



**AFRL-AFOSR-UK-TR-2023-0051**

---

**Platinum Acetylides in Cholesteric Liquid Crystal Glasses for Nonlinear Optical Applications**

**Patrick Norman  
KUNGLIGA TEKNISKA HOGSKOLAN  
VALHALLAVAGEN 79  
STOCKHOLM, , 10044  
SE**

---

**03/15/2023  
Final Technical Report**

**DISTRIBUTION A: Distribution approved for public release.**

Air Force Research Laboratory  
Air Force Office of Scientific Research  
European Office of Aerospace Research and Development  
Unit 4515 Box 14, APO AE 09421

## REPORT DOCUMENTATION PAGE

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

<b>1. REPORT DATE</b> 20230315		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED</b>	
				<b>START DATE</b> 20191215	<b>END DATE</b> 20221214
<b>4. TITLE AND SUBTITLE</b> Platinum Acetylates in Cholesteric Liquid Crystal Glasses for Nonlinear Optical Applications					
<b>5a. CONTRACT NUMBER</b>		<b>5b. GRANT NUMBER</b> FA8655-20-1-7010		<b>5c. PROGRAM ELEMENT NUMBER</b> 61102F	
<b>5d. PROJECT NUMBER</b>		<b>5e. TASK NUMBER</b>		<b>5f. WORK UNIT NUMBER</b>	
<b>6. AUTHOR(S)</b> Patrick Norman					
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> KUNGLIGA TEKNISKA HOGSKOLAN VALHALLAVAGEN 79 STOCKHOLM 10044 SE				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> EOARD UNIT 4515 APO AE 09421-4515			<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> AFRL/AFOSR IOE		<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> AFRL-AFOSR-UK-TR-2023-0051
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> A Distribution Unlimited: PB Public Release					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> This project has involved studies of molecular structure and dynamics, electronic structure and excited states, and the development of software packages and platforms. The structure, behavior, and spectroscopic properties of a cholesteric liquid crystal platinum acetylate was investigated, including the characterization and interpretation of self-assembly using scanning tunneling microscopy (STM) imaging and molecular dynamics (MD) simulations. Excellent agreement between theory and experiment was achieved, demonstrating that the computational protocol can provide valuable insight. A similar protocol was utilized to investigate the structure of spider silk on different surfaces, which is important for the functionalization of this compound for technological and biomedical applications. For the investigation of electronic structure and excited states, highly efficient linear response solvers in the VeloxChem program package were utilized for elucidating the properties of large molecular systems, here focusing on polarizabilities and circular dichroism of fullerenes and helicenes of varying sizes. Finally, three different software development projects have been supported, including packages for treating large molecular systems with density functional theory, efficient ab initio methods for considering excited states, and a platform for supporting the exploration and education of computational chemistry.					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>		<b>18. NUMBER OF PAGES</b>
<b>a. REPORT</b> U	<b>b. ABSTRACT</b> U	<b>c. THIS PAGE</b> U	SAR		12
<b>19a. NAME OF RESPONSIBLE PERSON</b> ATTILA SZEP				<b>19b. PHONE NUMBER (Include area code)</b> 314 235 6044	

Standard Form 298 (Rev. 5/2020)  
Prescribed by ANSI Std. Z39.18

## Final Performance

# Platinum Acetylides in Cholesteric Liquid Crystal Glasses for Nonlinear Optical Applications

Dr. Thomas Fransson and Prof. Patrick Norman

The work supported by this grant have been divided into three main areas:

- 1) Molecular structure and dynamics
- 2) Development of software packages and platforms
- 3) Electronic structure and excited states

In addition, several studies initiated and primarily conducted before the start of this project were finalized during this project, and thus gratefully acknowledged.

## Developed technologies

### Educational aids

An educational aid named eChem<sup>[1]</sup> has been developed and published, featuring a web page collecting a repository of Jupyter notebooks.<sup>[2]</sup> This has been developed for the dual purpose of explaining and exploring the theory underlying computational chemistry in a highly interactive manner as well as providing a tutorial-based presentation of the complex workflows needed to simulate embedded molecular systems of real biochemical and/or technical interest. The eChem book is well suited for self-directed learning, with workshops led by experienced instructors and targeting student bodies with specific needs and interests being readily formed from its components. This has been done by using eChem as the base for a workshop directed towards graduate students learning the theory and practices of quantum chemistry, resulting in very positive assessment of the interactive nature of this framework. This e-book is published under the Creative Commons Attribution-ShareAlike license CC BY-SA.

### Software

An open-source program named VeloxChem<sup>[3]</sup> is being developed for calculations of electronic real and complex linear response functions at the levels of Hartree–Fock and Kohn–Sham

density functional theories. This grant has supported further developments of this software package, including a new integral library which will enable the efficient treatment of very large molecular systems. VeloxChem distributed under the GNU Lesser General Public License version 2.1 (LGPLv2.1) license and made available for download from the homepage <https://veloxchem.org>.

The Gator<sup>[4]</sup> program has been developed for computational spectroscopy and calculations of molecular properties using real and complex propagators at the correlated level of wave function theory. This project has supported this development, with focus on using Gator for exploration and education. Gator is freely available under the GPLv3 license.

## Accomplishments

### Molecular structure and dynamics

In order to improve the nonlinear optical properties of functionalized materials such as liquid crystal glasses, a good understanding of the molecular structure and dynamics is imperative. Here, a molecular dynamics (MD) protocol has been used to investigate the molecular structure of a cholesteric liquid crystal platinum acetylide glass,<sup>[5]</sup> achieving excellent comparison to experimental measurements. Such a protocol has further been used to investigate the structure of spider silk at hydrophobic and hydrophilic surfaces,<sup>[6]</sup> demonstrating the versatility of this approach.

