Geneva Chemistry Day 2016

13 January 2016, 09:00–16:20
Sciences II – auditoire A100 – quai Ernest-Ansermet 30 – 1205 Genève
No registration required
Followed by *2016 International Symposium on Chemical Biology*
Campus Biotech – chemin des Mines 9 – 1202 Genève

Prof. Tim Clark
Friedrich-Alexander-Universität Erlangen-Nürnberg

Prof. Ron M.A. Heeren
Universiteit Maastricht

Junior speakers: • **Lucille Babel** • **Marie Humbert-Droz** • **Zdeňka Jarolímová** • **Tamas Oncsik** • **Nadezda Pankratova** • **Elia Previtera** • **Manish Sharma** • **Quinchao Sun** • **Birte Varnholt** • **Oleksandr Yushchenko** • **Davood Zare** • **Jingying Zhai** •

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FACULTÉ DES SCIENCES
SECTION DE CHIMIE ET BIOCHIMIE

UNIVERSITÉ DE GENÈVE

FOREWORD

Tradition is meant at evolving rather than being set in stone!

This is why, for its 6th edition, the "***Geneva Chemistry and Biochemistry Days***" becomes "***Geneva Chemistry Day***", still organised by the *Section de chimie et biochimie*, University of Geneva, but without its *Département de chimie organique* and *Département de biochimie*.

The vocation of the event remains, namely giving our students who are close to finishing their PhD studies the opportunity to present their research as short talks to an audience from academia and industry, and the steering committee is glad to welcome you in this context

Two distinguished lecturers further enrich the programme. They have been invited by our *Département de chimie minérale et analytique* and *Département de chimie physique,* and they will illustrate the extent and quality of top-level fundamental research in chemistry today.

Our BSc and MSc students are also welcome to smell the very flavour of the research held in our School and abroad, and to learn a bit more about how to present results to a scientific audience.

Our 1-day symposium will be followed by the tentative first edition of the "***2016 International Symposium on Chemical Biology***" (see http://symposium.nccr-chembio.ch/) organised by the National Centre of Competence in Research Chemical Biology with the participation of our *Département de chimie organique* and *Département de biochimie*, thus bridging the gap between fundamental chemistry and biochemistry / life science.

It is hoped that the two consecutive events will catalyse fruitful discussions between young and advanced researchers, and give our students an opportunity to get ready for their professional careers, yet offering our guests an overview of the high quality of the fundamental research performed in our School.

Looking forward to meeting you at this event, we hope that you will enjoy the lectures and interactions!

Prof. Éric Vauthey
Président de la Section de chimie et biochimie

Steering and organising committee

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PROGRAMME

Session 1 – Morning

Chairmen: **Prof. Tomasz Wesolowski + Dr Max Lawson Daku**

09:00- -09:05	**Prof. Eric Vauthey**	Welcome message Introduction
09:05- -09:50	**Prof Tim Clark** Friedrich-Alexander-Universität Erlangen-Nürnberg	Very large quantum mechanical calculations: A new world
09:50- -10:10	**Lucille Babel**	Allosteric cooperativity in every directions
10:10- -10:30	**Elia Previtera**	Directional energy transfer in nanocrystals of $[Ru(bpy)_3][NaCr(ox)_3]$
10:30- -10:45	Coffee break	Main hall of Sciences III
10:45- -11:05	**Zdeňka Jarolímová**	Ion-selective fluorescent nanospheres based on functionalized polyether macrocycles
11:05- -11:25	**Quinchao Sun**	Establishing the ligand-field state of ruthenium(II) polypyridyl complexes
11:25- -11:45	**Nadezda Pankratova**	Local acidification of electrode surfaces for potentiometric sensing of anions in environmental samples
11:45- -12:05	**Oleksandr Yushchenko**	Ultrafast excited-state dynamics of naphthalenediimide-based multichromophoric systems
12:05- -13:15	Lunch (senior speakers + junior lecturers)	Restaurant-pizzeria Sole Mio, boulevard Carl-Vogt

Session 2 – Afternoon

Chairmen: **Prof. Gérard Hopfgartner + Dr Plinio Maroni**

13:15- 14:00	**Prof. Ron M.A. Heeren** Universiteit Maastricht	Types of tumors: Towards personalized medicine
14:00- -14:20	**Jingying Zhai**	Ionophore-based ion selective nanospheres as novel class of complexometric titration reagents
14:20- -14:40	**Manish Sharma**	Single route synthesis of borohydrides, their characterization and applications
14:40- -14:55	Coffee break	Main hall of Sciences III
14:55- -15:15	**Tamas Oncsik**	Tuning particle aggregation in ionic liquids
15:15- -15:35	**Marie Humbert-Droz**	Computing excited state properties of chromophores
15:35- -15:55	**Davood Zare**	Implementing near-infrared to visible light upconversion in discrete triple-stranded polynuclear d-f complexes
15:55- -16:15	**Birte Varnholt**	Vibrational spectroscopy on functionalized and chiral monolayer protected gold clusters
16:15- 16:20	**Prof. Eric Vauthey**	Concluding remark
16:20-	*Verre de l'amitié*	Main hall of Sciences III
16:25-	Start of *2016 International Symposium on Chemical Biology* http://symposium.nccr-chembio.ch/	Campus Biotech

