

Foreword

C²TN - Radiation for Science and Society

We are very pleased to walk you through C²TN's scientific, technical, education, training and services endeavors and achievements of 2017!

C²TN, acronym for “Centro de Ciências e Tecnologias Nucleares” is an interdisciplinary Research Unit of Instituto Superior Técnico (IST), Universidade de Lisboa, established in 2013, located in Campus Tecnológico e Nuclear, one of the IST science and technology poles. It groups several tens of researchers (physicists, chemists, biologists, geologists, among others) recognized internationally as the Portuguese experts in matters related to Nuclear Sciences and Technologies and applications of Ionizing Radiation. This stems from the unique combination of C²TN's knowledge, skills and competence with its experimental facilities.

Indeed, C²TN has specialized scientific equipment, laboratories and infrastructures, some unique in Portugal, used as nodes in research networks: Laboratories for Synthesis & Characterization of Materials (licensed to handle radioisotopes), including at Low Temperature and High Magnetic Fields; facilities for Synthesis, Characterization & Preclinical Evaluation of Radioactive Tools for Nuclear Molecular Imaging and Therapy; Clean Rooms; Luminescence, Radiocarbon and Tritium Dating; Spectroscopy facilities – Mössbauer, Inductively Coupled Plasma Mass Spectrometer; alpha and gamma spectrometry laboratories; liquid scintillation counters; irradiation facilities for metrological verification of radiation detection equipment; linear electron accelerator; and access to Tandem and Van de Graaff accelerators and a Gamma Irradiation Unit, located in the Campus.

During 2017, C²TN reinforced its role in the Portuguese Scientific and Technology System and in the international arena. The main axes of activities undertaken aimed at strengthening C²TN's excellence in RD&I and to reinforce:

- ✧ Internationalization, pursuing the collaboration with reference institutions worldwide, in European platforms, international organizations and networks, nurturing new links and consolidating existing ones;
- ✧ Engagement of young researchers, students and stakeholders in Portugal and abroad, fostering new collaborations between C²TN and RD&I and academic institutions, hospitals, municipalities, environmental, industrial, energy and services companies;
- ✧ Outreach, dissemination and communication of Science and its activities.

The motto “*Radiation for Science and Society*” was adopted, in order to make explicit the outstanding contributions of C²TN to several societal challenges, namely:

- Better management of cancer and neurodegenerative diseases with more effective and personalized diagnosis and treatments;
- Assessment of detrimental effects due to the exposure to ionizing radiation of patients and medical staff, aiming at the Quality and Safety of health care;
- Radiological and nuclear emergency response and preparedness;
- Prevention of infectious diseases and outbreaks;
- Improving the air quality and reducing the carbon footprint;
- Environmental protection, management of natural resources and global changes;
- Sustainable agro-industry and food safety;
- Cultural Heritage leverage and safeguard;
- Advanced materials for applications in physics and engineering, electronic sensors and devices, energy conversion, cybersecurity and medical applications.

2017 was a very demanding year for C²TN with sizable uncertainties that affect the sustainability of its financial and human resources and the need to mitigate the precarious contractual link of a part of its researchers.

The scientific strength of C²TN is illustrated by the number of projects (42) led by its researchers submitted in May to the national Foundation for Science and Technology (FCT) Call, with additional participation in 27 projects led by other institutions. The rich variety and pluridisciplinarity of its activities were exhibited during the 1st C²TN Annual Meeting held in December of 2017 that was considered a success.

The highlights of C²TN’s activities during 2017, detailed in the sequence, follow closely its structure, namely the organization in 6 interdisciplinary Groups:

ES – Solid State: New Materials with Unconventional Electrical and Magnetic properties and characterization using Low Temperature and High Magnetic Field Techniques

NET – Nuclear Engineering and Techniques: Nuclear Physics, Geo-environments and Cultural Heritage using neutrons, radioactive nuclei and ion beams

RPS – Radiation Protection and Safety: Dosimetry, Radiobiology, Environmental Radioactivity, Radioecology, Radioactive Waste and Metrology

RS – Radiopharmaceutical Sciences: Nuclear Tools for Molecular Imaging and Theranostics

REI – Environmental Processes: Archaeological Material Culture and Macromolecular Materials using Nuclear Analytical Techniques and Ionizing Radiation

QEf – f-Element Chemistry: Synthesis, Characterization, Reactivity, Catalysis and Energetics

The RD&I activities synergistically interwoven into 3 Thematic Strands: I) Advanced Materials II) Radiopharmaceutical Sciences and Health Physics III) Earth Systems, Radioactivity & Cultural Heritage

The most important asset of C²TN is its members. The Executive Commission would like to acknowledge and thank all C²TN members for their efforts, contributions and accomplishments that made possible the journey throughout 2017!

C²TN Executive Commission

Pedro Vaz
(President)

Fernanda Margaça
(Vice-President)

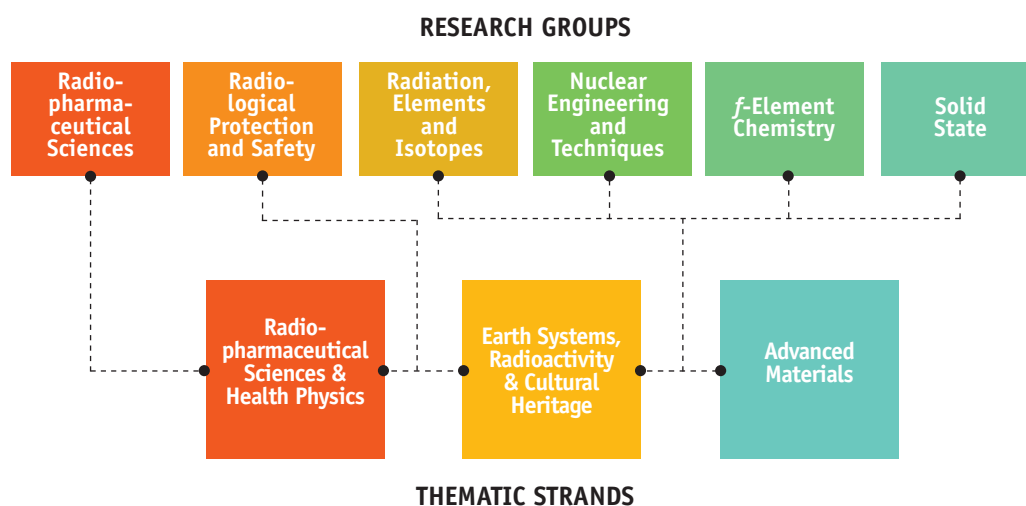
Dulce Belo
(Vogal)

C²TN Organization and Coordination

Considering the complementary know-how, common interests and facilities, the C²TN members are organized in six Research Groups: Radiopharmaceutical Sciences (RS), Radiological Protection and Safety (RPS), Radiation, Elements and Isotopes (REI), Nuclear Engineering and Techniques (NET), *f*-Element Chemistry (QE_f) and Solid State (ES). For the period 2015-2020, the 6 groups of scientists will converge and collaborate on 3 main Thematic Strands (TS):



The scheme below shows the C²TN research groups and their contribution to the three Thematic Strands. Within these TS the role of the groups is well established and the overall research objectives are in line and nicely intersect with the EU HORIZON 2020 initiative.



The Research Group Coordinators are:

RS – António Rocha Paulo; RPS – Pedro Vaz; REI – Maria de Fátima Araújo;
NET – Maria Isabel Dias; QE_f – João Paulo Leal; ES – Manuel Leite de Almeida

The Thematic Strands Coordinators are:

RSHP – António Rocha Paulo; ESRCH – Maria Isabel Prudêncio;
AM – Manuel Leite de Almeida

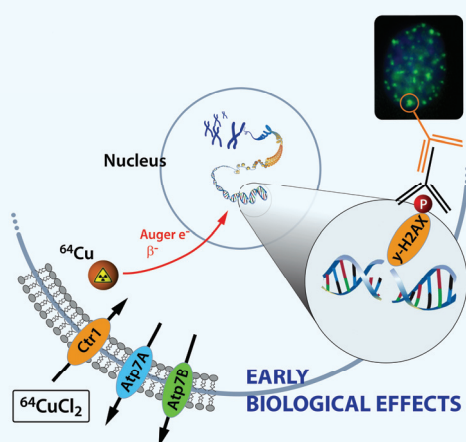
Thematic Strands

Scientific Report 2017

Radiopharmaceutical Sciences and Health Physics (RSHP)

Researchers of this TS used their unique know-how, expertise, competence, techniques and infrastructures to carry out cutting edge studies on Radiopharmaceutical Sciences, Radiation Protection and Dosimetry, Biological Effects of Ionizing Radiation and Metrology, aiming to contribute to the following major topics:

- Design, Synthesis and Pre-Clinical Evaluation of Radioactive Tools for Molecular Imaging and Theranostics;



Schematic representation of the cellular response to $^{64}\text{CuCl}_2$ in prostate cancer cells.

