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TOMO XLVIII

Celebratory Symposium

B – Metal Centres in Supramolecular and Biological Structures

Nanoporous Materials: Functional Silicates and Metal Organic Frameworks

João Rocha

ACADEMIA DAS CIÊNCIAS
DE LISBOA

LISBOA • 2022

B – Metal Centres in Supramolecular and Biological Structures

Nanoporous Materials: Functional Silicates and Metal Organic Frameworks

João Rocha[8]

João Rocha (b. 1962) is Full Professor of Chemistry and Professor of Chemistry, Coordinator of the Council of Associated Laboratories, and was the Director of the University of Aveiro Institute of Materials (CICECO, ca. 480 people) from 2002 to 2021.

He got his Ph.D. in 1990 from the Department of Chemistry, University of Cambridge. This was followed by a post-doc in the same group. He obtained his 'Agregação' (Habilitation) in 1997 in the University of Aveiro, Portugal.

Rocha is member and 'officer' of the Chemistry Division of the European Academy of Sciences (EURASC). He is a member of the Lisbon Academy of Sciences since 2006. He is also Fellow of both the Royal Society of Chemistry and Chemistry Europe. In 2012-2014, he was advisor for the Prime Minister of Portugal, as a member of the National Science and Technology Council. He has received the prize Ferreira da Silva (highest distinction bestowed by the Portuguese Chemical Society), and the Madinabeitia-Lourenço award from the Real Sociedad Española de Química. In 2005, he received the prize for Scientific Excellence from the Portuguese Science Foundation, and in 1990 a prize from Emmanuel College, Cambridge.

Rocha is one of the most cited Portuguese scientists, having published over 520 SCI papers and 25 book chapters, with ca. 26,000 citations and Google Scholar h-index 78 (Scopus: over 22,000 citations, h=68), and 5 patent applications, and gave over 250 invited talks at conferences (mostly international). He has mentored 43 post-docs and 33 Ph.D. students, coordinated over two-dozen projects (6 European, as national PI), and consulted widely for industry.

His present research interests encompass microporous transition metal and lanthanide (Ln) silicates, photoluminescent Ln-bearing materials, and Metal Organic Frameworks for sensing applications, including nanothermometry, and for batteries; organic-inorganic hybrid ferroelectric materials; nanosystems for multimodal (magnetic resonance, optical and thermometry) imaging and small molecules drug delivery; solid-state NMR and X-ray diffraction.

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For decades, there has been much interest in crystalline materials with frameworks exhibiting channels and cavities ('pores') of small-molecule dimensions. For historical reasons, these nanoporous solids are known as microporous materials. Zeolites, the archetypal microporous solids, are crystalline hydrated aluminosilicates with open framework structures assembled from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units interconnected to each other by sharing all the oxygen atoms. The negative charge of the frameworks is balanced by extra-framework, exchangeable, cations. Zeolites have found real-world applications, particularly in catalysis, gas sorption and separation, and ion-exchange. Other zeolitic materials comprise aluminophosphates dubbed AlPOs, or when doped with silicon or transition metals, respectively, SAPOs or MeAPOS. Pure AlPOs are built up of alternating corner-sharing $[AlO_4]^{5-}$ and $[PO_4]^{3-}$ tetrahedra and, thus, their frameworks have no net charge, no cation-exchange properties, and little catalytic potential.

An outstanding feature of zeolites, AlPOs, and related materials is that their frameworks are all based on tetrahedral (Si, Al, and P) building units. However, microporous silicate solids built from heteropolyhedra such as tetrahedra, pentahedra, and octahedra are also known, even if they are, comparatively, much less studied and commercially explored [1]. Typically, these (so-called OPT) materials contain transition metals, in particular titanium and zirconium, or lanthanides and, in addition to the conventional zeolite properties, exhibit new features, such as magnetism and light emission, that enable a range of new applications. This talk presents selected examples of OPT materials with applications in the treatment of a medical condition, hyperkalemia (excess K^+ in serum), and in light emission (photoluminescence).

Metal Organic Frameworks (MOFs) are crystalline organic–inorganic hybrid materials with nanoporous frameworks built by linking polyatomic metal clusters entirely by strong covalent interactions. While zeolite-like silicates are highly (thermally and chemically) robust systems, allowing applications in relatively harsh conditions, it is very challenging to synthesise the desired architectures and to modify them post-synthesis. In contrast, MOFs operate in milder conditions and often lack robustness, but they are much more amenable to 'rational synthesis' and post-synthetic modification using the conventional methods of organic synthesis. Concerning applications, zeolitic materials and MOFs, thus, complement each other. In this talk I shall present some examples of my groups' research on MOFs. For example, I show that calcium bisphosphonate MOFs are promising for treating bone diseases, and that MIL-125, a Ti-MOF, supported on textile fibres exhibits excellent anti-mosquito activity. Moreover, lanthanide-bearing MOFs for sensing temperature via light emission will also be highlighted. On a different note, MOFs post-synthetic modification allows engineering optical centres and tuning materials' light emission. A case study will be provided.

1. HEALTH-RELATED APPLICATIONS

Hyperkalemia Treatment

Hyperkalemia is a serious medical condition characterised by elevated levels (>5 mmol/L) of potassium in the blood. It is a common electrolyte disorder associated with substantial morbidity. The risk of developing hyperkalemia is increased in patients with chronic kidney disease, diabetes, or heart failure, and in those receiving RAAS inhibitors. A modification of a microporous zirconium silicate

developed in my laboratory (AV-13) [2] was eventually explored by the US company ZS Pharma, now part of AstraZeneca, to treat hyperkalemia [3]. The new drug Lokelma (oral intake) has been approved by FDA and the EMA and is already on the market. Lokelma binds K^+ in the gastrointestinal tract, decreasing the serum levels within one hour, following 10 g drug intake. The other drug on the market to treat hyperkalemia is a nonspecific organic ion exchange polymer resin, sodium polystyrene sulfonate, poorly tolerated by the patients. In contrast, Lokelma has a nine-fold larger K^+ binding capacity and is much more (125 times) selective than polymer resins for K^+ over Ca^{2+}, being also well tolerated.

