Summary

Pseudorotaxane Strategies for Guiding Self-Assembly

and the Application of Molecular Machinery in

Photoelectrochemical Devices

Over the years, chemists have become masters of covalent bond formation, demonstrated by the ability to synthesize complicated natural products and their derivatives. Conversely, control of structures beyond the molecule has not yet reached the same level of sophistication. Supramolecular organization is ubiquitous in biology and non-covalent interactions are extensively applied to (pre-)organize the individual compositional elements to achieve optimal operation as emergent functionality. Hence, non-covalent chemistry imparts the crucial reactions and interactions in the biological cells. Understanding (supra)molecular organization could enable the creation of novel types of materials and chemical systems with new functions. This thesis aims to explore the use of supramolecular organization to create functional chemical systems. As both fundamental understanding and application will be investigated in this thesis, the work is divided into two parts.
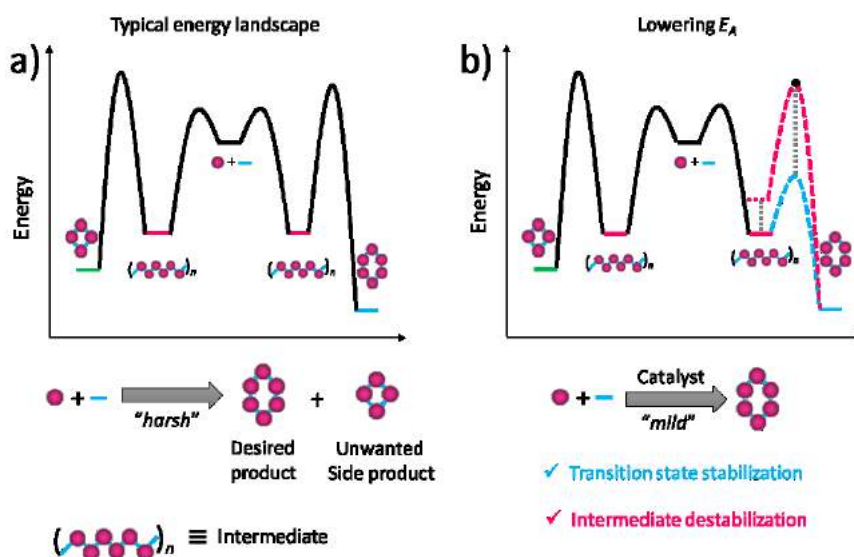

Figure 1. a) Schematic representation of pathway engineering of a typical energy landscape for formation of the desired product (blue) via an intermediate state (pink) and unwanted side product (green). As the activation barrier E_A is high, harsh conditions are required. b) Lowering the E_A can be achieved by transition state stabilization or intermediate destabilization.

First, the fundamentals of molecular organization and self-assembly are investigated in Part A, to study the ability of the reversible supramolecular bond for controlling the formation of non-covalent architectures. **Chapter 1** describes supramolecular approaches to guide self-assembly based on examples from recent literature. In addition, the level of control over kinetic pathways in covalent chemistry and non-covalent strategies have been compared in