$^{64}\text{CuCl}_2$ AS A TOOL FOR PROSTATE CANCER THERANOSTICS

Copper plays a critical role for cancer development and progression, and multiple copper isotopes are explored for cancer imaging and therapy. Studies using the simpler ionic form of a medically relevant copper radioisotope, ^{64}Cu , have been conducted with promising results for prostate cancer theranostics. High levels of $^{64}\text{CuCl}_2$ uptake were observed in prostate

cancer cells, which might correlate with the different expression of native copper cellular transporters exhibited by those cell lines. The biological effects of exposure to ^{64}Cu were also assessed using the γ -H2AX assay, evidencing higher early DNA damage in tumoral cells.

MULTIMODAL GOLD NANOPARTICLES FOR PROSTATE CANCER RADIOSENSITIZATION

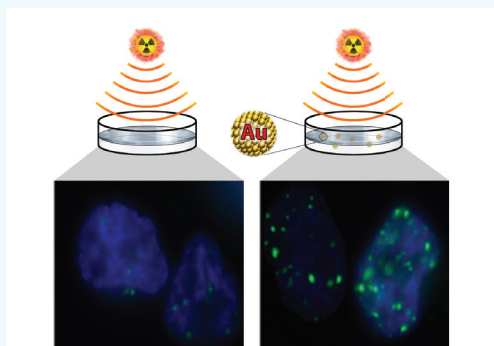
C²TN researchers introduced multifunctional gold nanoparticles (AuNPs) decorated with bombesin (BBN) peptide analogues to target the gastrin releasing peptide receptor, which is overexpressed in a variety of human tumors including prostate cancer. These AuNPs can be armed with imaging capabilities and show an augmented uptake in human PC3 prostate cancer cells. These favorable features pinpointed their potential relevance as multimodal radiosensitizing agents within a theranostic approach of prostate cancer. *In vitro* cellular studies demonstrated that the AuNPs carrying the BBN peptide possess enhanced radiosensitization properties when compared

- ❄ Evaluation of Biological Effects of Ionizing Radiation and Mechanisms of Action;
- ❄ Medical Dosimetry and Metrology of Ionizing Radiation.

During 2017, the scientific output of the RSHP team included: the publication of 44 papers in peer-reviewed journals, 1 proceedings, 8 invited and 14 contributed lectures in conferences, and the completion of 1 PhD and 5 MSc theses. The team's research has been supported by European, FCT and bilateral projects. The team has participated in the organization of 5 conferences and workshops and 3 national training courses. A significant participation in the scientific and technical activities of European Union Technology Platforms and Networks, namely MELODI, EURADOS NERIS, EURAMET and COST ACTIONS CM1105, TD1004 has also taken place. During 2017 the team has also prepared and submitted several common projects under calls from EC, FCT, CERN-FCT, and Horizon 2020.

From all the R&D activities performed during 2017, some relevant examples are highlighted below.

with the same nanoplateforms without the peptide. Altogether, these data corroborate the promising potential of BBN-containing AuNPs as multimodal tools for targeted cancer theranostics.

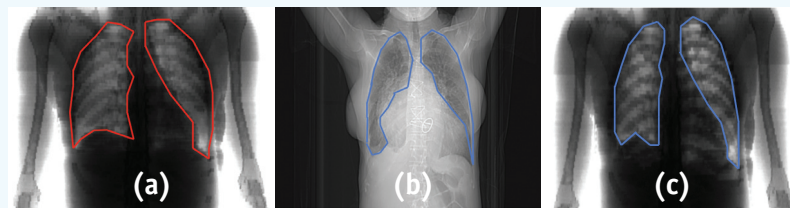


Radiosensitization effects of multifunctional gold nanoparticles (AuNPs) in PC3 prostate cancer cells.

COMPUTATIONAL VOXEL PHANTOMS FOR PERSONALIZED PATIENT DOSIMETRY

Computational voxel phantoms are models of the human anatomy used in the field of radiation protection and dosimetry, medical imaging and radiotherapy that enable the evaluation of organ doses with

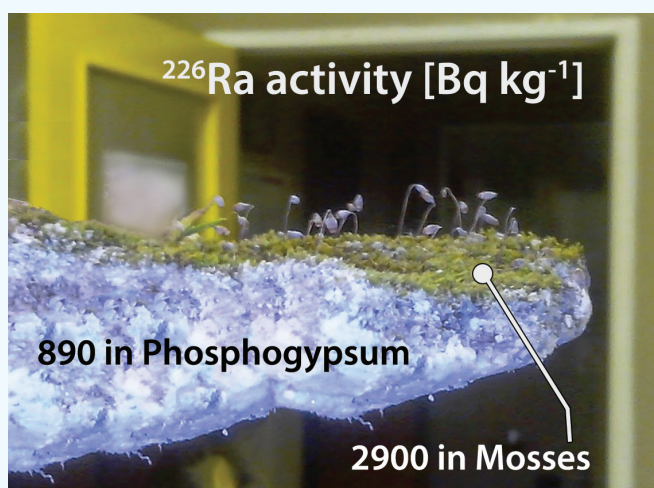
a high degree of precision. In this field, a FORTRAN-based program was developed to semi-automatically modify the volumetric information of organs of interest in a standard voxel phantom (ICRP standard). Monte Carlo simulations were used to mimic CT scan conditions and assess organ dose in ICRP standard phantoms and in modified phantoms matched to patients' size and overall anatomy. The modified phantoms allowed an increased accuracy in organ dose estimation, which can exhibit up to 20% underestimation and 40% overestimation using the standard phantoms. In summary, the voxel phantoms developed using single patient data provide more precise organ dose assessments, towards a personalized patient dosimetry.



(a) ICRP standard phantom; (b) patient CT image; (c) modified phantom according to patient lung volume.

Earth Systems, Radioactivity and Cultural Heritage (ESRCH)

During 2017, the scientific output of the ESRCH team included the publication of 55 papers in peer-reviewed journals, 12 book chapters, 21 conference proceedings, 9 invited and 33 contributed lectures in conferences and the completion of 2 PhD and 4 MSc theses. The team research has been supported by EC (LIFE, ERA-MIN, Interreg Sudoe and Interreg Mediterranean), FCT, IAEA, and bilateral projects. The team has participated in the



Close up of a fragment of PG detached from the surface of the stockpile, covered with mosses (*Bryum* sp.). Exhibited values of activity concentrations are referred to dry weight.

NORM - THE WILD VEGETATION ON THE PHOSPHOGYPSUM STOCKPILE

The availability of natural radionuclides in a phosphogypsum (PG) stockpile (Barreiro) was evaluated by analyzing the transfer to herbaceous plants and mosses growing on the PG. Activity concentrations of ^{226}Ra and ^{210}Pb in mosses exceeded 3 to 4 times those measured in the underlying PG. In herbaceous plants, concentrations were lower than those measured in the PG from the rhizosphere, with higher levels in roots relative to aerial parts. Only 1.6% of ^{226}Ra in the PG matrix is bioavailable, meaning that it is bounded strongly in a crystalline matrix and just a small amount is in an ion-exchangeable form.

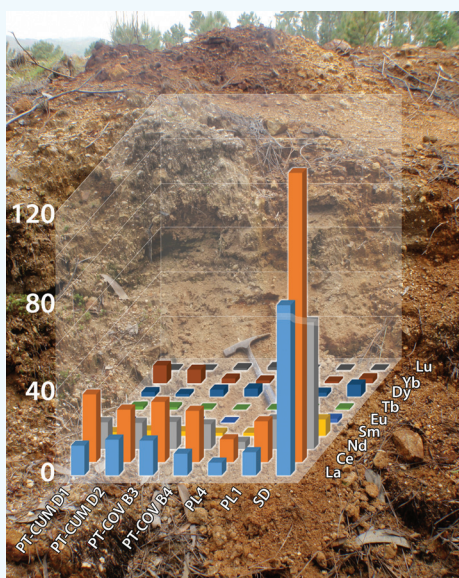
FOSTERING A LOW CARBON-ECONOMY IN SCHOOLS

Following the EU Roadmap – by 2050, the EU should cut greenhouse gas emissions to 80% below 1990 levels. The ongoing project Interreg Sudoe ClimACT coordinated by C²TN, promotes the transition to a Low Carbon-Economy in schools. During 2017 environmental and energy performance was assessed in 39 European schools, from primary to university level. Complementary approaches such as energy efficiency, sustainable transportation, green procurement, resources conservation and behavioural change were designed to support school managers, energy and environment players and students in the identification of smart solutions for schools for the greenhouse gas emission reduction.



ClimACT activities: awareness campaigns (left) and environmental and energy audits in schools (right).

organization of 10 conferences and workshops and 5 national training courses. A significant participation in the scientific and technical activities of European Union Technology Platforms and Networks, namely ALLIANCE, IGD-TP and NERIS, and in the COST ACTIONS CA16109 and ES1407 has also taken place. During 2017, the team has also prepared and submitted several common projects under calls from EC, FCT, and Horizon 2020. Two contracts were established with private companies.



Rare earth elements abundances in mine tailings from Portugal (PT), Poland (PL) and Sweden (SD).