Very large quantum mechanical calculations: A new world

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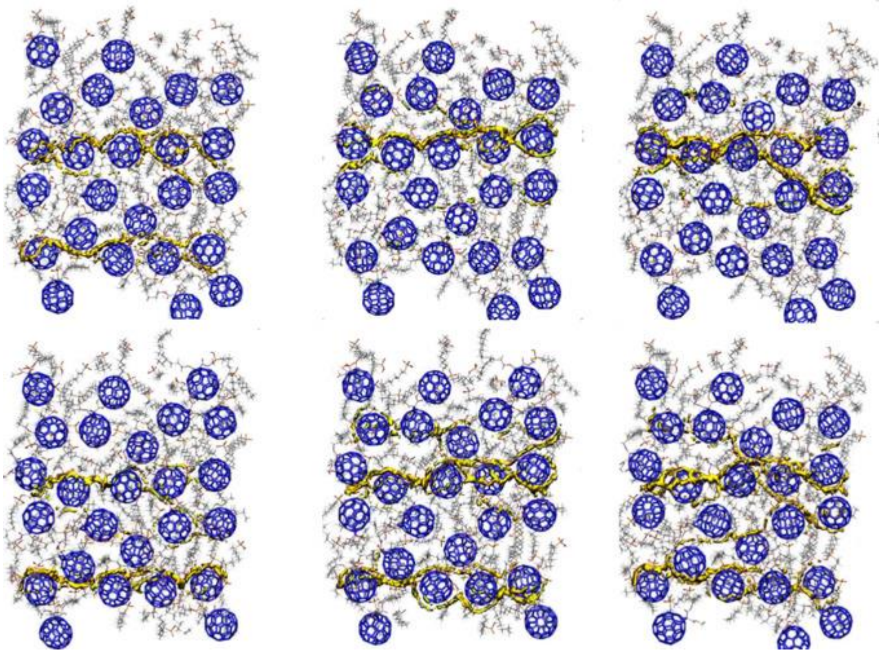
Moore's Law[1] is often cited, but its impact is seldom really understood. In the world of quantum chemistry, Moore's Law means that we can now treat small systems with unprecedented accuracy or (the subject of this lecture) simulate extremely large (currently up to 100,000 atoms) systems with approximate molecular-orbital (MO) theory without local approximations. We have conceived, designed and implemented a massively parallel semiempirical MO-program (EMPIRE[2,3]) that can treat nanoscale systems on high-performance compute clusters.



Such calculations allow us to treat organic electronic devices[4] using the semi-empirical wavefunction as the basis for simulations of electron- or hole-conduction through flexible organic molecular aggregates.

The Figure shows electron-conduction paths at different times through a self-assembled monolayer substituted with C_{60}-fullerenes as n-type semiconductor channel. In this respect, it is important that we can perform many quantum chemical calculations on snapshots of the system at different times.

However, very large scale MO-calculations are not limited to technical systems. They can also be used to investigate phenomena such as electron transfer in complete proteins in their water surroundings.

Examples of such applications will be discussed.

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Types of tumors:
Towards personalized medicine

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The chemical complexity of biological surfaces is highly dynamic and subject to local changes in response to a changing environment. This chemical heterogeneity is a particular important parameter when considering treatment of diseases such as cancer. It is this inconceivably complex heterogeneity that makes tumors so difficult to treat as no single therapy targets all permutations of phenotypes and environment precisely. This implies that to make truly personalized tumor therapy reality a diagnostic method is needed that unravels this spatial and molecular complexity of tumor tissue. The study of molecular signaling processes related to these diseases requires the detection and analysis of the molecules involved as well as the evaluation of their spatial organization. This allows the detailed molecular typing of cells under duress and can provide critical insight in the activated pathways related to the progression of disease. Molecular imaging in the post-genome era provides insight in metabolomic and proteomic changes during the progression of disease on different scales; from single cells to whole biological systems.

Innovations in high throughput molecular imaging with MS now enable tissue screening at clinically relevant time-scales. In this lecture we will demonstrate how mass spectrometry based multimodal molecular imaging can be used to reveal the tumor phenotype. We will discuss the development and application of new MS based chemical microscopes that target biomedical tissue analysis in various diseases as well as other chemically complex surfaces. We will demonstrate how to elucidate the way in which local environments can influence molecular signaling pathways on various scales. The integration of this pathway information in a surgical setting is imminent, but innovations that push the boundaries of the technology and its application are still needed. The imaging MS community is driving translational molecular imaging research and these needed developments rapidly forward. This lecture will highlight fundamental research, innovative developments, and unique applications in multimodal imaging MS. Results already demonstrated that rapid, direct tumor phenotyping is now reality and pointing the way towards personalized diagnostic and therapy.

Allosteric cooperativity in every directions

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The thermodynamics of complexation of bisbenzimidazolpyridine ligands with lanthanide carriers have been widely investigated.[1-3] For polymers ($N \geq 2$), the Ising model expresses the binding isotherms with the help of two microscopic thermodynamic parameters: (i) the non-cooperative intrinsic affinity f_{N3}^{Ln} of one lanthanide for a tridentate binding unit and (ii) the intermetallic interactions $\Delta E_{1-2}^{Ln,Ln}$ which operates between two occupied neighboring sites. Those parameters were estimated for the loading of different multi-tridentate ligands with $[Ln(hfac)_3dig]$ (hfac = hexafluoroacetylacetonate, dig = diglyme) on.[2-3] The influence of the number of sites and of the relative orientations of the tridentate subunits reveals unexpected trends in term of cooperativity concepts. The titrations were conducted in deuterated dichloromethane and monitored by ^{1}H and ^{19}F NMR in order to assess the successive complexation processes. The microscopic thermodynamic parameters can be rationalized with the help of solvation energies modulated by intramolecular electrostatic interactions.

