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### Ferrocene-based light-responsive carbon nano hoops

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# Summary

The research presented in this thesis centers on cycloparaphenylenes (CPPs), a family of macrocycles composed only of phenylene rings connected through the *para* position, with particular emphasis on new synthetic strategies and the development of novel CPP derivatives. The first part investigates the use of specific silyl protecting groups as an alternative route for the synthesis of carbon nanohoops. The main section then describes the preparation and characterization of a series of CPPs incorporating either a simple or *ansa*-bridged ferrocene (Fc) unit within the macrocyclic backbone. The results provide important insights into the effect of molecular strain on the structural, optoelectronic, and electrochemical properties of the nanohoops and highlight its critical role in driving the photochemical uncaging of  $\text{Fe}^{2+}$ .

Chapter 1, which serves as the introduction to this thesis, begins by discussing the different allotropes of carbon and presents CPPs as the shortest cross-sections of armchair carbon nanotubes (CNTs). Various synthetic approaches to CPPs are then outlined, followed by an overview of their structural, electrochemical, and optoelectronic properties, as well as their applications. Next, previously reported CPPs capable of shape alteration or incorporating metals are reviewed in detail to provide context for the work described in this thesis.

Chapter 2 explores improved protecting-group strategies for synthesizing strained carbon nanohoops such as CPPs. Sterically bulky silyl groups such as *tert*-butyldimethylsilyl (TBDMS) and triisopropylsilyl (TIPS) are evaluated as alternatives to alkyl and triethylsilyl (TES) groups. In particular, TBDMS can be readily installed and removed under mild conditions while offering superior stability and high stereoselectivity. Additionally, two methods are proposed for the selective deprotection of TES in the presence of TBDMS under mild conditions.

Chapter 3 describes the synthesis and full characterization of **Fc[6]CPP**, a nanohoop consisting of Fc enclosed in a loop of six *para*-phenylene rings. The strong molecular strain induces unprecedented photochemical reactivity under visible light. Green-light irradiation with 1,10-phenanthroline opens the hoop, releasing  $\text{Fe}^{2+}$  as  $[\text{Fe}(\text{phen})_3]^{2+}$  in high yield, even in water-rich media. Quantum yields reveal a thousand-fold boost in photoreactivity compared to unstrained

Fc. The data indicate that dissociation proceeds via interception of the nanohoop's photoexcited triplet state by nucleophilic solvent or ligands.

Chapter 4 reports the synthesis of **Fc[n]CPPs** ( $n = 7, 8$ ) as two novel photoactivable  $\text{Fe}^{2+}$  carriers. Spectroscopic, electrochemical, and computational studies of **Fc[n]CPPs** ( $n = 6-8$ ) reveal how nanohoop strain affects the geometry and photoreactivity of the Fc center. Remarkably, efficient Fe–Cp bond dissociation occurs even in less distorted systems, indicating that kinetic effects from strain, not just structural distortion, drive the reactivity. These results demonstrate the tunability of CPP strain for controlled  $\text{Fe}^{2+}$  uncaging.

Chapter 5 presents the efforts towards the synthesis of **Fc[5]CPP**, the smallest macrocycle of the Fc[n]CPP family. Notably, Suzuki coupling produced the pro-aromatic intermediate **pro-Fc[5]CPP**, whose triangular structure was confirmed by X-ray analysis. The final aromatization step proved challenging due to the high strain of **Fc[5]CPP**, leading to poor reproducibility and difficult purification. Nevertheless, the desired macrocycle was observed for the first time.

Chapter 6 demonstrates the synthesis of two ferrocene-based nanoscrolls, **a-Fc[6]CPP** and **a-Fc[8]CPP**, featuring an *ansa* ether bridge that locks the ferrocene conformation. Obtained as single enantiopure diastereomers, the strained macrocycles show up to 20-fold enhanced visible-light-induced  $\text{Fe}^{2+}$  uncaging via Fe–Cp bond dissociation. Quantum yields indicate that photoreactivity is retained even with reduced excess of the ligand, highlighting the critical role of the *ansa* bridge in modulating metallocene behavior.

# Samenvatting

Het onderzoek dat in dit proefschrift wordt beschreven richt zich op cycloparafenylenen (CPP's), een familie van macrocyclische verbindingen die uitsluitend bestaan uit fenyleenringen verbonden via de para-posities. De nadruk ligt hierbij op nieuwe synthetische strategieën en de ontwikkeling van nieuwe CPP-derivaten. Het eerste deel onderzoekt het gebruik van specifieke silyl-beschermgroepen als een alternatieve methode in de synthese van koolstofnanohoeplets. Vervolgens komt het hoofddoel van het onderzoek aan de orde, namelijk de bereiding en karakterisering van een reeks CPP's waarin een eenvoudige of *ansa*-gebonden ferroceen (Fc)-eenheid is geïntegreerd in het macrocyclische skelet. De resultaten verschaffen belangrijke inzichten in het effect van de spanning in de ringstructuur van de nanohoeplets op hun structurele, opto-elektronische en elektrochemische eigenschappen, en benadrukken de cruciale rol ervan bij het sturen van de fotochemische vrijgave van  $\text{Fe}^{2+}$ .

