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Preface

Excited state dynamics in light harvesting materials (in honor of Villy Sundström)

This issue is dedicated to Villy Sundström on the occasion of his 60th birthday. The articles herein span the wide range of topics to which Villy has made major contributions, from photosynthetic light harvesting to reaction dynamics and solar energy. His research has focused on the application of time-resolved spectroscopy techniques to the understanding of basic principles of dynamics and function of complex molecular systems. A respected member of the science community, his longstanding and fruitful collaborations with numerous research groups around the world are reflected in the contributions to this issue.

Villy is a proud member of the 49ers Club, celebrating the year in which many of his closest collaborators also got their start. He was born on February 6, 1949 in northern Sweden. He studied chemistry at the University of Umeå, and was fortunate to have the opportunity to perform part of his education at Bell Labs in Murray Hill, New Jersey, USA, under the guidance of Prof. Peter Renzepis. There, he obtained hands-on experience with state-of-the-art ultrafast dye lasers, providing picosecond pulses that gave an unprecedented glimpse of the first steps in biological processes such as the rhodopsin photocycle. He came home to defend his doctoral degree in 1977, and immediately set to work at building a picosecond laser laboratory in Umeå, thereby introducing the field of ultrafast spectroscopy to Scandinavia.

The first studies were made together with Tomas Gillbro in Umeå, focusing on photoisomerization reactions in cyanine dyes. In the mid-eighties, a very productive collaboration started with Rienk van Grondelle at the Vrije University of Amsterdam, shedding light on primary excitation transfer in antenna systems of photosynthetic purple bacteria. Low intensity high repetition rate mode locked synchronously pumped dye lasers were ideal for such studies, but in those days getting stable picosecond laser pulses in the 800–950 nm range required a 'feel' for the laser that was absolutely unprecedented in the hands of Villy, especially during the 'everlasting' nights of Umeå in December.

In 1994, he was appointed professor of Chemical Dynamics and head of the Chemical Physics Department at Lund University, Sweden. Studies on energy transfer and trapping in photosynthetic antenna systems continued, but also new research directions emerged. Villy's research continues to advance our understanding of the fundamental relationships between molecular structure, dynamics, reaction mechanism, and ultimately function in biological and biomimetic systems. The studies of natural photosynthetic systems inspired efforts in the area of artificial photosynthesis, biomimetic (Grätzel-type) solar cells, conjugated polymers, and carotenoid photophysics. The most recent research direction is in developing X-ray absorption spectroscopy for monitoring (bio)molecular motions in real time. This project was successful in the first call of the ERC Advanced Grants.

Villy is active in coordinating and organizing networks and conferences. Two landmark events organized by him and his group were the 1996 Nobel symposium "Femtochemistry and Femtobiology: Ultrafast Reaction Dynamics at Atomic-Scale Resolution" and the international conference "Femtochemistry III" held in Lund in 1997. He is a member of the Swedish Consortium for Artificial Photosynthesis, spanning experimental and theoretical physics, chemistry and biology groups. During 2000–2003 he served as Chairman of the ESF ULTRA programme, and is currently active in the Steering Committee of the follow-up programme DYNA.

Villy has served as a mentor to many young and talented students and postdocs from all over the world. His contagious enthusiasm and passion for his work inspires both hard work and creative dreams. His spirit is exemplified in the image portrayed in Pablo Picasso's "Circle of Friendship," which is often included in his scientific presentations. In Villy's interpretation, the vividly colored dancers encircling a dove of peace conjure up the schematic representation of a light harvesting antenna surrounding a reaction center, complete with both spectral and temporal disorder.

The collection of papers in this Special Issue reflects Villy's interest in a broad variety of time-resolved spectroscopic techniques from the 'old-time' single-wavelength pump-probe experiments in the visible and near-IR regions, up to recent developments of coherent multidimensional spectroscopy. Although Villy's primary interest has always been in the ultrafast time scale, a connection

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between the primary fast processes and the resulting slow photophysics is also mirrored in the selection of papers. The phenomena described in the Issue span the time scales from 30 fs (fast solvation dynamics) to processes occurring in minutes (response to illumination in plants). The papers are all related to Villy's scientific interests and many are in areas where he has made significant research contributions.

