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## Exciton dynamics in self-assembled molecular nanotubes

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## Summary

Photosynthetic systems that exist in plants, algae and some bacteria are Earth's powerhouse by harnessing its most abundant energy source: sunlight. As one of the key elements to achieve this, they employ a functional nano-machinery that is typically built from many thousands of autonomously assembled molecules. Many of these tiny structures compose a dense and interconnected network – so-called light-harvesting antennae – that maximize light absorption, transport the energy to its destination (the reaction center) with minimal losses and ultimately fuel the photosynthetic reaction. In billions of years of evolution, nature has engineered these systems to perform their tasks under physiological (warm and humid) conditions that would be considered detrimental to most lab-based applications. In order to replicate nature's design principles for light-harvesting antennae for potential applications, for example in the steadily growing field of organic photovoltaics or for the generation of solar fuels, their essential functional elements have to be identified and their working principles understood.

Inspired by the success of natural light-harvesting complexes, lab-made molecular aggregates such as micelles, vesicles, bilayer sheets, nanofibers, and nanotubes have recently experienced great attention. These systems are typically built via molecular self-assembly, which refers to the spontaneous organization of individual molecules under near-thermodynamic equilibrium conditions into structurally well-defined and stable arrangements through non-covalent interactions without human intervention. The interest in these systems has further been fueled, as some of them closely resemble the structure of their natural counterparts, but remedy a number of their drawbacks. In fact, these synthetic analogues feature a high degree of internal homogeneity (different systems are remarkably alike), while also being easier to produce, control and modify than the natural systems via *re-programming* of the constituting building blocks (i.e., molecules). The molecular packing within these aggregates facilitates strong intermolecular couplings and, thus, the formation of so-called excitons upon absorption of a photon. The term 'exciton' here refers to an excited state that is collectively shared by many molecules and, thus, spatially stretches over substantial parts of the aggregate, which in turn is considered a key ingredient for efficient energy transport. With these systems at hand, the ultimate goal is to combine the best from both worlds: to mimic the (excitonic) functionality of natural systems, while retaining the controllability of synthetic systems.

In this Thesis, we study how artificial light-harvesting complexes absorb photons, how the deposited energy is transported, and how this transport is affected by the morphology and dimensionality of the system. We investigate the optical (excitonic) properties of double-walled molecular nanotubes based on the amphiphilic cyanine dye derivative C8S3 – structurally reminiscent of chlorosomes of green sulfur bacteria. The formed double-walled concentric nanotubes measure only ~13 nm and ~7 nm for the outer and inner tube diameter, respectively, but extend over several micrometer in length along which excitons can potentially propagate. The excitonic properties and exciton dynamics of this system are studied in a multi-disciplinary approach by combining results from steady-state and time-resolved spectroscopy, optical and transmission electron microscopy, microfluidics, and Monte-Carlo simulations. Such an approach is able to provide a conclusive picture of the excitonic properties by effectively eliminating the ambiguity that is inherent to using one particular technique alone.

Conventional spectroscopic techniques are typically carried out using solutions or dried films of the sample containing an extremely large number ( $> 10^{10}$ ) of individual systems (molecular nanotubes in our case) that are all probed simultaneously. Hence, if these systems are inhomogeneous in structure with for example slightly different sizes or molecular packings resulting in slightly different spectral signatures, the properties of each individual system will be *washed out* due to so-called ensemble averaging. In other words, the information on an individual system can hardly be retrieved from ensemble spectra, as it is masked by the overlapping, yet slightly different signals from all other systems. That means the measured optical spectra are dictated by the inhomogeneity of the ensemble rather than the properties of the individual system. **Chapter 3** quantifies the spectral inhomogeneity at the level of individual molecular nanotubes by combining single-nanotube photoluminescence spectroscopy/microscopy with advanced 2D correlation spectroscopy. These measurements reveal that the structural variations between different nanotubes have a negligible contribution to the optical properties of an ensemble of nanotubes, i.e., the characteristic sizes and molecular packing of individual nanotubes drawn from a large ensemble are remarkably similar. Instead, it is interactions of the molecules within the nanotubes with their dynamically fluctuating environment occurring on ultrafast timescales that govern the optical properties observed in single-nanotube spectroscopy. Such high degree of structural homogeneity has profound implications for conventional spectroscopic experiments performed on ensembles of nanotubes, as their results can equally be ascribed to individual nanotubes. Furthermore, these findings will ultimately help to understand how the propagation of excitons is constrained by static and dynamic molecular disorder in complex (multi-layered) supramolecular systems.

