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COMPTES RENDUS CHIMIE

Foreword

Dendrimers and nanosciences

Nanotechnology is one of the major concerns of 21st century Society. It involves new advances for the miniaturization of computers, manipulation of electric, magnetic and optical signals and sensors for information and, on the biological side, the understanding and control of complex biochemical principles for drug transport and gene therapy. The appearance of nanotechnology has been impressive during the last decade as witnessed among the public in everyday life with, for instance, the popularity of personal computers and portable phones. Yet, progress is expected to accelerate at an even faster pace in the very near future. Examples of key challenges include the elaboration of nanowires, nanomagnets, nanoporous materials, single electron transistors, solar cells, light-emitting devices, solid-state lasers and multifunctional nanomaterials for the fabrication of nanodevices. So far, the miniaturization of technological devices has been achieved using the top-down approach that consisted in devising always-smaller chips of bulk metal and semi-conductors, but this strategy has now reached its limits. It is clearly apparent that the next step necessarily requires the involvement of the molecular level, whereby molecular components will be crucial parts of nanometer-sized devices containing both molecules and bulk metal and/or semi-conductors connected together. This strategy is called the bottom-up approach, and it is now the subject of intense scrutiny and formidable funding programs in the countries whose governments have understood its enormous impact on the control of future technology.

The importance of nanosciences en route for nanotechnology is thus obvious. An increasing number of nanosized molecules are now being synthesized. Polymers are the most well known examples, although they often still suffer from the lack of bio-degradability and of polydispersity beyond the precise technological requirements. Dendrimers, some series of which are now commercially available, are the first precise synthetic macromolecules with a polydispersity near 1.00 even at high molecular weights, and have therefore attracted considerable attention in the last decade. Their potential applications are in medicine, ecologically viable catalytic processes and nanotechnology. For instance, they have been shown to remove prions from solutions and are excellent mediators for gene therapy; also potentially efficient anti-cancer reagents involving boron capture of neutrons, easily recoverable nanocatalysts and NMR imaging agents. Being often of the same order of size as a biomolecule, they can be designed to mimic or insure a number of biological functions of metalloproteins, viruses and enzymes such as molecular recognition and supramolecular catalysis. Indeed, one of the great interests of dendrimers is that they can be decorated with metals at precisely selected and designed locations such as the periphery, center, focal points or branches. The magnetic, electronic and optical properties that are searched in nanoscopic dendritic systems are most of the time those of appropriately designed metal centers that one is able to locate in the dendritic framework. Therefore, the dendrimer field itself is interdisciplinary in that it gathers organic, inorganic, organometallic, polymer, physical and biochemists as well as scientists engaged in nanomaterials.

Dendrons are heterobifunctional dendrimers that resemble molecular trees, whereas dendrimers evoke califlowers. Dendrons are thus an exceptionally useful type of dendrimers, because they are bifunctional. They can be decorated with an appropriate function on the branches, and they can also be attached via their focal point to molecular or solid supports such as dendritic cores, dendrimers, nanoparticles, nanoporous materials and solid surfaces to build up mono- or controlled polylayers of molecules. Dendrons represent one way to link molecular and material compo-

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nents in devices, but they are not the only one. A diversity of nano-architectures derived with dendritic frames have been designed including combs and dendritic polymers, and dendrimers themselves can be physically adsorbed onto metal surfaces, nanoporous materials, etc. A considerable fundamental knowledge of dendrimers and dendrons is now accessible, in particular from two recent excellent books that have appeared in 2001, one of which already has a superb second edition, and from a multitude of review articles. We are now seeking for specific properties and true applications that need the connecting of these molecular materials to other materials and nanodevices such as self-assembled monolayers, nanoparticles, nanocrystals and superlattices. Thus, in editing this book-like special issue of *Comptes rendus Chimie*, one goal was to highlight the most recent concepts, progress and applications of dendrimers and dendrons. Another goal, most importantly, was to bring together the communities of molecular chemists involved in the dendrimer field (and others) and the nanomaterials scientists searching magnetic, electronic and optical properties and involved in the challenges of nanosciences and nanotechnology. Therefore, we have chosen to invite the most visible scientists in these fields to write an 'account' of their works emphasizing the key concepts and achievements as well as the general literature context. Each article is of a relatively reduced length in order to privilege the multiple aspects and the multiple orientations and fields that can potentially provide a productive interface between the molecular and material aspects. The yield of positive answers to the invitations has been gratifyingly, and referees have reviewed the articles.

This book-like issue is divided in six parts: the assembly of dendrimers and supramolecular aspects, dendritic polymers, dendritic nanodevices, metal nanoparticles, metallodendritic catalysis and nanoscopic materials and their physical properties.

The first part contains nine chapters. George R. Newkome (Akron, Ohio) was, with Drs. Denkewalter, Tomalia, and Vögtle, the pioneer of dendrimer chemistry in the early 1980s, and co-authored with C. N. Moorefield and F. Vögtle the most authoritative book on dendrimers (*Dendrimers and Dendrons: Concepts, Synthesis, Application*, Wiley-VCH, Weinheim, Germany, 2001). He now presents, together with C.N. Moorefield, the first chapter discussing dendrimers as molecular containers, whereas the second chapter by J.-F. Nierengaten (IPCMS, Strasbourg) treats encapsulated functions. Specific dendrimer effects and phenomena are emphasized in the two following chapters by H.-F. Chow's group (Hong Kong) and M.E. Mackay (East Lansing, Michigan). Then, Y. Tor's chapter (San Diego) is concerned with metal containing dendrimers, and the following chapter by S. Thayumanavan's group (Tulane, New Orleans) deals with biomimetic dendrimers. In chapter 7, J.R. Parquette (Columbus, Ohio) treats the intramolecular self-organization of dendrimers. The two last chapters on synthesis concern respectively the phosphorus dendrimer chemistry by the A.-M. Caminade and Majoral group (LCC, Toulouse) and carbosilane dendrimers by the O. Russell group (Barcelona).

