The Research Group
General Chemistry

has the honor to invite you to the public defense of the PhD thesis of

Eline Desmedt

to obtain the degree of Doctor of Sciences

Title of the PhD thesis:

Exploring the chemical compound space of hexaphyrin-based nonlinear optical switches with inverse molecular design

Promotors:
Prof. dr. Mercedes Alonso
Prof. dr. ir. Freija De Vleeschouwer

The defense will take place on

Friday, January 10, 2025 at 5 p.m. in auditorium I.0.01
VUB Etterbeek campus, Pleinlaan 2 Elsene.

The defense can be followed through a live stream. Contact Eline Desmedt for more information.

Members of the jury

Prof. dr. Ulrich Hennecke (VUB, chair)
Prof. dr. Frank De Proft (VUB, secretary)
Prof. dr. Jan De Beule (VUB)
Prof. dr. Benoît Champagne (UNamur)
Dr. Eduard Matito (DIPC, UPV/EHU, ES)
Dr. Julia Contreras-Garcia (Sorbonne Université & CNRS, FR)

Curriculum vitae

Eline Desmedt obtained her degree of Master of Science in Chemistry at the Vrije Universiteit Brussel in 2019. Afterwards, she joined the General Chemistry research group (ALGC) as a PhD student with a predoctoral fellowship awarded by FWO.

She is co-author of eight scientific papers in peer-reviewed international journals, among which five times as a first author. Eline Desmedt presented her work at international conferences as five oral and five poster presentations, respectively, and was awarded with two poster prizes. Besides teaching activities, she supervised three bachelor and four master students in the framework of their thesis. She disseminated her research to the broad public via a podcast and EOS blog post.

Abstract of the PhD research

Driven by their curiosity, humans have explored unchartered parts of the Earth and beyond. Similarly, researchers in chemistry investigate the chemical compound space (CCS) to search for new and undiscovered molecules for potential applications in medicine and material sciences. For instance, the search for efficient molecular electronic devices has recently spiked in importance as they show the potential to replace the current silicon-based technologies. Thanks to their tunable chemical and photophysical properties, porphyrins and their expanded analogs have been recently put forward as excellent candidates for new materials such as infrared dyes and molecular electronics such as nonlinear optical switches. One successful strategy to enhance the nonlinear optical properties of these systems is to directly introduce functionalizations such as core-modifications and *meso*-substitutions into their macrocycles based on chemical intuition. Due to the enormous size of the CCS, only small regions are traversed with traditional direct molecular design approaches making the discovery of novel functionalized molecules for nonlinear optical applications challenging. By applying inverse molecular techniques, we aim to efficiently explore larger regions of the compound space in search of promising expanded porphyrin-based molecular switches as measured by their first-hyperpolarizability related to the Hyper-Rayleigh Scattering (β_{HRS}) and the NLO contrast between the switch's ON and OFF states.

In this work, we start by scrutinizing the influence of functionalizations on the structural properties, aromaticity, UV/Vis absorption spectrum, and β_{HRS} of different selected unfunctionalized hexaphyrin configurations with various π-conjugation topologies and redox states. From this initial study, we derived structure-property relationships linking aromaticity to the photophysical properties, and β_{HRS} responses. Building further on these relationships, we performed several inverse design procedures with the best-first search algorithm starting from the most favorable redox (**26R** ⇌ **28R** & **30R** ⇌ **28R**) and topological switches (**28M** ⇌ **28R**) to further explore the combinatorial CCS of *meso*-substituted and core-modified hexaphyrins with high-contrast NLO switches based on different definitions of this contrast. No matter the contrast definition, the efficiency of the **26R** ⇌ **28R** and **30R** ⇌ **28R** is enhanced to a much greater extent than for the **28M** ⇌ **28R**. In the process, an extensive dataset was collected and statistical analysis revealed how each type of functionalization affects the NLO responses of the [26]- and [30]hexaphyrins, and in which aspects both redox switches differ. In addition, we extended our search to multistate switches of the type **26R** ⇌ **28R** ⇌ **30R**, where we aimed at designing switches with a similar NLO response for both ON states. By visualizing the CCS, we observe that our best-performing switches are found in regions shared by high-responsive [26]- and [30]hexaphyrins. To further understand why these two hexaphyrins behave so differently, machine-learning (ML) models with explainable ML techniques were designed using several physical and chemical properties. Finally, we exploit our hexaphyrin dataset to generalize the structure-property relationships between aromaticity and UV/Vis derived spectroscopic properties.