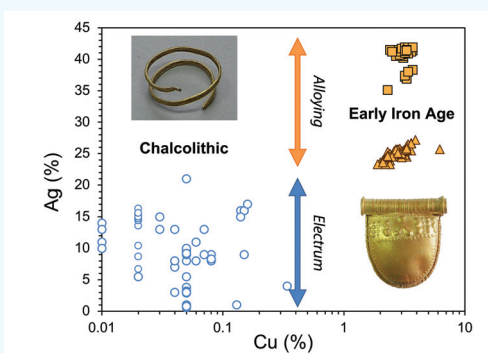
RECOVERING RARE EARTH ELEMENTS FROM OLD MINE TAILINGS

The ENVIREE project funded by ERA-MIN program (EU, FP7) is focused on a holistic perspective (from environmental systems, life-cycle assessment (LCA), leaching techniques, separation technology to remediation) to recover REE with minimal environmental impact, yet in an economically sustainable process. After the identification of the tailings with favorable conditions to contain metals (Covas and Cumieira, Northern Portugal) a more detailed chemical and mineralogical characterization of these heterogeneous materials was done during 2017.

Training and dissemination headed by C²TN has been a main achievement of this project through the organization of Workshops and Summer Courses on Rare Earth Elements, recovery and environmental issues.

CHALCOLITHIC AND EARLY IRON AGE JEWELLERY – 2000 YEARS OF GOLD TECHNOLOGY

In the Portuguese territory, the complex typologies of gold jewellery from the Early Iron Age (c. 850-400 BC) differ significantly from the simple types of the Chalcolithic (c. 3000-2000 BC). This typological evolution was found to be related with two technological developments: the use of less expensive and more workable resources by alloying Au with Ag (up to 42%) and/or Cu (up to 6%), and the use of autogenous welding and copper-rich solder alloys that allowed the manufacture of intricate shapes by joining different components and filigree decorations.



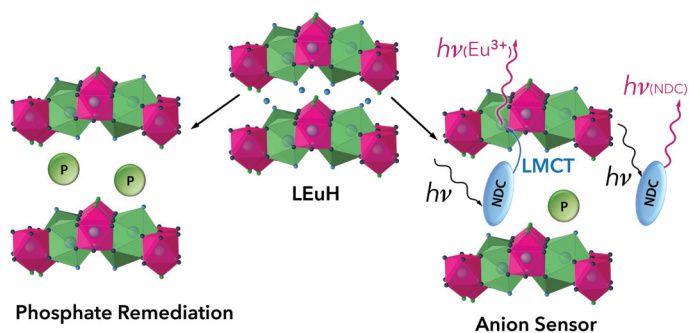
The composition of Chalcolithic and Early Iron Age gold jewellery of southern Portugal.

Advanced Materials (AM)

The research activities under this thematic strand have been focused in different advanced materials, with emphasis on multifunctional and unconventional electrical and magnetic materials, with potential applications in the fields of electronic and optoelectronics, health, catalysis and energy. These activities were possible thanks to a valuable combination of a wide range of complementary techniques existing at C²TN for both preparation and characterization of materials, enabling to address current challenges in materials science research and contributing to the establishment of more detailed correlations between the structure and the physical properties.

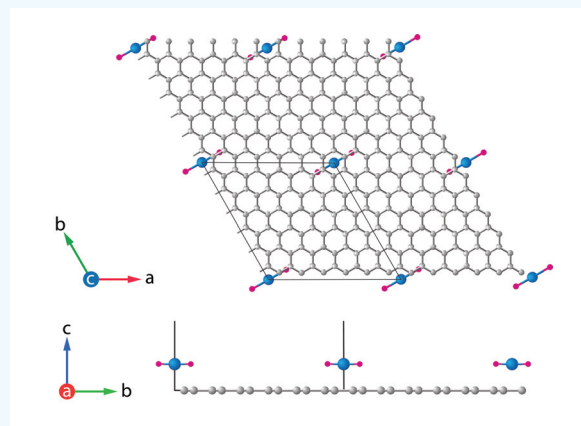
A significant part of the activities in this area has been possible by the operation and development of infrastructures and research tools, rare or even unique at national level, which have been placed open at the benefit of a large external community through an extensive network of scientific collaborations. These facilities include materials modification by ion implantation, neutrons, gamma and electron irradiation, neutron tomography, several ion beam techniques for elemental composition analysis and the low temperatures

A LAYERED EUROPIUM HYDROXIDE SYSTEM FOR PHOSPHOROUS SENSING



A dual-channel sensor (LEuH-2,6-NDC) towards anions, highlighting the significant potential of LLHs as new scavenging agents for inorganic phosphate.

AD-ATOMS AND AD-MOLECULES ON GRAPHENE



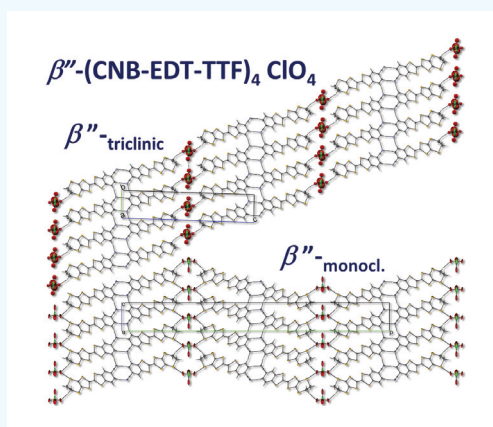
The configurations of freestanding Hg and HgO₂ molecules with respect to the graphene surface were analyzed with Density Functional Theory (DFT) probed by Perturbed Angular Correlation with ^{199m}Hg.

and high magnetic field facilities for the study of electrical transport, magnetic properties of materials and Mössbauer spectroscopy.

During 2017, the scientific output of the team involved in Advanced Materials studies included the publication of 49 papers in peer-reviewed journals, 1 book chapter, 4 invited and 28 contributed lectures in conferences and the completion of 3 PhD, 2 MSc and 2 graduation theses. The team research has been supported by European projects (namely a Marie Curie ITN) and by FCT. The team has participated in the organization of 2 conferences and workshops. A significant participation in the scientific and technical activities of European Union Technology Platforms and Networks, and in COST ACTIONS CA15128 CM1105, TD1004 has also taken place. During 2017 the team has also prepared and submitted several common projects under calls from EC, FCT, CERN-FCT, and Horizon 2020.

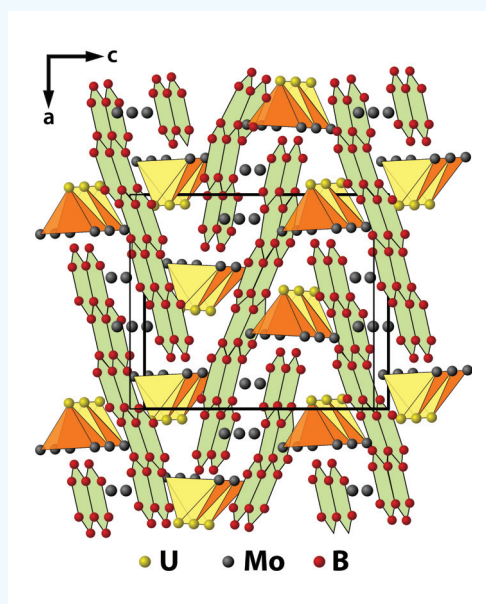
The activities had contributions from different research groups (ES, ETN, QEf, and REI) as more detailed described in their reports. The following major achievements in 2017 are highlighted.

BILAYER POLYMORPHISM IN $(\text{CNB-EDT-TTF})_4\text{ClO}_4$



Two polymorphs (monoclinic and triclinic), β'' -(CNB-EDT-TTF) $_4\text{ClO}_4$ illustrate a new aspect of polymorphism in bilayer metal.

MAGNETISM AND STRONGLY CORRELATED ELECTRON BEHAVIOR IN INTERMETALLICS



A novel ternary compound, UMo_3B_7 , showing spin fluctuations and enlarged Sommerfeld coefficient.

Radiopharmaceutical Sciences (RS)

MISSION AND OBJECTIVES

The RS Group develops research activities on the design and preclinical evaluation of innovative target-specific radiopharmaceuticals for Positron Emission Tomography (PET) or Single Photon Emission Computed Tomography (SPECT) Imaging and Targeted Radionuclide Therapy (TRT). This research field has important translational potential in the diagnosis and/or treatment of oncological, cardiovascular or neurodegenerative diseases, and contributes for the rise of molecular and personalized medicine. The group is a key partner of renowned national/international institutions involved in radionuclide production, nuclear medicine and biomedical research due to its rare combination of radiopharmaceutical chemistry expertise with preclinical evaluation skills. There is also an active collaboration with research groups engaged in the discovery and development of novel drugs, as well as technology transfer activities within research contracts with national/international biotech companies, namely in the field of antibody-based biopharmaceuticals.

MAIN ACHIEVEMENTS

1 ACRIDINE ORANGE DERIVATIVES FOR DNA-TARGETING

The RS Group has introduced a new family of ^{125}I - and $^{99\text{m}}\text{Tc}$ -containing acridine orange (AO) DNA intercalators and evaluated their relevance as Auger-emitting radiopharmaceuticals for cancer theranostics. Some of these DNA-targeted radioconjugates were shown to undergo a high internalization in tumoral cells, localizing in the nucleus and inducing DNA damage in an activity-dependent manner. Furthermore, in collaboration with Carla Cruz's group (CICS-UBI, Covilhã), we have proved that some of these AO derivatives are potent binders of G-quadruplex (G4) structures formed within the KRAS promoter, which might open new avenues in the design of Auger-emitting radiopharmaceuticals.