To understand these properties, the general features of the crystal structure of AV-13, ($Na_{2.27}ZrSi_3O_9Cl_{0.27}\cdot 2.5H_2O$) are now described (Figure 1). The framework consists of corner-sharing ZrO_6 octahedra and SiO_4 tetrahedra. The latter form six-membered $[Si_6O_{18}]^{12-}$ rings interconnected by ZrO_6 octahedra. In a given layer, successive distorted-cube Zr_8 cages contain extra-framework $[Na_{6-x}(H_2O)_x]$ (H_2O,Cl^-) octahedra and framework cyclohexasilicate units. The cages are accessed via seven-membered $[Zr_3Si_4O_{27}]^{26-}$ windows, with free aperture ca. 2.3×3.2 Å, one per each pseudo-cube face. The latter windows account for the high affinity and selectivity of the material (and also of Lokelma) for K^+ over, say H_3O^+, Ca^{2+} or Mg^{2+}: the former, with an unhydrated ionic diameter of 2.98 Å fits well this window while the other ions do not (respectively, 2.30, 2.00 and 1.44 Å). Because AV-13 contains considerable amounts of exchangeable Na^+ and Cl^- ions, an inconvenient feature for a drug, Lokelma was formulated to avoid this issue as $Na_{1.5}H_{0.5}ZrSi_3O_9\cdot 2H_2O$. It is interesting to note that this discrimination mechanism is reminiscent of the potassium ion channel in cells [4].

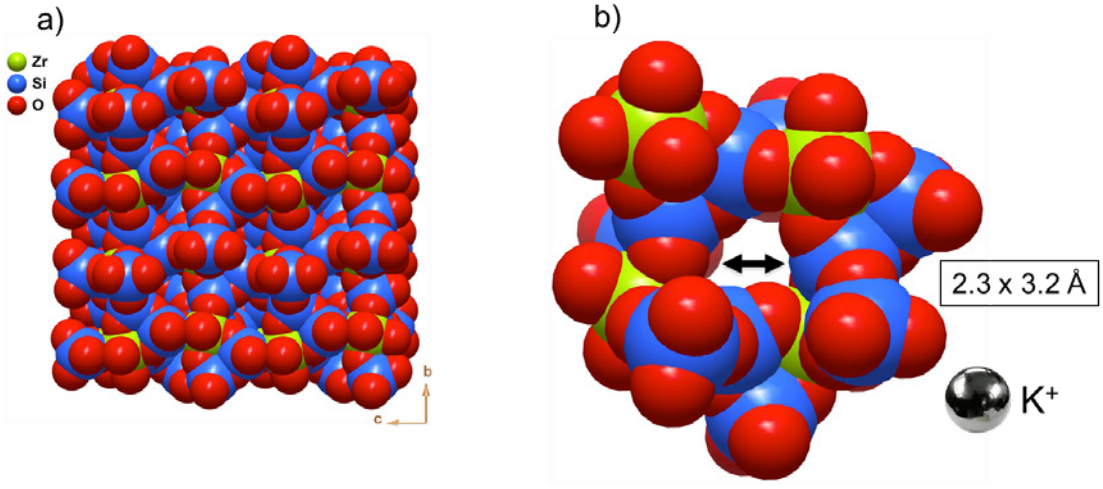

Figure 1
a) Crystal structure of nanoporous zirconium silicate AV-13. b) Cut away showing the seven-membered $[Zr_3Si_4O_{27}]^{26-}$ windows with free aperture ca. 2.3×3.2 Å. K^+ with an unhydrated ionic diameter of 2.98 Å fit well these windows.

Bone Tissue Disorders Treatment

Bisphosphonates are primary drugs against osteoclast-mediated bone loss due to osteoporosis, Paget's disease of bone, metastasis to the bone, and malignancy-associated hypercalcemia. They were introduced to clinical practice four decades ago. Although the maintenance of an adequate calcium (and vitamin D) intake is crucial for patients receiving bisphosphonate therapy, this is frequently

overlooked. We have, thus, prepared bioactive MOFs comprising Ca^{2+} and a bisphosphonate molecule, rather than supplying calcium and bisphosphonate separately [5]. One such material is [$Ca(H_2O)_3$(p--xylylenebisphosphonate)], in which the organic ligand coordinates to four Ca atoms (Figure 2). The sevenfold Ca atoms are coordinated by four O atoms from four symmetry-related organic ligands and three water molecules. The phosphonate ligands act as pillars linking neighbouring Ca atoms, forming a framework enclosing one-dimensional inorganic chains.

