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Inorganic, Analytical and Applied Chemistry

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Abstract: The recent history and the current activities in the fields of inorganic, analytical and applied chemistry are described briefly.

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Recent History

It is fitting, in this bicentenary year of Darwin's birth, to describe the recent history of this department as one of mutation and evolution to adapt to a changing environment. Certainly, the considerable changes that have occurred have often been the result of external decisions rather than any scientific logic. In 1970 the Department of Inorganic and Analytical Chemistry was in fact a very active department of analytical chemistry, directed by *Denys Monnier*, and carrying out research in a wide variety of analytical methods including groups led by *Werner Haerdi* (neutron activation analysis), *Minas Marcantonatos* (optometry and fluorescence) and *Jacques Buffle* (electrochemistry). The first change occurred in 1971 when *Christian Jørgensen* was transferred from physical chemistry. This was probably a good idea from a purely administrative point of view, but Jørgensen's research in spectroscopy was much closer to physical chemistry, and he always disliked quantitative analysis. Furthermore, it is difficult to imagine two temperaments more different than Jørgensen's and Monnier's; unsurprisingly, this move did not lead to any useful synergies. Denys Monnier retired in 1974, and Werner Haerdi took over the direction.

Administrative convenience struck again in 1976 when *Robert Monnier* retired from the chair of Applied Chemistry, and it was decided that the Applied Chemistry department, which had run the fourth and fifth year programme of the *Diplôme d'ingénieur chimiste*, was too small for an independent existence, and it was merged with Analytical and Inorganic Chemistry to produce the department with the longest name in the faculty. The structure was now essentially tripodal: the inorganic leg comprised Jørgensen and *Alan Williams* who had a small group in coordination chemistry and Mössbauer spectroscopy; that of analytical chemistry Werner Haerdi, Minas Marcantonatos and Jacques Buffle, and in applied chemistry *Hans Schmid* (the successor of Robert Monnier), *Paul Tissot* and *Jan Augustynski*. This structure was maintained essentially until the mid 1990's.

The research themes evolved slowly. The advances in atomic spectroscopy made techniques such as neutron activation less attractive, and Haerdi's research evolved towards methods of separation and preconcentration, and particularly chromatography. Marcantonatos became progressively more interested in the photophysics and photochemistry of the lanthanides and the uranyl ion. Jacques Buffle, while still active in electrochemistry, became more and more interested in the chemical processes in the aqueous environment. Denys Monnier had recognised the importance of chemistry for the study of the environment, and in 1972 the department had created the Certificate of Analytical Chemistry of the Environment. This was in many respects an idea well in advance of its time, a post-graduate course bringing together lecturers from analytical chemistry, environmental chemistry (*Werner Stumm, Paul Schindler, Jürgen Troe*), and from industry. For over twenty years it was followed by students from Geneva and other Swiss universities.

In applied chemistry, Hans Schmid developed an active research programme in solid-state chemistry, with particular interest in the synthesis and characterisation of ferroelectric materials. Paul Tissot and Jan Augustynski continued the traditional area of research in electrochemistry. Jørgensen, whose research is described elsewhere in this issue and Alan Williams, active in coordination chemistry, covered inorganic chemistry.

In 1992 Jacques Buffle was appointed to a chair of environmental and analytical chemistry funded by the Swiss National Science Foundation with the object of building up aquatic environmental chemistry. His vision of the subject involved not only the analytical aspects (development of new sensors) but also *in vitro* and field studies of metal ion uptake by organisms (*Kevin Wilkinson*) and modelling of interactions between particulate matter and biopolymers (*Serge Stoll*). Marcantonatos retired in 1992, and in 1993 Alan Williams was promoted professor of inorganic chemistry.

1996 was a year of major changes, marked by the retirement of Hans Schmid and Werner Haerdi. Jacques Buffle succeeded to Haerdi's chair, but Schmid's post was a victim of budget cuts. This condemned the *Diplôme d'ingénieur chimiste*, although courses in applied chemistry have been maintained as options in the fourth and fifth year programme of chemistry students. The development of the department would now be concentrated on inorganic and analytical chemistry, the latter with a strong environmental leaning. Inorganic chemistry was reinforced by *Claude Piguet* who created his own research group in 1995, later winning a Werner fellowship, and succeeding to Jørgensen's chair in 1999 after the latter's retirement. Further stimulus for inorganic chemistry came with the arrival in 1998 of *Katharina Fromm* as a research fellow.