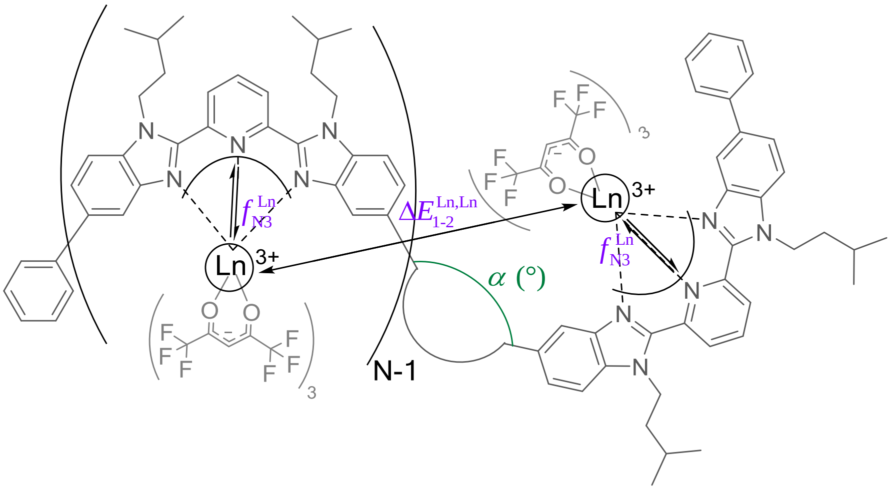

Figure. Schematic representation of the lanthanidopolymers $[Ln_N(hfac)_{3N}\mathbf{L}]$ highlighting the two microscopic thermodynamic parameters.

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Computing excited state properties of chromophores

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When it comes to computation of excited states of molecules, a large pool of methods is available.[1] Among those, Time-Dependent Density Functional Theory (TDDFT)[2] is usually a method of choice, as it can be very accurate and treat large systems. On the other hand, TDDFT has well known flaws especially when charge transfer states, double excitations or π-π^* excitation of large conjugated systems[3] are computed. Although TDDFT is an exact theory, approximations for the exchange-correlation potential are used in practice, introducing such typical errors. In this regard, wavefunction based methods are more robust and new developments in this field make it accessible for medium to large systems. As an illustration of this problem, excited state properties of several experimentally relevant chromophores are evaluated and analysed.[4,5]

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Ion-selective fluorescent nanospheres based on functionalized polyether macrocycles

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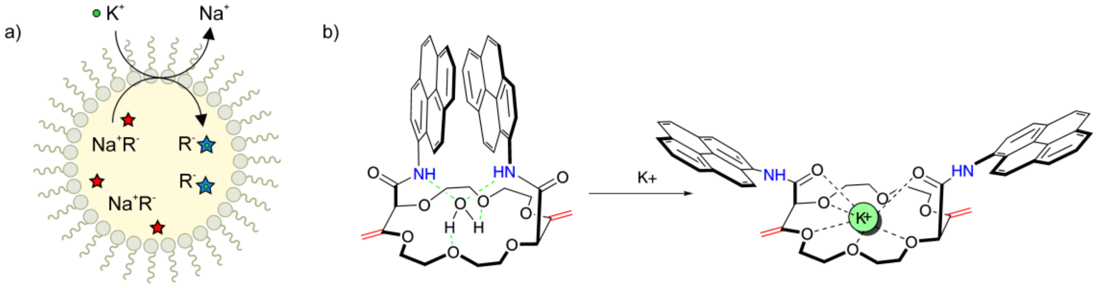
Ion sensors are important research tools in fundamental chemical science as well as in applied work such as clinical medicine or environmental analysis. During the past decades, the exploration and development of optochemical sensors (optodes, sensors layers, nano/micro particles) and their miniaturization have been the subjects of growing scientific attention.[1] The working mechanism such sensors is based on chemical equilibria where electroneutrality is maintained by ion-exchange or co-extraction processes and the spectral properties of the chromoionophores depend on the activity of two competing ions, H^+ and the target ion. Because of this, a major disadvantage of so-called ion-selective bulk optical sensors is the strong dependence of the sensor readout on the sample pH in the entire response range. The pH must be known or kept constant for a reliable measurement.[2]

The main interest of this work has been focused on the development of an optical sensor by eliminating the pH cross-sensitivity of bulk optodes while maintaining compatibility with aqueous solutions. We present here a new family of ion-selective optical sensors based on emulsified nanospheres containing densely functionalized 5-, 16-, 18- and 20-membered pyreneamide derivatives. Their specific structure consisting of a crown ether ring linked to pyrene moieties through amide groups exhibits on-off switchable behavior upon binding of specific cations without having to control the sample pH and allows one to incorporate these fluorosensors into ion-exchange nanospheres operating in an exhaustive manner.[3]



Scheme. Sensing mechanism of the ligand with potassium cation (a) and the specific interaction of functionalized 18-membered pyreneamide derivatives with potassium ion (b).