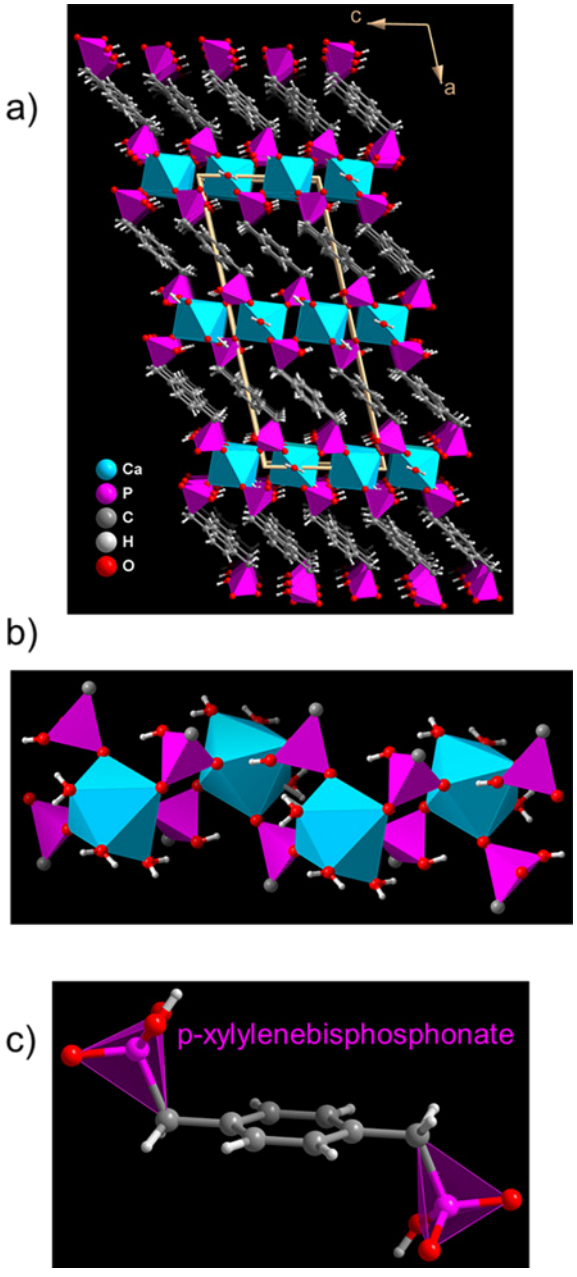

Figure 2
a) Unit cell of [$Ca(H_2O)_3$(p-xylylenebisphosphonate)] viewed along b axis. b) Ca^{2+} ions are interconnected via double phosphonate groups forming an infinite inorganic chain. c) The p-xylylenebisphosphonate ligands act as pillars linking neighbouring Ca^{2+}.

Immersion of pressed pellets of this material in a simulated body fluid (Kokubo's) solution for 3-14 days evidenced the precipitation of bone-precursor phases on the surfaces, octacalcium phosphate and hydroxyapatite (Figure 3). Studies with MG63 osteoblast-like cells indicate that CaP1 is not toxic and stimulates bone mineralization and, thus, holds considerable potential for treating bone diseases, such as osteoporosis.

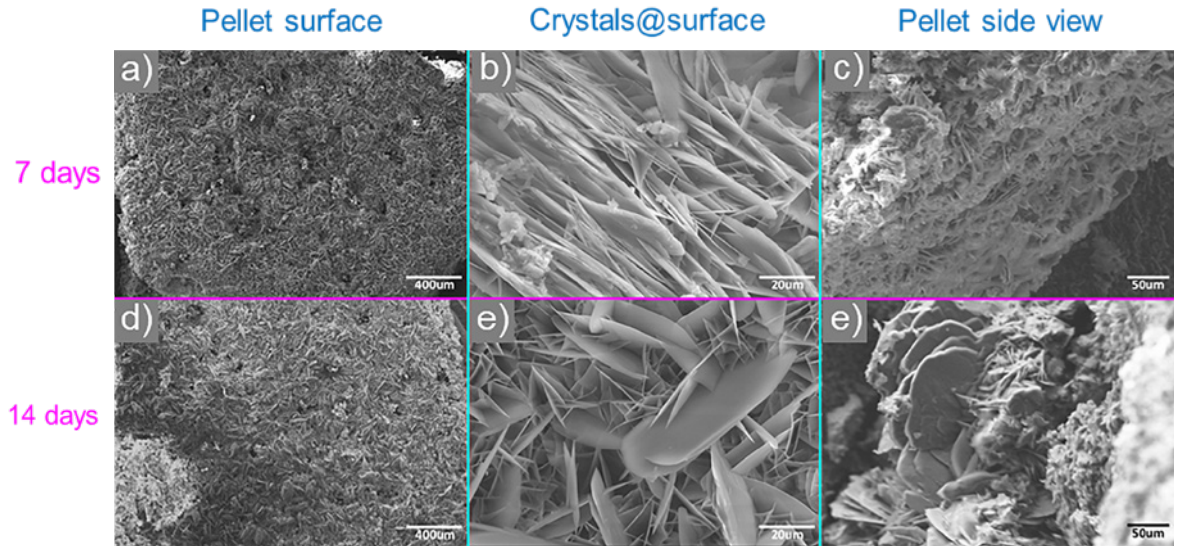

Figure 3
SEM images of [$Ca(H_2O)_3$(p-xylylenebisphosphonate)] pellet surface after soaking in simulated body fluid for 7 and 14 days exhibiting a clear surface modification with lamellar calcium phosphate crystals: a) overview of the pellet surface; (b) high magnification showing lamellar crystal particles on the surface; c) side view of the pellet; d) overview of the pellet surface; e) high magnification showing lamellar crystal particles on the surface; f) side view of the pellet.

Antimosquito Nets Protection

Mosquitoes are the main vectors of diseases like dengue fever, yellow fever, malaria, lymphatic filariasis, and Japanese encephalitis. Fabrics offer mosquito protection, being deployed in nets, curtains, military uniforms, garments, etc., loaded with insecticides or repellents. These methods have limited efficacy due to lack of durability of the finished fabrics, as insecticide and repellents are removed during washing. Trying to overcome these caveats, we have devised [6] composites of the traditional natural fibers' cotton, viscose, and linen and a Ti-bearing metal–organic framework, NH_2-MIL-125 (Figure 4 [7]), that are very effective against mosquitoes, in the absence of any conventional insecticides. To ensure a good adhesion of the MOFs crystals to the fibers' surface, prior to coating, the fabrics were modified with 3-glycidyloxypropyltrimethoxysilane.