In 2001 *Michal Borkovec* was appointed professor to reinforce the analytical side in anticipation of the retirement of Paul Tissot who retired in 2002, and he introduced new expertise in the study of surfaces and colloidal phenomena. In

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2006 *Josef Hamacek* created his own research group in inorganic chemistry, and *Oliver Wenger* joined the department as a Fonds National professor in inorganic chemistry working on photo-induced electron transfer. Jan Augustynski retired in 2006 and Jacques Buffle in 2008. The successor of Jacques Buffle will, we hope, join the department in 2010 to restore the equilibrium between inorganic and analytical chemistry.

Throughout this period, the department has maintained a constant output of research in international journals. A recent highlight was the award this year of the Lecoq de Boisbaudran prize to Claude Piguet to mark his major contributions to lanthanide chemistry, thereby continuing a tradition of lanthanide chemistry in Geneva after Jørgensen and Marignac. We are particularly pleased by the number of young chemists who have obtained professorial appointments after beginning their career as independent researchers in our department. Apart from Claude Piguet, we may mention Katharina Fromm (professor in Fribourg), *Vera Slaveykova* (Fonds National professor in environmental chemistry at the EPFL), Kevin Wilkinson (professor in Montreal), and very recently *Oliver Wenger* (professor in Göttingen) and *Georg Papastavrou* (professor in Bayreuth).

Teaching

The department has always had a heavy teaching load, including not only the three specialities in its name, but a major part of the teaching of general chemistry to students in medicine, pharmacy, biology and earth sciences. This general teaching has changed considerably in recent years, with the emphasis on aspects of chemistry relevant to the students' future studies. Considerable effort has been dedicated to illustrating the relevance of chemistry to studies in other sciences while maintaining a solid intellectual framework for the subject itself. In teaching for students of the Chemistry section an effort is made to illustrate the pertinence of chemistry for other subjects such as biochemistry or materials sciences.

An extensive programme of practical work is offered at all levels. For general chemistry for students in other fields, the emphasis is on illustration of theoretical concepts whereas for chemistry students this is also associated with instilling general experimental competence. Analytical chemistry labs allow students to familiarise themselves with a wide palette of experimental methods, while the inorganic labs cover not only classical solution chemistry, but also characterisation methods and examples taken from materials and solid state chemistry.

Research

The number of research groups active in the department is currently unusually low, and new groups are expected to join us in 2010. A theme common to all groups is the assembly of complex structures.

Inorganic Chemistry

Claude Piguet's research group combines a supramolecular approach to chemistry with coordination reactions, especially those involving lanthanide ions.[1] The synthesis of stable luminescent lanthanide complexes led to studies of the thermodynamics of formation of complex polynuclear species, especially helicates.[2] Careful design of ligands has allowed the control of nuclearity and the formation of heteronuclear complexes, and thrown a critical insight on the factors contributing to self assembly.[3] Assembly at a larger scale has also been studied in his work on thermotropic liquid crystals, and in particular those containing luminescent lanthanide ions (Fig. 1).[4]

Josef Hamacek's group is focussed on the preparation and characterisation of polynuclear lanthanide complexes, which allows the introduction of multiple functionalities into the final assembly. A typical example of such systems is the tetranuclear helicate with a three-dimensional arrangement of lanthanide cations (**1,** Fig. 2), which is achieved using a tripodal ligand with incorporated structural constraints.[5] The trinuclear complexes **2** obtained with a small ditopic ligand adopt unusual trian-

