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## ◆ How angular momentum is conserved in multisublattice ferrimagnets after a femtosecond laser excitation

Femtosecond laser pulses can be used to induce ultrafast reduction of the magnetization in magnetic materials. Such a process occurs via electronic excitation in the sub-picosecond time scale, before any lattice excitation. One of the so far unsolved questions is the understanding of the mechanism allowing for the conservation of the total angular momentum during the loss of the magnetic angular momenta.

Recently, we have reported new experimental results obtained in CoTb multisublattice ferrimagnets by means of time-resolved X-ray magnetic circular dichroism.

The experiment conducted at the femtoslicing beamline of the HZB BESSY II synchrotron has proved that the ultrafast demagnetization is driven by the transfer of angular momenta between two exchange-coupled sublattices while the total angular momentum is conserved. They conclude that the exchange coupling between both sub-lattices Co and Tb drives, at the atomic scale, an ultrafast transfer of angular momenta during ~150 fs.

This work is a collaboration between different European researchers of the Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS – CNRS), Institut Jean Lamour de Nancy (IJL- CNRS), ETH Zürich and the HZB- BESSY II - Berlin. This work has recently been published in Nature Communication. ■

N. Bergeard, V. Lopez-Flores, V. Halté, M. Hehn, C. Stamm, N. Pontius, E. Beaurepaire, and C. Boeglin, *Nature Communications*, 2014, **5**, 3466.

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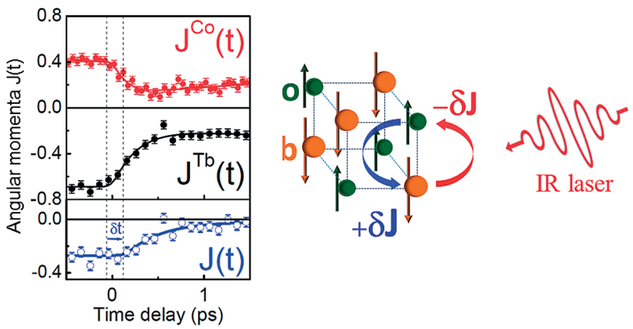






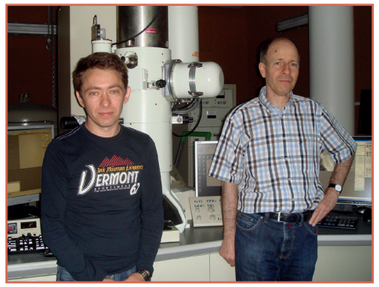



◀ *(Left) Femtosecond evolution of the total angular momenta measured by time resolved XMCD for Co and Tb in $Co_{0,74}Tb_{0,26}$. The continuous lines are simulations of $J^{Co}(t)$ (red line), $J^{Tb}(t)$ (black line) and J(t) (blue line). The loss of the total angular momentum J(t) is delayed by δt = 140 ± 60 fs compared to the time at which the demagnetization of both sublattices starts.*

*(Right) The illustration of the inter-atomic transfer of angular momenta during the first 150 femtoseconds.*

## Nominations

Within the french research and academic environments, the "Institut Universitaire de France" plays the role of a national agency highlighting and rewarding the achievements of outstanding researchers involved in university teaching. For the year 2014, IPCMS is proud to count on two of them, namely Ovidiu Ersen and Florian Banhart, recently appointed.



Ovidiu Ersen works in the area of structural and morphology of nanomaterials. He has developed three-dimensional imaging by electron tomography combined with energy electron loss spectroscopy allowing for a three-dimensional chemical analysis of nanoobjects. Ovidiu Ersen plans to develop enviromental adapted TEM microscopy together with ultra-fast Lorenz microscopy.

Florian Banhart's main interest is the study of one- and two-dimensional carbon and, more generally, inorganic nanosystems. Florian Banhart has established himself as a world renowned expert of in-situ electron microscopy, mastering also other techniques such as electron irradiation, heating or electrical biasing to investigate growth and structural properties. Very recently, he has become involved on the implementation of an «ultrafast» transmission electron microscope within the framework of the national excellence program EQUIPEX (UTEM project). This new facility will be focused on the study of processing characterized by very high spatial and temporal resolution.

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## Summary



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## Editorial

Observations on nanoscale objects (clusters, nanoparticles) can unravel unexpected properties and contribute to the understanding of macroscopic phenomena, such as multiferroic behavior, magnetism and, on the applicative side, diagnostic and/or therapeutic techniques. Among the five contributions selected for IPCMS news to highlight the wealth of breakthrough activities of the institute, three of them feature the keywords "clusters" and "nanoparticles". This exemplifies the leading role of IPCMS in the area of nanosciences through achievements that combine material synthesis, chemical characterization and measurement of physical properties.