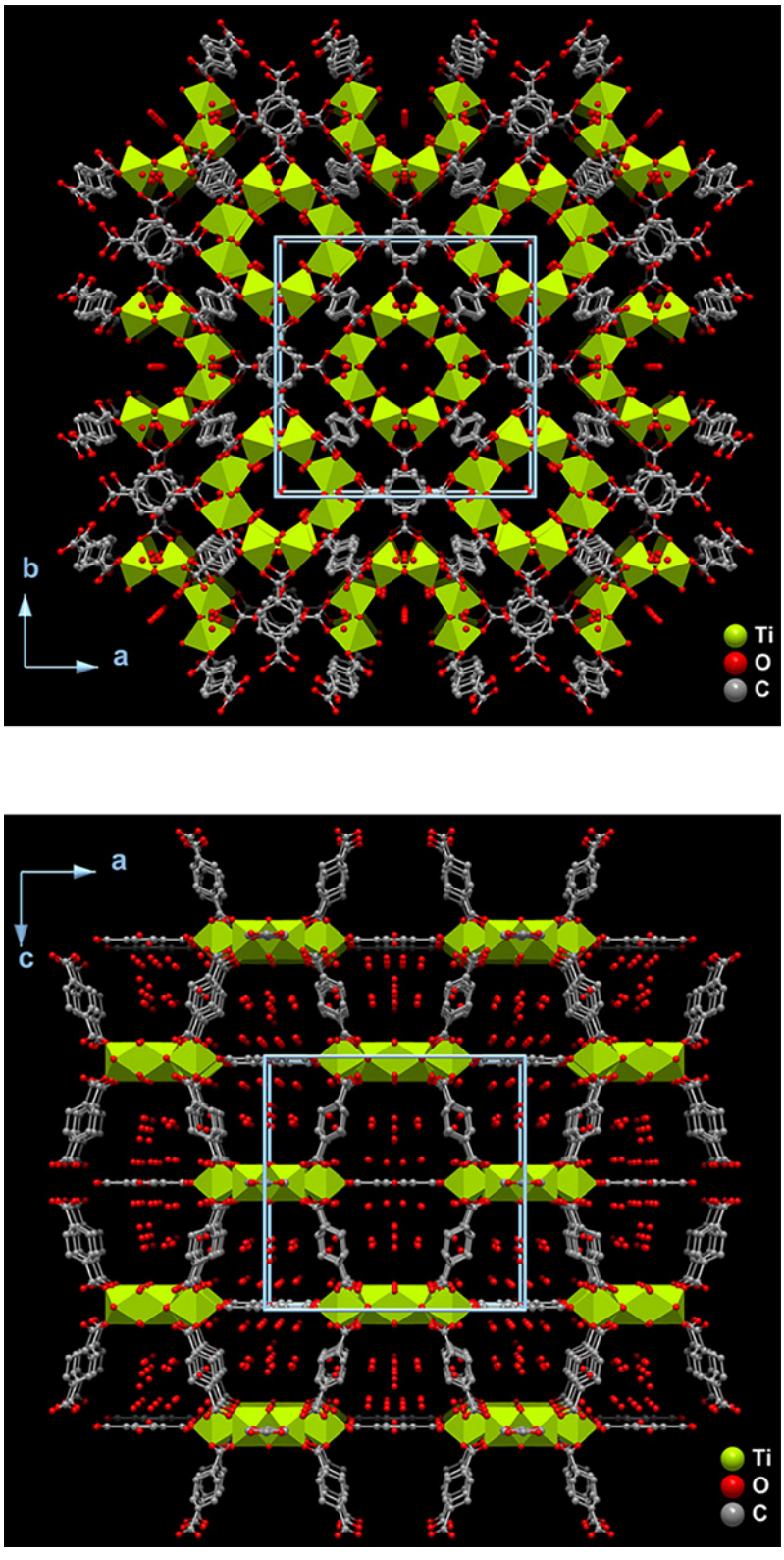

Figure 4
Crystal structure of MOF NH_2-MIL-125 viewed along the c axis (top) and b axis (bottom).

NH_2-MIL-125 is an efficient photocalyst that decomposes the modified urea resin usually present on the surface of cotton fabrics and certain volatile organics in the air, producing CO_2 that attracts mosquitoes. For, as yet, unknown reasons, the MOF kills the landing mosquitoes (Figure 5). Modified fabrics show good washing resistance, surviving more than five washing cycles.