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Tuning particle aggregation in ionic liquids

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Ionic liquids (ILs) are composed entirely of ions resulting in unusual properties, such as low vapor pressure, good stability and electrochemical window. They are called “designer solvents” due to their tunable physical properties by varying their constituent anions and cations. Particle suspensions in ILs are of great interest in materials science applications.[1] This class of materials has increasing relevance, e.g. in catalysis, electrochemistry or in printing inks. An important parameter of such systems is their stability, which depends on the nature of surface-IL interactions.

My talk will focus on aggregation of polymeric latex particles in ILs and IL-water mixtures. The aggregation rates were determined by static and dynamic light scattering. At low IL concentrations the rates are initially small, and then they start to increase rapidly with increasing IL content, resulting in a maximum value. Further increasing the IL concentration a slowdown in aggregation can be seen, where viscous and solvation stabilizations take place. The viscous stabilization mainly occurs in highly viscous ILs, where the diffusion of the particles is hindered by the increased viscosity of the medium. The solvation stabilization is due to the layering of IL constituents on the particle surface, resulting in a repulsive interparticle force.[2]

Further investigations in dilute IL solutions show clear ion-specific interactions between IL constituents with the surfaces. Several ILs were used, where the constituent cations and anions are systematically varied. Specific adsorption of the different ionic species is responsible for the difference in aggregation behavior. The effect of different alkyl chain length on the IL constituent cations was also investigated. In general, the more hydrophobic cations tend to adsorb more onto the particle surface leading to lower surface charge densities, thus they make the particles aggregate at lower concentrations. The adsorption can lead to charge neutralization and reversal with ILs of long alkyl chain which leads to restabilization of the dispersions at intermediate concentrations. With the knowledge generated by these results, particle aggregation can be tuned by choosing ILs of appropriate composition and/or concentration.[3]

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Local acidification of electrode surfaces for potentiometric sensing of anions in environmental samples

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The determination of inorganic and hydrophilic anions is essential in many areas of applied analytical chemistry, particularly for the analysis of environmental samples. Potentiometric sensors are very attractive for practical application due to their reasonably fast response, small dimensions, portability, low energy consumption and simple operation.[1,2] However, due to strong hydroxide interference, most anion sensors reported so far are not suitable for application above pH 7 while the pH of environmental samples normally ranges from 6.5 to 8.5.[3]

The hydroxide interference can be suppressed by acidification of the sample. The latter is normally achieved either with a cation exchanger column or a loop injector/mixing coil where the sample is mixed with acid at adequate proportion.[4,5] Yet both procedures suggest pre-treatment and removal of the sensor from direct contact with the natural sample. The approaches reported here allow for local acidification of membrane surface without removing the sensor from contact with the sample phase. Three localized acidification strategies are explored with ionophore-based membrane electrodes selective for nitrite and phosphate as guiding examples. In a first approach, a concentrated acetic acid solution is placed in the inner filling solution of the PVC-based membrane electrode, forcing a significant acid gradient across the membrane. A second strategy achieves the same type of passive acidification by using an external proton source placed in front of a potentiometric solid contact anion selective electrode where the thin layer gap allows one to observe spontaneous acidification at the opposing detection electrode. The third approach shares the same configuration, but protons are here released by electrochemical control from the selective proton source into the thin layer sample. All three protocols improve the limit of detection by more than two orders of magnitude at environmental pH.[6]

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Directional energy transfer in nanocrystals of [Ru(bpy)₃][NaCr(ox)₃]

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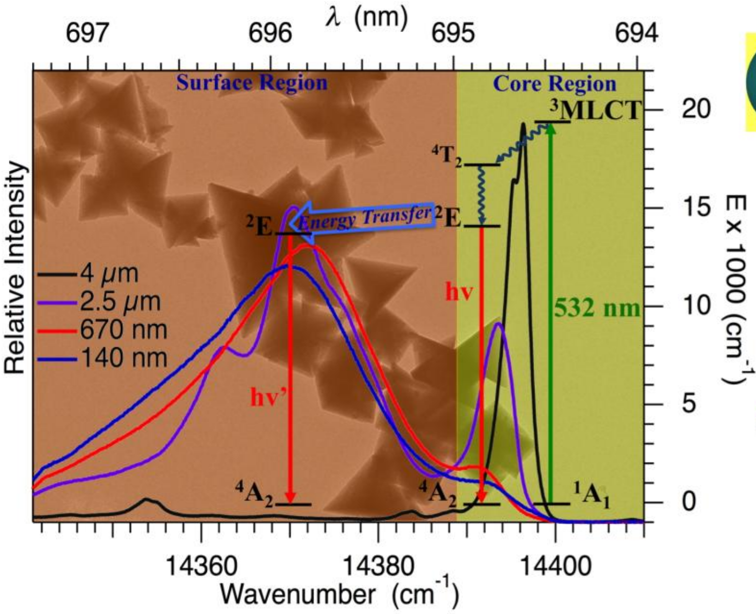
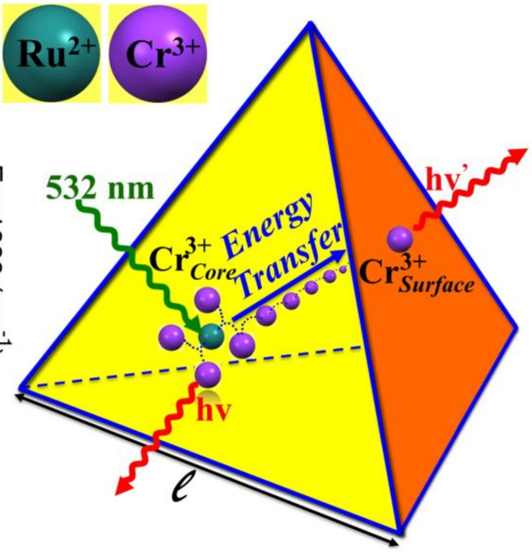
A reverse micelle technique was used to prepare size-controlled tetrahedral nanocrystals of 140 and 670 nm and microcrystals of 2.5 µm edge lengths of $[Ru(bpy)_3][NaCr(ox)_3]$, ox = oxalate, bpy = 2,2'-bipyridine, where $[NaCr(ox)_3]^{2-}$ forms a three-dimensional network.

