorm van spectroscopie die het verschil meet in de emissie van links- en rechtsdraaiend circulaire gepolariseerd licht door een materiaal. De grootte van dit verschil wordt uitgedrukt in de dissymmetriefactor. Daarnaast is een hoge fluorescentiekwantumopbrengst van belang voor een sterk CPL signaal. Het proefschrift geeft een overzicht van strategieën om deze factoren te optimaliseren in nanohoepels. Daarbij wordt bijzondere aandacht besteed aan de invloed van chiraliteit, symmetrie en moleculaire spanning op de chiroptische eigenschappen van deze systemen. Het eerste deel van het proefschrift richt zich op het ontwerp en de synthese van chirale koolstof-nanohoepels die eenheden bevatten die zorgen voor chiraliteit, zoals [2.2]paracyclofaan (PCP) en heliceen, en onderzoekt hoe excitondelokalisatie hun chiroptische eigenschappen beïnvloedt. Het tweede deel bestudeert de rol van moleculaire spanning in het stereodynamische gedrag van op heliceen gebaseerde koolstof-nanohoepels.

Hoofdstuk 1 licht de essentiële rol van chiraliteit in de chemie toe en introduceert twee belangrijke spectroscopische technieken: Circulair Dichroïsme (CD) en Circulair Gepolariseerde Luminescentie (CPL). Het hoofdstuk benadrukt de groeiende behoefte aan chirale emitterende materialen voor gebruik in opto-elektronica en definieert de sleutelparameters voor het kwantificeren van CPL, zoals dissymmetriefactoren voor absorptie en emissie en de helderheid van de fluorescentie. Vervolgens bespreekt het hoofdstuk strategieën voor het ontwerpen van heldere emitters met grote dissymmetriefactoren, waarbij het belang wordt benadrukt van een optimale hoek tussen de elektrische en magnetische overgangsdipoolmomenten. Daarna volgt een overzicht van voorbeelden van π -geconjugeerde macrocycli, in het bijzonder koolstof-nanohoepels. Hierbij worden de synthetische uitdagingen besproken die gepaard gaan met het buigen van benzeenringen en worden actuele methoden onderzocht om chiraliteit te introduceren in anderszins achirale cycloparafenyleenstructuren, waarmee het fundament wordt gelegd voor de moleculaire ontwerpstrategieën voor chirale koolstof-nanohoepels die in latere hoofdstukken worden ontwikkeld.

Hoofdstuk 2 beschrijft de systematische synthese van chirale koolstof-nanohoepels met [2.2]paracyclofaan (PCP) als rigide, vlak-chirale bouwsteen. Het hoofdstuk behandelt de synthetische uitdagingen, waaronder de complexe macrocyclisatie- en aromatisatiestappen, en geeft een geoptimaliseerd protocol voor de synthese van gespannen geconjugeerde nanohoepels dat in latere hoofdstukken zal worden toegepast. Daarnaast wordt een elektronaccepterende groep geïntroduceerd, wat de emissie naar langere golflengte verschuift maar ook een cruciale balans blootlegt tussen moleculaire spanning en chemische instabiliteit.

Hoofdstuk 3 presenteert de synthese van koolstof-nanohoepels die een vlak-chirale PCP-eenheid en een sterk fluorescerende acceptorgroep in een cycloparafenyleen-raamwerk bevatten. Deze verbindingen vertonen een uitgesproken roodverschuiving in hun emissie terwijl zij hoge fluorescentiekwantumopbrengsten behouden. Hoewel de gemeten dissymmetriefactoren voor absorptie en emissie bescheiden waren, maakte deze studie het mogelijk om voor het eerst systematisch te onderzoeken hoe excitondelokalisatie de chiroptische eigenschappen in deze nanohoepel-structuren beïnvloedt. Met de verkregen inzichten in structuur-eigenschapsrelaties kunnen de chiroptische prestaties van toekomstige nanohoepel-ontwerpen worden verbeterd.

