

NMR in Supramolecular Chemistry

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NMR in Supramolecular Chemistry

edited by

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FOREWORD

The challenge of developing large but well characterized discrete systems for technological or other applications is being met by exploiting non-covalent interactions between smaller subunits to form unique supramolecular structures. The weakness of the forces involved in the stabilization of the desired structures make them inherently dynamic and the desired uniqueness has to be built in during the design of the subunits. Careful experimental characterization of the final equilibrium structure is mandatory.

The power of NMR as a tool for the structural determination of complex systems has been proven in the field of biomolecules. In addition, NMR has a unique capability for the study of dynamics in different time scales that is being extensively exploited at present in the field of molecular biology. The strong interaction between NMR specialists and structural and molecular biologists has been crucial for the success of NMR in this field : it has guided the development of new NMR techniques needed for specific problems but has also led to the development of labeling techniques that have expanded the range of feasible NMR experiments.

Supramolecular systems have obvious connections with biomolecules. Most processes inside a living organisms are based on non-covalent interactions between different macromolecules and many designed supramolecular systems have been inspired by natural models. On the other hand, the range of possible supramolecular systems extends well beyond the biological models. The Advanced Research Workshop "Applications of NMR to the study of structure and dynamics of supramolecular systems" was conceived as a way of stimulating the interaction between Supramolecular Chemists and NMR specialists, including biomolecular NMR experts.

This idea was encouraged by the steering committee of the NATO Supramolecular Chemistry Program and benefitted from the advice and suggestions of the colleagues, and friends, that accepted invitations to sit on the international organizing committee. Additional financial support was provided by the Ministerio de Educación y Cultura and the Generalitat de Catalunya. The meeting was held in Sitges, near Barcelona (Spain) from the 4th to the 9th of May, 1998.

The presentations could be broadly classified under three general categories: the first class illustrated the state of the art in the design of supramolecular systems and included examples of different classes of supramolecular complexes: catenanes, rotaxanes, hydrogen-bonded rosettes, tubes, capsules, dendrimers, and metal-containing hosts. A second class comprised contributions to NMR methods that can be applied to address the main structural problems that arise in supramolecular chemistry. The third class included biological supramolecular systems studied by state of the art NMR techniques.

Specific structural problems in supramolecular chemistry were identified. These include determining the conformation of a bound molecule in equilibrium with a free state; avoiding the degeneracy problems that complicate the study of symmetrical molecules; avoiding the spin-diffusion problems arising from chemical exchange; coping with ensembles of different conformations in fast exchange; characterizing the dynamics of the systems at different time scales or determining the size or aggregation state of the system.

In addition to the traditional NMR techniques already used extensively, the meeting highlighted some special NMR methods that are not exploited very often in "ordinary" chemistry but that may find increased applications in supramolecular systems: the use of paramagnetic ions, the creation of coherence due to the special properties of quadrupolar nuclei in anisotropic environments, the exploitation of the interference between different relaxation mechanisms, the use of optical pumping to increase NMR sensitivity or the combination of multiple-quantum filtration with diffusion measurements.

The true interdisciplinary atmosphere that developed during the Sitges meeting is difficult to reflect in the pages of a book but browsing through the titles of the contributions may provide a hint. If some of the readers of this volume are encouraged to walk out of their labs and talk to the colleagues in the Department next door, the main purpose of this book of Proceedings and of the Advanced Research Workshop itself will have been achieved.

Miquel Pons

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PROBING SELF-ASSEMBLY BY NMR

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1. NMR Spectroscopy in Supramolecular Chemistry

One of the major challenges in supramolecular chemistry [1] is the characterization of the (super)structural properties of the (supra)molecular species resulting from self-assembly [2,3] processes. Although the stereoelectronic properties of the supramolecular synthons are responsible for determining the geometries of the final self-assembled (super)structures, in most instances the experimental conditions (*e.g.*, solvent, temperature, pressure, and stoichiometry) play a dominant role. As a result, the prediction of the geometries of supramolecular entities is difficult and, more often than not, impossible even by means of computational methods [4]. Experimental techniques that are able to establish the (super)structural properties of (supra)molecular species unequivocally are much in demand. X-Ray crystallography has played a major role in determining the superstructures of supermolecules and supramolecular arrays, as well as the structures of large and complex molecular assemblies, in the solid state [5]. The characterization of self-assembled monolayers at the air/water interface — and on solid supports — has been achieved employing sophisticated microscopic techniques (*e.g.*, Brewster angle microscopy [6], scanning and transmission electron microscopies (SEM and TEM) [7], atomic force microscopy (AFM) [8] and scanning tunneling microscopy (STM) [9]). The combination of absorption and emission spectroscopies [10], along with electrochemical techniques [11], has permitted the characterization of self-assembled products in solution. Chromatographic methods (*e.g.*, high performance liquid chromatography (HPLC) [12] and gel permeation chromatography (GPC) [13]), often coupled with mass spectrometric techniques (*e.g.*, fast atom bombardment and liquid secondary ion mass spectrometries (FABMS and LSIMS) [14], electrospray mass spectrometry (ESMS) [15], and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) [16]), are becoming more and more powerful analytical methods for the characterization of (supra)molecular species. However, the most informative and widely used analytical method employed for the study of such species in solution is nuclear magnetic resonance (NMR) spectroscopy [17]. By relying on the evaluation of simple parameters (*e.g.*, chemical shifts, relative signal intensities, and spin-spin couplings) inter-component interactions, thermodynamic (*e.g.*,