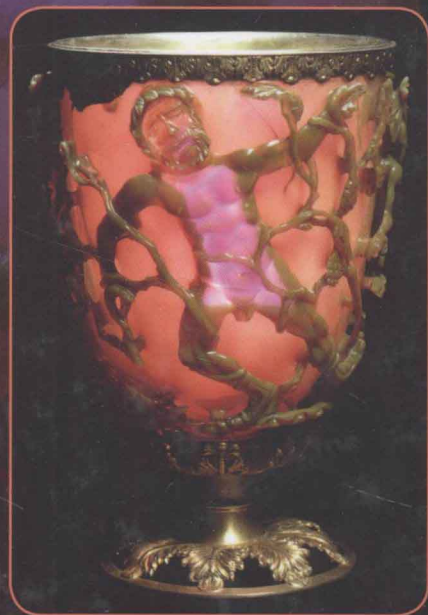


Supramolecular Chemistry

Jonathan W. Steed
and
Jerry L. Atwood

Second Edition



 WILEY

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Second Edition

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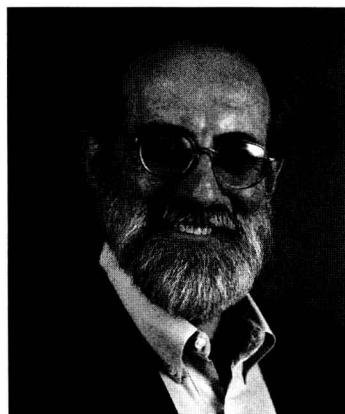
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In loving memory of Joan Edwina Steed, 1922–2008

About the Authors



Jonathan W. Steed was born in London, UK in 1969. He obtained his B.Sc. and Ph.D. degrees at University College London, working with Derek Tocher on coordination and organometallic chemistry directed towards inorganic drugs and new metal-mediated synthesis methodologies. He graduated in 1993, winning the Ramsay Medal for his Ph.D. work. Between 1993 and 1995 he was a NATO postdoctoral fellow at the University of Alabama and University of Missouri, working with Jerry Atwood. In 1995 he was appointed as a Lecturer at Kings College London and in 1998 he was awarded the Royal Society of Chemistry Meldola Medal. In 2004 he joined Durham University where he is currently Professor of Inorganic Chemistry. As well as *Supramolecular Chemistry* (2000) Professor Steed is co-author of the textbook *Core Concepts in Supramolecular Chemistry and Nanochemistry* (2007) and more than 200 research papers. He has published a large number of reviews, book chapters and popular articles as well as two major edited works, the *Encyclopaedia of Supramolecular Chemistry* (2004) and *Organic Nanostructures* (2008). He has been an Associate Editor of *New Journal of Chemistry* since 2001 and is the recipient of the Vice Chancellor's Award for Excellence in Postgraduate Teaching (2006). His interests are in supramolecular sensing and molecular materials chemistry.



Jerry L. Atwood was born in Springfield MO, USA in 1942. He attended Southwest Missouri State University, where he obtained his B.S. degree in 1964. He carried out graduate research with Galen Stuckey at the University of Illinois, where he obtained his Ph.D. in 1968. He was immediately appointed as an Assistant Professor at the University of Alabama, where he rose through Associate Professor (1972) to full Professor in 1978. In 1994 he was appointed Professor and Chair at the University of Missouri – Columbia. Professor Atwood is the author of more than 600 scientific publications. His research interests revolve around a number of themes in supramolecular chemistry including gas storage and separation and the control of confined space. He has also worked on the self-assembly of non-covalent capsules, liquid clathrate chemistry, anion binding and fundamental solid state interactions, and is a world-renown crystallographer. He co-founded the journals *Supramolecular Chemistry* (1992) and *Journal of Inclusion Phenomena* (1983). He has edited an enormous range of seminal works in supramolecular chemistry including the five-volume series *Inclusion Compounds* (1984 and 1991) and the 11-volume *Comprehensive Supramolecular Chemistry* (1996). In 2000 he was awarded the Izatt-Christensen Prize in Supramolecular Chemistry