Hoofdstuk 4 bouwt voort op de eerdere ontwerpstrategie door de PCP-eenheid te vervangen door een [5]heliceenmotief als chiraal element. De resulterende volledig geconjugeerde heliceen-koolstof-nanohoepel vertoont sterk roodverschoven emissie die reikt tot in het nabij-infrarood, met een aanzienlijke fluorescentiekwantumopbrengst. Resultaten van spectroscopische studies van de gescheiden enantiomeren ondersteunen de hypothese die π -conjugatie, excitondelokalisatie en de grootte van dissymmetriefactoren met elkaar verbindt. De sterke correlatie tussen experimentele en berekende gegevens bevestigt het theoretische model, wat de weg opent voor grootschalige computationele screening om potentiële CPL-kandidaten te identificeren.

Hoofdstuk 5 gaat in op de stereodynamische eigenschappen van chirale nanohoepels die heliceen-eenheden bevatten. Een reeks heliceen-nanohoepels met verschillende grootte en ringspanning werd succesvol gesynthetiseerd en hun enantiomeren werden gescheiden. Kinetische metingen van de snelheid van racemisatie laten een directe relatie zien met structuurkenmerken van de macrocyclische ring. Dit biedt duidelijke ontwerprichtlijnen voor het beheersen van de configuratiestabiliteit van heliceen-nanohoepels en dat is belangrijk voor de ontwikkeling van stabiele chirale materialen voor chiroptische toepassingen.

Tot slot biedt **Hoofdstuk 6** een vooruitblik op een strategie voor het vergroten van de ringspanning binnen een reeds gespannen nanohoepel. De aanpak omvat de synthese van macrocyclische ringmoleculen die zowel een heliceen- als een peryleendiimide- (PDI) eenheid bevatten, gevolgd door een poging tot een fotocyclisatie-ringfusiereactie die ontworpen is om de moleculaire spanning verder te vergroten. Computatieve analyse ondersteunt deze strategie sterk en voorspelt een substantiële toename in spanning na ringfusie. De eerste fotofysische metingen tonen een grote hypsochrome verschuiving in absorptie en emissie na ringfusie. Dit is consistent met de voorspelde verbreding van de energiekloof en bevestigt daarmee het ontwerpconcept.

List of Publications

Publications covered in this dissertation

1. **Kovida, K**[†]; Malinčík, J[†]; Groot, T.D.; Šolomek, T.
How Do Nanohoops Exercise Their Strain in [5]Helicene Racemization?
J. Org. Chem. **2025**, *90* (46), 16607–16614.
2. **Kovida, K**; Malinčík, J.; Šolomek, T.
Effect of π -Electron Conjugation on the Chiroptical Properties of Helicene Carbon Nanohoops.
Helv. Chim. Acta **2025**, *108* (4), e202400166.
3. **Kovida, K**; Malinčík, J.; Cruz, C.M.; Campaña, A.G.; Šolomek, T.
Role of Exciton Delocalization in Chiroptical Properties of Benzothiadiazole Carbon Nanohoops.
Chem. Sci. **2025**, *16* (3), 1405–1410.

Other Publications

4. Roy, R.; Pramanik, A.; Dutta, T.; Sharma, V.; **Kovida**; Koner, A. L.
Harnessing Solution and Solid-State Emissive Materials from Aliphatic Biogenic Amine-Induced Transient Assembly and Spontaneous Disassembly.
Mater. Chem. Front. **2022**, *6* (23), 3489–3503.
5. **Kovida**[†]; Sharma, V[†]; Koner, A. L.
Rapid On-Site and Naked-Eye Detection of Common Nitro Pesticides with Ionic Liquids.
Analyst **2020**, *145* (12), 4335–4340.
6. Sharma, V[†]; **Kovida**[†]; Sahoo, D.; Varghese, N.; Mohanta, K.; Koner, A. L.
Synthesis and Photovoltaic Application of NIR-Emitting Perylene-Monoimide Dyes with Large Stokes-Shift.
RSC Adv. **2019**, *9* (52), 30448–30452.