2 INDIUM(III) COMPLEXES FOR DUAL TARGETING OF BREAST CANCER

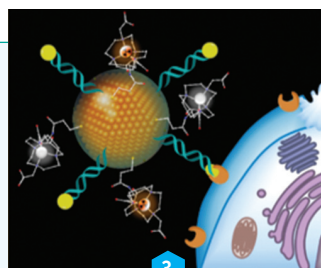
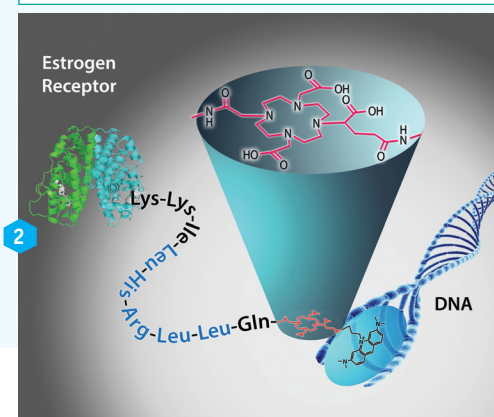
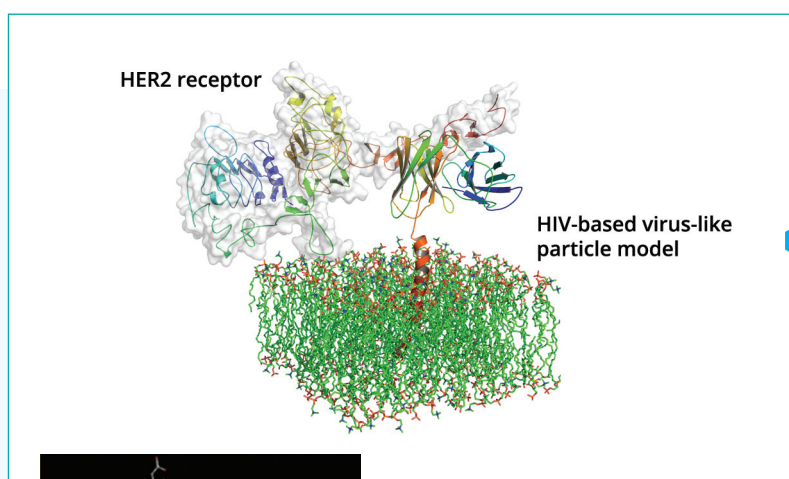
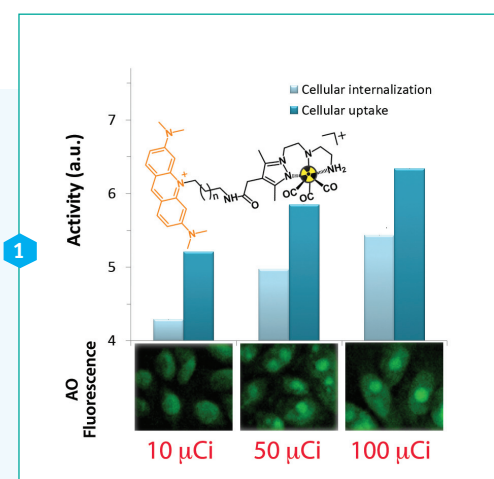
Despite the enhancement in the survival rate of breast cancer (BC) patients, there is still a need for more effective and personalized treatments to improve BC management. We have prepared a ^{111}In -hybrid compound containing two different biological targeting moieties, an estrogen receptor (ER) ligand (LXXLL peptide) and an antitumoral agent (the DNA intercalating agent, acridine orange - AO) aiming at the enhancement of breast cancer therapeutic efficacy. Biological evaluation of this ^{111}In -ERAO compound in tumor-bearing mice suggests it has potential for breast cancer theranostics.

3 MULTIFUNCTIONAL GOLD NANOPARTICLES FOR TARGETED CANCER THERANOSTICS

AuNPs stabilized with a thiolated DOTA derivative and decorated with a bombesin (BBN) analogue, for specific targeting of the gastrin releasing peptide receptor overexpressed in a variety of cancers, were simultaneously coordinated with Gd and ^{67}Ga to study their multimodal imaging capabilities. The Gd containing AuNPs displayed favorable relaxivity properties that make them potential candidates for T1- and T2- MR imaging application. Biodistribution studies in prostate cancer PC-3 xenografts, performed by gamma-counting measurements of ^{67}Ga , showed that the multimodal AuNPs have a reasonable tumor uptake, indicating its promising potential for cancer theranostics.

4 DESIGN OF HER2-SPECIFIC VIRUS-LIKE PARTICLES FOR IMAGE-GUIDED DRUG DELIVERY

Modelling, docking and fitting of an HER2-specific single chain variable fragment with the transmembrane viral protein (Gp41) was the key to define the best pairwise residues, allowing the modelling of a fusion protein to be expressed onto the viral capsid. Considering this information, DNA recombinant technologies were used to prepare the retargeted VLP containing the fusion protein with Gp41. The tropism of the constructed HIV-based VLPs was manipulated and the particles were engineered for the specific delivery of drugs and/or radionuclides for theranostics of HER2 positive breast cancer.



- 1 Internalization of a ^{99m}Tc -AO derivative in prostate cancer cells showing its preferential accumulation in the nucleus.
- 2 Dual targeting compound for theranostics of ER-positive tumors.
- 3 Gold nanoparticles carrying a radionuclide and gadolinium for cancer-specific multimodal imaging.
- 4 Schematic representation of the interaction of a recombinant HIV-based virus-like particle with HER2 receptor.

Radiological Protection and Safety (RPS)



MISSION AND OBJECTIVES

The RPS Group is a unique research group in Portugal, undertaking fundamental and applied research activities addressing multidisciplinary, cross-cutting and leading edge topics in:

- ⦿ Dosimetry and Radiobiology,
- ⦿ Environmental Radioactivity and Radioecology,
- ⦿ Radioactive Waste,
- ⦿ Metrology,
- ⦿ Nuclear and radiological emergencies and accidents.

The objectives of the Group's activities encompass I) the deployment of unique scientific and technical expertise, skills and competence in radiological protection and safety in Portugal II) keeping abreast of the state-of-the-art in scientific and technical topics and in international regulations and safety standards in radiation protection and radiation safety III) higher education and training of students and professionals and the supervision of PhD or MSc students IV) the provision of scientific advice to the Portuguese authorities and stakeholders in policies related to the application of ionizing radiations and radioisotopes V) raising the awareness about hot topics and multidisciplinary issues associated to the biological effects arising from the medical, industrial and environmental exposures to ionizing radiation of workers, patients and members of the public.

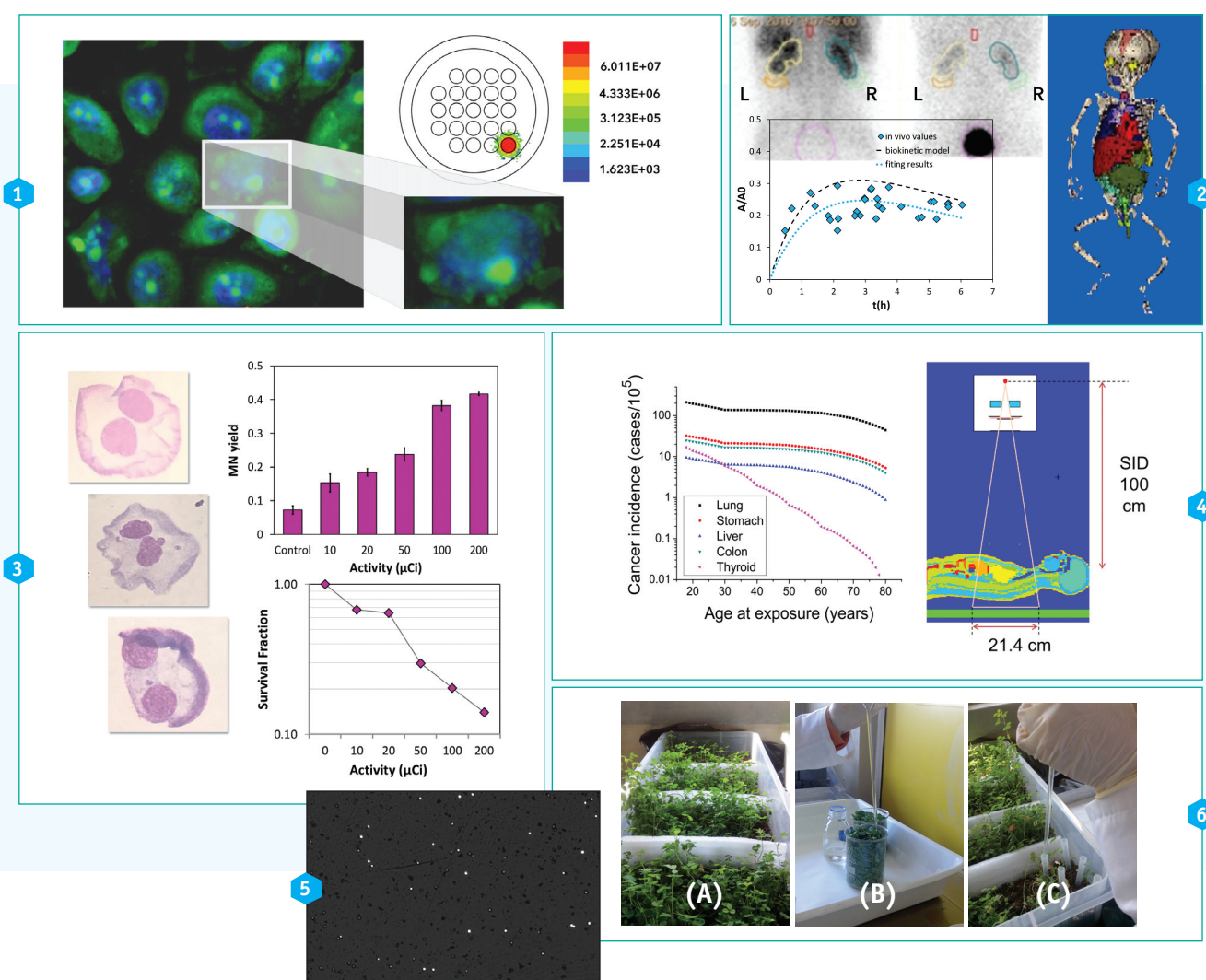
The RPS Group researchers use laboratory infrastructures and equipment and state-of-the-art radiobiology, radioanalytical, dosimetry and metrology techniques. They master computational techniques, namely Monte Carlo simulations and modelling, in support of radiological protection activities related to medical, occupational and environmental exposures.