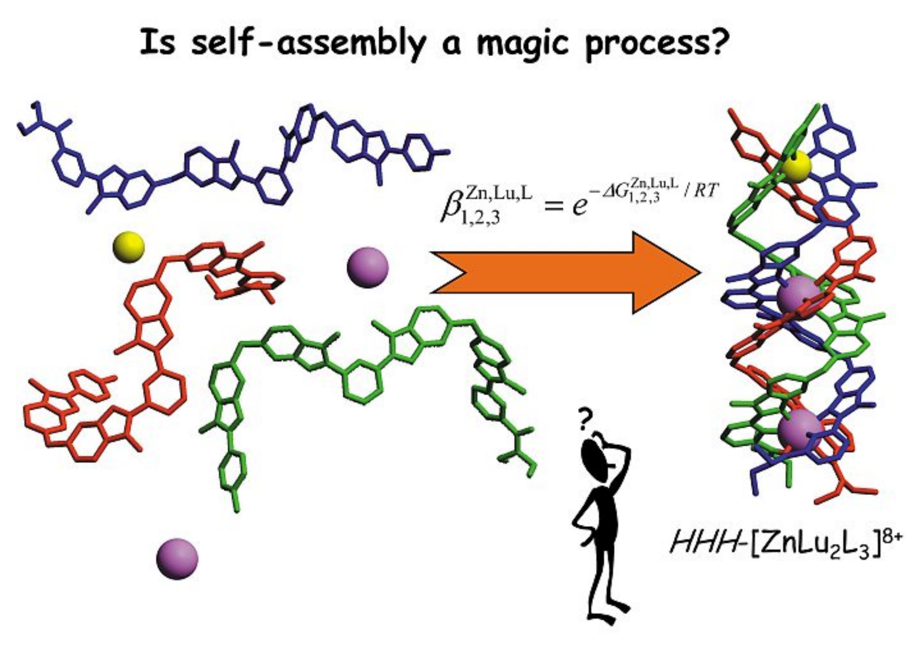

Fig. 1. Thermodynamics of self assembly.

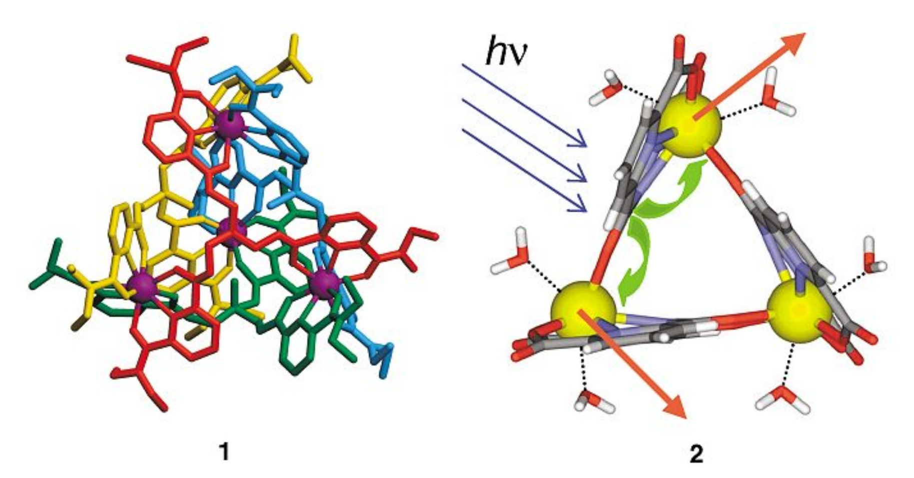

Fig. 2. Tetranuclear and trinuclear lanthanide complexes.

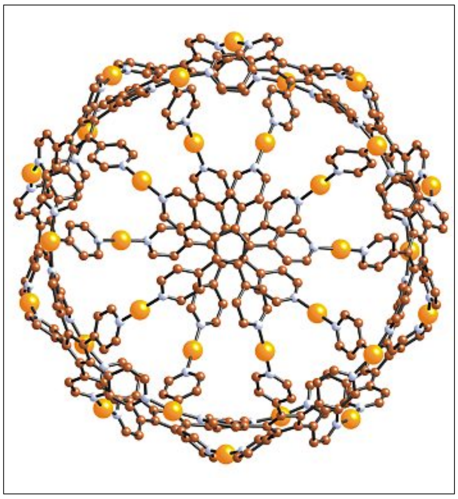

Fig. 3. A self-assembled molecular sphere.[10]

gular topology, which results in good luminescence and relaxivity.[6] Related heterometallic compounds are thus promising for multimodal imaging. The current effort is directed to the development of stable water-soluble compounds necessary for *in vivo* responsive probes. In this context, the development of asymmetrical tripodal systems is under progress. A deep interest obviously concerns fundamental aspects of the above mentioned self-assembly processes and comprises thermodynamic and kinetic investigations. A retrospective analysis of the *structure–properties* relation has been used for a better understanding of key factors governing intra- and intermolecular interactions.[7]

Alan Williams' group is mainly interested in polynuclear transition metal complexes. The transition metal cubanes have a general core of composition $\{M_4X_4\}$ where M is a transition metal and X is a bridging atom, typically S or O. Such complexes are frequently found in biology (iron sulphur proteins, the oxygen evolving centre) and exhibit magnetic exchange and multiple redox activity, and the structural properties and the ligands favouring the formation of such ligands have been studied.[8,9] Another field of interest is the generation of molecular cages by complexation reactions where symmetry is used to generate closed surfaces rather than infinite polymers (Fig. 3).[10] Finally, the use of chelating hydrogen bond donors for anion binding is being studied.[11]