The interplay between chemistry and life science is particularly effective in the contribution by C. Ghobril, et al. (team D. Felder, *Chem. Commun.*, 2013, **49**, 9158). Inorganic nanoparticles (superparamagnetic iron oxide) combined to a dendritic shell are found to be optimal tools for theranostics (diagnostic and therapeutic purposes), bound to be rapidly eliminated after injection. In a further contribution, nanospecies containing uranium centers are described as being of great interest in the context of geochemical reactions in nature. The long-standing competency of IPCMS in the area of magnetic characterization has allowed establishing a clear-cut correlation between structural and magnetic properties for a new poly-oxo-metalate containing as many as 38 uranium centers (*J. Amer. Chem. Soc.*, 2013, **135** (42), 15678–15681.). As a third example of new findings on nanoclusters, it has been demonstrated that a large strain due to nanoscale size reduction is very efficient for increasing substantially magnetoelectric coefficients. This is indeed the case for the epitaxial cluster $Cr_2O_3$ deposited in a MgO matrix (*Nature Comm.*, 2014, **5**, 3167).

This issue features also the response of the magnetization to the action of a femtosecond laser pulse. Such property has been addressed through time-resolved X-ray magnetic circular dichroism. In CoTb ferrimagnets the exchange coupling between sublattices is at the very origin of an ultra-fast transfer of angular momentum (*Nature Comm.*, 2014, **5**, 3466). As a further demonstration of the multidisciplinary character of IPCMS' research, we draw attention on a breakthrough in the understanding of the mechanisms rectifying pulsatile propagation in vascular networks. In collaboration with the partner institute IGBMC, this has been achieved by using fast imaging microscopy, optical tweezers *in vivo* and simulation models, allowing to quantify the blood-flow mechanism in the zebrafish (*Development*, 2013, **140**, 4426).

Stefan Haacke, *Director*



Institut de Physique et Chimie des Matériaux de Strasbourg

## • How a dendritic organic coating influences the bioelimination of iron oxide nanoparticles

Research on inorganic nanoparticles (NPs) is rapidly expanding with a large variety of applications as well as strategies for their synthesis. Most often their surface modification is critical, in particular to avoid their aggregation, make them dispersible in liquid media or functionalize them. Many research groups worldwide are actively developing superparamagnetic iron oxide (SPIO) NPs with the emergence of a vast number of applications in health sciences including combined *in vivo* magnetic resonance (MR) and optical imaging via multimodal NPs, hyperthermia or drug delivery. In parallel, biodendrimers (biocompatible and branched molecules) are being developed due to their precisely defined structure and composition and high tuneable surface chemistry. A clear input is brought by these branched molecules as they are discrete entities in which size, hydrophilicity, molecular weight and biocompatibility can easily be tuned as a function of their generation. Furthermore, a dendritic shell allows versatile polyfunctionalization at its periphery which could lead to multimodal imaging probes through dye grafting and theranostics through specific drug anchoring. Optimized biokinetics of a diagnostic and/or therapeutic probe show both low unspecific uptake and complete elimination of the untargeted probe within a few days. This is a prerequisite for human and clinical use. Therefore, designing versatile nanohybrids that display both high selective tumour uptake and low unspecific uptake is a major challenge. The functionalization of spherical SPIO NPs with PEGylated poly(amido)amine (PAMAM) dendrons through a bisphosphonate tweezers yielded 15 and 30 nm dendritic nano-objects stable in physiological media. PEG chains were introduced on PAMAM dendrons to ensure water molecule capture and retention for improved contrast enhancement. The NPs were additionally functionalized with a fluorescent dye and *in vitro* and *in vivo* MR and fluorescence imaging were simultaneously evaluated. The latter clearly highlighted that the dendritic organic coating impacts the nanoobjects aggregation state, thus influencing the bioelimination speed: NPs covered with small dendrons are rapidly and completely eliminated within 24 hours post intravenous injection, predominantly by urinary elimination. ■

C. Ghobril, G. Popa, A. Parat, C. Billotey, J. Taleb, P. Bonazza, S. Begin-Colin, D. Felder-Flesch,
*Chem. Commun.*, 2013, **49**, 9158–60.