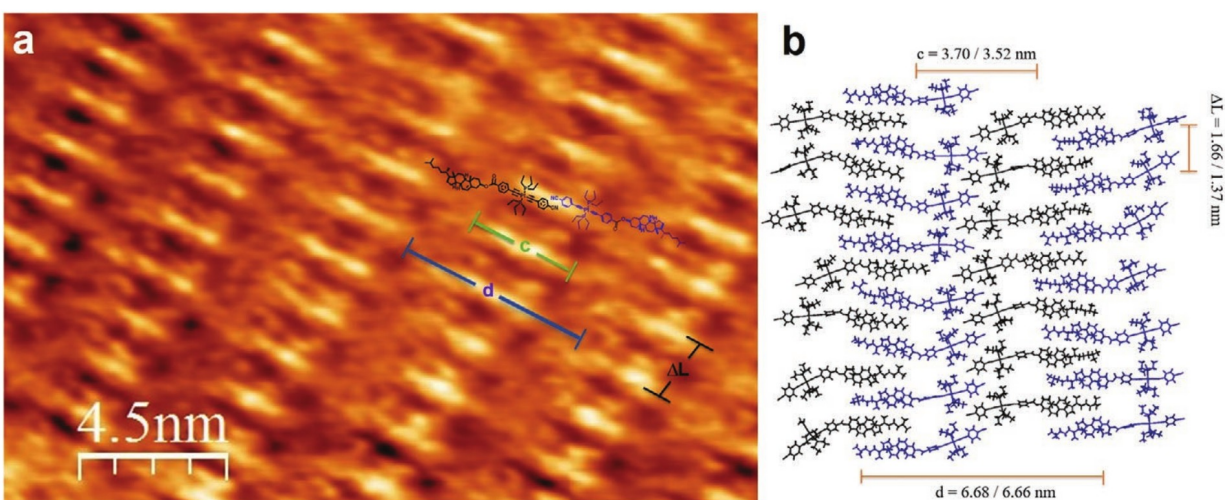
#### 1. Cholesteric liquid crystal Pt-acetylide glass<sup>[5]</sup>

Here, we describe the liquid crystalline behavior and spectroscopic properties of a cholesteric liquid crystal platinum acetylide (PE1-CN-Chol), which represents the ultimate concentration limit for enhancement of optical responses. We achieve microscale organization of the chromophore by attaching it to a cholesterol unit. We also provide characterization and interpretation of the self-assembly studied by scanning tunneling microscopy (STM) imaging and molecular dynamics (MD) simulations. Polarized optical microscopy, differential scanning calorimetry, and wide-angle X-ray scattering experiments show room temperature glassy/crystalline texture with crystal formation upon heating to 165 °C, with further heating results in conversion to cholesteric phase. Cooling to room temperature leads to the formation of a cholesteric liquid crystal glass.

Scanning tunneling microscopy (STM) of a PE1-CN-Chol monolayer reveals self-assembly at the solid-liquid interface with an array of two molecules arranged in pairs, oriented head-to-head through the CN groups, giving rise to a lamella arrangement (Fig. 1a). To support the STM data on the PE1-CN-Chol organization, molecular dynamics (MD) simulations were performed (Fig. 1b). There is a clear separation between the cholesteryl, and platinum and conjugated/benzene units of the chromophore. The calculated dimensions are in excellent agreement with STM results. We see that PE1-CN-Chol self-assembles at the solid-liquid interface on the surface as two molecules arranged in pairs through dipole-dipole interactions

between CN groups. This arrangement gives rise to a lamella or plate-like arrangement. The MD protocol used was constructed in a bottom-up approach, starting with a single molecule and increasing the number of molecules to identify higher order structures. We repeated the process by replication of the 6-chromophore system to arrive at a 12-chromophore system for which we could observe the formation of a layered structure with the cholesteric unit organizing in a plane with the platinum acetylide moieties organizing on top and bottom of the complex aggregate. The MD simulations predict a phase separation between the conjugated platinum acetylide and the hydrophobic cholesterol groups and the formation of lamellae (Fig. 2).