Analytical Chemistry

Michal Borkovec's group focusses on colloid and surface chemistry, with a particular emphasis on water-solid interfaces, simple ions, and polyelectrolytes. Strong emphasis is given to the development of surface analytical techniques, especially atomic force microscopy (AFM) and *in situ* optical reflectivity techniques. Two research areas will be discussed below; a third, the self-assembly of polyelectrolytes on water-solid interfaces, was recently highlighted in this journal.[12]

AFM is explored as a unique tool to study interaction forces between the micron-sized colloidal objects down to the single molecule level. Single molecule force spectroscopy is a particularly exciting area of research.[13–15] The principle of the technique is shown in Fig. 4. A polymer layer is adsorbed to a substrate and is brought into contact with an AFM-tip with a strong affinity for the polymer. This can be achieved either by grafting reactive groups to the surface of the tip or by providing an appropriate surface functionality. When the interaction with the polymer is sufficiently strong, upon retracting the AFM-tip from the substrate, several polymer chains will be pulled along with the tip. This situation can immediately be identified from the appearance of characteristic spikes in the retraction part of the force curve (see Fig. 4a). Strongly adsorbed chains can be identified with characteristic spikes, which indicate the stretching of the adsorbed polymer chains. This situation is encountered in adsorbed poly(vinyl amine) layers at the water-solid interface, and by analyzing these events the corresponding loop-distribution could be obtained.[13,14] Weakly adsorbed chains, on the other hand, lead to plateau-like events, which correspond to peeling of the polymer chains from the surface. Such events were identified in thin cellulose layers.[15]

Another research area carried out in collaboration with Claude Piguet is the resolution of the binding mechanism of simple ions to polyfunctional ligands, such as water–solid interfaces or polyelectrolytes.[2,16] As an example of this work, let us briefly discuss how a microscopic site-binding model can capture the protonation mechanism of dendrimers.[17,18] The relevance of interactions between the ionisable sites can be illustrated by the difference in the protonation mechanism of two types of dendritic polyamines, namely poly(amino amine) (PAMAM) and poly(propylene imine) (PPI) dendrimers. Both are globular and highly-branched polyelectrolytes of similar structure, and as ionisable groups they carry primary amine groups on the rim and tertiary ones in the centre (Fig. 5).