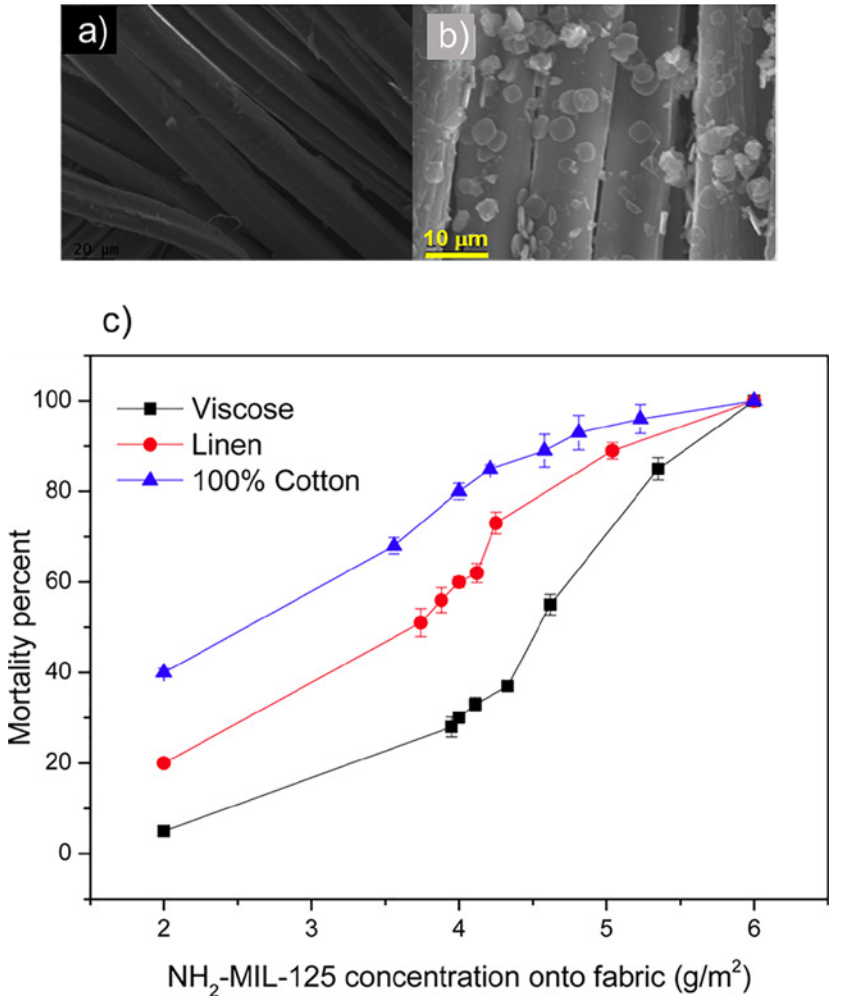

Figure 5
SEM images of a) silica modified 100% cotton; b) NH_2-MIL-125 modified 100% cotton, showing the fabrics surface coated with small MOFs crystals. c) Relation between NH_2-MIL-125 amounts in treated fabrics and mosquito mortality, after 24 h exposed to light. In the dark, the mortality for the highest dose, 6 gm^{-2}, is 11.0% (viscose), 15.0% (linen), and 18.0% (100% cotton).

2. LIGHT EMISSION-RELATED APPLICATIONS

Light Emission by Lanthanide Silicates

In reference 1, I have reviewed the foundations of this field. The trivalent ions of the lanthanide series are characterized by a gradual filling of the 4f orbitals, from $4f^0$ (La^{3+}) to $4f^{14}$ (Lu^{3+}) with the general electronic configuration [Xe]$4f^n$. Several lanthanide ions exhibit luminescence in the visible or near-infrared (NIR) spectral regions upon irradiation with UV light. The spectroscopic features of the

trivalent ions arise from intraconfigurational f–f transitions inside their partially filled 4f shell, which is shielded by the outer filled 5s and 5p shells. My group has prepared dozens of microporous and layered lanthanide silicates and studied their luminescence properties. A case in point is the system $Na_4K_2X_2Si_{16}O_{38}\cdot 10H_2O$, X = Eu, Tb, which illustrates the possibility of combining in a given silicate microporosity and optical activity [8]. The Tb-rich material is the first example of a microporous X-ray scintillator, *i.e.*, it exhibits X-ray (CuKα) induced luminescence (60% of the integrated intensity of Gd_2O_2S:Tb, one of the most efficient X-ray phosphors used in imaging detectors, Figure 6) [9]. The Er-rich material, in turn, is a C-band (1.54 μm) infrared emitter, particularly in the dehydrated form (Figure 7) [9].