this literature overview. Pathway engineering in covalent chemistry is often established with catalysts, cofactors and other reagents to promote formation of the desired product, while side product formation is suppressed (Figure 1). Non-covalent chemistry needs navigators and catalysts as well, if non-covalent chemistry is to reach the same level of sophistication. **Chapter 2** studies pathway engineering for the self-assembly of Fujita-type $M_{12}L_{24}$ nanospheres by circumventing the slowest step in the formation (Figure 2).
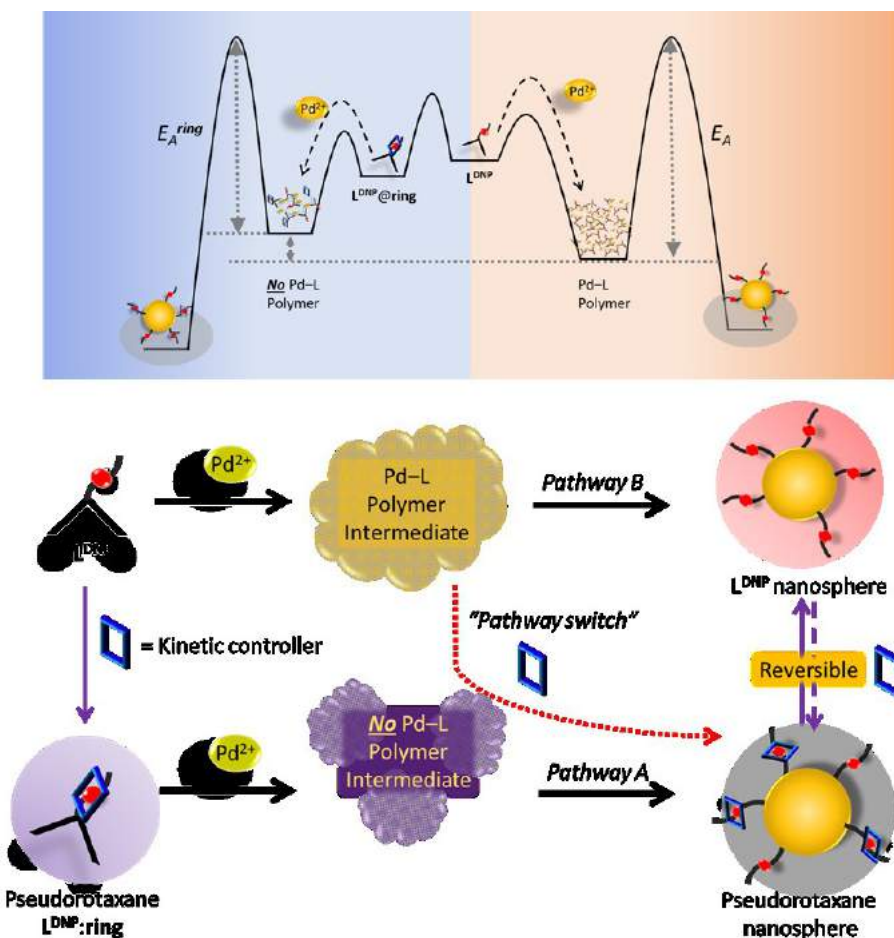

Figure 2. Proposed energy landscape for $L_{STATION}$ nanosphere formation via large coordination polymer, which has to occur via a high activation barrier (right, orange), making the large coordination polymer a kinetically trapped species. Pseudorotaxane-nanosphere formation (left, blue) takes place via small coordination clusters that have a lower activation barrier than nanosphere formation from the big coordination polymer as revealed by the kinetic study at varying temperatures.

As the geometry of the resting state is changed, and is much higher in energy, the overall energy barrier is lowered ($E_A^{ring} < E_A$). This was achieved by using bipyridyl ligands (L^{DNP}) that are *exo*-functionalized with the 1,5-dioxynaphthalene unit (**DNP**) for the binding cyclophane cyclobis(paraquat-*p*-phenylene) (**ring**) enabling the formation of $(Pd^{2+})_{12}(L_{STATION})_{24}(ring)_{8\pm5}$ pseudorotaxane nanosphere. In absence of **ring,** formation of the Pd–L polymer was identified as the fastest step, leading to a low-energy intermediate, from where nanospheres evolve slowly. The Pd–L polymer intermediate even becomes a kinetically trapped state at lower temperatures (≤10°C). In presence of **ring** this Pd–L polymer is not formed due to electrostatic repulsion between tetracationic **ring** and Pd–L assemblies, while promoting the rapid formation of nanospheres even at 10°C. This **ring** is not consumed in the process and can be removed after nanosphere formation, hence this navigator operates as a supramolecular catalyst in the self-assembly process conforming to the IUPAC definition.