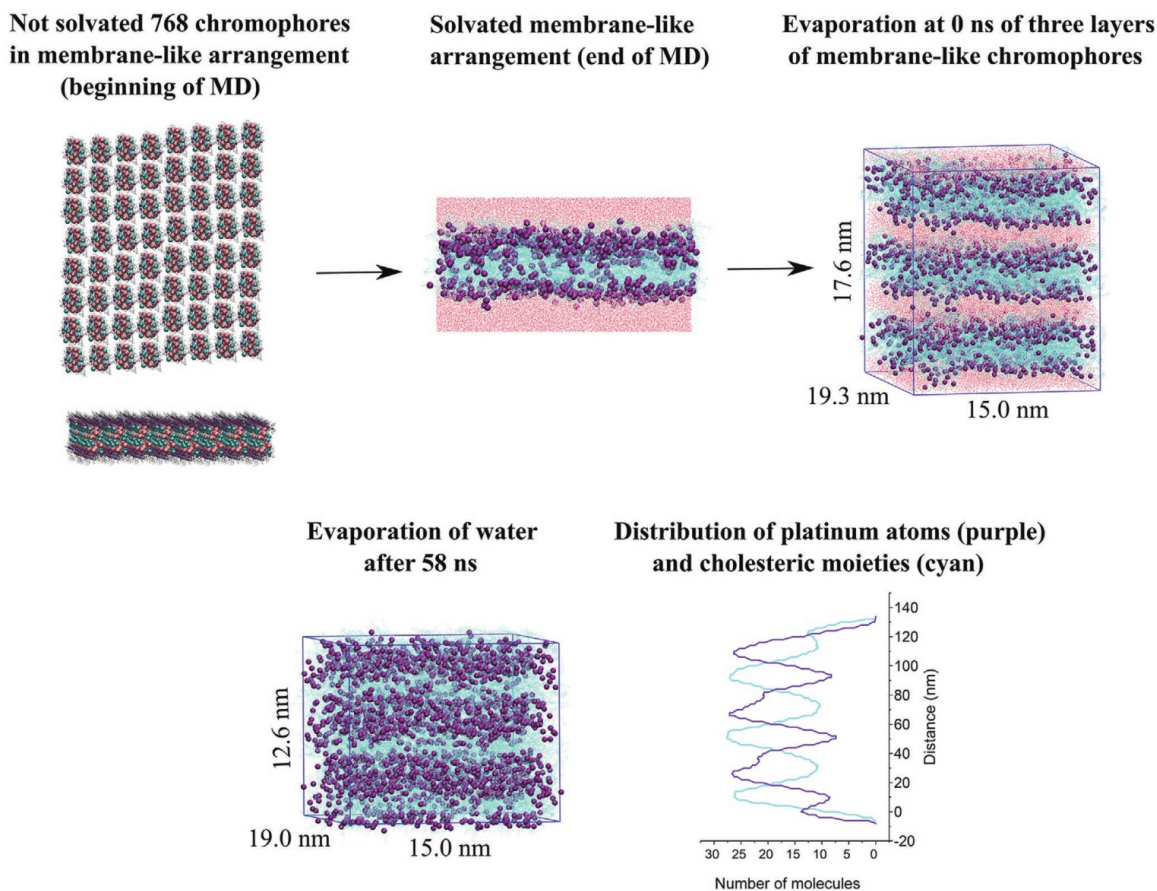
Ultrafast transient absorption and flash photolysis spectra of the glass show intersystem crossing to the triplet state occurring within 100 ps following excitation. The triplet decay time of the film compared to aerated and deoxygenated solutions is consistent with oxygen quenching at the film surface but not within the film. The high chromophore concentration, high glass thermal stability, and long triplet lifetime in air show that these materials have potential as nonlinear absorbing materials.



**Fig. 1:** a) Uncorrected high resolution scanning tunneling microscopy (STM) image showing the lamella-like assembly pattern of PE1-CN-Chol, superimposed with the organization obtained by molecular dynamics (MD); b) PE1-CN-Chol self-assembly, depicting the entire supramolecular organization, with average dimensions found by MD.

