Tuesday, December 10th

Session : NANOCHEMISTRY: SYNTHESIS AND FUNCTIONALIZATION OF NANOSYSTEMS FOR BIOAPPLICATIONS

10h45 - 12h45
Keynote speaker: Yannick GUARI
Iron oxide nanoparticles and nanocomposites: their biosafety and applications

14h15 – 15h45
Keynote speaker: Tanja WEIL
Biomaterials inspired by Nature to solve Medical Challenges

Romanée-Conti Amphitheater

Abstracts

The SFNano C'NANO joint meeting 2019

Thematic Session: Nanoparticles & targeting
Keywords: polymer, prodrug, nanoparticles, cancer therapy, combination therapy, imaging

Heterotelechelic polymer prodrug nanoparticles for imaging and combination therapy

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Polymer prodrug nanocarriers have been developed to circumvent the main limitations associated with traditional drug-loaded nanoparticles. They are typically synthesized following the "*grafting to*" strategy (i.e., coupling drugs onto a preformed polymer). However, the newly developed "*drug-initiated*" approach,[1] for which the polymer is grown from a drug, offers important benefits, such as its simplicity, a quantitative functionalization of the polymer by the drug and high drug loadings.

In the biomedical field, heterotelechelic polymers (i.e., polymers bearing different functional end-groups) are particularly interesting as they offer an opportunity to embed two different biologically active entities at both chain-ends, such as drugs, ligands or imaging agents. However, synthetic strategies to achieve such constructs are generally laborious and not versatile. Also, no example of heterotelechelic polymers bearing two different drugs for combination therapy has ever been reported.

In this context, we propose a versatile, yet simple methodology to design heterotelechelic polymers for both imaging and combination therapy.[2,3] The idea was to grow a well-defined polymer chain from a drug-bearing initiator by the "*drug-initiated*" approach, followed by a nitroxide exchange reaction from a functional nitroxide to quantitatively functionalize the other chain-end by another molecule of interest. The efficiency of our approach was illustrated by the design of many different combinations for: (i) drug delivery and imaging; (ii) combination therapy and (iii) drug delivery and targeting.

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The SFNano C'NANO joint meeting 2019

Thematic Session: Nanochemistry: synthesis and functionalization of nanosystems for bioapplications

Keywords: organic nanoparticles, nanochemistry, *in vitro* imaging, internalization, theranostics

Soft fluorescent organic nanodots as novel nanocarriers for photoactivated drugs

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Novel highly water-soluble soft fluorescent organic nanoparticles (FONPs) have been obtained using green synthesis protocols. These nanoparticles show remarkable solubility in aqueous environment (>250 g/L), as well as bright blue fluorescence in water that are fully retained in cell culture medium. Furthermore, they offer versatile opportunities for surface functionalization, including the possibility to tune the surface potential. These FONPs were shown to internalize into cancer cells while showing no cytotoxicity. Moreover, hydrophobic drugs can be covalently attached to the FONPs yielding conjugated FONPs which maintain both large water-solubility and fluorescence in aqueous environment. These unique features were applied to photoactivated cancer therapy. Both photosensitizers and photoactive cage moieties (caging anticancer drugs) were grafted onto the nanoparticles. Thanks to their bright fluorescence, the uptake of conjugated FONPs was monitored by fluorescence microscopy, demonstrating that the FONPs act as effective nanocarriers promoting efficient internalization of photoactive compounds into U87 cancer cells. Moreover selective light irradiation was shown to promote cell death, opening the route to novel biocompatible theranostics nanotools for cancer treatment.

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The SFNano C'NANO joint meeting 2019

Thematic Session: Nanochemistry

Keywords: Sepiolite, DNA transfer, mammalian cells, bionanocomposites

Sepiolite as a new nanocarrier for DNA transfer into mammalian cells

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Abstract:

Nanofibers of sepiolite, a natural silicate belonging to the clay minerals family, might constitute a potential promising nanocarrier for the non-viral transfer of bio-molecules. Using physic-chemical approach and transmission electron microscopy analyses, we show that sepiolite nanofibers efficiently bind different types of DNA molecules through mainly the external silanol groups. Due to its nano-size dimension sepiolite can be naturally internalized into mammalian cells. Therefore, deciphering the mechanisms of sepiolite cell internalization constitutes a question interesting biotechnology, for the use of sepiolite as nanocarrier, as well as environmental and public health concerns. Though it is low, the perfectly stable and natural intrinsic fluorescence of sepiolite nanofibers allows to follow their fate into cells. By combining fluorescence microscopy, time-lapse video microscopy, fluorescence activated cell sorting and transmission electron microscopy, we show that sepiolite can be spontaneously internalized into mammalian cells through both non-endocytic and endocytic pathways, macropinocytosis being one of the main pathways. As a proof of concept, we show that sepiolite is able to stably transfer plasmid DNA into mammalian cells and that the efficiency can be optimized. Indeed, sonication of sepiolite prior assembly with DNA 100-fold stimulated DNA transfection efficiency. Moreover, exposure of the cells to endocytosis inhibitors, such as chloroquine, two-fold increase the efficiency of sepiolite-mediated gene transfer, in addition to the 100-fold increased resulting from sepiolite sonomechanical treatment. These results open the way to the use of sepiolite-based bionanocomposites as a novel class of nanoplatform for gene transfer.