The papers devoted to photosynthetic light-harvesting systems including excited-state dynamics in light-harvesting complexes of purple bacteria, the LH2 and LH1 complexes, represent a topic where Villy has been active from the early stages of his scientific career and where he has made substantial contributions [1–4]. Despite the numerous experimental and theoretical studies during the past twenty years, purple bacterial light-harvesting complexes still have a lot to divulge. They serve as an ideal model system with controlled atomic structure that forms a platform for testing theories and understanding more complex systems. The papers in this Issue show how the old themes from the nineties of the last century – annihilation [5], energy transfer between B800 and B850 rings in LH2 [6], relation between the structure and excitonic properties [7], or polaron formation [8] – come back in more sophisticated versions that provide valuable information about delicate details of processes occurring at the ultrafast time scales in purple bacterial antennae. Through his numerous collaborations Villy has also participated in studies of other antenna systems [9]. In the current collection, antenna systems of Photosystem II are represented by the LHCII and CP29 proteins. Energy transfer and excited-state processes in these proteins are of key importance not only for understanding the energy transfer pathways in Photosystem II, but also for the photoprotection mechanism. This process is crucial for survival of plants under high-light conditions and it is studied over a wide range of time scales and system sizes as demonstrated in the papers in this Issue describing ultrafast annihilation kinetics in LHCII on one hand, and slow fluorescence induction curves in whole plants on the other. Contrary to the Photosystem II, Photosystem I of cyanobacteria has no separate antenna proteins and both antenna and reaction center pigments and cofactors bind to the same protein. One of the most intriguing features of the PSI antenna is the presence of the so-called red chlorophylls whose energy is clearly below that of the chlorophylls of the reaction center. Their role has been extensively studied since the discovery of these pigments and their potential role is also discussed in the Issue which includes descriptions of the energy transfer pathways in a carotenoid-dominating antenna of certain Dinoflagellates, the peridinin-chlorophyll protein (PCP) [10]. The PCP complex has become a benchmark in studies of energy transfer between carotenoids and chlorophylls, and the Issue also addresses how different spectroscopic techniques can tackle various aspects of energy transfer processes, and span the broad time scales on which the energy transfer occurs.

Other papers are devoted to excited-state and reaction dynamics of various molecules, a topic that has a solid place in Villy's scientific career [11]. Photoinduced isomerization is a widespread photochemical process that triggers many events in chemistry and biology, and cyanine has been one of the typical model systems with which to study it [12]. Therefore a paper studying isomerization of pseudocyanine and its dependence on solvent properties is included. However, isomerization and its effect on excited-state properties are much less understood for carotenoids, molecules that have a significant place in Villy's research achievements [13,14] and the experiments on carotenoid isomers in this Issue represent a systematic study of their excited states. Electron transfer in donor–acceptor systems is another key process and a study of the electronic coupling attenuation factor as a function of bridge properties is to be found in the Issue. Many essential processes in biology and chemistry concern the dynamics of H-bonds, which have been the subject of a large literature. Recent achievements in near-infrared time-resolved spectroscopy have enabled new views of H-bond dynamics and an example of such experimental techniques, applied to adenine–thymine base pairs, is included in the Issue.

Based on the research on natural light-harvesters, Villy has also turned his attention to a development and spectroscopic characterization of various synthetic systems that could eventually serve as artificial light-gathering complexes in solar energy conversion devices. Therefore the Issue contains contributions that map Villy's research interests in this field, ranging from electron injection processes in TiO_2-based solar cells [15], electron-hole pair and excitation dynamics in conjugated polymers [16,17], to electron transfer processes in supramolecular complexes [18]. The efficiency of electron injection and probability of recombination are the key factors for determining the overall performance of a solar cell. Various dyes have been tested to improve the electron injection efficiency while maintaining low recombination rate. One of the examples, terrylene, is presented in this collection as are contributions where various aspects of conjugated polymers and their potential applications in nano-devices and solar cells are studied.

The past decade has witnessed many efforts to design and synthesize supramolecular complexes aiming for efficient electron and/or energy transfer. The most common systems are covalently bound dyads, consisting of an energy/electron donor that ideally absorbs in the visible part of the spectrum where the solar irradiance is maximal, and an energy/electron acceptor that can be further chained to other molecular systems that ultimately perform the desired light-driven task. A selection of contributions in this Issue show examples of both synthetic energy transfer system (an artificial antenna containing a carotenoid donor and purpurin acceptor) and a few examples of dyads aiming for electron transfer. Finally, studies of excitonic structure and exciton dynamics in attractive new materials, CdSe semiconductor nanocrystals, add to the selection of systems that are of considerable interest in a view of potential applications.

Also highlighted in the Issue are recent developments in ultrafast spectroscopy – coherent multidimensional electronic spectroscopy. Such studies are now being carried out also in Lund. Photon echo spectroscopy has been used for investigation of solute–solvent or chromophore–protein interactions for many years, its intricate details and interpretation of the results are still heavily discussed. One of the most discussed themes is how to extract proper time constants of various solvation processes, and it is natural that the well-investigated dyes Nile Blue and Rhodamine are used to explore how the solvent affects the solvation dynamics that is monitored by the three-pulse photon echo peak shift. Contributions on two-dimensional electronic spectroscopy describe the exciton dynamics in aggregates of a relatively small molecule, carbocyanine, and a theoretical model for the 2D spectra of a light-harvesting antenna of green sulfur bacteria, the FMO complex.

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