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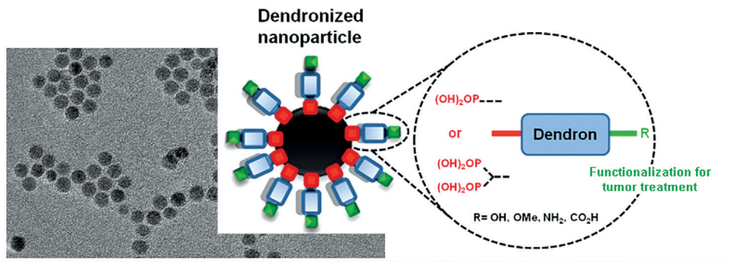
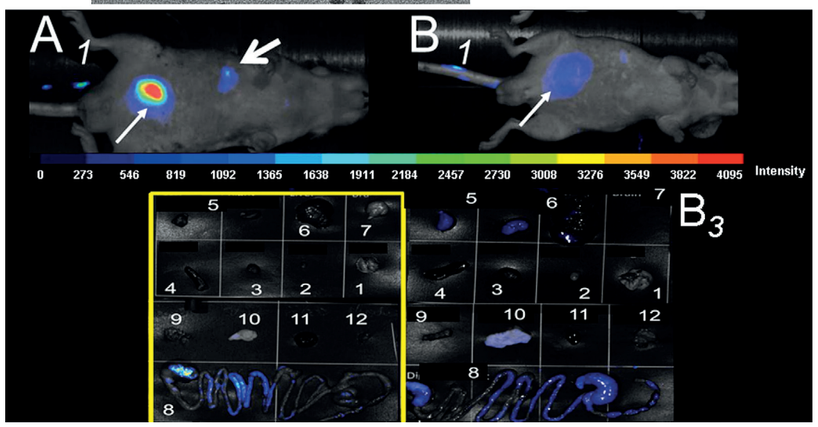



▶ *Top: TEM image of dendronized IO NPs (Inset: schematic view).*




▲ *Bottom:* In vivo *whole body (A1, B1) and* ex vivo *organs (B3) optical images of NP@dendron@Alexa647 performed at 7 minutes (A1), 20 minutes (B1) and 24 hours (B3) post intravenous injection. The yellow square includes* ex vivo *organ images of control mouse imaged with the same parameters [1 = lungs, 2 = urines, 3 = heart, 4 = spleen, 5 = kidney, 6 = liver, 7 = brain, 8 = digestive tract, 9 = bone sample, 10 = skin sample, 11 = blood sample, 12 = muscle sample]. Fine arrows indicate bladder signal, large arrow indicates liver signal.*

## • Structure-Magnetic property Relationships in Large {Uranium}$_{38}$ Poly-oxo Cluster

The chemistry of polynuclear oxo/hydroxo complexes of actinides with a wide range of oxidation states is extensively investigated. Regarding uranium, a large number of molecular uranyl-based moieties have been identified, among which fullerene-type nanospheres with a wide range of nuclearities (from $U_{24}$ to $U_{68}$). Beyond fundamental interest, these structural records give insight in the oligomerization of nanospecies formed during geochemical reactions in nature. As well, the knowledge of how uranium combines with carboxylate ligands is of significant interest for recycling spent nuclear fuel.

In collaboration with researchers of the university of Lille (UCCS, UMR CNRS 8181 USTL-ENSCL) a researcher of IPCMS contributed to better understanding of the magnetic behavior of large actinide oxo-clusters.

A new poly-oxo-metalate species containing 38 uranium centers has been solvothermally synthesized in the presence of benzoic acid in tetrahydrofuran (THF). This complex is, up to now, the largest low-valent uranium polyoxo cluster and was characterized by X-ray diffraction, photoelectron spectroscopy and magnetic analyses. The $\{U_{38}\}$ motif contains a distorted $UO_2$ core of fluorite type, with a cubic coordination geometry for the uranium centers. The $UO_2$ core is capped by additional uranium centers related to a truncated octahedral configuration of U nodes. The cluster is stabilized during the first steps of the poly-oxo condensation process by controlling the water content, preventing the formation of the 3D extended $UO_2$ fluorite-type network.