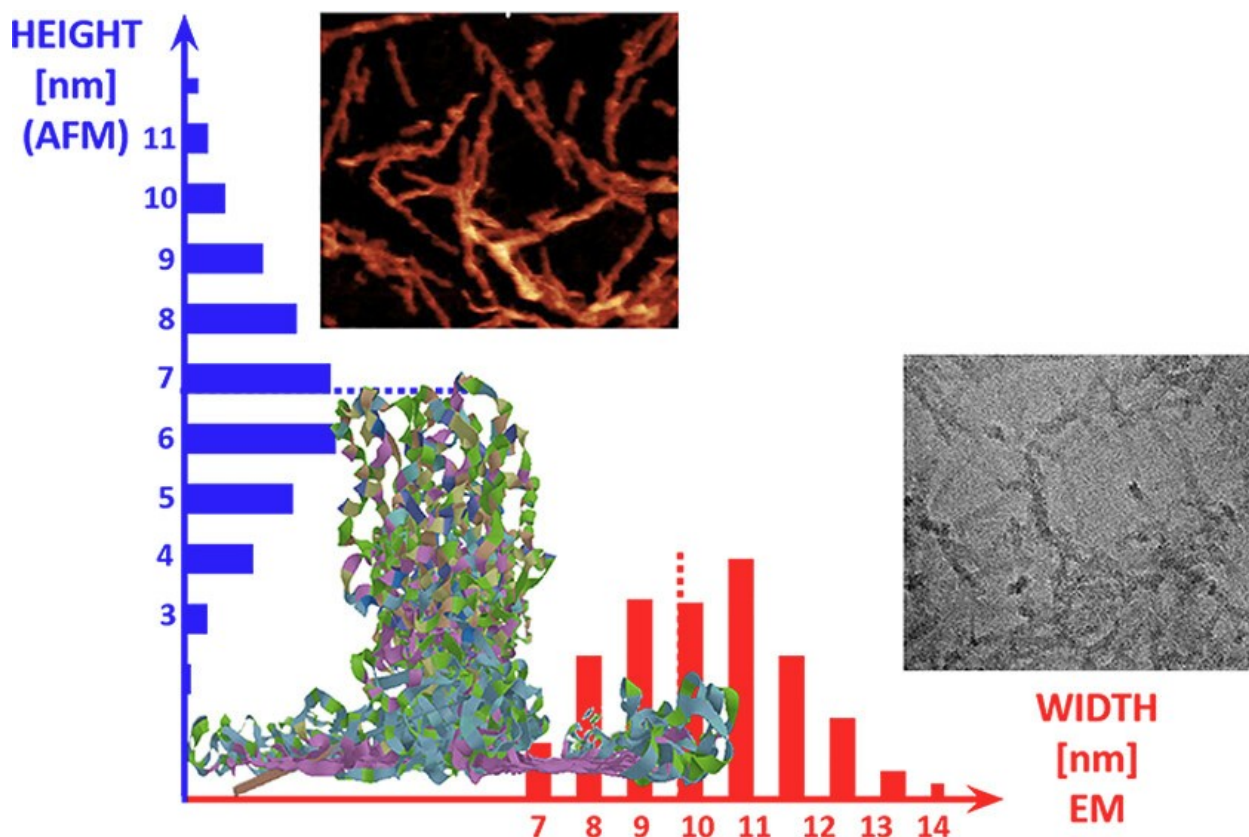
## 2. Spider silk<sup>[6]</sup>

A detailed insight about the molecular organization behind spider silk assembly is valuable for the decoding of the unique properties of silk. Spider silk has been claimed as the utmost biopolymer surpassing the mechanical properties of many modern synthetic fibers. In addition to the tensile strength and elasticity, silk has become attractive due to good biocompatibility and natural degradation. Thus, various ways of developing silk-based materials are being explored for biomedical applications, such as tissue regeneration, wound dressings, and drug delivery.



**Fig. 2:** From beginning of molecular dynamics (MD) simulation (membrane-like cholesteric platinum acetylides chromophore before running MD simulation), through solvated arrangement after MD simulation, to three membrane-like layers. Profile of platinum and cholesteric moieties shows a distribution of the moieties after the evaporation process. Platinum atoms in purple, and water in red.

Spider silk is made of sophisticated proteins, called spidroins, which are produced and stored in glands in the back of the spider. Spidroins are large proteins (size ranging from 200 to 350 kDa) composed of three main segments: a central repetitive region flanked by non-repetitive and conserved N- and C-terminal domains. The recombinant partial spider silk protein 4RepCT contains four polyaniline/glycine-rich repeats followed by an amphiphilic C-terminal domain and has shown the capacity to self-assemble into fibrils on hydrophobic surfaces. We have used molecular dynamic simulations to address the structure of 4RepCT and its different parts on hydrophobic versus hydrophilic surfaces. When the protein is placed in a wing arrangement model and periodically repeated on a hydrophobic surface,  $\beta$ -sheet structures of the polyaniline repeats are preserved, while the CT part is settled on top, presenting a fibril with a height of  $\sim 7$  nm and a width of  $\sim 11$  nm. Both atomic force microscopy and cryo-electron microscopy imaging support this model as a possible fibril formation on hydrophobic surfaces (Fig. 3). These results contribute to the understanding of silk assembly and alignment mechanism onto hydrophobic surfaces.



**Fig. 3:** Overview of fibril height and width obtained by AFM and EM, respectively, in comparison with the wing arrangement of 4RepCT model.

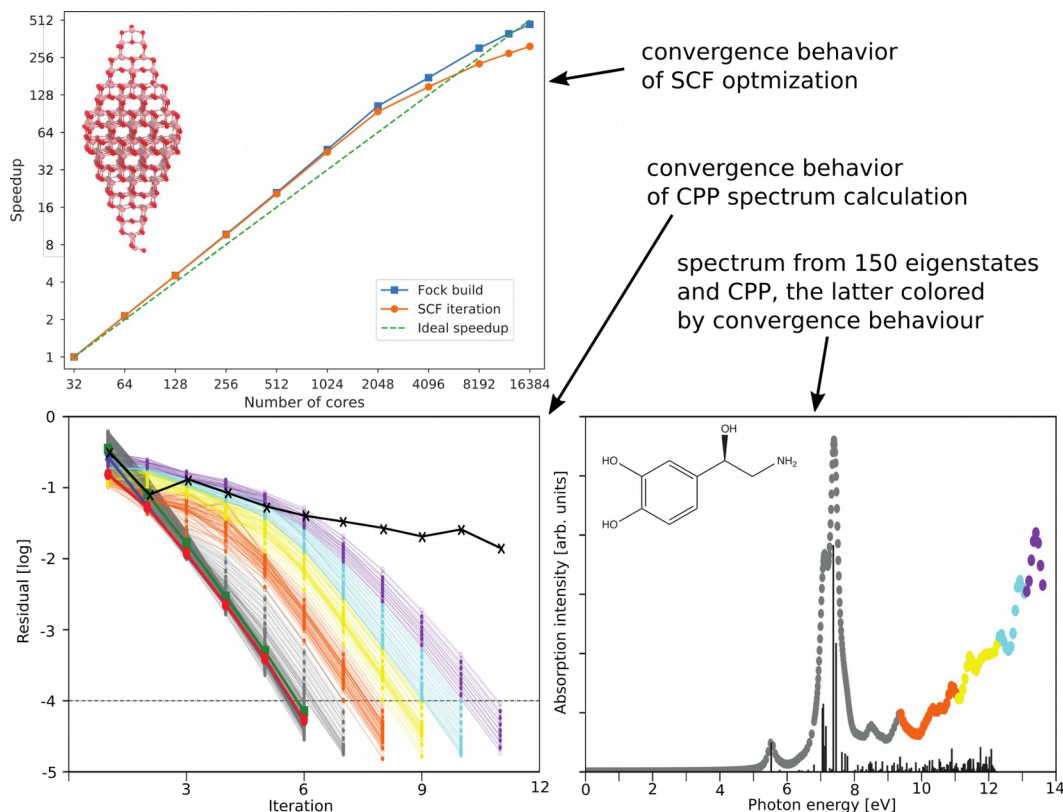
## Development of software packages and platforms

The development and improvement of several software packages and platforms has been carried out, including further development of VeloxChem<sup>[3]</sup> and Gator<sup>[4]</sup>, as well as the development and publication of the eChem<sup>[5]</sup> platform.