Hoofdstuk 1, dat dient als de inleiding van dit proefschrift, begint met een bespreking van de verschillende allotropen van koolstof en presenteert CPP's als de kortste dwarsdoorsneden van "armchair"-koolstofnanobuisjes (CNT's). Vervolgens worden diverse synthetische benaderingen voor CPP's besproken, gevolgd door een overzicht van hun structurele, elektrochemische en opto-elektronische eigenschappen, evenals hun toepassingen. Daarna worden eerder gerapporteerde CPP's die vormverandering kunnen ondergaan of metalen kunnen incorporeren uitvoerig besproken, om zo context te bieden voor het werk dat in dit proefschrift wordt beschreven.

Hoofdstuk 2 onderzoekt verbeterde beschermende-groep-strategieën voor de synthese van gespannen koolstof nanohoeplets zoals CPPs. Silylgroepen die veel ruimte innemen —*tert*-butyldimethylsilyl (TBDMS) en triisopropylsilyl (TIPS)— worden onder de loep genomen als alternatieven voor kleinere alkyl- en triethylsilylgroepen (TES). Vooral TBDMS kan eenvoudig worden aangebracht en verwijderd onder milde omstandigheden, terwijl het superieure stabiliteit en hoge stereoselectiviteit biedt. Daarnaast worden twee methoden voorgesteld voor de selectieve ontscherming van TES in aanwezigheid van TBDMS.

Hoofdstuk 3 beschrijft de synthese en volledige karakterisering van **Fc[6]CPP**, een nanohoepel bestaande uit ferroceen ingebouwd in een lus van zes *para*-fenyleenringen. De grote spanning in de ringstructuur induceert ongekende fotochemische reactiviteit onder zichtbaar licht. Bestraling met groen licht in aanwezigheid van 1,10-fenantroline opent de lus, waarbij  $\text{Fe}^{2+}$  wordt vrijgegeven als  $[\text{Fe}(\text{phen})_3]^{2+}$  in hoge opbrengst, zelfs in waterrijke media. Kwantumopbrengsten laten een duizendvoudige toename van de fotoreactiviteit zien vergeleken met vrij ferroceen. De gegevens wijzen erop dat dissociatie verloopt via onderschepping van de elektronisch aangeslagen triplettoestand van de nanohoepel door nucleofiele oplosmiddelen of liganden.

Hoofdstuk 4 beschrijft de synthese van **Fc[n]CPPs (n = 7, 8)** als twee nieuwe fotoactiveerbare  $\text{Fe}^{2+}$ -dragers. Spectroscopische, elektrochemische en computationele studies van **Fc[n]CPPs (n = 6–8)** tonen hoe de ringspanning van de nanohoepel de geometrie en fotoreactiviteit van het Fc-centrum beïnvloedt. Opmerkelijk is dat efficiënte Fe–Cp bindingsdissociatie zelfs optreedt in minder vervormde systemen, wat aangeeft dat kinetische effecten door spanning—en niet alleen structurele vervorming—de reactiviteit sturen. Deze resultaten tonen aan dat CPP-spanning kan worden benut voor gecontroleerde  $\text{Fe}^{2+}$ -vrijgave.

Hoofdstuk 5 presenteert de inspanningen voor de synthese van **Fc[5]CPP**, de kleinste macrocyclus van de Fc[n]CPP-familie. Via Suzuki-koppeling werd het pro-aromatische intermediair **pro-Fc[5]CPP** gemaakt, waarvan de driehoekige structuur werd bevestigd met behulp van röntgendiffractie. De laatste aromatiseringsstap bleek uitdagend door de grote ringspanning van **Fc[5]CPP**, wat leidde tot slechte reproduceerbaarheid en moeizame zuivering. Desondanks werd de gewenste macrocyclische verbinding voor het eerst waargenomen.

Hoofdstuk 6 beschrijft de synthese van twee op ferroceen gebaseerde "nanoscrollen", **a-Fc[6]CPP** en **a-Fc[8]CPP**, die worden gekenmerkt door een *ansa*-etherbrug die de ferroceenconformatie vastlegt. Geïsoleerd als enkelvoudige enantiozuivere diastereomeren vertonen deze gespannen macrocycli tot een twintigvoudige toename in zichtbaar-lichtgeïnduceerde  $\text{Fe}^{2+}$ -vrijgave via Fe–Cp-bindingsdissociatie. Metingen van de kwantumopbrengst tonen aan dat de fotoreactiviteit zelfs behouden blijft bij een verminderde ligandovermaat, wat het cruciale belang van de *ansa*-brug benadrukt bij het moduleren van het gedrag van metalocenen.

# List of publications

1. **R. B. Krećijas**, J. Malinčík, T. Šolomek. Exploring Silyl Protecting Groups for the Synthesis of Carbon Nanohoops. *Synthesis* **2023**, *55*, 1355–1366.
2. **R. B. Krećijas**, J. Malinčík, S. Mathew, P. Štacko, T. Šolomek. Strain-Induced Photochemical Opening of Ferrocene[6]cycloparaphenylene: Uncaging of Fe<sup>2+</sup> with Green Light. *J. Am. Chem. Soc.* **2025**, *147*, 10231–10237.



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