Preface to the First Edition

Supramolecular chemistry is one of the most popular and fastest growing areas of experimental chemistry and it seems set to remain that way for the foreseeable future. Everybody's doing it! Part of the reason for this is that supramolecular science is aesthetically appealing, readily visualised and lends itself to the translation of everyday concepts to the molecular level. It might also be fair to say that supramolecular chemistry is a very greedy topic. It is highly interdisciplinary in nature and, as a result, attracts not just chemists but biochemists, biologists, environmental scientists, engineers, physicists, theoreticians, mathematicians and a whole host of other researchers. These supramolecular scientists are people who might be described as goal-orientated in that they cross the traditional boundaries of their discipline in order to address specific objectives. It is this breadth that gives supramolecular chemistry its wide allure, and sometimes leads to grumbling that 'everything seems to be supramolecular these days'. This situation is aided and abetted by one of the appealing but casual definitions of supramolecular chemistry as 'chemistry beyond the molecule', which means that the chemist is at liberty to study pretty much any kind of interaction he or she pleases – except some covalent ones. The situation is rather reminiscent of the hubris of some inorganic chemists in jokingly defining that field as 'the chemistry of all of the elements except for some of that of carbon'.

The funny thing about supramolecular chemistry is that despite all of this interest in doing it, there aren't that many people who will actually teach it to you. Most of today's practitioners in the field, including the present authors, come from backgrounds in other disciplines and are often self-taught. Indeed, some people seem as if they're making it up as they go along! As university academics, we have both set up undergraduate and postgraduate courses in supramolecular chemistry in our respective institutions and have found that there are a lot of people wanting to learn about the area. Unfortunately there is rather little material from which to teach them, except for the highly extensive research literature with all its jargon and fashions. The original idea for this book came from a conversation between us in Missouri in the summer of 1995. Very few courses in 'supramol,' existed at the time, but it was clear that they would soon be increasingly common. It was equally clear that, with the exception of Fritz Vögtle's 1991 research-level book, there was nothing by way of a teaching textbook of the subject out there. We drew up a contents list, but there the idea sat until 1997. Everybody we talked to said there was a real need for such a book; some had even been asked to write one. It finally took the persuasive powers of Andy Slade from Wiley to bring the book to fruition over the summers of 1998 and 1999. We hope that now we have written a general introductory text for supramolecular chemistry, many more courses at both undergraduate and postgraduate level will develop in the area and it will become a full member of the pantheon of chemical education. It is also delightful to note that Paul Beer, Phil Gale and David Smith have recently written a short primer on supramolecular chemistry, which we hope will be complementary to this work.

In writing this book we have been very mindful of the working title of this book, which contained the words 'an introduction'. We have tried to mention all of the key systems and to explain in detail all of the jargon, nomenclature and concepts pertaining to the field. We have not tried to offer any kind of comprehensive literature review (for which purpose JLA has co-edited the 11 volumes of *Comprehensive Supramolecular Chemistry*). What errors there are will be, in the main, ones of over-simplification in an attempt to make accessible many very complicated, and often still rapidly evolving, topics. To the many fine workers whose insights we may have trivialised we offer humble apology. We hope that the overwhelming advantages will be the excitement of the reader who can learn about any or all aspects of this hydra-like field of chemistry either by a tobogganing plunge from cover to cover, or in convenient, bite-sized chunks.

Preface to the Second Edition

Since the publication of the first edition of *Supramolecular Chemistry* in 2000 the field has continued to grow at a tremendous pace both in depth of understanding and in the breadth of topics addressed by supramolecular chemists. These developments have been made possible by the creativity and technical skill of the international community and by continuing advances in instrumentation and in the range of techniques available. This tremendous activity has been accompanied by a number of very good books particularly at more advanced levels on various aspects of the field, including a two-volume encyclopaedia that we edited.

In this book we have tried to sample the entire field, bringing together topical research and clear explanations of fundamentals and techniques in a way that is accessible to final year undergraduates in the chemical sciences, all the way to experienced researchers. We have been very gratified by the reception afforded the first edition and it is particularly pleasing to see that the book is now available in Russian and Chinese language editions. For a short while we attempted to keep the book current by updating our system of key references on a web site; however it has become abundantly clear that a major overhaul of the book in the form of a refreshed and extended second edition is necessary. We see the strengths of the book as its broad coverage, the care we have tried to take to explain terms and concepts as they are encountered, and perhaps a little of our own personal interpretation and enthusiasm for the field that we see evolving through our own research and extensive contact with colleagues around the world. These strengths we have tried to build upon in this new edition while at the same time ameliorating some of the uneven coverage and oversimplifications of which we may have been guilty.