Throughout 2017, the Group's activities:

- ⦿ were sustained by the participation in R&D projects funded by the European Union (EU) FP7 and HORIZON 2020 Programs, and by organizations such as EURADOS (European Radiation Dosimetry Group) and EURAMET (European Association of National Metrology Institutes), in collaboration with CERN (European Council for Nuclear Research) and other research centers in Europe;

- included the participation in the EU Technological Platforms MELODI (Multidisciplinary European Low Dose Research), IGD-TP (Implementing Geological Disposal of Radioactive Waste), NERIS-TP (Preparedness for Nuclear and Radiological Emergency Response and Recovery) and Alliance (European Radioecology Alliance);
- fostered collaborative links with Portuguese research groups, academia, hospitals and other stakeholders in Radiation Protection, in the context of scientific projects and academic, education and training activities.

MAIN ACHIEVEMENTS



- Developing of computational cell models starting from PC3 fluorescence microscopy images for innovative cellular dosimetric formalisms.
- Biokinetic analysis of ^{99m}Tc -DMSA in pediatric patients and dose assessment using the BABY voxel phantom (8 weeks old).
- Late biological effects induced by ^{99m}Tc -exposure in PC3 prostate cancer cells.
- Radiological risk for cancer incidence in thorax CBCT scans during a complete course of IGRT treatment for lung cancer, for justification of medical procedures and for the optimization of patient protection which is a Public Health concern.
- Microscope image of radon alpha particles tracks on a solid state nuclear track detector.
- Experimental studies on ^{137}Cs release to soil from the degradation of plant biomass contaminated by soil-to-root transfer (A, B) and by wet deposition (C). Outcomes will provide a deeper understanding on the fate of radiocesium in contaminated areas.

Radiation, Elements and Isotopes (REI)

MISSION AND OBJECTIVES

The REI Group is an interdisciplinary group with expertise in nuclear related analytical techniques, atomic physics and ionizing radiation dedicated to the investigation of Environmental Processes, Ancient Materials & Materials Processing.

The group operates an Ionizing Radiation Facility with gamma and e-beam sources and a set of laboratory facilities and equipment to perform: elemental, isotopic and trace element determinations; radiocarbon dating; tritium determinations in water samples; microbiological and chemical analysis of radiation effects in products; and MeV ion microbeam analytical techniques.

Major research fields include environmental pollution; coastal palaeoenvironmental evolution and climate changes; water quality, protection and management; wastewater treatment; provenance, manufacturing technologies and chronological framework of ancient artefacts; materials processing by ionizing radiation for biomedical and industrial applications and conservation of cultural artefacts.

MAIN ACHIEVEMENTS

1 ROMAN METALLURGY IN LUSITANIA: SOURCES AND METAL FLUXES FROM REPUBLICAN PERIOD TO THE ROMAN EMPIRE

Lead isotope and elemental characterization of lead pipes, from Roman urban centers in Lusitania Province (Conimbriga, Augusta Emerita and Mirobriga) ascribed to the Roman Empire and of lead sling bullets from Late Republic identified the lead sources to the Iberian Pyrite Belt (argentiferous jarosite ores) and Sierra Morena and Ossa Morena Zone (galena ores). Study of anthropomorphic *situlae* attachments differentiate a diversity of alloys without standardized compositions (copper, leaded copper, leaded bronze, gunmetal, leaded brass). Research evidences that Roman metallurgical production was strongly influenced by economic concerns, with an important re-use of scrap metal especially during the Empire.

2 STRATEGIES TO MITIGATE CORK WASTEWATERS POLLUTANTS

Cork wastewater (CW) contains phenolic acids that are recalcitrant compounds with high antioxidant activity, requiring treatment before discharge. However, phenolics recovery opens a possibility to valorize the wastewater. CW toxicity, antioxidant activity and the effects of gamma radiation on these parameters were studied to access the feasibility of irradiation to reduce the environmental impact. CW radiolytic products showed increased

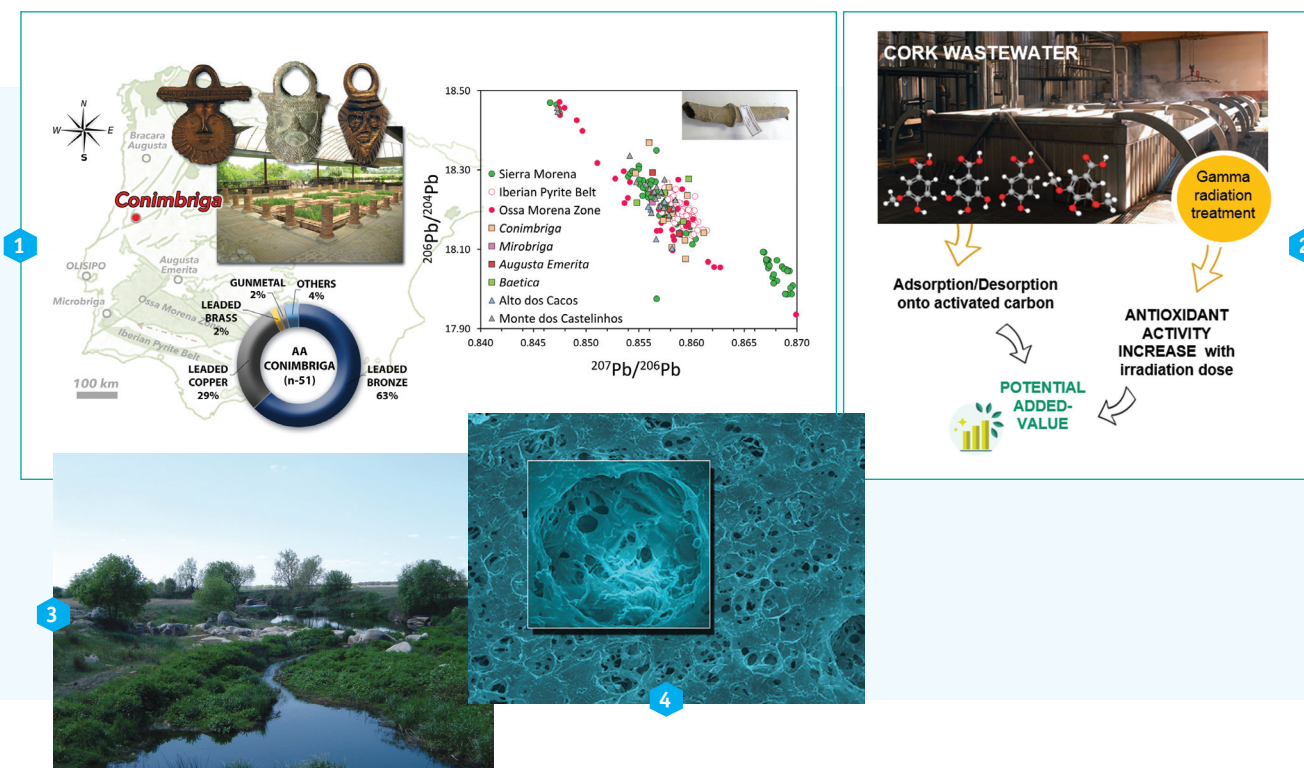
antioxidant potential and higher toxicity than parental ones. This could be relevant for CW valorization through application of extractable phenolics in other industries. The removal of four phenolic compounds from CW was investigated using mesoporous carbons. Results suggested the use of activated carbon to reduce phenolic compounds in cork wastewaters.