The photophysical properties of the Cr^{3+} chromophores in these systems were investigated by high-resolution optical spectroscopy at low temperature and compared to the energy migration properties within ^2E states of Cr^{3+} in 4 µm microparticles[1] prepared by fast precipitation.

Significant differences in the luminescence spectra of nanoparticles are observed compared to the luminescence spectrum of the 4 µm microparticles after laser excitation at 532 nm at 4 K. For the larger particles the luminescence originates from the R_1 line of the ^2E emission of bulk $[Cr(ox)_3]^{3-}$ chromophores. Time-resolved fluorescence line narrowing techniques demonstrate that for the smaller particles, the luminescence of the lower energy broad band originates from chromophores at or near the surface region having their ^2E state at lower energy. These are excited via efficient directional energy transfer towards the surface from the initially excited chromophores in the centre (core region) of the nanocrystals.[2,3]





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Single route synthesis of borohydrides, their characterization and applications

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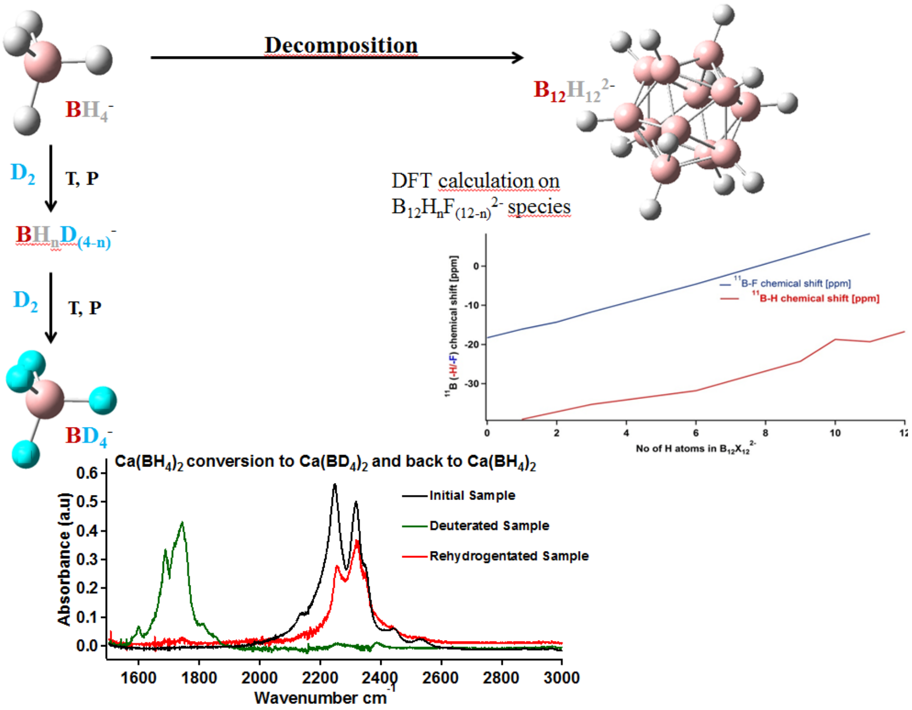
Borohydrides are actively considered as potential hydrogen storage materials. But to design safe and efficient hydrogen storage systems is a key challenge. Current work shows the synthesis of borohydrides and their characterization using vibrational spectroscopy, thermal analysis, XRD and computational calculations. In order to understand the mechanism of hydrogen release from borohydrides it is important to have the fundamental understanding of the mechanism of breaking and forming the boron–hydrogen bond. Isotope exchange reactions allow in principle to isolate some parts of this reaction without having to consider the chemical and structural changes associated with thermal decomposition reactions. Current work involves the reaction of $Ca(BH_4)_2$ with D_2 gas releasing $Ca(BD_4)_2$ as the product.

Borohydride can also be used for decomposing CO_2 and a part of current work shows the experiments involving the calculation of rate constant of reaction between CO_2 and $Mg(BH_4)_2$.

Anion exchange is considered to be a way to improve the kinetics of hydrogen release in borohydrides. Species like $BH_nX_{(4-n)}$ (X= halogen Cl, F) instead of BH_4. Thus there is a possibility of formation of $B_{12}H_nX_{(12-n)}$ instead of $B_{12}H_{12}$ as an end product. Current work also involves the computationally calculated IR and NMR spectra to decipher the difference between different species formed as an end product of $BH_nX_{(4-n)}$ decomposition.