The SFNano C'Nano joint meeting 2019

Thematic Session: (Nanochemistry: synthesis and functionalization of nanosystems for bioapplications)
Keywords: (zwitterion, ligand, antifouling, quantum dots, FCS)

Antifouling zwitterionic nanoparticles surface chemistry: impact on intracellular diffusion

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Minimizing protein corona around nanoparticles by using stealth polymer is a current strategy to limit non-specific cellular uptake. In addition, the antifouling property is a prerequisite for specific targeting and drug delivery. PEG coating is most commonly used for this purpose but zwitterionic surface chemistry appears as an interesting alternative. The wide range of possible variations of zwitterionic materials is clearly an advantage compared to PEG but in return, the impact of the molecular design on protein-adsorption properties must be optimized. Here, we present some results about interactions between polyzwitterionic coated quantum dots nanoparticles and albumin or whole serum. Sulfobetaine, phosphorylcholine and carboxybetaine based polymers have been synthesized by RAFT. A terminal vinylimidazole block was added at the end of the polyzwitterion to ensure anchoring at the quantum dots surface. Fluorescence Correlation Spectroscopy was used to characterize dynamic interactions between proteins and QDs directly.

We found that sulfobetaine based polymer is able to totally prevent hard and soft corona formation with BSA and proteins of serum around nanoparticles making this polymer ideal for antifouling applications. The phosphorylcholine and carboxybetaine ligands are less efficient and induce formation of few aggregates in serum. Intracellular trajectories of individual QD injected into Hela cells have been analyzed. The high diffusion coefficient (D_{60ms} ~0.8 um^2s^{-1}) and the purely Brownian motion point to the remarkable cytoplasmic inertness of these zwitterionic coated nanoparticles. Finally, I will show that the exceptional antifouling properties observed in the case of sulfobetaine-coated QDs can be transposed to iron oxide nanoparticles.

The SFNano C'Nano joint meeting 2019

Thematic Session: Nanomaterials

Keywords: Nanoconjugates; glioblastoma; hyaluronicacid

Hyaluronic acid modified stimuli responsive nanoconjugates for multimodal therapy of glioblastoma

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Abstract:

The FePt alloy nanoparticles were synthesized with controlled size and elemental composition followed by surface modification using (3-Aminopropyl) triethoxysilane (APTES). Lenalidomide was covalently bound to FePt-NH2 by pH-sensitive hydrazone bonding. Hyaluronic acid was conjugated to amino groups of APTES while lactoferrin (Lf) was directly conjugated to excess carboxylic group present on hyaluronic acid (HA) to form surface-modified pH-sensitive alloy-drug nanoconjugates (SPANs). The multifunctional nanoconjugates were characterized and evaluated using extensive *in vitro* and *in vivo* techniques. The nanoconjugates demonstrated excellent heating ability on exposure to alternating magnetic field and near-infrared laser irradiation. The acidic microenvironment of lysozome triggered release of LND from SPANs. Owing to leaching of Fe and Pt contents, SPANs demonstrated ability to generate reactive oxygen species (ROS) in U87MG cell line which further enhanced therapeutic effect of SPANs. A significant difference in cell viability suppression was observed in *in vitro* photothermal, chemo-photothermal and chemo-magnetophotothermal killing of cancer cells using SPANs in U87MG cell lines. A significant difference in heating ability and cell cytotoxicity of SPANs in comparison to alternative magnetic field and NIR irradiation was observed for DUAL-mode exposure of SPANs. The results of cellular internalization study showed efficient internalization of SPANs inside U87MG cells. The *in vivo* results (both qualitative and quantitative) confirmed enhanced uptake of SPANs in brain after intranasal administration with enhanced nasal and mucus penetration owing to presence of Lf. No significant interaction was observed with ECM and mucin due to presence of carboxyl group on SPANs.

