

Main research achievements of Claude Piguet (www.unige.ch/sciences/chiam/piguet/)

Basic formation and first contributions (1980-1995)

Claude Piguet studied inorganic and coordination chemistry during his PhD thesis dedicated to the design of low-molecular compounds modelling copper-based dioxygen transporters found in molluscs and in arthropods (1989). He then joined the research group of Prof. J.-M. Lehn (Strasbourg 1989-1990) for investigating copper-helicates displaying specific intramolecular interligand recognitions. Returned at the Inorganic Chemistry Department of the University of Geneva as a junior lecturer (1991), CP initiated research projects aiming at controlling the formation of discrete architectures incorporating d-block and f-block transition metals. This work was distinguished in 1995 by the Swiss Chemical Society with the attribution of the Werner Prize for *innovative work in metallosupramolecular chemistry*. CP was appointed as an assistant professor in 1995 thanks to the support of the Werner Foundation.

The initiation of lanthanide supramolecular chemistry (1995-1999)

Reasoning that the achievements of supramolecular chemistry with transition d-block complexes may be transposed for 4f-block ions, polynuclear homometallic f-f and heterometallic d-f assemblies possessing predetermined magnetic and optical properties were designed. This effort resulted in the emergence of polynuclear lanthanide bioprobes for cell monitoring. In 1999, CP was appointed as a full professor in chemistry at the University of Geneva, where he succeeded Prof. Christian K. Jørgensen at the chair of f-elements.

A renewal of basic thermodynamics in metallosupramolecular chemistry (1999-2010)

The rational growing of discrete metallosupramolecular structures in solution was hindered by the lack of clear and quantitative thermodynamic concepts controlling the subtle driving forces responsible for molecular recognition, cooperativity and for preorganization in multi-component self-assemblies. After intense efforts made possible by close collaborations with Prof. M. Borkovec (Geneva, statistical mechanics) and Prof. G. Ercolani (Roma, effective molarities and cooperativity), the thermodynamic site-binding model was introduced in the community of the coordination chemists in 2005. Its most obvious application concerned supramolecular complexes in solution, but the recognition of the crucial role played by solvation effects in the electrostatic balance controlling inter-cationic interactions in polynuclear complexes opened novel perspectives for stabilizing sophisticated metal–ligand assemblies in liquid crystalline phases and polymers. This advance was distinguished in 2009 by the 4th Lecoq de Boisbaudran award attributed by the European Rare-Earth and Actinide Society for *his seminal contribution to supramolecular chemistry of lanthanides and more particularly to its rational understanding through thermodynamic models*.

Phase transition controlled by chemical perturbations: toward coordination chemistry in liquid crystals (2005-2017)

Entered into the field of metal-containing liquid crystals during the nineties, CP was surprised that standard phase diagrams considered chemical perturbations as substitute of physical pressure contribution without any theoretical link with the only existing predictive theory based on Clapeyron equation. Building on the microsegregation Huggins-Flory theory reactivated at the turn of the century by Prof. C. Tschierske (Halle) who introduced the concept of cohesive energy density for tuning the vaporization temperature of liquids, CP extended it to any phase transitions with a special focus on solid→liquid-crystalline→liquid sequences, which are at the origin of the

formation of thermotropic liquid crystalline phases. The latter general concept of Cohesive Free Energy Density (CFED) slowly emerged and its application to phase transitions operating in organic, organometallic and inorganic materials rapidly established its virtues for rationalizing any transition temperatures. The last step considered the transformation of any chemical perturbations in term of pressure increments in Pascal units, which allows the unprecedented programming of luminescent lanthanidomesogens at room temperature. These efforts ended in 2017 with the provision of this novel method for pushing the limit of coordination chemistry, with a novel access to semi-organized phases and materials sensitive to external stimuli.

Inducing light upconversion in molecular complexes (2011-currently)

Light-upconversion based on linear optics was thought to be impossible to occur in molecular coordination complexes because of the coupling of electronic states with bond vibrations. This field was thus limited to doped low-phonon solid-state inorganic materials since the discovery of linear upconversion in 1966. Using a special complex design, the implementation of indirect chromium-centred energy transfer upconversion overcame this limitation in 2011. Lanthanide-centred near-infrared to visible light upconversion, despite its low quantum yield, may favourably compete for specific applications with non-coherently sensitized upconversion based on triplet-triplet annihilation, currently considered as the only pertinent method for performing the conversion of the NIR part of the solar light into green emission compatible with its absorption by dye-sensitized or by crystalline silica solar cells.

Mastering metal loading and organization of luminescent organic polymers (2013-currently)

When looking at the possibility of introducing luminescent lanthanide stains into processible polymers, CP was startled by the very limited reproducibility and the lack of reliable methods for organizing and mastering metal loading in polymers, resorting to basic statistical mechanics for programming cooperative binding leading to either metal clustering or metal alternation, multi-terdentate linear receptors were exposed to various neutral lanthanide carriers. The considerable difficulties encountered for inducing detectable intersite interactions justifies the recurrent production of uncontrolled novel metallopolymeric materials. Having realized that solvation processes caught by Onsager equations are essential for a rational tuning, the first anti-cooperative procedure, for which the intersite interactions largely overcome thermal energy could be designed only in 2017.