The original intent of this book was to serve as a concise introduction to the field of supramolecular chemistry. One of us (JWS) has since co-authored a short companion book *Core Concepts in Supramolecular Chemistry and Nanochemistry* that fulfils that role. We have therefore taken the opportunity to increase the depth and breadth of the coverage of this longer book to make it suitable for, and hopefully useful to, those involved at all stages in the field. Undergraduates encountering Supramolecular Chemistry for the first time will find that we have included careful explanations of core concepts building on the basics of synthetic, coordination and physical organic chemistry. At the same time we hope that senior colleagues will find the frontiers of the discipline well represented with plenty of recent literature. We have retained the system of key references based on the secondary literature that feedback indicates many people found useful, but we have also extended the scope of primary literature references for those wishing to undertake more in-depth reading around the subjects covered. In particular we have tried to take the long view both in temporal and length scales, showing how 'chemistry beyond the molecule' continues to evolve naturally and seamlessly into nanochemistry and molecular materials chemistry.

We have added a great deal to the book in this new edition including new chapters and subjects (*e.g.* supramolecular polymers, microfabrication, nanoparticles, chemical emergence, metal-organic frameworks, ion pairs, gels, ionic liquids, supramolecular catalysis, molecular electronics, polymorphism, gas sorption reactions, anion- π interactions... the list of exciting new science is formidable). We have also extensively updated stories and topics that are a part of ongoing research with new results published since 2000. The book retains some of the 'classics' which no less striking and informative for being a little long in the tooth these days. As before we apologise to the many fine colleagues whose work we did not include. The objective of the book is to cover the scope of the field with interesting and

representative examples of key systems but we cannot be comprehensive. We feel this second edition is more complete and balanced than the first edition and we have really enjoyed putting it together. We hope you enjoy it too.

Jonathan W. Steed, Durham, UK

Jerry L. Atwood, Columbia, Missouri, USA

Acknowledgements

Our thanks go to the many fine students, researchers and colleagues who have passed through our groups over the years, whose discussions have helped to both metaphorically and literally crystallize our thinking on this rapidly evolving field. Many colleagues in both Europe and the USA have been enormously helpful in offering suggestions and providing information. In particular we are grateful to Jim Tucker, Mike Hannon, Jim Thomas and the late Fred Armitage for their help in getting the ball rolling and constructive comments on the first edition. The second edition has benefited tremendously from input by Kirsty Anderson and Len Barbour, and we are also very grateful to Len for the brilliant X-Seed which has made the crystallographic diagrams much easier to render. David Turner also provided some excellent diagrams. We thank Graeme Day for useful information on crystal structure calculation and a number of colleagues for providing artwork or additional data, particularly Sir Fraser Stoddart, John Ripmeester, Peter Tasker, Travis Holman and Bart Kahr. Beth Dufour, Rebecca Ralf and Hollie Budge, Andy Slade, Paul Deards, Richard Davies and Gemma Valler at Wiley have worked tirelessly to bring the book to the standard and accessibility it needs to have. JWS is very grateful to Durham University for providing a term of research leave which made this book so much easier to write, and we are both as ever indebted to the many fine co-workers who have passed through our labs over the years who make chemistry such an enjoyable subject to work in.

About the Front Cover

The front cover shows two views of the Lycurgus cup – a 4th century Roman chalice made of dichroic glass impregnated with nanoparticles made of gold-silver alloy. When viewed under normal lighting conditions the cup appears green but if light is shone through the glass the nanoparticles impart a gorgeous crimson colour. The chemistry of metallic nanoparticles remains a highly topical field in supramolecular chemistry. (Images courtesy of the British Museum, London, UK).

Website

Powerpoint slides of all figures from this book, along with the answers to the problems, can be found at <http://www.wiley.com/go/steed>

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