Establishing the ligand-field state of ruthenium(II) polypyridyl complexes

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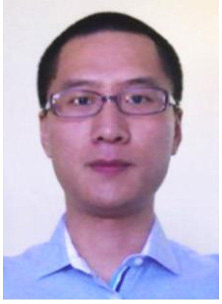
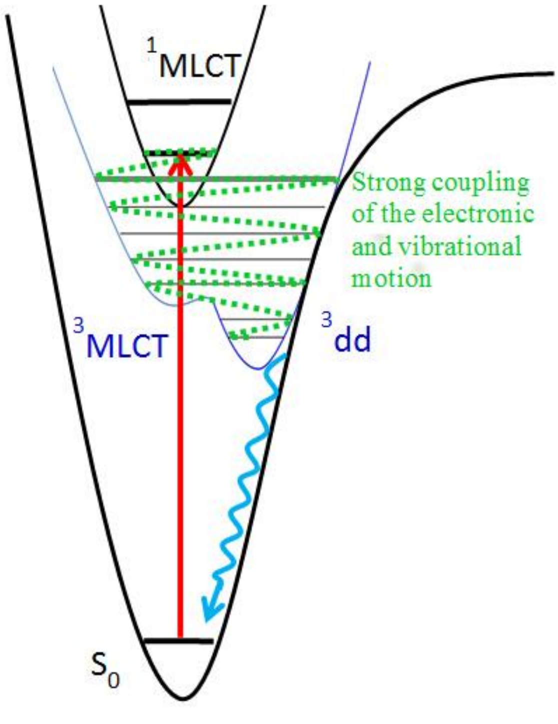


The lowest-energy ^{3}dd state is considered to be the dark quenching state for the ^{3}MLCT luminescence of $[\mathrm{Ru(bpy)_3}]^{2+}$ in solution at elevated temperature. The energy level of this state can be controlled by adjusting the ruthenium(II)-bipyridyl ligand bond length.[1] $[\mathrm{Ru(mbpy)_3}]^{2+}$ (6-methyl-2,2'-bipyridine) and $[\mathrm{Ru(mphen)_3}]^{2+}$ (mphen = 2-methyl-1,10'-phenanthroline) were designed to achieved this goal. Through steric effects, the methyl groups force a slightly longer Ru-N bond length, leading to smaller ligand-field strength, which in turn lowers the energy of the ^{3}dd state. Ultrafast transient absorption spectroscopy revealed that in the latter two complexes the ^{3}MLCT state decays within around 1.6 ps, while the return to the ground state takes around 450 ps.[1,2] The intermediate state was assigned to the ^{3}dd state.[1,2] In order to further characterize this intermediate state, time-resolved infrared spectroscopy was performed. The species associated IR spectra (SAIRS) of this intermediate state agree well with the ones calculated for the ^{3}dd state. The potential energy curves were scanned for all the complexes on the lowest energy triplet state along the metal ligand bond length. For $[\mathrm{Ru(bpy)_3}]^{2+}$, the ^{3}dd state was found to be higher in energy than the ^{3}MLCT state with a large barrier between them. The ^{3}dd state is lower in energy than the ^{3}MLCT state for $[\mathrm{Ru(mbpy)_3}]^{2+}$ and $[\mathrm{Ru(mphen)_3}]^{2+}$, and no barrier was found for the $[\mathrm{Ru(mbpy)_3}]^{2+}$.



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Vibrational spectroscopy on functionalized and chiral monolayer protected gold clusters

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The structure of monolayer protected gold clusters can be described by the divide-and-protect-model,[1] i.e. they are built up from a gold core and a protecting shell of gold-thiolate units.

Vibrational spectroscopy is one way to discriminate bond strengths and geometry sensitively.[2,3] The low-wavenumber region, which contains the Au-S and Au-S-C vibrations, can be investigated with far-infrared and Raman spectroscopy. With these means we studied thiolate-protected gold clusters with surface structures composed of monomeric (S-Au-S) and dimeric (S-Au-S-Au-S) binding units.

DFT calculations on the well-known $Au_{38}L_{24}$ cluster allow discriminating the spectral contributions of such units. The assignment can be transferred to clusters with different surface composition. A systematic shift of the Au-S-C bending allows estimating the number of monomeric and dimeric units.

Moreover, the ligand type used for the stabilization of the cluster influences the low-wavenumber range of the vibrational spectrum. Raman measurements reveal information about ligand-ligand interactions between long aliphatic chains. The distortion of the shell upon partial ligand exchange with di-thiolate ligands is reflected in the spectra.

It was found that intrinsic chirality is a common feature of monolayer protected gold clusters. The enantiomers of $Au_{38}L_{24}$ could recently be separated by high performance liquid chromatography.[4] Vibrational circular dichroism measurements on the enantiomers show that the chiral cluster transfers its handedness to the achiral ligand.[5] Chirality transfer of surfaces to adsorbed molecules is a phenomenon playing an important role in asymmetric catalysis.

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Ultrafast excited-state dynamics of naphthalenediimide-based multichromophoric systems

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Excitation energy transfer (EET) and charge separation (CS) are crucial steps in natural photosynthesis, that allows conversion of solar light into chemical energy. Understanding the nature of these processes is crucial for designing efficient synthetic analogues of these natural systems.

We have investigated various multichromophoric systems based on similar chromophores arranged according to different motifs.[1,2] To better understand the properties of these complex multichromophoric systems, systematic investigations of the individual units have first been performed.