The SFNano C'NANO joint meeting 2019

Thematic Session: Nanochemistry: synthesis & functionalization of nanosystems for bioapplications

Keywords: iron oxide nanoparticles, shape effects, defect, dendron coating, relaxivity and hyperthermia-structure relationships

Shape, functionnalisation and defect effects on theranostic anisotropic nano-objects coated with antifouling dendrons

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Among the virtues of theranostic agents for nanomedicine, it is the stealthiness to evade the reticulo-endothelial system, showing a good biodistribution to enable specific targeting of diseases and an image-guided therapy. Here, a series of biocompatible iron oxide nanoparticles with different shapes (spherical, plate, cubic, octopod), were designed and screened in vitro and in vivo to test their abilities as high-end theranostic agents. Octopod-shaped nanoparticles coated with dendrons showed an unprecedented combination of characteristics as image contrast and magnetic hyperthermia agent especially at low frequency. The anti-fouling properties of the dendron coating, together with a small hydrodynamic size ensuring an extended *in vivo* circulation, are evidenced. The extensive structural and magnetic characterization of all dendronized nanoparticles series evidences a clear shape and defect effect affecting their performance. Besides the octopods, dendronized nanospheres with size around 20 nm also offer interesting combined theranostic properties, whereas nanoplates and nanocubes showed adequate relaxivity values for magnetic resonance imaging, performing less well as heaters for hyperthermia properties. The octopod and nanoplate shapes appear to induce unusual surface effects demonstrated by Electron Energy Loss and Mossbauer spectroscopies when nanospheres were shown

to display high internal defects favoring Neel relaxation for magnetic hyperthermia. NMRD profiles and magnetic measurements evidenced also a particular signature of octopods which is attributed to surface effects and/or magnetic field inhomogeneity induced by the octopod shape with elongated corners. A size effect is noticed with octopods showing a Neel relaxation favored at sizes around 18 nm while the Brownian one raises at higher sizes.

The SFNano C'NANO joint meeting 2019

Thematic Session: Nanochemistry: synthesis and functionalization for bioapplications / Nano for imaging, diagnosis and theranostics / Nanophotonics & nano-optics
Keywords: fluorescent organic nanoparticles, microfluidics, energy and electron transfer, nanomechanics, cell uptake mechanism

Morphology Control and Electronic Confinement within Photoactive Organic Nanoparticles for Bioimaging and Drug Release

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Functional organic nanomaterials (FONs), initially restricted to the field of data display and lighting, have crossed the field of nanomedicine at a staggering rate for the last decade. Based on self-assembled hydrophilic and lipophilic structures, most of them are exclusively composed of fluorescent π-conjugated polymeric or monomeric units. Their common fabrication process relies on the manual injection of concentrated solutions of hydrophobic fluorophores into a large volume of water. Nevertheless, the conditions of nanoprecipitation appear to be very "operator" dependent. We have thus investigated how microfluidic mixing chambers, implying high-rate impinging flows, allow for a fine and reproducible control of the FON size and provide improved narrowness of size distributions (Figure 1a,b). Moreover, the high structural confinement of fluorophores within FONs (up to 10^5 per FON) yields very efficient electron and energy transfer when various partners are self-assembled together (Figure 1c). All these transfers, occurring with hardly a few % of one partner, have thus been harnessed to fabricate off-on probes, signaling FON entrance upon disassembling into malignant cells. Finally, in order to understand the specific cell uptake mechanism of FONs and the possible influence of FON rheological properties, comparative mechanical measurements at the nanoscale and biological studies have been performed using nanoparticles of varying elasticity while keeping the charge and size identical. Such investigations should provide novel benchmarks to rationalize the potentiality of FONs to serve as theranostic tools, offering all in one drug vectorization and on-command drug delivery.

The SFNano C'NANO joint meeting 2019

Thematic Session: Nanochemistry: synthesis & functionalization of nanosystems for bioapplications

Keywords: Gold nanoparticles, Polyoxometalates, bisphosphonates, antibiofilm

One-pot synthesis of a new generation of hybrid bisphosphonate polyoxometalate gold nanoparticles as antibiofilm agents

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The excessive use of antibiotics caused the emergence of resistant bacteria, which is at the origin of a major public health problem. It is therefore essential to reduce their consumption and to find an alternative to current treatments. Recently, the use of antimicrobial nanomaterials has attracted great attention[1], to facilitate cellular internalization of the active agents while limiting their quantity. Many emerging antibacterial agents are explored, among them, Polyoxometalates (POMs), a class of molecular oxides composed of metals in high oxidation states, typically W^{VI} and Mo^{VI}, have proven to be efficient to promote antibiotic activity.[2] When reduced, POMs can be used to synthesize metallic nanoparticles.[3] In this context, the use of POMs as active agents supported by gold nanoparticles (AuNPs) combined with antibiotics is a very promising alternative to synthesized nanomaterials with enhanced antibacterial properties.

