Pseudorotaxane strategies for guiding self-assembly and the application of molecular machinery in photoelectrochemical devices

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Preface

Chemistry beyond the Molecule: Fundaments and Applications

i. Chemistry and Society

The ever-growing ability to manipulate chemical bonds has led to the development of the chemical sciences, such that it has shaped modern society by playing an essential role in several sectors vital to the modern industrialized economy.[1,2] From the 20th century, the chemical industry enabled the development of crop enhancing chemicals providing a constant food supply. Likewise, the pharmaceutical industry's ability to combat mortality demonstrate how the central science of chemistry can suppress poverty and disease, while solving prevalent problems in society.[3] Moreover, the chemical industry also made life more pleasant with the development of plastics and synthetic fibers for all kinds of consumer products. Chemistry in this sense can be considered as a scientific tool to solve obvious societal problems. The 1935 marketing slogan of DuPont "Better things for better living… through chemistry" illustrates this idea.[4,5]

Chemical science, and, modern technology are intertwined in a way that aids humanity by quality of life enhancements. In its fundaments, chemistry studies how matter can undergo changes. Matter is composed of atoms that are listed in the periodic table, the building blocks of everything that we can find on Earth and beyond. The peculiar thing in chemistry is that when atoms are combined, they make up something new and unique, allowing for endless possibilities in the composition of multiatomic materials.[6,7] The main pursuit in chemistry is unraveling the structure, composition and properties of (newly made) substances by employing physicochemical analyses to understand emergent phenomena and potentially use this knowledge for specific purposes. Hence, the connection between fundamental understanding and application is irrefutable in chemical sciences, and therefore both aspects will have a prominent place in this thesis.

ii. Order, Chaos and Chemistry

Looking at our universe, we can find all kinds of highly ordered structures. From our galaxy, to salt crystals to the extremely complex organization of a single cell.[8] One of the biggest questions in science is why do we get order instead of just randomness? How do we get components to work together to achieve a global level of organization, from where simple matter becomes more and more complex? It is hypothesized that this observed type of organization must somehow be self-generated internally without external control, and therefore, this idea became to be known as **self-organization**. The impetes behind the emergence of organization can be unraveled when asking the right scientific questions. The key role of chemistry as the bridge between physics and biology makes it the ideal research area to explore the boundary where matter becomes life, i.e. to study the science of complex matter.[9] Chemistry has always been a creating science that traditionally works with molecules, helping humanity progress by the development of medicines and food industries, and thereby making life easier and more pleasant. Over the years chemists have become masters of synthesizing extremely complicated natural products, evidently demonstrating control over the covalent bond. Conversely, the control of structures "beyond the molecule" has not yet reached the same level of sophistication. Understanding molecular organization could lead to control over nanoscale organization to ultimately create new types of materials and chemical systems. The next quest in chemistry is to uncover what complex matter appertains to and how complexity relates to molecular organization. The following section deals with how complexity is described, and what role it plays in chemistry.

iii. Complexity Theory

The term **complexity** is often explained as an interplay between multiple elements (i.e. components) that is irreproducible to the single element.[8] The word complexity stems from *plectere* in Latin, which means to entwine or to weave. By bringing elements together, new properties and functions come into existence that cannot be deduced from that of the single element, known as **emergence**.[10] To exemplify this, one could think of a school of fish.[11] One fish on its own is a very simple target for a predator. Contrary, when fish assemble in a school, they form a collective and a potential predator has a much harder job catching a fish. Organizing themselves forming a school is an effective strategy to protect individual fish from predator attacks by following only three simple rules: 1) stay close to the school; 2) avoid collisions with your neighbors; 3) move in the same directions your neighbors are moving. Considering an individual fish one could not deduce this behavior. Yet, only when the whole system is studied these rules become evident, known as **emergent behavior**. It is important to note that the collective is somehow organized without centralized coordination, as fish assemble by themselves. This collective behavior is part of swarm theory, which is also found with birds, insects, bacteria and algae. Complexity theory aims to deal with the problem of how relatively simple elements organize themselves without a central controller by using information, forming a collective from where new behavior and functions emerge.