The magnetic behavior of $U_{38}O_{56}Cl_{18}(THF)_8(bz)_{24}{\cdot}8THF$ was investigated. The effective moment value at room temperature ($\mu_{eff}$ = 2.57 μB/U) is consistent with that expected for $U^{IV}$. The thermal variation of $\mu_{eff}$ is quite complex and difficult to rationalize as often reported for $U^{IV}$ compounds in the literature. The lowering of $\mu_{eff}$ with temperature can stem from antiferromagnetic coupling and/or coupling of the nonmagnetic ($m_J$ = 0) ground state of $U^{IV}$ in low-symmetry environments with low-lying excited states. The magnetization versus field curve indicates a small magnetic moment for the $\{U_{38}\}$ compound, still paramagnetic at 2 K. It confirms that the lowering of $\mu_{eff}$ is mainly due to thermal depopulation of excited states. Yet, the magnetic data suggest antiferromagnetic coupling between U ions owing to the presence of a fluorite-type $UO_2$ core. The behavior is thus the results of several contributions arising from $U^{IV}$ in different environments. ■

C. Falaise, Ch. Volkringer, J.-F. Vigier, A. Beaurain, P. Roussel, P. Rabu, T. Loiseau
*J. Amer. Chem. Soc.* 2013, **135** (42), 15678–15681.
http://pubs.acs.org/doi/abs/10.1021/ja4067207.

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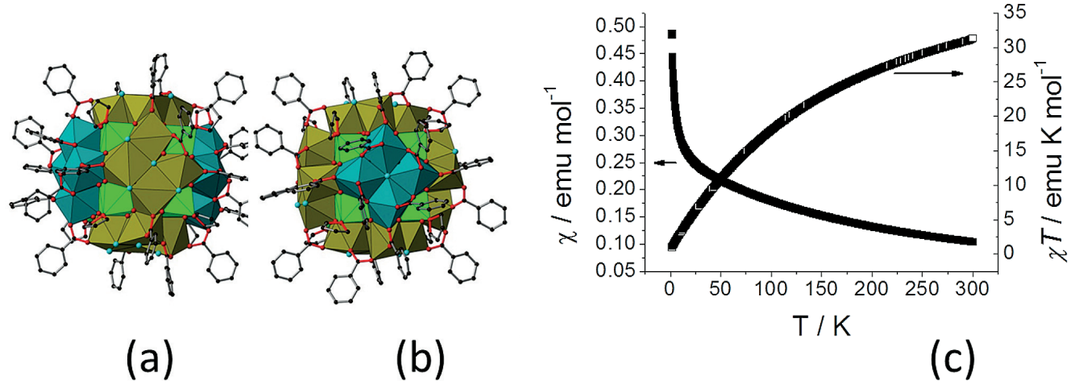


▲ *Two perpendicular views of the $\{U_{38}\}$ nano cluster in $U_{38}O_{56}Cl_{18}(THF)_8(bz)_{24}{\cdot}8THF$.*
*(a) Capped face of the $UO_2$ like ($U_{14}$) core showing the 3-chloro group bridging three uranium centers (brown polyhedra) together with a bidentate benzoate ligand.*
*(b) Capped face of the ($U_{14}$) core showing the 4-chloro group bridging four uranium centers (teal polyhedra).*
*(c) Temperature variation of the magnetic susceptibility.*

# ◆ *Size-induced enhancement of the magnetoelectric effect in chromium oxide nanoclusters*

Magnetoelectric materials combine the presence of magnetisation and electric polarisation, with a possible mutual interaction between both quantities. Such a property gives the opportunity of controlling the magnetic dipole of a device by applying an electric field: an applied bias voltage can modify the electric polarisation and subsequently the magnetisation that is linked to it. This explains the renewed interest for magnetoelectric materials within the field of magnetic memories and spintronics, as those materials would make possible the design and the integration of novel electronic devices. Nevertheless, the scarcity of the magnetoelectric materials and the smallness of the magnetoelectric effects have prevented so far the application of these materials. Different ways to enhance the magneto-electric coefficient are therefore investigated: for instance, theoretical predictions of a magnetoelectric effect enhancement under strain have recently been put for.

We have demonstrated at the IPCMS a proof-of-principle experiment showing that a large strain due to nanoscale size reduction is very efficient for increasing magnetoelectric coefficients by orders of magnitude. We studied the archetype magnetoelectric material, $Cr_2O_3$, that is deposited in the form of epitaxial clusters in a MgO matrix which induces a large epitaxial strain in the clusters. The MgO layer is thin enough to behave as a tunnel barrier: electrons can be injected from a magnetic electrode into the $Cr_2O_3$ clusters by tunnel effect. This enables us to measure the tunnel magneto-resistance effect and thus probe the magnetisation of those nanometric clusters under applied voltage. This original technique showed that the highly strained clusters exhibit an unprecedented 600% change in the magnetization magnitude under 1 V applied through the MgO tunnel barrier. Furthermore, a multiferroic phase, with both permanent magnetic and electric polarizations, is found in the clusters, while absent in the bulk. ■

D. Halley, N. Najjari, H. Majjad, L. Joly, P. Ohresser, F. Scheurer, C. Ulhaq-Bouillet, S. Berciaud, B. Doudin and Y. Henry, *Nature Communications*,2014, **5**, 3167.