### 1. VeloxChem<sup>[3]</sup>

An open-source program named VeloxChem has previously been developed for the calculation of electronic real and complex linear response functions at the levels of Hartree–Fock and Kohn–Sham density functional theories. With an object-oriented program structure written in a Python/C++ layered fashion, VeloxChem enables time-efficient prototyping of novel scientific approaches without sacrificing computational efficiency, so that molecular systems involving up to and beyond 500 second-row atoms (or some 10,000 contracted and in part diffuse Gaussian basis functions) can be routinely addressed. Ongoing development on a new integral library will enable the treatment of even larger systems, and a hybrid message passing interface/open multiprocessing scheme makes VeloxChem suitable for execution in high-performance computing cluster environments, showing even slightly beyond linear scaling for the Fock matrix construction with use of up to 16,384 central processing unit (CPU) cores.

An efficient multifrequency/gradient complex linear response equation solver enables calculations not only of conventional spectra, such as visible/ultraviolet/X-ray electronic absorption and circular dichroism spectra, but also time-resolved linear response signals as due to ultra-short weak laser pulses. As an example, Fig. 4 illustrate the excellent scaling for SCF optimization, here shown for calculations on  $\text{Ti}_{165}\text{O}_{330}$  (using up to 512 cluster nodes), as well as for spectrum calculations. For the latter we have considered noradrenalin, comparing the calculation of 150 excited states to using the complex polarization propagator (CPP), and for the latter we see more rapid convergence when considering all frequencies at once, compared to considering them each at a time.



**Fig. 4:** The convergence behavior of VeloxChem for SCF optimization of a titanium oxide (top) and for the calculation of the absorption spectrum of noradrenalin (bottom).

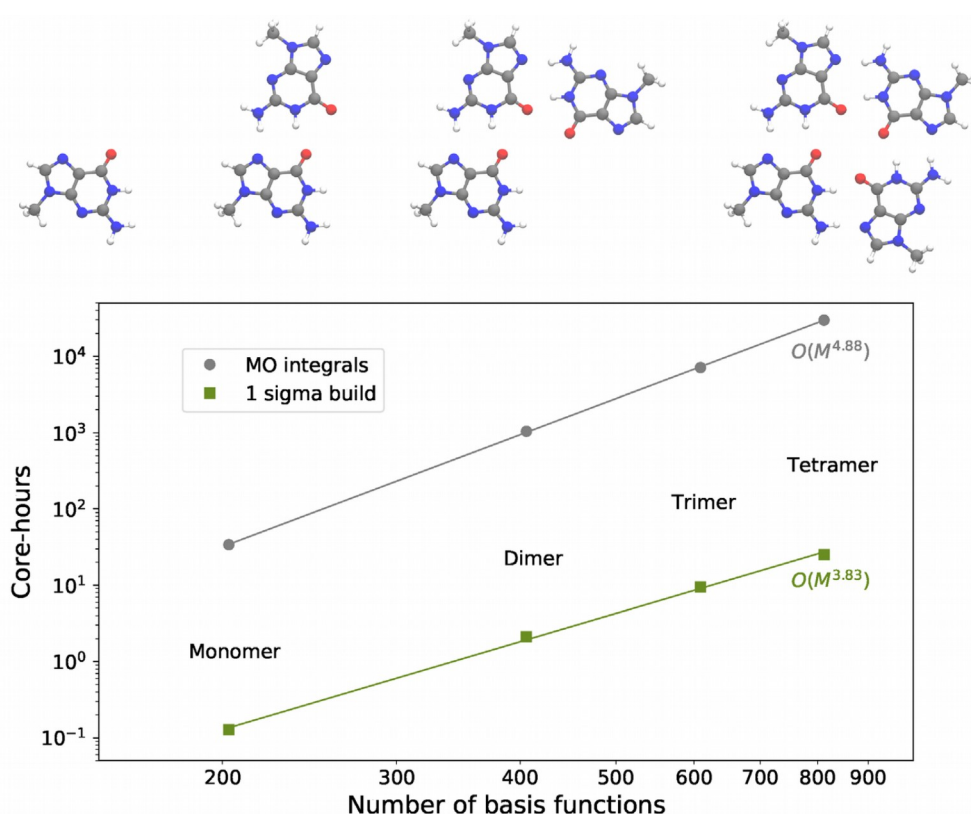
When studying excited states and dynamics of chromophores, the construction of excited state potential energy surfaces is vital, but typically very demanding. We are collaborating with a group which has developed an approach in which the surface is interpolated using a limited number of high-cost calculations, enabling the calculation of topologies at a dramatically reduced cost.<sup>[7]</sup> Together with the calculation of couplings between the different excited states, this enables us to look at a large number of excited state properties and processes.

## 2. Gator<sup>[4]</sup>

The Gator program has been developed for computational spectroscopy and calculations of

molecular properties using real and complex propagators at the correlated level of wave function theory. Currently, the focus lies on methods based on the algebraic diagrammatic construction (ADC) scheme up to the third order of perturbation theory.