In **Chapter 3**, the electrostatic character of the **ring**@L^{DNP} pseudorotaxane is used to control the distribution of $Pd_{12}(L^{\alpha})_{24-n}(L^{\beta})_n$ type nanosphere mixtures when more than one ligand type is used (Figure 3). The two different ditopic building blocks are the non-functionalized L^{EtO} bipyridyl ligand and the L^{DNP}. In absence of **ring**, we observe with ESI–MS that a statistical mixture of $Pd_{12}(L^{EtO})_{24-n}(L^{DNP})$ structures is formed (with $n = 8\pm5$), as there is no control over the distribution. In the presence of **ring**, the repulsive interactions between the **rings** at various L^{DNP} building blocks induces a narrow distribution of $(ring)_m@Pd_{12}(L^{EtO})_{24-n}(L^{DNP})_n$ ($n = 8\pm4$), which shows 55% less variance. We also observed that presence of **ring** controls the internal organization of the functionalized building block within the nanospheres, to minimize electrostatic repulsion. This level of organization was indirectly demonstrated by binding experiments of the **ring**, which is 40% higher when **ring** is present during nanosphere formation. Upon addition of **ring** to the $Pd_{12}(L^{EtO})_{24-n}(L^{DNP})$ nanosphere sample that was formed in absence of **ring**, the system is triggered to undergo adaptation by reorganizing and reshuffling the ligands within the nanospheres resulting a more organized sample. In this Chapter, **ring** promotes certain geometries that facilitate optimum **ring** binding leading to a narrow distribution of nanosphere species. We envisioned that this level of programmable self-assembly can be applied for non-covalent synthesis to pursuit more complex structures.
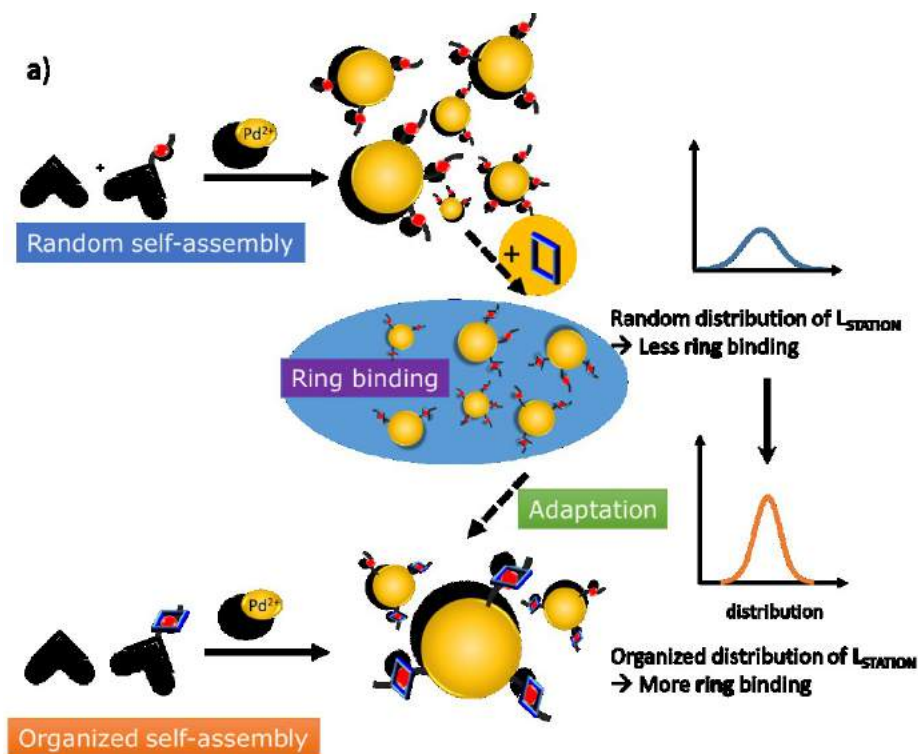
Figure 3. Overview of organized self-assembly investigated in Chapter 3. Self-assembly of two different ligands will lead to a random, broad distribution of nanosphere species. When **ring** is added to the randomly distributed sample, the system undergoes an adaptation to facilitate maximum **ring** binding by reorganizing and reshuffling of the ligands over the nanosphere.