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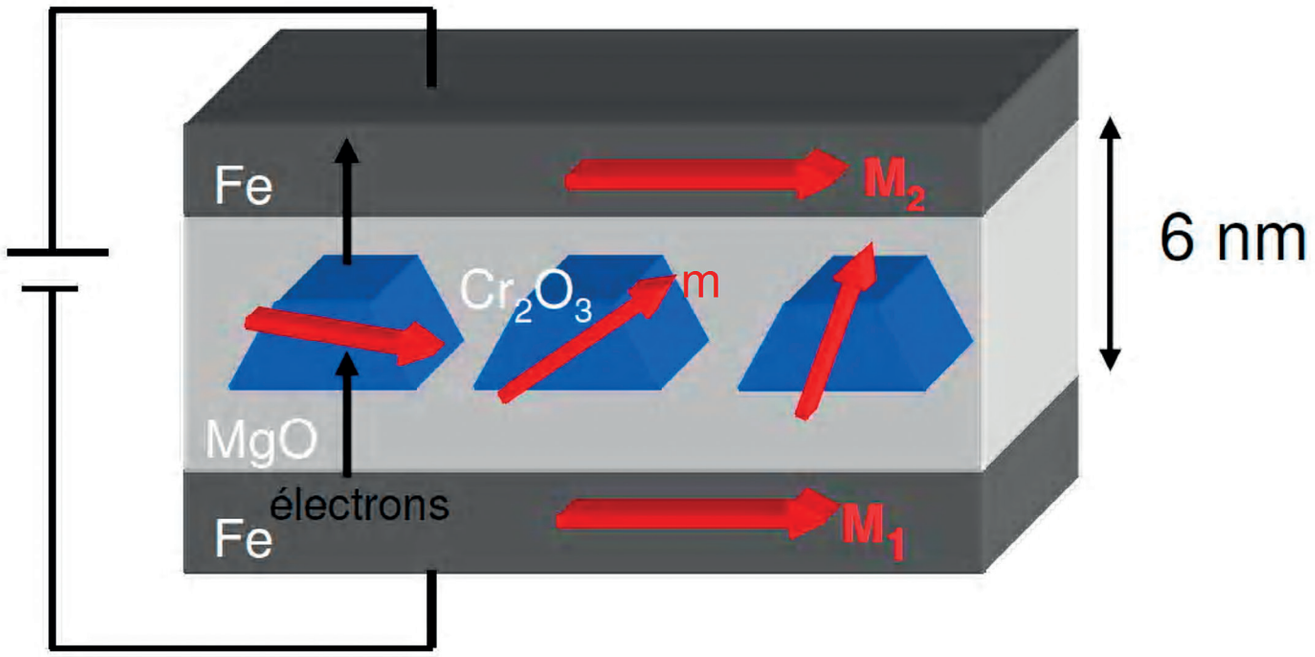


▲ *Epitaxial magnetic tunnel junction with nanometric $Cr_2O_3$ clusters inserted in the insulating MgO tunnel barrier. Electrons can tunnel from the Fe electrodes through the strained magnetic clusters. The tunnel magnetoresistance effect is used as a probe of the $Cr_2O_3$ clusters magnetic moment.*

## Visco-Elastic tubing propagates pulsatile embryonic blood flow

Pulsatile flow is a universal feature of vertebrates' blood circulatory system, which can lead to diseases when abnormal. In the embryo, blood flow forces stimulate vessel remodeling and stem cell proliferation. At these early stages, when vessels lack muscle cells, the heart is valveless and the Reynolds number (Re) is low, few details are available regarding the mechanisms controlling pulses propagation in the developing vascular network.

Researchers at IGBMC and IPCMS developed original techniques to tackle this problem. Taking advantage of the relative optical transparency of the Zebrafish embryo, they followed blood cells close to intersegmental vessels (ISV) using fast imaging microscopy. These observations led to unexpected results. The cells were able not only to move against the arterial flow toward the ISV, but also to continue moving even if no arterial flow was present, which is in contradiction with low Reynolds numbers where the flow directly follows the heartbeat.