The performance-determining tasks in post-HF spectroscopy calculations are the atomic-to-molecular orbital integral transformations followed by the tensor operations defined in the iterative solution of the underlying response equations. Conventional implementations suited for shared-memory computers typically store the full tensor of transformed antisymmetrized two-electron integrals in memory. While this approach works well for calculations of molecular systems up to about 700 one-particle basis functions on standard computers, it quickly becomes unfeasible for larger systems due to a memory bottleneck. As a complement to a conventional integral transformation, we have also implemented an MPI/OpenMP parallel auxiliary Fock matrix-driven transformation routine, with scaling properties illustrated in Fig. 5. This has been realized with an underlying hybrid MPI/OpenMP parallelization scheme suitable for execution in high-performance computing cluster environments. With a modular and object-oriented program structure written in a Python/C++ layered fashion, Gator thus additionally enables time-efficient prototyping of novel scientific approaches, as well as efficient excited state solver implementations for practical calculations.

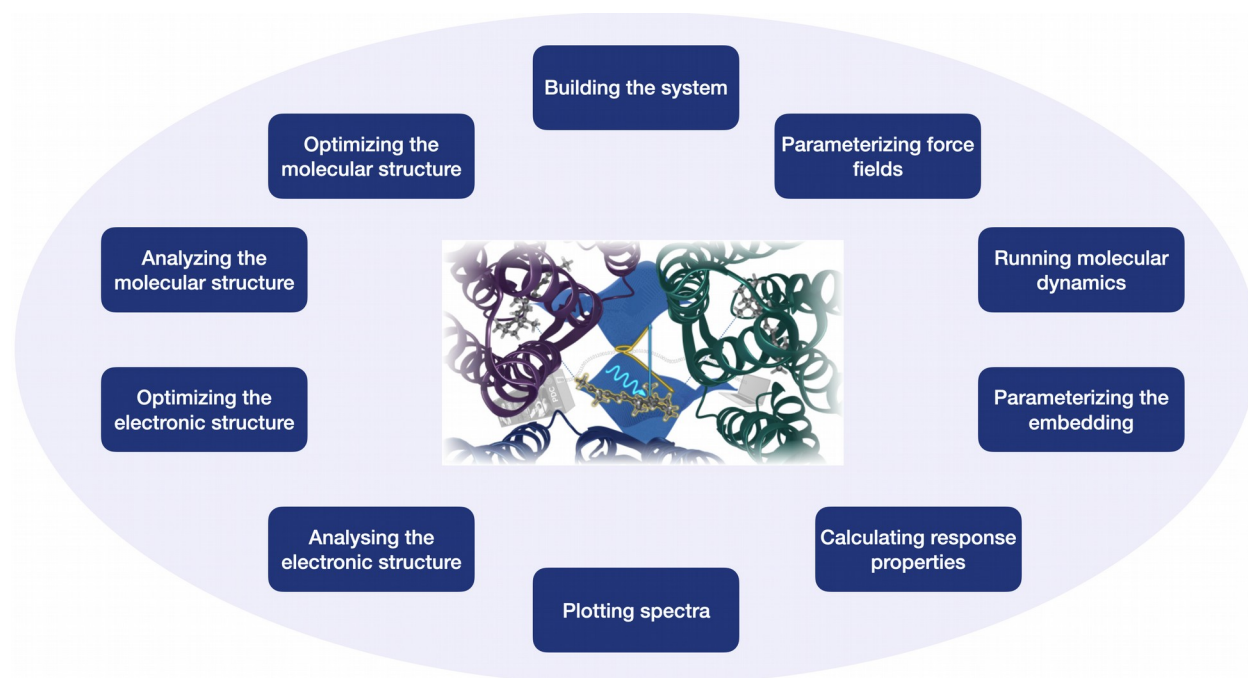


**Fig. 5:** Scaling of the construction of molecular orbital (MO) integrals and ADC(2)  $\sigma$ -vectors with respect to the number of contracted basis functions.

### 3. eChem<sup>[1]</sup>

Performing computational studies of chromophores, including steps such as setting up and running dynamics simulations, sampling and analyzing the resulting trajectories, and looking at excited states and excited state properties, is currently a rather challenging task for experts and non-experts alike (Fig. 6). Part of this challenge is due to the opaqueness of the methods and software packages used, as well as complications in performing multi-step studies, which often need to utilize several software packages which do not integrate well.

Here, the eChem project features an e-book published as a web page, collecting a repository of Jupyter notebooks developed for the dual purpose of explaining and exploring the theory underlying computational chemistry in a highly interactive manner as well as providing a tutorial-based presentation of the complex workflows needed to simulate embedded molecular systems of real biochemical and/or technical interest. The overarching vision and goal of our work is to provide a science- and education-enabling software platform for quantum molecular modeling on contemporary and future high-performance computing systems, and to document the resulting development and workflows in the eChem book.



**Fig. 6:** Different components for the modeling of, *e.g.* chromophores. These components are discussed on eChem and can be combined to construct a computational workflow.