In the first part, a study of a red core-substituted naphthalenediimide dye, r(ed)NDI, using a combination of steady-state and time-resolved techniques in the femto- to ms time domains will be presented.[3] Surprisingly, the fluorescence quantum yield of rNDI was found to decrease by a factor of almost 2 by going from $S_1 \leftarrow S_0$ to $S_2 \leftarrow S_0$ excitation. Time-resolved spectroscopic measurements reveal that this unusual deviation from the Kasha-Vavilov's rule is due to an ultrafast, < 200 fs, intersystem-crossing (ISC) from the S_2 state to the triplet manifold. In non-core substituted naphthalenediimide (pNDI), ISC is slower, ~2 ps, and was found to be reversible on a timescale shorter than that of vibrational cooling.[3] This unusual behavior allows to design rNDI-based systems with excitation-wavelength dependent properties.[2]

In the second part, the excited-state dynamics of two exemplary dyads consisting of zinc (ZnP) or free-base tetraphenylporphyrin (FbP) linked to a core-substituted NDI will be presented.[1] The excited-state behavior of these two dyads is rather complex and depends on the solvent polarity and on the excitation wavelength. Depending on the experimental conditions, ultrafast EET (ZnP to NDI or NDI to FbP) and/or CS are observed.[1] The dynamics of all these processes and the differences between the two dyads will be discussed.

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Implementing near-infrared to visible light upconversion in discrete triple-stranded polynuclear d-f complexes

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Nowadays, near-infrared to visible photon upconversion is extensively used for solar cells or for biological applications, in which solid-state rare earth-doped materials and nanoparticles play a prominent role.[1] One major issue in the design of these upconverting devices relies on the existence of intermediate excited states on the activator, which exhibit sufficiently long lifetimes for efficiently cumulating several linear excitations. Due to vibration-induced deactivation pathways occurring in discrete metallo-organic lanthanide complexes, in which molecular high-energy oscillators coexist with a series of closely spaced metal-centered excited states, the operation of upconversion processes was thought to be very unlikely.[2] However, the energy transfer upconversion (ETU) mechanism offers some underexploited perspectives for maximizing the efficiency of the light upconversion process according that the sensitizers and activators are judiciously coupled. Among promising sensitizer/activator pairs, the combination of kinetically inert strong-field octahedral Cr(III) with labile nine-coordinated saturated Er(III) appears particularly appealing for inducing efficient intermetallic energy transfers and long lived metal-centered excited state upon molecular design.[3,4] In this contribution, chemical requirements and design favoring upconversion at the molecular level will be presented.

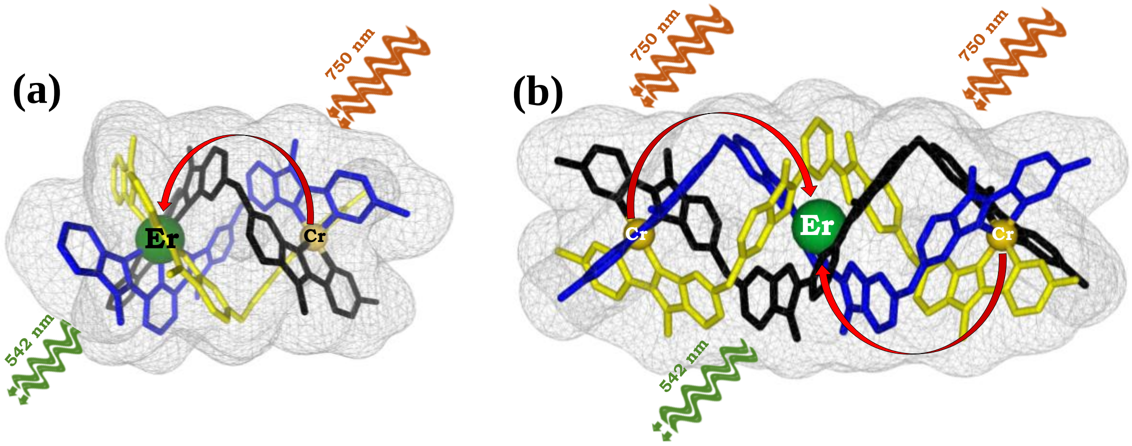

Figure. Molecular structures and photophysical processes for the molecular light-upconversion occurring in (a) dinuclear $[CrEr(\mathbf{L1})_3]^{6+}$ and (b) trinuclear triple-stranded $[CrErCr(\mathbf{L2})_3]^{9+}$ complexes.

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Ionophore-based ion selective nanospheres as novel class of complexometric titration reagents

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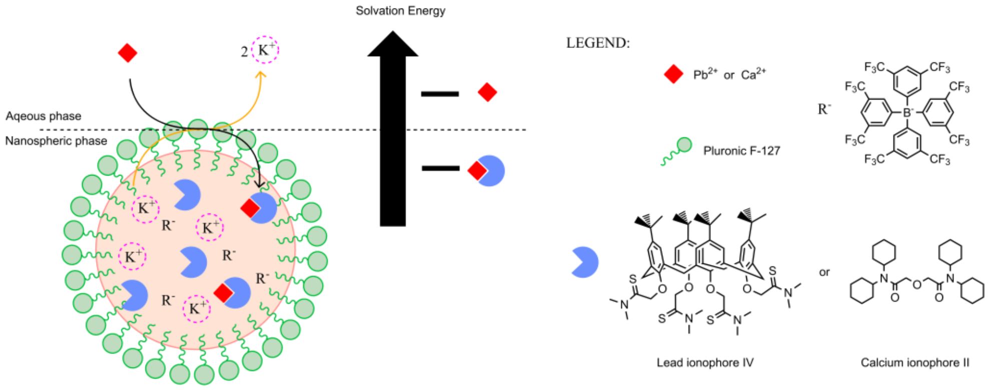
Complexometric titrations are routinely used to determine ion concentration, speciation as well as complexation reactions in various fields such as environmental, clinical and bioanalytical chemistry. Titration has now become an analytical technique used and taught all over the world in analytical science.