The molecular nanotubes considered in this Thesis are structurally simplified versions of their natural counterparts, because each nanotube comprises only two layers (instead of many) and different nanotubes are remarkably similar (*vide supra*). Despite this simplification, they are far from straight-forward to study due to the nanotubes' sheer size accommodating large numbers of molecules stacked together in a complex packing motif. This, in turn, leads to congestion of the optical spectra with multiple spectrally overlapping peaks. In addition to that, the interpretation of these spectra is further complicated by the fact that the two tubes are coupled leading to energy transfer between them. **Chapter 4** introduces a novel spectroscopic lab-on-a-chip approach to obtain *in-situ* control of the hierarchical complexity of the supramolecular nanotubes: microfluidic flash-dilution. The latter is an elegant means to simplify the double-walled structure of C8S3 nanotubes by physical dissolution (or *stripping*) of the outer layer and, thus, selectively switching off the coupling between the inner and outer tube. Time-resolved photoluminescence measurements on the double-walled and simplified single-walled nanotubes have shown that the latter feature optical (excitonic) properties that are remarkably robust against such perturbations of their supramolecular structure. Even upon physical removal of the adjacent nanotube layer, excitonic properties such as the exciton mobility are retained. Such robustness would prove extremely beneficial for utilizing such multi-chromophoric systems of a similar design in light-harvesting applications.

Multi-chromophoric systems are by definition built from thousands of strongly coupled molecules, which allows excitons to be highly mobile and, thus, propagate over 'large' distances on ultrafast timescales (i.e., in the femtosecond to picosecond regime). In presence of multiple of such excitons, two excitons may eventually meet (after having moved towards each other) and, as a consequence, start to mutually interact. This interaction, in turn, leads to the loss of one of the excitons via so-called exciton-exciton annihilation, which can be directly detected using advanced ultrafast 2D

spectroscopy. In **Chapter 5**, this type of 2D spectroscopy is interfaced with microfluidic flash-dilution to obtain an in-depth picture of the exciton dynamics within and between the individual layers of double-walled molecular nanotubes. The rate of these annihilation events then allows backtracking on what length and time scales the exciton propagation has occurred and, hence, extraction of the excitonic properties. Moreover, these experiments have shown that the outer layer acts as an exciton antenna at low excitation fluxes, but transitions to an exciton annihilator under intense illumination. In the double-walled configuration, molecular nanotubes are able to adapt to different illumination conditions, where the outer tube changes its functionality from an exciton antenna to an exciton annihilator. Understanding these excitonic properties of a system and how these properties relate to its supramolecular structure are important steps towards optimizing the exciton energy transport for potential (opto-)electronic applications.

One of the prevailing strategies to alter the final self-assembled supramolecular structure is to (chemically) modify the individual monomeric building blocks. Modifications of the composition and structure of these building blocks also changes the type and strength of their intermolecular interactions that drive and coordinate the self-assembly process. It is, however, extremely difficult to make *a priori* predictions of what the outcome of such modifications will be, which renders systematic studies on how the morphology of self-assembly systems relates to their spectral properties intrinsically challenging. In **Chapter 6**, minimalistic modifications of only four halogen atoms attached to the chromophore of the amphiphilic cyanine derivative C8S3 are used to steer the supramolecular motif in a controlled way. This allowed substantially inflating the nanotubes' radial size, while retaining the desired double-walled structure – reminiscent to the structure of natural light-harvesting complexes. Furthermore, we show that the delicate molecular packing inside the nanotubes is preserved, a crucial factor for the system's optical properties. Hence, subtle modifications of the chromophore via halogen exchange allowed studying the effects of purely radial growth on the nanotubes' optical properties.

Overall, this Thesis elucidates the exciton dynamics in double-walled molecular nanotubes and demonstrates how these excitonic properties are related to the overarching supramolecular structure. The capabilities of the system under study as an artificial light-harvesting complex are thoroughly assessed using a variety of (time-resolved) spectroscopic and microscopic techniques. This allowed this Thesis to paint a unifying picture of the exciton dynamics and excitonic properties by combining several complementary techniques. In that regard this Thesis covers the key elements for successful light-harvesting: exciton propagation on ultrafast timescales, role of heterogeneity and disorder for exciton transport, robustness towards structural perturbations, and strategies for controlled modifications of the supramolecular structure for optimization. The findings presented in this Thesis, hence, contribute to a better fundamental understanding of exciton dynamics in complex supramolecular structures and pave the way to incorporation of such systems as 'excitonic highways' in light-harvesting applications. Moreover, the experimentally obtained insights are highly valuable for refining molecular dynamics simulations and theoretical models that aim to elucidate the systems' molecular structure and self-assembly dynamics in unprecedented (atomistic) detail. All approaches combined will open exciting new possibilities for structure prediction and optimization of artificial light-harvesting systems.

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