

Jean-Claude Bünzli's research and interests

Initiation (1966-1974)

After training in organic chemistry (at Hofmann-La Roche, 1966), in inorganic reaction mechanisms (Diploma thesis and PhD thesis, Lausanne 1968-1971), JCB went to the Physical Chemistry Department of UBC in Vancouver, BC, Canada where he spent two years constructing photoelectron spectrometers and analyzing the PES spectra of small organic and inorganic molecules by means of semi-empirical molecular orbital calculations (INDO/2, MINDO, for instance). Back to Switzerland, he completed his initial education at ETH Zürich where he continued some work on PES while performing calorimetric measurements.

Main achievements during this period:

- use of NMR (^1H - and ^{31}P) to decipher ligand exchange mechanisms (HCA 1972, 55, 2867)
- high-resolution PES spectrometer, analysis of inductive effects in organic molecules (JACS 1974, 96, 1952)
- determination of the stabilization energy of [18]annulene and strain energy of quadricyclane (HCA 1974, 57, 2276, JACS 1975, 97, 1510).

The Lanthanide Kick (1974-present)

Solvation and coordination number in organic solvents (1974-1995)

The coordination numbers of trivalent lanthanide ions were still not very well known at the beginning of the 1970's, nor their interaction with anions. The problem was tackled by two experimental techniques, luminescence, which gives information on the excited state, and, for the most part of the work, FT-IR spectrometry, which was in its infancy at the time. The latter technique yielded the most interesting and systematic data; spectra were analyzed in terms of local symmetry of the coordinated and free anions and quantitative data could be obtained on nitrates and perchlorates, with or without the presence of a strong donor such as dmsO. The outcome was that

- coordination numbers in acetonitrile decrease by about 1-2 units in going from La to Lu
- the coordination number depends on the concentration of donor present in the solution, which means the coordination sphere can expand to accept an additional molecule or ion)
- perchlorate anions interact fairly strongly in acetonitrile

Main papers: *Inorg. Chem.* **1986**, 25, 2750, *Inorg. Chem.* **1990**, 29, 3875, ICA **1996**, 252, 221. Review: HPCRE, 1995, Vol. 21, 306.

Luminescent probes

In the late 1970's, rare-earth spectroscopy was beginning to be well understood, particularly in view of the work performed at Argonne National Laboratory by Wybourne and Carnall and in the CNRS laboratory of Bellevue in Paris by Caro. Solid state scientists were using these spectra to determine site-symmetry and, in parallel, at the beginning of the 1980's, W. deW. Horrocks was using lanthanide probe for the analysis of proteins.

Starting in the field, JCB was appealed by the vast potentiality of these intriguing spectra and my basic idea was to try to use lanthanide luminescent probe in coordination chemistry. This concept has remained the major thrust in my career and JCB tried to organize the other ideas around this theme, contributing in various fields, for instance:

- determination of the number of metal ion site in a complex, along with their symmetry (*J. Chem. Phys.* **1986**, 85, 2489 and *J. Phys. Chem.* **1989**, 93, 980)
- development of highly luminescent complexes (*Inorg. Chem.* **2000**, 41, 2459; *Inorg. Chem.* **2006**, 45, 732)
- directional energy transfers (*J. Phys. Chem.* **1994**, 98, 532, JACS **1993**, 115, 8197)
- quantum yield determination (*Spectrosc. Lett.* **2004**, 37, 517, and unpublished work)

- characterization of phase transition in liquid crystalline media (*Chem. Mater.* **2004**, *16*, 4063).

The book co-edited in 1989 (Lanthanide probes in Life, Chemical and Earth Sciences) has been instrumental in getting the attention of several coordination chemists and biochemists and the chapter that JCB wrote in it (Luminescent Probes) is by large its highest cited contribution and has brought to the field several prominent scientists (e.g. D. Parker and several of his pupils). The Lausanne group has established itself as one of the leading laboratories in lanthanide luminescence and as such collaborates with several other research groups worldwide.

Other recent reviews include: *Chem. Soc. Rev.* **2005**, *34*, 1048, Ch. 11 in Spectroscopic Properties of Rare Earths in Optical Materials (Springer Verlag, Berlin, 2005), Ch. 2 in Metal Complexes in Tumor Diagnosis and as Anticancer Agents (M. Dekker, 2004).

Besides luminescence, JCB always kept a wide interest for coordination chemistry and this translates in tackling several synthetic strategies to encapsulate lanthanide ions in functional (luminescent) molecular edifices. (see Chapter in Rare Earths, Editorial Complutense, 1998).