Complexity theory is a new field that has developed alongside systems theory as part of computer sciences and information sciences.[8] The power of complexity theory is that it connects all disciplines within science, finding applications at the micro- macro-level. For instance, complex systems can be found in the animal world (e.g swarms), the brain, the economy and even the World Wide Web is considered a complex system.[12] These systems have the following properties in common as they are: self-organizing, highly interconnected (network theory), adaptive, and they are showing non-linear behavior.[8] On the (supra)molecular level, we also observe complex behavior emerging from the interactions between individual components, rather than the properties of the components themselves. An example of this is the most extraordinary liquid of all, water.[13] Considering the H_2O molecule as an compositional element, how can we explain the patterns in snowflakes, its high boiling point, or the fact that its solid form has a lower density than that of the liquid form? We know water is comprised of atoms and atoms consist of quarks. However, by considering the atoms and quarks, there is no way that we can predict that water has such a high boiling point. We can only achieve this by looking at this network of interacting water molecules. Thus, the high boiling point of water emerges from the local-level interactions that cannot be deduced by just extrapolating the properties of the smallest elements (atoms or quarks) that water is composed of. The behavior of water as a substance is much more complex than what the simple molecular formula H_2O would predict. This touches upon a difference in approach in understanding phenomena via **reductionism** or **holism**.[12,14] Reductionism reasons that higher-level phenomena can be understood as a combination of lower-level properties, i.e. reducing a system to its most elementary parts and predicting the properties from those elements. Holism refers to an approach that emphasizes the whole rather than the individual parts. The properties of the whole cannot entirely be explained by the properties of its parts, which is the idea behind **emergence.** Considering networks, the most important aspects are the relationships and interactions between the elements from which new properties arise, such as the high boiling point of water.

iv. Complexity and Systems Chemistry

Biology is full of complexity.[15] If we consider a single cell, scientists have made great progress in unravelling what the general components are and what type of chemistry is used. Although the actions of the individual components of a cell have been studied thoroughly, scientists have struggled to mimic the workings of the cell. The lack of understanding is rooted in the comprehension how the individual components assemble, and ultimately, work together to perform a certain task. The field of systems biology studies whole biological systems such as the cell, focusing on the consequences of altering a single component on the network of reactions that take place.[16] In this thesis we seek to explore the newly emerging field of systems chemistry in supramolecular systems.[17] The field of systems chemistry uses a **holistic** approach to study how new properties arise when multiple components are added together in complex chemical systems, analogous to how systems biology studies biological systems such as the cell.[18,19]

Within systems chemistry there are two major areas. The first focuses on the origin of life,[20,21] while the second focuses on complex matter and how to integrate this to make smart materials and functional self-maintaining devices.[22,23] To advance chemistry further we should study whole chemical systems instead of individual molecules to transition to the next generation of materials. Yet, how do we start and what kind of chemistry is suitable for this?

Many biological structures come into existence via multiple non-covalent interactions with the resulting suprastructures possessing emergent functionality. These interactions include hydrophobic interactions (bilayer membranes), van der Waals interactions (DNA), hydrogen bond formation (DNA and protein folding) and many other electrostatic interactions (salt-bridges).[24] Unlike the covalent bond, non-covalent interactions are generally reversible, which imparts dynamicity to the larger structure. Nature uses non-covalent interactions to (pre-)organize the individual compositional elements involved to achieve optimal operation. By doing so, organisms can perform crucial reactions to compose and maintain their cellular structures. The field of supramolecular chemistry studies these non-covalent interactions and exploits molecular recognition to create large, supramolecular architectures. The world was introduced to chemistry beyond the molecule by Lehn, Pederson, Cram who were awarded with the Nobel Prize in chemistry in 1987.[25,26] This highly interdisciplinary science focuses on chemical, physical and biological properties of molecular assemblies held together by supramolecular bonds, as for example substrate binding (**guest**) by a receptor (**host**) (Figure 1).

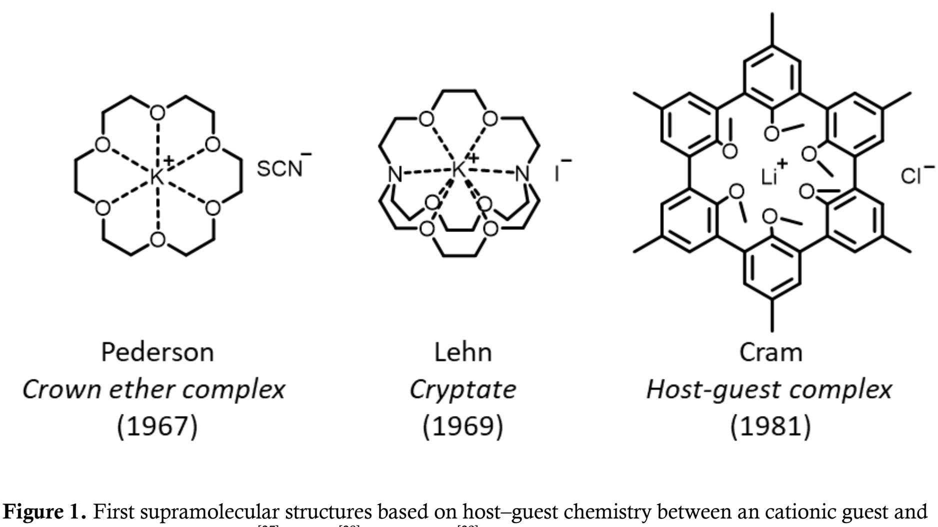

Figure 1. First supramolecular structures based on host–guest chemistry between an cationic guest and an organic host by Pederson[27], Lehn[28] and Cram[29].

