

Óbuda University

PhD thesis abstract



Study of complex nanostructures by infrared spectroscopy

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Introduction

The formation and breaking of hydrogen bonds is one of the most fundamental processes in biology, chemistry, and materials science. For example, hydrogen bonding is responsible for the formation of the DNA double helix and for the highly unusual phase diagram of water or the secondary and tertiary structures in proteins; it is therefore at the very heart of life sciences. Furthermore, with the continuous down-scaling of technology in mind, the self-assembly and molecular recognition properties of hydrogen bonds have found their way into the fabrication of nanoscale materials and devices [1–3]. It is therefore imperative to understand the microscopic mechanisms that lead to the formation and dissolution of hydrogen bonds, in particular their temperature dependence. The energy of these weak interactions between the supramolecular constituents is comparable to the thermal energy slightly above room temperature so such systems are very dynamic: weak interactions can be broken and formed back again within very short time scales [4]. In the first part of my PhD work I studied uracil and acetylamino-pyridine based molecules which form supramolecular assemblies through hydrogen bonds.

The second part of my thesis presents a study on silicon carbide quantum dots. Silicon carbide is a stable, chemically inert wide band gap semiconductor with excellent hardness, heat resistance and chemical resistivity [5, 6]. Silicon carbide is also known as a biocompatible material with very promising results in living cell implantation for bioimaging techniques [7, 8]. The emergence of nanotechnology in the field of cell biology gave rise to the implementation of quantum dots in cell labeling. Considering the requirements for the ideal *in vivo* luminescent biomarkers (to be nontoxic, bioinert, photostable, not blinking, ultra small size) and comparing to the widely used II-VI semiconductor quantum dots (e.g. CdSe), silicon carbide quantum dots are among the best candidates for biological applications [9]. Further applications of the silicon carbide quantum dots in medicine and drug delivery rely on the ability of engineering the desired surface properties by attaching different functional molecular groups. To obtain tailor-made functionalized surfaces it is necessary to understand the complex structure of the quantum dots surface. During my work I studied the surface structure of the silicon carbide quantum dots by surface sensitive infrared spectroscopy and photoluminescence spectroscopy.

Objectives

First task of my work was to prepare an infrared spectral library on the molecules synthesized by our partners. These molecules have different functional sites which permit the self-assembly through hydrogen bonding. Starting from the basic molecular units and finishing with the final supramolecular assemblies, I studied the supramolecular ordering of different imide-uracil and acetylaminopyridine based molecular constituents to understand the microscopic mechanisms that lead to the formation and dissolution of hydrogen bonds.

Silicon carbide quantum dots are very promising material for different biological applications due to their bioinert and biocompatibility properties. They show very interesting and promising luminescent properties as well as a complex surface structure. The main task during my work was to study the surface structure of the quantum dots by infrared and photoluminescence spectroscopy. Surface sensitive infrared spectroscopy revealed the presence of carboxyl and carboxylate groups on the surface of silicon carbide quantum dots, opening the possibility for further biological functionalization.

Methods

The main experimental method used during this work was infrared spectroscopy. In the first part of my thesis I used different methods of infrared spectroscopy to characterize the molecules in isolated and aggregated state. Matrix isolation infrared spectroscopy was used to study the molecules in their monomeric state when no interaction between them is possible. In the aggregated state hydrogen bonds represent the main interaction between the molecules. To reveal the exact dimeric or multimeric character of the hydrogen bonded structures, temperature dependent measurements were used to study the stability of the hydrogen bonds.

The study of the surface structure of silicon carbide quantum dots requires surface sensitive methods of infrared spectroscopy. These methods permit the identification of atomic monolayers and surface functional molecular groups. One of the methods used and implemented during my PhD work in our laboratory is attenuated total internal reflection (ATR) infrared spectroscopy. Using standard infrared spectroscopic methods I found clear evidence of chemical transformation of carboxylic groups on the surface of silicon carbide quantum dots to acid anhy-

dride groups at elevated temperatures. Finally, photoluminescence spectroscopy was used to reveal the luminescent properties of the quantum dots.