In order to understand this phenomenon, they quantified the blood-flow mechanics in the zebrafish main artery using optical tweezers combined to fast imaging. The measurements of the velocity profiles in the different vascular parts show strong changes between the dorsal aorta (DA) where the flow is pulsatile and the posterior cardinal vein (PCV) where it is relatively steady. The ISV has an average behavior between pulsatile and steady, indicating that the flow is rectified between the DA and the PCV. They further mapped the flow forces in the artery and measured the DA wall displacements at the same positions. By comparing axial and perpendicular force traces close to ISV they observed a phase shift, which is perfectly correlating with the arterial wall displacement, indicating that deformation is essential in the flow propagation.

They further used a mathematical model on the zebrafish to test the influence of a distensible vascular network. With the introduction of measured in vivo parameters, they obtained a rectified pulsatile flow in the ISV as observed in the embryo. To confirm this result, they performed simulation without elasticity and found out that ISV flow follows the DA one. Thus, features of ISV flow strongly depend on the DA elasticity. During the heartbeat contraction phase, the DA is 'inflated', and more slowly 'deflates' via the ISV flow: acting literally as a capacitor.
Overall these results demonstrate that the embryonic vascular network biomechanics is in many ways comparable to the adult vasculature and constitutes a good system to study cardiovascular biomechanics and related diseases. ■

H. Anton, S. Harlepp, D. Wu, F. Monduc, S. Bhat, M. Liebling, C. Paoletti, G. Charvin, J.B. Freund, J. Vermot, *Development*, 2013, **140**, 4426-34.

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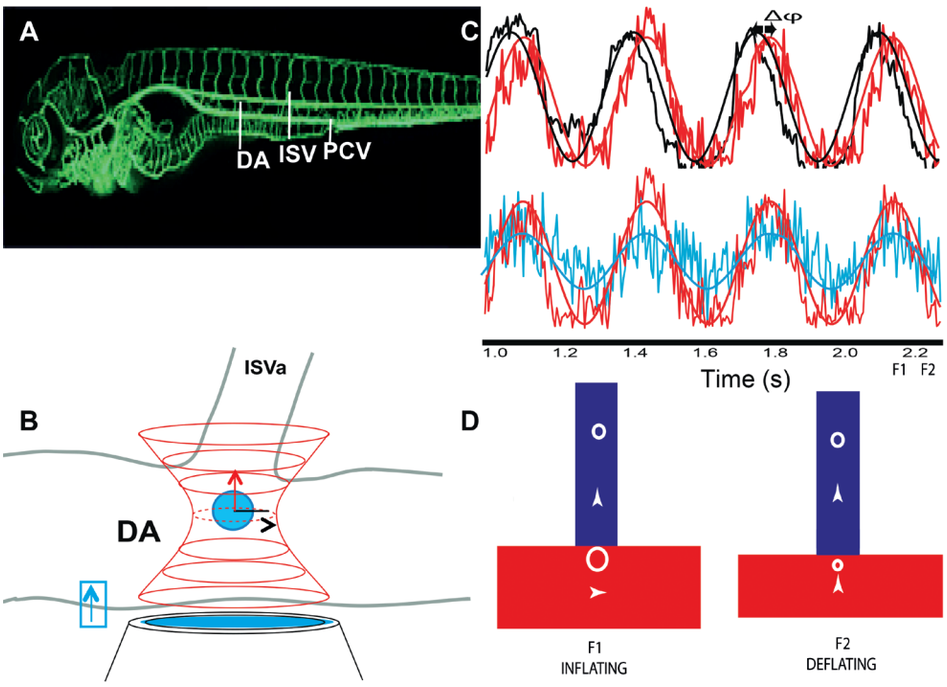


◀ *A. Fluorescent view of the Zebrafish vascular system. The 3 main domains are the dorsal aortia (DA), the intersegments either arterial or venous (ISVa or ISVv) and the posterior cardinal vein. B. Optical tweezing experiments in vivo. Trapping a red blood cell in the DA and measuring horizontal and vertical forces over time as well as the endothelium displacement. C. Time traces of a trapped red blood cell close an intersegment. The vertical displacement (red curve) shows a time delay compared to the horizontal one (black curve) but is completely in phase with the endothelium (blue curve). D. Push-Pull model due to visco-elastic properties of the tubing, derived from experiments and Winkessel modelling.*