3 MULTI-ISOTOPIC APPROACH IN COASTAL AQUIFERS AND THERMINERAL WATER SYSTEMS

Studies on the impact of groundwater over exploitation in coastal areas were accomplished in Algarve and Lower Sado basin (Portugal) and in Morocco W Atlantic, Essaouira basin. Major results include: evidences of mixing with ancient seawater trapped in the sediments during the Sado basin formation; evaporitic minerals dissolution at Tavira (Portugal) and Essaouira; active seawater mechanisms at Portimão/Faro. Investigation of thermomineral waters (N Portugal) established conceptual circulation models comprising the delimitation of the preferential recharge areas and evaluation of the mean residence time, essential for an appropriate management and protection of water resources.

4 BIODEGRADABLE POLYMER MATRICES OBTAINED BY IONIZING RADIATION FOR SKIN SCAFFOLDS

Progress was achieved in the optimization of biocompatible and biodegradable chitosan/polyvinyl alcohol (Chit/PVA) matrices prepared by gamma irradiation for tissue regeneration processes. These processes should occur in polymer matrices developed to act as skin scaffolds. It was found that, the use of low molecular weight chitosan with the addition of gelatine, favor cellular growth with improvement on cells' morphology and cytoskeletal organization.



- 1 The Pb isotope ratios of Roman lead pipes and sling bullets and the copper-based alloys of anthropomorphic situlae attachments from Lusitania Province.
- 2 Antioxidant activity improvement by gamma radiation treatment of cork wastewater and potential extractability of high-valuable cork bioactive compounds by adsorption.
- 3 Xarama river (Lower Sado Basin) - Identification of mixing processes between superficial waters and groundwater systems.
- 4 Surface's SEM micrographs of a Chit/PVA matrix obtained with a g-radiation dose of 3 kGy.

Nuclear Engineering and Techniques (NET)

MISSION AND OBJECTIVES

Multidisciplinary research is paramount at NET playing a significant role in nuclear physics and engineering and in the use of nuclear analytical techniques (NAT) in several domains. Gamma and alpha Spectroscopy and various ion-beam based techniques (Rutherford Backscattering, Elastic Recoil Detection, Nuclear Reaction Analysis and Resonant Elastic Scattering), Particle Induced X-ray Emission, complemented with other techniques like X-ray diffraction are all available within C²TN and are employed by NET towards a deep material's characterization. Moreover, the group maintains an experimental infrastructure at ISOLDE-CERN using short-lived isotopes. Upon emission and detection of the radiation, we probe their interactions with matter providing unique information regarding the structural, electronic, magnetic and dynamical local properties. Research on air pollution and indoor air quality, developing decision support tools to the transition to a low carbon economy is too a major goal. NATs are also applied to Cultural Heritage through dynamical characterization, provenance and absolute dating.

Besides basic research, NET is also involved in project and contract research. Moreover, education and training are a major mission, as well as dissemination, bridging expertise across disciplines, promoting integration beyond the university level and engaging academic into practical problem solving to better reach and influence society.

MAIN ACHIEVEMENTS

1 OVERCOMING THE DOPING LIMIT OF GaN OPTOELECTRONIC DEVICES

Mg-doped p-type GaN is a core component of optoelectronic devices but, with an inherent doping limit where substitutional Mg, introduced during growth, becomes interstitial above a certain concentration. Using the β -emission channeling radioactive technique, we obtained direct evidence for the amphoteric nature of Mg. Recent implantation studies show that above 400 °C interstitial ²⁷Mg progressively converts to substitutional Ga sites in all GaN doping types, as shown in the Arrhenius curves plotted as a function of temperature.

2 DYNAMICAL MODELLING OF CONSTRAINED FLEXIBLE SYSTEMS USING A MODAL UDWADIA-KALABA FORMULATION

Most structures consist on dynamical subsystems connected at constraining points. While standard modelling techniques use Lagrange multipliers or penalty methods, Udwadia & Kalaba (U-K) encapsulated the constraints into a single dynamical equation. We extended their approach to continuous flexible systems, through modal description,

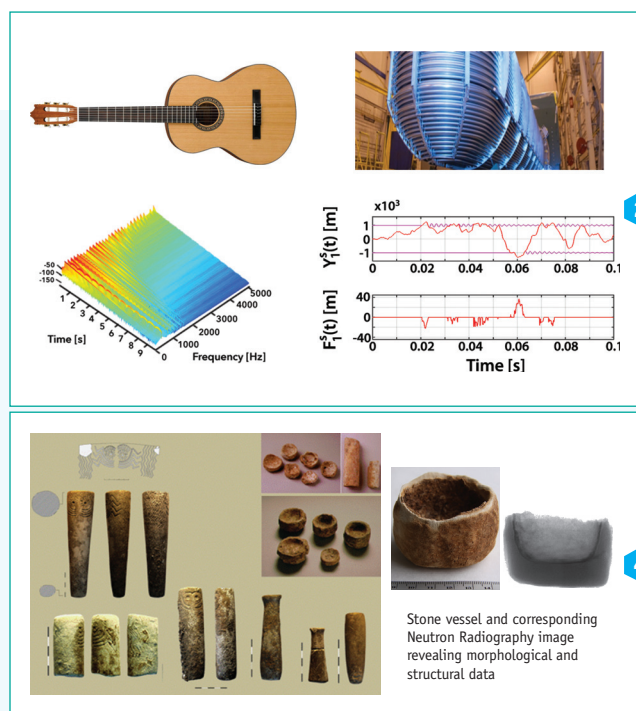
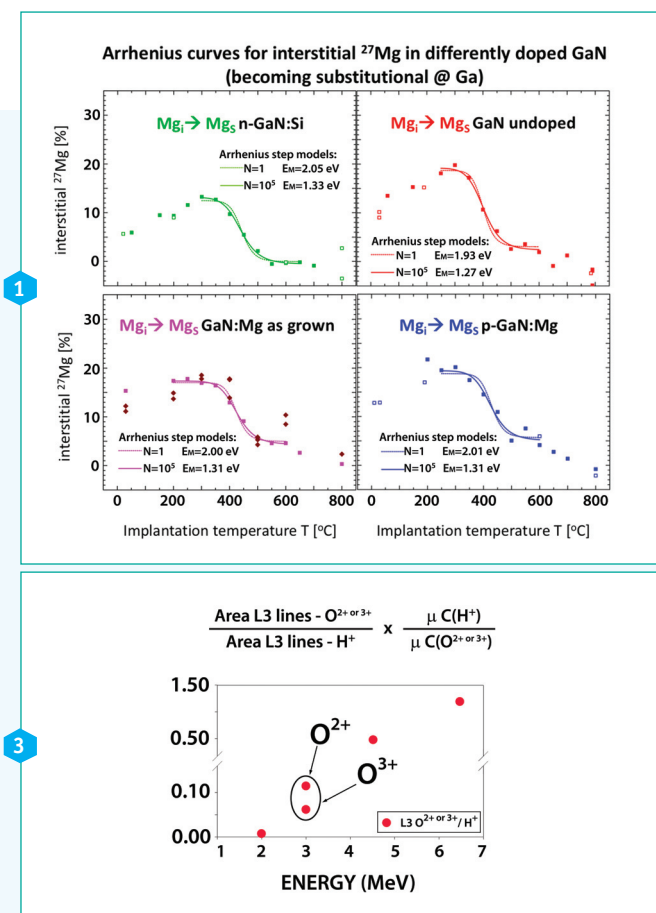
while addressing highly nonlinear intermittent constraints. Efficient numerical simulations performed include the (1) dynamics of a complete guitar, incorporating many modes and linear constraints; (2) flow-excited vibro-impact responses of multi-supported tubes with clearances, typical of nuclear steam generators.

3 DEVELOPMENT OF SOFTWARE FOR X-RAY ANALYTICAL METHODS AND QUANTITATIVE INSTRUMENTAL SPECIATION METHODS FOR PARTICLE INDUCED X-RAYS EMISSION (PIXE)

L3 yields of Yb measured during oxygen beam irradiations showed differences between O^{2+} and O^{3+} beam irradiations, for the same energy, after taking into account the collecting charge for each single spectrum, corrected to the ion charge. As one can observe, at 3.0 MeV the results for O^{2+} case are nearly as twice as for O^{3+} case.

4 X-RAY AND NEUTRON-BASED NON-INVASIVE ANALYSIS IN CULTURAL HERITAGE

A novel combination of X-ray and neutron-based non-invasive analysis was used for the first time to study prehistoric stone idols and vessels from Perdigões Chalcolithic site (Portugal), as a contribution to understand mobility and interaction networks in Pre-History of Southern Iberian Peninsula. We were capable to distinguish between marble/limestone samples originating from nearby, long-distance and unknown geological sources, and to match artefacts to sources.



- 1** Arrhenius curves for interstitial Mg becoming substitutional at Ga sites on differently doped GaN samples. The same activation energy is observed for all types of samples.
- 2** Modelling of a complete guitar (instrument body, strings, playing fingers): spectrogram of the dynamical force exerted by strings at the instrument bridge. Time-domain simulation of the flow-excited nonlinear vibration of a nuclear steam-generator tube: rattling tube motion at a clearance support and the impact force.
- 3** Ta L lines X-ray production cross-sections for oxygen ion beams collisions. Different values were obtained for 3 MeV 2^+ and 3^+ ions.

f-Element Chemistry (QE*f*)

MISSION AND OBJECTIVES

The research activities of the QE*f* Group are centered in the study of the chemistry of lanthanides and actinides at fundamental and applied levels, with focus on topics of relevance in environmental, nuclear and materials sciences.