In the second part of the thesis the central topic is supramolecular organization of molecular components to improve charge separation in artificial photosynthesis through molecular recognition, eventually leading to enhanced device performance. To this extent, **Chapter 4** discusses supramolecular strategies for artificial photosynthesis to achieve (pre-)organization of components promoting forward charge propagation in photoelectrochemical cells (PEC). The analogy is discussed between components found in *p*-type dye-sensitized solar cells (*p*-DSSC) and photosystem II (PSII) as part of the natural photosynthetic process. In PSII supramolecular organization is employed to achieve efficient charge transfer and pre-organization of the final Q_B acceptor that is exchanged after double reduction becoming QH_2 for a new quinone. Although in nature (pre-)organization is vital for efficient electron transfer, these type of strategies are absent in most photoelectrochemical devices. As *p*-DSSCs are challenged by low efficiencies caused by charge recombination, we propose a strategy

emphasizing the crucial interactions between components to favor electron propagation within the device. The aim is to address recombination issues found in *p*-DSSC by employing supramolecular machines inspired by binding and unbinding events of quinone found in PSII. Accordingly, we proposed to employ a pseudorotaxane strategy where the macrocycle interacts with the dye molecule as is illustrated in Figure 4. This **ring** acts as macrocyclic charge carrier and functions as redox mediator in the photoelectrochemical device. Upon photo-induced electron transfer (PET) from the dye the mediator, the **ring** loses its affinity, unbinds and is exchanged for a new **ring**. Hence, a charge separated state is created as the reduced mediator moves away from the D|NiO interface, ultimately suppressing recombination (Figure 4). Both pre-organization of the charge acceptor and ring launching of reduced mediator is carried out by the pseudorotaxane based molecular machine.
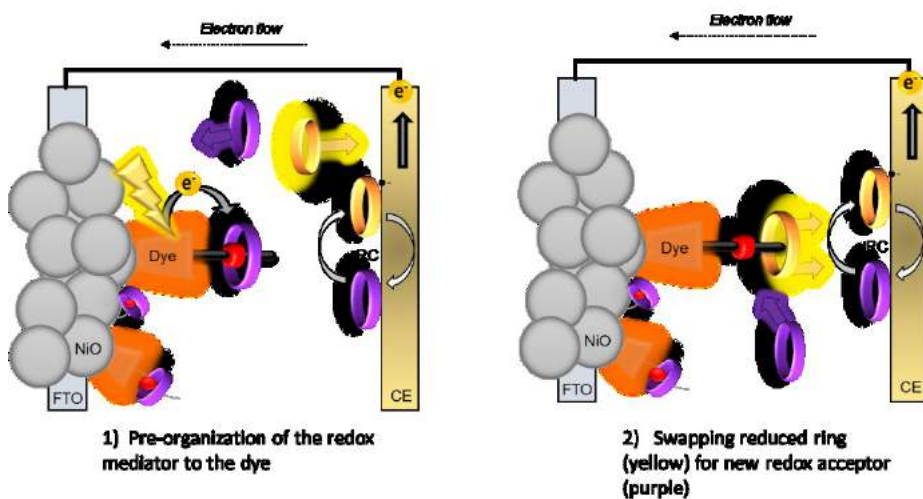

Figure 4. Schematic representation of pseudorotaxane strategy to suppress recombination while promoting forward electron propagation via pre-organization of the redox mediator to the dye for PET (1). After PET, the reduced ring is exchanged for a new acceptor (2).