The second part on hyperbranched or dendritic polymers contain five chapters starting with a general introductory chapter by B.I. Vogt (Dresden), a second chapter by Tang's group (Hong Kong) on hyperbranched polyarylenes, the following one by A.D. Schlüster (Berlin) on dendronized polymer and the last chapter by Tande et al. (Newark, Delaware) on hybrid dendron–linear copolymers.

The third part gathers dendritic nanodevices. The luminescent dendrimers, first disclosed in the early 1990s by V. Balzani's group (Bologna), are now discussed by him with F. Vögtle (Bonn) who published the first iterative synthesis in 1978. Other chapters on this area have been prepared by L. De Cola (Amsterdam), a former student of V. Balzani, and by S. Serroni et al. (Messina), J. Luo et al. (Seattle) and D.K.P. Ng (Hong Kong). Redox-active biomimetic dendrimers are carefully detailed in the chapters by C. B. Gorman (Raleigh, North Carolina) with the dendritic encapsulation of the redox core, M. Yamada and H. Nishihara (Tokyo) with the electrochemical deposition of metal nanoparticles and M. Venturi and P. Ceroni (Bologna) with electroactivity in the core or on the branches; the two last chapters by J.L. Serrano (Zaragoza) and R. Descheneaux (Neuchâtel) concern the remarkable field of liquid-crystal dendrimers.

The fourth part brings us into the world of metal nanoparticles that are intermediate between molecules and metals and present fascinating specific properties looking towards nanomaterials. For instance, nanocrystals in superlattices are nicely exposed in the first three chapters by M.-P. Pileni (Paris), T. Teranishi

(Ishikawa) and W. Guo and X. Peng (Fayetteville, Arkansas) before V. Kamat and D. Meisel (Notre Dame, Indiana) present their views on nanoscience opportunities in environmental remediaton. In the following chapter, Y.-S. Shon and H. Choo (Bowling Green, Kentucky) detail the chemistry of gold nanoparticles, then K. Philippot and B. Chaudret (LCC, Toulouse) show us an original route to nanoparticles from organometalic precursors. Finally, S. Efrima and N. Pradhan (Beer-Sheva) discuss an entry to nanoparticles using xanthate stabilization.

The fifth part deals with the promising field of dendrimers in catalysis. Indeed, metallodendrimers are recyclable catalysts that function in a homogeneous, thus fully controllable way. Yet, they can be easily removed from the reaction medium by precipitation, or ultra-filtration because of their large size, which is of great significance for the green chemistry of tomorrow when strict regulations will no longer allow chemists to let catalysts pollute the products. The first, elegant chapter by Y. Niu and M. Crooks (Texas A&M, College Station) describes an astute approach, combining dendrimers and nanoparticle catalysts. The second chapter by the P. van Leeuwen group (Amsterdam) brings us a spirit from industry where this distinguished scientist spent most of his career and pioneered the field. Then, van Koten's group (Amsterdam) details another pioneering approach involving dendritic catalysts that contain van Koten's famous magic pincer ligand. The two following chapters by the groups of L.H. Gade (ULP, Strasbourg) and K. Saoai and I. Sato (Tokyo) concern the essential results obtained with chiral dendritic catalysts. Then the chapter by J.L. Zhang's group (Hong Kong) reports dendritic catalysis with metalloporphyrin. Finally, the last chapter of this part by Astruc's group (Talence–Bordeaux) in collaboration with J.-C. Blais (Paris) details results comparing star-shaped and dendritic shaped catalysts and presents the design and applications (sensors, molecular electronics) of dendritic electron-reservoir structures including gold-nanoparticle-cored dendrimers.

The last, but not the least, part concerns nanomaterials at the border between the molecular and nanoscopic fields and whose combination with dendritic structures has provided, or should provide, exciting avenues. The two first chapters by the C. Sanchez group (Paris) and by P.-H. Mutin, G. Guerrero and A. Vioux (Montpellier) present the mesoporous approach, whereas the two following chapters by the group of A. Bleuzen, C. Cartier du Moulin and M. Verdaguer (Paris) and that of A. Bousseksou (LCC, Toulouse) report materials presenting remarkable magnetic properties. Then, the group of J. Won (Seoul) enlightens us about the area of thin films on polymer support. The following chapter by K. Naka and Y. Chujo (Kyoto) explains how dendrimers can orientate the crystallization of calcium carbonate in water. The final chapter of the volume presents the combination of chemistry and beauty in a superb piece of research by A. Müller (Bielefeld) in collaboration with M. Henry (ULP, Strasbourg) concerning giant, unique heteropolymetallate nanocapsules and their chemistry in water.

These new ventures are based on the control of molecular engineering involving organic, inorganic, bioorganic, bioinorganic and organometallic chemistry and catalysis, physical chemistry and physics, manipulating electron-transfer strategies at the interface between these molecular materials and solid-state components. This discipline needs bringing together synthetic molecular chemists, physicists and biologist as well as industry. Therefore, its success will involve the will of our Society to promote interdisciplinary research, as already exemplified, in several instances, in the present volume.

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