The available chemical toolbox of suitable chelating and indicating compounds are unfortunately limited because many promising complexing agents are not as water soluble as the widely used EDTA. However, there are a number of drawbacks for EDTA-based titrations, including pH dependence and poor selectivity. We recently introduced a novel class of complexometric titration reagents, a suspension of polymeric nanospheres whose hydrophobic core is doped with ion exchanger and complexing agent (ionophore) as chelators (chelating nanospheres). In this case, the complexometric titration process was moved from homogeneous phase to heterogeneous phase. The nanosphere-based titration reagents were successfully applied for titrating cations, such as Pb^{2+} and Ca^{2+},[1] as well as anions ClO_4^- and NO_3^-.[2]



Besides chelating nanospheres, we also introduced indicating nanospheres to indicate the endpoints. The indicating nanospheres contained additional hydrophobic chromoionophore (pH indicator) or solvatochromic dyes. Chromoionophore based indicating nanospheres rely on ion exchange between the hydrogen ions and analyte and are pH dependent.[3] Solvatochromic dye based indicating nanospheres are able to overcome this pH dependence.[4]

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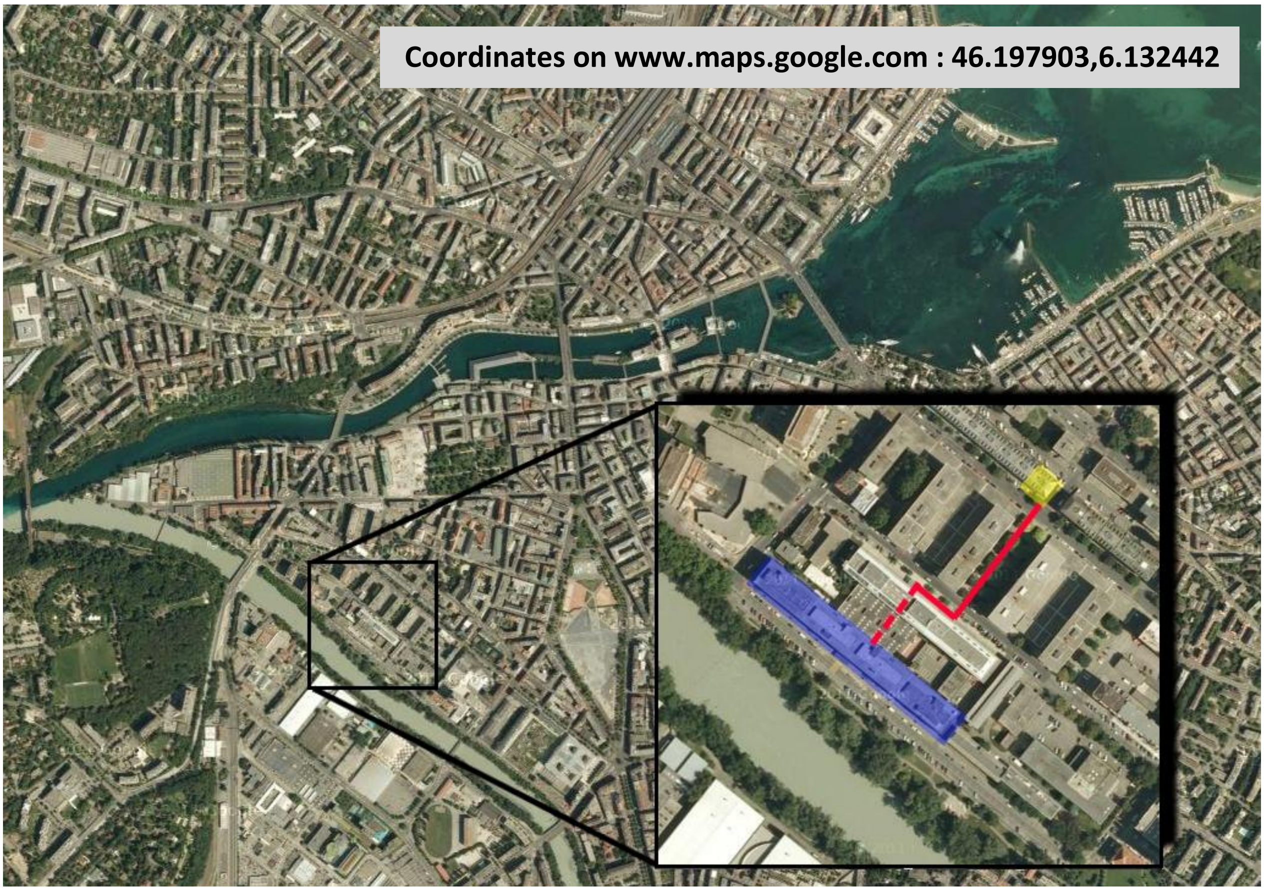

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