Classical coordination chemistry

By this, we refer to the use of multidentate chelating ligands or of podands for the complexation of lanthanide ions, taking advantage of the entropic effect generated by these molecules. Among the classes of ligands studied, a tetrapodal molecule fitted with 3-carboxylate pyrazole functional arms led to the formation of stable nanoparticles with a very high relaxivity, which could be useful as contrast agent (*JACS* **2000**, *122*, 10810). Another tetrapodal ligand, fitted with 8-hydroxyquinoline proved to have optimum sensitization of the luminescence of ytterbium in water, with the largest quantum yield reported for this ion in aqueous medium (*Inorg. Chem.* **2006**, *45*, 732). Tris(dipicolinates) have also been investigated, particularly with the aim of unraveling through space 4f→3d or 3d→4f energy transfer processes (*Inorg. Chem.* **1995**, *34*, 2068).

Macrocyclic chemistry

Crown ethers

JCB was the first to investigate in details the chemistry of lanthanide macrocyclic complexes with crown ethers, in the 1980's, as a logical follow on of the work on solvation, since including the metal ion into a ring-like cavity would allow the selective study of axial coordination. In particular he succeeded in unraveling the macrocyclic effect of crown ethers (*Inorg. Chem.* 1989, *28*, 2638).

Reviews: *Coord. Chem. Rev.* 1984, *60*, 191; *HPCRE* 1987, Vol. 9, Ch. 60; "Modern Aspects of Rare Earths and Complexes, Elsevier, 2003.

Schiff bases and calixarenes

The relatively poor complexation ability of simple crown ethers led him to rapidly turn to other types of macrocyclic receptors, compartmental Schiff base derivatives allowing the design of 3d-4f or 4f-4f bimetallic complexes (*JCS Dalton* 1990, 647), or derivatized calixarenes. The latter proved to be quite rewarding and were included in several projects, from the study of directional energy transfer mechanisms in 4f-4f⁺ heterometallic materials (*J. Phys. Chem.* 1994, *98*, 532), to the design of ligands able to separate lanthanide from actinides (unpublished).

Cyclen derivatives

Another small macrocycle amenable to easy substitution is cyclen and luminescent probed based on it have been developed within the frame of COST actions in the field of medical imaging. Grafting specific chromophores allows the sensitization of the luminescence of a given lanthanide ion (*Inorg. Chem.* 2000, *41*, 2459). The importance of chromophore orientation was also demonstrated. Presently some of the complexes are being tested *in vitro*.

Supramolecular chemistry: self-assembly processes

After Claude Piguet (now full professor of inorganic chemistry at Geneva University) spent 6 months in his laboratory, JCB became interested in self-assembly processes, another powerful strategy to recognize specific metal ions. A strong collaboration developed in the early 1990's, which is still active. Initially centred on the design of symmetric ditopic hexadentate ligands for the formation of triple-stranded bimetallic 4f-4f helicates (JACS **1993**, *115*, 8197) it soon evolved towards the control of the properties of one metal ion by another one through intermetallic communication in nd-4f edifices (JACS **2003**, *125*, 15698). Modifying the initial ligands to render them asymmetric allowed the recognition of a hetero-pair of 4f,4f' ions (*Inorg. Chem.* **2004**, *43*, 515).

Review article: **Chem. Rev.** *2002*, 1897.

Luminescent liquid crystals

The goal of this project conducted in collaboration with Prof. Claude Piguet was to produce lanthanide-containing luminescent liquid crystalline phases. Two approaches were used in Lausanne, one based on macrocyclic compounds (*New J. Chem.* **2005**, *29*, 1323) while in the other one, luminescent compounds were doped into an ionic liquid crystalline material leading to a range of tunable colored phases (*Chem. Mater.* **2004**, *16*, 4063). Another interesting result was the work out of a luminescence method allowing the determination of the phase transition (*Chem. Mater.* **2004**, *16*, 4063).

Present interests

Besides collaborative work with several other laboratories, the Lausanne group presently focuses on two main subjects. The first one is ambitious and aimed at developing heterobimetallic lanthanide helicates (either luminescent/luminescent or luminescent/magnetic) which are soluble in water and linkable to biological materials. The other one focuses on the sensitization of NIR luminescence initially by a podate approach, but subsequently by developing doped glasses and nanoparticles. Here again, medical imaging is targeted, although potential other applications are also sought for (light emitting diodes, solar energy conversion).

As far as biological probes are concerned, the luminescent complexes can now be tested in vitro, since the opening of a cell-culture facility in March 2006, within the Laboratory of Lanthanide Supramolecular Chemistry.

Spreading the Lanthanide Enthusiasm

Eager to keep the international f-element community together and in communication, JCB has been involved in the organization of international conferences in the field since 1985. In 1989 he has founded the European Rare Earths and Actinide Society, which sponsored a Europe-based broad-scope conference on f-element science every three years and has kept since then tight links with similar organizations worldwide, in particular in USA, China and Japan, so that a world scheme for international conferences on f-elements could be worked out.

He has also given several courses on lanthanide coordination chemistry and spectrophysics, in China (1989), Japan (1998), Holland (2003), Poland (2005), and France (2006).