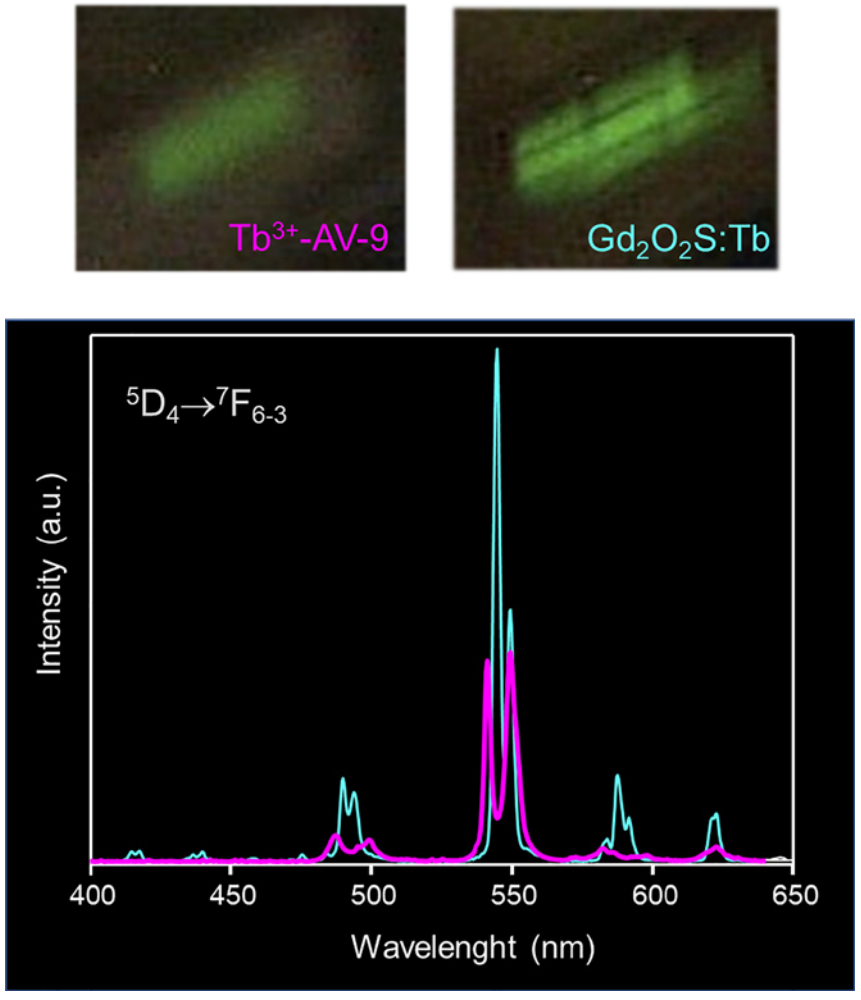

Figure 6
Luminescence spectra of microporous $Na_4K_2Tb_2Si_{16}O_{38}10H_2O$ (pink line) and standard Gd_2O_2S:Tb (blue line) excited by 8.050 keV X-rays (bottom). The top panels show photographs of the emissions acquired under identical experimental conditions.

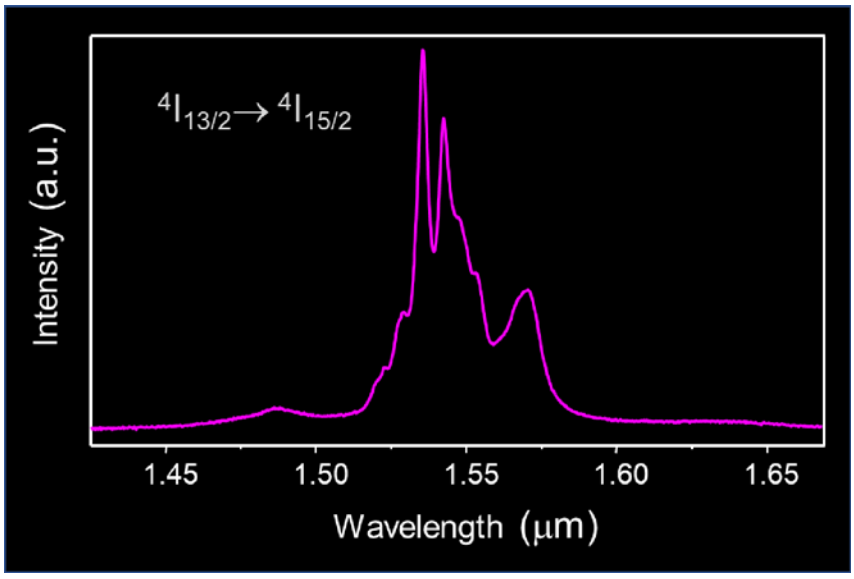

Figure 7
Infrared emission spectra of dehydrated $Na_4K_2Er_2Si_{16}O_{38}$ recorded at 300K and excited at 514.5 nm.

Luminescent Thermometry

MOFs thermometers ascertain the absolute temperature via the intensities of two transitions of distinct emitting centres (so-called dual-centre thermometers): a ligand (linker) and a Ln^{3+} ion (Eu^{3+} or Tb^{3+}), two Ln^{3+} ions (usually Eu^{3+} and Tb^{3+}), or a dye hosted in the MOFs nanopores and a Ln^{3+} ion [10]. Most MOFs thermometers use the intensity ratio of the $^5D_4 \rightarrow {}^7F_5$ (Tb^{3+}) and the $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) transitions as the thermometric parameter. The temperature dependence of the emission intensities is, mainly, governed by the thermally-activated energy transfer between the ligand and the metal ion (and by back transfer).

As an example, in this talk we show that spray-drying prepared MOF nanoparticles of $[(Tb_{0.914}Eu_{0.086})_2(PDA)_3(H_2O)]\cdot 2H_2O$ (PDA = 1,4-phenylenediacetic acid) (Figure 8) may be used as ratiometric luminescent nanothermometers operative over a wide range of temperatures, in particular, in the cryogenic range (<100 K), combining high sensitivity (up to 5.96 ± 0.04% K^{-1} at 25 K), reproducibility (in excess of 99%), and low-temperature uncertainty (0.02 K at 25 K) [11]. We have also reported luminescent thermometers based on OPT and other materials [12,13].

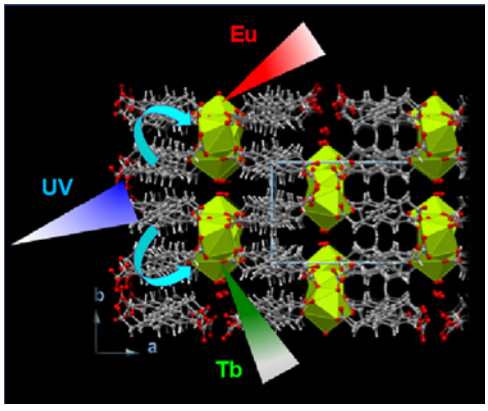

Figure 8
Schematic ('pedagogical') representation of the emission process of $[(Tb_{0.914}Eu_{0.086})_2(PDA)_3(H_2O)]\cdot 2H_2O$ used in luminescent thermometry. The PDA ligand works an antenna capturing the incoming ultraviolet light and transferring energy to Eu^{3+} and Tb^{3+}, thus boosting their emission.

