Inorganica Chimica Acta 417 (2014) 3–26

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Review

Metals in supramolecular chemistry

Carla Bazzicalupi [a], Antonio Bianchi [a,*], Enrique García-España [b,*], Estefanía Delgado-Pinar [b]

[a] Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
[b] Instituto de Ciencia Molecular, C/catedrático José Beltrán no. 2, 46098 Paterna (Valencia), Spain

ARTICLE INFO

Article history:
Received 22 February 2014
Received in revised form 1 March 2014
Accepted 4 March 2014
Available online 15 March 2014
Metals In Supramolecular Chemistry Special Issue

Keywords:
Supramolecular chemistry
Metal complexes
Molecular devices
Enzyme mimicking
Contrast agents
Chemosensors

ABSTRACT

Metals have played a fundamental role in the development of supramolecular chemistry. The main steps taken from the pre-supramolecular age to the present time are retraced with a brief description of salient examples from the unconscious use of gold nanoparticle in the preparation of the Lycurgus cup (5th or 4th century B.C.) to the modern use of metals as templates, for the preparation of large self-assembled structures, of molecular sensors, switches, motors and machines, for mimicking biological processes, for tissue and organ imaging or for the application of the Boolean logic at the molecular level.

Carla Bazzicalupi *graduated in chemistry in 1992 at the University of Firenze, Italy. In 1996 she received her PhD degree from the same University, under the supervision of Professor Piero Paoletti. Since 2001 she has been a researcher at the University of Firenze. Her research interests mainly concern the structural characterization of coordination compounds with synthetic macrocyclic ligands of both cations and anions. Recently her interest has been attracted by the structure of supramolecular adducts formed by biological macromolecules, such as DNA, with both natural and synthetic compounds and with their metal complexes.*

Estefanía Delgado Pinar *graduated in Chemistry at the University of Valencia in 2005. She is actually concluding her PhD in Inorganic Chemistry under the supervision of Prof. E. García-España. Her research focuses on modification of nanoparticles with organic molecules in order to achieve molecular recognition in water of charged species, using both surface science and supramolecular chemistry.*

* Corresponding author.
E-mail addresses: antonio.bianchi@unifi.it (A. Bianchi), enrique.garcia-es@uv.es (E. García-España).

http://dx.doi.org/10.1016/j.ica.2014.03.001
0020-1693/

Antonio Bianchi *received his Ph.D. in Chemistry at the University of Florence (Italy) in 1989 under the supervision of Prof. Piero Paoletti. He was employed by this university first as a tenured Researcher (1989-1991), then as an Associated Professor (1991-2000), and from 2000 as Professor of General and Inorganic Chemistry. From 2006 to 2009 he served as the Head of the Department of Chemistry at the said university. His research bridges across the fields of metal coordination chemistry, thermodynamic of coordination compounds, supramolecular chemistry and anion coordination chemistry. Within these areas, he paid special attention to molecular recognition of cationic, anionic and ion-pair substrates, to model systems for biological processes, MRI contrast agents, photochemical chemosensors, molecular devices, and chelating agents supported on solid phases. Nevertheless, anion coordination chemistry remains his preferred research topic. He has authored over 220 papers on international ISI journals and has served as co-editor and co-author of the books "The Supramolecular Chemistry of Anions" and "Anion Coordination Chemistry" edited by VCH-Wiley. He is the authors of many book chapters, mostly devoted to macrocyclic chemistry, to thermodynamics of cation and anion complexation and to photochemical chemosensors.*

Enrique García-España *Monsonís got his graduation in Chemistry from the University of Valencia in June 1977. After a period working in a private industry he returned to the University and performed the Ph.D. that defended in October 1984. He was a Postdoctoral Fellowship with the group of Professor Piero Paoletti at the University of Florence from November 1984 to January 1986. In 1986 he got a position of assistant professor at the University of Valencia. Since November 2000 he is full professor of Inorganic Chemistry at the University of Valencia. Since 1986 he is the scientific leader of the research group of Supramolecular Chemistry at the University of Valencia. His research interests covers enzyme mimicking, building of molecular probes for recognition of species of biomedical or environmental relevance, preparation of modified nanoparticles and development of new therapeutic agents. He has co-authored over 240 research articles. He has served as editor of two books of Wiley-VCH dealing with Anion Coordination Chemistry and he has been the editor of one volume devoted to Molecular Recognition of the eight-volume Encyclopedia of Supramolecular Chemistry published by Wiley in 2012 entitled: "Supramolecular Chemistry. From Molecules to Nanomaterials". In 2010 he was awarded with the Inorganic Chemistry prize by the Spanish Royal Society of Chemistry.*

Contents

1. Introduction

The modern concept of "supramolecular chemistry" was introduced by Lehn in 1978 [1]. Nevertheless, the term "supramolecular" had already appeared in Webster's Dictionary in 1903 and the word "übermoleküle" was coined in 1937 to describe species of higher organization derived from the association of smaller molecular entities [2].

Although the involvement of metal ions in supramolecular chemistry has been effective since the pioneering work of Pedersen, Cram and Lehn [3–5], who prepared cyclic and polycyclic molecules with cavities well suited to host metal cations, metals were not initially regarded as important tools for supramolecular chemistry. Only later, they were recognized as essential components of this emerging area, offering their coordination sites for the construction of fascinating architectures, for the geometrical regulation of self-assembling processes, for the propagation of catalytic, optical, electric and magnetic properties of metals.

When supramolecular chemistry was taking its first steps, coordination chemists demonstrated a certain interest toward cyclic and polycyclic ligands, mostly due to the occurrence that their metal complexes showed greater stability than the complexes formed by their acyclic counterparts, a phenomenon that was termed the "macrocyclic effect" by Cabbines and Margerum in 1969 [6]. In many cases, metal ions even took part in the synthesis of macrocyclic ligand via the "template reaction" procedure, a process that successively gained a wider denotation and attracted the interest of many chemists from different areas, whilst its name changed to "self-assembling" [7].

The convergence of supramolecular and coordination chemistry toward issues of common interests was initially fostered by the perception that both disciplines might furnish a synergistic help in the understanding of biological processes. The consequent construction of model systems, to reproduce or mimic natural processes, was a common challenge of supramolecular and coordination chemistry [8].

Nowadays, the "supramolecular coordination chemistry" is an established field [9], but the role of metals in the supramolecular age goes beyond the mere coordination chemistry toward a number of different applications, in both macro- and nanotechnology