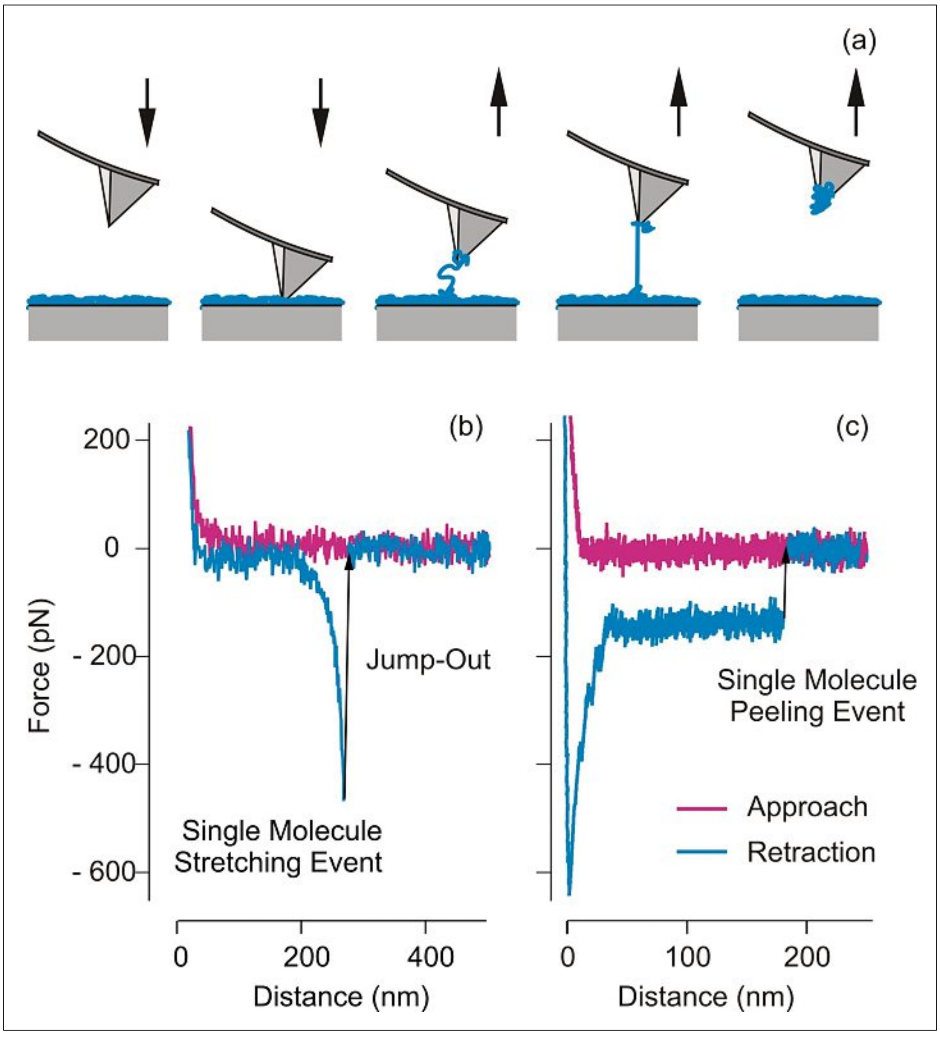

Fig. 4. (a) Single molecule events studied by AFM; (b) stretching event; and (c) peeling event.

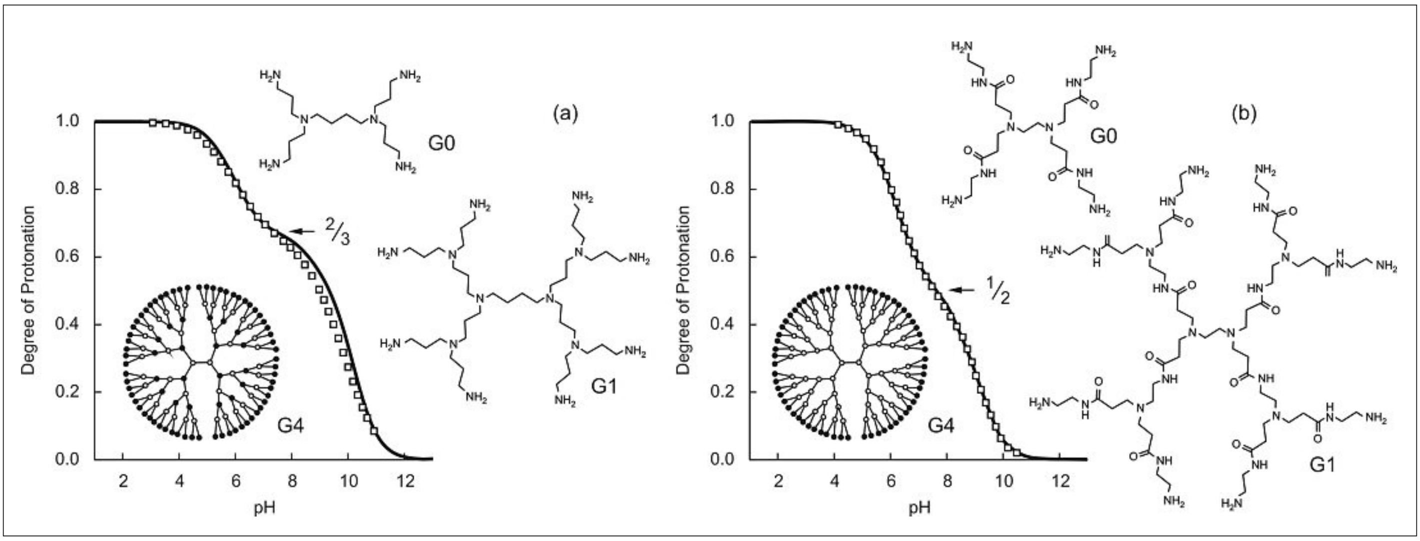

Fig. 5. Protonation of polyamine dendrimers 0.5 M KCl. (a) Poly(propylene imine) (PPI), and (b) poly(amido amine) (PAMAM) dendrimer.

However, these two polyelectrolytes protonate in a different fashion. One observes that PPI dendrimers show an intermediate plateau at 2/3, while for the PAMAM dendrimers a less pronounced plateau is located at 1/2. The quantitative interpretation of the charging curve is straightforward within the site-binding model. One immediately finds that the site–site interactions are strongly repulsive in the PPI system, while in the PAMAM system they are basically negligible. One concludes that the protonated sites in the intermediate state are the primary amine groups on the rim for the PAMAM dendrimer (1/2 of all sites), while for the PPI dendrimer these sites are the amine groups in odd shells (2/3 of all sites).

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