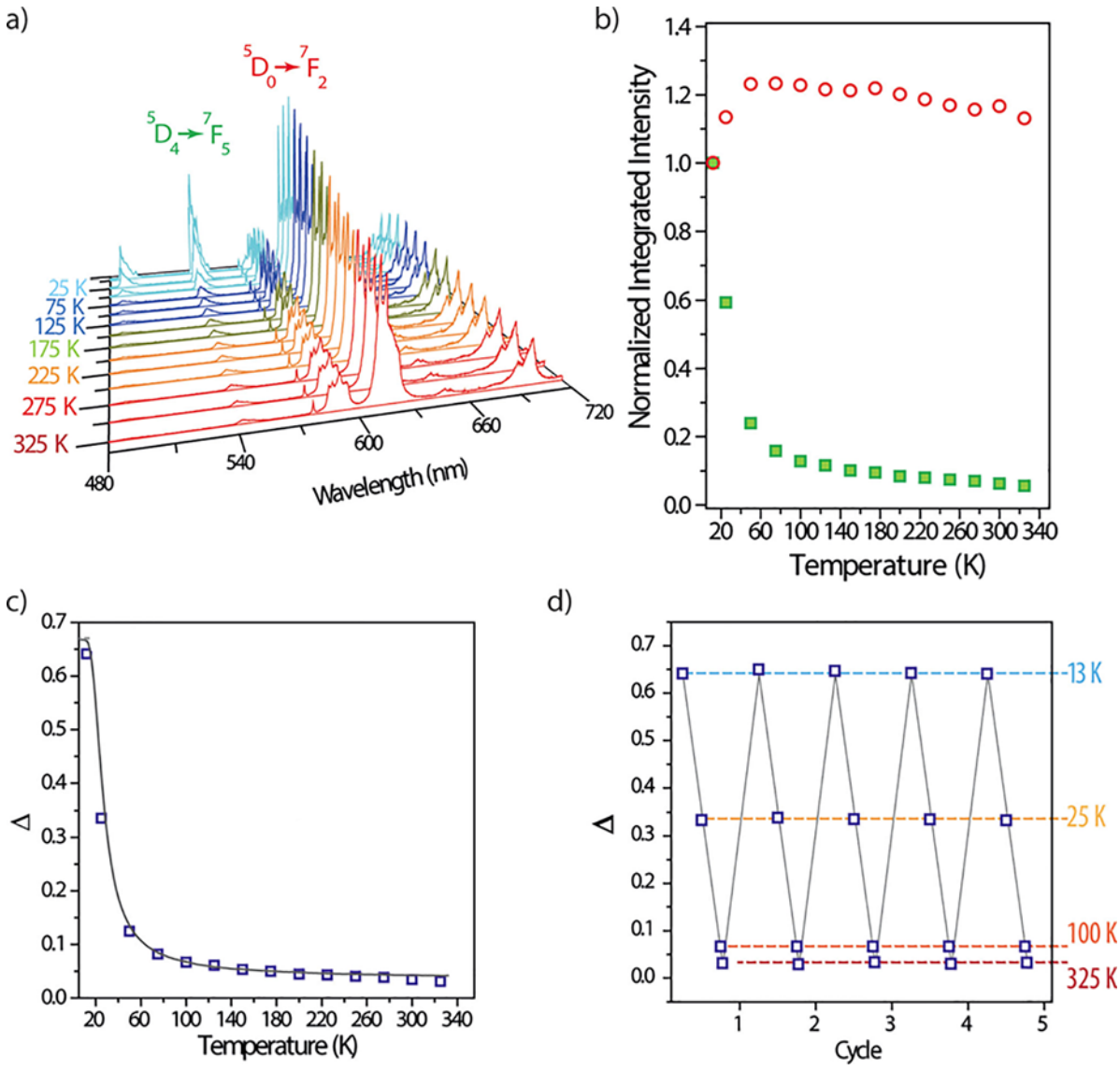

Figure 9

a) Emission spectra (excited at 377 nm, 10–325 K) of $[(Tb_{0.914}Eu_{0.086})_2(PDA)_3(H_2O)]\cdot 2H_2O$; b) I_1 (green) and I_2 (red) integrated areas; c) calibration curve. The open points depict the experimental Δ parameter (I_1/I_2) and the solid line is the best fit to the experimental points; d) temperature cycling between 13 and 325 K reveals reproducibility better than 99%.

MOFs Post-synthetic Modification

An attractive feature of MOFs is the possibility of post-synthetic modification (PSM), particularly the reaction of the linkers with organic reagents, to produce materials with new functionalities. This is, in general, not possible with OPT materials. In a case in point, PSM of IRMOF-3 amino group with ethyl oxalyl monochloride and ethyl acetoacetate followed by the chelation of trivalent lanthanide ions (Figure 10) afforded efficient near infrared (Nd^{3+}) (Figure 11) and visible (Eu^{3+} and Tb^{3+}) light emitters [14].