Chapter 5 describes the first-generation of *p*-DSSC based on molecular machines, where cyclophane cyclobis(paraquat-*p*-phenylene) **ring** (**ring⁴⁺/ring³·⁺**) functions as a redox mediator. The dye (**P$_{STATION}$**) functionalized with a **DNP** recognition site, promotes the supramolecular formation of a pseudorotaxane with the redox mediator. The binding affinity of **ring⁴⁺** to **P$_{STATION}$** is high ($K_{ass} = 3.4 \times 10^4$ M^{-1}), while reduced **ring³·⁺** exhibits a lower binding affinity to **P$_{STATION}$** facilitating exchange with the excess **ring⁴⁺** present in solution. Devices promoting pseudorotaxane formation show a tenfold enhancement in photocurrent, compared to analogous viologen systems that do not facilitate pseudorotaxane formation. Although this system is limited in its performance in terms of PCE (0.00033%), it demonstrates a proof-of-principle that our concept of forward electron propagation within *p*-DSSCs is promoted by pseudorotaxane mediated charge-transfer.

In **Chapter 6** the 2ⁿᵈ generation *p*-DSSC based on pseudorotaxane with a neutral naphthalene diimide based ring (**3-NDI-ring**) is reported. This new macrocycle also forms pseudorotaxanes with the **P$_{STATION}$** dye but has a lower binding affinity ($K_{ass} = 160$ M^{-1}) than the blue box **ring**. PET from **P$_{STATION}$** to **3-NDI-ring** enables a "ring launching" event, releasing **3-NDI-ring·⁻**. By integrating **P$_{STATION}$:3-NDI-ring** into *p*-DSSCs a fivefold increase in PCE was observed (0.048%) compared to benchmark dye **P1** (0.009%), that does not facilitate pseudorotaxane formation. Pre-organization of the redox mediator and repelling anionic **3-NDI-ring·⁻** with concomitant reformation **P$_{STATION}$:3-NDI-ring** circumvents recombination at the D|NiO interface. The difference in performance between **P$_{STATION}$** and **P1** is reflected by the twofold enhancement in hole lifetime, translating into higher V_{OC}, J_{SC} and finally PCE.

Lastly, **Chapter 7** describes the investigation of the influence of a permanently installed mediator on the DSSC performance. This rotaxane based system, represents a closer mimic to PSII consisting of a permanently fixed quinone (Q_A) while the second unit (Q_B) is non-covalently bound and exchanged after reduction. The **P$_{Rotaxane}$** dye outperforms the **P$_{Stopper}$** that does not have a permanently bound **3-NDI-ring** (PCE = 0.066%, 30% higher). Further analysis revealed that this difference in performance originates from the extremely long hole lifetimes approaching 1 s, which is a 16-fold improvement compared to the typical I⁻/I$_3$⁻ cells (τ_h = 50 ms). By suppressing charge recombination, these DSSCs display an exceptional V_{OC} (0.43 V). While recombination was successfully suppressed leading to relatively high PCE, the overall efficiencies of DSSC based on molecular machinery are still limited by low solubility and slow diffusion of the macrocyclic charge acceptors used as redox mediator.
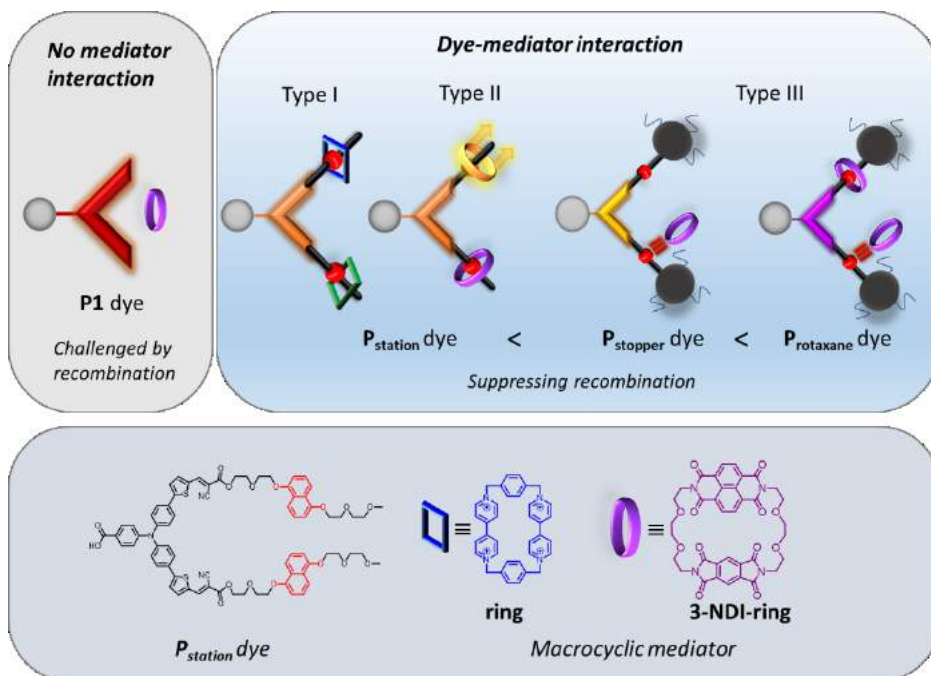
Figure 5. Overview of three different types of molecular machines suppressing charge recombination developed in this thesis.