Currently, the field of supramolecular chemistry explores large three-dimensional architectures based on the non-covalent bond often inspired by Nature. This enables studying, for example, pre-organization effects and the confinement effect in host–guest chemistry. Furthermore, the reversible character of the non-covalent bond has provided a method to construct complex structures with switchable entities that can be used for stimuli-responsive systems, which is the groundwork for creating molecular machines.[30] These insights are the starting point for realizing chemistry beyond the molecule, developing supramolecular structures that possess new features and function for creating the smart and complex materials of tomorrow.

v. The focus of this thesis

In this thesis we aim to explore the use of supramolecular organization to create functional chemical systems through two different approaches and in this pursuit the thesis is divided into two parts. Part A focuses on the fundamentals of molecular organization and self-assembly to discover the ability of the reversible supramolecular bond for controlling the formation non-covalent architectures. Part B utilizes a holistic approach to improve charge separation in photoelectrochemical devices through supramolecular organization to enhance device performance. These two approaches both explore the power of the non-covalent bond in self-organization by investigating possible applications and underlying concepts of chemistry beyond the molecule.

References

[1] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, **2000**.

[2] G. Rothenberg, *Catalysis*, WILEY-VHC Verlag GmbH & Co. KGaA, Weinheim, **2008**.

[3] J. R. Flower, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 118–118.

[4] B. Roemmele, “Why did DuPont drop ‘through chemistry’ from their old advertising,” can be found under https://www.quora.com/Why-did-DuPont-drop-through-chemistry-from-their-old-advertising-slogan, **2012**.

[5] DuPont, “DuPont Song : ‘Better things for better living ... through chemistry’ (1964 New York World´s Fair),” can be found under https://www.youtube.com/watch?v=tJtKkBYlHFw, **1964**.

[6] L. Ruddigkeit, R. van Deursen, L. C. Blum, J. Reymond, *J. Chem. Inf. Model.* **2012**, *52*, 2864–2875.

[7] D. Lowe, “Chemical space is big. Really big,” can be found under https://www.chemistryworld.com/opinion/chemical-space-is-big-really-big/7899.article, **2014**.

[8] M. Mitchell, *Complexity: A Guided Tour*, Oxford University Press, New York, **2011**.

[9] J. M. Lehn, *Angew. Chemie Int. Ed.* **2013**, *52*, 2836–2850.

[10] S. Carroll, in *Big Pict. Orig. Life, Mean. Universe Itself*, Dutton, New York, **2016**, pp. 225–316.

[11] T. J. Pitcher, J. K. Parrish, *Behaviour of Teleost Fishes*, Chapman & Hall, London, **1993**.

[12] F. Spier, *Big History and the Future of Humanity*, John Wiley & Sons, Ltd, Chichester, **2011**.

[13] H. Vandewall, *Philos. Sci.* **2007**, *74*, 906–919.
[14] J. F. Salmon, *Found. Chem.* **2009**, *11*, 21–32.
[15] A. Pross, *What Is Life?*, Oxford University Press, Oxford, **2012**.
[16] H.-Y. Chuang, M. Hofree, T. Ideker, *Annu. Rev. Cell Dev. Biol.* **2010**, *26*, 721–744.
[17] J. Stankiewicz, L. H. Eckardt, *Angew. Chemie Int. Ed.* **2006**, *45*, 342–344.
[18] G. Ashkenasy, T. M. Hermans, S. Otto, A. F. Taylor, *Chem. Soc. Rev.* **2017**, *46*, 2543–2554.
[19] A. de la Escosura, C. Briones, K. Ruiz-Mirazo, *J. Theor. Biol.* **2015**, *381*, 11–22.
[20] K. Ruiz-Mirazo, C. Briones, A. De La Escosura, *Chem. Rev.* **2014**, *114*, 285–366.
[21] P. Adamski, M. Eleveld, A. Sood, Á. Kun, A. Szilágyi, T. Czárán, E. Szathmáry, S. Otto, *Nat. Rev. Chem.* **2020**, *4,* 386–403.
[22] N. Giuseppone, *Acc. Chem. Res.* **2012**, *45*, 2178–2188.
[23] A. Walther, *Adv. Mater.* **2020**, *32*, 1–10.
[24] E. Mattia, S. Otto, *Nat. Nanotechnol.* **2015**, *10*, 111–119.
[25] J. M. Lehn, *Science* **2002**, *295*, 2400–2403.
[26] "The Nobel Prize in Chemistry 1987," can be found under https://www.nobelprize.org/prizes/chemistry/1987/press-release/, **n.d.**
[27] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
[28] B. Dietrich, J. M. Lehn, J. P. Sauvage, *Tetrahedron Lett.* **1969**, *10*, 2885–2888.
[29] K. N. Trueblood, C. B. Knobler, E. Maverick, R. C. Helgeson, S. B. Brown, D. J. Cram, *J. Am. Chem. Soc.* **1981**, *103*, 5594–5596.
[30] I. Aprahamian, *ACS Cent. Sci.* **2020**, *6*, 347–358.