We report the elaboration of gold nanoparticles using functionalized POMs as reducing and capping agent. In this study a reduced polyoxovanadate functionalized with bisphosphonate molecules was synthesized and used to prepare in one step hybrid organic–inorganic polyoxometalate decorated gold nanoparticles. These new composites were shown to strongly inhibit P. aeruginosa and S. epidermidis biofilm growth, with the three components constituting the nanoparticles (Au^0 core, vanadium and alendronate) acting synergistically.[4]

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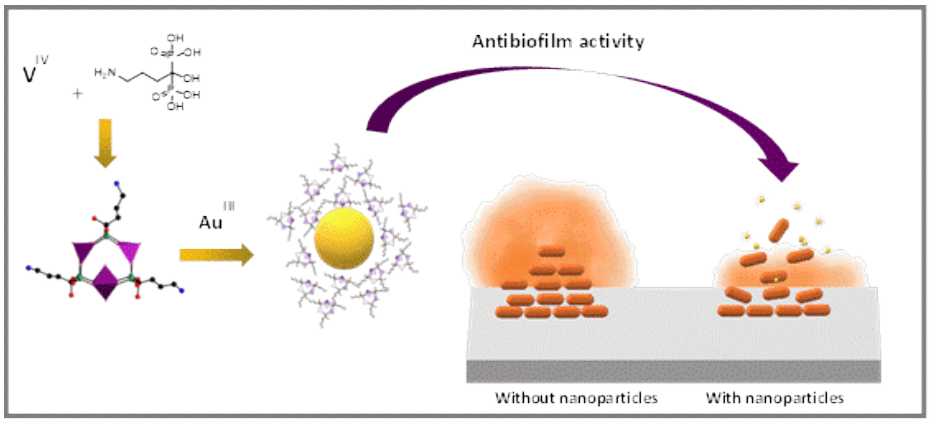

Fig 1 : A reduced polyoxovanadate functionalized by alendronate molecules was used for the synthesis of gold nanoparticles; these hybrid nanomaterials exhibit high antibiofilm activity.

imaging and magnetic hyperthermia and were investigated with cells in coll. with Dr M. Tasso (Univ La Plata, Argentina). [13]

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The SFNano C'Nano joint meeting 2019

Thematic Session: Nanochemistry: synthesis and functionalization of nanosystems for bioapplications, Bio-inspired nanosystems; Nano for imaging, diagnosis and theranostics etc.
Keywords: nanocomposites, magnetically or photo-induced hyperthermia, drug delivery

Magneto and photoresponsive nanoplatforms based on mesoporous silica for nanomedecine applications

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The design of magneto and photoresponsive hybrid nanoplatforms has become a great challenge in the field of nanomedecine[1,2]. Among the different starting materials needed for the realization of such multifunctional theranostic nanoplatforms, iron oxide nanoparticles (NPs) and carbon-based materials are suitable remotely wave-responsive materials respectively for magnetic hyperthermia[3] and phototherapy applications.[4] However, regarding their use in a physiological media, these both type of inorganic NPs need to be functionalized with a suitable surface state to ensure colloidal stability, biocompatibility and drug loading/release properties. To face these latter issues, mesoporous silica (MS) as shell coatings of these two nanoheaters are particularly choice materials. Indeed, MS are stable, easily chemically modified and has a high drug delivery capability thanks to its important pore volume. [5]

Since several years, at IPCMS, Strasbourg, we have developed a deep expertise in the synthesis of a range of various MS nanostructures having well-controlled pore size (from 2.5 to 15 nm) that were used for various design of stimuli responsive NPs. In a first work, such MS NPs were used as original sacrificial templates for the preparation of drug releasing protein capsules or NPs.[6–8] In another work, large pore stellate silica grafted with quantum dots and coated with polysaccharides were also used as hybrid fluorescent nanoplatforms and were assessed in zebra fish models.[9] Silica was also coated around magnetic NPs or carbon materials. Hence, MS shells were recently deposited at the surface of iron oxide NPs for simultaneous enzyme sensitive drug release and MRI applications.[10] They were also coated around carbon-based materials and the remote controlled and pulsatile drug release under application of NIR light laser was achieved in vitro in aqueous solutions[11,12] in coll. with Dr S.Harlepp (INSERM U1109). At least, recently, we coated large pores stellate mesoporous silica with around magnetic cores and achieved the grafting of small quantum dots and proteins coatings within these pores. Such magnetic luminescent nanocomposites were shown useful for bimodal fluorescence /MRI