The activities comprise the synthesis of new *f*-element compounds and materials (complexes with new coordination environments, metal-organic frameworks, ionic liquids, nanostructured intermetallic compounds and bimetallic oxides), the examination of their properties, searching for unusual or enhanced behavior, and reactivity and catalytic studies (activation of unsaturated and redox-active substrates, activation/elimination of major gaseous pollutants such as CO₂, CH₄ and N₂O, and production of value-added compounds such as CH₃OH). The investigation of the thermodynamic properties of key species in condensed and gas phases is conducted and methods for their prediction are developed. Also, the recovery of Rare Earths Elements (REE), considered as critical materials by the European Commission, is carried out by QE*f* group.

The QE*f* Group collaborates with other groups within C²TN: ES, REI, RPS and NET Groups – within a variety of projects including one European Project (ENVIREE).

Outside the Center, the QE*f* Group has collaborations with: IPFN; CQB-FCUL; IPMA/CERENA-IST-FCT project REEuse; REQUIMTE; and groups in the framework of the Portuguese Mass Spectrometry Network. The QE*f* Group participates also in the FCT Doctoral Program CATSUS-Catalysis and Sustainability and in COST ACTION ES1407 (ReCreew).

MAIN ACHIEVEMENTS

1 CO₂ AS RAW MATERIAL FOR THE PRODUCTION OF METHANE

The use of CO₂ as chemical feedstock is limited to a few processes so the hydrogenation of CO₂ to methane is a major catalytic goal. The production of methane was achieved in a continuous atmospheric pressure flow reactor using carbon dioxide and hydrogen as reagents that confirm the potentialities of *f*-block containing compounds as very good catalysts. The Figure shows the results of methane synthesis over nanoparticles of nickel bimetallic oxides containing *f*-block elements at 400 °C. The methanation of carbon dioxide has a range of applications where the conversion of the Martian CO₂-atmosphere into CH₄ and H₂O for fuel and astronaut support systems is a paradigmatic example.

2 PROBING HIGH OXIDATION STATES IN THE LANTHANIDE SERIES

Lanthanide (Ln) chemistry is dominated by the +3 oxidation state, although some Ln show significant +2 and +4 chemistry. Recently, the synthesis of molecular Pr(V) species, in the gas phase and/or in noble-gas matrices, was reported. We have previously demonstrated that

$[\text{Ln}(\text{NO}_3)_4]^-$ complexes presented a behavior that is related to the stability of the Ln +4 oxidation states. For Ce, Pr and Nd, $[\text{LnO}_2(\text{NO}_3)_2]^-$ ions revealed different reactivities with water, namely, hydrolysis for Ce, hydration for Nd and no reactivity for Pr. These differences seem to indicate that Pr is in a stable +5 oxidation state, which was confirmed by ab initio computations.

3 A LAYERED EUROPIUM HYDROXIDE SYSTEM FOR PHOSPHOROUS SENSING AND REMEDIATION

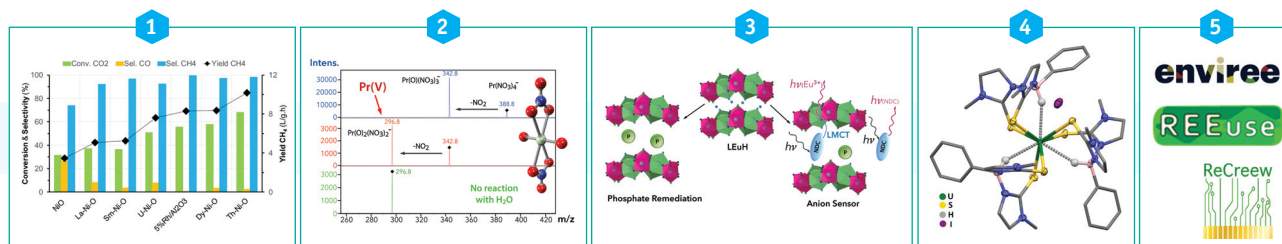
Addressing the societal challenge “Climate action, environment, resource efficiency and raw materials”, a study of a dual-channel sensor (LEuH-2,6-NDC) towards anions was made. The sensor was tested with several biological relevant anions and phosphate was found to have the highest degree of intercalation proven by fluorescence and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Taking advantage of LEuH selectivity towards phosphate, its applicability in phosphorus remediation was studied presenting high sequestration capacity, followed by controlled release of phosphate in three consecutive cycles and improved stability of the LEuH host material. These results highlight the significant potential of LLHs as new scavenging agents for inorganic phosphate.

4 U...H-B AGOSTIC INTERACTIONS IN HOMOLEPTIC URANIUM(IV) BIS(MERCAPTOIMIDAZOLYL)BORATE COMPLEXES

The choice of the ancillary ligand is crucial for the stabilization of metal complexes. Previously monoanionic hydrobis(mercaptoimidazolyl)borate ligands showed their ability to stabilize trivalent uranium complexes. Studies were pursued in order to access complexes with uranium in other oxidation states. New homoleptic cationic uranium(IV) complexes $[\text{U}(\text{K}^3\text{-}\{\text{H}(\text{Ph})\text{B}(\text{tim}^{\text{Me}})_2\})_3][\text{X}]$ ($\text{X} = \text{BPh}_4, \text{I}$; $\text{tim}^{\text{Me}} = 2\text{-mercapto-1-methylimidazolyl}$) were obtained with a $\text{K}^3\text{-H,S,S}$ coordination mode for the three hydrobis(mercaptoimidazolyl)borate ligands, favoring nine-coordinated U(IV) complexes in tricapped trigonal prismatic geometries. These recent results expand the field of non-aqueous uranium chemistry with soft donor ligands and demonstrate that hydrobis(mercaptoimidazolyl)borate ligands can also form robust complexes with U^{4+} ions.

5 RARE EARTH RECOVERY AND VALORISATION AND PROTECTION OF THE ENVIRONMENT

Among the critical materials defined by the European Commission are Rare Earths Elements (REE). They play an essential role in modern electronic technologies, industrial and medical products and innovative environmental technologies. The QEf group is involved in defining and improving ways of recovering REE from a variety of sources: secondary materials resulting from mining activities (ENVIREE), urban and industrial effluents (REEuse), or electric and electronic waste (ReCreew). It is also important to know the REE cycle in aquatic media and this is a second area that is also addressed in the REEuse project.



- 1 Methanation of CO_2 over nanoparticles of Ni- f block element bimetallic oxides at 400 °C ($\text{H}_2/\text{CO}_2=4$, GHSV=15000 mL $\text{CO}_2/\text{g.h}$)
- 2 Experimental and computational evidence for Pr(V) in $[\text{PrO}_2(\text{NO}_3)_2]^-$.
- 3 A dual-channel sensor (LEuH-2,6-NDC) towards anions, highlighting the significant potential of LLHs as new scavenging agents for inorganic phosphate.
- 4 Molecular structure of $[\text{U}\{\text{k}^3\text{-}(\text{Ph})\text{B}(\text{tim}^{\text{Me}})_2\}_3][\text{I}]$.
- 5 Logos of the projects related with recovery and valorisation of rare-earths.

Solid State Group (ES)

MISSION AND OBJECTIVES

The Solid State Group is a multidisciplinary research group focused on the study of selected new materials with unconventional electrical and magnetic properties. The group combines a wide range of expertise ranging from the synthetic chemistry of either molecular materials with transition metal complexes and electro active organic molecules or intermetallic compounds, to many different specialized solid state characterization techniques. Besides molecular synthesis, high temperature and crystal growth and X-ray diffraction laboratories, the facilities developed, maintained and operated by the group include the Low Temperature and High Magnetic Field Laboratory (LTHMFL). This laboratory, unique in Portugal, hosts different equipment for measurements at low temperatures down to 0.3 K and under high magnetic fields up to 18 T, including several magnetometers (SQUID, extraction and AC susceptibility) electronic transport and magnetotransport characterization and Mössbauer spectroscopy.

MAIN ACHIEVEMENTS

1 TWO CHAIN (CONDUCTING AND MAGNETIC) COMPOUNDS

The electrical and magnetic properties of the solid solutions $(\text{Per})_2[\text{Pt}_x\text{Au}_{(1-x)}(\text{mnt})_2]$ were investigated, probing the effects of paramagnetic centers in the diamagnetic chains, and the effects of breaking the paramagnetic chains with diamagnetic centers, for low and high Pt concentrations respectively. In the range $x=0.50-0.95$, only β -phase crystals were obtained.

2 BILAYER POLYMORPHISM IN $(\text{CNB-EDT-TTF})_4\text{ClO}_4$ SALTS

The salts β'' -(CNB-EDT-TTF) $_4\text{ClO}_4$ were obtained in two polymorphs (monoclinic and triclinic), putting into evidence a new aspect of polymorphism in these bilayer metals associated with the orientation of donor molecules in β'' - type consecutive bilayers.