[†] = authors contributed equally

Acknowledgements

I did not complete my PhD alone. Throughout this journey, I was fortunate to be surrounded by many people who supported me both intellectually and personally. Whether it was troubleshooting a failed experiment, engaging in stimulating scientific discussions or simply offering words of encouragement during challenging times, I am incredibly grateful to everyone who shared their time, expertise and kindness with me. This section is for all of you.

First and foremost, I would like to express my deepest gratitude to my supervisor, Dr. **Tomáš Šolomek**, for giving me the opportunity to pursue my PhD in your research group. Your patient supervision, invaluable feedback and constant encouragement kept me on the right path and made the successful completion of this thesis possible. Thank you for trusting me with new project ideas, granting me academic freedom while continuously challenging me to grow as a researcher. Most importantly, thank you for always having an open office door not only for scientific discussions, but also for conversations that made this journey lighter and more enjoyable.

I am extremely thankful to Prof. **Fred Brouwer** for accepting the role of my promotor. Your guidance has been invaluable, and I am sincerely grateful for the time and energy you devoted to providing insightful feedback on my research and thoughtful suggestions for improving this doctoral thesis. I also extend my sincere gratitude to my doctoral committee, Prof. **Jana Roithová**, Dr. **Bettina Baumgartner**, Dr. **Sonja Pullen**, Prof. **Jan van Maarseveen** and Prof. **Chris Slootweg** for dedicating their precious time to the assessment of my thesis and for their constructive and valuable feedback throughout this journey.

I gratefully acknowledge our collaborators, Dr. **Araceli G. Campaña** and Dr. **Carlos M. Cruz** for the fruitful collaborations on our work on CPL, for the insightful scientific discussions and for the valuable feedback that led to several joint publications. I also thank Dr. **Susanna Bertuletti** at AMOLF for the kind assistance with CD measurements and Dr. **Yingying Tang** for help with the quantum yield measurements. Thank you all for always being willing to help, sometimes also at short notice, and for teaching me how to work with various instruments.

I would also like to thank Prof. **Marcel Mayor** and the entire Mayor group at the University of Basel for their generosity and support during my PhD, especially for providing access to instruments such as MALDI and HPLC. A special thank you to the Basel crew, **Hua, Luise, Salome, Pascal, Laurent, Valerie, Henrik** and **Senta** for the wonderful times in Basel and for always making me feel welcome, especially during the group BBQ sessions.

My sincere thanks go to the management team at HIMS, **Laura, Saskia, Renate** and **Christina** for the warm welcome in Amsterdam and for making my transition from Bern smooth and stress-free. You truly made “moving across countries” easy for me. **Laura**, thank you for always being there for me, whether for IT issues, visa matters or simply sharing life updates and laughter. I am also deeply grateful to Dr. **Andreas Ehlers** and **Ed Zuidinga** for their support, insightful discussions on NMR and MS and for endless troubleshooting during my research.

I would like to express my deepest gratitude to the esteemed professors at the Molecular Photonics group for all the fruitful discussions and valuable feedback during the group meetings and afterwards. Thank you, Dr. **Annemieke Petrignani**, Dr. **Giulia Giubertoni**, Prof. **Sander Wouterson**, Prof. **Hong Zhang**, Dr. **René Williams** and Prof. **Wybren Jan Buma**. Thank you, **Wybren Jan**, for giving me the opportunity to be involved with the HIMS PhD council. I also warmly thank the incredibly skilled and supportive lab technicians **Wim**, **Michiel**, **Hans** and **Tim** for their constant technical support and guidance over the years and for all the memories together. Thank you **Hans** for being so patient and welcoming when we invaded the labs with our stuff and for helping us settle into the labs so smoothly. **Tim**, thank you for your invaluable advice on thesis writing and improving it. I always learn so much from you. **Michiel**, thank you for the quantum yield measurements and for always being so helpful and available when lab issues arose. A special thanks to the molphot HPLC for not dying during my final PhD project and to **Michiel** and **Tim** for repeatedly rescuing the blue screen of death stricken 90s computer with utmost importance and heroic dedication.