Theses

1. I prepared an infrared spectral library for the molecular constituents for hydrogen bonded systems. Starting from the basic molecular units and finishing with the final supramolecular assemblies I measured and interpreted the infrared spectra of the supramolecular ordering of different imide-uracil and acetylaminopyridine based molecular constituents by infrared transmission spectroscopy [T1, T2, T3].
2. I studied the direct evidence of the presence of hydrogen bonds for a pair of monotopic uracil-derivative molecules measuring the spectra of the isolated molecules and that of the aggregated state. For this I applied different methods of infrared spectroscopy: matrix isolation and conventional transmission spectroscopy. I could identify the weakening and subsequent disruption of hydrogen bonds by following the temperature dependence of the affected vibrational bands. The assignment of the processes responsible for the melting of hydrogen bonds was done: a gradual increase of the temperature to intermediate values induces large thermal fluctuations in the dimers that leads to a thermal equilibrium between different dimer configurations. I found that further increase of the temperature above the sublimation point of the molecules the hydrogen bonds are disrupted, indicating that the sublimation temperature provides a good estimate for hydrogen bond stability in such systems. These results are consistent with theoretical results [T2].
3. I studied the supramolecular ordering in the solid state of bis-uracil based linear molecules by different infrared spectroscopic methods. A temperature-induced transition from a highly ordered tetrameric into a linear assembly was observed by temperature dependent infrared measurements. The interaction between molecules in the three perpendicular directions of the solid crystal is governed by three different noncovalent interactions: double hydrogen bonds, van der Waals attraction and π - π stacking [T3].

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4. I performed room temperature infrared and photoluminescence measurements on silicon carbide quantum dots dispersed in different solvents (water, ethanol, and butanol). Infrared spectroscopy has revealed the complex surface structure of quantum dots involving the presence of COOH and COO- molecular groups which are important for further functionalization processes [T4, T5].
 5. Performing temperature dependent infrared and photoluminescence investigations I found evidence for chemical transformation of carboxylic groups to acid anhydride groups on the surface of silicon carbide quantum dots. Acid anhydride formation was observed above 370 K by water elimination between two neighboring carboxyl groups. Photoluminescence results show that silicon carbide quantum dots emission properties are highly sensitive to the surface structure of quantum dots and to the surface-solvent interactions [T6].

Conclusions and Outlook

After studying prototypical molecules able to form hydrogen bonded supramolecular systems and presenting basic spectroscopic properties of silicon carbide quantum dots one major question arises: how 'potential' are the potential applications? Even if many supramolecular approaches were suggested for the preparation of self-assembled systems, to the best of my knowledge, no final devices for real life applications have been created yet. However, the increasing knowledge in controlling the location and accessibility of the molecules in a supramolecular network demonstrates that the "bottom-up" approach is getting closer and closer to industrial applications. Challenging requirements are set up also for quantum dots. For applications in bioimaging and biolabelling techniques a quantum dot must fulfill, at the same time, the following criteria: it should be nontoxic, bioinert, photostable, should be no blinking, be small, be producible in large amounts and show luminescent emission in a range specific to the desired application. Even if no ideal quantum dot was found yet, there are several potential candidates like core-shell quantum dots prepared from group II-VI elements, nanodiamond, carbon dot, and of course silicon carbide. Which

of these will be finally used in real world applications? Hopefully the right answer is silicon carbide.

Publications related to the thesis points

- [T1] L. Piot, C. A. Palma, A. Llanes-Pallas, Zs. Szekrényes, K. Kamarás, M. Prato, D. Bonifazi and P. Samorì, Selective formation of bi-component arrays through H-bonding of multivalent molecular modules, *Adv. Funct. Mater.*, 19:1207, 2009 (cover page).
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- [T3] Zs. Szekrényes, K. Kamarás, P. Nagy, G. Tarczay, A. Llanes-Pallas, L. Maggini, M. Prato, D. Bonifazi, Direction-dependent secondary bonds and their stepwise melting in a uracil-based molecular crystal studied by infrared spectroscopy and theoretical modeling, *under submission*.
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- [T5] D. Beke, Zs. Szekrényes, I. Balogh, Zs. Czigány, K. Kamarás, A. Gali, Preparation of small silicon carbide quantum dots by wet chemical etching, *J. Mater. Res.*, 28:44, 2013.
- [T6] Zs. Szekrényes, B. Somogyi, D. Beke, Gy. Károlyházy, I. Balogh, K. Kamarás, and A. Gali, Chemical transformation of carboxyl groups on the surface of silicon carbide quantum dots, *J. Phys. Chem. C*, 118:19995, 2014.

Further publications

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- [F6] D. Beke, Zs. Szekrényes, D. Pálfi, G. Róna, I. Balogh, P. A. Maák, G. Katona, Zs. Czigány, K. Kamarás, B. Rózsa, L. Buday, B. Vértessy and A. Gali, Silicon carbide quantum dots for bioimaging, *J. Mater. Res.*, 28:205, 2013.

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