3 IRON OXIDE NANOPARTICLES FOR HYPERTHERMIA

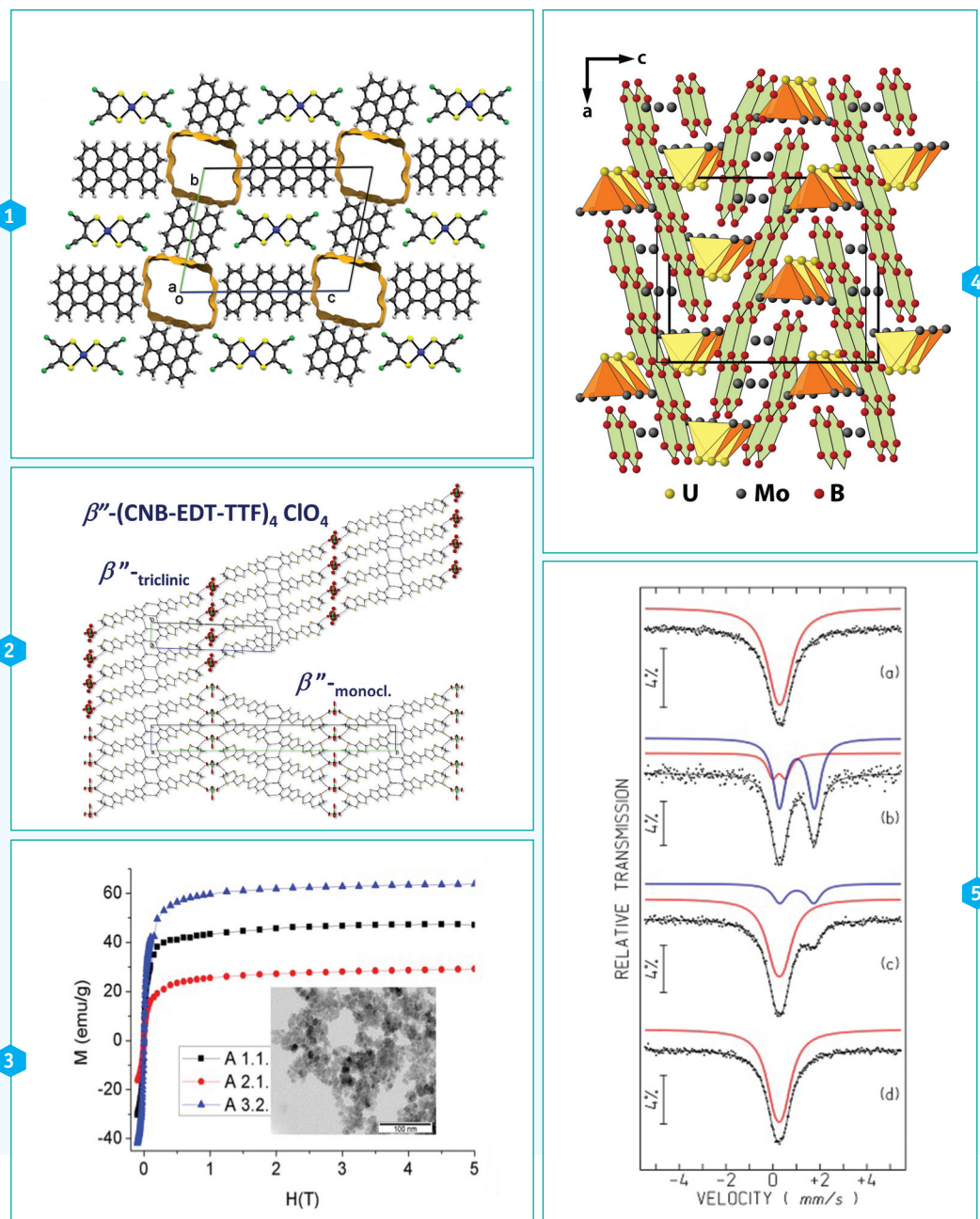
Aiming at the design and development of new nanoparticles for enhanced theranostic techniques, namely for magnetic resonance imaging and for directed drug delivery, silica-based matrices were prepared and decorated with iron oxide nanoparticles (Fe_3O_4 , SPIONs) SPIONs.

4 MAGNETISM AND STRONGLY CORRELATED ELECTRON BEHAVIOR IN INTERMETALLICS

A novel ternary compound, UMo_3B_7 , has been synthesized and characterized. Specific heat, magnetic susceptibility and electrical resistivity studies point to a spin fluctuation scenario with a moderately enlarged Sommerfeld value of $\gamma = 28 \text{ mJ}/(\text{molK}^2)$.

5 MÖSSBAUER SPECTROSCOPY OF PHOTORESPONSIVE MATERIAL

Fe Mössbauer spectroscopy clearly showed in a photoresponsive molecular polyanion that Fe(III) was reduced upon irradiation with UV light. The K salt of this material, in which two Fe(III) ions are simultaneously coordinated by two $[A-\alpha-PW_{934}]^{9-}$ polyoxometalate units and two oxalato ligands, when irradiated with UV light, exhibits a remarkable photocoloration effect, due to the partial reduction of the POM units to give rise to a mixed-valence species.



1 Crystal structure of β -(Per)₂[Pt(mnt)₂] viewed along a-axis.

2 Comparison of crystal structures of the monoclinic and triclinic polymorphs of β'' -(CNB-EDT-TTF)₄ClO₄.

3 Magnetization curves of silica-based matrices decorated with Iron oxide nanoparticles (Fe₃O₄ SPIONs) prepared under different conditions. The inset shows the SEM image of the particles.

4 Crystal structure of UMo₃B₇.

5 Mössbauer spectra of a sample taken before (a) and after 6 h UV irradiation for 0.75 h (b), 42 h (c), and 12 days (d) after irradiation was switched off. The lines over the experimental points are the sum of two quadrupole doublets.

C²TN Conferences at CTN Campus

During 2017 C²TN organized and hosted several scientific meetings, as well as a regular series of seminars by internal and external researchers.

MEETINGS

- ✧ 17th EAN Workshop (in collaboration with NERIS) / 15-16 May 2017, Bobadela, Campus Tecnológico e Nuclear of IST, Portugal.
- ✧ NERIS Workshop 2017 & 8th General Assembly / 17-19 May 2017, Bobadela, Campus Tecnológico e Nuclear of IST, Portugal.
- ✧ 3rd PETRUS-ANNETTE-ENEN PhD and Early-Stage Researchers Conference 2017: Radioactive Waste Management and Disposal / 26-30 June 2017, Lisbon, Portugal.
- ✧ Radiological Protection in Heath (PSR 2017) / 27-29 September 2017, Lisbon, Portugal.
- ✧ Workshop ESRCH - Respiratory Protection Against Aerosol Hazards in Occupational Environments / 3rd November 2016, Bobadela, Loures Pole of IST (Portugal).
- ✧ Workshop on Preclinical Small Animal in Vivo Imaging / 13th October 2017, Lisbon, Portugal.
- ✧ 1st C²TN Workshop / 6th December 2017, Bobadela, Campus Tecnológico e Nuclear of IST, Portugal.

SEMINARS / Bobadela (CTN Auditorium), Loures Pole of IST (Portugal)



January, 18

Olga Iranzo

Institut des Sciences Moléculaires de Marseille UMR CNRS 7313,
Marseille, France

Bioinspired approaches for biotechnological applications: expanding
Nature's repertoire



February, 23

Sérgio Dias

Instituto de Plasmas e Fusão Nuclear IPFN/IST

Dois Anos no Laboratório de Plasmas Hipersónicos

March, 27

Johannes van Lier

Departement de Médecine Nucléaire et Radiobiologie, Faculté de Médecine
et des Sciences de la Santé, Université de Sherbrooke, Québec, Canada

Radioligands and Fluorescence Probes to Image Estrogen Receptors



April, 27

Isabel Almeida

Maastric Clinic, Maastricht, The Netherlands

Imaging for Proton Therapy



June, 28

Dominique Lorc

Institut des Sciences Chimiques de Rennes,
Université de Rennes, Rennes, France

Effect of subtle steric differences on the conducting properties
of gold bis(dithiolene) complexes



July, 06

Helena Alves

CICECO, Universidade de Aveiro, Aveiro, Portugal

Graphene-coated textiles: a platform for wearable electronics



September, 06

Marta Ferraz Dias

DKFZ - German Cancer Research Centre, Heidelberg, Germany

Charged particle therapy: from treatment to imaging



October, 12

Nuno Marques

Sociedade Portuguesa de Psicologia, Portugal

Comunicação de Risco



October, 19

Vasco D. B. Bonifácio

CQFM/IN, IST-UL, Lisbon, Portugal

Polyurea Dendrimers: Life in a box



November, 30

Helena F. Florindo

Research Institute for Medicines, Faculty of Pharmacy,
Universidade Lisboa, Lisbon, Portugal

Multicomponent Nanoscale Systems for Immune Modulation
against solid tumors



C²TN Track Record

Information on the number of researchers from C²TN and peer – reviewed publications, the correspondent impact factor, PhD and MSc completed theses and values on the budget of C²TN is given for 2017 and compared with the corresponding values in previous years.