In both parts of the thesis, the power of the non-covalent bond is demonstrated, gaining insight in possible applications and underlying concepts of chemistry beyond the molecule. Part A demonstrates two examples of pathway engineering for non-covalent self-assembly by employing a pseudorotaxane strategy. In one example the **ring** is used as a catalyst to guide self-assembly, while in the second example the **ring** binding impedes on the possible outcomes of multi-ligand architectures, and thereby organizing the self-assembled structures. Part B demonstrates that photoelectrochemical devices benefit from implementing supramolecular organization promoting the forward electron propagation. Three different types of molecular machines were designed and applied to address electron-hole recombination issues found in *p*-DSSCs, as is illustrated in Figure 5.

This thesis is centered around supramolecular organization by using pseudorotaxane strategies. We foresee that supramolecular organization via other secondary interactions will further grant new structures beyond the molecule. By learning how to control kinetics and thermodynamics of supramolecular self-assembly, we hope to inspire others for designing reagents for non-covalent synthesis, such as navigators, kinetic controllers and catalysts. We

envision that pathway engineering of self-assembly processes can be applied to make new, multicomponent architectures and materials. Advancing non-covalent chemistry towards programmable self-organization could ultimately enable complex adaptive structures. By expanding to non-equilibrium systems, the transition to the next generation of materials can be facilitated.

Furthermore, we hope that the concept of supramolecular-directed charge-propagation will encourage further integration of molecular machinery into PEC devices. While recombination has been suppressed to a minimum, the PEC efficiency of the current system is still limited by slow mediator diffusion and low solubility of the macrocyclic charge acceptor. The next generation DSSC based on molecular machinery must address the apparent diffusion issues to further increase the performance. Next, faster hole mobility must be promoted in *p*-DSSC to further improve charge separation. We envision that by optimizing NiO semiconductor and combine this with dye-mediator interactions, new *p*-DSSC performance records are within reach. These optimizations are considered as an important step in closing the gap in performance between *n*-DSSC and *p*-DSSC, which enables successful integration of these devices into tandem cells. The next logical step is integrating mediator interaction in photocatalytic reaction to promote solar driven synthesis, for example by coupling molecular machinery to generate sustainable fuels in photoelectrochemical device. This would be a powerful contribution to the state-of-the-art artificial photosynthetic devices. Combining supramolecular organization with molecular machinery and coupling these to catalytic bond formation ultimately mimics Nature's instruments and is a huge step forward for the next generation photosynthetic devices.