## Electronic structure and excited states

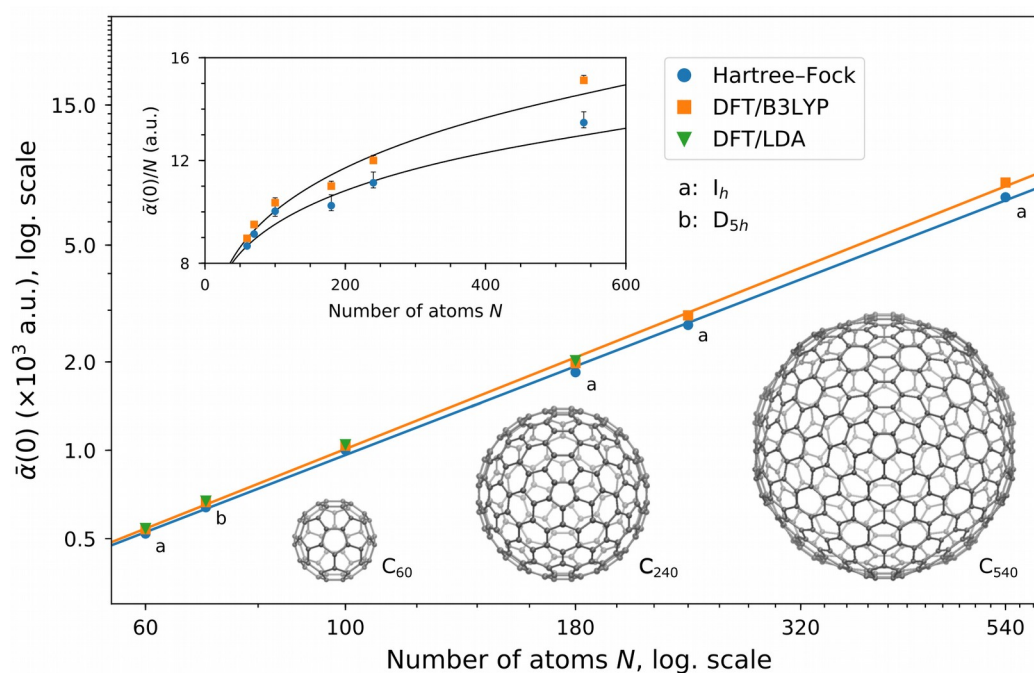
VeloxChem and Gator have been developed to enable the calculation of a wide range of molecular properties for large molecular systems, as exemplified by, *e.g.*, the calculation of

circular dichroism and polarizability of fullerenes and helicenes of varying sizes.<sup>[8,9]</sup>

## 1. Static polarizabilities and dispersion coefficients of fullerenes<sup>[8]</sup>

While the anomalous non-additive size-dependencies of static dipole polarizabilities and van der Waals dispersion coefficients of carbon fullerenes are well established, the widespread reported scalings for the latter call for a comprehensive first-principles investigation. We have further improved the solver algorithm/implementation so that the storage of reduced-space vectors and the associated vector–vector operations are carried out across the available cluster nodes, enabling linear-response calculations to be performed on large-scale systems as several terabytes of distributed memory are easily accessible. With an improved and efficient distributed memory handling in the complex linear-response equation solver, stable calculations of dynamic electric-dipole polarizabilities for systems involving up to and beyond 10,000 contracted and partly diffuse basis functions are made available.

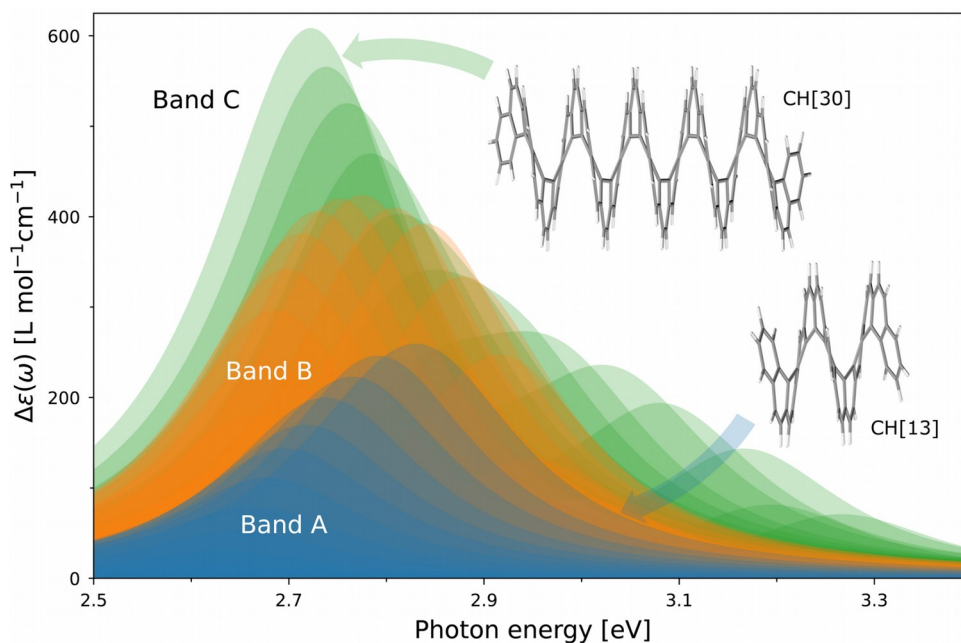
We have performed Hartree–Fock and Kohn–Sham density functional theory calculations of the frequency-dependent polarizabilities for fullerenes consisting of up to 540 carbon atoms (Fig. 7). Our results for the static polarizabilities and dispersion coefficients deviate significantly from the previously reported values obtained with the use of semi-classical and empirical methods. Arguably, our results are the most accurate to date as they represent the first *ab initio* or first-principles treatment of fullerenes up to a convincing system size.



**Fig. 7:** Static polarizability as a function of the number of atoms. The inset shows the scaling applied to the per-atom-polarizability.