I am deeply thankful to my colleagues and friends at the University of Bern and the University of Amsterdam. I would like to begin by thanking the Šolomek lab members in Bern: **Sergey**, **Remek**, **Noah**, **Simon**, and **Gianna** for the wonderful time we shared in the group. **Sergey**, thank you for teaching me GPC, for the valuable research discussions and not to forget, for being there when I used *t*-BuLi for the first time. **Remek**, thank you for the great time we shared in Bern, from picking me up at the train station with Tomas when I arrived in the country for the very first time, to the cooking sessions in Bolligen, the hiking trips and countless scientific discussions. Special thanks go to my friends at UniBern, **Eva**, **Kaila**, **Isabella**, **Cedric** and **Ivo** for basically adopting me during the early days of my PhD and making me feel at home. It was indeed fun and a great learning experience to start the PhD coalition with you at UniBern.

My sincere thanks go to all former and current members of the Molecular Photonics group for creating such a welcoming, positive and memorable environment. **Quentin**, thank you for the unforgettable crêpe and wine evenings and for so many good memories, you are always missed. Dear **Max**, **Ivan**, **Chao** and **Begüm**, even though our time together was short, I learned so much from each of you and will forever cherish those moments. You all have been my go to people had I any questions about work or life in general and I am very happy to have known you all. **Begüm**, you have been one of the kindest and most inspiring colleagues and friends I have ever met, I cannot thank you enough for being so helpful with even minor stuff, you always make me feel at home and at ease. Love you!

A big thank you and many warm hugs to **Maëva**, you have known me the longest and stood by me throughout my entire PhD journey in Amsterdam. I am forever grateful for your genuine friendship and for all the times you have lifted me up with your kind words and the Starbucks coffee. **Hugo**, **Carolyn** and **Leting**, thank you for all the coffee chats, for solving daily work problems together, and for organizing meetups outside of work, I have learnt so much about different cultures from you all. Talking to you all even for a short time is enough to make my day. **Orr**, thank you for the kindness and encouragement you bring with you everywhere, I always find myself smiling and feeling happier every time we meet even if it's for a short bit.

Robin, my lab bestie, thank you for joining our group and making the last few months of my PhD life even more enjoyable, thanks to your humor. I will never forget our memorable GPC-HPLC adventures working, chatting and solving problems together. Our beloved GPC is in your big hands now, good luck! I also warmly thank **Robert, Kefan, Jun, Sarah, Hoda, Prakash, Mahsa, Jana, Lucy, Daan, Sander** and **Theo** for being a big part of my journey and for all the shared memories, laughter and good times, whether during lunch or at Oerknal.

Special gratitude goes to the HIMS PhD council, **Renate, Tamika, Youri, Elia** and **Maria** for organizing many successful events together, particularly the annual Christmas party and the HIMS symposium. These experiences helped me better understand the insides of the academic administration and management, build a strong network of people and develop valuable skills.

I am immensely grateful to my family, especially my wonderful parents, Sh. **Roshan Lal** and Smt. **Meghawati** for their unwavering support with my career decisions and for giving me strength to move abroad for higher studies. I am forever grateful for the values and lessons you have taught me in life that shaped me into who I am today. Thanks to the best sister and brother in the world, **Rachita** and **Himanshu** for always being supportive of my choices, for being just a call away and for fighting for me in difficult times. Thank you from the bottom of my heart. I extend my huge thanks to my lifelong friends in India, **Sweety** and **Meenu** for being part of my chemistry journey for over twelve years. You filled my life with happiness, constant encouragement and joy, and I am forever grateful to have known such amazing souls.

Lastly, I want to thank my colleague and now fiancé, Dr. **Juraj Malinčík** for the unconditional love, support and encouragement that you have showered me with during this PhD journey. I have learned so much from you and you have been very patient with me especially while learning computations. Words are not enough to express my feelings so thank you for literally everything and Milujem ťa.

Kovida

Amsterdam, 2026