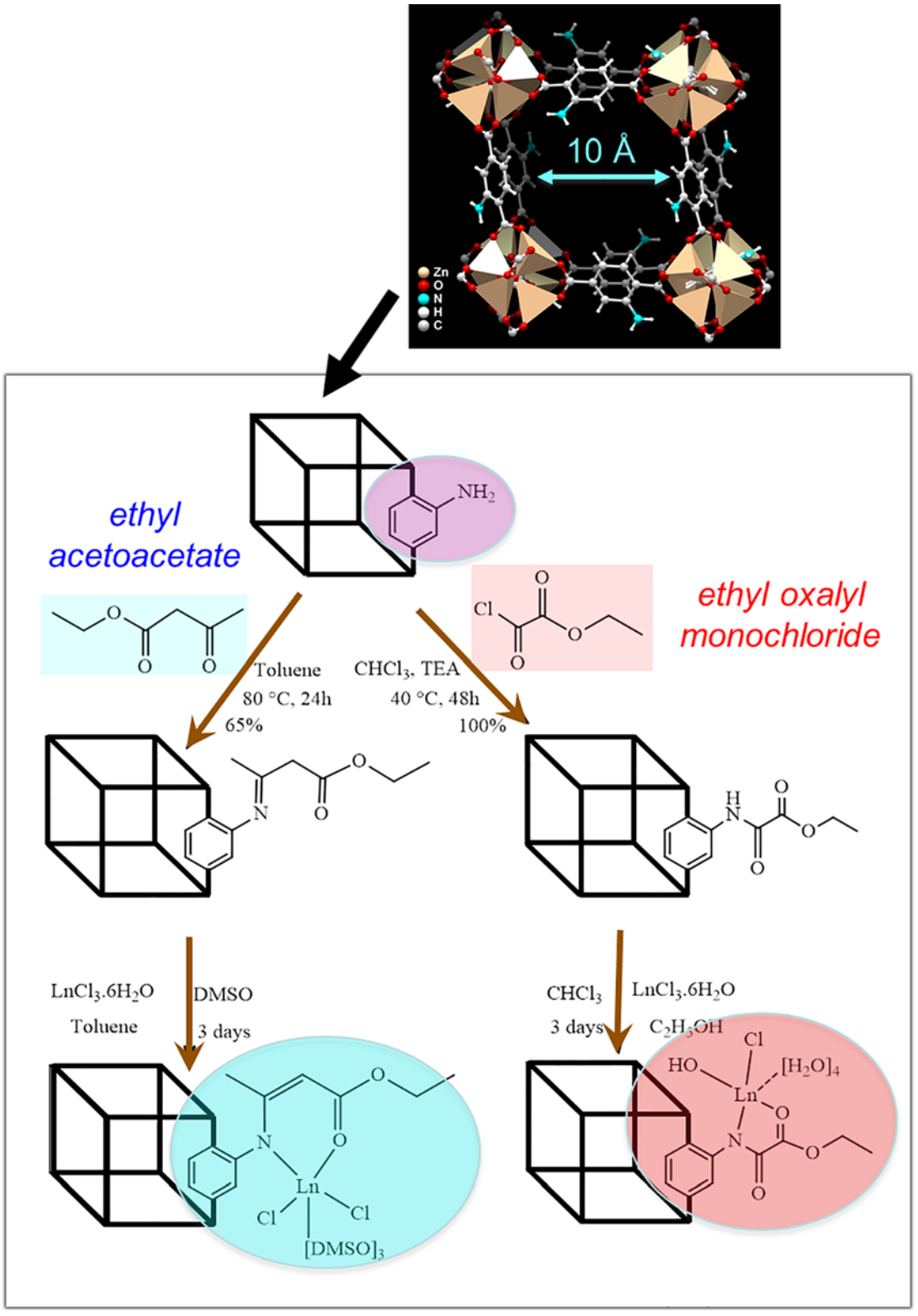

Figure 10
Post-synthetic covalent modification of IRMOF-3 with ethyl oxalyl monochloride and ethyl acetoacetate and subsequent Nd^{3+} coordination.

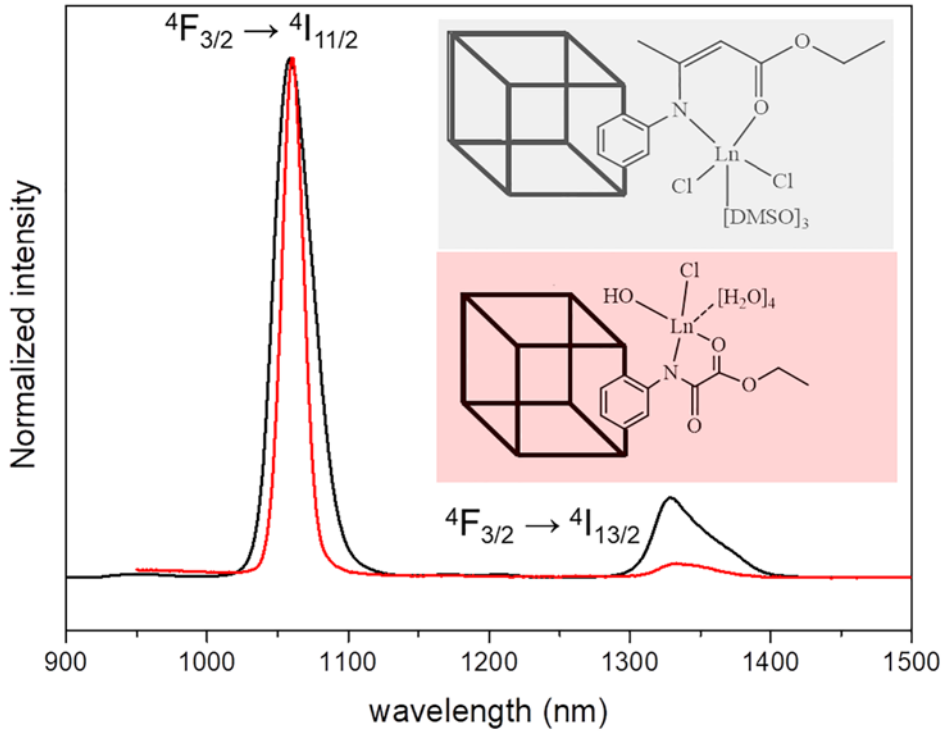

Figure 11
Room-temperature near-infrared emission of Nd-IRMOF-3-(ethyl acetoacetate) (black line) excited at 400 nm, and Nd-IRMOF-3-(ethyl oxalyl monochloride) (red) excited at 525 nm.

ACKNOWLEDGEMENTS

"This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement"

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