## 2. Circular dichroism of carbohelicenes<sup>[9]</sup>

We demonstrate that contemporary computational resources allow for accurate theoretical studies of systems matching recent advances in experimental helicene chemistry. Utilizing a highly efficient implementation of linear response algorithms, we present electronic circular dichroism (CD) spectra of carbohelicenes ranging from CH[5] to CH[30] at the level of Kohn–Sham density-functional theory, including the by far largest members of the homologous series treated with an *ab initio* approach to date. Our results for a systematic increase in system size show the emergence of new CD bands that subsequently rise to intensities dominating the spectrum (Fig. 8). The spectral band progressions exhibit a periodicity directly linked to the number of overlapping layers of conjugation. While our findings rectify the current understanding of the electronic structure of carbohelicenes, they also serve as a general call for caution regarding the extrapolation of trends from small system ranges.



**Fig. 8:** Isolated CD spectra of bands A, B, and C for systems CH[13]–CH[30].

## Impacts

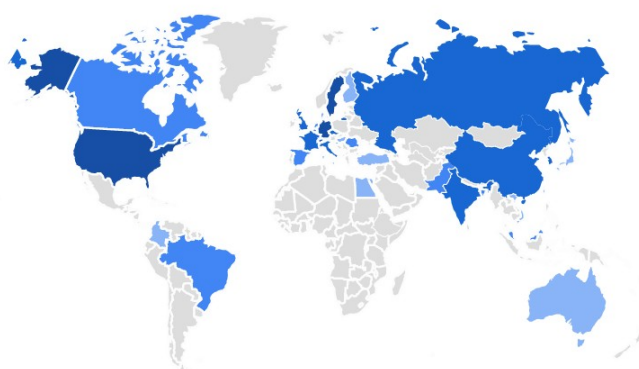
The impact of the published articles can be seen from the citation statistics:

	Year of publication	Citations on Google Scholar (03/13/23)
eChem <sup>[1]</sup>	2023	-
VeloxChem <sup>[3]</sup>	2020	25
Gator <sup>[4]</sup>	2021	10
Pt-acetylide glasses <sup>[5]</sup>	2020	4

Spider silk <sup>[6]</sup>	2023	-
Fullerenes <sup>[8]</sup>	2021	5
Helicenes <sup>[9]</sup>	2022	-

In particular the software development has been well received, and the applied studies have also been cited numerous times (with the exception of the papers published this or last year). Evaluating the impact of software packages and platforms is more difficult, but we note that VeloxChem has been downloaded through conda ~2000 times, and Gator ~150 times. The eChem repository has approximately one unique clone per day, and on average 18 viewers on the e-book page, with the largest user base being located in the United States (Fig. 9).

Users ▼ by Country ID ▼



COUNTRY ID	USERS
United States	33 ↑ 200.0%
Germany	22 ↑ 214.3%
Sweden	12 ↓ 14.3%
China	5 ↓ 50.0%
France	7 ↑ 40.0%
Italy	6 0.0
India	9 ↑ 350.0%

Last 7 days ▼

[View countries →](#)

**Fig. 9:** Google Analytics illustration of the user demography of the eChem web book. The trend of usage is steeply increasing as seen in the right-most column for the past 7-day period.

The eChem project disseminates new educational materials, useful for teachers, students, and others, and while we have had personal correspondence discussing how useful this is for colleagues, we lack any more objective assessments.

## Changes

There has been delays in the development of a new integral library which can fully use the advantages provided by a modern, heterogeneous HPC environment. These delays have been the result of the complexity of making such a framework able to fully leverage the capacities (and difficulties) of modern computational nodes, but progress is being made, and we expect

that the main barriers are overcome, and hope to be able to publish the results soon.

## References

- [1] T. Fransson, ..., and P. Norman, "eChem: A notebook exploration of quantum chemistry." *J. Chem. Educ.* (accepted); <https://kthpanor.github.io/echem/>
- [2] T. Kluyer *et al.*, "Jupyter Notebooks—a publishing format for reproducible computational workflows," in *Positioning and power in academic publishing: Players, agents and agendas*, pages 87–90 (2016); <https://jupyter.org/>
- [3] <https://veloxchem.org>; Z. Rinkevicius, ..., and P. Norman, "VeloxChem: A Python-driven density-functional theory program for spectroscopy simulations in high-performance computing environments." *WIREs Comp. Mol. Sci.* **10**, e1457 (2020)
- [4] D. R. Rehn, ..., and P. Norman, "Gator: A Python-driven program for spectroscopy simulations using correlated wave functions." *WIREs Comp. Mol. Sci.* **11**, e1528 (2021)
- [5] T. M. Cooper, ..., and P. Norman, "Nanoscale organization of a platinum(II) acetylide cholesteric liquid crystal molecular glass for photonics applications." *Adv. Funct. Mater.* **30**, 1910562 (2020)
- [6] D. H. De Oliveira, ..., and M. Hedhammar, "Silk assembly against hydrophobic surfaces—modeling and imaging of formation of nanofibrils," *ACS Appl. Bio. Mater.* (2023)
- [7] Y. M. Rhee and T. G. Lee, "Potential energy surfaces for polyatomic reactions by interpolation with reaction path weight:  $\text{CH}_2\text{OH}^+ \rightarrow \text{CHO}^+ + \text{H}_2$  reaction" *J. Chem. Phys.* **106**, 1003 (1997)
- [8] M. Brand, ..., and P. Norman. "Size-dependent polarizabilities and van der Waals dispersion coefficients of fullerenes from large-scale complex polarization propagator calculations." *J. Chem. Phys.* **154**, 074304 (2021)
- [9] M. Brand and P. Norman, "Nontrivial spectral band progressions in electronic circular dichroism spectra of carbohelicenes revealed by linear response calculations." *Phys. Chem. Chem. Phys.* **24**, 19321 (2022)